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U.S. DEPARTMENT OF THE INTERIOR
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Techniques of Water-Resources Investigations of the United States Geological Survey

METHODS FOR DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

BOOK 5

CHAPTER A1

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Chapter A1

METHODS FOR DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

By Marvin W. Skougstad, Marvin J. Fishman, Linda C. Friedman,
David E. Erdmann, and Saundra S. Duncan, Editors

Book 5

LABORATORY ANALYSIS

UNITED STATES DEPARTMENT OF THE INTERIOR

CECIL D. ANDRUS, Secretary

GEOLOGICAL SURVEY

H. William Menard, Director

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PREFACE

A series of manuals on techniques describes methods used by the Geological Survey for planning and conducting water-resources investigations. The material is arranged under major subject headings called books and is further subdivided into sections and chapters. Book 5 is on laboratory analyses; section A is on water. The unit of publication, the chapter, is limited to a narrow field of subject matter. "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments" is the first chapter under Section A of Book 5. The chapter number includes the letter of the section.

This chapter was prepared with the assistance of many chemists and hydrologists of the Geological Survey as a means of documenting and making available the methods used by the Geological Survey to analyze water, water and sediment, and sediment samples. The loose-leaf format of this methods manual is designed to permit flexibility in revision and publication. Supplements will be prepared as the need arises and issued to purchasers automatically as they become available.

Reference to trade names, commercial products, manufacturers, or distributors in this manual does not constitute endorsement by the Geological Survey nor recommendation for use.

This manual supersedes "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases" by Eugene Brown, M. W. Skougstad, and M. J. Fishman (U.S. Geol. Survey Techniques of Water-Resources Investigation, book 5, chapter A1, 1970) and "Selected Methods of the U.S. Geological Survey for the Analysis of Wastewaters," by M. J. Fishman and Eugene Brown (U.S. Geol. Survey Open-File Report 76-177, 1976).

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METHODS FOR DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

By Marvin W. Skougstad, Marvin J. Fishman, Linda C. Friedman, David E. Erdmann, and Suandra S. Duncan, editors

Abstract

Chapter A1 of the laboratory manual contains methods used by the Geological Survey to analyze samples of water, suspended sediments, and bottom material for their content of inorganic constituents. Included are methods for determining dissolved, total recoverable, and total concentrations of constituents in water-suspended sediment samples, and recoverable and total constituents in samples of bottom material. Essential definitions are included in the introduction to the manual, along with a brief discussion of the use of significant figures in calculating and reporting analytical results. Quality control in the water-analysis laboratory is discussed, including accuracy and precision of analyses, the use of standard reference water samples, and the operation of an effective quality assurance program. Methods for sample preparation and pretreatment are given also.

The analytical methods are arranged according to the analytical technique employed for the determination: atomic absorption spectrometric, calculation, colorimetric, electrometric, gravimetric, and titrimetric methods. More than 200 methods are given for the determination of 69 different inorganic constituents and physical properties of water, suspended sediment, and bottom material, and many of the methods given are identical except for the preparation step, which varies with the particular type of sample that is taken for analysis. Included in the manual are many automated methods, particularly the colorimetric methods that make use of the Technicon AutoAnalyzer system to automate the determination from sample introduction to final concentration readout.

A brief discussion of the principles of the analytical technique involved and its particular application to water analysis precedes each group of analytical methods. For each method given, the general topics covered are application, principle of the method, interferences, apparatus and reagents required, a detailed description of the analytical procedure, reporting results, units and significant figures, and analytical precision data, when available.

Methods for the following determinations are included in the manual:

Dissolved constituents and physical properties

Acidity
Alkalinity
Aluminum
Antimony
Arsenic
Barium
Beryllium
Boron

Dissolved constituents and physical properties

Bromide
Cadmium
Calcium
Carbon dioxide
Chloride
Chromium
Chromium(VI)
Cobalt
Copper
Cyanide
Fluoride
Hardness
Hardness, noncarbonate
Iodide
Iron
Iron(II)
Lead
Lithium
Magnesium
Manganese
Mercury
Molybdenum
Nickel
Nitrogen, ammonia plus organic
Nitrogen, ammonia
Nitrogen, nitrate
Nitrogen, nitrite
Nitrogen, nitrite plus nitrate
Oxygen, dissolved
pH
Phosphorus
Phosphorus, hydrolyzable
Phosphorus, organic
Phosphorus, orthophosphate
Potassium
Selenium
Silica
Silver
Sodium
Sodium adsorption ratio
Sodium, percent
Solids, sum of constituents
Solids, nonvolatile on ignition
Solids, volatile on ignition
Solids, residue on evaporation, at 105°C
Solids, residue on evaporation, at 180°C
Specific conductance
Strontium
Sulfate
Tin
Vanadium
Zinc

Suspended constituents

Solids, nonvolatile on ignition
Solids, suspended, residue at 105°C
Solids, volatile on ignition

Total recoverable constituents and physical property

Aluminum
Barium
Beryllium
Boron
Cadmium
Calcium
Chromium
Cobalt
Color
Copper
Iron
Lead
Lithium
Magnesium
Manganese
Mercury
Molybdenum
Nickel

Total recoverable constituents and physical property

Potassium
Silver
Sodium
Strontium
Tin
Zinc

Total constituents and physical properties

Antimony
Arsenic
Cyanide
Density
Fluoride
Nitrogen, ammonia
Nitrogen, ammonia plus organic
Nitrogen, nitrite
Nitrogen, nitrite plus nitrate
Oxygen demand, biochemical
Oxygen demand, chemical
Phosphorus
Phosphorus, hydrolyzable
Phosphorus, organic
Phosphorus, orthophosphate
Selenium
Solids, nonvolatile on ignition
Solids, residue on evaporation, at 105°C
Solids, volatile on ignition
Sulfide
Turbidity

Constituents recoverable from bottom material

Aluminum
Barium
Beryllium
Boron
Cadmium
Calcium
Chromium
Cobalt
Copper
Iron
Lead
Lithium
Magnesium
Manganese
Mercury
Molybdenum
Nickel
Potassium
Sodium
Strontium
Zinc

Total constituents in bottom material

Antimony
Arsenic
Boron
Cyanide
Nitrogen
Nitrogen, ammonia
Nitrogen, ammonia plus organic
Nitrogen, nitrite plus nitrate
Oxygen demand, chemical
Phosphorus
Selenium
Solids, volatile on ignition

Introduction

The Department of the Interior has a basic responsibility for the appraisal, conservation, and efficient utilization of the Nation's natural resources—including water as a resource as well as water involved in the use and development of other resources. As one of several Interior agencies, the Geological Surveys primary function in relation to water is to assess its availability and utility as a national resource for all uses. The Geological Survey's responsibility for water appraisal includes not only assessments of the location, quantity, and availability of water, but also determinations of water quality. Inherent in this responsibility is the need for extensive water-quality studies related to the physical, chemical, and biological adequacy of natural and developed surface- and ground-water supplies. Included, also, is a need for supporting research to increase the effectiveness of these studies.

As part of its mission the Geological Survey is responsible for generating a large part of the water-quality data for rivers, lakes, and ground water that is used by planners, developers, water-quality managers, and pollution-control agencies. A high degree of reliability and standardization of these data is paramount.

This manual is one of a series prepared to document and make available data collection and analysis procedures used by the Geological Survey. The series describes procedures for planning and executing specialized work in water-resources investigations. The unit of publication, the chapter, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as the need arises. For convenience the chapters on methods for water-quality analysis are grouped into the following categories:

Inorganic substances
Minor elements by emission spectroscopy
Organic substances
Aquatic biological and microbiological samples
Radioactive substances

Provisional drafts of new or revised analytical methods are distributed to field offices of the Geological Survey for their use. These drafts are subject to revision based on use or because of advancement in knowledge, techniques, or equipment. After a method is sufficiently developed and confirmed, it is incorporated in a supplement to the manual or a new edition of the manual and is then available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

Purpose

Rapid changes in technology are constantly providing new and improved methods for the study of water-quality characteristics. It is, therefore, necessary that methods manuals be updated frequently in order to gain the advantages of improved technology. The purpose of this chapter is to record and disseminate methods used by the Geological Survey to analyze samples of water, suspended sediment, and bottom material collected in connection with ongoing water-quality investigations. The manual is an update and enlargement of Techniques of Water-Resources Investigations (TWRI) of the U.S. Geological Survey, Book 5, Chapter A1, "Methods for collection and analysis of water samples for dissolved minerals and gases," by Brown, Skougstad, and Fishman, published in 1970. Of special note is the fact that this manual includes methods for analyzing samples of water-suspended sediment mixtures and of bottom material collected from streams, lakes, and reservoirs.

Although excellent and authoritative manuals on water analysis are available (American Public Health Association and others, 1976; American Society for Testing and Materials, 1966), most of them emphasize primarily either municipal, industrial, or agricultural water utilization. No single reference or combination meets all requirements as a guide to the broader phases of water-quality investigations conducted by the Geological Survey. These investigations are intended to define the chemical, physical, and biological characteristics of the Nation's surface- and ground-water resources, as well as to indicate the suitability of these resources for various beneficial uses.

Scope

This chapter includes techniques and procedures found to be suitable for the analysis of representative samples of water and fluvial sediments. The methods are grouped according to the analytical techniques involved and include—

Sample preparation and pretreatment
Atomic absorption spectrometry
Calculation methods
Colorimetry
Electrometry
Gravimetry
Titrimetry

Most of the groups are introduced by a brief description of the chemical or instrumental principles of the technique involved, followed, where appropriate, by a discussion of the types of analytical operations that may be required, the sensitivity that may be expected from the technique, interferences, applications of the technique, and general references. Each section also includes a detailed description of all methods in which that technique is used, first as they may apply to the determination of constituents in solution (dissolved), then to the determination of total or total recoverable constituents (substances both in solution and adsorbed on or a part of suspended sediment) and finally to the determination of total or recoverable constituents from samples of bottom material.

Each method has a single identifying four-digit number preceded by a letter. The letter prefix designates whether the method applies to a physical characteristic (P), an inorganic substance (I), an organic substance (O), a radioactive substance (R), a biological characteristic or determination (B), an element determined by emission spectrographic method (E), or a sediment characteristic (S). The first digit of the identifying number indicates the type of determination (or procedure) for which the method is suitable, according to the following:

0 ---------- Sample preparation.
1 ---------- Manual method for dissolved constituents.
2 ---------- Automated method for dissolved constituents.
3 ---------- Manual method for analyzing water-suspended sediment mixtures.
4 ---------- Automated method for analyzing water-suspended sediment mixtures.
5 ---------- Manual method for analyzinz samples of bottom material.
6 ---------- Automated method for analyzing samples of bottom material.
7 ---------- Method for suspended constituents.

The last three digits are unique to each method. Additionally, each method number has an appended two-digit number designating the year of last approval of that method. If revisions of a method are issued within the calendar year of last approval, suffixes A, B, . . . are added to the year designation to identify such a subsequent revision. This numbering system simplifies unequivocal identification of each method and also simplifies updating of the chapter as new or revised methods are introduced.

Definitions

Reporting the results of analyses of water and fluvial sediment samples requires the use of a number of terms that are based on the combination of physical phases sampled (water or sediments) and analytical methods used. These terms are defined below.

Dissolved. Pertaining to the material in a representative water sample which passes through a 0.45-μm membrane filter. This is a convenient operational definition used by Federal agencies that collect water data. Determinations of "dissolved" constituents are made on subsamples of the filtrate.

Suspended, recoverable. The amount of a given constituent that is in solution after the part of a representative water-suspended sediment sample that is retained on a 0.45-μm membrane filter has been digested by a method (usually using a dilute acid solution) that results in dissolution of only readily soluble substances. Complete dissolution of all the particulate matter is not achieved by the digestion treatment, and thus the determination represents something less than the "total" amount (that is, less than 95 percent) of the constituent present in the sample. To achieve comparability of analytical data, equivalent digestion procedures would be required of all laboratories performing such analyses, because different digestion procedures are likely to produce different analytical results.

Determinations of "suspended, recoverable" constituents are made either by analyzing portions of the material collected on the filter or, more commonly, by difference, based on determinations of (1) *dissolved* and (2) *total recoverable* concentrations of the constituent.

Suspended, total. The total amount of a given constituent in the part of a representative water-suspended sediment sample that is retained on a 0.45-μm membrane filter. This term is used only when the analytical procedure assures measurement of at least 95 percent of the constituent determined. A knowledge of the expected form of the constituent in the sample, as well as the analytical methodology used, is required to determine when the results should be reported as "suspended, total."

Determinations of "suspended, total" constituents are made either by analyzing portions of the material collected on the filter or, more commonly, by difference, based on determinations of (1) *dissolved* and (2) *total* concentrations of the constituent.

Total, recoverable. The amount of a given constituent that is in solution after a representative water-suspended sediment sample has been digested by a method (usually using a dilute acid solution) that results in dissolution of only readily soluble substances. Complete dissolution of all particulate matter is not achieved by the digestion treatment, and thus the determination represents something less than the "total" amount (that is, less than 95 percent) of the constituent present in the dissolved and suspended phases of the sample. To achieve comparability of analytical data, equivalent digestion procedures would be required of all laboratories performing such analyses, because different digestion procedures are likely to produce different analytical results.

Total. The total amount of a given constituent in a representative water-suspended sediment sample, regardless of the constituent's physical or chemical form. This term is used only when the analytical procedure assures measurement of at least 95 percent of the constituent present in both the dissolved and suspended phases of the sample. A knowledge of the expected form of the constituent in the sample, as well as the analytical methodology used, is required to judge when the results should be reported as "total." (Note that the word "total" does double duty here, indicating both that the sample consists of a water-suspended sediment mixture and that the analytical method determines all of the constituent in the sample.)

Recoverable from bottom material. The amount of a given constituent that is in solution after a representative sample of bottom material has been digested by a method (usually using an acid or mixture of acids) that results in dissolution of only readily soluble substances. Complete dissolution of all bottom material is not achieved by the digestion treatment and thus the determination represents less than the total amount (that is, less than 95 percent) of the constituent in the sample. To achieve comparability of analytical data, equivalent digestion procedures would be required of all laboratories performing such analyses because different digestion procedures are likely to produce different analytical results.

Total in bottom material. The total amount of a given constituent in a representative sample of bottom material. This term is used only when the analytical procedure assures measurement of at least 95 percent of the constituent determined. A knowledge of the expected form of the constituent in the sample, as well as the analytical methodology used, is required to judge when the results should be reported as "total in bottom material."

In describing an analytical method, it is necessary to compare the result obtained by the method to the value that is sought, normally the true concentration of the chemical substance in the sample. Definitions of terms that are used for this purpose are given below.

Accuracy. A measure of the degree of conformity of the values generated by a specific method or procedure with the true value. The concept of accuracy includes both bias (systematic error) and precision (random error).

Bias. A persistent positive or negative deviation of the values generated by a specific method or procedure from the true value, expressed as the difference between the true value and the mean value obtained by repetitive testing of the homogeneous sample.

Precision. The degree of agreement of repeated measurements by a specific method or procedure, expressed in terms of dispersion of the values generated about the mean value obtained by repetitive testing of a homogeneous sample.

Significant figures

The significant figures used by the Geological Survey in reporting the results of analysis in milligrams or micrograms per liter are the result of a compromise between precision of the measurement, importance of this precision to the use of the analytical data, and obvious advantages of some semblance of uniformity in tabulations of analytical data. One of the commonly used methods, which applies only to the expression of the precision of a determination, is to include all digits known with certainty and the first (and only the first) doubtful digit. This method has one obvious disadvantage: published data so reported may not be interpreted to mean the same thing by all users of the data.

TABLE 1.—Factors for converting milligrams per liter to milliequivalents per liter

[1975 atomic weights]

Ion	Sum of atomic weights	Conversion factor	Ion	Sum of atomic weights	Conversion factor
Ag^{+1}	107.868	0.00927	I^{-1}	126.9045	0.00788
Al^{+3}	26.9815	.11119	K^{+1}	39.0983	.02558
As^{+3}	74.9216	.04004	Li^{+1}	6.941	.14407
AsO_4^{-3}	138.9192	.02160	Mg^{+2}	24.305	.08229
Ba^{+2}	137.33	.01456	Mn^{+2}	54.9380	.03640
Be^{+2}	9.01218	.22192	Mn^{+4}	54.9380	.07281
BO_3^{-3}	58.8082	.05101	Mo^{+3}	95.94	.03127
Br^{-1}	79.904	.01252	Na^{+1}	22.9898	.04350
Ca^{+2}	40.08	.04990	NH_4^{+1}	18.0383	.05544
Cd^{+2}	112.41	.01779	Ni^{+2}	58.70	.03407
Cl^{-1}	35.453	.02821	NO_2^{-1}	46.0055	.02174
Co^{+2}	58.9332	.03394	NO_3^{-1}	62.0049	.01613
CO_3^{-2}	60.0092	.03333	OH^{-1}	17.0073	.05880
Cr^{+3}	51.996	.05770	Pb^{+2}	207.2	.00965
CrO_4^{-2}	115.9936	.01724	PO_4^{-3}	94.97136	.03159
CN^{-1}	26.0177	.03844	S^{-2}	32.06	.06238
Cu^{+2}	63.546	.03147	SeO_4^{-2}	142.9576	.01399
F^{-1}	18.9984	.05264	Sn^{+2}	118.69	.01685
Fe^{+2}	55.847	.03581	Sn^{+4}	118.69	.03370
Fe^{+3}	55.847	.05372	SO_4^{-2}	96.0576	.02082
H^{+1}	1.0079	.99216	Sr^{+2}	87.62	.02283
Hg^{+2}	200.59	.00997	V^{+2}	50.9414	.03926
HCO_3^{-1}	61.0171	.01639	VO^{+2}	66.9408	.02988
HPO_4^{-2}	95.97926	.02084	VO_3^{-1}	98.9396	.01011
$H_2PO_4^{-1}$	96.98716	.01031	Zn^{+2}	65.38	.03059

Chemical milliequivalents per liter are computed by multiplying the reported concentration of the individual constituents, in milligrams per liter, by the reciprocal of their equivalent weights. The factors for the conversion of milligrams per liter to milliequivalents per liter for the more commonly determined constituents are given in table 1.

Milliequivalents per liter as reported by the Geological Survey are numerical expressions of milligrams per liter and for uniformity are carried to three decimal places regardless of the magnitude of the milligrams-per-liter value; the significant figures shown in no way reflect the precision of the measurement as do the milligrams-per-liter values.

Quality control

Accuracy of analysis

Some errors are practically unavoidable in analytical work. Errors may result from the reagents used, from the limitations of the method or instruments employed, or even from impurities in distilled water. The analyst's skill and general judgment have a direct bearing on the accuracy of the analytical statement. After the chemical analysis of the water sample has been completed, there are several ways by which the validity of the results can be evaluated. No one method of checking gives conclusive proof of the accuracy of the determinations, but the process of checking may bring to light some dubious results or may suggest some additional constituents of the sample that were not considered in the analysis. No statement of accuracy is provided for the analytical determinations included in this chapter.

Chemical balance

One of the most commonly used procedures for checking water analyses is the balancing of the chemical equivalents of the major ions. Since water is an electrically neutral system, the sum of the milliequivalents of cations in solution equals the sum of the milliequivalents of the anions. If all of the predominant ions have been determined, the milliequivalents per liter (me/L) should be in balance. All major ionic species must, of course, be determined and properly identified.

The hydrogen-ion content of acid water is included in the balance. The hydrogen-ion concentration is approximated from the hydrogen ion activity as determined by the pH of the sample.

$$\mathrm{pH} = \log_{10} \frac{1}{\alpha_{\mathrm{H}} + 1}$$

or

$$\alpha_{\mathrm{H}} + 1 = 10^{-\mathrm{pH}}$$

where $\alpha_{\mathrm{H}} + 1$ is the effective hydrogen ion concentration (hydrogen ion activity).

The calculated pH of standard solutions of sulfuric acid has been compared with determined pH, and the agreement is good up to 2.0 me/L H^{+1} (pH 2.70). Reproducibility and accuracy of ±0.1 me/L H^{+1} is the best that can be anticipated under normal operating conditions and with most waters. Considerable error may be introduced in converting pH to hydrogen-ion concentration because of the effect of other ions on the activity of the hydrogen ion. The reader is referred to the works of Kolthoff and Laitinen (1941) and Bates (1964) for a full discussion of the subject.

Table 2 gives hydrogen ion concentrations approximated from selected pH values.

Multivalent ions present difficulties in the ionic balance unless the ionic states are differentiated by the analysis. Orthophosphates may occur in water as PO_4^{-3}, HPO_4^{-2}, and $H_2PO_4^{-1}$; the proportion of each of these ions is related to the pH of the water. The PO_4^{-3} ion occurs only above

TABLE 2.—Hydrogen ion concentrations as approximated from observed pH values

pH	H^{+1} concentration (me/L)	pH	H^{+1} concentration (me/L)
4.25–3.85	0.1	3.05	.9
3.80–3.60	.2	3.00	1.0
3.55–3.50	.3	2.95	1.1
3.45–3.40	.4	2.90	1.3
3.35–3.30	.5	2.85	1.4
3.25–3.20	.6	2.80	1.6
3.15	.7	2.75	1.8
3.10	.8	2.70	2.0

about pH 10.5. Because natural waters practically never attain this pH, a general assumption can be made that the PO_4^{-3} ion is not present in natural waters. For the purpose of ionic balance, the proportion of HPO_4^{-2} and $H_2PO_4^{-1}$ present can be calculated from the pH relation as shown in table 3 for waters having pH values 10.0 or less. If HPO_4^{-2} and $H_2PO_4^{-1}$ are included in the ionic balance, the milliequivalents per liter of alkalinity must be corrected because HPO_4^{-2} and $H_2PO_4^{-1}$ will partially titrate as alkalinity. Normally, the concentration of phosphorus in water is seldom high enough to enter into the ionic balance.

The values in table 3 were computed from the following chemical equilibrium relationships:

$$H_2PO_4^{-1} = H^{+1} + HPO_4^{-2}$$

$$K_i = \frac{[H^{+1}][HPO_4^{-2}]}{[H_2PO_4^{-1}]}$$

$$\frac{[H^{+1}]}{K_i} = \frac{[H_2PO_4^{-1}]}{[HPO_4^{-2}]}$$

where

Other forms of phosphorus cannot be easily differentiated in this manner. More accurate procedures for the calculation of anionic species from pH and for the correction of activities to stoichiometric concentrations are given by Hem (1961, 1970), but such methods are not usually needed for routine water analysis.

The deviations from ionic balance can be expressed in terms of absolute quantities or as a percentage of the total ionic concentration. Obviously, the analyst must use some type of sliding scale to evaluate the significance of the deviations for water of different concentrations. For example, normally, the deviation between milliequivalents per liter of cations and anions will approach 2 percent for a sample with a total (cations plus anions) milliequivalent-per-liter value of 20 and will approach 3 percent for a sample with a total milliequivalent-per-liter value of 7; however, the deviation may be as high as 12 percent for a sample with a total milliequivalent-per-liter value of 0.9.

Chemical balance is only an indication of the gross validity of the analysis. Using only chemical balance checks, very large errors in the determination of minor constituents can go unnoticed and compensating errors can go undetected. Large deviations indicate either a large error in one or more determinations or the presence of some undetermined constituent, but a good balance is not conclusive evidence that each of the determinations is accurate nor that all constituents have been determined. Chemical balance is one tool for evaluating the validity and comprehensiveness of an analysis, but it must not be a goal for the analyst.

TABLE 3.—Percent orthophosphate mixtures as related to pH

pH	HPO_4	H_2PO_4	pH	HPO_4	H_2PO_4
	(*percent*)			(*percent*)	
4.5	0.2	99.8	7.3	55.3	44.7
4.6	.2	99.8	7.4	60.9	39.1
4.7	.3	99.7	7.5	66.0	34.0
4.8	.4	99.6	7.6	71.2	28.8
4.9	.5	99.5	7.7	75.6	24.4
5.0	.6	99.4	7.8	79.7	20.3
5.1	.8	99.2	7.9	83.1	16.9
5.2	1.0	99.0	8.0	86.1	13.9
5.3	1.2	98.8	8.1	88.7	11.3
5.4	1.5	98.5	8.2	90.7	9.3
5.5	1.9	98.1	8.3	92.5	7.5
5.6	2.4	97.6	8.4	93.7	6.3
5.7	3.0	97.0	8.5	95.1	4.9
5.8	3.8	96.2	8.6	96.1	3.9
5.9	4.7	95.3	8.7	96.9	3.1
6.0	5.8	94.2	8.8	97.5	2.5
6.1	7.2	92.8	8.9	98.0	2.0
6.2	8.9	91.1	9.0	98.4	1.6
6.3	11.0	89.0	9.1	98.7	1.3
6.4	13.5	86.5	9.2	99.0	1.0
6.5	16.2	83.8	9.3	99.2	.8
6.6	19.8	80.2	9.4	99.4	.6
6.7	23.6	76.4	9.5	99.5	.5
6.8	28.2	71.8	9.6	99.6	.4
6.9	33.0	67.0	9.7	99.7	.3
7.0	38.3	61.7	9.8	99.7	.3
7.1	43.9	56.1	9.9	99.8	.2
7.2	49.5	50.5	10.0	99.8	.2

Relation of residue on evaporation to calculated dissolved solids

Comparison of the residue on evaporation and dissolved solids calculated from the analytical statement is a rough check on the comprehensiveness of an analysis. However, the residue on evaporation value will be higher than the calculated dissolved solids if appreciable amounts of organic or undetermined inorganic materials are present, or if water of hydration is contained in the residue, and the value will be lower if volatile solids are lost during evaporation. The calculated value may appear higher if weak acid radicals other than carbonate and bicarbonate (for example, phosphate, borate, and silicate) are included both individually and as part of the alkalinity value.

Specific conductance relation

For most natural waters of mixed type the specific conductance, in micromhos per centimeter at 25°C multiplied by a factor of 0.65 approximates the residue on evaporation in milligrams per liter. This equation is not an exact relation because the conductance of a solution is dependent on the type and total quantity of ions in solution. The specific conductance in micromhos per centimeter at 25°C divided by 100 approximates the milliequivalents per liter of anions and cations. This relation is particularly helpful in detecting the location of error (in anions or cations), as well as for estimating the comprehensiveness of an analysis. More precise relations can be developed for specific water types.

Precision of analysis

The analytical procedure for each determined constituent includes a statement, where data are available, indicating the precision to be expected for that procedure. The precision of procedures for water analysis is difficult to measure in absolute terms of either concentration or percentage. If possible, the precision is expressed in terms of a regression equation over a stated range. In general, these statements have been calculated from data obtained through multi laboratory analysis of test samples prepared by Geological Survey laboratories.

The precision is also expressed in terms of the relative deviation (coefficient of variation), the ratio of the standard deviation to the mean times 100 percent. A convenient formula to calculate the standard deviation is—

$$S_T = \sqrt{\frac{\sum_{i=1}^{m} (X_i - \overline{X})^2}{m - 1}}$$

where

i = an analysis,
n = number of analyses,
X_i = individual values of analyses,
$\overline{X}$ = average value of analyses, and
S_T = standard deviation.

Quality assurance

A quality assurance program is essential to ensure the validity of analytical data (Office of Water Planning and Standards, 1976). A well designed program must provide unbiased monitoring of the accuracy and precision of reported data and must also provide timely information to the analyst on errors and potential errors.

Within the laboratory, quality assurance should be practiced in all areas and on all levels with at least 10 percent of both dollar and man-power budgets devoted to quality control and quality assurance activities. Operationally, a quality assurance program should consist of standardization of all analytical methods, the preparation and use of reference materials, analysis of replicate samples, and a manual and (or) computer-assisted review of the analytical results.

Sample collection

The analysis of an improperly collected sample is meaningless. To keep errors and variation in data due to sampling to a minimum, records on sampling, including field measurements, should be maintained by field personnel. Appropriate field measurements and information peculiar to the sample should be supplied along with the sample to the laboratory. Samples must be shipped without delay, in bottles and containers appropriate to the individual analyses. Time-critical analyses should be performed within the allowable time either in the laboratory or in the field.

Use and documentation of standard laboratory procedures

The acceptance of a new method or modification of an existing method for use in the Geological Survey Central Laboratories requires that several criteria be met:

1. A copy of the method in its final form along with a research report must be presented. The report must include all raw analytical data used in evaluating the method, an evaluation of known and possible interferences, a single operator precision statement for distilled water and natural water solutions of the constituent being determined over the applicable concentration range of the method, and an estimate of the method's productivity and personnel requirements.
2. The method must be tested in one or more operating laboratories in parallel with the currently accepted method or methods for the same determination in order to develop a set of data that cover the concentration range of the method and the variety of natural water types which would be expected to occur nationwide. The evaluation of the results of this testing is the principal basis for accepting a new or modified method and establishing its precision.
3. For general use, the proposed method should be at least equivalent to the current method with regard to precision, accuracy, limitation of interferences, productivity, and the use of hazardous or toxic substances, and should be an improvement over the current method in at least one of these areas.

Methods that do not meet all of the criteria may be conditionally accepted but are limited to the application for which they were specifically developed. Extension of the application requires additional verification.

Clear records must be maintained on the preparation of all standard solutions. All chemicals must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, and dilution water must be distilled or demineralized (passage through mixed bed exchange resins). The latter process must be used if ammonia-free water is necessary, while the water must be boiled immediately before use for carbon dioxide-free water.

The periodic calibration and recalibration of each instrument must be recorded by the analyst. Records must include the number of standards used, the type and date of preparation of stock solution, if applicable, and sample identification (such as a sample number). Noticeable blank drift or changes in readings of standards must also be recorded and corrected.

The monitoring of analyses by use of reference materials must be part of the operational routine. Within the Geological Survey Central Laboratories each section chief ensures that a sufficient number of both standards and reference materials are incorporated in each set of analyses to give confidence in the results of the set. Data are examined for indications of noticeable bias or inadequate precision; data are kept on file in the section and are available for regular inspection.

In addition, each section chief promptly receives and evaluates information on all reference samples submitted by the management. The largest proportion of reference materials is submitted daily by the laboratory management directly to the laboratory as unknowns. Depending on the frequency of an analysis, samples which are totally "blind" are submitted weekly or monthly via field personnel to the laboratory.

Reference material

Reference materials of known concentration are used to monitor the analyses. Two forms of reference materials are used for water analyses: ampouled concentrates and prepared natural waters. Both types have certain advantages for quality control.

Ampouled concentrates are obtained from the U.S. Environmental Protection Agency, National Bureau of Standards, or commercial sources, or are prepared by the USGS Water Resources Division's quality assurance support project, which is independent of the laboratories. Most constituents can be prepared as ampouled concentrates. These can later be diluted quantitatively with either distilled or natural water to provide a variety of matrices and final concentration levels. Such concentrates are particularly useful in method-development or method-comparison studies because data can be obtained both on precision and on percentage recovery.

Reference samples with working level concentrations of stable constituents can be prepared in distilled or natural water. The quality assurance support project prepares a natural water reference sample by collecting a sample of river water, running a preliminary analysis for the constituents of interest, spiking to higher levels of concentration if necessary, and stabilizing the solution. Stabilization is accomplished by filtering, stirring, and aerating quantities of up to 300 gallons of the solution for 3 days, then irradiating it with ultraviolet radiation. The prepared reference solution is then bottled and stored in sterile Teflon containers. Concentrations of the constituents in the solution are not quantitatively known, but the most probable values are determined from the mean results of determinations by several laboratories. Because these solutions are ready for immediate use without further dilution, they are suitable for introduction to the laboratory as "blind" samples for quality control purposes.

Spiked or unspiked natural water or sediment of unknown concentrations, split in a central location and supplied simultaneously to several laboratories, is a further source of reference material. This type of reference material is of particular use in bottom-material analyses. Similarly, although probably of more limited usefulness, the duplicate samples submitted occasionally by field personnel can be evaluated for precision information.

The Geological Survey requires participation of its water laboratories in a designated quality control program. A part of this program requires frequent analysis of standard reference water samples and of blind samples of known composition. Complete records are maintained of each laboratory's performance on these reference samples, and deficiencies are promptly corrected.

Analytical review procedures

Control charts for each method on which the concentration of a constituent is plotted against the date of analysis with a line depicting the known reference value must be kept by the section chief. The amount of scatter and trends in values can then be easily spotted. Control charts on which reference samples near both the upper and lower range of the method are plotted may be found to be particularly useful.

Where it is known that duplicate samples have been submitted, the difference between duplicates can be plotted against the date of analysis (Youden and Steiner, 1975). Because the duplicates are actual samples, this type of control chart may yield as much or more information on the usefulness of the data obtained as the one based on known reference samples.

In addition to reference sample evaluation, the analysis of each sample must be reviewed for quality assurance prior to releasing the information outside of the laboratory. The analysis for the major ionic constituents must be checked, as elaborated on in the section on chemical balance, to see if the sum of the milliequivalents per liter of cations is equal to the sum of the milliequivalents per liter of anions.

The reviewer must be aware of the problems in achieving a balance when multivalent ions or partially dissociated substances are present and must also be aware that the milliequivalents per liter cannot be expected to balance if the concentrations of all major ionic contributors are not determined. Likewise, the reviewer must realize that only predominant ions are checked by this equivalence and that a chemical balance does not ensure accuracy, even of these major ions, since compensating errors can exist in both cations and anions.

Depending on reference sample results or on other checks and after considering the precision of the method, the reviewer may decide to have a water-quality sample reanalyzed. The reviewer must take into account possible interferences in a method and should consider recommending to the analyst that a different method be used. The resulting concentration of the reanalysis must be examined carefully, possibly with further analyses made on the sample, before the value is accepted.

Basic laboratory and field requirements

Any laboratory performing work for the U.S. Geological Survey, Water Resources Division, must be clean, free from atmospheric contaminants, and safety features and programs must meet State and Federal health and safety requirements. Personnel with education and experience in water chemistry must be involved both in performing the analyses and in the supervision of the laboratories.

The use of reference materials, spiked samples, and samples split between laboratories must constitute at least 15 percent of the workload for any parameter. The percentage for rarely used methods must be considerably higher. A data-review program must provide for continual review and evaluation of the laboratory performance data.

Analyses performed in the field must also be carefully monitored. In addition to the use of reference materials, instruments must be calibrated regularly prior to going out in the field, and personnel must be thoroughly trained for field analyses.

The Central Laboratories

In addition to reference material data evaluation, the Central Laboratories, quality control staff reviews the completed analysis report for each sample prior to releasing the information. This review is aided by more than 100 computerized checks that are made prior to printing the analysis report. All checks that fall outside prescribed limits are printed on a sheet following each analysis report. The computerized checks include computation of the ionic balance and comparison to an allowable error curve; comparison of dissolved solids to specific conductance and the dissolved solids-specific conductance ratio to predetermined expected ranges; a check on whether a total constituent concentration is equal to or greater than the corresponding dissolved concentration; and a check on the constituents known to interfere in current methodology above a certain level. The reviewer determines the validity of the individual error messages for each sample and examines the analysis report for anomalies. Reanalysis of individual constituents is requested by the reviewer when it is suspected that an error may have been made, and if errors are indicated, updated values are entered into the data file, and a revised analytical report is generated. This report receives another check by the laboratory's quality control staff and is then released to the requestor.

Laboratory equipment and techniques

Glassware and other containers

All glass apparatus and containers used in analytical work must be carefully selected to meet the requirements of its particular use. Although several types of special-purpose glasses are available, borosilicate thermal-resistant types, such as Pyrex or Kimax, are generally satisfactory for all ordinary laboratory purposes in water analysis. Borosilicate glass is especially suitable for storage of neutral or acid solutions, for volumetric glassware, and for conducting reactions. Since borosilicate glass is not entirely resistant to attack by strongly alkaline solutions, bottles of polyethylene or teflon must be used for storage of standard solutions of silica, boron, and the alkali metals.

All volumetric glassware, such as burets, pipets, and volumetric flasks, must be of borosilicate glass and must contain or deliver volumes within the tolerances of the method. In addition if such glassware is frequently used to measure strongly alkaline solutions, it must be recalibrated at frequent intervals. Directions for such calibration and testing of volumetric glassware are given by the National Bureau of Standards (1959) and in standard texts of quantitative analysis.

Evaporations may be carried out in glass, porcelain, or platinum dishes. Platinum is preferred if the weight of the residue must be determined accurately, because the weight of platinum vessels is very constant.

Although platinum is one of the most resistant metals, it is not completely inert and is subject to embrittlement. The following precautions are recommended: Never put solutions containing tin, mercury, or lead in a reducing environment in platinum; if the free metal should be formed it will alloy with the platinum, especially if heated. Do not heat mixtures of hydrochloric acid with oxidizing substances, such as nitrate or manganese dioxide; ferric chloride in hydrochloric acid attacks platinum appreciably. Place hot platinum vessels on a refractory material, never on a cold metal surface or on a dirty surface. Use only clean platinum-tipped tongs to handle hot platinum vessels. Coarse crystal growth and embrittlement may result from prolonged heating at high temperatures, heating under reducing conditions, and heating phosphates or sulfates in the presence of organic compounds. Embrittlement can be counteracted by rubbing the platinumware with moistened sea sand. Gentle rubbing with sea sand cold-works the metal and breaks down the coarse crystal structure. Detailed instructions for the care and use of platinumware are distributed by manufacturers of these vessels and are described in textbooks of quantitative analysis.

Chemicals and solutions

Purity

Unless indicated to the contrary, all chemicals specified for use in the analytical procedures shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Those chemicals not listed by this organization may be tested as indicated by Rosin (1955). Chemicals used for primary standards may be obtained from the National Bureau of Standards or from manufacturers marketing chemicals of comparable purity.

Water used to dilute samples or to prepare chemical solutions shall first be demineralized by passage through mixed cation-anion exchange resins or by distillation. Its specific conductance at 25°C must not exceed 1.5 μmho/cm, and it shall be stored in resistant glass or polyethylene bottles.

Carbon dioxide-free water may be prepared by boiling and cooling demineralized water immediately before use. Its pH should be between 6.2 and 7.2.

Ammonia-free water may be prepared by

passing distilled water through a mixed-bed ion-exchange resin.

Standard solutions

The concentrations of standard solutions are indicated as the weight of a given element equivalent to, or contained in, 1 mL of solution. The strengths of acids and bases are given in terms of molarities or normalities.

Nonstandard solutions

The concentrations of nonstandard solutions are indicated in terms of the weight of solute dissolved in a solvent and diluted to a given volume. Unless specifically indicated otherwise, it is understood that the solvent is demineralized water of required purity. Designation of concentration in terms of percent is not used.

Accuracy of measurement

Within the methods, significant figures are utilized to define the accuracy of weights and measures. Weighings will be accurate to the last figure shown. For example: A mass designated as 4.532 g must be weighed accurately to ±0.0005 g, whereas a mass designated as 4.5 g must be weighed accurately to only ±0.05 g.

Required accuracy for measurement of volume in the analysis and preparation of reagents is shown similarly. Standard solutions are always prepared in and measured from volumetric glassware. The significant figures given for such measurements are in practical agreement with the tolerance limits for volumetric glassware used. For example: "Add 2.00 mL of reagent" shows that a volumetric pipet must be used for the addition, but "add 2 mL" or "add 1.5 mL" shows that a serological pipet may be used; "dilute to 1,000 mL" shows that a volumetric flask is essential, but "dilute to 1 L" permits the use of a graduated cylinder.

Test-sample volumes less than 5 mL should not be measured directly, because the calibration of 1–mL and 2–mL pipets is not as precise as that of the larger volume pipets. Less error is incurred if a suitable sample dilution is prepared and part of this dilution taken for the test sample. Although the glassware is calibrated to deliver a specific volume at 20°C, the error in measurement incurred by pipetting samples at room temperature is insignificant for water analysis. One gram of pure water is contained in 1.002 mL at 20°C and in 1.007 mL at 38°C; the maximum error in volume that will result from those temperature differences is only 0.5 percent. Brine samples should be brought to as near 20°C as possible before making dilutions for analysis.

Dilution of water samples

The concentration of some inorganic constituents in a water sample many times will exceed the working range as recommended in the application section of each method. For example, sodium in brines will exceed the recommended range several fold. Dilution is normally used to bring the concentration of any of these constituents into the appropriate range. This procedure with proper technique is satisfactory for dilutions of 1 to 1,000. The following techniques must be observed:

1. A volumetric pipet (Class A) smaller than 5.0 mL must never be used.
2. All volumetric flasks used must be Class A.
3. No more than two sequential dilutions can be made on a sample; for example (1:1,000), 5.0 mL diluted to 500 mL and then 5.0 mL diluted to 50.0 mL.

The dilution procedure above is for single pass data only. If more than a 1 to 1,000 dilution must be made, the sample must be analyzed in triplicate. This will require making sequential dilutions of the sample in triplicate, and reporting the average of the three determinations.

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Sample preparation and pretreatment

To determine the total concentrations of metals (dissolved plus suspended forms), it is necessary to digest completely the unfiltered sample (water-suspended sediment mixture) with a strong mineral acid or mixture of acids to bring the metals into solution. Digestion is also necessary when analyzing samples of bottom material. In addition, the organic matter which is nearly always present must be removed by oxidation and volatilization. On samples of bottom material, analytical data are reported on a dry-weight basis. If, however, there is a possibility of volatilizing during air or oven drying any of the constituents to be determined, the analysis must be made on a weighed portion of the as-received (wet) sample; the percent of moisture is then determined on a separate portion. The concentration values obtained on the wet sample may then be converted and reported on a dry-weight basis.

The proper subsampling of bulk samples of bottom material presents unique problems. For most samples, splitting the sample using a Jones-type splitter is satisfactory. Alternatively, subsamples may be conveniently extracted with a small-diameter coring device, commonly glass tubing to minimize risk of metal contamination of the sample. Ordinarily, bottom material samples are sieved before analysis and only the portion passing a 2–mm screen is taken for analysis. The use of an all-plastic screen eliminates the risk of introducing metals into the sample.

Sample preparation and pretreatment methods

Extraction procedure, bottom material (I–5485–78)

1. Application

This method must be used as a preliminary treatment of bottom-material samples to destroy organic matter and to desorb and solubilize readily acid-soluble metals and other minor elements. If there is reason to believe that ≥95 percent of the solution to be determined is solubilized, the results should be reported as "total." If <95 percent is solubilized, the results should be reported as "total recoverable." Only that portion of bottom material that passes a 2–mm sieve is taken for analysis.

2. Summary of method

2.1 The determination of acid-soluble minor elements occurring in, or associated with, sediments and bed materials involves (1) preliminary destruction and removal of all organic matter, followed by (2) treatment to dissolve acid-soluble substances, and (3) the analytical determination of each sought constituent in the resulting solution.

2.2 Removal or destruction of organic matter is a necessary preliminary treatment when acid-soluble minor elements are to be determined in samples of bottom material. This is conveniently accomplished with a strong oxidizing agent that has only a minimal effect on the mineral composition of the particulate material. The following procedure, employing hydrogen peroxide (H_2O_2), is generally satisfactory for destroying organic matter present in samples of bottom material prior to the determination of acid-soluble metals.

2.3 The procedure also provides for a hot, dilute acid (HCl) digestion of the sample after destruction of organic matter. The digestion is designed to ensure dissolution of all sorbed metals and other minor elements as well as all readily acid-soluble components of the bottom material mixture without appreciably attacking the mineral components of the sediment. The treatment is comparable to that used to desorb and dissolve soluble metals and other minor elements associated with particulate material present in water-suspended sediment samples (Method I–3485).

3. Interferences

There are no interferences in the acid digestion.

4. Apparatus

Filter paper, Whatman No. 41, or equivalent.

5. Reagents

5.1 *Hydrochloric acid,* double distilled, 6*M*: Dilute reagent-grade concentrated HCl (sp gr 1.19) with an equal volume of demineralized water. Purify this acid by double distillation, retaining only the middle one–half of the total volume of acid being distilled in each case. Collect the distillate in a clean polyethylene or teflon reagent bottle and protect the purified acid from contamination. The concentration of the distillate will be approx 6*M*. Double distillation of HCl may be omitted if each lot of acid is analyzed prior to use and is determined to yield a negligible blank for all metals of interest.

5.2 *Hydrochloric acid,* double distilled, dilute (1 + 19): Add 50 mL HCl (double distilled, 6*M*) to 950 mL demineralized water.

5.3 *Hydrogen peroxide* solution (H_2O_2), 30 percent w/v.

6. Procedure

Immediately before each use, clean all glassware used in this determination by rinsing, first with warm dilute HNO_3 (1 + 4), and then with demineralized water.

6.1 Weigh to the nearest milligram, between 5 and 10 g dry weight of undried sample that has passed a 2-mm nonmetallic sieve. Compute the dry weight of the sample by determining the percent moisture on a separate subsample.

6.2 Quantitatively transfer each sample to a 600-mL beaker. Add sufficient demineralized water to provide a volume ratio of water to sample of between 1:1 and 2:1. Cover the beaker with a ribbed watchglass.

6.3 If necessary, make the solution acid to litmus paper by the dropwise addition of 1*M* HCl.

6.4 Add 30 percent H_2O_2 in increments of about 5 mL, stir the suspension and allow time for any strong effervescence or frothing to subside. Continue adding H_2O_2 in small amounts until the sample ceases to froth.

6.5 Transfer the sample beaker to a steam bath or hotplate at low heat (65°C to 70°C), and observe it closely until certain that all danger of further strong reaction has passed. Continue to add small increments of H_2O_2 until all organic matter is destroyed, as evidenced by absence of any dark-colored material and cessation of conspicuous effervescence. Evaporate excess liquid between additions of H_2O_2 to keep the water-to-sediment ratio between 1:1 and 2:1. Do not allow the mixture to evaporate to dryness at any time.

6.6 Dilute the mixture to 200 mL with demineralized water.

6.7 Add 10 mL double distilled HCl, 6*M*, mix thoroughly and heat on a hotplate to just below boiling. Continue heating for 30 min.

6.8 Filter the hot mixture (Whatman No. 41 filter paper, or equivalent) and collect the filtrate in a 250-mL volumetric flask. Wash the residue on the filter paper at least three times with hot, dilute, double distilled HCl (1 + 19).

6.9 Cool the filtrate to room temperature and dilute to volume with dilute HCl (1 + 19); mix thoroughly.

6.10 Use appropriate aliquots of this solution to determine acid-soluble metals as required.

7. Calculations

See each individual method.

8. Report

See each individual method for significant figures to be reported.

9. Precision

Precision data are not available for this method.

Extraction procedures, water-suspended sediment mixtures (I–3485–78)

1. Application

This method is used as a preliminary treatment of samples of water-suspended sediment mixtures to desorb and solubilize readily acid-soluble metals and other minor elements associated with the suspended sediment phase of the sample. If there is reason to believe that ≥ 95 percent of the substance to be determined is solubilized, the results should be reported as "total." If <95 is solubilized, the results should be reported as "total recoverable."

2. Summary of method

2.1 The sample is digested by heating with dilute hydrochloric acid. Following digestion, the sample is filtered to remove particulate matter and aliquots of the filtrate are analyzed by standard atomic absorption spectrophotometric or other appropriate method for the following:

Aluminum
Barium
Beryllium
Boron
Cadmium
Calcium
Chromium
Cobalt
Copper
Iron
Lead
Lithium
Magnesium
Manganese
Molybdenum
Nickel
Potassium
Silver
Sodium
Strontium
Zinc

2.2 For additional information on the principles of the methods, see each individual method for each of the substances.

3. Interferences

There are no interferences in the acid digestion.

4. Apparatus

Filter paper, Whatman No. 41, or equivalent.

5. Reagents

5.1 *Hydrochloric acid*, double distilled, 6*M*: Dilute reagent-grade concentrated HCl (sp gr 1.19) with an equal volume of demineralized water. Purify this acid by double distillation, retaining only the middle one-half of the total volume of acid being distilled in each case. Collect the distillate in a clean polyethylene or teflon reagent bottle and protect the purified acid from contamination. The concentration of the distillate will be approx 6*M*. Double distillation of HCl may be omitted if each lot of acid is analyzed prior to use and is determined to yield a negligible blank for all metals of interest.

5.2 *Hydrochloric acid*, double distilled, dilute (1 + 19): Add 50 mL HCl (double distilled, 6*M*) to 950 mL demineralized water.

6. Procedure

Immediately before each use, clean all glassware used in this determination by rinsing, first with warm dilute HNO_3 (1 + 4), and then with demineralized water.

6.1 Weigh the sample bottle plus sample.

6.2 Transfer the entire contents of the sample bottle to a beaker.

6.3 Add to the sample bottle 5 mL double distilled HCl (6*M*) for each 100 mL of original sample. Shake vigorously and add this solution to the beaker. Heat to just below boiling, and continue heating for 30 min.

6.4 Filter the hot mixture (Whatman No. 41 filter paper, or equivalent). Wash the residue on the filter paper three times with 5-mL portions of hot, dilute, double distilled HCl (1 + 19).

6.5 Cool the filtrate to room temperature, transfer it to the original sample bottle which has been cleaned with demineralized water and dilute to the original weight with dilute, distilled HCl (1 + 19). Mix thoroughly.

6.6 Use appropriate aliquots of this solution to determine acid-soluble metals as required.

7. Calculations

See each individual method for each metal.

8. Report

See each individual method for significant figures to be reported.

9. Precision

Precision data are not available for this method.

Percent moisture, total, in bottom material, gravimetric (P–0590–78)

1. Application

1.1 This method may be used to determine the percent moisture in bottom material less than 2 mm in size which has not been air-dried (Method P–0810 or P–0811). To determine percent moisture of air-dried bottom material samples see Method P–0520.

1.2 Information obtained by this method is used to compute the dry weight of subsamples used for analysis of bottom material. The result obtained is not applicable to the bottom material in situ.

2. Summary of method

A portion of well mixed sample less than 2 mm in size is dried at 103°C to 105°C. The loss of weight on drying is computed as percentage of the total wet weight and represents the percent moisture of the sample.

3. Interferences

None.

4. Apparatus

4.1 *Crucible,* platinum or porcelain.

4.2 *Desiccator.*

4.3 *Oven,* 103°C to 105°C.

5. Reagents

None.

6. Procedure

6.1 Place a subsample of sieved bottom material, between 1 and 2 g, into a crucible that has been dried in an oven for 1 h at 105°C to 110°C, cooled and weighed to the nearest 0.1 mg.

6.2 Weigh the sample and crucible to the nearest 0.1 mg.

6.3 Place the crucible containing the sample in an oven and dry to constant weight at 105°C to 110°C.

7. Calculations

$$\text{Moisture (percent} = \frac{W - D}{W} \times 100$$

where

W = total wet weight of sample, grams, and

D = dry weight of sample, grams.

8. Report

The percent moisture is used only to compute the dry weight of other bottom material subsamples used for analysis. It is not reported outside the laboratory.

9. Precision

Precision data are not available for this method.

Sample preparation, bottom material (P–0520–78)

1. Application

This method may be used to air dry samples of bottom material for subsequent analysis.

2. Summary of method

2.1 The sample is sieved, using a 2-mm plastic sieve, and the material passing through this sieve saved for analysis. A portion of the sample is then air dried.

2.2 The percent moisture remaining in the air-dried sample is determined by heating at 105°C to 110°C. This permits recomputation of all constituents determined to an oven-dried basis if desired.

3. Interferences

None.

4. Apparatus

4.1 *Desiccator,* charged with "Drierite" or its equivalent.

4.2 *Drying oven,* 105°C to 110°C, uniform temperature throughout.

4.3 *Sieve,* plastic, with 2.00-mm openings.

4.4 *Tray,* drying, white enameled, size 34 cm (13-1/2 in.) by 24.5 cm (9-5/8 in.) by 2 cm (3/4 in.), or equivalent.

4.5 *Weighing bottle,* cylindrical, 12-mL capacity.

5. Reagents

None required.

6. Procedure

6.1 Transfer the entire sample to a plastic sieve having 2.00-mm openings. Shake and tap the sieve firmly but gently, washing with the minimal amount of distilled water necessary to sieve all material less than 2-mm diameter. Discard material retained on the sieve.

6.2 Air dry the sample. Spread a representative portion of the sample in a thin layer on a flat, enamelware tray or glass watch glass and allow it to stand exposed for 24 h, or until dry. The drying must be conducted in a place free of potential contamination.

6.3 Portions of the resulting air-dried representative sample may be taken for subsequent analysis, as required.

6.4 Determine the percent moisture in the air-dried and sieved sample. Weigh between 1 and 2 g, to nearest 0.1 mg, into a tared weighing bottle. Place the weighing bottle containing the accurately weighed sample in a drying oven and heat for 2 h at 105°C to 110°C. Cool in a desiccator for 30 min and immediately weigh.

7. Calculations

7.1 Compute the loss in weight of the sample, in grams, on heating at 110°C.

7.2 Compute the percent moisture in the air-dried and sieved sample as follows:

$$\text{Percent moisture} = \frac{\text{loss in weight (g)}}{\text{sample weight (g)}} \times 100.$$

8. Report

Report percentage of moisture to two significant figures.

9. Precision

Precision data are not available for this method.

Subsampling, bottom material, coring (P–0810–78)

1. Application

1.1 This method may be used to subsample wet bottom material samples for subsequent analysis.

1.2 If the amount of material less than 2 mm in size is insufficient for adequate coring, a Jones-type teflon splitter may be used (Method P–0811).

2. Summary of method

2.1 The entire wet sample is sieved, using a 2-mm plastic sieve. The material passing through the sieve is subsampled by coring.

2.2 The percent moisture is determined by drying a suitable portion of the sieved wet sample (Method P–0590) in order to permit computation of all constituents determined on an oven-dried basis (105°C to 110°C).

2.3 Care must be taken that the sieved sample is well mixed and that the percent moisture determined on the separate subsample adequately reflects the moisture content of the subsample analyzed.

2.4 In general, when peat-like material comprises the majority of a sample, it should be considered as part of the sample even though it will not pass easily through a 2-mm sieve. (This is not to be confused with samples consisting almost solely of leaves and twigs.)

3. Interferences

None.

4. Apparatus

4.1 *Glass tubes*, both 10-mm i.d. and 20-mm i.d. have been found satisfactory.

4.2 *Sieve*, plastic, with 2-mm openings.

5. Reagents

None.

6. Procedure

6.1 Transfer the entire sample to the plastic sieve. Shake the sieve firmly, washing with a minimum amount of demineralized water as necessary to sieve all material less than 2-mm diameter.

6.2 Thoroughly mix the sieved portion, returning it to the sample container in which it was received or to a beaker.

6.3 Core the sample, using either a 10-mm or a 20-mm glass tube, and place the core material (subsample) in a tared container. In some cases it may be necessary to withdraw more than one core in order to have sufficient bed material for the particular determination to be made (NOTE 1).

NOTE 1. The type of container and the amount of bed material required will depend on the individual method for which the subsample will be used.

6.4 Weigh the subsample to determine its wet weight.

6.5 At the same time as the other subsamplings, use the small bore (10-mm) tube to withdraw a separate subsample for a moisture determination (Method P–0590).

7. Calculations

Compute the dry weight of a subsample as follows:

$$\text{Sample, dry weight (g)} = W\,\frac{(100 - M)}{100}$$

where

W = wet weight of the sample, grams, and
M = percent of moisture as determined by Method P–0590.

8. Report

See each individual determination for the number of significant figures to be reported.

9. Precision

Precision data are not available for this method.

Subsampling, bottom material, splitting (P–0811–78)

1. Application

1.1 This method may be used to subsample wet bottom material samples for subsequent analysis if the amount of material that is less than 2 mm in size is insufficient for adequate coring (Method P–0810).

1.2 Samples that clog the splitter may be subsampled by coring (Method P–0810).

2. Summary of method

2.1 The entire wet sample is sieved, using a 2-mm plastic sieve. The material passing through the sieve is subsampled with a Jones-type teflon splitter.

2.2 The percent moisture is determined by drying a suitable portion of the sieved wet sample (Method P–0590) in order to permit computation of all constituents determined on an oven-dried basis (105°C to 110°C).

2.3 Care must be taken that the sieved sample is well mixed and that the percent moisture determined on the separate subsample adequately reflects the moisture content of the subsample analyzed.

2.4 In general, when peat-like material comprises the majority of a sample, it should be considered as part of the sample even though it will not pass easily through a 2-mm sieve. (This is not to be confused with samples consisting almost solely of leaves and twigs.)

3. Interferences

Certain samples, especially those with a large proportion of sand size material, may clog the Jones type splitter, and an uneven split may result.

4. Apparatus

4.1 *Sieve*, plastic, with 2-mm openings.

4.2 *Splitter*, teflon, Jones-type.

5. Reagents

None.

6. Procedure

6.1 Thoroughly mix the sieved portion and determine the percent moisture (Method P–0590) of a subsample obtained by coring with a 10-mm tube (NOTE 1).

NOTE 1. Alternatively, the moisture content may be determined on one of the last splits; however, since samples do not split into equal weight subsamples, the amount of wash water used in each split would be extremely critical and would have to be calculated accurately.

6.2 Accurately weigh the rest of the sample.

6.3 Pass the sample through a Jones-type teflon splitter.

6.4 Accurately weigh the split subsample.

6.5 Using one of the split subsamples, repeat steps 6.3 and 6.4 until a sufficient number of subsamples are available.

7. Calculations

Compute the dry weight of a split subsample, as follows:

$$\text{Sample dry weight (g)} = \frac{W_1}{W_1 + W_2} W_0 \frac{100 - M}{100}$$

where

W_1 = wet weight, grams, of the split subsample,

W_2 = wet weight, grams, of the other subsample produced by the splitting,

W_0 = weight, grams, of the sample before splitting, and,

M = percent moisture as determined by Method P–0590.

8. Report

See each individual determination for the number of significant figures to be reported.

9. Precision

Precision data are not available for this method.

Atomic absorption spectrometry

Instrumental principles

When a metal salt in solution is aspirated into a flame, the solvent evaporates, and the salt decomposes and vaporizes, producing some atoms. Some of these atoms can be raised to an excited state by the thermal energy of the flame, although a major portion of the atoms present in the flame remain in the ground state (Walsh, 1955). The return of the excited atoms to the ground state results in the emission of radiant energy characteristic of the element atomized. The quantitative measurement of this radiation is the basis of emission flame spectrometry. The essential difference between this form of analysis and classical arc-emission spectrometry is the temperature of the source used to excite the atoms. Since the gas-air and gas-oxygen flames are much cooler than spark and arc sources, analysis by emission flame spectrometry is usually limited to the more easily excitable elements such as lithium, sodium, and potassium.

The unexcited or ground-state atoms produced in the flame can absorb radiant energy when a suitable external radiation source is supplied through the flame at a frequency coinciding with that of the emission frequencies of the element atomized. The measurement of this absorbed radiation forms the basis of absorption flame spectrometry—or atomic-absorption spectrometry, as it is usually referred to (Elwell and Gidrey, 1966; Robinson, 1966).

Analytical procedures

Direct

In a great many samples the concentration of the element desired is sufficiently high, and interference effects so negligible, that the sample in solution may be aspirated directly into the flame of the spectrometer. It may be necessary to adjust the element concentration of the more sensitive elements by sample dilution. When the percent-absorption figures are read from the instrument, converted to absorbance values, and compared with absorbance curves for standard solutions, concentration of the element desired is easily obtained.

When scale expansion is used to increased sensitivity, the percent-absorption values are small, and it is unnecessary to convert percent-absorption to absorbance before plotting an analytical curve. However, most instruments provide for direct readout in absorbance or concentration units and even provide for analytical curve fitting, thus eliminating the necessity for plotting an analytical curve.

Chelation-extraction

In some samples, where the analyte concentration is less than the minimum detectable amount for the particular element sought, some means of sample treatment must be used. This also becomes necessary when the effect of interferences present cannot otherwise be avoided.

For the concentration of samples, or removal of interferences, several alternate procedures may be utilized; among these are chemical separation, ion exchange, or solvent extraction. Of these, solvent extraction is most commonly used, as it is usually less time consuming, and greater sensitivity is frequently obtained by enhancement of emission or absorption by the organic solvent. For example, in the determination of cadmium by direct flame absorption, the lowest reliable determinable concentration is 10 μg/L (micrograms per liter). When determined following chelation and solvent extraction, as little as 0.2 μg/L may be determined with an equivalent scale reading. In this solvent extraction procedure, ammonium pyrrolidine dithiocarbamate (APDC) is used to form the metal chelate, which is then extracted into methyl isobutyl ketone (MIBK) for aspiration into the flame of the spectrometer (Slavin, 1964).

Standard-addition

Another technique widely used in both emission and absorption analysis, when interferences are unknown or otherwise cannot be avoided, is the standard-addition method. An important advantage of this method is that it avoids the necessity of preparing synthetic standards of composition comparable to the unknown sample. It also compensates for matrix effects and interferences, since both sample and standard will be affected equally.

In this method, equal volumes of sample are added to a demineralized-water blank and to three standards containing different known amounts of the test element. The volume of the blank and standards must be the same. In the case of flame atomic-absorption spectrometric analysis, the absorbance of each solution is determined and then plotted on the vertical axis of a graph, and the concentrations of the known standards are plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in figure 1. Although illustrated for flame absorption, the standard-addition technique may be applied equally well to flame-emission analysis.

Internal-standard

The accuracy and precision of both emission and absorption procedures may be improved by the use of internal standards, although such standards have been used primarily in the emission procedure.

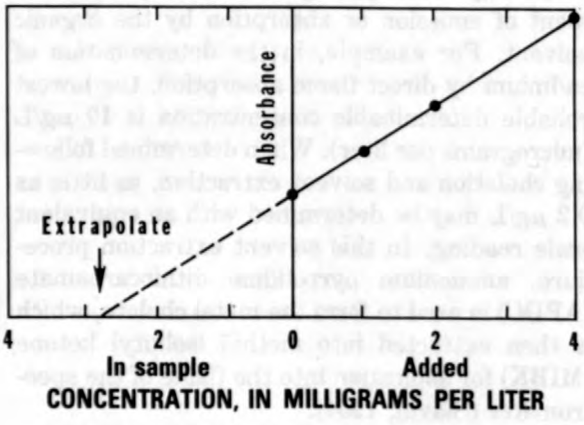


FIGURE 1.—Example of standard-addition method.

The method involves the addition to each sample, and to a series of standards, of a known quantity of an internal-standard element different from that to be determined in the sample. The amount of radiant energy emitted by the element sought and by the internal standard element is measured by successive scanning of the two emission lines. The ratio of the net intensity of the element line to that of the internal-standard line is plotted against concentration of the element sought in the series of standards on log-log paper. This plot of logarithm of intensity ratio versus logarithm of concentration produces a straight line from which the concentration of the element sought in the sample can be obtained. An excellent discussion of the use of the internal-standard method is presented in Dean (1960).

Interferences

Ionization effects

If a significant number of the atoms of the element being determined become ionized in the flame, an error in the analysis will result. This ionization is due to excessive flame temperature, which may be altered to control this interference. Another type of interference may be caused by the presence in the sample of other, more easily ionizable elements than the one sought. The signal enhancement which results may be controlled by the addition of a sufficient amount of the interfering element to both sample and standards to produce a "plateau" in the absorbance curve, above which no further increase occurs.

Chemical effects

This type of interference is due to the formation, in the flame, of compounds of the element sought which are difficult to decompose, thus reducing the amount of the element available for absorption. The formation of such compounds may often be precluded by the addition of another element, such as lanthanum, which forms a less-soluble salt with the interfering anion than does the element desired. The interfering anion is thus effectively reduced in concentration in the flame, and the interference is minimized.

A modification of the fuel-to-oxidant ratio of the flame as well as the choice of fuel and oxidant can also be used to reduce this type of interference.

Matrix effects

Unequal amounts of dissolved solids in samples and standards may cause errors in the analysis due to different nebulization of such solutions by the atomizer. This may usually be controlled by matching the density or viscosity of samples and standards, or by adding a noninterfering salt to the standards. Usually, if matrix effects are severe, the standard-addition technique is used.

Spectral line effects

Spectral-line interference is not commonly encountered. It occurs when there is overlap of a spectral line of the element sought and that of another element that is present in the test sample. Usually, sufficiently high resolution of the spectrometer precludes these problems. However, when a nonanalyte element is present at very high concentration, its atomic line becomes broadened to the extent that it may overlap the line of the sought-for element. The analyst should always be alert to the possibility of errors due to interference of this type.

Background absorption

Background absorbance is a collective term used to describe the combined effects of flame absorption, molecular absorption, and "light scattering," and it is caused by samples with complex matrices which produce erroneously high analyte absorbance readings. This effect is usually eliminated by the use of background correction such as the deuterium arc (continuum source). When the background corrector is in operation, light from a continuum source is passed through the flame simultaneously with the light from the hollow cathode lamp (sharp line source). The element of interest shows atomic absorption only with the sharp line source, while background absorption generally is equal with both sources. When the ratio of the continuum and line source signal is taken automatically, the effects of background absorption are removed, leaving only the atomic absorption signal.

Flameless atomic absorption spectrometric techniques

Atomic absorption measurements may be made without using a flame, providing the absorbing atoms can be introduced in some manner into the light path of the spectrometer. Such methods are common, for example, in determining mercury, where mercury vapor is swept from the sample solution into an absorption cell placed in the light path of the spectrometer. A somewhat analogous situation exists in the method for determining arsenic: arsine gas, produced in the sample solution, is swept into a quartz tube heated to a fairly high temperature, and its absorption measured.

Several devices are available for volatilizing a sample directly in the spectrometer light path. A commonly used device for this purpose is the heated graphite furnace, consisting of a graphite tube that can be heated electrically to a high temperature. A few microliters of sample are placed inside the tube, and the heating unit is then programmed to (1) evaporate the solvent at a comparatively low temperature, (2) ash the evaporated residue at somewhat higher temperature, and (3) finally volatilize the ashed residue at a high temperature. The technique has the advantage of requiring only a very small volume of sample, and providing greater sensitivity than flame techniques, sometimes one or two orders of magnitude greater. Matrix effects may be serious, however, and it is frequently necessary to use a standard addition method to ensure reliable data.

It should be pointed out that a minimum of two additions is required, and that each addition should produce a change in absorbance equal to the observed absorbance of the sample. It is important that the additions show a linear relationship with concentration and that there be no background component to the absorbance of the sample. If either of these premises is violated, the standard-addition method is invalid.

Automation techniques of atomic absorption spectrometers

Atomic absorption spectrometers may be automated by the addition of a continuously flowing system consisting of a series of individual modules, each a separate component performing one specific function in a programmed sequence. A sampler, proportioning pump, if needed, and printer are the modules required.

When pretreatment is unnecessary, samples are aspirated directly into the spectrometer and results are recorded with a printer. In some atomic absorption spectrometric determinations, pretreatment of the samples is necessary to eliminate chemical and ionization interferences.

With the proportioning pump, reagents are added to the sample stream and mixed in coils to eliminate interferences. The solutions are then aspirated automatically in the atomic absorption spectrometer, and results recorded with a printer.

References

Dean, J. A., 1960, Flame photometry: New York, McGraw-Hill Book.

Elwell, W. T., and Gidley, J. A. F., 1966, Atomic-absorption spectrophotometry: New York, McMillan, 138 p.

Robinson, J. W., 1966, Atomic absorption spectroscopy: New York, Marcel Dekker, 204 p.

Slavin, Walter, 1964, Some data on ammonium pyrrolidine dithiocarbamate: Atomic Absorption Newsletter, v. 3, p. 141.

———1968, Atomic absorption spectroscopy: New York, Interscience Publishers, 307 p.

Walsh, A., 1955, The application of atomic absorption spectra to chemical analysis: Spectrochim. Acta, v. 7, p. 108.

Automated atomic absorption spectrometric methods

Metals, dissolved, atomic absorption spectrometric, automated

(I–2470–78)

Parameters and Codes: See individual metal method

1. Application

Automated atomic absorption spectrometric methods may be used to analyze the same types of samples as by the corresponding nonautomated methods. See the individual methods for a discussion of applications.

2. Summary of method

Atomic absorption spectrometric procedures for the determination of several metals can be automated by the addition of a sampler, a proportioning pump, if needed, and a printer. Cooper, iron, lithium, manganese, potassium, sodium, and zinc may be determined by direct aspiration from the sampler; no pretreatment of the sample is necessary. In the determination of calcium, magnesium, and strontium, however, chemical interferences are present, and an ionization interference occurs in the strontium determination. The proportioning pump, in the automated system, adds the required volume of suppressant solution to the sample, mixes the solution thoroughly, and feeds the mixture to the aspirator (Fishman and Erdmann, 1970).

3. Interferences

Interferences in the automated atomic absorption methods are identical to those encountered in nonautomated methods. See the individual methods for a discussion of interferences.

4. Apparatus

4.1 *Atomic absorption spectrometer* with printer.

4.2 Refer to each individual manual method to optimize output of the instrument for the determination of that metal.

4.3 *Technicon AutoAnalyzer* consisting of sampler and proportioning pump.

4.4 With this equipment the following operating conditions have been used (NOTE 1):

Element	*Concentration range*	*Samples per hour*
	(mg/L)	
Ca	0.1 to 60	40
Mg	0.1 to 50	40
K	0.1 to 10	60
Na	0.1 to 80	60
	(µg/L)	
Cu	10 to 1,000	50
Fe	10 to 1,000	30
Li	10 to 1,000	30
Mn	10 to 1,000	40
Sr	10 to 5,000	30
Zn	10 to 200	40

NOTE 1. All cams used must provide 2 parts of sample to 1 part of wash solution.

5. Reagents

5.1 *Lanthanum chloride* solution: See the individual, nonautomated methods for the preparation of the required solution when needed.

5.2 *Metal* standard solutions: See individual, nonautomated methods for the preparation of the required standard solutions of the metal to be determined.

6. Procedure

6.A Procedure for Cu, Fe, K, Li, Mn, Na, and Zn

6.A.1 Manually aspirate a blank and use auto zero to set the instrument digital display to read zero concentration. Similarly aspirate standards and use auto concentration to set the instrument digital display to read the concentration of the standards. Calibrate the instrument each time a set of samples is analyzed.

6.A.2 To check for stability at reasonable intervals, place a complete set of standard solutions of the metal being determined in the first position of the first sample tray. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill the remainder of each sample tray with unknown samples.

6.A.3 Begin analysis.

6.B Procedure for Ca, Mg, and Sr

6.B.1 Set up manifold (NOTES 2 and 3) (fig. 2).

NOTE 2. When maximum sensitivity is required for strontium and low concentrations of calcium and magnesium, a stream splitter may be used so that the 2.1-mm (0.081-in.) diameter water-tube also carries the sample stream.

NOTE 3. The manifold can be used for automatic dilution of samples for any determination.

6.B.2 Manually aspirate a blank and use auto zero to set the instrument digital display to read zero concentration. Similarly, aspirate standards and use auto concentration to set the instrument digital display to read the concentration of the standards. Calibrate the instrument each time a set of samples is analyzed.

6.B.3 To check for stability at reasonable intervals, place a complete set of standard solutions of the metal being determined in the first position of the first sample tray. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill the remainder of each sample tray with unknown samples.

6.B.4 Begin analysis.

7. Calculations

Determine the concentration of the metal being determined in each sample from the printer output. Dilute those samples whose concentrations exceed the working range of the method. Repeat those analyses and multiply by the proper dilution factors.

8. Report

Report as directed in the individual, nonautomated methods.

9. Precision

See the individual, nonautomated methods.

Reference

Fishman, M. J., and Erdmann, D. E., 1970, Automation of atomic absorption analyses: Atomic Absorption Newsletter, v. 9, p. 88–89.

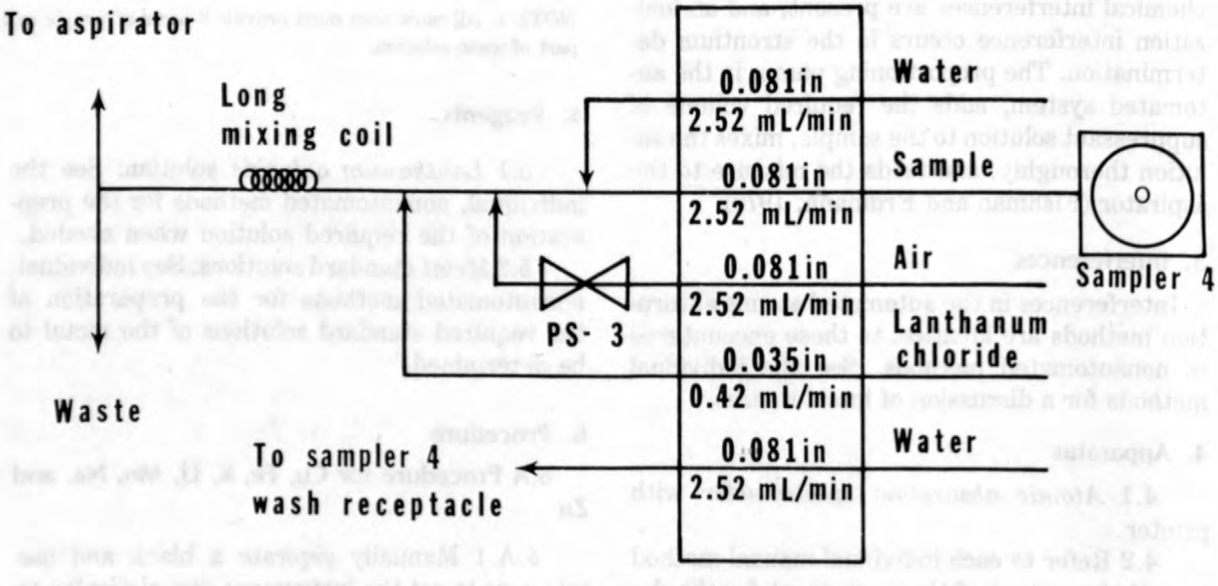


FIGURE 2.—Metals manifold.

Metals, total recoverable, atomic absorption spectrometric automated (I–4470–78)

Parameters and Codes: See individual metal method

1. Application

1.1 Automated atomic absorption spectrometric methods may be used to determine total or total recoverable metals in the same types of water-suspended sediment mixtures as the corresponding nonautomated methods. See the individual methods for a discussion of applications.

1.2 All samples of water-suspended sediment mixtures to be analyzed for total or total recoverable metals must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

Atomic absorption spectrometric procedures for the determination of several metals can be automated by the addition of a sampler, a proportioning pump, if needed, and a printer. Copper, iron, lithium, manganese, potassium, sodium, and zinc may be determined by direct aspiration from the sampler; no pretreatment of the sample is necessary. In the determination of calcium, magnesium, and strontium, however, chemical interferences are present, and an interference occurs in the strontium determination. The proportioning pump, in the automated system, adds the required volume of ionization-suppressant solution to the sample, mixes the solution thoroughly, and feeds the mixture to the aspirator (Fishman and Erdman, 1970).

3. Interferences

Interferences in the automated atomic absorption methods are identical to those encountered in nonautomated methods. See the individual methods for a discussion of interferences.

4. Apparatus

4.1 *Atomic absorption spectrometer* with printer.

4.2 Refer to the corresponding nonautomated method to optimize output of the instrument for each metal to be determined.

4.3 *Technician AutoAnalyzer II*, consisting of sampler and proportioning pump.

4.4 With this equipment the following operating conditions have been used (NOTE 1).

Element	*Concentration range*	*Samples per hour*
	(mg/L)	
Ca	0.1 to 60	40
Mg	0.1 to 50	40
K	0.1 to 10	60
Na	0.1 to 80	60
	(µg/L)	
Cu	10 to 1,000	50
Fe	10 to 1,000	30
Li	10 to 1,000	30
Mn	10 to 1,000	40
Sr	10 to 5,000	30
Zn	10 to 200	40

NOTE 1. All cams used must provide 2 parts of sample to 1 part of wash solution.

5. Reagents

5.1 *Lanthanum chloride* solution: See the individual, nonautomated methods for the preparation of the required solution when needed.

5.2 *Metal* standard solutions: See individual, nonautomated methods for the preparation of the required standard solutions of the metal to be determined.

6. Procedure

6.A Procedure for Cu, Fe, K, Li, Mn, Na, and Zn

6.A.1 Manually aspirate a blank and use auto zero to set the instrument digital display to read zero concentration. Similarly, aspirate standards and use auto concentration to set the instrument digital display to read the concentration of each standard. Calibrate the instrument each time a set of samples is analyzed.

6.A.2 To check for stability at reasonable intervals, place a complete set of standard solutions of the metal being determined in the first position of the first sample tray. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill the remainder of each sample tray with unknown samples that have undergone preliminary digestion-solubilization (Method I–3485).

6.A.3 Begin analysis.

6.B Procedure for Ca, Mg, and Sr.

6.B.1 Set up manifold (NOTES 2 and 3) (fig. 3).

NOTE 2. When maximum sensitivity is required for strontium and low concentrations of calcium and magnesium, a stream splitter may be used so that the 2.1 mm (0.081-in.) diameter water-tube also carries the sample stream.

NOTE 3. The manifold can be used for automatic dilution of samples for any determination.

6.B.2 Manually aspirate a blank and use auto zero to set the instrument digital display to read zero concentration. Similarly aspirate standards and use auto concentration to set the instrument digital display to read the concentrations of the standards. Calibrate the instrument each time a set of samples is analyzed.

6.B.3 To check for stability at reasonable intervals, place a complete set of standard solutions of the metal being determined in the first positions of the first sample tray. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill the remainder of each sample tray with unknown samples that have undergone the preliminary digestion-solubilization (Method I–3485).

6.B.4 Begin analysis.

7. Calculations

Determine the concentration of the metal being determined in each sample from the printer output. Dilute those samples whose concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report as directed in the individual, nonautomated methods for water-suspended sediment mixtures.

9. Precision

See the individual, nonautomated methods for water-suspended sediment mixtures.

Reference

Fishman, M. J., and Erdman, D. E., 1970, Automation of atomic absorption analyses: Atomic Absorption Newsletter, v. 9, p. 88–89.

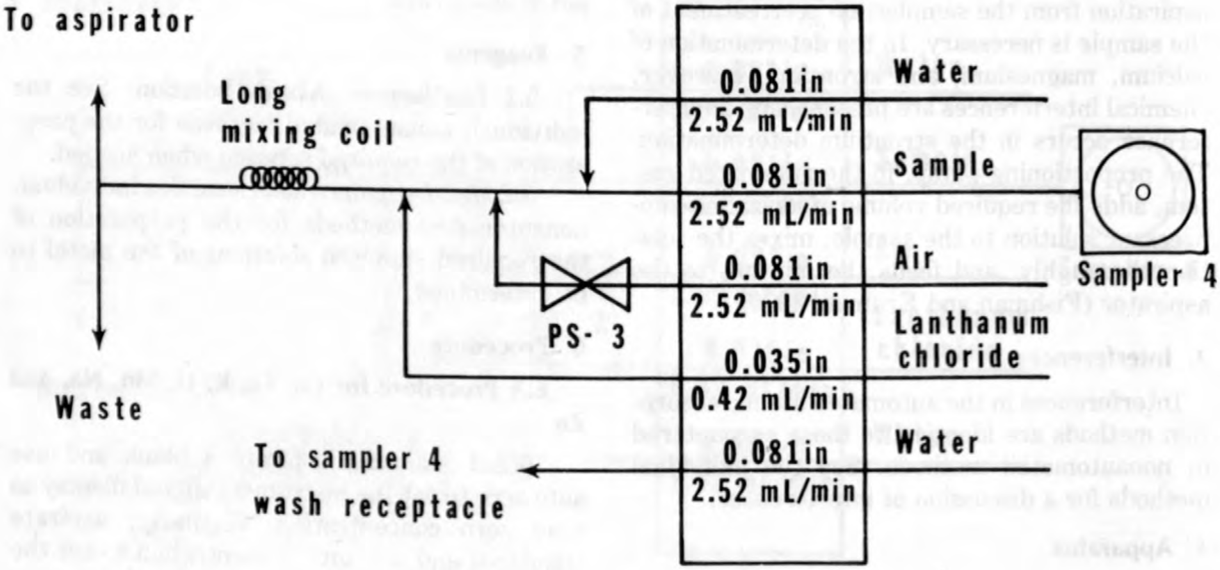


FIGURE 3.—Metals manifold.

Atomic absorption spectrometric methods

Aluminum, dissolved, atomic absorption spectrometric, chelation-extraction (I–1052–78)

Parameter and Code: Aluminum, dissolved (μg/L as Al): 01106

1. Application

1.1 This method may be used to analyze waters and brines containing from 10 to 1,000 μg/L of aluminum. Water samples containing more than 1,000 μg/L may be either diluted prior to chelation-extraction, or a smaller sample volume taken for analysis, or analyzed by Method I–1051.

1.2 If the iron concentration of the sample exceeds 10,000 μg/L, determine aluminum by direct atomic absorption (Method I–1051).

2. Summary of method

2.1 Aluminum is determined by atomic absorption spectrometry following chelation with 8-hydroxyquinoline and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the nitrous oxide-acetylene flame of the spectrometer.

2.2 Additional information about the principles of the method may be found in Snell and Snell (1959) and in Fishman (1972).

3. Interferences

3.1 Concentrations of iron greater than 10,000 μg/L interfere by suppressing the aluminum absorption.

3.2 Manganese concentrations up to 80,000 μg/L do not interfere if the turbidity in the MIBK extract is allowed to settle.

3.3 Magnesium forms an insoluble chelate with 8-hydroxyquinoline at pH 8.0 and tends to coprecipitate aluminum 8-hydroxyquinolate. However, the magnesium 8-hydroxyquinolate forms rather slowly (approximately 4 to 6 min); its interference can be avoided if the aluminum 8-hydroxyquinolate is extracted with MIBK immediately after the sample is buffered to pH 8.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	309.3 nm.
Source (hollow-cathode lamp)	Aluminum.
Burner	Nitrous-oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

5. Reagents

5.1 *Aluminum* standard solution I, 1.00 mL = 100 μg Al: Dissolve 1.758 g $AlK(SO_4)_2+12H_2O$ in demineralized water, add 1 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL with demineralized water.

5.2 *Aluminum* standard solution II, 1.00 mL = 1.00 μg Al: Dilute 10.0 mL aluminum standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.3 *Ammonium hydroxide-ammonium acetate buffer* solution: Dissolve 200 g $NH_4C_2H_3O_2$ and 70 mL concentrated NH_4OH (sp gr 0.90) in water and dilute to 1 L with demineralized water.

5.4 *8-Hydroxyquinoline* solution: Dissolve 20 g 8-hydroxyquinoline in 57 mL glacial acetic acid (sp gr 1.06) and 200 mL demineralized water, and dilute to 1 L with demineralized water.

5.5 *Methyl isobutyl ketone* (*MIBK*).

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.1 Pipet a volume of sample containing less than 100 μg Al (100 mL maximum) into a 200-mL volumetric flask and adjust the volume to approx 100 mL.

6.2 Prepare a blank and at least six standards and adjust the volume of each to approx 100 mL with demineralized water.

6.3 Add 2 mL 8-hydroxyquinoline solution and mix.

6.4 Add 10 mL ammonium hydroxide-ammonium acetate buffer solution to *one* sample and *immediately* add 10.0 mL MIBK. Shake vigorously for 15 sec. Each sample must be treated individually to avoid interference from magnesium. Each remaining sample, blank, and standard is treated in a like manner.

6.5 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask (NOTE 1).

NOTE 1. If the layers do not separate, allow to stand overnight.

6.6 While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter aluminum in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of aluminum exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

8. Report

Report aluminum, dissolved (01106), concentrations as follows: less than 100 μg/L nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 75 to 800 μg/L may be expressed as follows:

$$S_T = 0.073X + 14.97$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of aluminum, micrograms per liter.

9.2 The precision may also be expressed in terms of relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
4	75.0	23
3	433	9

References

Fishman, M. J., 1972, Determination of aluminum in water: Atomic Absorption Newsletter, v. 11, p. 46–47.

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 22.

Snell, F. D., and Snell, C. T., 1959, Colorimetric methods of analysis: Princeton, D. Van Nostrand Company, Incorporated, p. 181–183.

Aluminum, dissolved, atomic absorption spectrometric, direct (I–1051–78)

Parameter and Code: Aluminum, dissolved (μg/L as Al): 01106

1. Application

This method may be used to analyze water containing at least 100 μg/L of aluminum. If the sample solution prepared for analysis contains more than 5,000 μg/L Al, it must be either diluted or less scale expansion used. Sample solutions containing less than 100 μg/L, and brines, must be analyzed by Method I–1052, providing that the interferences discussed in that method are not exceeded.

2. Summary of method

Aluminum is determined by atomic absorption spectrometry by direct aspiration of the sample into a nitrous oxide-acetylene flame without preconcentration or pretreatment of the sample other than the addition of sodium chloride to control ionization of aluminum, and bis(2-ethoxyethyl)ether to enhance the sensitivity (Ramakrishna and others, 1967).

3. Interferences

3.1 Aluminum ionizes slightly in the nitrous oxide-acetylene flame; to control this effect the sodium ion concentration of each standard and sample is adjusted to at least 850 mg/L.

3.2 Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (9,000 mg/L), and iron (9×10^6 μg/L) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	309.3 nm.
Source (hollow-cathode lamp)	Aluminum.
Burner	Nitrous-oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

5. Reagents

5.1 *Aluminum* standard solution, 1.00 mL = 100 μg Al: Dissolve 1.758 g $AlK(SO_4)_2 \cdot 12H_2O$ in demineralized water, add 1 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL with demineralized water.

5.2 *Aluminum* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 5,000 μg/L of aluminum by appropriate dilution of aluminum standard solution I. To each standard working solution, add 1.0 mL sodium chloride solution and 1.0 mL bis(2-ethoxyethyl)ether for each 10 mL of standard solution. Prepare fresh daily.

5.3 *Bis(2-ethoxyethyl)ether:* Eastman Kodak Co. Chemical No. 4738 or equivalent.

5.4 *Sodium chloride* solution, 25.4 g/L: Dissolve 25.4 g NaCl in demineralized water and dilute to 1 L.

6. Procedure

6.1 Add 1.0 mL NaCl solution and 1.0 mL bis(2-ethoxyethyl)ether to 10.0 mL of sample and mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter aluminum in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of aluminum exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report aluminum, dissolved (01106), concentrations as follows: less than 10,000 μg/L, nearest 100 μg/L; 10,000 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of approximately 100 to 1,000 μg/L may be expressed as follows:

$$S_T = 0.158X + 35.3$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of aluminum, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μgL)*	*Relative deviation (percent)*
6	158	23
7	7	811

References

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 19.

Ramakrishna, T. V., West, P. W., and Robinson J. W., 1967, The determination of aluminum and beryllium by atomic absorption spectroscopy: Analytical Chemical Acta, v. 39, p. 81–87.

Aluminum, recoverable from bottom material, atomic absorption spectrometric, direct (I–5051–78)

Parameter and Code: Aluminum, recoverable from bottom material, dry wt (μg/g as Al): 01108

1. Application

1.1 This method may be used to analyze bottom material containing at least 10 μg/g of aluminum. If the sample solution prepared for analysis contains more than 5,000 μg/L Al, it must be either diluted or less scale expansion used.

1.2 Bottom material must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

Aluminum is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution into a nitrous oxide-acetylene flame without further preconcentration or pretreatment of the sample solution other than the addition of sodium chloride to control ionization of aluminum and bis(2-ethoxyethyl)ether to enhance the sensitivity (Ramakrishna and others, 1967).

3. Interferences

3.1 Aluminum ionizes slightly in the nitrous oxide-acetylene flame; to control this effect the sodium ion concentration of each standard and sample is adjusted to at least 850 mg/L.

3.2 Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (9,000 mg/L), and iron (9×10^6 μg/L) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	309.3 nm.
Source (hollow-cathode lamp)	Aluminum.
Burner	Nitrous-oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

5. Reagents

5.1 *Aluminum* standard solution, 1.00 mL = 100 μg Al: Dissolve 1.758 g $AlK(SO_4)_2 \cdot 12H_2O$ in demineralized water, add 1 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL with demineralized water.

5.2 *Aluminum* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 5,000 μg/L of aluminum by appropriate dilution of aluminum standard solution I. To each standard working solution, add 1.0 mL sodium chloride solution and 1.0 mL bis(2-ethoxyethyl)ether for each 10 mL of standard solution. Prepare fresh daily.

5.3 *Bis(2-ethoxyethyl)ether:* Eastman Kodak Co. Chemical No. 4738 or equivalent.

5.4 *Sodium chloride* solution, 25.4 g/L: Dissolve 25.4 g NaCl in demineralized water and dilute to 1 L.

6. Procedure

6.1 Add 1.0 mL NaCl solution and 1.0 mL bis(2-ethoxyethyl)ether to 10.0 mL of sample and mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use auto concentration to set instrument digital display to read concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter aluminum in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of aluminum exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per gram aluminum in bottom material samples, first determine the micrograms per liter aluminum in each sample as in 7.1; then

$$\text{Al}\ (\mu\text{g/g}) = \frac{\mu\text{g/L Al} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report aluminum, total in bottom material (01108), concentrations as follows: less than 1,000 μg/g, nearest 10 μg/g; 1,000 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 23 percent in the lower portion of the analytical range.

Reference

Ramakrishna, T. V., West, P. W., and Robinson, J. W., 1967, The determination of aluminum and beryllium by atomic absorption spectroscopy: Analytical Chemical Acta, v. 39, p. 81–87.

Aluminum, total recoverable, atomic absorption spectrometric, chelation-extraction (I–3052–78)

Parameter and Code: Aluminum, total recoverable (μg/L as Al): 01105

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing from 10 to 1,000 μg/L of aluminum. Water samples containing more than 1,000 μg/L may be either diluted prior to chelation-extraction or a smaller sample volume taken for analysis, or analyzed by Method I–3051.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

1.3 If the iron concentration of the prepared sample solution exceeds 10,000 μg/L, determine aluminum by direct atomic absorption (Method I–3051).

2. Summary of method

2.1 Aluminum is determined by atomic absorption spectrometry following chelation with 8-hydroxyquinoline and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the nitrous oxide-acetylene flame of the spectrometer.

2.2 Additional information about the principles of the method may be found in Snell and Snell (1959) and in Fishman (1972).

3. Interferences

3.1 Concentrations of iron greater than 10,000 μg/L interfere by suppressing the aluminum absorption.

3.2 Manganese concentrations up to 80,000 μg/L do not interfere if the turbidity in the MIBK extract is allowed to settle.

3.3 Magnesium forms as insoluble chelate with 8-hydroxyquinoline at pH 8.0 and tends to coprecipitate aluminum 8-hydroxyquinolate. However, the magnesium 8-hydroxyquinolate forms rather slowly (approximately 4 to 6 min); its interference can be avoided if the aluminum 8-hydroxyquinolate is extracted with MIBK immediately after the sample is buffered to pH 8.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	309.3 nm.
Source (hollow-cathode lamp)	Aluminum.
Burner	Nitrous-oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

5. Reagents

5.1 *Aluminum* standard solution I, 1.00 mL = 100 μg Al: Dissolve 1.758 g $AlK(SO_4)_2 \cdot 12H_2O$ in demineralized water, add 1 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL with demineralized water.

5.2 *Aluminum* standard solution II, 1.00 mL = 100 μg Al: Dilute 10.0 mL aluminum standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.3 *Ammonium hydroxide-ammonium acetate buffer* solution: Dissolve 200 g $NH_4C_2H_3O_2$ and 70 mL concentrated NH_4OH (sp gr 0.90) in water and dilute to 1 L with demineralized water.

5.4 *8-Hydroxyquinoline* solution: Dissolve 20 g 8-hydroxyquinoline in 57 mL glacial acetic acid (sp gr 1.06) and 200 mL demineralized water, and dilute to 1 L with demineralized water.

5.5 *Methyl isobutyl ketone* (MIBK).

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.1 Pipet a volume of sample containing less than 100 μg Al (100 mL maximum) into a 200-mL volumetric flask and adjust the volume to approx 100 mL.

6.2 Prepare a blank and at least six standards and adjust the volume of each to approx 100 mL with demineralized water.

6.3 Add 2 mL 8-hydroxyquinoline solution and mix.

6.4 Add 2.2 mL NH_4OH (concentrated, sp gr 0.90).

6.5 Add 10 mL ammonium hydroxide-ammonium acetate buffer solution to *one* sample and *immediately* add 10.0 mL MIBK. Shake vigorously for 15 sec. Each sample must be treated individually to avoid interference from magnesium. Each remaining sample, blank, and standard is treated in a like manner.

6.6 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask (NOTE 1).

NOTE 1. If the layers do not separate, allow to stand overnight.

6.7 While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter aluminum in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of aluminum exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

8. Report

Report aluminum, total (01105), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 23 percent at 75 μg/L and greater than 9 percent at 433 μg/L.

References

Fishman, M. J., 1972, Determination of aluminum in water: Atomic Absorption Newsletter, v. 11, p. 26–47.

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 22.

Snell, F. D., and Snell, C. T., 1959, Colorimetric methods of analysis: Princeton, D. Van Nostrand, p. 181–183.

Aluminum, total recoverable, atomic absorption spectrometric, direct (I–3051–78)

Parameter and Code: Alumimum, total recoverable (μg/L as Al): 01105

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 100 μg/L of aluminum. Sample solutions containing more than 5,000 μg/L must be either diluted or less scale expansion used. Sample solutions containing less than 100 μg/L, and brines, must be analyzed by Method I–3052, providing that the interferences discussed in that method are not exceeded.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

Aluminum is determined by atomic absorption spectrometry by direct aspiration of the sample into a nitrous oxide-acetylene flame without preconcentration or pretreatment of the sample other than the addition of sodium chloride to control ionization of aluminum, and bis(2-ethoxyethyl)ether to enhance the sensitivity (Ramakrishna and others, 1967).

3. Interferences

3.1 Aluminum ionizes slightly in the nitrous oxide-acetylene flame; to control this effect the sodium ion concentration of each sample and standard is adjusted to at least 850 mg/L.

3.2 Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (9,000 mg/L), and iron (9×10^6 μg/L) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	309.3 nm.
Source (hollow-cathode lamp)	Aluminum.
Burner	Nitrous-oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

5. Reagents

5.1 *Aluminum* standard solution, 1.00 mL = 100 μg Al: Dissolve 1.758 g $AlK(SO_4)_2 \cdot 12H_2O$ in demineralized water, add 1 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL with demineralized water.

5.2 *Aluminum* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 5,000 μg/L of aluminum by appropriate dilution of aluminum standard solution I. To each standard working solution, add 1.0 mL sodium chloride solution and 1.0 mL bis(2-ethoxyethyl)ether for each 10 mL of standard solution. Prepare fresh daily.

5.3 *Bis(2-ethoxyethyl)ether:* Eastman Kodak Co. Chemical No. 4738 or equivalent.

5.4 *Sodium chloride* solution, 25.4 g/L: Dissolve 25.4 g NaCl in demineralized water and dilute to 1 L.

6. Procedure

6.1 Add 1.0 mL NaCl solution and 1.0 mL bis(2-ethoxyethyl)ether to 10.0 mL of sample and mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter aluminum in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of aluminum exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report aluminum, total (01105), concentrations as follows: less than 10,000 μg/L, nearest 100 μg/L; 10,000 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 23 percent at 158 μg/L and greater than 9 percent at 811 μg/L.

References

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 19.

Ramakrishna, T. V., West, P. W., and Robinson, J. W., 1967, The determination of aluminum and beryllium by atomic absorption spectroscopy: Analytical Chemical Acta, v. 39, p. 81–87.

Antimony, dissolved, atomic absorption spectrometric, hydride (I–1055–78)

Parameter and Code: Antimony, dissolved (μg/L as Sb): 01095

1. Application

This method may be used to analyze waters containing at least 1 μg/L of antimony. Samples containing more than 15 μg/L must first be diluted.

2. Summary of method

Organic antimony-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The antimony so liberated, together with inorganic antimony originally present, is subsequently reacted with potassium iodide and stannous chloride, and finally with sodium borohydride to form stibine. The stibine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame, where it is determined by atomic absorption at 217.6 nm.

3. Interferences

3.1 Since the stibine is freed from the original sample matrix, interferences in the flame are minimized.

3.2 Selenium and arsenic, which also form gaseous hydrides, do not interfere at concentrations of 100 μg/L. Higher concentrations were not tested.

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Wavelength	217.6 nm.
Source (electrodeless discharge lamp).	Antimony.
Burner	Three-slot.
Fuel	Hydrogen.
Diluent	Nitrogen.
Carrier	Nitrogen.

4.3 Stibine vapor analyzer, figure 4, consisting of—

4.3.1 *Beaker*, berzelius, 200-mL capacity.

4.3.2 *Gas dispersion tube*, coarse frit (Scientific Glass Apparatus Co. No. JG–8500 has been found satisfactory).

4.3.3. *Medicine dropper* 2-mL capacity, minimum, or automatic pipettor, 5-mL capacity.

5. Reagents

5.1 *Antimony* standard solution I, 1.00 mL = 100 μg Sb: Dissolve 274.3 mg antimony potassium tartrate, $KSbOC_4H_4O_6 \cdot \frac{1}{2}H_2O$, in demineralized water and dilute to 1,000 mL with demineralized water.

5.2 *Antimony* standard solution II, 1.00 mL = 10 μg Sb: Dilute 50.0 mL antimony standard solution I to 500.0 mL with demineralized water.

5.3 *Antimony* standard solution III, 1.0 mL = 0.10 μg Sb: Dilute 5.0 mL antimony solution II to 500.0 mL with demineralized water. Prepare fresh before each use.

5.4 *Hydrochloric acid*, concentrated (sp gr 1.19).

5.5 *Nitric acid*, concentrated (sp gr 1.41).

5.6 *Potassium iodide* solution, 15 g/100 mL: Dissolve 15 g KI in 100 mL demineralized water. This solution is stable when stored in an amber bottle.

5.7 *Sodium borohydride* solution, 4 g/100 mL: Dissolve 4 g $NaBH_4$ pellets in 100 mL demineralized water (Alfa Products No. 14122 has been found satisfactory). Prepare fresh just before each use.

5.8 *Stannous chloride* solution, 4.2 g/100 mL concentrated HCl: Dissolve 5 g $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl (sp gr 1.19). This solution is stable if a few small pieces of mossy tin are added to prevent oxidation.

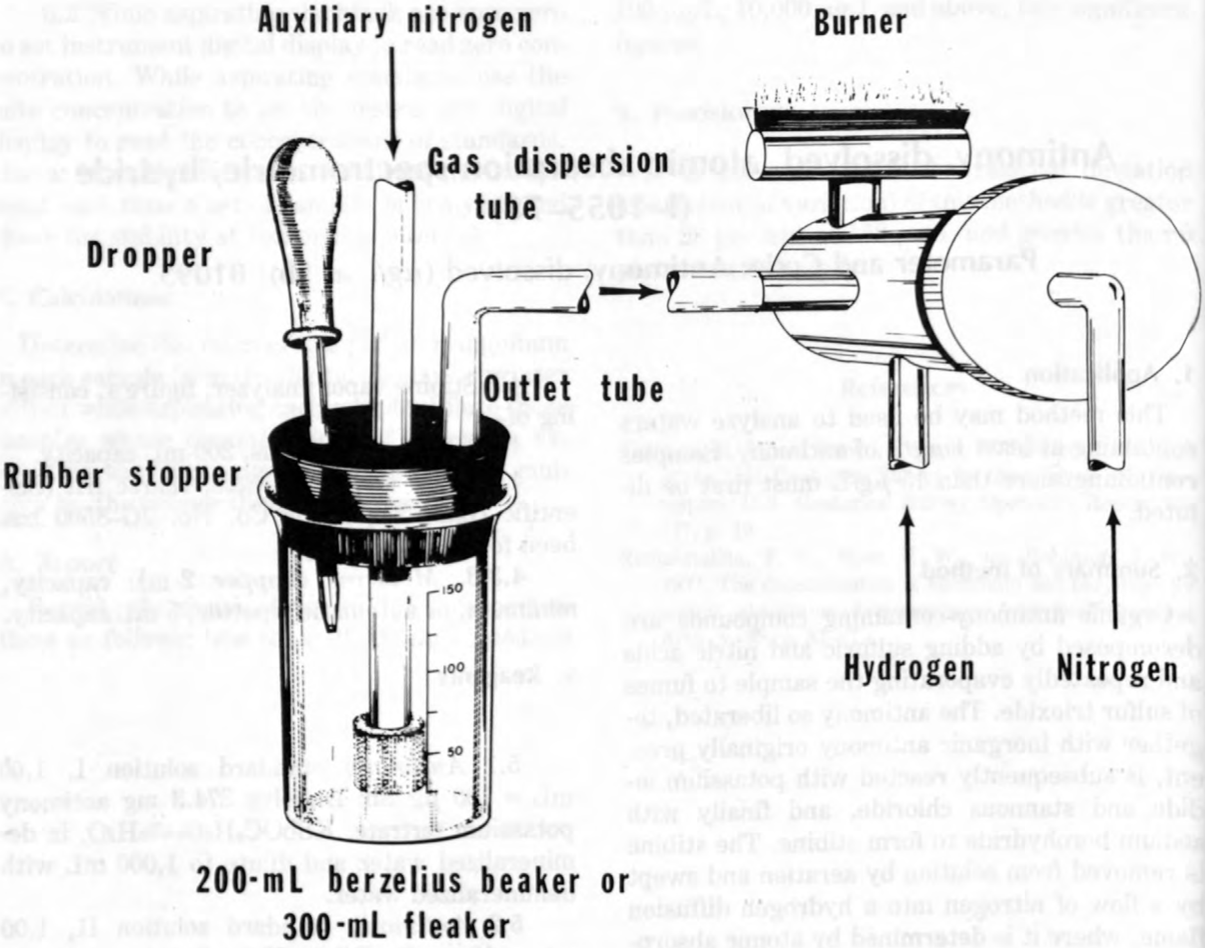


FIGURE 4.—Stibine vapor analyzer.

5.9 *Sulfuric acid 9M*: *Cautiously*, and with constant stirring and cooling, add 250 mL concentrated H_2SO_4 (sp gr 1.84) to 250 mL demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 1.5 μg Sb (100 mL maximum) into a 200-mL berzelius beaker and dilute to 100 mL with demineralized water.

6.2 Prepare, in 200-mL berzelius beakers, a blank and sufficient standards containing from 0.0 to 1.5 μg Sb by diluting 0.0 to 15.0 mL portions of antimony standard solution III to 100 mL with demineralized water.

6.3 To each beaker, add 7 mL 9*M* H_2SO_4 and 5 mL concentrated HNO_3. Add a small boiling chip and carefully evaporate to fumes of SO_3. Maintain an excess of HNO_3 until all organic matter is destroyed. This prevents darkening o the solution and possible reduction and loss of antimony. Cool, add 25 mL demineralized water, and again evaporate to fumes of SO_3 to expel oxides of nitrogen.

6.4 Cool, and adjust the volume of each beaker to approx 100 mL with demineralized water.

6.5 To each beaker, add successively, with thorough mixing after each addition, 8 mL concentrated HCl, 1 mL KI solution, and 0.5 mL $SnCl_2$ solution. Allow about 15 min for reaction to proceed.

6.6 Attach one beaker at a time to the rubber stopper containing the gas dispersion tube.

6.7 Fill the medicine dropper with 2 mL $NaBH_4$ solution and insert into hole in rubber stopper.

6.8 Add the $NaBH_4$ solution to the sample solution. After the absorbance has reached a maximum and has returned to the baseline, remove the beaker. Rinse the gas dispersion tube in demineralized water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

7. Calculations

7.1 Determine the micrograms of antimony in each sample from a plot of absorbances of standards. Exact reproducibility is not obtained, and an analytical curve must be prepared with each set of samples.

7.2 Determine the concentration of antimony in each sample as follows:

$$\text{Sb } (\mu\text{g/L}) = \frac{1{,}000}{\text{mL sample}} \times \mu\text{g Sb in sample.}$$

8. Report

Report antimony, dissolved (01095), concentrations as follows: less than 100 μg/L, nearest microgram per liter; 100 μg/L and above, two significant figures.

9. Precision

The statistical results expressed in terms of the relative deviation (coefficient of variation) are as follows:

Number of labs	*Mean (µg/L)*	*Relative deviation (percent)*
3	4.3	4
2 (13 replicates)	20.3	3

Reference

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 26.

Antimony, total in bottom material, atomic absorption spectrometric, hydride (I–5055–78)

Parameter and Code: Antimony, total in bottom material, dry wt (μg/g as Sb): 01098

1. Application

1.1 This method may be used to analyze bottom material containing at least 1 μg/L of antimony. Ordinarily, a 100-mg sample of prepared bottom material (Method P–0520) is taken for analysis. However, if the sample contains more than 15 μg/g of antimony, a smaller sample must be used.

1.2 Bottom-material samples must be prepared for analysis as directed in Method P–0520.

2. Summary of method

Organic antimony-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The antimony so liberated, together with inorganic antimony originally present, is subsequently reacted with potassium iodide and stannous chloride, and finally with sodium borohydride to form stibine. The stibine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame, where it is determined by atomic absorption spectrometry at 217.6 nm.

3. Interferences

3.1 Since the stibine is freed from the original sample matrix, interferences in the flame are minimized.

3.2 Selenium and arsenic, which also form gaseous hydrides, do not interfere at concentrations of 100 μg/L. Higher concentrations were not tested.

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	217.6 nm.
Source (electrodeless discharge lamp).	Antimony.
Burner	Three-slot.
Fuel	Hydrogen.
Diluent	Nitrogen.
Carrier	Nitrogen.

4.3 Stibine vapor analyzer, figure 5, consisting of—

4.3.1 *Beaker*, berzelius, 200-mL capacity.

4.3.2 *Gas dispersion tube*, coarse frit (Scientific Glass Apparatus Co. No. JG–8500 has been found satisfactory).

4.3.3. *Medicine dropper* 2-mL capacity, minimum, or automatic pipettor, 5-mL capacity.

5. Reagents

5.1 *Antimony* standard solution I, 1.00 mL = 100 μg Sb: Dissolve 274.3 mg antimony potassium tartrate, $KSbOC_4H_4O_6 \cdot \frac{1}{2}H_2O$, in demineralized water and dilute to 1,000 mL with demineralized water.

5.2 *Antimony* standard solution II, 1.00 mL = 10 μg Sb: Dilute 50.0 mL antimony standard solution I to 500.0 mL with demineralized water.

5.3 *Antimony* standard solution III, 1.0 mL = 0.10 μg Sb: Dilute 5.0 mL antimony standard solution II to 500.0 mL with demineralized water. Prepare fresh before each use.

5.4 *Hydrochloric acid*, concentrated (sp gr 1.19).

5.5 *Nitric acid*, concentrated (sp gr 1.41).

5.6 *Potassium iodide* solution, 15 g/100 mL: Dissolve 15 g KI in 100 mL demineralized water. This solution is stable when stored in an amber bottle.

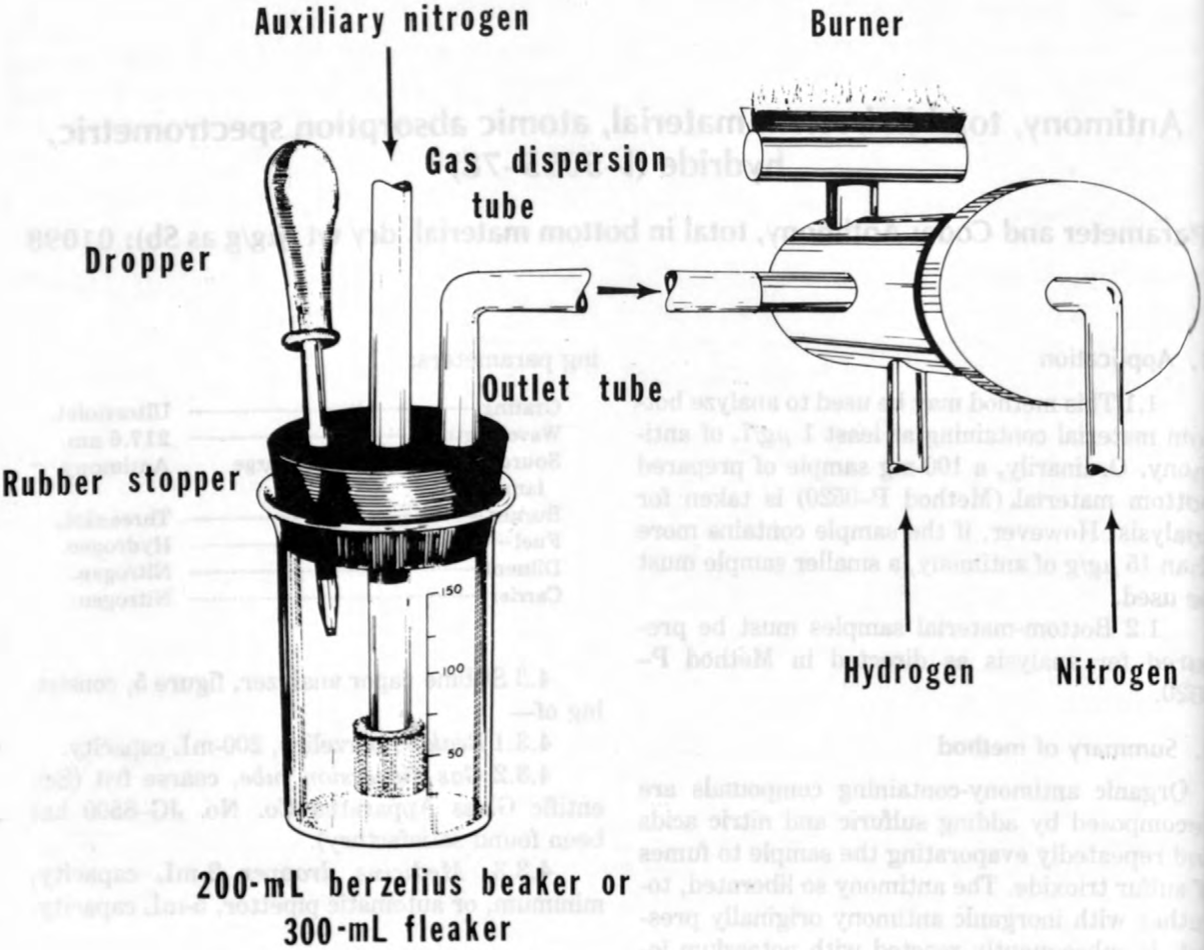


FIGURE 5.—Stibine vapor analyzer.

5.7 *Sodium borohydride* solution, 4 g/100 mL: Dissolve 4 g $NaBH_4$ pellets in 100 mL demineralized water (Alfa Products No. 14122 has been found satisfactory). Prepare fresh just before each use.

5.8 *Stannous chloride* solution, 4.2 g/100 mL concentrated HCl: Dissolve 5 g $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl (sp gr 1.19). This solution is stable if a few small pieces of mossy tin are added to prevent oxidation.

5.9 *Sulfuric acid 9M*: *Cautiously*, and with constant stirring and cooling, add 250 mL concentrated H_2SO_4 (sp gr 1.84) to 250 mL demineralized water.

6. Procedure

6.1 Weigh a portion of the prepared bottom-material sample (Method P–0520) containing less than 1.5 μg Sb (100 mg maximum); transfer to a 200-mL berzelius beaker and add 100 mL demineralized water (NOTE 1).

NOTE 1. Do not use more than 100 mg of bottom material; else severe bumping and loss of antimony may occur during the subsequent digestion of the sample.

6.2 Prepare, in 200-mL berzelius beakers, a blank and sufficient standards containing from 0.0 to 1.5 μg Sb by diluting 0.0 to 15.0 mL portions of antimony standard solution III to 100 mL with demineralized water.

6.3 To each beaker, add 7 mL 9M H_2SO_4 and 5 mL concentrated HNO_3. Add a small boiling chip and carefully evaporate to fumes of SO_3. Maintain an excess of HNO_3 until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of antimony. Cool, add 25 mL demineralized water, and again evaporate to fumes of SO_3 to expel oxides of nitrogen.

6.4 Cool, and adjust the volume of each beaker to approx 100 mL with demineralized water.

6.5 To each beaker, add successively, with thorough mixing after each addition, 8 mL concentrated HCl, 1 mL KI solution, and 0.5 mL $SnCl_2$ solution. Allow about 15 min for reaction to proceed.

6.6 Attach one beaker at a time to the rubber stopper containing the gas dispersion tube.

6.7 Fill the medicine dropper with 2 mL $NaBH_4$ solution and insert into hole in rubber stopper.

6.8 Add the $NaBH_4$ solution to the sample solution. After the absorbance has reached a maximum and has returned to the baseline, remove the beaker. Rinse the gas dispersion tube in demineralized water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

7. Calculations

7.1 Determine the micrograms of antimony in each sample from a plot of absorbances of standards. Exact reproducibility is not obtained, and an analytical curve must be prepared with each set of samples.

7.2 Determine the concentration of antimony in micrograms per gram of air-dried bottom material as follows:

$$\text{Sb } (\mu g/g) = \frac{\mu g \text{ Sb in sample}}{\text{sample weight (g)}}$$

8. Report

Report antimony, total in bottom material (01098), concentrations as follows: less than 100 μg/g, nearest microgram per gram; 100 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of the method is greater than 4 percent.

Antimony, total, atomic absorption spectrometric, hydride (I–3055–78)

Parameter and Code: Antimony, total (μg/L as Sb): 01097

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 1 μg/L of antimony. Samples containing more than 15 μg/L must first be diluted.

1.2 Water-suspended sediment mixtures may be analyzed by this procedure after sample has been thoroughly mixed by vigorous shaking and a suitable sample portion has been rapidly withdrawn from the mixture.

2. Summary of method

Organic antimony-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The antimony so liberated, together with inorganic antimony originally present, is subsequently reacted with potassium iodide and stannous chloride, and finally with sodium borohydride to form stibine. The stibine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame, where it is determined by atomic absorption at 217.6 nm.

3. Interferences

3.1 Since the stibine is freed from the original sample matrix, interferences in the flame are minimized.

3.2 Selenium and arsenic, which also form gaseous hydrides, do not interfere at concentrations of 100 μg/L. Higher concentrations were not tested.

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

4.2 Refer to manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	217.6 nm.
Source (electrodeless discharge lamp).	Antimony.
Burner	Three-slot.
Fuel	Hydrogen.
Diluent	Nitrogen.
Carrier	Nitrogen.

4.3 Stibine vapor analyzer, figure 6, consisting of—

4.3.1 *Beaker*, berzelius, 200-mL capacity.

4.3.2 *Gas dispersion tube*, coarse frit (Scientific Glass Apparatus Co. No. JG–8500 has been found satisfactory).

4.3.3. *Medicine dropper* 2-mL capacity, minimum, or automatic pipettor, 5-mL capacity.

5. Reagents

5.1 *Antimony* standard solution I, 1.00 mL = 100 μg Sb: Dissolve 274.3 mg antimony potassium tartrate, $KSbOC_4H_4O_6 \cdot \frac{1}{2}H_2O$, in demineralized water and dilute to 1,000 mL with demineralized water.

5.2 *Antimony* standard solution II, 1.00 mL = 10 μg Sb: Dilute 50.0 mL antimony standard solution I to 500.0 mL with demineralized water.

5.3 *Antimony* standard solution III, 1.0 mL = 0.10 μg Sb: Dilute 5.0 mL antimony standard solution II to 500.0 mL with demineralized water. Prepare fresh before each use.

5.4 *Hydrochloric acid*, concentrated (sp gr 1.19).

5.5 *Nitric acid*, concentrated (sp gr 1.41).

5.6 *Potassium iodide* solution, 15 g/100 mL: Dissolve 15 g KI in 100 mL demineralized water. This solution is stable when stored in an amber bottle.

5.7 *Sodium borohydride* solution, 4 g/100 mL: Dissolve 4 g $NaBH_4$ pellets in 100 mL de-

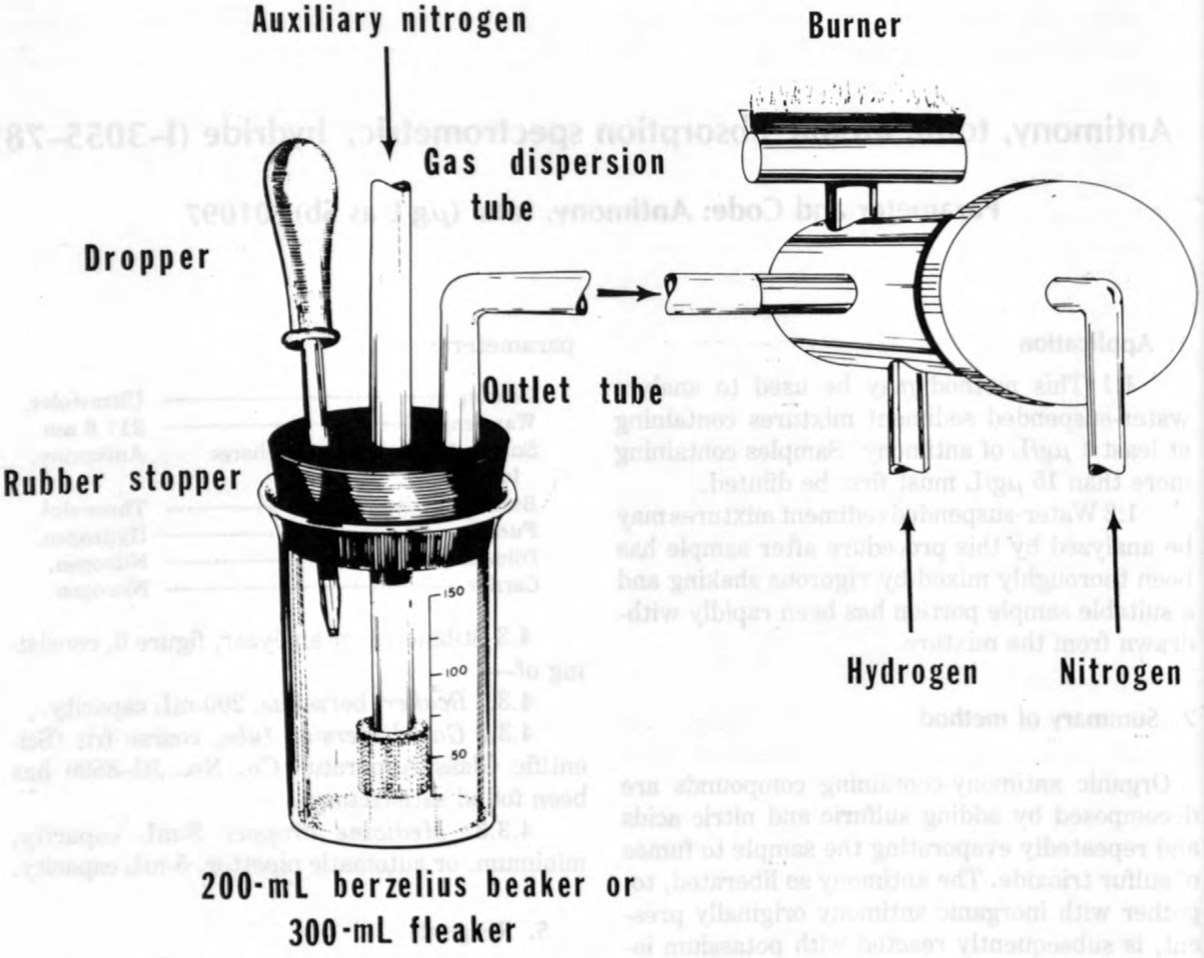


FIGURE 6.—Stibine vapor analyzer.

mineralized water (Alfa Products No. 14122 has been found satisfactory). Prepare fresh just before each use.

5.8 *Stannous chloride* solution, 4.2 g per 100 mL concentrated HCl: Dissolve 5 g $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl (sp gr 1.10). This solution is stable if a few small pieces of mossy tin are added to prevent oxidation.

5.9 *Sulfuric acid 9M*: *Cautiously*, and with constant stirring and cooling, add 250 mL concentration H_2SO_4 (sp gr 1.84) to 250 mL demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 1.5 μg Sb (100 mL maximum) into a 200-mL berzelius beaker and dilute to 100 mL with demineralized water.

6.2 Prepare, in 200-mL berzelius beakers, a blank and sufficient standards containing from 0.0 to 1.5 μg Sb by diluting 0.0 to 15.0 mL portions of antimony standard solution III to 100 mL with demineralized water.

6.3 To each beaker, add 7 mL $9M$ H_2SO_4 and 5 mL concentrated HNO_3. Add a small boiling chip and carefully evaporate to fumes of SO_3. Maintain an excess of HNO_3 until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of antimony. Cool, add 25 mL demineralized water, and again evaporate to fumes of SO_3 to expel oxides of nitrogen.

6.4 Cool, and adjust the volume of each beaker to approx 100 mL with demineralized water.

6.5 To each beaker, add successively, with thorough mixing after each addition, 8 mL con centrated HCl, 1 mL KI solution, and 0.5 mL $SnCl_2$ solution. Allow about 15 min for reaction to proceed.

6.6 Attach one beaker at a time to the rubber stopper containing the gas dispersion tube (fig. 6).

6.7 Fill the medicine dropper with 2 mL $NaBH_4$ solution and insert into hole in rubber stopper.

6.8 Add the $NaBH_4$ solution to the sample solution. After the absorbance has reached a maximum and has returned to the baseline, remove the beaker. Rinse the gas dispersion tube in demineralized water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

7. Calculations

7.1 Determine the micrograms of antimony in each sample from a plot of absorbances of standards. Exact reproducibility is not obtained, and an analytical curve must be prepared with each set of samples.

7.2 Determine the concentration of antimony in each sample as follows:

$$\text{Sb } (\mu\text{g/L}) = \frac{1{,}000}{\text{mL sample}} \times \mu\text{g Sb in sample.}$$

8. Report

Report antimony, total (01097), concentrations as follows: less than 100 μg/L, nearest microgram per liter; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of the method is greater than 4 percent at 4.3 μg/L and greater than 3 percent at 20.3 μg/L.

Reference

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 26.

Arsenic, dissolved, atomic absorption spectrometric, hydride (I–1062–78)

Parameter and Code: Arsenic, dissolved (μg/L as As): 01000

1. Application

1.1 This method may be used to analyze waters containing at least 1 μg/L of arsenic. Samples containing more than 20 μg/L must first be diluted.

1.2 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the strong-acid digestion, paragraphs 6.3 to 6.4 of the procedure.

2. Summary of method

Organic arsenic-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The arsenic(V) so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsenic(III) by potassium iodide and stannous chloride, and finally to gaseous arsine by zinc in hydrochloric acid solution. The arsine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame, where it is determined by atomic absorption at 193.7 nm (fig. 7).

3. Interferences

Since the arsine is freed from the original sample matrix, interferences in the flame are minimized.

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	193.7 nm.
Source (electrodeless discharge lamp).	Arsenic.
Burner	Three-slot.
Fuel	Hydrogen.
Diluent	Nitrogen.
Carrier	Nitrogen.

4.3 *Beaker, berzelius,* tall form without pouring spout, 200-mL capacity, or fleaker, 300-mL capacity.

4.4 *Gas dispersion tube,* coarse frit (Scientific Glass Apparatus Co. No. JG–8500 has been found to be satisfactory).

4.5 *Medicine dropper,* 2-mL capacity, minimum, or automatic pipettor, 5-mL capacity.

5. Reagents

5.1 *Arsenic* standard solution I, 1.00 mL = 1.00 mg As: Dissolve 1.320 g As_2O_3, dried for 1 h at 110°C, in 10 mL 10*M* NaOH and dilute to 1,000 mL with demineralized water. This solution is stable. However, it should probably be prepared fresh every 6 months.

5.2 *Arsenic* standard solution II, 1.00 mL = 10.0 μg As: Dilute 5.00 mL arsenic standard solution I to 500.0 mL with demineralized water. Discard after 3 months.

5.3 *Arsenic* standard solution III, 1.00 mL = 0.10 μg As: Dilute 5.00 mL arsenic standard solution II to 500.0 mL with demineralized water. Prepare fresh before each use.

5.4 *Hydrochloric acid,* concentrated (sp gr 1.19): Use analytical-grade acid with arsenic content not greater than 1×10^{-6} percent.

5.5 *Nitric acid,* concentrated (sp gr 1.41): Use analytical-grade acid with arsenic content not greater than 5×10^{-7} percent.

5.6 *Potassium iodide* solution, 15 g/100 mL: Dissolve 15 g KI in 100 mL demineralized water. This solution is stable when stored in an amber bottle.

5.7 *Stannous chloride* solution, 33.6 g/100 mL concentrated HCl: Dissolve 40 g arsenic-free

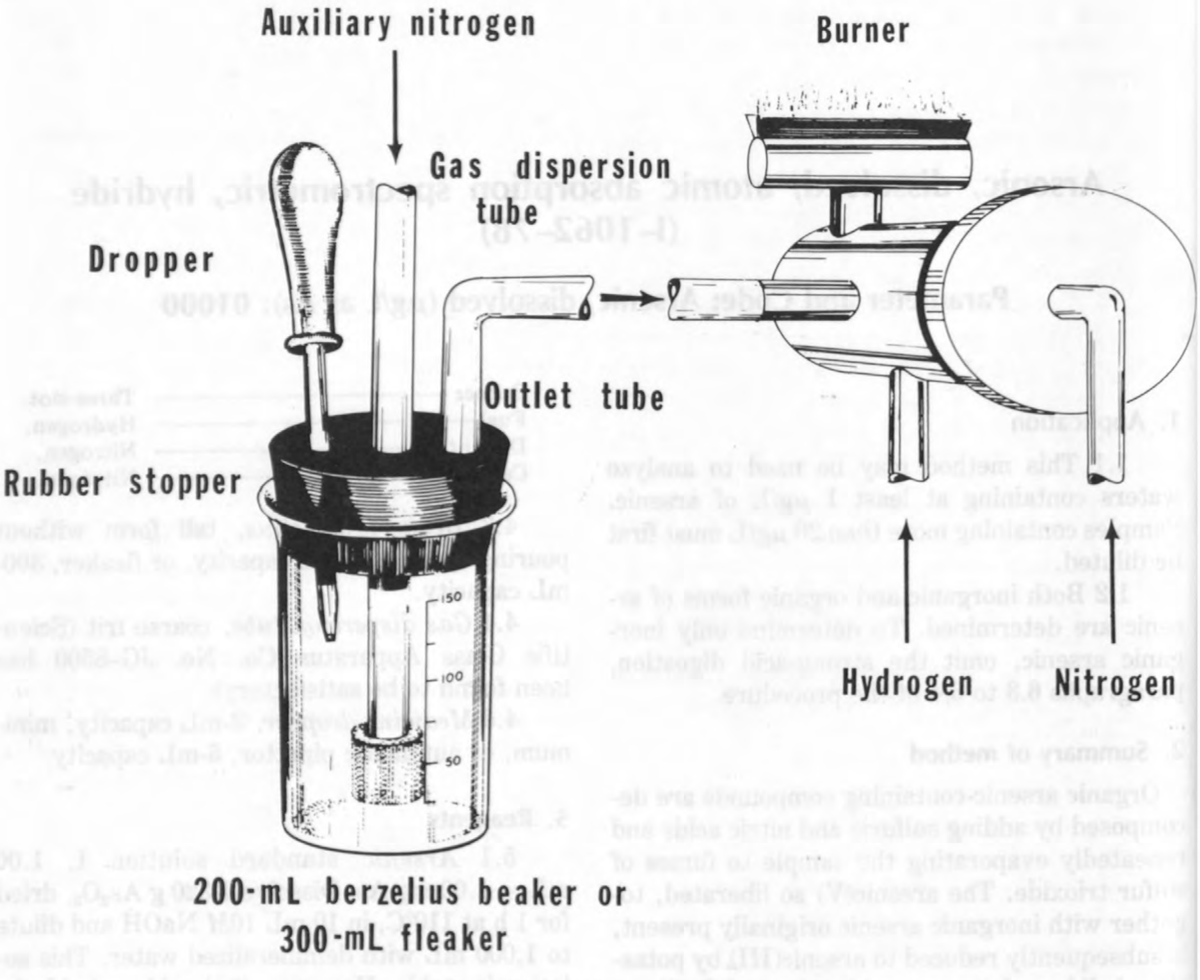


FIGURE 7.—Arsine vapor analyzer.

$SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl. This solution is stable if a few small pieces of mossy tin are added to prevent oxidation.

5.8 *Sulfuric acid 9M*: *Cautiously*, and with constant stirring and cooling, add 250 mL concentrated H_2SO_4 (sp gr 1.84) to 250 mL demineralized water.

5.9 *Zinc metal (dust)* suspension: Add 10 g zinc dust to 20 mL demineralized water. Fisher Scientific Co. reagent-grade zinc metal (dust) No. Z–5 has been found to be satisfactory.

6. Procedure

Clean all glassware used in this determination with dilute HCl (1 + 4) and rinse with demineralized water immediately before each use.

6.1 Pipet a volume of sample containing less than 1.0 μg As (50 mL maximum) into a 200-mL berzelius beaker and dilute to 50 mL (NOTE 1).

NOTE 1. If fleakers are used, maximum volume can be 100 mL. Reagent volumes should then be doubled.

6.2 Prepare, in 200-mL berzelius beakers or 300-mL fleakers, a blank and sufficient standards containing from 0.0 to 1.0 μg As by diluting 0.0 to 10.0-mL portions of arsenic standard solution III. Dilute each to approx 50 mL.

6.3 To each beaker, add 7 mL 9*M* H_2SO_4 and 5 mL concentrated HNO_3. Add a small boiling chip or glass beads and carefully evaporate to fumes of SO_3. Maintain an excess of HNO_3 until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of arsenic. Cool, add 25 mL demineralized water, and again evaporate to fumes of SO_3 to expel oxides of nitrogen (NOTE 2).

NOTE 2. If only inorganic arsenic is to be determined, omit steps 6.3 and 6.4.

6.4 Cool, and adjust each beaker to approx 50 mL with demineralized water.

6.5 To each beaker, add successively, with thorough mixing after each addition, 8 mL concentrated HCl, 4 mL KI solution, and 1.0 mL $SnCl_2$ solution. Allow about 15 min for reduction of the arsenic to the tervalent state.

6.6 Attach one beaker at a time to the rubber stopper containing the gas dispersion tube (fig. 7).

6.7 Fill the medicine dropper with 2 mL zinc dust suspension (NOTE 3) and insert into the hole in the rubber stopper. Alternatively, the zinc dust suspension may be delivered from an automatic pipettor.

NOTE 3. The zinc dust must be kept in suspension by continuous stirring. A magnetic stirrer is satisfactory.

6.8 Add the zinc dust suspension to the sample solution. After the absorbance has reached a maximum and has returned to the baseline, remove the beaker. Rinse the gas dispersion tube first in nitric acid (1 + 4), and then in distilled water before proceeding to next sample. Test each succeeding sample, blank, and standard in a like manner.

7. Calculations

7.1 Determine the micrograms of arsenic in the sample from a plot of absorbances of standards.

7.2 Determine the concentration of arsenic in each sample as follows:

$$\text{As } (\mu g/L) = \mu g \text{ As in sample} \times \frac{1{,}000}{\text{mL sample}}$$

8. Report

Report arsenic, dissolved (01000), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 2 to 20 μg/L may be expressed as follows:

$$S_T = 0.082X + 1.94$$

where

S_T=overall precision, micrograms per liter, and

X=concentration of arsenic, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
3	4.3	58
5	17.8	19

Reference

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 37.

Arsenic, dissolved, atomic absorption spectrometric, hydride, automated (I–2062–78)

Parameter and Code: Arsenic, dissolved (μg/L as As): 01000

1. Application

1.1 This method may be used to analyze waters containing at least 1 μg/L of arsenic. Samples containing more than 15 μg/L must first be diluted.

1.2 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the acid-persulfate digestion or the ultraviolet radiation.

2. Summary of method

2.1 Organic arsenic-containing compounds are decomposed either by sulfuric acid-potassium persulfate digestion or by ultraviolet radiation. The arsenic so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsine with sodium borohydride. The arsine is stripped from the solution with the aid of nitrogen and is then decomposed in a tube furnace placed in the optical path of an atomic absorption spectrometer.

2.2 For additional information on the determination of inorganic arsenic in water, see Pierce and others (1976).

3. Interferences

3.1 Since the arsine is freed from the original sample matrix, interferences are minimized.

3.2 A detailed inorganic interference study showed that most trace elements at concentration levels of less than 300 μg/L do not interfere (Pierce and Brown, 1976).

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

4.2 Refer to manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	193.7 nm.
Source (electrodeless discharge lamp).	Arsenic.

4.3 *Pyrometer,* portable, 0°C to 1,200°C. Thermolyne Model PM–20700 or equivalent.

4.4 *Stripping-condensing column,* pyrex, packed with 3- to 5-mm pyrex beads (fig. 8) (NOTE 1). Cooling of the condensing column is not required.

NOTE 1. Nitrogen is used to carry arsine to the tube furnace. Adjust the flow rate for maximum sensitivity by analyzing several identical standards. A flow rate of approx 200 mL/min has been found satisfactory.

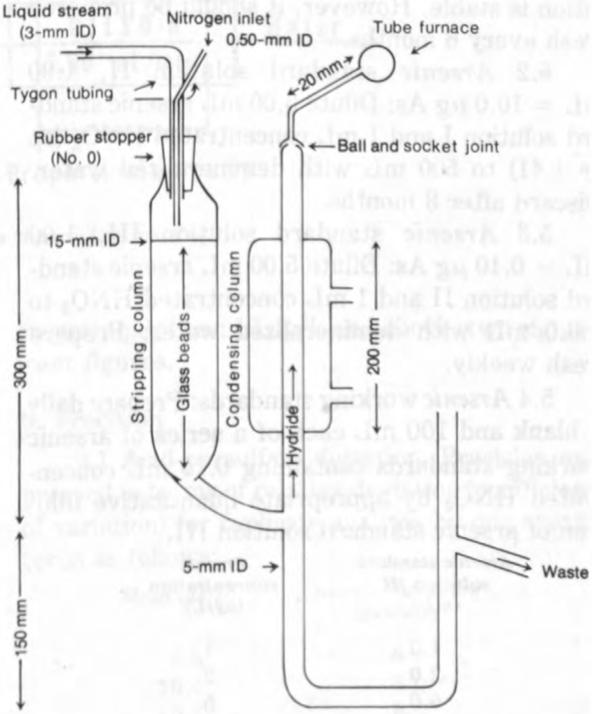


FIGURE 8.—Stripping-condensing column and quartz tube furnace.

4.5 *Tube furnace*, quartz, 10-mm i.d. by 100-mm long, with a quartz eyelet at each end of tube to anchor nickel-chrome wire and with a 2-mm i.d. quartz inlet tube attached at the center (fig. 8). Wrap the tube furnace with 5.5 m (18 ft) of 26-gauge nickel-chrome wire and cover with asbestos cloth. Mount in the optical path of the atomic absorption spectrometer.

4.6 *Technicon AutoAnalyzer II*, consisting of sampler with stirrer, manifold, ultraviolet digestor (optional—NOTE 2), proportioning pump, and heating bath (optional—NOTE 3).

Heating bath temperature-------------------- 95° C.

NOTE 2. The ultraviolet digestor can be used only when determining dissolved arsenic; it cannot be used when analyzing water-suspended sediment mixtures or bottom material.

NOTE 3. The heating bath is used only in the acid-persulfate digestion procedure.

4.7 *Autotransformer, variable:* Superior Powerstat type 3 PN 1010 or equivalent.

5. Reagents

5.1 *Arsenic* standard solution I, 1.00 mL = 1.00 mg As: Dissolve 1.320 g As_2O_3, dried for 1 h at 110°C, in 10 mL 10*M* NaOH and dilute to 1,000 mL with demineralized water. This solution is stable. However, it should be prepared fresh every 6 months.

5.2 *Arsenic* standard solution II, 1.00 mL = 10.0 μg As: Dilute 5.00 mL arsenic standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 500 mL with demineralized water. Discard after 3 months.

5.3 *Arsenic* standard solution III, 1.00 mL = 0.10 μg As: Dilute 5.00 mL arsenic standard solution II and 1 mL concentrated HNO_3 to 500.0 mL with demineralized water. Prepare fresh weekly.

5.4 *Arsenic* working standards: Prepare daily a blank and 100 mL each of a series of arsenic working standards containing 0.15 mL concentrated HNO_3 by appropriate quantitative dilution of arsenic standard solution III.

Arsenic standard solution III (mL)	*Arsenic concentration (µg/L)*
1.0	1
2.0	2
5.0	5
10.0	10
15.0	15

5.5 *Hydrochloric acid*, 6*M*: Add 500 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.6 *Potassium iodide* solution, 100 g/L: Dissolve 100 g KI in demineralized water and dilute to 1 L.

5.7 *Potassium persulfate* solution, 50 g/L: Dissolve 50 g $K_2S_2O_8$ in demineralized water with warming and dilute to 1 L after the solution has cooled.

5.8 *Sodium borohydride* solution, 5 g/L: Dissolve 5 g $NaBH_4$ and 40 g NaOH in demineralized water and dilute to 1 L.

5.9 *Sodium hydroxide* solution, 10*M*: *Cautiously* dissolve 400 g NaOH in demineralized water and dilute to 1 L.

5.10 *Sulfuric acid* solution, 3*M*: Add slowly with constant stirring, 167 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Apply a voltage of 47 volts or more (variable transformer) as necessary to the tube furnace to maintain a constant temperature of 800°C (NOTE 4).

NOTE 4. Use the portable pyrometer to check the temperature of the tube furnace. Place the tip of the thermocouple just inside the end of the tube.

6.2 Set up manifold—acid persulfate (fig. 9) or ultraviolet radiation (fig. 10).

6.3 Feed all reagents through the system, using demineralized water in the sample line. Allow the heating bath to warm to 95°C.

6.4 Beginning with the most concentrated standard (NOTE 5), place a complete set of standards in the first positions of the first sample tray. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent trays. Fill remainder of each sample tray with unknown samples.

NOTE 5. It is best to place two or three samples of the most concentrated standard at the beginning, since the first peak is usually low. The first standard should not be used in any of the calculations.

6.5 Remove the sample line from the demineralized water wash solution when the baseline stabilizes and begin the analyses.

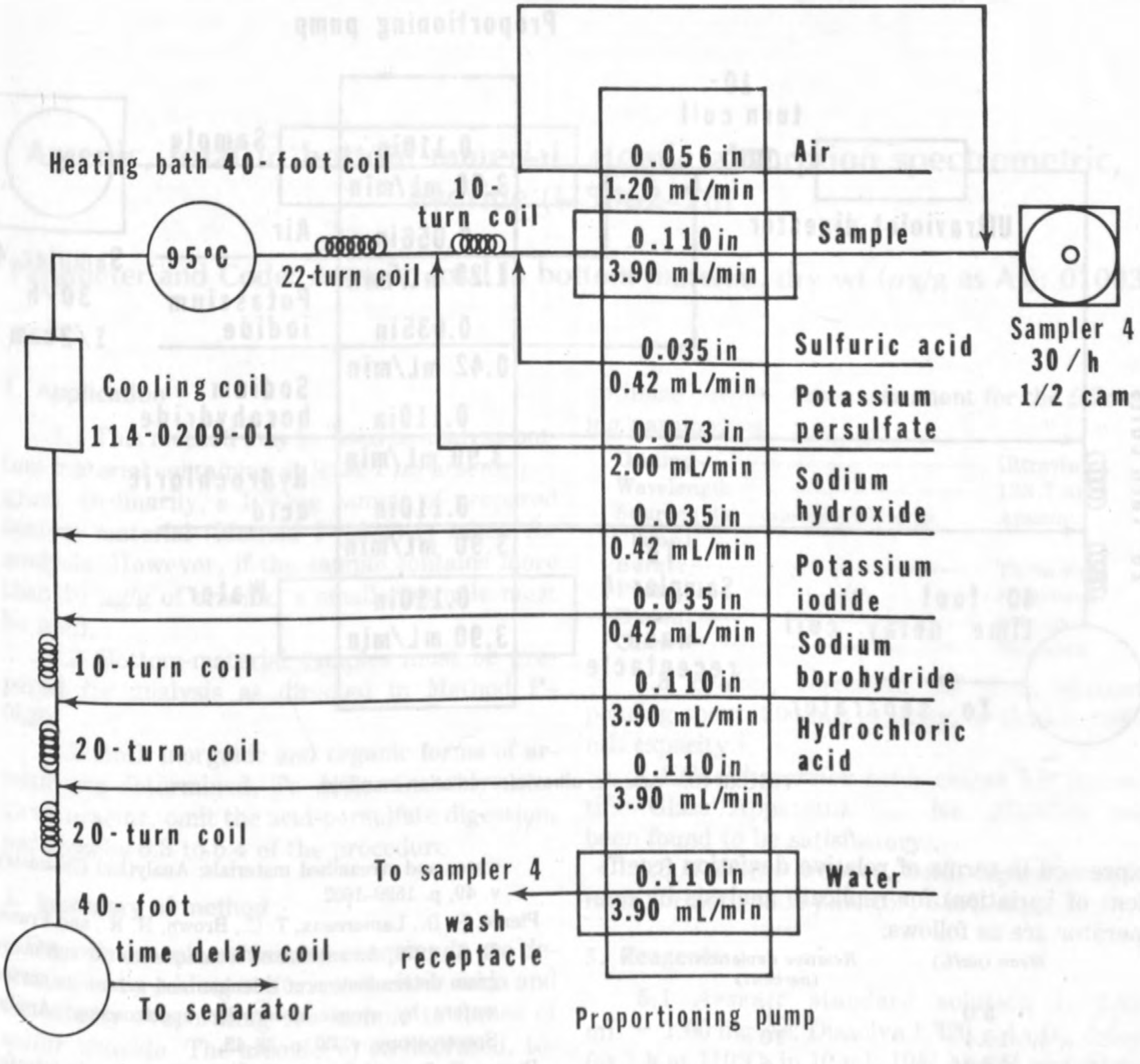


FIGURE 9.—Arsenic, acid-persulfate manifold.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective arsenic concentration.

7.2 Compute the concentration of arsenic in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report arsenic, dissolved (01000), concentrations as follows: less than 10 µg/L, nearest microgram per liter; 10 µg/L and above, two significant figures.

9. Precision

9.1 Acid-persulfate digestion: Precision expressed in terms of relative deviation (coefficient of variation) for replicate analysis by one operator is as follows:

Mean (µg/L)	*Relative deviation (percent)*
5.8	5
10.4	5
15.5	5

9.2 Ultraviolet radiation: Statistical results

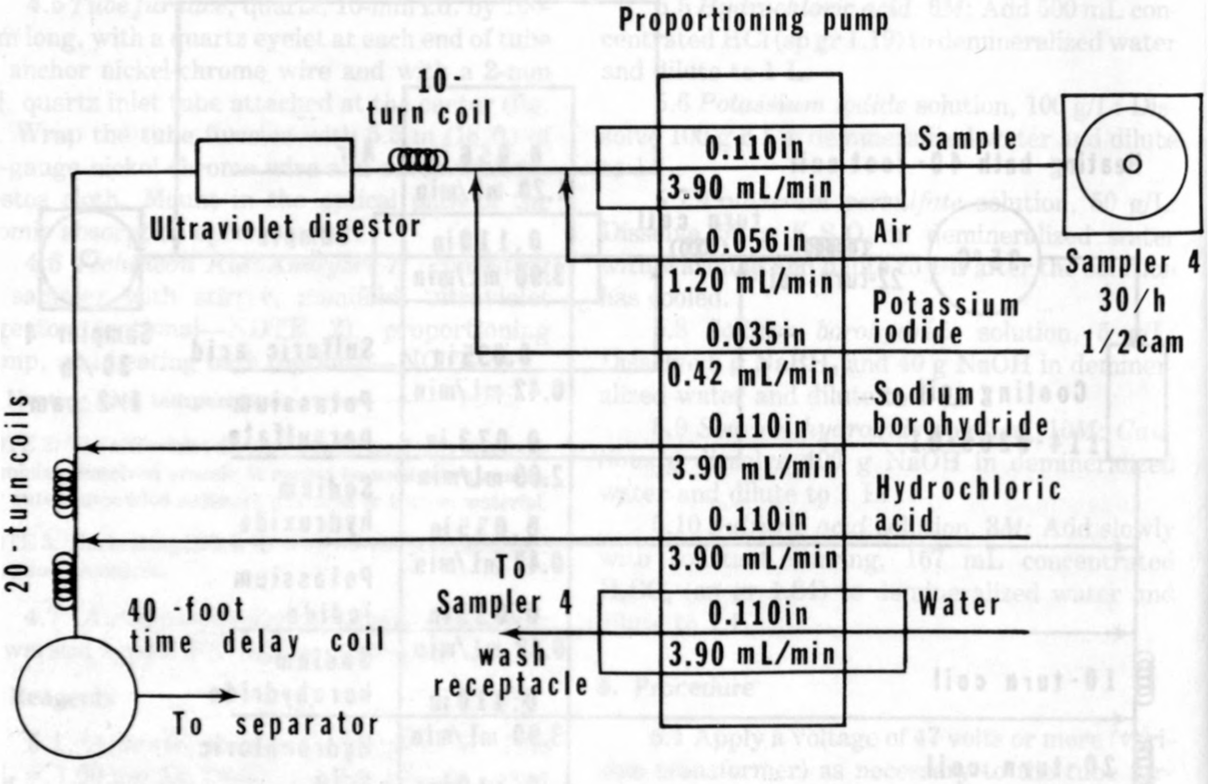


FIGURE 10.—Arsenic, ultraviolet radiation manifold.

expressed in terms of relative deviation (coefficient of variation) for replicate analysis by one operator are as follows:

Mean (µg/L)	*Relative deviation (percent)*
5.0	10
10.4	10
13.8	4

References

Fishman, M. J., Spencer, R. R., 1977, Automated atomic absorption spectrometric determination of total arsenic in water and streambed materials: Analytical Chemistry, v. 49, p. 1599–1602.

Pierce, F. D., Lamoreaux, T. C., Brown, H. R., and Fraser, R. S., 1976, An automated technique for the sub-microgram determination of selenium and arsenic in surface waters by atomic absorption spectroscopy: Applied Spectroscopy, v. 30, p. 38–42.

Pierce, F. D., and Brown, H. R., 1976, Inorganic interference study of automated arsenic and selenium determination with atomic absorption spectrometry: Analytical Chemistry, v. 48, p. 693–695.

Arsenic, total in bottom material, atomic absorption spectrometric, hydride (I–5062–78)

Parameter and Code: Arsenic, total in bottom material, dry wt (μg/g as As): 01003

1. Application

1.1 This method may be used to analyze bottom material containing at least 1 μg arsenic per gram. Ordinarily, a 100-mg sample of prepared bottom material (Method P–0520) is taken for analysis. However, if the sample contains more than 10 μg/g of arsenic, a smaller sample must be used.

1.2 Bottom-material samples must be prepared for analysis as directed in Method P–0520.

1.3 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the acid-persulfate digestion, paragraphs 6.3 to 6.4 of the procedure.

2. Summary of method

Organic arsenic-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The arsenic(V) so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsenic(III) by potassium iodide and stannous chloride, and finally to gaseous arsine by zinc in hydrochloric acid solution. The arsine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame, where it is determined by atomic absorption at 193.7 nm (fig. 11).

3. Interferences

Since the arsine is freed from the original sample matrix, interferences in the flame are minimized.

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	193.7 nm.
Source (electrodeless discharge lamp).	Arsenic.
Burner	Three-slot.
Fuel	Hydrogen.
Diluent	Nitrogen.
Carrier	Nitrogen.

4.3 *Beaker, berzelius,* tall form without pouring spout, 200-mL capacity, or fleaker, 300-mL capacity.

4.4 *Gas dispersion tube,* coarse frit (Scientific Glass Apparatus Co. No. JG–8500 has been found to be satisfactory).

4.5 *Medicine dropper,* 2-mL capacity, minimum, or automatic pipettor, 5-mL capacity.

5. Reagents

5.1 *Arsenic* standard solution I, 1.00 mL = 1.00 mg As: Dissolve 1.320 g As_2O_3, dried for 1 h at 110°C, in 10 mL 10*M* NaOH and dilute to 1,000 mL with demineralized water. This solution is stable. However, it should be prepared fresh every 6 months.

5.2. *Arsenic* standard solution II, 1.00 mL = 10.0 μg As: Dilute 5.00 mL arsenic standard solution I to 500.0 mL with demineralized water. Discard after 3 months.

5.3 *Arsenic* standard solution III, 1.00 mL = 0.10 μg As: Dilute 5.00 mL arsenic standard solution II to 500.0 mL with demineralized water. Prepare fresh weekly.

5.4 *Hydrochloric acid,* concentrated (sp gr 1.19): Use analytical-grade acid with arsenic content not greater than 1×10^{-6} percent.

5.5 *Nitric acid,* concentrated (sp gr 1.41): Use analytical-grade acid with arsenic content not greater than 5×10^{-7} percent.

5.6 *Potassium iodide* solution, 15 g/100 mL:

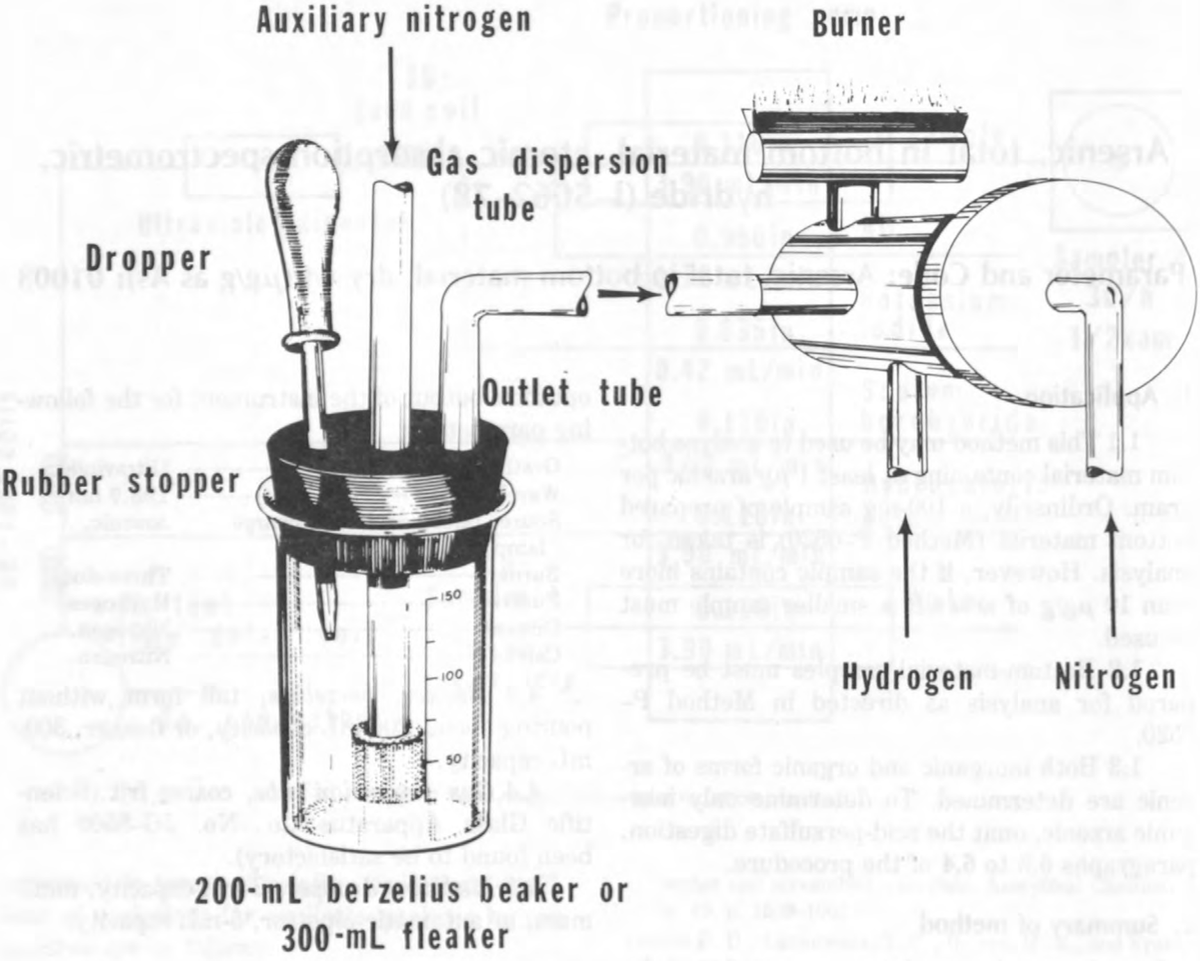


FIGURE 11.—Arsine vapor analyzer.

Dissolve 15 g KI in 100 mL demineralized water. This solution is stable when stored in an amber bottle.

5.7 *Stannous chloride* solution, 33.6 g/100 mL concentrated HCl: Dissolve 40 g arsenic-free $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl. This solution is stable if a few small pieces of mossy tin are added to the bottle to prevent oxidation.

5.8 *Sulfuric acid, 9M*: *Cautiously*, and with constant stirring and cooling, add 250 mL concentrated H_2SO_4 (sp gr 1.84) to 250 mL demineralized water.

5.9 *Zinc metal (dust)* suspension: Add 10 g zinc dust to 20 mL demineralized water. Fisher Scientific Co. reagent-grade zinc metal (dust) No. Z–5 has been found to be satisfactory.

6. Procedure

Clean all glassware used in this determination with dilute HCl (1 + 4) and rinse with demineralized water immediately before each use.

6.1 Weigh a portion of the prepared bottom-material sample (Method P–0520) containing less than 1 μg of As (100 mg max) (NOTE 1); transfer to a 200-mL berzelius beaker and add 100 mL demineralized water (NOTE 2).

NOTE 1. Do not use more than 100 mg of bottom material to avoid severe bumping and loss of arsenic.

NOTE 2. If fleakers are used, maximum volume can be 100 mL. Reagent volumes should then be doubled.

6.2 Prepare, in 200-mL berzelius beakers or 300-mL fleakers, a blank and sufficient standards containing from 0.0 to 1.0 μg As by diluting 0.0 to 10.0-mL portions of arsenic standard solution III. Dilute each to approx 50 mL.

6.3 To each beaker, add 7 mL 9*M* H_2SO_4 and 5 mL concentrated HNO_3. Add a small boiling chip or glass beads and carefully evaporate to fumes of SO_3. Maintain an excess of HNO_3 until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of arsenic. Cool, add 25 mL demineralized water, and again evaporate to fumes of SO_3 to expel oxides of nitrogen (NOTE 3).

NOTE 3. If only inorganic arsenic is to be determined, omit steps 6.3 to 6.4.

6.4 Cool, and adjust each beaker to approx 50 mL with demineralized water.

6.5 To each beaker, add successively, with thorough mixing after each addition, 8 mL concentrated HCl, 4 mL KI solution, and 1.0 mL $SnCl_2$ solution. Allow about 15 min for reduction of the arsenic to the tervalent state.

6.6 Attach one beaker at a time to the rubber stopper containing the gas dispersion tube.

6.7 Fill the medicine dropper with 2 mL zinc dust suspension (NOTE 4) and insert into the hole in the rubber stopper. Alternatively, the zinc dust suspension may be delivered from an automatic pipettor.

NOTE 4. The zinc dust must be kept in suspension by continuous stirring. A magnetic stirrer is satisfactory.

6.8 Add the zinc dust suspension to the sample solution. After the absorbance has reached a maximum and has returned to the baseline remove the beaker. Rinse the gas dispersion tube first in nitric acid (1 + 4), and then in distilled water before proceeding to next sample. Test each succeeding sample, blank, and standard in a like manner.

7. Calculations

7.1 Determine the micrograms of arsenic in each sample from a plot of absorbances of standards.

7.2 Determine the concentration of arsenic in micrograms per gram of air-dried bottom material sample as follows:

$$\text{AS } (\mu g/g) = \frac{\mu g \text{ As in sample}}{\text{sample weight (g)}}$$

8. Report

Report arsenic, total in bottom material (01003), concentrations as follows: less than 10 $\mu g/g$, nearest microgram per gram; 10 $\mu g/g$ and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of the method is greater than 58 percent in the lower portion of the analytical range and is greater than 19 percent in the upper portion of the analytical range.

Arsenic, total in bottom material, atomic absorption spectrometric, hydride, automated (I–6062–78)

Parameter and Code: Arsenic, total in bottom material, dry wt ($\mu g/g$ as As): 01003

1. Application

1.1 This method may be used to analyze bottom material containing at least 1 $\mu g/g$ of arsenic (NOTE 1). For samples containing more than 15 $\mu g/g$, use less sediment.

NOTE 1. Do not use more than 100 mg sediment, because erratic results and large blanks will occur.

1.2 Bottom materials may be analyzed by this procedure after they have been prepared as directed in Method P–0520.

1.3 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the acid-persulfate digestion.

2. Summary of method

2.1 Organic arsenic-containing compounds are decomposed by sulfuric acid-potassium persulfate digestion. The arsenic so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsine with sodium borohydride. The arsine is stripped from the solution with the aid of nitrogen and is then decomposed in a tube furnace placed in the optical path of an atomic absorption spectrometer.

2.2 For additional information on the determination of inorganic arsenic in water, see Pierce and others (1976).

3. Interferences

3.1 Since the arsine is freed from the original sample matrix, interferences in the flame are minimized.

3.2 A detailed inorganic interference study showed that most trace elements at concentration levels of less than 300 $\mu g/L$ do not interfere (Pierce and Brown, 1976).

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

4.2 Refer to manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	193.7 nm.
Source (electrodeless discharge lamp).	Arsenic.

4.3 *Pyrometer,* portable, 0°C to 1,200°C. Thermolyne Model PM–20700 or equivalent.

4.4 *Stripping-condensing column,* pyrex, packed with 3- to 5-mm pyrex beads (fig. 12)

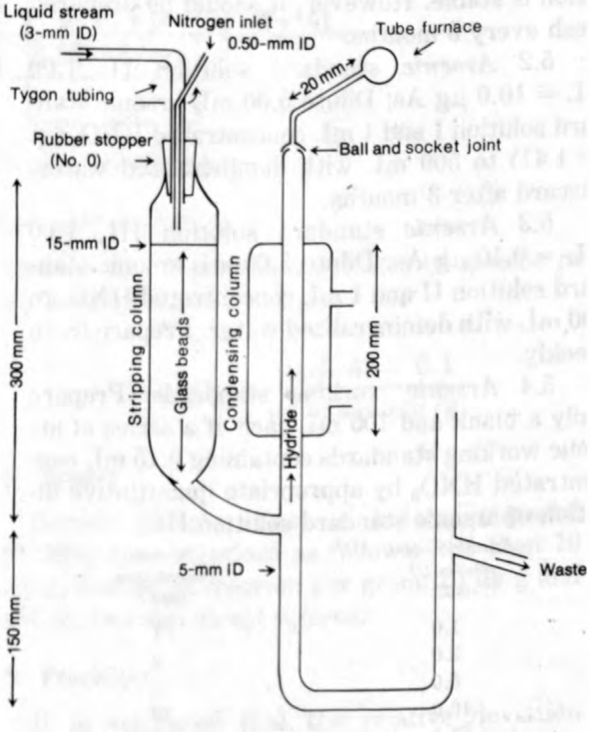


FIGURE 12.—Stripping-condensing column and quartz tube furnace.

(NOTE 2). Cooling of condensing column is not required.

NOTE 2. Nitrogen is used to carry arsine to the tube furnace. Adjust the flow rate for maximum sensitivity by analyzing several identical standards. A flow rate of approx 200 mL/min has been satisfactory.

4.5 *Tube furnace*, quartz, 10-mm i.d. by 100-mm long, with a quartz eyelet at each end of the tube to anchor nickel-chrome wire and with a 2-mm i.d. quartz inlet tube attached at the center (fig. 12). Wrap the tube furnace with 5.5 m (18 ft) of 26-gauge nickel-chrome and cover with asbestos cloth. Mount in the optical path of the atomic absorption spectrometer.

4.6 *Tecnicon AutoAnalyzer II*, consisting of sampler with stirrer, manifold, proportioning pump, and heating bath.

Heating bath temperature .... 95° C.

4.7 *Autotransformer, variable;* Superior Powerstat type 3 PN 1010 or equivalent.

5. Reagents

5.1 *Arsenic* standard solution I, 1.00 mL = 1.00 mg As: Dissolve 1.320 g As_2O_3, dried for 1 h at 110°C, in 10 mL 10*M* NaOH and dilute to 1,000 mL with demineralized water. This solution is stable. However, it should be prepared fresh every 6 months.

5.2 *Arsenic* standard solution II, 1.00 mL = 10.0 μg As: Dilute 5.00 mL arsenic standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 500 mL with demineralized water. Discard after 3 months.

5.3 *Arsenic* standard solution III, 1.00 mL = 0.10 μg As: Dilute 5.00 mL arsenic standard solution II and 1 mL concentrated HNO_3 to 500 mL with demineralized water. Prepare fresh weekly.

5.4 *Arsenic* working standards: Prepare daily a blank and 100 mL each of a series of arsenic working standards containing 0.15 mL concentrated HNO_3 by appropriate quantitative dilution of arsenic standard solution III.

Arsenic standard solution III (mL)	*Arsenic concentration (µg/L)*
1.0	1
2.0	2
5.0	5
10.0	10
15.0	15

5.5 *Hydrochloric acid*, 6*M*: Add 500 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.6 *Potassium iodide* solution, 100 g/L: Dissolve 100 g KI in demineralized water and dilute to 1 L.

5.7 *Potassium persulfate* solution, 50 g/L: Dissolve 50 g $K_2S_2O_8$ in demineralized water with warming and dilute to 1 L after the solution has cooled.

5.8 *Sodium borohydride* solution, 5 g/L: Dissolve 5 g $NaBH_4$ and 40 g NaOH in demineralized water and dilute to 1 L.

5.9 *Sodium hydroxide* solution, 10*M*: *Cautiously* dissolve 400 g NaOH in demineralized water and dilute to 1 L.

5.10 *Sulfuric acid* solution, 3*M*: Add slowly with constant stirring, 167 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Apply a voltage of 47 volts or more (variable transformer) as necessary to the tube furnace to maintain a constant temperature of 800°C (NOTE 3).

NOTE 3. Use a portable pyrometer to check the temperature of the tube furnace. Place the tip of the thermocouple just inside the end of the tube.

6.2 Set up manifold (fig. 13).

6.3 Feed all reagents through the system, using demineralized water in the sample line. Allow the heating bath to warm to 95°C.

6.4 Weigh 100 mg or less of bottom material sample (1.5 μg As, max), transfer to a 100-mL flask and dilute to volume with demineralized water.

6.5 Beginning with the most concentrated standard (NOTE 4), place a complete set of standards in the first positions of the first sample tray. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent trays. Fill remainder of each sample tray with unknown samples (well mixed).

NOTE 4. It is best to place two or three samples of the most concentrated standard at the beginning, since the first peak is usually low. The first standard should not be used in any of the calculations.

6.6 Remove the sample line from the demin-

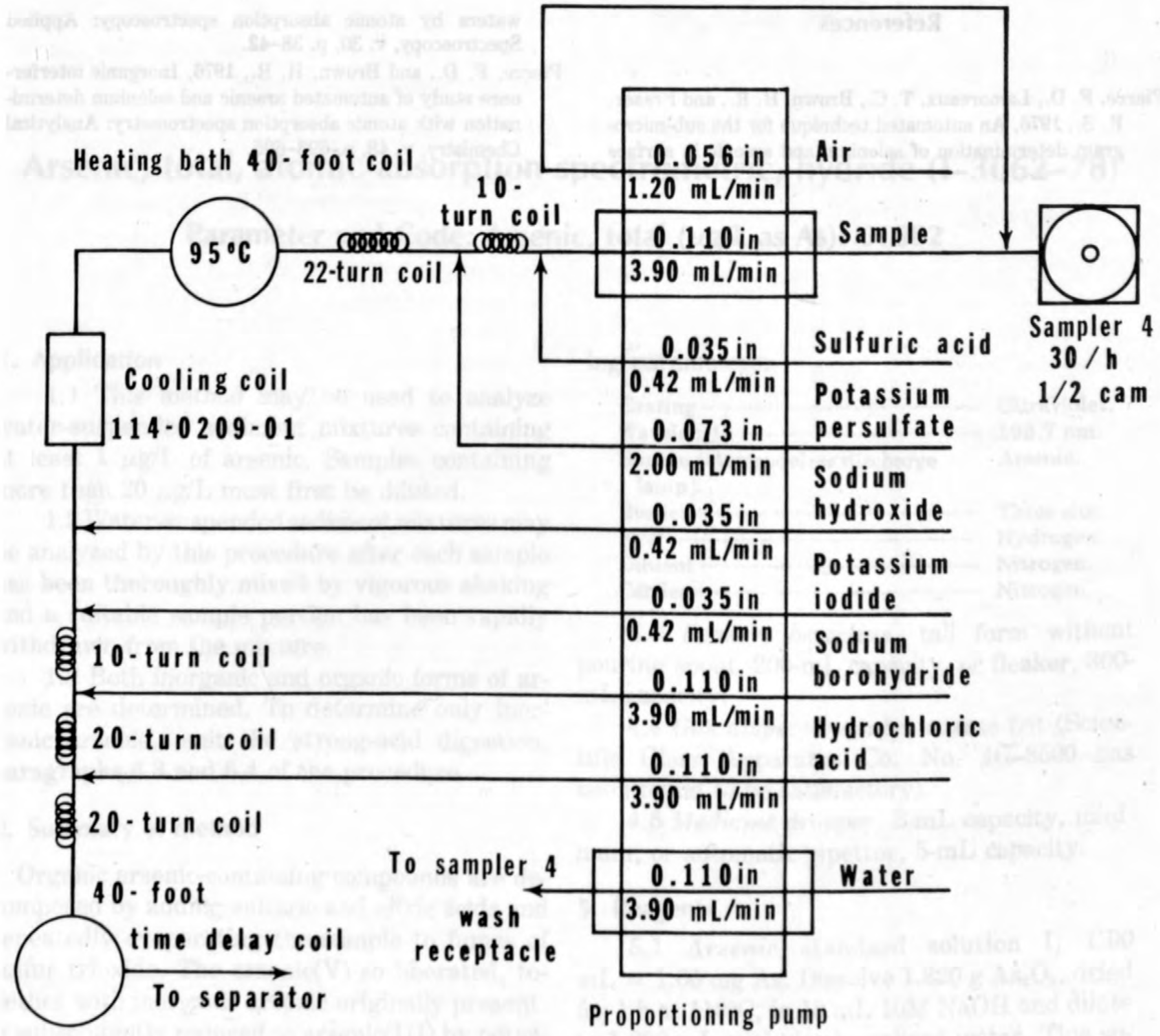


FIGURE 13.—Arsenic, acid-persulfate manifold.

eralized water wash solution when the baseline stabilizes and begin the analyses (NOTE 5).

NOTE 5. When the analyses are complete, the tubes in the manifold and the separator-condenser column should be cleaned if any sediment is present.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective arsenic concentration.

7.2 Compute the concentration of arsenic in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 To determine the micrograms per gram of arsenic in bottom material samples, first determine the micrograms per liter of arsenic in each sample as in 7.2, then

$$\text{As } (\mu g/g) = \frac{\mu g/L \text{ As} \times 0.1}{\text{wt of sample (g)}}$$

8. Report

Report arsenic, total in bottom material (01003), concentrations as follows: less than 10 $\mu g/g$, nearest microgram per gram; 10 $\mu g/g$ and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 5 percent.

References

Pierce, F. D., Lamoreaux, T. C., Brown, H. R., and Fraser, R. S., 1976, An automated technique for the sub-microgram determination of selenium and arsenic in surface waters by atomic absorption spectroscopy: Applied Spectroscopy, v. 30, p. 38–42.

Pierce, F. D., and Brown, H, R., 1976, Inorganic interference study of automated arsenic and selenium determination with atomic absorption spectrometry: Analytical Chemistry, v. 48, p. 693–695.

Arsenic, total, atomic absorption spectrometric, hydride (I–3062–78)

Parameter and Code: Arsenic, total (μg/L as As): 01002

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 1 μg/L of arsenic. Samples containing more than 20 μg/L must first be diluted.

1.2 Water-suspended sediment mixtures may be analyzed by this procedure after each sample has been thoroughly mixed by vigorous shaking and a suitable sample portion has been rapidly withdrawn from the mixture.

1.3 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the strong-acid digestion, paragraphs 6.3 and 6.4 of the procedure.

2. Summary of method

Organic arsenic-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The arsenic(V) so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsenic(III) by potassium iodide and stannous chloride, and finally to gaseous arsine by zinc in hydrochloric acid solution. The arsine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame, where it is determined by atomic absorption at 193.7 nm (fig. 14).

3. Interferences

Since the arsine is freed from the original sample matrix, interferences in the flame are minimized.

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	193.7 nm.
Source (electrodeless discharge lamp).	Arsenic.
Burner	Three-slot.
Fuel	Hydrogen.
Diluent	Nitrogen.
Carrier	Nitrogen.

4.3 *Beaker, berzelius,* tall form without pouring spout, 200-mL capacity, or fleaker, 300-mL capacity.

4.4 *Gas dispersion tube,* coarse frit (Scientific Glass Apparatus Co. No. JG–8500 has been found to be satisfactory).

4.5 *Medicine dropper,* 2-mL capacity, minimum, or automatic pipettor, 5-mL capacity.

5. Reagents

5.1 *Arsenic* standard solution I, 1.00 mL = 1.00 mg As: Dissolve 1.320 g As_2O_3, dried for 1 h at 110°C, in 10 mL 10*M* NaOH and dilute to 1,000 mL with demineralized water. This solution is stable. However, it should be prepared fresh every 6 months.

5.2 *Arsenic* standard solution II, 1.00 mL = 10.0 μg As: Dilute 5.00 mL arsenic standard solution I to 500.0 mL with demineralized water. Discard after 3 months.

5.3 *Arsenic* standard solution III, 1.00 mL = 0.10 μg As: Dilute 5.00 mL arsenic standard solution II to 500.0 mL with demineralized water. Prepare fresh weekly.

5.4 *Hydrochloric acid,* concentrated (sp gr 1.19): Use analytical-grade acid with arsenic content not greater than 1×10^{-6} percent.

5.5 *Nitric acid,* concentrated (sp gr 1.41): Use analytical-grade acid with arsenic content not greater than 5×10^{-7} percent.

5.6 *Potassium iodide* solution, 15 g/100 mL: Dissolve 15 g KI in 100 mL demineralized water.

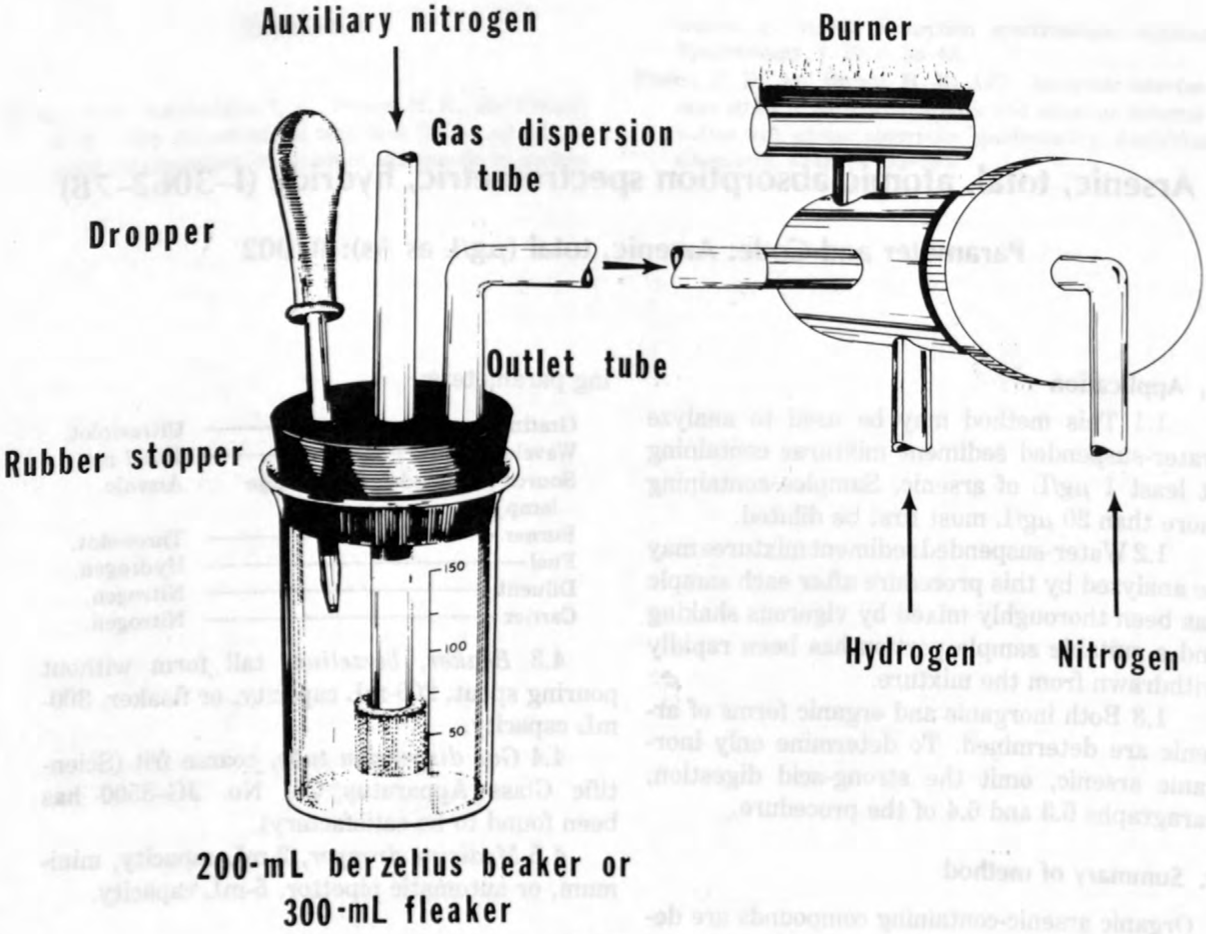


FIGURE 14.—Arsine vapor analyzer.

This solution is stable when stored in an amber bottle.

5.7 *Stannous chloride* solution, 33.6 g/100 mL concentrated HCl: Dissolve 40 g arsenic-free $SnCl_2 \cdot 2H_20$ in 100 mL concentrated HCl. This solution is stable if a few small pieces of mossy tin are added to the bottle to prevent oxidation.

5.8 *Sulfuric acid, 9M: Cautiously*, and with constant stirring and cooling, add 250 mL concentrated H_2SO_4 (sp gr 1.84) to 250 mL demineralized water.

5.9 *Zinc metal (dust)* suspension: Add 10 μg zinc dust to 20 mL demineralized water. Fisher Scientific Co. reagent-grade zinc metal (dust) No. Z–5 has been found to be satisfactory.

6. Procedure

Clean all glassware used in this determination with dilute HCl (1 + 4) and rinse with demineralized water immediately before each use.

6.1 Pipet a volume of sample containing less than 1.0 μg As (50 mL maximum) into a 200-mL berzelius beaker and dilute to 50 mL (NOTE 1).

NOTE 1. If fleakers are used, maximum volume can be 100 mL. Reagent volumes should then be doubled.

6.2 Prepare, in 200-mL berzelius beakers or 300-mL fleakers, a blank and sufficient standards containing from 0.0 to 1.0 μg As by diluting 0.0- to 10.0-mL portions of arsenic standard solution III. Dilute each to approx 50 mL.

6.3 To each beaker, add 7 mL 9*M* H_2SO_4 and 5 mL concentrated HNO_3. Add a small boiling chip or glass beads and carefully evaporate to fumes of SO_3. Maintain an excess of HNO_3 until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of arsenic. Cool, add 25 mL demineralized water, and again evaporate to fumes of SO_3 to expel oxides of nitrogen (NOTE 2).

NOTE 2. If only inorganic arsenic is to be determined, omit steps 6.3 and 6.4.

6.4 Cool, and adjust each beaker to approx 50 mL with demineralized water.

6.5 To each beaker, add successively, with thorough mixing after each addition, 8 mL concentrated HCl, 4 mL KI solution, and 1.0 mL $SnCl_2$ solution. Allow about 15 min for reduction of the arsenic to the tervalent state.

6.6 Attach one beaker at a time to the rubber stopper containing the gas dispersion tube.

6.7 Fill the medicine dropper with 2 mL zinc dust suspension (NOTE 3) and insert into the hole in the rubber stopper. Alternatively, the zinc dust suspension may be delivered from an automatic pipettor.

NOTE 3. The zinc dust must be kept in suspension by continuous stirring. A magnetic stirrer is satisfactory.

6.8 Add the zinc dust suspension to the sample solution. After the absorbance has reached a maximum and has returned to the baseline remove the beaker. Rinse the gas dispersion tube first in nitric acid (1 + 4), and then in distilled water before proceeding to next sample. Test each succeeding sample, blank, and standard in a like manner.

7. Calculations

7.1 Determine the micrograms of arsenic in each sample from a plot of absorbances of standards.

7.2 Determine the concentration of arsenic in each sample as follows:

$$\text{As } (\mu g/L) = \mu g \text{ As in sample} \times \frac{1{,}000}{\text{mL sample}}$$

8. Report

Report arsenic, total (01002), concentrations as follows: less than 10 $\mu g/L$, nearest microgram per liter; 10 $\mu g/L$ and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 58 percent at 4.3 $\mu g/L$ and greater than 19 percent at 17.8 $\mu g/L$.

Reference

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 37.

Arsenic, total, atomic absorption spectrometric, hydride, automated (I–4062–78)

Parameter and Code: Arsenic, total (μg/L as As): 01002

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 1 μg/L of arsenic. Samples containing more than 15 μg/L must be diluted.

1.2 Water-suspended sediment mixtures may be analyzed by this procedure after each sample has been thoroughly mixed by vigorous shaking and a suitable portion has been rapidly withdrawn from the mixture (NOTE 1).

NOTE 1. Do not use a sample containing more than 1/g/L sediment. Concentrations greater than 1 g/L cause erratic results.

1.3 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the acid-persulfate digestion.

2. Summary of method

2.1 Organic arsenic-containing compounds are decomposed by sulfuric acid-potassium persulfate digestion. The arsenic so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsine with sodium borohydride. The arsine is stripped from the solution with the aid of nitrogen and is then decomposed in a tube furnace placed in the optical path of an atomic absorption spectrometer.

2.2 For additional information on the determination of inorganic arsenic in water, see Pierce and others (1976).

3. Interferences

3.1 Since the arsine is freed from the original sample matrix, interferences in the tube furnace are minimized.

3.2 A detailed inorganic interference study showed that most trace elements at concentration levels of less than 300 μg/L do not interfere (Pierce and Brown, 1976).

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	193.7 nm.
Source (electrodeless discharge lamp).	Arsenic.

4.3 *Pyrometer*, portable, 0°C, to 1,200°C. Thermolyne Model PM–20700 or equivalent.

4.4 *Stripping-condensing column*, pyrex, packed with 3- to 5-mm pyrex beads (fig. 15)

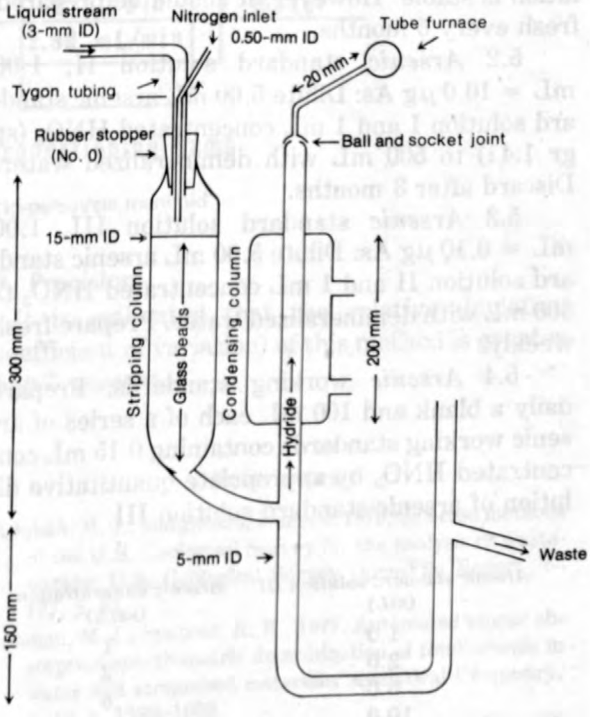


FIGURE 15.—Stripping-condensing column and quartz tube furnace.

(NOTE 2). Cooling of condensing column is not required.

NOTE 2. Nitrogen is used to carry arsine to the tube furnace. Adjust the flow rate for maximum sensitivity by analyzing several identical standards. A flow rate of approx 200 mL/min has been found satisfactory.

4.5 *Tube furnace,* quartz, 10-mm i.d. by 100-mm long, with a quartz eyelet at each end of the tube to anchor nickel-chrome wire and with a 2-mm i.d. quartz inlet tube attached at the center (fig. 15). Wrap the tube furnace with 5.5 m (18 ft) of 26-gauge nickel-chrome wire and cover with asbestos cloth. Mount in the optical path of the atomic absorption spectrometer.

4.6 *Technicon AutoAnalyzer II,* consisting of sampler with stirrer, manifold, proportioning pump, and heating bath.

Heating bath temperature ---------- 95° C.

4.7 *Autotransformer, variable;* Superior Powerstat type 3 PN 1010 or equivalent.

5. Reagents

5.1 *Arsenic* standard solution I, 1.00 mL = 1.00 mg As: Dissolve 1.320 g As_2O_3, dried for 1 h at 110°C, in 10 mL 10*M* NaOH and dilute to 1,000 mL with demineralized water. This solution is stable. However, it should be prepared fresh every 6 months.

5.2 *Arsenic* standard solution II, 1.00 mL = 10.0 μg As: Dilute 5.00 mL arsenic standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 500 mL with demineralized water. Discard after 3 months.

5.3 *Arsenic* standard solution III, 1.00 mL = 0.10 μg As: Dilute 5.00 mL arsenic standard solution II and 1 mL concentrated HNO_3 to 500 mL with demineralized water. Prepare fresh weekly.

5.4 *Arsenic* working standards: Prepare daily a blank and 100 mL each of a series of arsenic working standards containing 0.15 mL concentrated HNO_3 by appropriate quantitative dilution of arsenic standard solution III.

Arsenic standard solution III (mL)	*Arsenic concentration (µg/L)*
1.0	1
2.0	2
5.0	5
10.0	10
15.0	15

5.5 *Hydrochloric acid,* 6*M*: Add 500 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.6 *Potassium iodide* solution, 100 g/L: Dissolve 100 g KI in demineralized water and dilute to 1 L.

5.7 *Potassium persulfate* solution, 50 g/L: Dissolve 50 g $K_2S_2O_8$ in demineralized water with warming and dilute to 1 L after the solution has cooled.

5.8 *Sodium borohydride* solution, 5 g/L: Dissolve 5 g $NaBH_4$ and 40 g NaOH in demineralized water and dilute to 1 L.

5.9 *Sodium hydroxide* solution, 10*M*: *Cautiously* dissolve 400 g NaOH in demineralized water and dilute to 1 L.

5.10 *Sulfuric acid* solution, 3*M*: Add slowly with constant stirring, 167 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Apply a voltage of 47 volts or more (variable transformer) as necessary to the tube furnace to maintain a constant temperature of 800°C (NOTE 3).

NOTE 3. Use the portable pyrometer to check the temperature of the tube furnace. Place the tip of the thermocouple just inside the end of the tube.

6.2 Set up manifold (fig. 16).

6.3 Feed all reagents through the system, using demineralized water in the sample line. Allow the heating bath to warm to 95°C.

6.4 Beginning with the most concentrated standard (NOTE 4), place a complete set of standards in the first positions of the first sample tray. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent trays. Fill remainder of each sample tray with unknown samples (well mixed).

NOTE 4. It is best to place two or three samples of the most concentrated standard at the beginning, since the first peak is usually low. The first standard should not be used in any of the calculations.

6.5 Remove the sample line from the demineralized water wash solution when the baseline stabilizes and begin the analyses (NOTE 5).

NOTE 5. When the analyses are completed, the tubes in the manifold and the separator-condenser column should be cleaned if any sediment is present.

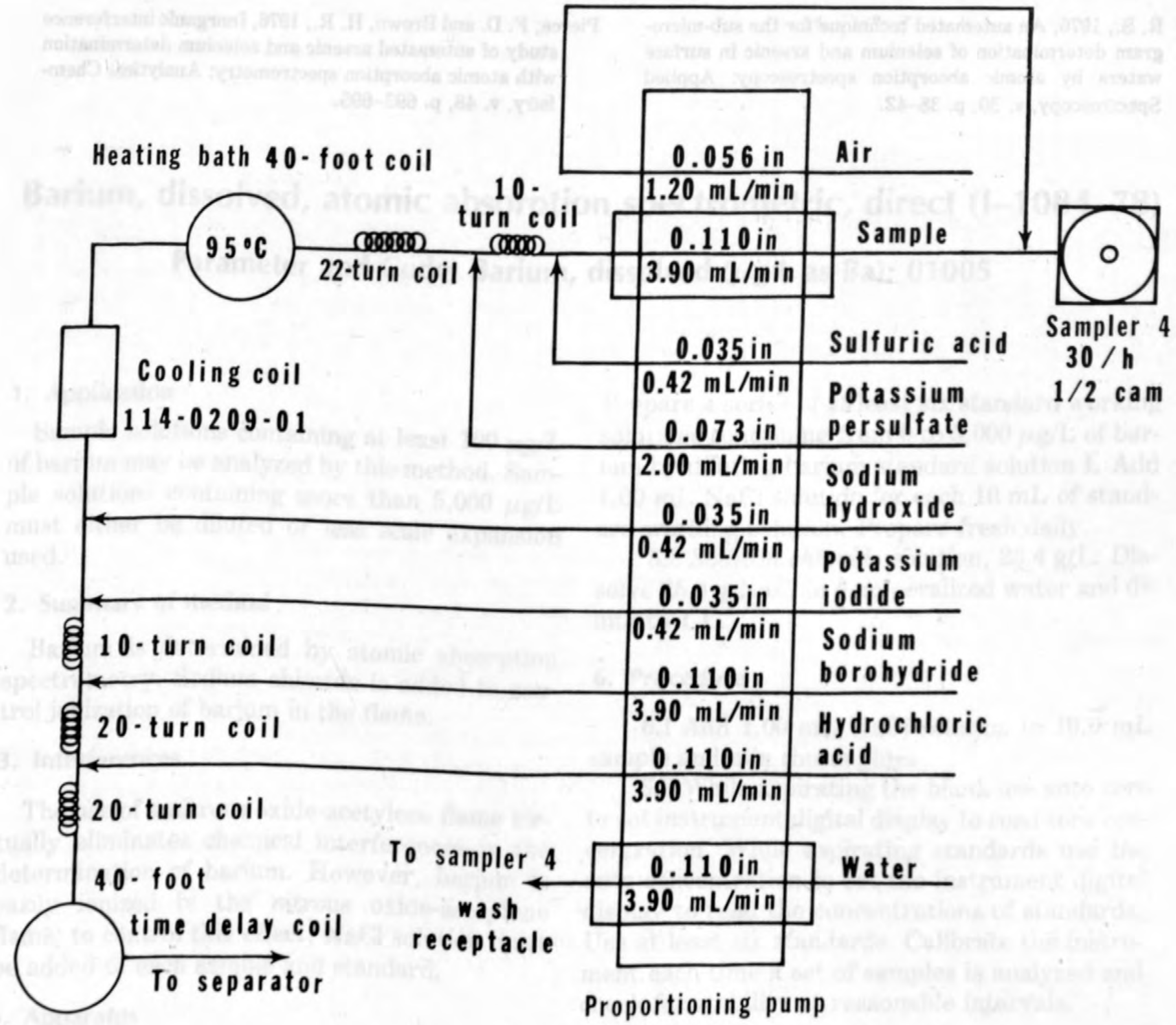


FIGURE 16.—Arsenic, acid-persulfate manifold.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective arsenic concentration.

7.2 Compute the concentration of arsenic in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report arsenic, total (01002), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 5 percent.

References

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 37.

Fishman, M. J., Spencer, R. R., 1977, Automated atomic absorption spectrometric determination of total arsenic in water and streambed materials: Analytical Chemistry, v. 49, p. 1599–1602.

Pierce, F. D., Lamoreaux, T. C., Brown, H. R., and Fraser,

R. S., 1976, An automated technique for the sub-microgram determination of selenium and arsenic in surface waters by atomic absorption spectroscopy: Applied Spectroscopy, v. 30, p. 38–42.

Pierce, F. D. and Brown, H. R., 1976, Inorganic interference study of automated arsenic and selenium determination with atomic absorption spectrometry: Analytical Chemistry, v. 48, p. 693–695.

Barium, dissolved, atomic absorption spectrometric, direct (I–1084–78)

Parameter and Code: Barium, dissolved (μg/L as Ba): 01005

1. Application

Sample solutions containing at least 100 μg/L of barium may be analyzed by this method. Sample solutions containing more than 5,000 μg/L must either be diluted or less scale expansion used.

2. Summary of method

Barium is determined by atomic absorption spectrometry. Sodium chloride is added to control ionization of barium in the flame.

3. Interferences

The use of a nitrous oxide-acetylene flame virtually eliminates chemical interferences in the determination of barium. However, barium is easily ionized in the nitrous oxide-acetylene flame; to control this effect, NaCl solution must be added to each sample and standard.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Visible.
Wavelength	553.6 nm.
Source (hollow-cathode lamp)	Barium.
Burner	Nitrous-oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

5. Reagents

5.1 *Barium* standard solution, 1.00 mL = 100 μg Ba: Dissolve 0.178 g $BaCl_2 \cdot 2H_2O$ in demineralized water and dilute to 1,000 mL.

5.2 *Barium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 5,000 μg/L of barium by diluting barium standard solution I. Add 1.00 mL NaCl solution for each 10 mL of standard working solution. Prepare fresh daily.

5.3 *Sodium chloride* solution, 25.4 g/L: Dissolve 25.4 g NaCl in demineralized water and dilute to 1 L.

6. Procedure

6.1 Add 1.00 mL NaCl solution to 10.0 mL sample and mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of barium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of barium exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report barium, dissolved (01005), concentrations as follows: less than 1,000 μg/L, nearest 100 μg/L; 1,000 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 100 to 800 μg/L may be expressed as follows:

$$S_T = 0.069X + 69.1$$

where

S_T = overall precision, micrograms per liter, and
X = concentration of barium, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
16	162	38
10	800	16

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 50.

Barium, recoverable from bottom material, atomic absorption spectrometric, direct (I–5084–78)

Parameter and Code: Barium, recoverable from bottom material, dry wt (µg/g as Ba):01008

1. Application

1.1 This method may be used to analyze bottom material containing at least 2.5 µg/g of barium. If the preliminary digestion-solubilization of the sample results in a sample solution containing more than 5,000 µg/L, it must be either diluted or less scale expansion used.

1.2 Bottom material must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

Barium is determined by atomic absorption spectrometry. Sodium chloride is added to control ionization of barium in the flame.

3. Interferences

The use of a nitrous oxide-acetylene flame virtually eliminates chemical interferences in the determination of barium. However, barium is easily ionized in the nitrous oxide-acetylene flame; to control this effect, NaCl solution must be added to each sample and standard.

4. Apparatus

4.1 *Atomic absorption spectrometer.*

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Visible.
Wavelength	553.6 nm.
Source (hollow-cathode lamp)	Barium.
Burner	Nitrous-oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

5. Reagents

5.1 *Barium* standard solution, 1.00mL = 100 µg Ba: Dissolve 0.178 g $BaCl_2 \cdot 2H_2O$ in demineralized water and dilute to 1,000 mL.

5.2 *Barium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 5,000 µg/L of barium by diluting barium standard solution I. Add 1.00 mL NaCl solution for each 10 mL of standard working solution. Prepare fresh daily.

5.3 *Sodium chloride* solution, 25.4 g/L: Dissolve 25.4 g NaCl in demineralized water and dilute to 1 L.

6. Procedure

6.1 Add 1.0 mL NaCl solution to 10.0 mL sample and mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of barium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of barium exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per gram of barium, in bottom material samples, first determine the micrograms-per-liter concentration of barium in each sample as in 7.1 then

$$\text{Ba } (\mu\text{g/g}) = \frac{\mu\text{g/L Ba} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report barium, total in bottom material (01008), as follows: less than 100 μg/g, nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 38 percent in the lower portion of the analytical range.

Barium, total recoverable, atomic absorption spectrometric, direct (I–3084–78)

Parameter and Code: Barium, total recoverable (μg/L as Ba): 01007

1. Application

1.1 Sample solutions containing at least 100 μg/L of barium may be analyzed by this method. Sample solutions containing more than 5,000 μg/L must be diluted or less scale expansion used.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

Barium is determined by atomic absorption spectrometry. Sodium chloride is added to control ionization of barium in the flame.

3. Interferences

The use of a nitrous oxide-acetylene flame virtually eliminates chemical interferences in the determination of barium. However, barium is easily ionized in the nitrous oxide-acetylene flame; to control this effect, NaCl solution must be added to each sample and standard.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Visible.
Wavelength	553.6 nm.
Source (hollow-cathode lamp)	Barium.
Burner	Nitrous-oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

5. Reagents

5.1 *Barium* standard solution, 1.00 mL = 100 μg Ba: Dissolve 0.178 g $BaCl_2 \cdot 2H_2O$ in demineralized water and dilute to 1,000 mL.

5.2 *Barium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 5,000 μg/L barium by diluting barium standard solution I. Add 1.00 mL NaCl solution for each 10 mL of standard working solution. Prepare fresh daily.

5.3 *Sodium chloride* solution, 25.4 g/L: Dissolve 25.4 g NaCl in demineralized water and dilute to 1 L.

6. Procedure

6.1 Add 1.00 mL NaCl solution to 10.0 mL sample and mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of barium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of barium exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report barium, total (01007), concentrations as follows: less than 1,000 μg/L, nearest 100 μg/L; 1,000 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 38 percent at 62 μg/L andμgreater than 16 percent at 800 μg/L.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 50.

Beryllium, dissolved, atomic absorption spectrometric, direct (I–1095–78)

Parameter and Code: Beryllium, dissolved (μg/L as Be): 01010

1. Application

Sample solutions containing at least 10 μg/L of beryllium may be analyzed by this method. Sample solutions containing more than 200 μg/L must either be diluted or less scale expansion used.

2. Summary of method

Beryllium is determined by atomic absorption spectrometry. Calcium chloride is added to control ionization of beryllium in the flame.

3. Interferences

Beryllium is slightly ionized in the nitrous oxide-acetylene flame; to control this effect, $CaCl_2$ solution must be added to each standard and sample. Bicarbonate ion interferes; however, this interference is of no consequence if samples preserved by the addition of acid are used for the analysis (NOTE 1).

NOTE 1. It has been reported that aluminum at concentrations greater than 500 μg/L depresses the absorbance. U.S. EPA reports that sodium and silicon at concentrations in excess of 1,000 mg/L have been found to severely depress the beryllium absorbance.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	235.2 nm.
Source (hollow-cathode lamp)	Beryllium.
Burner	Nitrous-oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

5. Reagents

CAUTION: Beryllium compounds and samples with high concentrations of beryllium should be handled with care; they may be carcinogenic.

5.1 *Beryllium* standard solution I, 1.00 mL = 1,000 μg Be: Dissolve 9.83 g $BeSO_4 \cdot 4H_2O$ in demineralized water and dilute to 500.0 mL.

5.2 *Beryllium* standard solution II, 1.00 mL = 10.0 μg Be: Dilute 10.0 mL beryllium standard solution I to 1,000 mL with demineralized water.

5.3 *Beryllium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 200 μg/L beryllium by diluting beryllium standard solution II. Add 1.0 mL $CaCl_2$ solution for each 10.0 mL of standard working solution. Prepare fresh daily.

5.4 *Calcium chloride* solution, 27.8 g/L: Suspend 25 g $CaCO_3$ in demineralized water and dissolve with a minimum of dilute HCl. Dilute to 1 L with demineralized water.

6. Procedure

6.1 Add 1.0 mL $CaCl_2$ solution to 10.0 mL sample and mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of beryllium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of beryllium exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report beryllium, dissolved (01010), concentrations as follows: less than 1,000 μg/L to the nearest 10 μg/L.

9. Precision

9.1 The precision of this method within the range of 10 to 60 μg/L may be expressed as follows:

$$S_T = -0.015X + 5.62$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of beryllium, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
4	27	19
5	38	12

Reference

Brown, Eugene, Skougstad, M. W. and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 53.

Beryllium, recoverable from bottom material, atomic absorption spectrometric, direct (I–5095–78)

Parameter and Code: Beryllium, recoverable from bottom material, dry wt (μg/g as Be): 01013

1. Application

1.1 This method may be used to analyze bottom material containing at least 2.5 μg/g of beryllium. If the preliminary digestion-solubilization of the sample results in a solution containing more than 200 μg/L, it must either be diluted or less scale expansion used.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

Beryllium is determined by atomic absorption spectrometry. Calcium chloride is added to control ionization of beryllium in the flame.

3. Interferences

Beryllium is slightly ionized in the nitrous oxide-acetylene flame; to control this effect, $CaCl_2$ solution must be added to each standard and sample (NOTE 1).

NOTE 1. It has been reported that aluminum at concentrations greater than 500 μg/L depresses the absorbance. U.S. EPA reports that sodium and silicon at concentrations in excess of 1,000 mg/L have been found to severely depress the beryllium absorbance.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	235.2 nm.
Source (hollow-cathode lamp)	Beryllium.
Burner	Nitrous-oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

5. Reagents

CAUTION: Beryllium compounds and samples with high concentrations of beryllium should be handled with care; they may be carcinogenic.

5.1 *Beryllium* standard solution I, 1.00 mL = 1,000 μg Be: Dissolve 9.83 g $BeSO_4 \cdot 4H_2O$ in demineralized water and dilute to 500.0 mL.

5.2 *Beryllium* standard solution II, 1.00 mL = 10.0 μg Be: Dilute 10.0 mL beryllium standard solution I to 1,000 mL with demineralized water.

5.3 *Beryllium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 200 μg/L of beryllium by diluting beryllium standard solution II. Add 1.0 mL $CaCl_2$ solution for each 10.0 mL of standard working solution. Prepare fresh daily.

5.4 *Calcium chloride* solution, 27.8 g/L: Suspend 25 g $CaCO_3$ in demineralized water and dissolve with a minimum of dilute HCl. Dilute to 1 L with demineralized water.

6. Procedure

6.1 Add 1.0 mL $CaCl_2$ solution to a 10.0-mL portion of the sample solution obtained by the digestion-solubilization procedure of Method I–5485. Mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards.

Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of beryllium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of beryllium exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per gram of beryllium in bottom material samples, first determine the micrograms per liter of beryllium in each sample as in 7.1, then:

$$\text{Be } (\mu g/g) = \frac{\mu g/L \text{ Be} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report beryllium, total in bottom material (01013), as follows: less than 10 $\mu g/g$, nearest microgram per gram; 10 μ/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 19 percent at 27 $\mu g/L$ and greater than 12 percent at 38 $\mu g/L$.

Beryllium, total recoverable, atomic absorption spectrometric, direct (I–3095–78)

Parameter and Code: Beryllium, total recoverable (μg/L as Be): 01012

1. Application

1.1 Sample solutions containing at least 10 μg/L of beryllium may be analyzed by this method. Sample solutions containing more than 200 μg/L must either be diluted or less scale expansion used.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

Beryllium is determined by atomic absorption spectrometry. Calcium chloride is added to control ionization of beryllium in the flame.

3. Interferences

Beryllium is slightly ionized in the nitrous oxide-acetylene flame; to control this effect, $CaCl_2$ solution must be added to each standard and sample (NOTE 1).

NOTE 1. It has been reported that aluminum at concentrations greater than 500 μg/L depresses the absorbance. U.S. EPA reports that sodium and silicon at concentrations in excess of 1,000 mg/L have been found to severely depress the beryllium absorbance.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	235.2 nm.
Source (hollow-cathode lamp)	Beryllium.
Burner	Nitrous-oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

5. Reagents

CAUTION: Beryllium compounds and samples with high concentrations of beryllium should be handled with care; they may be carcinogenic.

5.1 *Beryllium* standard solution I, 1.00 mL = 1,000 μg Be: Dissolve 9.83 g $BeSO_4 \cdot 4H_2O$ in demineralized water and dilute to 500.0 mL.

5.2 *Beryllium* standard solution II, 1.00 mL = 10.0 μg Be: Dilute 10.0 mL beryllium standard solution I to 1,000 mL with demineralized water.

5.3 *Beryllium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 200 μg/L beryllium by diluting beryllium standard solution II. Add 1.0 mL $CaCl_2$ solution for each 10.0 mL standard working solution. Prepare fresh daily.

5.4 *Calcium chloride* solution, 27.8 g/L: Suspend 25 g $CaCO_3$ in demineralized water and dissolve with a minimum of dilute HCl. Dilute to 1 L with demineralized water.

6. Procedure

6.1 Add 1.0 mL $CaCl_2$ solution to a 10.0-mL portion of the sample solution obtained by the preliminary digestion-solubilization procedure of Method I–3485. Mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of beryllium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of beryllium exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report beryllium, total (01012), concentrations as follows: less than 1,000 μg/L to the nearest 10 μg/L.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 19 percent at 27 μg/L and greater than 12 percent at 38 μg/L.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigation of the United States Geological Survey, book 5, chapter A1, p. 53.

Cadmium, dissolved, atomic absorption spectrometric, chelation-extraction (I–1136–78)

Parameter and Code: Cadmium, dissolved (μg/L as Cd): 01025

1. Application

1.1 This method may be used to analyze sample solutions containing from 1 to 50 μg/L of cadmium. Sample solutions containing more than 50 μg/L may be either diluted prior to chelation-extraction or aspirated directly into the spectrometer (Method I–1135).

1.2 If the iron concentration of the sample exceeds 25,000 μg/L, determine cadmium by direct atomic absorption (Method I–1135).

2. Summary of method

Cadmium is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the air-acetylene flame of the spectrophotometer.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by depressing the cadmium absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	228.8 nm.
Source (hollow-cathode lamp)	Cadmium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate APDC* solution, 1.0 g/100 mL: Dissolve 1.0 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 1 g/L: Dissolve 1.0 g bromophenol blue in 1 L 50-percent ethanol.

5.3 *Citric acid-sodium citrate buffer* solution: Dissolve 252 g citric acid monohydrate and 88.2 g of sodium citrate dihydrate in demineralized water. Add 100 mL bromophenol blue indicator solution and dilute to 1 L with demineralized water. (Use only in procedure 6.A.)

5.4 *Cadmium* standard solution I, 1.00 mL = 50 μg Cd: Dissolve 0.0571 g CdO in a minimum quantity of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.5 *Cadmium* standard solution II, 1.00 mL = 0.50 μg Cd: Dilute 10.0 mL cadmium standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.6 *Cadmium* standard solution III, 1.00 mL = 0.05 μg Cd: Immediately before use, dilute 10.0 mL cadmium standard solution II to 100.0 mL with demineralized water. This standard is used to prepare working standards at time of analysis.

5.7 *Hydrochloric acid 0.3M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L. (Use only in procedure 6.B.)

5.8 *Methyl isobutyl ketone (MIBK)*.

5.9 *Sodium hydroxide, 2.5M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 mL. (Use only in procedure 6.B.)

6. Procedure

Two procedures, 6.A and 6.B, are given for adjusting the pH of the sample solution prior to chelation and extraction. The two procedures are considered to give equivalent results, and the preference is left to the analyst.

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.A Procedure A

6.A.1 Pipet a volume of sample containing less than 5.0 μg Cd (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.A.2 Prepare a blank with 1.5 mL HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.A.3 Add 10 mL buffer solution and mix (NOTE 1).

NOTE 1. If the proper amount of acid is present, the color will be a greenish yellow. If the color is yellow, add buffer solution dropwise until the proper color is obtained. If the color is green or greenish blue, add concentrated nitric acid dropwise until the proper color is obtained.

6.A.4 Add 2.5 mL APDC solution and shake for 3 min.

6.A.5 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.A.6 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.A.7 Aspirate the ketone layer within 1 h. While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

6.B Procedure B

6.B.1 Pipet a volume of sample containing less than 5.0 μg Cd (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.B.2 Prepare a blank with 1.5 mL HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.B.3 Add 2 drops of bromophenol blue indicator solution to each sample and standard.

6.B.4 Adjust the pH of each by addition of 2.5*M* NaOH by drops until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears. Then add 2.0 mL in excess. The pH at this point should be 2.4 (NOTE 2). Return to step 6.A.4 and proceed through step 6.A.7.

NOTE 2. The pH adjustment in steps 6.B.3 and 6.B.4 may be made with a pH meter instead of using indicator.

7. Calculations

Determine the micrograms per liter of cadmium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose cadmium concentrations exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

8. Report

Report cadmium, dissolved (01025), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 2 to 16 μg/L may be expressed as follows:

$$S_T = 0.192X + 0.093$$

where

S_T = overall precision, micrograms per liter, and
X = concentration of cadmium, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
6	2.5	22
6	10.2	17

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 63.

Cadmium, dissolved atomic absorption spectrometric, direct (I–1135–78)

Parameter and Code: Cadmium, dissolved (μg/L as Cd): 01025

1. Application

This method may be used to analyze water containing at least 10 μg/L of cadmium. Sample solutions containing more than 250 μg/L must either be diluted or less scale expansion used. Sample solutions containing less than 10 μg/L and brines must be analyzed by Method I–1136, providing that the interferences discussed in that method are not exceeded.

2. Summary of method

Cadmium is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment of the sample.

3. Interferences

3.1 Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), magnesium (4,500 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (100 mg/L), iron (4×10^6 μg/L), and cobalt, nickel, copper, zinc, lead, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

3.2 Calcium at concentrations greater than 1,000 mg/L suppresses the cadmium absorption. At 2,000 mg calcium per liter, the suppression is approximately 19 percent.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	228.8 nm.
Source (hollow-cathode lamp)	Cadmium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The Perkin–Elmer flathead single slot burner allows a scale expansion of 0.0 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Cadmium* standard solution I, 1.00 mL = 50 μg Cd: Dissolve 0.0571 g CdO in a minimum quantity of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Cadmium* standard solution II, 1.00 mL = 0.5 μg Cd: Dilute 10.0 mL cadmium standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.3 *Cadmium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 250 μg/L cadmium by appropriate dilution of cadmium standard solutions I and II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set the instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of cadmium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose cadmium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report cadmium, dissolved (01025), concentrations as follows: less than 1,000 μg/L, nearest 10 μg/L; 1,000 μg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
12	12	49
6	14	31

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 62.

Cadmium, recoverable from bottom material, atomic absorption spectrometric, direct (I–5135–78)

Parameter and Code: Cadmium, recoverable from bottom material, dry wt (μg/g as Cd): 01028

1. Application

1.1 This method may be used to analyze bottom material containing at least 1 μg/g of cadmium. If the prepared sample solution (Method I–5485) contains more than 250 μg/L, it must either be diluted or less scale expansion used.

1.2 Bottom material must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

Cadmium is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–5485) into an air-acetylene flame without further preconcentration or pretreatment of the sample solution.

3. Interferences

3.1 Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), magnesium (4,500 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (100 mg/L), iron (4×10^6 μg/L), and cobalt, nickel, copper, zinc, lead, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

3.2 Calcium at concentrations greater than 1,000 mg/L suppresses the cadmium absorption. At 2,000 mg/L of calcium, the suppression is approximately 19 percent.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	228.8 nm.
Source (hollow-cathode lamp)	Cadmium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The Perkin–Elmer flathead single slot burner allows a working range of 10 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Cadmium* standard solution I, 1.00 mL = 50 μg Cd: Dissolve 0.0571 g CdO in a minimum quantity of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Cadmium* standard solution II, 1.00 mL = 0.5 μg Cd: Dilute 10.0 mL cadmium standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.3 *Cadmium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 250 μg/L of cadmium by appropriate dilution of cadmium standard solutions I and II. Prepare fresh daily.

6. Procedure

6.1 For this determination, use a portion of the sample solution obtained by the digestion-solubilization procedure of Method I–5485.

6.2 While aspirating the blank use auto zero to set the instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of cadmium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of cadmium exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per gram of cadmium in bottom material samples, first determine the micrograms per liter of cadmium in each sample as in 7.1, then

$$\text{Cd } (\mu\text{g/g}) = \frac{\mu\text{g/L Cd} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report cadmium, total in bottom material (01028), concentrations as follows: less than 10 μg/g, nearest microgram per gram; 10 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 31 percent at the lower portion of the analytical range.

Cadmium, total recoverable, atomic absorption spectrometric, chelation-extraction (I–3136–78)

Parameter and Code: Cadmium, total recoverable (μg/L as Cd): 01027

1. Application

1.1 This method may be used to analyze sample solutions containing from 1 to 50 μg/L of cadmium. Sample solutions containing more than 50 μg/L may be either diluted prior to chelation-extraction or aspirated directly into the spectrometer (Method I–3135).

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

1.3 If the iron concentration of the prepared sample solution (Method I–3485) exceeds 25,000 μg/L, determine cadmium by direct atomic absorption (Method I–3135).

2. Summary of method

Cadmium is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the air-acetylene flame of the spectrophotometer.

3. Interferences

Concentrations of iron in the prepared solution (Method I–3485) greater than 25,000 μg/L interfere by suppressing the cadmium absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating ---------------------------------- Ultraviolet.
Wavelength ----------------------------- 228.8 nm.
Source (hollow-cathode lamp)------ Cadmium.
Oxidant ---------------------------------- Air.
Fuel -------------------------------------- Acetylene.
Type of flame ---------------------------- Oxidizing.

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution, 1.0 g/100 mL: Dissolve 1.0 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 1 g/L: Dissolve 1.0 g bromophenol blue in 1 L 50-percent ethanol.

5.3 *Sodium citrate buffer* solution: Dissolve 450 g sodium citrate dihydrate in demineralized water. Add 100 mL bromophenol blue indicator solution and dilute to 1 L with demineralized water. (Use only in procedure 6.A.)

5.4 *Cadmium* standard solution I, 1.00 mL = 50 μg Cd: Dissolve 0.0571 g CdO in a minimum quantity of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.5 *Cadmium* standard solution II, 1.00 mL = 0.50 μg Cd: Dilute 10.0 mL cadmium standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.6 *Cadmium* standard solution III, 1.00 mL = 0.05 μg Cd: Immediately before use, dilute 10.0 mL cadmium standard solution II to 100.0 mL with demineralized water. This standard is used to prepare working standards at time of analysis.

5.7 *Hydrochloric acid*, 0.3*M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L. (Use only in procedure 6.B.)

5.8 *Methyl isobutyl ketone* (*MIBK*).

5.9 *Sodium hydroxide*, 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 mL. (Use only in procedure 6.B.)

6. Procedure

Two procedures, 6.A and 6.B, are given for adjusting the pH of the sample solution prior to chelation and extraction. The two procedures are considered to give equivalent results, and the preference is left to the analyst.

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.A Procedure A

6.A.1 Pipet a volume of prepared sample solution (Method I–3485) containing less than 5.0 μg Cd (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL (NOTE 1).

NOTE 1. If the samples must be diluted prior to chelation-extraction, a specially prepared dilution water must be used. It is prepared as follows: Mix 25 mL HCl with demineralized water and dilute to 1 L.

6.A.2 Prepare a blank and at least six standards, and adjust the volume of each to approx 100 mL with the specially prepared dilution water (NOTE 1).

6.A.3 Add 10 mL buffer solution and mix (NOTE 2).

NOTE 2. If the proper amount of acid is present, the color will be a greenish yellow. If the color is yellow, add buffer solution dropwise until the proper color is obtained. If the color is green or greenish blue, add concentrated nitric acid dropwise until the proper color is obtained.

6.A.4 Add 2.5 mL APDC solution and shake for 3 min.

6.A.5 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.A.6 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.A.7 Aspirate the ketone layer within 1 h. While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

6.B Procedure B

6.B.1 Pipet a volume of prepared sample solution (Method I–3485) containing less than 5.0 μg Cd (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.B.2 Prepare a blank with 1.5 mL HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.B.3 Add 2 drops of bromophenol blue indicator solution to each sample and standard.

6.B.4 Adjust the pH of each by addition of 2.5*M* NaOH by drops until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears. Then add 2.0 mL in excess. The pH at this point should be 2.4 (NOTE 3). Return to step 6.A.4 and proceed through step 6.A.7.

NOTE 3. The pH adjustment in steps 6.B.3 and 6.B.4 may be made with a pH meter instead of using indicator.

7. Calculations

Determine the micrograms per liter cadmium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose cadmium concentrations exceed the working range of the method; repeat the chelation-extraction, and multiply by the proper dilution factors.

8. Report

Report cadmium, total (01027), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 22 percent at 2.5 μg/L and greater than 17 percent at 10.2 μg/L.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 63.

Cadmium, total recoverable, atomic absorption spectrometric, direct (I–3135–78)

Parameter and Code: Cadmium, total recoverable (μg/L as Cd): 01027

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 10 μg/L of cadmium. Sample solutions containing more than 250 μg/L must either be diluted or less scale expansion used. Sample solutions containing less than 10 μg/L must be analyzed by Method I–3136, providing that the interferences discussed in that method are not exceeded.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

Cadmium is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment of the sample.

3. Interferences

3.1 Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), magnesium (4,500 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (100 mg/L), iron (4×10^6 μg/L), and cobalt, nickel, copper, zinc, lead, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

3.2 Calcium at concentrations greater than 1,000 mg/L suppresses the cadmium absorption. At 2,000 mg calcium per liter, the suppression is approximately 19 percent.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	228.8 nm.
Source (hollow-cathode lamp)	Cadmium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The Perkin–Elmer flathead single slot burner allows a working range of 10 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Cadmium* standard solution I, 1.00 mL = 50 μg Cd: Dissolve 0.0571 g CdO in a minimum quantity of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Cadmium* standard solution II, 1.00 mL = 0.5 μg Cd: Dilute 10.0 mL cadmium standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.3 *Cadmium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 250 μg/L of cadmium by appropriate dilution of cadmium standard solutions I and II. Prepare fresh daily.

6. Procedure

6.1 For this determination, use a portion of the sample solution obtained by the digestion-solubilization procedure of Method I–3485.

6.2 While aspirating the blank use auto zero to set the instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of cadmium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of cadmium exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report cadmium, total (01027), concentrations as follows: Less than 1,000 μg/L, nearest 10 μg/L; 1,000 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 49 percent at 12 μg/L.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 62.

Calcium, dissolved, atomic absorption spectrometric, direct (I–1152–78)

Parameter and Code: Calcium, dissolved (mg/L as Ca): 00915

1. Application

This method may be used to analyze waters and brines. Sample solutions containing from 0.1 to 60 mg/L of calcium may be analyzed without dilution, whereas those containing more than 60 mg/L must first be diluted.

2. Summary of method

2.1 Calcium is determined by atomic absorption spectrometry (Fishman and Downs, 1966). Lanthanum chloride is added to mask interferences.

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and a strip-chart recorder or printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 Phosphate, sulfate, and aluminum interfere but are masked by the addition of lanthanum. It has been reported that silica also interferes. Since low calcium values result if the pH of the sample is above 7, standards are prepared in hydrochloric acid solution and samples are preserved in the field with use of nitric acid solution. Concentrations of magnesium greater than 1,000 mg/L also cause low calcium values.

3.2 Nitrate interferes, but in the presence of lanthanum chloride-hydrochloric acid solution at least 2,000 mg/L can be tolerated. The addition of nitric acid to the sample causes no problem in the following procedure.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Visible.
Wavelength	422.7 nm.
Source (hollow-cathode lamp).	Calcium.
Oxidant	Air
Fuel	Acetylene.
Type of flame	Slightly reducing.

4.3 Different burners may be used according to manufacturer's instructions.

A nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences; however, sodium or potassium chloride will have to be added to control ionization of calcium.

5. Reagents

5.1 *Calcium* standard solution, 1.00 mL = 0.500 mg Ca: Suspend 1.250 g $CaCO_3$, dried at 180°C for 1 h before weighing, in demineralized water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 mL with demineralized water.

5.2 *Calcium* standard working solutions: Prepare at least six standard working solutions containing from 0 to 60 mg/L of calcium by diluting the calcium standard solution. To each standard working solution, add 1.0 mL of $LaCl_3$ solution for each 10 mL of standard.

5.3 *Lanthanum chloride* solution, 87 g/L: Mix 29 g of La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

6. Procedure

6.1 Add 1.0 mL of $LaCl_3$ solution per 10.0 mL of sample.

6.2 While aspirating the blank use auto zero to set the instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the milligrams per liter of calcium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose calcium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report calcium, dissolved (00915), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 3 to 110 mg/L may be expressed as follows:

$$S_T = 0.057X + 0.343$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of calcium, milligrams per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
17	12.6	7
23	110	8

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 66.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. C26-C28.

Calcium, recoverable from bottom material, atomic absorption spectrometric, direct (I–5152–78)

Parameter and Code: Calcium, recoverable from bottom material, dry wt (mg/kg as Ca): 00917

1. Application

1.1 This method may be used to analyze bottom material containing at least 10 mg/kg of calcium. Prepared sample solutions (Method I–5485) containing from 0.1 to 60 mg/L calcium may be analyzed without dilution, whereas those containing more than 60 mg/L must first be diluted.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

2.1 Calcium is determined by atomic absorption spectrometry (Fishman and Downs, 1966). Lanthanum chloride is added to mask interferences.

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and a strip-chart recorder or printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 Phosphate, sulfate, and aluminum interfere but are masked by the addition of lanthanum. It has been reported that silica also interferes.

3.2 Nitrate interferes but in the presence of lanthanum chloride-hydrochloric acid solution at least 2,000 mg/L can be tolerated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Visible.
Wavelength	422.7 nm.
Source (hollow-cathode lamp)	Calcium.
Oxidant	Air.

4.3 Different burners may be used according to manufacturer's instructions.

A nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences; however, sodium or potassium chloride will have to be added to control ionization of calcium.

5. Reagents

5.1 *Calcium* standard solution, 1.00 mL = 0.500 mg Ca: Suspend 1.250 g $CaCO_3$, dried at 180°C for 1 h before weighing, in demineralized water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 mL with demineralized water.

5.2 *Calcium* standard working solutions: Prepare at least six standard working solutions containing from 0 to 60 mg/L of calcium by diluting the calcium standard solution. To each standard working solution, add 1.0 mL of $LaCl_3$ solution for each 10 mL of standard.

5.3 *Lanthanum chloride* solution, 87 g/L: Mix 29 g of La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

6. Procedure

6.1 Add 1.0 mL of $LaCl_3$ solution per 10.0 mL of sample solution prepared as directed in

Method I–5485.

6.2 While aspirating the blank use auto zero to set the instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the milligrams per liter of calcium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose calcium concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine milligrams per kilogram of calcium in bottom material samples, first determine the milligrams per liter of calcium in each sample as in 7.1, then

$$\text{Ca (mg/kg)} = \frac{\text{mg/L Ca} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report calcium, total in bottom material (00917), concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 7 percent.

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. C26–C28.

Calcium, total recoverable, atomic absorption spectrometric, direct (I–3152–78)

Parameter and Code: Calcium, total recoverable (mg/L as Ca): none assigned

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures. Sample solutions containing from 0.1 to 60 mg/L of calcium may be analyzed without dilution, whereas those containing more than 60 mg/L must first be diluted.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

2.1 Calcium is determined by atomic absorption spectrometry (Fishman and Downs, 1966). Lanthanum chloride is added to mask interferences.

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and a strip-chart recorder or printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 Phosphate, sulfate, and aluminum interfere but are masked by the addition of lanthanum. It has been reported that silica also interferes.

3.2 Nitrate interferes, but in the presence of lanthanum chloride-hydrochloric acid solution at least 2,000 mg/L can be tolerated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Visible.
Wavelength	422.7 nm.
Source (hollow-cathode lamp)	Calcium.
Oxidant	Air.
Fuel	Acetylene.

4.3 Different burners may be used according to manufacturer's instructions.

A nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences; however, sodium or potassium chloride will have to be added to control ionization of calcium.

5. Reagents

5.1 *Calcium* standard solution, 1.00 mL = 0.500 mg Ca: Suspend 1.250 g $CaCO_3$, dried at 180°C for 1 h before weighing, in demineralized water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 mL with demineralized water.

5.2 *Calcium* standard working solutions: Prepare at least six standard working solutions containing from 0 to 60 mg/L of calcium by diluting the calcium standard solution. To each standard working solution, add 1.0 mL of $LaCl_3$ solution for each 10 mL of standard.

5.3 *Lanthanum chloride* solution, 87 g/L: Mix 29 g of La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

6. Procedure

6.1 Add 1.0 mL of $LaCl_3$ solution per 10.0 mL of sample solution prepared as directed in Method I–3485.

6.2 While aspirating the blank use auto zero to set the instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the milligrams per liter of calcium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose calcium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report calcium, total, concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 7 percent at 12.6 mg/L and greater than 8 percent at 110 mg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 66.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. C26–C28.

Calcium, total recoverable, atomic absorption spectrometric, direct-EPA (I–3153–78)

Parameter and Code: Calcium, total recoverable (mg/L as Ca): 00916

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures. Sample solutions containing from 0.1 to 60 mg/L of calcium may be analyzed without dilution, whereas those containing more than 60 mg/L must first be diluted.

1.2 For ambient waters, analysis may be made on a measured portion of the acidified water-suspended sediment sample.

1.3 For all other waters, including domestic and industrial effluents, the atomic absorption procedure must be preceded by a digestion-solubilization as specified below. In cases where the analyst is uncertain about the type of sample, the digestion-solubilization procedure must be used.

2. Summary of method

2.1 Calcium is determined by atomic absorption spectrometry (Fishman and Downs, 1966). Lanthanum chloride is added to mask interferences.

2.2 Effluent samples must undergo a preliminary nitric acid digestion followed by a hydrochloric acid solubilization.

2.3 The atomic absorption procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 Phosphate, sulfate, and aluminum interfere but are masked by the addition of lanthanum. It has been reported that silica also interferes. Since low calcium values result if the pH of the sample is above 7, standards are prepared in hydrochloric acid solution and samples are preserved in the field with use of nitric acid solution. Concentrations of magnesium greater than 1,000 mg/L also cause low calcium values.

3.2 Nitrate interferes, but in the presence of lanthanum chloride-hydrochloric acid solution at least 2,000 mg/L can be tolerated. The addition of nitric acid to the sample as a preservative at the time of collection causes no problem in the following procedure. Samples should be evaporated just to dryness following HNO_3 digestion to avoid any possible nitrate interference.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Visible.**
Wavelength	**422.7 nm.**
Source (hollow-cathode lamp).	**Calcium.**
Oxidant	**Air**
Fuel	**Acetylene.**
Type of flame	**Slightly reducing.**

4.3 Different burners may be used according to manufacturer's instructions. A nitrous oxide-acetylene flame provides 2 to 5 times greater sensitivity and freedom from chemical interferences; however, sodium or potassium chloride must be added to control ionization of calcium.

5. Reagents

5.1 *Calcium* standard solution, 1.00 mL = 0.500 mg Ca: Suspend 1.250 g $CaCO_3$, dried at 180°C for 1 h before weighing, in demineralized water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 mL with demineralized water.

5.2 *Calcium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 200 mg/L of calcium by dilution of calcium standard solution I. To each standard working solution, add 1.0 mL of $LaCl_3$ solution for each 10 mL of standard.

5.3 *Hydrochloric acid*, 6*M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.4 *Hydrochloric acid*, 0.3*M*: Dilute 25 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.5 ***Lanthanum chloride*** solution, 87 g/L: Mix 29 g La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

5.6 *Nitric acid*, concentrated HNO_3 (sp gr 1.41).

6. Procedure

6.1 Transfer the entire sample to a beaker.

6.2 Rinse the sample bottle with 3 mL concentrated HNO_3 for each 100 mL of sample and add to the beaker. Prepare a blank using 3 mL concentrated HNO_3 per 100 mL demineralized water.

6.3 Evaporate samples and blank to dryness on a hot plate, making sure the samples do not boil.

6.4 Cool and add an additional 3 mL concentrated HNO_3 to the beaker. Cover with a watch glass, return to the hot plate and gently reflux the sample.

6.5 Continue heating, adding additional acid as necessary, until the digestion is complete (indicated by a light colored residue). Evaporate just to dryness.

6.6 Add 6 mL 6*M* HCl solution per 100 mL of original sample and warm the beaker to dissolve the residue.

6.7 Wash the watch glass and beaker with demineralized water and filter the sample (Whatman No. 41 or equivalent), rinsing the filter with hot, 0.3*M* HCl. Dilute to the original volume with demineralized water.

6.8 Add 1.0 mL lanthanum chloride solution per 10.0 mL of sample.

6.9 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the milligrams per liter of calcium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose calcium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report calcium, total (00916), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 7 percent at 12.6 mg/L and greater than 8 percent at 110 mg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 66.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. C26–C28.

U.S. Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 82–83.

Chromium, dissolved, atomic absorption spectrometric, chelation-extraction (I–1238–78)

Parameter and Code: Chromium, dissolved (μg/L as Cr): 01030

1. Application

1.1 This method may be used to analyze waters and brines containing from 1 to 25 μg/L of chromium. Water samples containing more than 25 μg/L may be either diluted prior to chelation-extraction or analyzed by Method I–1236.

1.2 If the iron concentration of the sample exceeds 5,000 μg/L, determine chromium by direct atomic absorption (Method I–1236).

2. Summary of method

The procedure used for the determination of hexavalent plus tervalent chromium is the same as that for hexavalent chromium (Method I–1232), except for an additional step to oxidize any tervalent chromium present to the hexavalent state. A modification of a method described by Saltzman (1952), whereby Cr^{+3} is oxidized by potassium permanganate, has been found satisfactory. Excess permanganate is reduced with sodium azide, which must not be present in excess, as it interferes with subsequent pH adjustment and chelation.

3. Interferences

3.1 The optimum pH for the extraction of the Cr^{+6}–ammonium pyrrolidine dithiocarbamate (Cr^{+6}–APDC) complex by methyl isobutyl ketone (MIBK) is 3.1. At this pH, however, manganese is also partially extracted. The Mn–APDC complex is unstable and decomposes to a fine suspension of manganese oxides which clog the atomizer-burner. If the pH of the sample is adjusted to 2.4 prior to chelation and extraction, less manganese is extracted, and there is only a slight loss in extraction efficiency for chromium. If the extract is not clear after overnight standing, it must be centrifuged.

3.2 Concentrations of iron greater than 5,000 μg/L interfere by suppressing the chromium absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters.

Grating	Ultraviolet.
Wavelength	357.9 nm.
Source (hollow-cathode lamp)	Chromium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Reducing.

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution, 1.0 g/100 mL: Dissolve 1.0 g APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 0.1 g/100 mL: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.

5.3 *Chromium* standard solution I, 1.00 mL = 100 μg Cr^{+6}: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.4 *Chromium* standard solution II, 1.00 mL = 2.00 μg Cr^{+3}: Pipet 5.0 mL chromium standard solution I into an erlenmeyer flask.

Add approx 15 mg Na_2SO_3 and 0.5 mL concentrated HNO_3 (sp gr 1.41). Gently evaporate just to dryness; strong heating reoxidizes the Cr. Add 0.5 mL concentrated HNO_3 and again evaporate to dryness to destroy any excess sulfite. Dissolve the residue in 1 mL concentrated HNO_3 with warming. Cool, transfer to a 250-mL volumetric flask, and dilute to the mark with demineralized water.

5.5 *Chromium* standard solution III, 1.00 mL = 0.50 μg Cr^{+3}: Dilute 25.0 mL chromium standard solution II to 100 mL with demineralized water. Prepare immediately before use.

5.6 *Methyl isobutyl ketone* (MIBK).

5.7 *Potassium permanganate* solution, 0.32 g/100 mL: Dissolve 0.32 g $KMnO_4$ in demineralized water and dilute to 100 mL. Allow to stand several days and decant if necessary.

5.8 *Sodium azide* solution, 0.10 g/100 mL: Dissolve 0.10 g NaN_3 in 100 mL demineralized water.

5.9 *Sodium hydroxide* solution, 1*M*: Dissolve 40 g NaOH in demineralized water and dilute to 1 L.

5.10 *Sulfuric acid*, 0.12*M*: Slowly add 6.5 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1+9) and rinse with demineralized water immediately before use.

6.1 Pipet a volume of sample containing less than 2.5 μg chromium (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL. The pH must be 2.0 or less. Add concentrated HNO_3 if necessary.

6.2 Acidify a liter of demineralized water with 1.5 mL concentrated HNO_3 (sp gr 1.41). Prepare a blank and at least six standards, and adjust the volume of each to approx 100 mL with the acidified demineralized water.

6.3 Add $KMnO_4$ solution by drops to blank, standards, and samples until a faint pink color persists.

6.4 Heat on a steam bath for 20 min. If the color disappears, add $KMnO_4$ solution by drops to maintain a slight excess.

6.5 While still on the steam bath, add sodium azide solution by drops until the $KMnO_4$ color just disappears. Heat for about 2 min between each addition and avoid adding any excess. Continue heating for 5 min after adding the last drop of sodium azide solution.

6.6 Transfer to a water bath and cool to room temperature.

6.7 Remove from the water bath and filter through Whatman No. 40 filter paper any sample that has a brownish precipitate or coloration that may interfere with the pH adjustment.

6.8 Add 2.0 mL of 1*M* NaOH and 2 drops bromophenol blue indicator solution. Continue the addition of 1*M* NaOH by drops to all samples and standards in which the indicator change from yellow to blue has not occurred. Add 0.12*M* H_2SO_4 by drops until the blue color just disappears, then add 2.0 mL in excess. The pH at this point should be 2.4 (NOTE 1).

NOTE 1. The pH adjustment in step 6.8 may be made with a pH meter instead of using an indicator, in which case the filtration called for in sec. 6.7 would not be necessary.

6.9 Add 5.0 mL APDC solution and shake for 3 min. The pH at this point should be 2.8.

6.10 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.11 Allow the layers to separate and then add demineralized water until the ketone layer is completely in the neck of the flask.

6.12 Stopper and allow to stand overnight. The Cr^{+6}–APDC complex is stable for at least 36 h.

6.13 While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of chromium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose chromium concentrations exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

8. Report

Report chromium, dissolved (01030), concentrations as follows: less than 100 μg/L, the nearest microgram per liter; 100 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 8 to 25 μg/L may be expressed as follows:

$$S_T = 1.005X - 5.36$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of chromium, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (µg/L)*	*Relative deviation (percent)*
3	8.0	25
12	23	82

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 78.

Saltzman, B., 1952, Microdetermination of chromium with diphenyl carbazide by permanganate oxidation: Analytical Chemistry, v. 24, p. 1016.

Chromium, dissolved, atomic absorption spectrometric, direct
(I–1236–78)

Parameter and Code: Chromium, dissolved (μg/L as Cr): 01030

1. Application

This method may be used to analyze waters containing at least 10 μg/L of chromium. Sample solutions containing more than 400 μg/L must be diluted or less scale expansion must be used. Sample solutions, containing less than 10 μg/L, and brines, must be analyzed by Method I–1238, providing that the interferences discussed in that method are not exceeded.

2. Summary of method

Chromium is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment of the sample other than the addition of ammonium chloride to mask certain interferences.

3. Interferences

3.1 Iron, nickel, and cobalt at 100 μg/L and magnesium at 30 mg/L interfere by suppressing the absorption of chromium. These interferences are eliminated in solutions containing about 18,000 mg/L of ammonium chloride (Barnes, 1966, and Giammarise, 1966). Samples adjusted to this concentration of ammonium chloride show no interferences from 7×10^5 μg/L of iron and 10,000 μg/L each of nickel and cobalt, or from 1,000 mg/L of magnesium.

3.2 Individual concentrations of sodium (8,000 mg/L), calcium (4,000 mg/L), nitrate (100 mg/L), sulfate (8,000 mg/L), and chloride (10,000 mg/L) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	357.9 nm.
Source (hollow-cathode lamp)	Chromium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Reducing.

4.3 The 102-mm flathead single slot burner allows a scale expansion of 10 to 400 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium chloride* solution, 200 g/L: Dissolve 200 g NH_4Cl in demineralized water and dilute to 1 L.

5.2 *Chromium* standard solution I, 1.00 mL = 100 μg Cr: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.3 *Chromium* standard solution II, 1.00 mL = 1 μg Cr: Dilute 10.0 mL chromium standard solution I to 1,000 mL with demineralized water.

5.4 *Chromium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 400 μg/L of chromium by diluting chromium standard solution II. To each standard working solution, add 1.0 mL of NH_4Cl solution for each 10 mL of standard. Prepare fresh daily.

6. Procedure

6.1 Add 1.0 mL ammonium chloride solution to 10 mL sample and mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero con-

centration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of chromium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose chromium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report chromium, dissolved (01030), concentrations as follows: less than 1,000 μg/L, nearest 10 μg/L; 1,000 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 10 to 55 μg/L may be expressed as follows:

$$S_T = 0.173X + 2.44$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of chromium, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
10	22	27
12	31	23

References

American Society for Testing and Materials, 1975, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 345.

Barnes, L., Jr., 1966, Determination of chromium in low alloy steels by atomic absorption spectrometry: Analytical Chemistry, v. 38, p. 1083–1085.

Giammarise, A., 1966, The use of ammonium chloride in analyses of chromium samples containing iron: Atomic Absorption Newsletter, v. 5, p. 113–115.

Chromium, hexavalent, dissolved, atomic absorption spectrometric, chelation-extraction (I–1232–78)

Parameter and Code: Chromium, hexavalent, dissolved (μg/L as Cr): 01032

1. Application

1.1 This method may be used to analyze waters and brines containing from 1 to 25 μg/L of chromium. Water samples containing more than 25 μg/L must be diluted prior to chelation-extraction.

1.2 If the iron concentration of the sample exceeds 5,000 μg/L, determine chromium (Cr^{+3} and Cr^{+6}) by direct atomic absorption (Method I–1236); hexavalent chromium cannot be determined by this method in this case.

2. Summary of method

Hexavalent chromium is determined by atomic absorption spectrometry. The element is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the air-acetylene flame of the spectrometer (Midgett and Fishman, 1967).

3. Interferences

Concentrations of iron greater than 5,000 μg/L interfere by suppressing the chromium absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**357.9 nm.**
Source (hollow-cathode lamp)	**Chromium.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Reducing.**

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution, 1.0 g/100 mL: Dissolve 1.0 g APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 0.1 g/100 mL: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.

5.3 *Chromium* standard solution I, 1.00 mL = 100 μg Cr^{+6}: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.4 *Chromium* standard solution II, 1.00 mL = 10.0 μg Cr^{+6}: Dilute 100 mL chromium standard solution I to 1,000 mL with demineralized water.

5.5 *Chromium* standard solution III, 1.00 mL = 0.10 μg Cr^{+6}: Dilute 10.0 mL chromium standard solution II to 1,000 mL with demineralized water.

5.6 *Methyl isobutyl ketone* (MIBK).

5.7 *Sodium hydroxide* solution, 1*M*: Dissolve 40 g NaOH in demineralized water and dilute to 1 L.

5.8 *Sulfuric acid*, 0.12*M*: Slowly add 6.5 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1+9) and rinse with demineralized water immediately before use.

6.1 Pipet a volume of sample containing less than 2.5 μg Cr^{+6} (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.2 Prepare a blank with a 1.5 mL HNO_3 per liter of demineralized water and at least six standards containing from 1 to 25 μg/L of chromium, and adjust the volume of each to approx 100 mL.

6.3 Add 2 drops bromophenol blue indicator solution to each sample and standard.

6.4 Adjust the pH of each by addition of 1*M* NaOH solution by drops until a blue color persists. Add 0.12*M* H_2SO_4 by drops until the blue color just disappears. Then add 2.0 mL of 0.12*M* H_2SO_4 in excess. The pH at this point should be 2.4 (NOTE 1).

NOTE 1. The pH adjustment in steps 6.3 and 6.4 may be made with a pH meter instead of using an indicator.

6.5 Add 5.0 mL APDC solution and shake for 3 min. The pH at this point should be 2.8.

6.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask. The Cr^{+6}–APDC complex is stable for at least 36 h.

6.8 While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating the standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of chromium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose chromium concentrations exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factor.

8. Report

Report chromium, hexavalent (01032), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

It is estimated that the precision of this method is equal to that of Method I–1238.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 76.

Midgett, M. R., and Fishman, M. J., 1967, Determination of total chromium in fresh waters by atomic absorption: Atomic Absorption Newsletter, v. 6, p. 128–131.

Chromium, recoverable from bottom material, atomic absorption spectrometric, direct (I–5236–78)

Parameter and Code: Chromium, recoverable from bottom material, dry wt ($\mu g/g$ as Cr): 01029

1. Application

1.1 This method may be used to analyze bottom material containing at least 1 $\mu g/g$ of chromium. Prepared sample solutions (Method I–5485) containing more than 400 $\mu g/L$ must either be diluted or less scale expansion must be used.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

Chromium is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–5485) into an air-acetylene flame without further preconcentration or pretreatment of the sample solution other than the addition of ammonium chloride to mask certain interferences.

3. Interferences

3.1 Iron, nickel, and cobalt at 100 $\mu g/L$, and magnesium at 30 mg/L in the prepared sample solution interfere by suppressing the absorption of the chromium. These interferences are eliminated in solutions containing about 18,000 mg/L of ammonium chloride (Barnes, 1966, and Giammarise, 1966). Samples adjusted to this concentration of ammonium chloride show no interferences from 7×10^5 $\mu g/L$ of iron and 10,000 $\mu g/L$ each of nickel and cobalt, or from 1,000 mg/L of magnesium.

3.2 Individual concentrations of sodium (8,000 mg/L), calcium (4,000 mg/L), nitrate (100 mg/L), sulfate (8,000 mg/L), and chloride (10,000 mg/L) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	357.9 nm.
Source (hollow-cathode lamp)	Chromium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Reducing.

4.3 The 102-mm flathead single slot burner allows a working range of 10 to 400 $\mu g/L$. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium chloride* solution, 200 g/L: Dissolve 200 g NH_4Cl in demineralized water and dilute to 1 L.

5.2 *Chromium* standard solution I, 1.00 mL = 100 μg Cr: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.3 *Chromium* standard solution II, 1.00 mL = 1 μg Cr: Dilute 10.0 mL chromium standard solution I to 1,000 mL with demineralized water.

5.4 *Chromium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 400 $\mu g/L$ of chromium by diluting chromium standard solution II. To each standard working solution, add 1.0 mL of NH_4Cl solution for each 10 mL of standard.

6. Procedure

6.1 Add 1.0 mL ammonium chloride solution to 10.0 mL prepared sample solution (Method I–5485) and mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero con-

centration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of chromium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose chromium concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per gram of chromium in bottom material samples first determine the micrograms per liter of chromium in each sample as in 7.1, then

$$\mathrm{Cr}\ (\mu g/g) = \frac{\mu g/L\ \mathrm{Cr} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report chromium, total in bottom material (01029), as follows: less than 10 μg/g, nearest microgram per gram; 10–100 μg/g, nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 27 percent in the lower portion of the analytical range.

References

Barnes, L., Jr., 1966, Determination of chromium in low alloy steels by atomic absorption spectrometry: Analytical Chemistry, v. 38, p. 1083–1085.

Giammarise, A., 1966, The use of ammonium chloride in analyses of chromium samples containing iron: Atomic Absorption Newsletter, v. 5, p. 113–115.

Chromium, total recoverable, atomic absorption spectrometric, chelation-extraction (I–3238–78)

Parameter and Code: Chromium, total recoverable (μg/L as Cr): 01034

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing from 1 to 25 μg/L of chromium. Samples containing more than 25 μg/L may be either diluted prior to chelation-extraction or analyzed by Method I–3236.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

1.3 If the iron concentration of the sample exceeds 5,000 μg/L, determine chromium by direct atomic absorption (Method I–3236).

2. Summary of method

The procedure used for the determination of hexavalent plus tervalent chromium is the same as that for hexavalent chromium (Method I–1232), except for an additional step to oxidize any tervalent chromium present to the hexavalent state. A modification of a method described by Saltzman (1952), whereby Cr^{+3} is oxidized by potassium permanganate, has been found satisfactory. Excess permanganate is reduced with sodium azide, which must not be present in excess, as it interferes with subsequent pH adjustment and chelation.

3. Interferences

3.1 The optimum pH for the extraction of the Cr^{+6}–ammonium pyrrolidine dithiocarbamate (Cr^{+6}–APDC) complex by methyl isobutyl ketone (MIBK) is 3.1. At this pH, however, manganese is also partially extracted. The Mn–APDC complex is unstable and decomposes to a fine suspension of manganese oxides which clog the atomizer-burner. If the pH of the sample is adjusted to 2.4 prior to chelation and extraction, less manganese is extracted, and there is only a slight loss in extraction efficiency for chromium. If the extract is not clear after overnight standing, it must be centrifuged.

3.2 Concentrations of iron greater than 5,000 μg/L interfere by suppressing the chromium absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	357.9 nm.
Source (hollow-cathode lamp)	Chromium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Reducing.

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution, 1.0 g/100 mL: Dissolve 1.0 g APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 0.1 g/100 mL: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.

5.3 *Chromium* standard solution I, 1.00 mL = 100 μg Cr^{+6}: Dissolve 0.2829 g primary standard $K_2Cr_2 0_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.4 *Chromium* standard solution II, 1.00 mL = 2.00 μg Cr^{+3}: Pipet 5.0 mL chromium standard solution I into an erlenmeyer flask.

Add approximately 15 mg Na_2SO_3 and 0.5 mL concentrated HNO_3 (sp gr 1.41). Gently evaporate just to dryness; strong heating reoxidizes the Cr. Add 0.5 mL concentrated HNO_3 and again evaporate to dryness to destroy any excess sulfite. Dissolve the residue in 1 mL concentrated HNO_3 with warming. Cool, transfer to a 250-mL volumetric flask, and dilute to the mark with demineralized water.

5.5 *Chromium* standard solution III, 1.00 mL = 0.50 μg Cr^{+3}: Dilute 25.0 mL chromium standard solution II to 100 mL with demineralized water. Prepare immediately before use.

5.6 *Methyl isobutyl ketone* (MIBK).

5.7 *Potassium permanganate* solution, 0.32 g/100 mL: Dissolve 0.32 g $KMnO_4$ in demineralized water and dilute to 100 mL. Allow to stand several days and decant if necessary.

5.8 *Sodium azide* solution, 0.10 g/100 mL: Dissolve 0.10 g NaN_3 in 100 mL demineralized water.

5.9 *Sodium hydroxide* solution, 1*M*: Dissolve 40 g NaOH in demineralized water and dilute to 1 L.

5.10 *Sulfuric acid*, 0.12*M*: Slowly add 6.5 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1+9) and rinse with demineralized water immediately before use.

6.1 Pipet a volume of the prepared sample (Method I-3485) containing less than 2.5 μg chromium (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL. The pH must be 2.0 or less. Add concentrated HNO_3 if necessary.

6.2 Acidify a liter of demineralized water with 1.5 mL concentrated HNO_3 (sp gr 1.41). Prepare a blank and at least six standards, and adjust the volumes of each to approx 100 mL with the acidified demineralized water.

6.3 Add $KMnO_4$ solution by drops to blank, standards, and samples until a faint pink color persists.

6.4 Heat on a steam bath for 20 min. If the color disappears, add $KMnO_4$ solution by drops to maintain a slight excess.

6.5 While still on the steam bath, add sodium azide solution by drops until the $KMnO_4$ color just disappears. Heat for about 2 min between each addition and avoid adding any excess. Continue heating for 5 min after adding the last drop of sodium azide solution.

6.6 Transfer to a water bath and cool to room temperature.

6.7 Remove from the water bath and filter through Whatman No. 40 filter paper any sample that has a brownish precipitate or coloration that may interfere with the pH adjustment.

6.8 Add 2.0 mL 1*M* NaOH and 2 drops bromophenol blue indicator solution. Continue the addition of 1*M* NaOH by drops to all samples and standards in which the indicator change from yellow to blue has not occurred. Add 0.12*M* H_2SO_4 by drops until the blue color just disappears, then add 2.0 mL in excess. The pH at this point should be 2.4 (NOTE 1).

NOTE 1. The pH adjustment in step 6.8 may be made with a pH meter instead of using an indicator, in which case the filtration called for in sec. 6.7 will not be necessary.

6.9 Add 5.0 mL APDC solution and shake for 3 min. The pH at this point should be 2.8.

6.10 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.11 Allow the layers to separate and then add demineralized water until the ketone layer is completely in the neck of the flask.

6.12 Stopper and allow to stand overnight. The Cr^{+6}–APDC complex is stable for at least 36 h.

6.13 While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of chromium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose chromium concentrations exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

8. Report

Report chromium, total (01034), concentrations as follows: less than 100 μg/L, nearest microgram per liter; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 25 percent at 8.0 μg/L and greater than 82 percent at 23 μg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 78.

Saltzman, B., 1952, Microdetermination of chromium with diphenyl carbazide by permanganate oxidation: Analytical Chemistry, v. 24, p. 1016.

Chromium, total recoverable, atomic absorption spectrometric, direct

(I–3236–78)

Parameter and code: Chromium, total recoverable (μg/L as Cr): 01034

1. Application

1.1 This method may be used to analyze water-suspended sediments mixtures containing at least 10 μg/L of chromium. Sample solutions containing more than 400 μg/L must either be diluted or less scale expansion must be used. Sample solutions containing less than 10 μg/L and brines must be analyzed by Method I–3238, providing that the interferences discussed in that method are not exceeded.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

Chromium is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–3485) into an air-acetylene flame without preconcentration or pretreatment of the sample solution other than the addition of ammonium chloride to mask certain interferences.

3. Interferences

3.1 Iron, nickel, and cobalt at 100 μg/L, and magnesium at 30 mg/L interfere by suppressing the absorption of the chromium. These interferences are eliminated in solutions containing about 18,000 mg/L of ammonium chloride (Barnes, 1966, and Giammarise, 1966). Samples adjusted to this concentration of ammonium chloride show no interferences from 7 × 10^5 μg/L of iron and 10,000 μg/L each of nickel, and cobalt, or from 1,000 mg/L of magnesium.

3.2 Individual concentrations of sodium (8,000 mg/L), calcium (4,000 mg/L), nitrate (100 mg/L), sulfate (8,000 mg/L), and chloride (10,000 mg/L) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	357.9 nm.
Source (hollow-cathode lamp)	Chromium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Reducing.

4.3 The 102-mm flathead single slot burner allows a working range of 10 to 400 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium chloride* solution, 200 g/L: Dissolve 200 g NH_2Cl in demineralized water and dilute to 1 L.

5.2 *Chromium* standard solution I, 1.00 mL = 100 μg Cr: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.3 *Chromium* standard solution II, 1.00 mL = 1 μg Cr: Dilute 10.0 mL chromium standard solution I to 1,000 mL with demineralized water.

5.4 *Chromium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 400 μg/L of chromium by diluting chromium standard solution II. To each standard working solution, add 1.0 mL of NH_4Cl solution for each 10 mL of standard. Prepare fresh daily.

6. Procedure

6.1 Add 1.0 mL ammonium chloride solution to 10.0 mL prepared sample solution (Method I-3485) and mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of chromium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose chromium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report chromium, total (01034), concentrations as follows: less than 1,000 μg/L, nearest 10 μg/L; 1,000 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 27 percent at 22 μg/L.

References

American Society for Testing and Materials, 1975, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 345.

Barnes, L., Jr., 1966, Determination of chromium in low alloy steels by atomic absorption spectrometry: Analytical Chemistry, v. 38, p. 1083-1085.

Giammarise, A., 1966, The use of ammonium chloride in analyses of chromium samples containing iron: Atomic Absorption Newsletter, v. 5, p. 113-115.

Cobalt, dissolved, atomic absorption spectrometric, chelation-extraction (I–1240–78)

Parameter and Code: Cobalt, dissolved (μg/L as Co): 01035

1. Application

1.1 This method may be used to analyze waters and brines containing from 1 to 50 μg/L of cobalt. Water samples containing more than 50 μg/L may be either diluted prior to chelation-extraction or analyzed by Method I–1239.

1.2 If the iron concentration of the sample exceeds 25,000 μg/L, determine cobalt by direct atomic absorption spectrometry (Method I–1239).

2. Summary of method

2.1 Cobalt is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer (Fishman and Midgett, 1968).

2.2 Two procedures are given (6A and 6B), differing only in the manner of adjusting the pH of the sample solution prior to chelation and extraction of the cobalt. Both methods are believed to be equally reliable, and the choice of method is left to the analyst.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the cobalt absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	240.7 nm.
Source (hollow-cathode lamp)	Cobalt.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate (APDC)* solution, 1 g/100 mL: Dissolve 1.0 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution: Dissolve 252 g bromophenol blue in 1 L 50-percent ethanol.

5.3 *Citric acid-sodium citrate buffer* solution: Dissolve 252 g citric acid monohydrate and 88.2 g sodium citrate dihydrate in demineralized water. Add 100 mL bromophenol blue indicator solution and dilute to 1 L with demineralized water. (Procedure A only.)

5.4 *Cobalt* standard solution I, 1.00 mL = 200 μg Co: Dissolve 0.9877 g $Co(NO_3)_2\ 6H_2O$ in demineralized water, add 1 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL.

5.5 *Cobalt* standard solution II, 1.00 mL = 2.0 μg Co: Dilute 10.0 mL cobalt standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.6 *Cobalt* standard solution III, 1.00 mL = 0.2 μg Co: Immediately before use, dilute 10.0 mL cobalt standard solution II to 100.0 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.7 *Hydrochloric acid,* 0.3*M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L. (Procedure B only.)

5.8 *Methyl isobutyl ketone (MIBK).*

5.9 *Sodium hydroxide,* 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 mL. (Procedure B only.)

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.A Procedure A

6.A.1 Pipet a volume of sample containing less than 5.0 μg Co (100 mL maximum) into a 200-mL volumetric flask, and adjust volume to approx 100 mL.

6.A.2 Prepare a blank with 1.5 mL HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.A.3 Add 10 mL buffer solution and mix (NOTE 1).

NOTE 1. If the proper amount of acid is present, the color will be a greenish yellow. If the color is yellow, add buffer solution dropwise until the proper color is obtained. If the color is green or greenish blue, add concentrated nitric acid dropwise until the proper color is obtained.

6.A.4 Add 2.5 mL APDC solution and shake for 3 min.

6.A.5 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.A.6 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.A.7 Aspirate the ketone layer within 1 h. While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

6.B Procedure B

6.B.1 Pipet a volume of sample containing less than 5.0 μg Co (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.B.2 Prepare a blank with 1.5 mL HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.B.3 Add 2 drops of bromophenol blue indicator solution to each sample and standard.

6.B.4 Adjust the pH of each by addition of 2.5*M* NaOH by drops until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears. Then add 2.0 mL in excess. The pH at this point should be 2.4 (NOTE 2). Return to step 6.A.4 and proceed through step 6.A.7.

NOTE 2. The pH adjustment in steps 6.B.3 and 6.B.4 may be made with a pH meter instead of using an indicator.

7. Calculations

Determine the micrograms per liter of cobalt in each sample from the digital display or printer output. Dilute those samples whose cobalt concentrations exceed the working range of the method; repeat the chelation-extraction, and multiply by the proper dilution factors.

8. Report

Report cobalt, dissolved (01035), concentrations as follows: less than 100 μg/L, nearest microgram per liter; 100 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 5 to 15 μg/L may be expressed as follows:

$$S_T = 0.100X + 0.732$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of cobalt, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
5	5	20
8	14	14

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 80.

Fishman, M. J., and Midgett, M. R., 1968, Extraction techniques for the determination of cobalt, nickel, and lead in fresh water by atomic absorption, *in* Trace inorganics in water: American Chemical Society, Advances in Chemistry Series, no. 73, p. 230.

Cobalt, dissolved, atomic absorption spectrometric, direct (I-1239-78)

Parameter and Code: Cobalt dissolved (µg/L as Co): 01035

1. Application

This method may be used to analyze water ontaining at least 50 µg/L of cobalt. Sample olutions containing more than 1,000 µg/L must ither be diluted or less scale expansion must be sed. Sample solutions containing less than 50 g/L and brines must be analyzed by Method -1240, providing the interferences discussed in hat method are not exceeded.

Summary of method

Cobalt is determined by atomic absorption pectrometry by direct aspiration of the sample nto an air-acetylene flame without preconcenration or pretreatment of the sample other than he addition of ammonium chloride to mask cerain interferences.

Interferences

3.1 Nitrate at 1 mg/L interferes by depressng the absorption of the cobalt. This interfernce is eliminated in solutions containing about 8,000 mg/L of ammonium chloride. Samples adusted to this concentration of ammonium chlode show no interference from 800 mg/L of nirate.

3.2 Individual concentrations of sodium 000 mg/L), potassium [illegible] mg/L), calcium ,500 mg/L), magnesium (4,500 mg/L), sulfate ,000 mg/L), chloride (15,000 mg/L), iron (4 × 10^4 g/L), and cadmium, nickel, copper, zinc, lead, d chromium (10,000 µg/L each) do not interre. Higher concentrations of each constituent are not investigated.

Apparatus

4.1 *Atomic absorption spectrometer* equipped th electronic digital readout, automatic zero, d automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	240.7 nm.
Source (hollow-cathode lamp)	Cobalt.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The Perkin-Elmer flathead single slot burner allows a working range of 50 to 1,000 µg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ammonium chloride solution*, 200 g/L: Dissolve 200 g NH_4Cl in demineralized water and dilute to 1 L.

5.2 *Cobalt standard solution I*, 1.00 mL = 200 µg Co: Dissolve 0.9877 g $Co(NO_3)_2 \cdot 6H_2O$ in demineralized water, add 1 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL with demineralized water.

5.3 *Cobalt standard solution II*, 1.00 mL = 10 µg Co: Dilute 50.0 mL cobalt standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.4 *Cobalt standard working solutions*: Prepare a series of at least six standard working solutions containing from 0 to 1,000 µg/L of cobalt by appropriate dilution of cobalt standard solution II. To each standard working solution, add 1.0 mL of NH_4Cl solution for each 10 mL of standard solution. Prepare fresh daily.

6. Procedure

6.1 Add 1.0 mL NH_4Cl solution to 10.0 mL of sample and mix thoroughly.

6.2 While aspirating the blank use auto-zero to set instrument digital display at zero con-

Cobalt, dissolved, atomic absorption spectrometric, direct (I–1239–78)

Parameter and Code: Cobalt dissolved (µg/L as Co): 01035

1. Application

This method may be used to analyze water containing at least 50 µg/L of cobalt. Sample solutions containing more than 1,000 µg/L must either be diluted or less scale expansion must be used. Sample solutions containing less than 50 µg/L, and brines must be analyzed by Method I–1240, providing the interferences discussed in that method are not exceeded.

2. Summary of method

Cobalt is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment of the sample other than the addition of ammonium chloride to mask certain interferences.

3. Interferences

3.1 Nitrate at 1 mg/L interferes by depressing the absorption of the cobalt. This interference is eliminated in solutions containing about 18,000 mg/L of ammonium chloride. Samples adjusted to this concentration of ammonium chloride show no interference from 800 mg/L of nitrate.

3.2 Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,500 mg/L), magnesium (4,500 mg/L), sulfate (9,000 mg/L), chloride (15,000 mg/L), iron (4×10^6 µg/L), and cadmium, nickel, copper, zinc, lead, and chromium (10,000 µg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	240.7 nm.
Source (hollow-cathode lamp)	Cobalt.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The Perkin–Elmer flathead single slot burner allows a working range of 50 to 1,000 µg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ammonium chloride* solution, 200 g/L: Dissolve 200 g NH_4Cl in demineralized water and dilute to 1 L.

5.2 *Cobalt* standard solution I, 1.00 mL = 200 µg Co: Dissolve 0.9877 g $Co(NO_3)_2\ 6H_2O$ in demineralized water, add 1 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL with demineralized water.

5.3 *Cobalt* standard solution II, 1.00 mL = 10 µg Co: Dilute 50.0 mL cobalt standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.4 *Cobalt* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 µg/L of cobalt by appropriate dilution of cobalt standard solution II. To each standard working solution, add 1.0 mL of NH_4Cl solution for each 10 mL of standard solution. Prepare fresh daily.

6. Procedure

6.1 Add 1.0 mL NH_4Cl solution to 10.0 mL of sample and mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero con-

centration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of cobalt in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose cobalt concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report cobalt, dissolved (01035), concentrations to the nearest 50 μg/L.

9. Precision

Precision data are not available for this method.

Reference

American Society for Testing and Materials, 1975, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 345.

Cobalt, recoverable from bottom material, atomic absorption spectrometric, direct (I–5239–78)

Parameter and Code: Cobalt, recoverable from bottom material, dry wt (μg/g as Co): 01038

1. Application

1.1 This method may be used to analyze bottom material containing at least 5 μg/g of cobalt. Prepared sample solutions (Method I–5485) containing more than 1,000 μg/L must either be diluted or less scale expansion used.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

Cobalt is determined by atomic absorption spectrometry by direct aspiration of a prepared sample solution (Method I–5485) into an air-acetylene flame without further treatment of the sample solution other than the addition of ammonium chloride to mask certain interferences.

3. Interferences

3.1 Nitrate at 1 mg/L interferes by suppressing the absorption of the cobalt. This interference is eliminated in solutions containing about 18,000 mg/L of ammonium chloride. Samples adjusted to this concentration of ammonium chloride show no interference from 800 mg/L of nitrate.

3.2 Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,500 mg/L), magnesium (4,500 mg/L), sulfate (9,000 mg/L), chloride (15,000 mg/L), iron (4,000 mg/L), and cadmium nickel, copper, zinc, lead, and chromium (10 mg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	240.7 nm.
Source (hollow-cathode lamp)	Cobalt.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The Perkin–Elmer flathead single slot burner allows a working range of 50 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium chloride* solution, 200 g/L: Dissolve 200 g NH_4Cl in demineralized water and dilute to 1 L.

5.2 *Cobalt* standard solution I, 1.00mL = 200 μg Co: Dissolve 0.9877 g $Co(NO_3)_2 \cdot 6H_2O$ in demineralized water, add 1 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL with demineralized water.

5.3 *Cobalt* standard solution II, 1.00 mL = 10 μg Co: Dilute 50.0 mL cobalt standard solution I and 1 mL concentrated HNO_3 to 1,000 mL with demineralized water.

5.4 *Cobalt* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 μg/L of cobalt by appropriate dilution of cobalt standard solution II. Add 1.0 mL of NH_4Cl solution for each

10 mL of standard working solution. Prepare fresh daily.

6. Procedure

6.1 Add 1.0 mL NH_4Cl solution to 10.0 mL of prepared sample solution (Method I–5485) and mix thoroughly.

6.2 While aspirating the blank use auto zero to set the instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of cobalt in each prepared sample solution (Method I–5485) from the digital display or printer output while aspirating each sample. Dilute those samples whose cobalt concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per gram of cobalt in bottom material samples, first determine the micrograms per liter of cobalt in each sample as in 7.1, then

$$\text{Co } (\mu g/g) = \frac{\mu g/L \text{ Co} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report cobalt, recoverable from bottom material (01038), concentrations as follows: less than 100 $\mu g/g$, the nearest 10 $\mu g/g$; 100 $\mu g/g$ and above, two significant figures.

9. Precision

Precision data are not available for this method.

Cobalt, total recoverable, atomic absorption spectrometric, chelation-extraction (I–3240–78)

Parameter and Code: Cobalt, total recoverable (μg/L as Co): 01037

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing from 1 to 50 μg/L of cobalt. Water samples containing more than 50 μg/L may be either diluted prior to chelation-extraction or analyzed by Method I–3239.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

1.3 If the iron concentration of the prepared sample solution (Method I–3485) exceeds 25,000 μg/L, determine cobalt by direct atomic absorption spectrometry (Method I–3239).

2. Summary of method

2.1 Cobalt is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer (Fishman and Midgett, 1968).

2.2 Two procedures are given (6A and 6B), differing only in the manner of adjusting the pH of the sample solution prior to chelation and extraction of the cobalt. Both methods are believed to be equally reliable, and the choice of method is left to the analyst.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the cobalt absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	240.7 nm.
Source (hollow-cathode lamp)	Cobalt.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate (APDC)* solution, 1 g/100 mL: Dissolve 1.0 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 1 g/L: Dissolve 1 g bromophenol blue in 1 L 50-percent ethanol.

5.3 *Sodium citrate buffer* solution: Dissolve 450 g sodium citrate dihydrate in demineralized water. Add 100 mL bromophenol blue indicator solution and dilute to 1 L with demineralized water. (Procedure A only.)

5.4 *Cobalt* standard solution I, 1.00 mL = 200 μg Co: Dissolve 0.9877 g $Co(NO_3)_2$ $6H_2O$ in demineralized water, add 1 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL.

5.5 *Cobalt* standard solution II, 1.00mL = 2.0 μg Co: Dilute 10.0 mL cobalt standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.6 *Cobalt* standard solution III, 1.00 mL = 0.2 μg Co: Immediately before use, dilute 10.0 mL cobalt standard solution II to 100.0 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.7 *Hydrochloric acid,* 0.3*M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L. (Procedure B only.)

5.8 *Methyl isobutyl ketone (MIBK).*

5.9 *Sodium hydroxide,* 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 mL. (Procedure B only.)

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.A Procedure A

6.A.1 Pipet a volume of prepared sample solution (Method I–3485) containing less than 5.0 μg Co (100 mL maximum) into a 200-mL volumetric flask, and adjust volume to approximately 100 mL (NOTE 1).

NOTE 1. If the samples must be diluted prior to chelation-extraction, a specially prepared dilution water must be used. It is prepared as follows: Dilute 25 mL HCl to 1 L with demineralized water.

6.A.2 Prepare a blank and at least six standards, and adjust the volume of each to approx 100 mL with the specially prepared dilution water (NOTE 1).

6.A.3 Add 10 mL buffer solution and mix (NOTE 2).

NOTE 2. If the proper amount of acid is present, the color will be a greenish yellow. If the color is yellow, add buffer solution dropwise until the proper color is obtained. If the color is green or greenish blue, add concentrated nitric acid dropwise until the proper color is obtained.

6.A.4 Add 2.5 mL APDC solution and shake for 3 min.

6.A.5 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.A.6 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.A.7 Aspirate the ketone later within 1 h. While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

6.B Procedure B

6.B.1 Pipet a volume of prepared sample solution (Method I–3485) containing less than 5.0 μg Co (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approximately 100 mL.

6.B.2 Prepare a blank with 1.5 mL HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.B.3 Add 2 drops of bromophenol blue indicator solution to each sample and standard.

6.B.4 Adjust the pH of each by addition of 2.5*M* NaOH by drops until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears. Then add 2.0 mL in excess. The pH at this point should be 2.4 (NOTE 3). Return to step 6.A.4 and proceed through step 6.A.7.

NOTE 3. The pH adjustment in steps 6.B.3 and 6.B.4 may be made with a pH meter instead of using indicator.

7. Calculations

Determine micrograms per liter of cobalt in each sample from the digital display or printer output. Dilute those samples whose cobalt concentrations exceed the working range of the method; repeat the chelation-extraction, and multiply by the proper dilution factors.

8. Report

Report cobalt, total (01037), concentrations as follows: less than 100 μg/L, nearest microgram per liter; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 20 percent at 5.0 μg/L and greater than 14 percent at 14.0 μg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter Al, p. 80.

Fishman, M. J., and Midgett, M. R., 1968, Extraction techniques for the determination of cobalt, nickel, and lead in fresh water by atomic absorption, *in* Trace inorganics in water: American Chemical Society, Advances in Chemistry Series, no. 73, p. 230.

Cobalt, total recoverable, atomic absorption spectrometric, direct (I–3239–78)

Parameter and Code: Cobalt, total recoverable (μg/L as Co): 01037

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 50 μg/L of cobalt. Prepared sample solutions (Method I–3485) containing more than 1,000 μg/L must either be diluted or less scale expansion used. Sample solutions containing less than 50 μg/L must be analyzed by Method I–3240 providing the interferences discussed in that method are not exceeded.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

Cobalt is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–3485) into an air-acetylene flame without additional treatment of the sample other than the addition of ammonium chloride to mask certain interferences.

3. Interferences

3.1 Nitrate at 1 mg/L interferes by suppressing the absorption of the cobalt. This interference is eliminated in solutions containing about 18,000 mg/L of ammonium chloride. Samples adjusted to this concentration of ammonium chloride show no interference from 800 mg/L of nitrate.

3.2 Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,500 mg/L), magnesium (4,500 mg/L), sulfate (9,000 mg/L), chloride (15,000 mg/L), iron (4×10^6 μg/L), and cadmium nickel, copper, zinc, lead, and chromium (10,000 μg/L) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturers' manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**240.7 nm.**
Source (hollow-cathode lamp)	**Cobalt.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

4.3 The Perkin–Elmer flathead single slot burner allows a working range of 50 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium chloride* solution, 200 g/L: Dissolve 200 g NH_4Cl in demineralized water and dilute to 1 L.

5.2 *Cobalt* standard solution I, 1.00mL = 200 μg Co: Dissolve 0.9877 g $Co(NO_3)_2$ $6H_2O$ in demineralized water, add 1 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL with demineralized water.

5.3 *Cobalt* standard solution II, 1.00mL = 10 μg Co: Dilute 50.0 mL cobalt standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.4 *Cobalt* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 μg/L cobalt by appropriate dilution of cobalt standard solution II. Add 1.0 mL NH_4Cl solution for each 10 mL standard working solution. Prepare fresh daily.

6. Procedure

6.1 Add 1.0 mL NH_4Cl solution to 10.0 mL prepared sample solution (Method I–3485) and mix thoroughly.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of cobalt in each prepared sample solution (Method I–3485) from the digital display or printer output while aspirating each sample. Dilute those samples whose cobalt concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report cobalt, total recoverable (01037), concentrations as follows: less than 1,000 μg/L to the nearest 50 μg/L; 1,000 μg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

Reference

American Society for Testing and Materials, 1975, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 345.

Copper, dissolved, atomic absorption spectrometric, chelation-extraction (I–1271–78)

Parameter and Code: Copper, dissolved (μg/L as Cu): 01040

1. Application

1.1 This method may be used to analyze water containing from 1 to 75 μg/L of copper. Samples containing more than 75 μg/L may be either diluted prior to chelation-extraction or determined by direct atomic absorption spectrometry (Method I–1270).

1.2 If the iron concentration of the sample exceeds 25,000 μg/L, determine copper by direct atomic absorption spectrometry (Method I–1270).

2. Summary of method

2.1 Copper is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer.

2.2 Two procedures are given (6A and 6B), differing only in the manner of adjusting the pH of the sample solution prior to chelation and extraction of the copper. Both methods are believed to be equally reliable, and the choice of method is left to the analyst.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the copper absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	324.7 nm.
Source (hollow-cathode lamp)	Copper.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate (APDC)* solution, 1 g/100 mL. Dissolve 1 g APDC in 100 ml demineralized water. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 1 g/L: Dissolve 1 g bromophenol blue in 1 L 50-percent ethanol.

5.3 *Citric acid-sodium citrate buffer* solution: Dissolve 252 g citric acid monohydrate and 88.2 g sodium citrate dihydrate in demineralized water. Add 100 mL bromophenol blue indicator solution and dilute to 1 L with demineralized water. (Procedure A only.)

5.4 *Copper* standard solution I, 1.00 mL = 100 μg Cu: Dissolve 0.100 g metallic copper in a minimum quantity of dilute HNO_3 and dilute to 1,000 mL with demineralized water.

5.5 *Copper* standard solution II, 1.00 mL = 1.00 μg Cu: Dilute 10.0 mL copper standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at time of analysis.

5.6 *Hydrochloric acid*, 0.3*M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L. (Procedure B only.)

5.7 *Methyl isobutyl ketone (MIBK)*.

5.8 *Sodium hydroxide*, 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 mL. (Procedure B only.)

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.A Procedure A

6.A.1 Pipet a volume of sample containing less than 7.5 μg Cu (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.A.2 Prepare a blank with 1.5 mL HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.A.3 Add 10 mL buffer solution and mix (NOTE 1).

NOTE 1. If the proper amount of acid is present, the color will be a greenish yellow. If the color is yellow, add buffer solution dropwise until the proper color is obtained. If the color is green or greenish blue, add concentrated nitric acid dropwise until the proper color is obtained.

6.A.4 Add 2.5 mL APDC solution and shake for 3 min.

6.A.5 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.A.6 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.A.7 Aspirate the ketone layer within 1 h. While aspirating the ketone layer of the blank use the auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

6.B Procedure B

6.B.1 Pipet a volume of sample containing less than 7.5 μg Cu (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.B.2 Prepare a blank with 1.5 mL HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.B.3 Add 2 drops bromophenol blue indicator solution to each sample and standard.

6.B.4 Adjust the pH of each by addition of 2.5*M* NaOH by drops until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears. Then add 2.0 mL in excess. The pH should then be 2.4 (NOTE 2). Return to step 6.A.4 and proceed through step 6.A.7.

NOTE 2. The pH adjustment in steps 6.B.3 and 6.B.4 may be made with a pH meter instead of using indicator.

7. Calculations

Determine the micrograms per liter of copper in each sample from the digital display or printer output. Dilute those samples whose copper concentrations exceed the working range of the method; repeat the chelation-extraction, and multiply by the proper dilution factors.

8. Report

Report copper, dissolved (01040), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
5	25.0	23

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 84.

Copper, dissolved, atomic absorption spectrometric, direct (I–1270–78)

Parameter and Code: Copper, dissolved (μg/L as Cu): 01040

1. Application

This method may be used to analyze water containing at least 10 μg/L of copper. Sample solutions containing more than 1,000 μg/L must either be diluted or less scale expansion used. Brines must be analyzed by Method I–1271, providing that the interferences discussed in that method are not exceeded.

2. Summary of method

2.1 Copper is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (2,000 mg/L), iron (4×10^6 g/L), lead, cadmium, zinc, and chromium (10,000 g/L each) do not interfere. Higher concentrations of each constituent were not investigated. Nickel and cobalt concentrations greater than 8,000 μg/L suppress the copper absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	324.7 nm.
Source (hollow-cathode lamp)	Copper.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The 100-mm (4-in.) flathead single slot burner allows a scale expansion of 10 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Copper* standard solution I, 1.00 mL = 1,000 μg Cu: Dissolve 1.00 g metallic copper in a slight excess of dilute HNO_3, and dilute to 1,000 mL with demineralized water.

5.2 *Copper* standard solution II, 1.00 mL = 500 μg Cu: Dilute 5.0 mL copper standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at time of analysis.

5.3 *Copper* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 μg/L of copper by appropriate dilution of copper standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of copper in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose copper concentrations exceed the working range of the method and multiply by proper dilution factors.

8. Report

Report copper, dissolved (01040), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 50 to 600 μg/L may be expressed as follows:

$$S_T = 0.063X + 9.34$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of copper, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (µg/L)*	*Relative deviation (percent)*
24	79	15
23	595	9

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 83.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 28.

Copper, recoverable from bottom material, atomic absorption spectrometric, direct (I–5270–78)

Parameter and Code: Copper, recoverable from bottom material, dry wt (μg/g as Cu): 01043

1. Application

1.1 This method may be used to analyze bottom material containing at least 1 μg/g of copper. Prepared sample solutions (Method I–5485) containing more than 1,000 μg/L must either be diluted or less scale expansion used.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

2.1 Copper is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–5485) into an air-acetylene flame (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (2,000 mg/L), iron (4×10^6 μg/L), lead, cadmium, zinc, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated. Nickel and cobalt concentrations greater than 8 mg/L suppress the copper absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	324.7 nm.
Source (hollow-cathode lamp)	Copper.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The 100-mm (4-in.) flathead single slot burner allows a scale expansion of 10 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Copper* standard solution I, 1.00 mL = 1,000 μg Cu: Dissolve 1.00 g metallic copper in a slight excess of dilute HNO_3, and dilute to 1,000 mL with demineralized water.

5.2 *Copper* standard solution II, 1.00 mL = 5.00 μg Cu: Dilute 5.0 mL copper standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at time of analysis.

5.3 *Copper* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 μg/L of copper by appropriate dilution of copper standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument

each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of copper in each prepared sample solution (Method I–5485) from the digital display or printer output while aspirating each sample. Dilute those samples whose copper concentrations exceed the working range of the method and multiply by proper dilution factors.

7.2 To determine the micrograms per gram of copper in bottom material samples, first determine the micrograms per liter of copper in each sample as in 7.1, then

$$\text{Cu } (\mu g/g) = \frac{\mu g/L \text{ Cu} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample in grams}}$$

8. Report

Report copper, recoverable from bottom material (01043), concentrations as follows: less than 10 μg/g, nearest microgram per gram; 10 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 15 percent in the lower portion of the analytical range and greater than 9 percent in the mid-portion of the analytical range.

Reference

Fishman M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 28.

Copper, total recoverable, atomic absorption spectrometric, chelation-extraction (I–3271–78)

Parameter and Code: Copper, total recoverable (μg/L as Cu): 01042

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing from 1 to 75 μg/L of copper. Samples containing more than 75 μg/L may be either diluted prior to chelation-extraction or determined by direct atomic absorption spectrometry (Method I–3270).

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

1.3 If the iron concentration of the sample exceeds 25,000 μg/L, determine copper by direct atomic absorption spectrometry (Method I–3270).

2. Summary of method

2.1 Copper is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer.

2.2 Two procedures are given (6A and 6B), differing only in the manner of adjusting the pH of the sample solution prior to chelation-extraction of the copper. Both methods are believed to be equally reliable, and the choice of method is left to the analyst.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the copper absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	324.7 nm.
Source (hollow-cathode lamp)	Copper.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate (APDC)* solution, 1 g/100 mL. Dissolve 1 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 1 g/L: Dissolve 1 g bromophenol blue in 1 L 50-percent ethanol.

5.3 *Sodium citrate buffer* solution: Dissolve 450 g sodium citrate dihydrate in demineralized water. Add 100 mL bromophenol blue indicator solution and dilute to 1 L with demineralized water. (Procedure A only.)

5.4 *Copper* standard solution I, 1.00 mL = 100 μg Cu: Dissolve 0.100 g metallic copper in a minimum quantity of dilute HNO_3 and dilute to 1,000 mL with demineralized water.

5.5 *Copper* standard solution II, 1.00 mL = 1.00 μg Cu: Dilute 10.0 mL copper standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.6 *Hydrochloric acid*, 0.3*M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L. (Procedure B only.)

5.7 *Methyl isobutyl ketone* (MIBK).

5.8 *Sodium hydroxide*, 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 mL. (Procedure B only.)

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.A Procedure A

6.A.1 Pipet a volume of prepared sample solution (Method I–3485) containing less than 7.5 μg Cu (100 mL maximum) into a 200-mL volumetric flask, and adjust volume to approx 100 mL (NOTE 1).

NOTE 1. If the samples must be diluted prior to chelation-extraction, a specially prepared dilution water must be used. It is prepared as follows: dilute 25 mL HCl to 1 L with demineralized water.

6.A.2 Prepare a blank and at least six standards, and adjust the volume of each to approx 100 mL with the specially prepared dilution water (NOTE 1).

6.A.3 Add 10 mL buffer solution and mix (NOTE 2).

NOTE 2. If the proper amount of acid is present, the color will be a greenish yellow. If the color is yellow, add buffer solution dropwise until the proper color is obtained. If the color is green or greenish blue, add concentrated nitric acid dropwise until the proper color is obtained.

6.A.4 Add 2.5 mL APDC solution and shake for 3 min.

6.A.5 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.A.6 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.A.7 Aspirate the ketone layer within 1 h. While aspirating the ketone layer of the blank use the auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

6.B Procedure B

6.B.1 Pipet a volume of prepared sample solution (Method I–3485) containing less than 7.5 μg Cu (100 mL maximum) into a 200-mL volumetric flask and adjust the volume to approx 100 mL.

6.B.2 Prepare a blank with 1.5 mL concentrated HNO_3 per liter of demineralized water and sufficient standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.B.3 Add 2 drops bromophenol blue indicator solution to each sample and standard.

6.B.4 Adjust the pH of each by addition of 2.5*M* NaOH by drops until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears. Then add 2.0 mL in excess. The pH should then be 2.4 (NOTE 3). Return to step 6.A.4 and proceed through step 6.A.7.

NOTE 3. The pH adjustment in steps 6.B.3 and 6.B.4 may be made with a pH meter instead of using indicator.

7. Calculations

Determine the micrograms per liter of copper in each sample from the digital display or printer output. Dilute those samples whose copper concentrations exceed the working range of the method; repeat the chelation-extraction, and multiply by the proper dilution factors.

8. Report

Report copper, total recoverable (01042), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 23 percent at 25 μg/L.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 84.

Copper, total recoverable, atomic absorption spectrometric, direct (I–3270–78)

Parameter and Code: Copper, total recoverable (μg/L as Cu): 01042

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 10 μg/L of copper. Sample solutions containing more than 1,000 μg/L must either be diluted or less scale expansion used. Brines must be analyzed by Method I–3271, providing that the interferences discussed in that method are not exceeded.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

2.1 Copper is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–3485) into an air-acetylene flame without additional treatment (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer or both. (See Metals, I–2470.)

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (2,000 mg/L), iron (4×10^6 μg/L), lead, cadmium, zinc, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated. Nickel and cobalt concentrations greater than 8,000 μg/L suppress the copper absorption.

4. Apparatus

4.1 Atomic absorption spectrometer equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	324.7 nm.
Source (hollow-cathode lamp)	Copper.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The 100-mm (4-in.) flathead single slot burner allows a working range of 10 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Copper* standard solution I, 1.00 mL = 1,000 μg Cu: Dissolve 1.00 g metallic copper in a slight excess of dilute HNO_3, and dilute to 1,000 mL with demineralized water.

5.2 *Copper* standard solution II, 1.00 mL = 5.00 μg Cu: Dilute 5.0 mL copper standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at time of analysis.

5.3 *Copper* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 μg/L of copper by appropriate dilution of copper standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument

each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of copper in each prepared sample solution (Method I–3485) from the digital display or printer output while aspirating each sample. Dilute those samples whose copper concentrations exceed the working range of the method and multiply by proper dilution factors.

8. Report

Report copper, total recoverable (01042), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 15 percent at 79 μg/L and greater than 9 percent at 595 μg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1 p. 83.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 28.

Iron, dissolved, atomic absorption spectrometric, direct (I–1381–78)

Parameter and Code: Iron, dissolved (μg/L as Fe): 01046

1. Application

This method may be used to analyze waters containing at least 10 μg/L of iron. Sample solutions containing more than 1,000 μg/L must be diluted or less scale expansion used. Brines must be either diluted to below 20,000 mg/L of dissolved solids, or analyzed by the colorimetric method I–1379.

2. Summary of method

2.1 Iron is determined by atomic absorption spectrometry. The sample is aspirated directly with no pretreatment other than filtration or dilution as required.

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer, or both. (See Metals I–2470.)

3. Interferences

Individual concentrations of sodium, potassium, chloride, and sulfate (5,000 mg/L each), calcium and magnesium (1,000 mg/L each), nitrate (100 mg/L), and chromium, manganese, cobalt, nickel, copper, zinc, silver, cadmium, tin, lead, lithium, mercury, selenium, aluminum, antimony, arsenic, vanadium, boron, and molybdenum (1×10^5 μg/L each), do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**248.3 nm.**
Source (hollow-cathode lamp)	**Iron.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Iron* standard solution I, 1.00 mL = 400 μg Fe: Weigh 0.400 g analytical grade iron wire which has been cleaned in dilute HCl, rinsed, and dried. Dissolve in 5 mL concentrated HNO_3 (sp gr 1.41), warming if necessary, and dilute to 1,000 mL with demineralized water.

5.2 *Iron* standard solution II, 1.00 mL = 4.00 μg Fe: Dilute 10.0 mL iron standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.3 *Iron* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 μg/L of iron by appropriate dilution of iron standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of iron in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose iron concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report iron, dissolved (01046), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 80 to 1,000 μg/L may be expressed as follows:

$$S_T = 0.056X + 23.90$$

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
17	100	31
13	445	

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissoved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 102.

Iron, recoverable from bottom material, atomic absorption spectrometric, direct (I–5381–78)

Parameter and Code: Iron, recoverable from bottom material dry wt (μg/g as Fe): 01170

1. Application

1.1 This method may be used to analyze bottom material containing at least 1 μg/g of iron. Prepared sample solutions (Method I–5485) containing more than 1,000 μg/L must either be diluted or less scale expansion used.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

2.1 Iron is determined by atomic absorption spectrometry. The prepared sample solution (Method I–5485) is aspirated directly into an air-acetylene flame with no further pretreatment other than dilution as may be required.

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer, or both. (See Metals I–2470.)

3. Interferences

Individual concentrations of sodium, potassium, chloride, and sulfate (5,000 mg/L each), calcium and magnesium (1,000 mg/L each), and nitrate (100 mg/L), and chromium, manganese, cobalt, nickel, copper, zinc, silver, cadmium, tin, lead, lithium, mercury, selenium, aluminum, antimony, arsenic, vanadium, boron, and molybdenum (1×10^5 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	248.3 nm.
Source (hollow-cathode lamp)	Iron.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Iron* standard solution I, 1.00 mL = 400 μg Fe: Weigh 0.400 g analytical grade iron wire which has been cleaned in dilute HCl, rinsed, and dried. Dissolve in 5 mL concentrated HNO_3 (sp gr 1.41), warming if necessary, and dilute to 1,000 mL with demineralized water.

5.2 *Iron* standard solution II, 1.00 mL = 4.00 μg Fe: Dilute 10.0 mL iron standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at time of analysis.

5.3 *Iron* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 μg/L of iron by appropriate dilution of iron standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of iron in each prepared sample solution (Method I–5485) from the digital display or printer output while aspirating each sample. Dilute those samples whose iron concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per gram of iron in bottom material samples, first determine the micrograms per liter of iron as in 7.1, then

$$\text{Fe } (\mu g/g) = \frac{\mu g/L \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}.$$

8. Report

Report iron, recoverable from bottom material (01170), concentrations as follows: less than 100 μg/g, nearest microgram per gram; 100 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 3 percent in the lower portion of the analytical range and greater than 10 percent in the upper portion of the analytical range.

Iron, total recoverable, atomic absorption spectrometric, direct (I–3381–78)

Parameter and Code: Iron, total recoverable (μg/L as Fe): 01045

1. Application

This method may be used to analyze water-suspended sediment mixtures containing at least 10μg/L of iron. Sample solutions containing more than 1,000 μg/L must either be diluted or less scale expansion used.

2. Summary of method

2.1 Iron is determined by atomic absorption spectrometry. The prepared sample solution (Method I–3485) is aspirated directly into an air-acetylene flame with no further pretreatment other than dilution as may be required.

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer, or both. (See Metals I–2470.)

3. Interferences

Individual concentrations of sodium, potassium, chloride, and sulfate (5,000 mg/L each), calcium and magnesium (1,000 mg/L each), and nitrate (100 mg/L), and chromium, manganese, cobalt, nickel, copper, zinc, silver, cadmium, tin, lead, lithium, mercury, selenium, aluminum, antimony, arsenic, vanadium, boron, and molybdenum (1×10^5 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**248.3 nm.**
Source (hollow-cathode lamp)	**Iron.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Iron* standard solution I, 1.00 mL = 400 μg Fe: Weigh 0.400 g analytical grade iron wire which has been cleaned in dilute HCl, rinsed, and dried. Dissolve in 5 mL concentrated HNO_3 (sp gr 1.41), warming if necessary, and dilute to 1,000 mL with demineralized water.

5.2 *Iron* standard solution II, 1.00 mL = 4.00 μg Fe: Dilute 10.0 mL iron standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at time of analysis.

5.3 *Iron* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 μg/L of iron by appropriate dilution of iron standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of iron in each prepared sample solution (Method I–3485) from the digital display or printer output while aspirating each sample. Dilute those samples whose iron concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report iron, total recoverable (01045), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 31 percent at 100 μg/L and greater than 10 percent at 445 μg/L.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 112.

Lead, dissolved, atomic absorption spectrometric, chelation-extraction (I–1400–78)

Parameter and Code: Lead, dissolved (μg/L as Pb): 01049

1. Application

1.1 This method may be used to analyze waters and brines containing from 1 to 100 μg/L of lead. Water samples containing more than 100 μg/L may be either diluted prior to chelation-extraction or analyzed by Method I–1399.

1.2 If the iron concentration of the sample exceeds 25,000 μg/L, determine lead by direct atomic absorption spectrometry (Method I–1399).

2. Summary of method

2.1 Lead is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer (Fishman and Midgett, 1968).

2.2 Two procedures are given (6A and 6B), differing only in the manner of adjusting the pH of the sample solution prior to chelation-extraction of the lead. Both methods are believed to be equally reliable, and the choice of method is left to the analyst.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the lead absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**283.3 nm.**
Source (hollow-cathode lamp or electrodeless discharge lamp).	**Lead.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate (APDC)* solution, 1 g/100 mL: Dissolve 1.0 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 1 g/L: Dissolve 1 g bromophenol blue in 1 L 50-percent ethanol.

5.3 *Citric acid-sodium citrate buffer* solution: Dissolve 252 g citric acid monohydrate and 88.2 g sodium citrate dihydrate in demineralized water. Add 100 mL bromophenol blue indicator solution and dilute to 1 L with demineralized water. (Procedure A only.)

5.4 *Hydrochloric acid,* 0.3*M*: Mix 25.0 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L. (Procedure B only.)

5.5 *Lead* standard solution I, 1 mL = 200 μg Pb: Dissolve 0.3197 g $Pb(NO_3)_2$ in demineralized water containing 1 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL.

5.6 *Lead* standard solution II, 1 mL = 2.00 μg Pb: Dilute 10.0 mL lead standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.7 *Methyl isobutyl ketone (MIBK).*

5.8 *Sodium hydroxide,* 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 mL. (Procedure B only.)

ples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 105.

Fishman, M. J., and Midgett, M. R., 1968, Extraction techniques for the determination of cobalt, nickel, and lead in fresh water by atomic absorption, *in* Trace inorganics in water: American Chemical Society, Advances in Chemistry Series, no. 73, p. 230.

Lead, dissolved, atomic absorption spectrometric, direct (I-1399-78)

Parameter and Code: Lead, dissolved (µg/L as Pb): 01049

1. Application

This method may be used to analyze waters containing at least 100 µg/L of lead. Sample solutions containing more than 4,000 µg/L must either be diluted or less scale expansion used. Sample solutions containing less than 100 µg/L and brines must be analyzed by Method I-1400 providing that the interferences discussed in that method are not exceeded.

2. Summary of method

Lead is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment of the sample.

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (900 mg/L), iron (4×10^4 µg/L) and cadmium, nickel, copper, zinc, cobalt, and chromium (10,000 µg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	283.3 nm.
Source (hollow-cathode lamp)	Lead.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Slightly oxidizing.

4.3 The 100-mm (4-in.) slot-head single-slo burner allows a scale expansion of 100 to 4,00 µg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Lead standard solution I*, 1.00 mL = 20 µg Pb: Dissolve 0.3197 g $Pb(NO_3)_2$ in demineralized water containing 1 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Lead standard solution II*, 1.00 mL = 2 µg Pb: Dilute 100.0 mL lead standard solution I and 1 mL concentrated HNO_3 to 1,000 mL with demineralized water.

5.3 *Lead standard working solutions*: Prepare a series of at least six standard working solutions containing from 0 to 4,000 µg/L of lead by appropriate dilution of lead standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto-zero to set instrument digital display to read zero concentration. While aspirating standards use the automatic concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of lead in each sample from the digital display or printo

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.A Procedure A

6.A.1 Pipet a volume of sample containing less than 10.0 μg Pb (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.A.2 Prepare a blank with 1.5 mL HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.A.3 Add 10 mL buffer solution and mix (NOTE 1).

NOTE 1. If the proper amount of acid is present, the color will be a greenish yellow. If the color is yellow, add buffer solution dropwise until the proper color is obtained. If the color is green or greenish blue, add concentrated nitric acid dropwise until the proper color is obtained.

6.A.4 Add 2.5 mL APDC solution and shake for 3 min.

6.A.5 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.A.6 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.A.7 Aspirate the ketone layer within 1 h. While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

6.B Procedure B

6.B.1 Pipet a volume of sample containing less than 10.0 μg Pb (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.B.2 Prepare a demineralized-water blank with 1.5 mL HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.B.3 Add 2 drops bromophenol blue indicator solution to each sample and standard.

6.B.4 Adjust the pH of each by addition of 2.5*M* NaOH by drops until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears. Then add 2.0 mL 0.3*M* HCl in excess. The pH at this point should be 2.4 (NOTE 2). Return to 6.A.4 and proceed through 6.A.7.

NOTE 2. The pH adjustment in steps 6.B.3 and 6.B.4 may be made with a pH meter instead of using indicator.

7. Calculations

Determine the micrograms per liter of lead in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose lead concentrations exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

8. Report

Report lead (Pb), dissolved (01049), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 4 to 50 μg/L may be expressed as follows:

$$S_T = 0.097X + 1.45$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of lead, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
7	4.0	38
7	45.6	10

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water sam-

Lead, dissolved, atomic absorption spectrometric, direct (I–1399–78)

Parameter and Code: Lead, dissolved (μg/L as Pb): 01049

1. Application

This method may be used to analyze waters containing at least 100 μg/L of lead. Sample solutions containing more than 4,000 μg/L must either be diluted or less scale expansion used. Sample solutions containing less than 100 μg/L and brines must be analyzed by Method I–1400 providing that the interferences discussed in that method are not exceeded.

2. Summary of method

Lead is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment of the sample.

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (900 mg/L), iron (4×10^6 μg/L), and cadmium, nickel, copper, zinc, cobalt, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	283.3 nm.
Source (hollow-cathode lamp or electrodeless discharge lamp).	Lead.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Slightly oxidizing.

4.3 The 100-mm (4-in.) flathead single slot burner allows a scale expansion of 100 to 4,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Lead* standard solution I, 1.00 mL = 200 μg Pb: Dissolve 0.3197 g $Pb(NO_3)_2$ in demineralized water containing 1 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Lead* standard solution II, 1.00 mL = 20 μg Pb: Dilute 100.0 mL lead standard solution I and 1 mL concentrated HNO_3 to 1,000 mL with demineralized water.

5.3 *Lead* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 4,000 μg/L of lead by appropriate dilution of lead standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of lead in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose lead concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report lead, dissolved (01049), concentrations to the nearest 100 μg/L.

9. Precision

Precision data are not available for this method.

Reference

American Society for Testing and Materials, 1975, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 345.

Lead, recoverable from bottom material, atomic absorption spectrometric, direct (I–5399–78)

Parameter and Code: Lead, recoverable from bottom material dry wt (μg/g as Pb): 01052

1. Application

1.1 This method may be used to analyze bottom material containing at least 10 μg/g of lead. Prepared sample solutions (Method I–5485) containing more than 4,000 μg/L must be diluted or less scale expansion used.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

Lead is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–5485) into an air-acetylene flame.

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (900 mg/L), iron (4×10^6 μg/L), and cadmium, nickel, copper, zinc, cobalt, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	283.3 nm.
Source (hollow-cathode lamp or electrodeless discharge lamp).	Lead.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Slightly oxidizing.

4.3 The 100-mm (4-in.) flathead single slot burner allows a working range of 100 to 4,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Lead* standard solution I, 1.00 mL = 200 μg Pb: Dissolve 0.3197 g $Pb(NO_3)_2$ in demineralized water containing 1 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Lead* standard solution II, 1.00 mL = 20 μg Pb: Dilute 100.0 mL lead standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.3 *Lead* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 4,000 μg/L of lead by appropriate dilution of lead standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of lead in each prepared sample solution (Method I–5485) from the digital display or printer output while aspirating each sample. Dilute those samples whose lead concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per gram of lead in bottom material samples, first determine the micrograms-per-liter of lead as in 7.1, then

$$\text{Pb } (\mu g/g) = \frac{\mu g/L \text{ Pb} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report lead, recoverable from bottom material (01052), concentrations as follows: less than 100 μg/g, nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

Precision data are not available for this method.

Lead, total recoverable, atomic absorption spectrometric, chelation-extraction (I–3400–78)

Parameter and Code: Lead, total recoverable (μg/L as Pb): 01051

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing from 1 to 100 μg/L of lead. Sample solutions containing more than 100 μg/L may be either diluted prior to chelation-extraction or analyzed by Method I–3399.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

1.3 If the iron concentration of the sample exceeds 25,000 μg/L, determine lead by direct atomic absorption spectrometry (Method I–3399).

2. Summary of method

2.1 Lead is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer (Fishman and Midgett, 1968).

2.2 Two procedures are given (6A and 6B), differing only in the manner of adjusting the pH of the sample solution prior to chelation and extraction of the lead. Both methods are believed to be equally reliable, and the choice of method is left to the analyst.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the lead absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**283.3 nm.**
Source (hollow-cathode lamp or electrodeless discharge lamp).	**Lead.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate (APDC)* solution, 1 g/100 mL: Dissolve 1.0 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 1 g/L: Dissolve 1 g bromophenol blue in 1 L 50-percent ethanol.

5.3 *Sodium citrate buffer* solution: Dissolve 450 g sodium citrate dihydrate in demineralized water. Add 100 mL bromophenol blue indicator solution and dilute to 1 L with demineralized water.

5.4 *Hydrochloric acid*, 0.3*M*: Mix 25.0 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.5 *Lead* standard solution I, 1 mL = 200 μg Pb: Dissolve 0.3197 g $Pb(NO_3)_2$ in demineralized water containing 1 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL.

5.6 *Lead* standard solution II, 1 mL = 2.00 μg Pb: Dilute 10.0 mL lead standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.7 *Methyl isobutyl ketone (MIBK)*.

5.8 *Sodium hydroxide*, 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 mL.

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.A Procedure A

6.A.1 Pipet a volume of prepared sample solution (Method I-3485) containing less than 10.0 μg Pb (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL (NOTE 1).

NOTE 1. If the samples must be diluted prior to chelation-extraction, a specially prepared dilution water must be used. It is prepared as follows: Mix 25 mL HCl with demineralized water and dilute to 1 L.

6.A.2 Prepare a blank and at least six standards, and adjust the volume of each to approx 100 mL with specially prepared dilution water (NOTE 1).

6.A.3 Add 10 mL buffer solution and mix (NOTE 2).

NOTE 2. If the proper amount of acid is present, the color will be a greenish yellow. If the color is yellow, add buffer solution dropwise until the proper color is obtained. If the color is green or greenish blue, add concentrated nitric acid dropwise until the proper color is obtained.

6.A.4 Add 2.5 mL APDC solution and shake for 3 min.

6.A.5 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.A.6 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.A.7 Aspirate the ketone layer within 1 h. While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

6.B Procedure B

6.B.1 Pipet a volume of prepared sample solution (Method I-3485) containing less than 10.0 μg Pb (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.B.2 Prepare a demineralized-water blank with 1.5 mL HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.B.3 Add 2 drops bromophenol blue indicator solution to each sample and standard.

6.B.4 Adjust the pH of each by addition of 2.5*M* NaOH by drops until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears. Then add 2.0 mL 0.3*M* HCl in excess. The pH at this point should be 2.4 (NOTE 3). Return to step 6.A.4 and proceed through step 6.A.7.

NOTE 3. The pH adjustment in steps 6.B.3 and 6.B.4 may be made with a pH meter instead of using indicator.

7. Calculations

Determine the micrograms per liter of lead in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose lead concentrations exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

8. Report

Report lead, total recoverable (01051), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 38 percent at 4 μg/L and greater than 10 percent at 45.6 μg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 105.

Fishman, M. J., and Midgett, M. R., 1968, Extraction techniques for the determination of cobalt, nickel, and lead in fresh water by atomic absorption, *in* Trace inorganics in water: American Chemical Society, Advances in Chemistry Series, no. 73, p. 230.

Lead, total recoverable, atomic absorption spectrometric, direct
(I–3399–78)

Parameter and Code: Lead, total recoverable (μg/L as Pb): 01051

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 100 μg/L of lead. Sample solutions containing more than 4,000 μg/L must be diluted or less scale expansion used. Sample solutions containing less than 100 μg/L must be analyzed by Method I–3400, providing that the interferences discussed in that method are not exceeded.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

Lead is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–3485) into an air-acetylene flame.

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (900 mg/L), iron (4×10^6 μg/L), and cadmium, nickel, copper, zinc, cobalt, and chromium (10,000 μg/L) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**283.3 nm.**
Source (hollow-cathode lamp or electrodeless discharge lamp).	**Lead.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Slightly oxidizing.**

4.3 The 100-mm (4-in.) flathead single slot burner allows a working range of 100 to 4,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Lead* standard solution I, 1.00 mL = 200 μg Pb: Dissolve 0.3197 g $Pb(NO_3)_2$ in demineralized water containing 1 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Lead* standard solution II, 1.00 mL = 20 μg Pb: Dilute 100.0 mL lead standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.3 *Lead* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 4,000 μg/L of lead by appropriate dilution of lead standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of lead in each prepared sample solution (Method I–3485) from the digital display or printer output while aspirating each sample. Dilute those samples whose lead concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report lead, total recoverable (01051), concentrations to the nearest 100 µg/L.

9. Precision

Precision data are not available for this method.

Reference

American Society for Testing and Materials, 1975, ASTM Standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 345.

Lithium, dissolved, atomic absorption spectrometric, direct (I–1425–78)

Parameter and Code: Lithium, dissolved (μg/L as Li): 01130

1. Application

1.1 This method may be used to analyze waters and brines containing at least 10 μg/L of lithium.

1.2 Brines must first be diluted to eliminate interference from other elements. (See Section 3 "Interferences".) If the lithium concentrations in the diluted samples are below detection, the undiluted samples may be analyzed by the standard-addition method.

1.3 The analytical range is from 10 to 1,000 μg/L.

2. Summary of method

2.1 Lithium is determined by atomic absorption spectrometry. The sample is aspirated directly with no pretreatment other than filtration or dilution as required (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

The following elements interfere when the indicated concentrations are exceeded: sodium, 1,000 mg/L; potassium, 100 mg/L; magnesium, 200 mg/L; calcium, 200 mg/L; chloride, 1,000 mg/L; sulfate, 2,000 mg/L; nitrate, 100 mg/L; and strontium, 5,000 μg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Visible.
Wavelength	670.8 nm.
Source (hollow-cathode lamp)	Lithium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The 50-mm (2-in.) flathead single slot burner allows a scale expansion of 10 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Lithium* standard solution I, 1.00 mL = 1,000 μg Li: Dissolve 9.936 g $LiNO_3$ in demineralized water and dilute to 1,000 mL.

5.2 *Lithium* standard solution II, 1.00 mL = 10.0 μg Li: Dilute 10.0 mL lithium standard solution I to 1,000 mL with demineralized water. This solution is used to prepare working standards at time of analysis.

5.3 *Lithium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 μg/L of lithium by appropriate dilution of lithium standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of lithium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose lithium concentrations exceed working range of the method and multiply by the proper dilution factors.

8. Report

Report lithium, dissolved (01130), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 30 to 500 μg/L may be expressed as follows:

$$S_T = 0.048X + 4.84$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of lithium, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
10	54	9
18	484	5

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 107.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 30–32.

Lithium, recoverable from bottom material, atomic absorption spectrometric, direct (I–5425–78)

Parameter and Code: Lithium, recoverable from bottom material, dry wt (μg/g as Li): not assigned

1. Application

1.1 This method may be used to analyze bottom material containing at least 1 μg/g of lithium.

1.2 Bottom material must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

1.3 The analytical range is from 10 to 1,000 μg/L in the prepared sample solution.

2. Summary of method

2.1 Lithium is determined by atomic absorption spectrometry. The prepared sample solution (Method I–5485) is aspirated directly with no pretreatment other than dilution as may be required (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

The following elements interfere when the indicated concentrations are exceeded: sodium, 1,000 mg/L; potassium, 100 mg/L; magnesium, 200 mg/L; calcium, 200 mg/L; chloride, 1,000 mg/L; sulfate, 2,000 mg/L; nitrate, 100 mg/L; and strontium, 5,000 μg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Visible.**
Wavelength	**670.8 nm.**
Source (hollow-cathode lamp)	**Lithium.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

4.3 The 50-mm (2-in.) flathead single slot burner allows a working range of 10 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Lithium* standard solution I, 1.00 mL = 1,000 μg Li: Dissolve 9.936 g $LiNO_3$ in demineralized water and dilute to 1,000 mL.

5.2 *Lithium* standard solution II, 1.00 mL = 10.0 μg Li: Dilute 10.0 mL lithium standard solution I to 1,000 mL with demineralized water. This solution is used to prepare working standards at time of analysis.

5.3 *Lithium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 μg/L of lithium by appropriate dilution of lithium standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of lithium in each prepared sample solution (Method I–5485) from the digital display or printer output while aspirating each sample. Dilute those samples whose lithium concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per gram of lithium in bottom material samples, first determine micrograms per liter of lithium as in 7.1, then

$$\text{Li}\ (\mu\text{g/g}) = \frac{\mu\text{g/L} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report lithium, recoverable from bottom material, concentrations as follows: less than 10 μg/g, nearest microgram per gram; 10 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 9 percent in the lower portion of the analytical range and greater than 5 percent in the mid portion of the analytical range.

Reference

Fishman M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 30–32.

Lithium, total recoverable, atomic absorption spectrometric, direct (I–3425–78)

Parameter and Code: Lithium, total recoverable (μg/L as Li): 01132

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 10 μg/L of lithium.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

1.3 The analytical range is from 10 to 1,000 μg/L.

2. Summary of method

2.1 Lithium is determined by atomic absorption spectrometry. The prepared sample solution (Method I–3485) is aspirated directly with no pretreatment other than dilution as may be required (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

The following elements interfere when the indicated concentrations are exceeded: sodium, 1,000 mg/L; potassium, 100 mg/L; magnesium, 200 mg/L; calcium, 200 mg/L; chloride, 1,000 mg/L; sulfate, 2,000 mg/L; nitrate, 100 mg/L; and strontium, 5,000 μg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Visible.
Wavelength	670.8 nm.
Source (hollow-cathode lamp)	Lithium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The 50-mm (2-in.) flathead single slot burner allows a working range of 10 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Lithium* standard solution I, 1.00 mL = 1,000 μg Li: Dissolve 9.936 g $LiNO_3$ in demineralized water and dilute to 1,000 mL.

5.2 *Lithium* standard solution II, 1.00 mL = 10.0 μg Li: Dilute 10.0 mL lithium standard solution I to 1,000 mL with demineralized water. This solution is used to prepare working standards at time of analysis.

5.3 *Lithium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 μg/L of lithium by appropriate dilution of lithium standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of lithium in each prepared sample solution (Method I–3485) from the digital display or printer output while aspirating each sample. Dilute those samples whose lithium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report lithium, total recoverable (01132), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 9 percent at 54 μg/L and greater than 5 percent at 484 μg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 107.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 30–32.

Magnesium, dissolved, atomic absorption spectrometric, direct (I–1447–78)

Parameter and Code: Magnesium, dissolved (mg/L as Mg): 00925

1. Application

1.1 This method may be used to analyze waters and brines.

1.2 Two analytical ranges for magnesium are included: from 0.1 to 10 mg/L and from 2.5 to 50 mg/L. Samples containing magnesium concentrations greater than 50 mg/L must first be diluted.

2. Summary of method

2.1 Magnesium is determined by atomic absorption spectrometry (Fishman and Downs, 1966). Lanthanum chloride is added to mask interferences.

2.2 This procedure may be automated by the addition of a sampler, proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 The interference caused by aluminum at concentrations greater than 2,000 μg/L is masked by addition of lanthanum. Since low magnesium values result if the pH of the sample is above 7, standards are prepared in hydrochloric acid solution and samples are preserved in the field with use of nitric acid solution.

3.2 Nitrate, sulfate, and silica interfere, but in the presence of lanthanum chloride-hydrochloric acid solution at least 2,000 mg/L, 1,000 mg/L, and 200 mg/L, respectively, can be tolerated. The addition of nitric acid at the time of collection to preserve the samples causes no problem in the following procedure.

3.3 Sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	285.2 nm.
Source (hollow-cathode lamp).	Magnesium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Slightly reducing.

4.3 The 50-mm (2-in.) flathead single slot burner allows a working range of 0.1 to 10 mg/L. This burner rotated 90° allows a working range of 2.5 to 50 mg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Lanthanum chloride* solution, 87 g/L: Mix 29 g La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

5.2 *Magnesium* standard solution I, 1.00 mL = 0.50 mg Mg: Dissolve 0.500 g pure metallic Mg in a minimum amount of dilute HCl, and dilute to 1,000 mL with demineralized water.

5.3 *Magnesium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 50 mg/L magnesium by appropriate dilution of magnesium standard solution I. Add 1.0 mL $LaCl_3$ solution for each 10 mL of standard working solution.

6. Procedure

6.1 Add 1.0 mL lanthanum chloride solution to 10.0 mL of sample.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the milligrams per liter of magnesium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose magnesium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report magnesium, dissolved (00925), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 0.5 to 36 mg/L may be expressed as follows:

$$S_T = 0.043X + 0.134$$

where

S_T = overall precision, milligrams per liter, and
X = concentration magnesium, milligrams per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
23	1.98	9
20	22.0	5
17	35.6	17

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 109.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 32–34.

Magnesium, recoverable from bottom material, atomic absorption spectrometric, direct (I–5447–78)

Parameter and Code: Magnesium, recoverable from bottom material dry wt (mg/kg as Mg): 00924

1. Application

1.1 This method may be used to analyze bottom material containing at least 10 mg/kg of magnesium.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

1.3 Two analytical ranges for magnesium in the prepared sample solution (Method I–5485) are included: from 0.1 to 10 mg/L and from 2.5 to 50 mg/L. Samples containing magnesium concentrations greater than 50 mg/L must first be diluted.

2. Summary of method

2.1 Magnesium is determined by atomic absorption spectrometry (Fishman and Downs, 1966). Lanthanum chloride is added to mask interferences.

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 The interference caused by aluminum at concentrations greater than 2,000 μg/L is masked by addition of lanthanum. Since low magnesium values result if the pH of the sample is above 7, standards are prepared in hydrochloric acid solution and samples are preserved in the field with use of nitric acid solution.

3.2 Nitrate, sulfate, and silica interfere, but in the presence of lanthanum chloride-hydrochloric acid solution at least 2,000 mg/L, 1,000 mg/L, and 200 mg/L, respectively, can be tolerated. The addition of nitric acid at the time of collection to preserve the samples causes no problem in the following procedure.

3.3 Sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	285.2 nm.
Source (hollow-cathode lamp).	Magnesium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Slightly reducing.

4.3 The 50-mm (2-in.) flathead single slot burner allows a working range of 0.1 to 10 mg/L. This burner rotated 90° allows a working range of 2.5 to 50 mg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Lanthanum chloride* solution, 87 g/L: Mix 29 g La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

5.2 *Magnesium* standard solution I, 1.00 mL = 0.50 mg Mg: Dissolve 0.500 g pure metallic Mg in a minimum amount of dilute HCl, and dilute to 1,000 mL with demineralized water.

5.3 *Magnesium* standard working solutions:

Prepare a series of at least six standard working solutions containing from 0 to 50 mg/L magnesium by appropriate dilution of magnesium standard solution I. Add 1.0 mL $LaCl_3$ solution for each 10 mL of standard working solution.

6. Procedure

6.1 Add 1.0 mL lanthanum chloride solution to 10.0 mL of sample solution (Method I–5485).

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the milligrams per liter of magnesium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose magnesium concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine milligrams per kilogram of magnesium in bottom material samples, first determine the milligrams per liter of magnesium as in 7.1, then

$$\text{Mg (mg/kg)} = \frac{\text{mg/L Mg} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}.$$

8. Report

Report magnesium, recoverable from bottom material (00924), concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 9 percent in the lower portion of the analytical range and greater than 5 percent in the mid portion of the analytical range.

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 32–34.

Magnesium, total recoverable, atomic absorption spectrometric, direct (I–3447–78)

Parameter and Code: Magnesium, total recoverable (mg/L as Mg): not assigned

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

1.3 Two analytical ranges for magnesium are included: from 0.1 to 10 mg/L and from 2.5 to 50 mg/L. Samples containing magnesium at concentrations greater than 50 mg/L must first be diluted.

2. Summary of method

2.1 Magnesium is determined by atomic absorption spectrometry (Fishman and Downs, 1966). Lanthanum chloride is added to mask interferences.

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 The interference caused by aluminum at concentrations greater than 2,000 μg/L is masked by addition of lanthanum. Since low magnesium values result if the pH of the sample is above 7, standards are prepared in hydrochloric acid solution and samples are preserved in the field with use of nitric acid solution.

3.2 Nitrate, sulfate, and silica interfere, but in the presence of lanthanum chloride-hydrochloric acid solution at least 2,000 mg/L, 1,000 mg/L, and 200 mg/L, respectively, can be tolerated. The addition of nitric acid at the time of collection to preserve the samples causes no problem in the following procedure.

3.3 Sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	285.2 nm.
Source (hollow-cathode lamp).	Magnesium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Slightly reducing.

4.3 The 50-mm (2-in.) flathead single slot burner allows a working range of 0.1 to 10 mg/L. This burner rotated 90° allows a working range of 2.5 to 50 mg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Lanthanum chloride* solution, 87 g/L: Mix 29 g La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

5.2 *Magnesium* standard solution I, 1.00 mL = 0.50 mg Mg: Dissolve 0.500 g pure metallic Mg in a minimum amount of dilute HCl, and dilute to 1,000 mL with demineralized water.

5.3 *Magnesium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 50 mg/L magnesium by appropriate dilution of magnesium standard solution I. Add 1.0 mL $LaCl_3$ solution for each 10 mL of standard working solution.

6. Procedure

6.1 Add 1.0 mL lanthanum chloride solution to 10.0 mL of prepared sample solution (Method I–3485).

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the milligrams per liter of magnesium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose magnesium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report magnesium, total recoverable, concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 9 percent at 1.98 mg/L and greater than 17 percent at 35.6 mg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 109.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 32–34.

Magnesium, total recoverable, atomic absorption spectrometric, direct-EPA (I–3448–78)

Parameter and Code: Magnesium, total recoverable(mg/L as Mg): 00927

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures.

1.2 For ambient waters, analysis may be made on a measured portion of the acidified water-suspended sediment sample.

1.3 For all other waters, including domestic and industrial effluents, the atomic absorption procedure must be preceded by a digestion-solubilization as specified below. In cases where the analyst is uncertain about the type of sample, the digestion-solubilization procedure must be used.

1.4 Two analytical ranges are provided: from 0.1 to 10 mg/L of Mg and from 2.5 to 50 mg/L. Samples containing magnesium at concentrations greater than 50 mg/L must first be diluted.

2. Summary of method

2.1 Magnesium is determined by atomic absorption spectrometry (Fishman and Downs, 1966). Lanthanum chloride is added to mask interferences.

2.2 Effluent samples must undergo a preliminary nitric acid digestion followed by a hydrochloric acid solubilization.

2.3 This atomic absorption procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 The interference caused by aluminum at concentrations greater than 2,000 μg/L is masked by addition of lanthanum. Since low magnesium values result if the pH of the sample is above 7, standards are prepared in hydrochloric acid solution and samples are preserved in the field with use of nitric acid solution.

3.2 Nitrate, sulfate, and silica interfere, but in the presence of lanthanum chloride acid solution at least 2,000 mg/L, 1,000 mg/L, and 200 mg/L, respectively, can be tolerated. The addition of nitric acid to the sample as a preservative at the time of collection causes no problem in the following procedure. Samples should be evaporated just to dryness following HNO_3 digestion to avoid any possible nitrate interference.

3.3 Sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	285.2 nm.
Source (hollow-cathode lamp).	Magnesium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Slightly reducing.

4.3 The 50-mm (2-in.) flathead single slot burner allows a working range of 0.1 to 10 mg/L. This burner rotated 90° allows a range of 2.5 to 50 mg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Hydrochloric acid*, 6*M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.2 *Hydrochloric acid,* 0.3*M*: Dilute 25 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.3 *Lanthanum chloride* solution, 87 g/L: Mix 29 g La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

5.4 *Magnesium* standard solution I, 1.00 mL = 0.50 mg Mg: Dissolve 0.500 g pure metallic Mg in a minimum amount of dilute HCl, and dilute to 1,000 mL with demineralized water.

5.5 *Magnesium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 50 mg/L magnesium by diluting magnesium standard solution I. Add 1.0 mL $LaCl_3$ solution for each 10 mL of standard working solution.

5.6 *Nitric acid,* concentrated HNO_3 (sp gr 1.41).

6. Procedure

6.1 Transfer the entire sample to a beaker.

6.2 Rinse the sample bottle with 3 mL concentrated HNO_3 for each 100 mL of sample and add to the beaker. Prepare a blank using 3 mL concentrated HNO_3 per 100 mL of demineralized water.

6.3 Evaporate samples and blank to dryness on a hot plate, making sure the samples do not boil.

6.4 Cool and add an additional 3 mL concentrated HNO_3 to the beaker. Cover with a watch glass, return to the hot plate and gently reflux the sample.

6.5 Continue heating, adding additional acid as necessary, until digestion is complete (indicated by a light-colored residue). Evaporate just to dryness.

6.6 Add 6 mL 6*M* HCl solution per 100 mL of original sample and warm the beaker to dissolve the residue.

6.7 Wash the watch glass and beaker with demineralized water and filter the sample (Whatman No. 41 or equivalent), rinsing the filter with hot, dilute 0.3*M* HCl. Dilute to the original volume with demineralized water.

6.8 Add 1.0 mL lanthanum chloride solutio per 10.0 mL of sample.

6.9 While aspirating the blank use auto zer to set instrument digital display to read zero concentration. While aspirating standards use th auto concentration to set the instrument digit display to read the concentrations of standard Use at least six standards. Calibrate the instrument each time a set of samples is analyzed an check for stability at reasonable intervals.

7. Calculations

Determine the milligrams per liter of magnesium in each sample from the digital display o printer output while aspirating each sample. Dilute those samples whose magnesium concentrations exceed the working range of the metho and multiply by the proper dilution factors.

8. Report

Report magnesium, total recoverable (00927) concentrations as follows: less than 10 mg/L, on decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greate than 9 percent at 1.98 mg/L and greater than 17 percent at 35.6 mg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 109.

Environmental Protection Agency, 1974, Methods for Chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 82.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, pp. 32–34.

Manganese, dissolved, atomic absorption spectrometric, chelation-extraction (I–1456–78)

Parameter and Code: Manganese, dissolved (μg/L as Mn): 01056

1. Application

This method may be used to analyze waters and brines containing from 1 to 100 μg/L of manganese. Brines containing more than 100 μg/L must either be diluted or less scale expansion used. Waters containing more than 100 μg/L may either be diluted prior to chelation-extraction or analyzed by Method I–1454.

2. Summary of method

Manganese is determined by atomic absorption spectrometry. The element is first chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with chloroform. The extract is evaporated to dryness, treated with hot nitric acid to destroy organic matter, dissolved in hydrochloric acid, and diluted to a specified volume with demineralized water. The resulting solution is then aspirated into the air-acetylene flame of the spectrometer.

3. Interferences

Iron up to 4×10^6 μg/L does not interfere; higher concentrations were not tested.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	279.5 nm.
Source (hollow-cathode lamp)	Manganese.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate (APDC)* solution, 4 g/100 mL: Dissolve 4 g APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.

5.2 *Bromocresol green indicator* solution, 0.1 g/100 mL. Dissolve 0.1 g bromocresol green in 100 mL 20-percent ethanol.

5.3 *Chloroform.*

5.4 *Hydrochloric acid, 4M*: Mix 333 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.5 *Manganese* standard solution I, 1.00 mL = 100 μg Mn: Heat 0.5 g $MnSO_4 \cdot H_2O$ for 1 h at 180°C. Dissolve 0.2749 g in demineralized water containing 1 mL concentrated H_2SO_4 (sp gr 1.84) and dilute to 1,000 mL with demineralized water.

5.6 *Manganese* standard solution II, 1.00 mL = 1.00 μg Mn: Immediately before use, dilute 10.0 mL manganese standard solution I to 1,000 mL with demineralized water. This solution is used to prepare working standards at time of analysis.

5.7 *Sodium hydroxide, 0.25M*: Dissolve 10 g NaOH in demineralized water and dilute to 1 L.

6. Procedure

Clean all glassware used in this determination with warm dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.1 Pipet a volume of sample containing less than 5 μg Mn (50 mL maximum) into a 125-mL separatory funnel. Adjust the volume to approx 50 mL.

6.2 Prepare a blank and at least six standards, and adjust the volume of each to approx 50 mL with demineralized water.

6.3 Add 2 drops bromocresol green indicator solution and adjust the pH of each sample, standard, and blank to 4.0 (light olive-green color) with the addition of 0.25*M* NaOH.

6.4 Add 5.0 mL APDC solution and mix.

6.5 Add 10 mL chloroform and shake for 2 min.

6.6 Allow the phases to separate and drain the chloroform phase into a 100-mL beaker.

6.7 Repeat the extraction with an additional 10 mL chloroform and drain the chloroform phase into the same beaker.

6.8 Place the beaker on a steam bath and evaporate just to dryness.

6.9 Hold the beaker at a 45° angle, and slowly add 2 mL concentrated HNO_3 (sp gr 1.41), rotating the beaker to effect thorough contact of the acid with the residue (CAUTION—NOTE 1).

NOTE 1. If acid is added to the beaker in a vertical position, a violent reaction may occur accompanied by high heat and spattering.

6.10 Place the beaker on a hotplate at low heat and evaporate just to dryness.

6.11 Add 2 mL 4*M* HCl and heat, while swirling, for 1 min.

6.12 Cool and transfer the solution to a 10-mL volumetric flask and dilute to volume with demineralized water.

6.13 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of manganese in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of manganese exceed the working range of the method. Repeat those analyses and multiply by the proper dilution factors.

8. Report

Report manganese, dissolved (01056), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 112.

Manganese, dissolved, atomic absorption spectrometric, direct (I–1454–78)

Parameter and Code: Manganese, dissolved (μg/L as Mn): 01056

1. Application

This method may be used to analyze waters containing at least 10 μg/L of manganese. Sample solutions containing more than 1,000 μg/L must first be diluted or less scale expansion used. Brines must be analyzed by Method I–1456, providing that the interferences discussed in that method are not exceeded.

2. Summary of method

2.1 Manganese is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment.

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

Magnesium (100 mg/L) and silica (100 mg/L) do not interfere. Magnesium in excess of 100 mg/L may present some interference, especially when the manganese concentration exceeds 500 μg/L. Silica interferes above 100 mg/L. Iron up to 4 × 10^6 μg/L does not interfere.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**279.5 nm.**
Source (hollow-cathode lamp)	**Manganese.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

4.3 The 100-mm (4-in.) single slot burner allows scale expansion from 10 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Manganese* standard solution I, 1.00 mL = 100 μg Mn: Heat 0.5 g $MnSO_4 \cdot H_2O$ for 1 h at 180°C. Dissolve 0.2749 g in demineralized water containing 1 mL concentrated H_2SO_4 (sp gr 1.85) and dilute to 1,000 mL with demineralized water.

5.2 *Manganese* standard solution II, 1.00 mL = 10.0 μg Mn: Immediately before use, dilute 10.0 mL manganese standard solution I to 100 mL with demineralized water.

5.3 *Manganese* standard working solutions: Prepare a series of at least six standard working solutions containing from 0.0 to 1,000 μg/L manganese by appropriate dilution of manganese standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of manganese in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose manganese concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report manganese, dissolved (01056), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 40 to 300 μg/L may be expressed as follows:

$$S_T = 0.049X + 9.59$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of manganese, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
23	70	20
34	256	9

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 111.

Manganese, recoverable from bottom material, atomic absorption spectrometric, direct (I–5454–78)

Parameter and Code: Manganese, recoverable from bottom material, dry wt (μg/g as Mn): 01053

1. Application

1.1 This method may be used to analyze bottom material containing at least 1 μg/g of manganese. Prepared sample solutions (Method I–5485) containing more than 1,000 μg/L must first be diluted or less scale expansion used.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

2.1 Manganese is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–5485) into an air-acetylene flame.

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

Magnesium (100 mg/L) and silica (100 mg/L) do not interfere. Magnesium in excess of 100 mg/L may present some interference, especially when the manganese concentration exceeds 500 μg/L. Silica interferes above 100 mg/L. Iron up to 4 × 10^6 μg/L does not interfere.

4. Apparatus

4.1 *Atomic absorption spectrometer* with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	279.5 nm.
Source (hollow-cathode lamp)	Manganese.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The 100-mm (4-in.) single slot burner allows a working range from 10 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Manganese* standard solution I, 1.00 mL = 100 μg Mn: Heat 0.5 g $MnSO_4 \cdot H_2O$ for 1 h at 180°C. Dissolve 0.2749 g in demineralized water containing 1 mL concentrated H_2SO_4 (sp gr 1.85) and dilute to 1,000 mL with demineralized water.

5.2 *Manganese* standard solution II, 1.00 mL = 10.0 μg Mn: Immediately before use, dilute 10.0 mL manganese standard solution I to 100 mL with demineralized water.

5.3 *Manganese* standard working solutions: Prepare a series of at least six standard working solutions containing from 0.0 to 1,000 μg/L manganese by appropriate dilution of manganese standard solution II.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of manganese in each prepared sample solution (Method I–5485) from the digital display or printer output while aspirating each sample. Dilute those samples whose manganese concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per gram of manganese in bottom material samples, first determine the micrograms per liter of manganese as in 7.1, then

$$\text{Mn } (\mu g/g) = \frac{\mu g/L \text{ Mn} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}.$$

8. Report

Report manganese, recoverable from bottom material (01053), concentations as follows: less than 10 $\mu g/g$, nearest microgram per gram; 10 $\mu g/g$ and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 20 percent in the lower portion of the analytical range.

Manganese, total recoverable, atomic absorption spectrometric, direct (I–3454–78)

Parameter and Code: Manganese, total recoverable (μg/L as Mn): 01055

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 10 μg/L of manganese. Sample solutions containing more than 1,000 μg/L must first be diluted or less scale expansion used.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

2.1 Manganese is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–3485) into an air-acetylene flame.

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

Magnesium (100 mg/L) and silica (100 mg/L) do not interfere. Magnesium in excess of 100 mg/L may present some interference, especially when the manganese concentration exceeds 500 μg/L. Silica interferes above 100 mg/L. Iron up to 4×10^6 μg/L does not interfere.

4. Apparatus

4.1 *Atomic absorption spectrometer* with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**279.5 nm.**
Source (hollow-cathode lamp)	**Manganese.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

4.3 The 100-mm (4-in.) single slot burner allows a working range from 10 to 1,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Manganese* standard solution I, 1.00 mL = 100 μg Mn: Heat 0.5 g $MnSO_4 \cdot H_2O$ for 1 h at 180°C. Dissolve 0.2749 g in demineralized water containing 1 mL concentrated H_2SO_4 (sp gr 1.85) and dilute to 1,000 mL with demineralized water.

5.2 *Manganese* standard solution II, 1.00 mL = 10.0 μg Mn: Immediately before use, dilute 10.0 mL manganese standard solution I to 100 mL with demineralized water.

5.3 *Manganese* standard working solutions: Prepare a series of standard working solutions containing from 0 to 1,000 μg/L of manganese by appropriate dilution of manganese standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument

each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of manganese in each prepared sample solution (Method I–3485) from the digital display or printer output while aspirating each sample. Dilute those samples whose manganese concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report manganese, total recoverable (01055), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 20 percent at 70.4 μg/L and greater than 90 percent at 256 μg/L.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 111.

Mercury, dissolved, atomic absorption spectrometric, flameless (I–1462–78)

Parameter and Code: Mercury, dissolved (μg/L as Hg): 71890

1. Application

This method may be used to analyze waters containing at least 0.5 μg/L of mercury. Samples containing mercury concentrations greater than 10 μg/L must first be diluted. Industrial and sewage effluents may be analyzed, as well as samples of fresh and saline water.

2. Summary of method

2.1 The cold-vapor flameless atomic absorption procedure is based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds, if present, are decomposed by hot (95°C) digestion with potassium permanganate and potassium persulfate in acid solution. The mercuric ions are then reduced to the elemental state with stannous chloride, and the mercury vapor subsequently removed from solution by aeration and passed through a cell positioned in the light path of an atomic absorption spectrometer.

2.2 This method is based on a procedure described by Hatch and Ott (1968) and is similar in substance to the flameless atomic absorption method in "Methods for Chemical Analysis of Water and Wastes", published by the Water Quality Office of the Environmental Protection Agency (1974).

3. Interferences

Some samples may contain volatile organic compounds that absorb radiation at 253.7 nm and that may be swept from the solution along with the mercury vapor. These constitute a positive interference and the possibility of their presence must not be overlooked.

4. Apparatus

4.1 *Absorption cell* (fig. 17). Mount and align an absorption cell (10- to 20-cm path length) in the light path of the spectrometer. Position a 60-watt lamp over the cell (10 to 15 cm) to prevent condensation of water vapor. Attach a sufficient length of tubing to the outlet of the cell and vent to a hood. Connect the inlet of the cell to the aerator with a minimum length of plastic tubing. Attach a water aspirator to the outlet of the stopcock (NOTE 1).

NOTE 1. The stopcock must remain closed during analysis and opened only briefly, between samples, to remove residual mercury vapor from the absorption cell.

4.2 *Aerator* (fig. 17).

4.3 *Atomic absorption spectrometer* and recorder.

4.4 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	253.7 nm.
Source	Mercury-vapor discharge, hollow-cathode, or electrodeless discharge lamp.

4.5 *BOD bottle*, 300-mL capacity.

4.6 *Water bath*, 95°C.

5. Reagents

5.1 *Hydroxylamine hydrochloride-sodium chloride* solution: Dissolve 10 g $NH_2OH \cdot HCl$ and 12 g NaCl in demineralized water and dilute to 100 mL (NOTE 2). Prepare fresh daily. Alternatively, 12 g hydroxylamine sulfate may be used instead of the hydroxylamine hydrochloride.

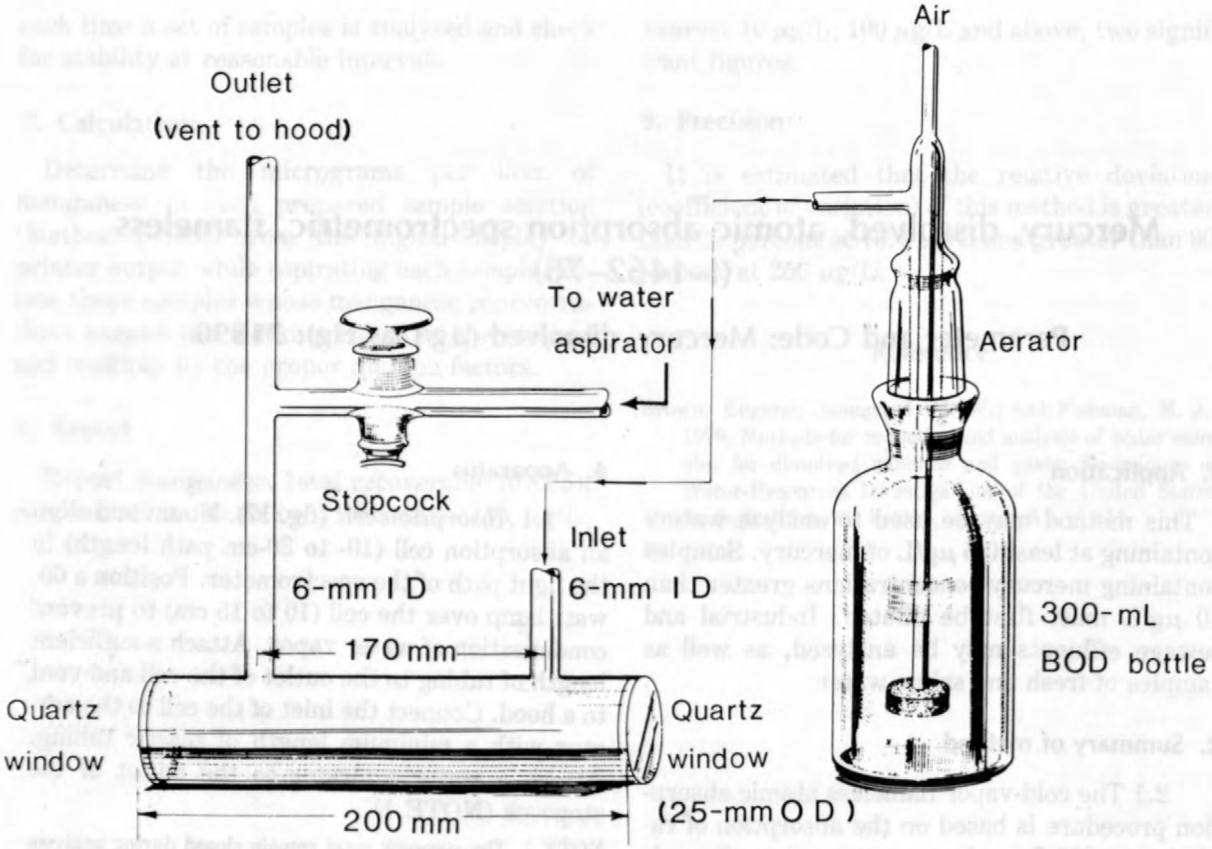


FIGURE 17.—Absorption cell and aerator.

NOTE 2. A larger volume of this reagent can be prepared if it is kept refrigerated.

5.2 *Mercury* standard solution I, 1.00 mL = 100 μg Hg: Dissolve 0.1712 g $Hg(NO_3)_2 \cdot H_2O$ in demineralized water. Add 1.5 mL concentrated HNO_3 and dilute to 1,000 mL with demineralized water.

5.3 *Mercury* standard solution II, 1.00 mL = 1.00 μg Hg: Dilute 5.00 mL mercury standard solution I and 1.5 mL concentrated HNO_3 to 500 mL with demineralized water. This and the following mercury standard solutions must be prepared fresh daily.

5.4 *Mercury* standard solution III, 1.00 mL = 0.050 μg Hg: Dilute 10.0 mL mercury standard solution II and 1.5 mL concentrated HNO_3 to 200 mL with demineralized water (NOTE 3). Use this solution to prepare working standards at the time of analysis.

NOTE 3. Mercury standard solution III, 1.00 mL = 0.01 μg Hg has also been found useful. Dilute 5.0 mL mercury standard solution II and 4.0 mL concentrated HNO_3 to 500 mL with demineralized water.

5.5 *Nitric acid*, concentrated (sp gr 1.41), with low mercury content: du Pont reagent grade acid has been found to be satisfactory.

5.6 *Potassium permanganate* solution, 50 g/L: Dissolve 5 g $KMnO_4$ in demineralized water and dilute to 100 mL. Prepare fresh weekly. Store in brown glass bottle.

5.7 *Potassium persulfate* solution, 50 g/L: Dissolve 5 g $K_2S_2O_8$ in demineralized water and dilute to 100 mL.

5.8 *Stannous chloride* solution, 74 g/L: Add 22 g $SnCl_2 \cdot 2H_2O$ to 250 mL 0.25*M* H_2SO_4. Prepare fresh daily.

5.9 *Sulfuric acid*, concentrated (sp gr 1.84).

5.10 *Sulfuric acid, 0.25M*: *Cautiously* add 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

Immediately before each use, clean all glassware used in this determination by rinsing, first with warm, dilute HNO_3 (1 + 4), and then with demineralized water.

6.1 Pipet a volume of sample containing less than 1.0 μg Hg (100 mL maximum) into a 300-mL capacity BOD bottle and adjust the volume to approx 100 mL.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.3 Add 5 mL concentrated H_2SO_4 and 2.5 mL concentrated HNO_3, mixing after each addition.

6.4 Add 5 mL $KMnO_4$ solution and shake. Add additional small portions of $KMnO_4$ solution, if necessary, until the purple color persists for at least 15 min.

6.5 Add 2 mL $K_2S_2O_8$ solution, mix, and heat for 2 h in a boiling-water bath or for 3 h in an oven at 95°C.

6.6 Remove from water bath, cool, and add $NH_2OH \cdot HCl\text{–}NaCl$ solution in 2-mL increments to reduce the excess permanganate, as evidenced by the disappearance of the permanganate color.

6.7 Add 5 mL $SnCl_2$ solution to *one* sample and immediately attach the bottle to the aerator (NOTE 4). Record the maximum absorbance. After maximum absorbance has been recorded, remove the BOD bottle and open the stopcock to the vacuum. Momentarily pinch off the vent tube in order to remove residual mercury vapor from the absorption cell. Treat each succeeding sample, blank, and standard in a like manner.

NOTE 4. Use either the atomic absorption compressed-air supply or a peristaltic pump to aerate the sample. Adjust the rate of air flow to approx 2 L/min.

7. Calculations

7.1 Determine the micrograms of mercury in the sample from a plot of absorbances of standards. Exact reproducibility is not obtained, and an analytical curve must be prepared with each set of samples.

7.2 Compute the concentration of mercury in each sample as follows:

$$\text{Hg} (\mu\text{g/L}) = \mu\text{g Hg} \times \frac{1{,}000}{\text{mL sample aliquot}}$$

8. Report

Report mercury, dissolved (71890), concentrations as follows: less than 10 μg/L and greater than or equal to 0.5 μg/L, nearest 0.1 μg/L; 10 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 0.5 to 7.0 μg/L may be expressed as follows:

$$S_T = 0.171X + 0.132$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of mercury, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
15	0.60	46
7	6.54	18

References

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 51.

Hatch, W. R., and Ott, W. L., 1968, Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry: Analytical Chemistry, v. 40, p. 2085–2087.

U.S. Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 118–126.

Mercury, dissolved, atomic absorption spectrometric, flameless automated (I–2462–78)

Parameter and Code: Mercury, dissolved ($\mu g/L$ as Hg): 71890

1. Application

This method may be used to analyze waters and waste waters containing at least 0.1 $\mu g/L$ mercury. Samples containing mercury concentrations greater than 8.0 $\mu g/L$ must first be diluted.

2. Summary of method

2.1 The cold-vapor flameless atomic absorption procedure is based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds, if present, are decomposed by hot (95°C) digestion with potassium dichromate and potassium persulfate in acid solution. The mercuric ions are then reduced to the elemental state with stannous chloride, and the mercury vapor subsequently removed from solution by aeration and passed through a cell positioned in the light path of an atomic absorption spectrometer.

2.2 The method is based on a procedure described by El-Awady, Miller, and Carter (1976).

3. Interferences

3.1 Chloride concentrations up to 5,000 mg/L do not interfere; higher concentrations were not tested.

3.2 Hydroxylamine hydrochloride-sodium chloride solution is added to prevent interference from residual chlorine.

3.3 El-Awady, Miller, and Carter (1976) report that copper sulfate (1,000 mg/L) does not interfere and that chemical oxygen demand (COD) concentrations of less than 700 mg/L can be tolerated. Ethyl alcohol, methyl alcohol, glycerol, chloroform, and carbon tetrachloride did not interfere when added in concentrations as high as 0.5 percent. Major interferences were observed from benzene and toluene. A maximum tolerance of 500 $\mu g/L$ was obtained for these compounds.

4. Apparatus

4.1 *Absorption cell*, 100-mm long, 10-mm diameter with quartz windows.

4.2 *Atomic absorption spectrometer and recorder.*

4.3 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength counter.	**253.7 nm.**
Source	**Mercury-vapor discharge, hollow-cathode, or electrodeless discharge lamp.**
Carrier	**Nitrogen (flow approx 20 mL/min; adjust for maximum sensitivity with use of a standard).**

4.4 *Technicon AutoAnalyzer system*: Consisting of sampler, manifold (fig. 18), proportioning pump, and high temperature heating bath.

4.5 *Vapor-liquid separator* (fig. 19).

5. Reagents

5.1 *Hydroxylamine hydrochloride-sodium chloride* solution: Dissolve 30 g of hydroxylamine hydrochloride and 30 g of sodium chloride in demineralized water and dilute to 1 L.

5.2 *Mercury* standard solution I, 1.00 mL = 100 μg Hg: Dissolve 0.1712 g $Hg(NO_3)_2 \cdot H_2O$ in demineralized water. Add 1.5 mL concentrated HNO_3 (sp gr 1.41), 25 mL potassium dichromate solution, and dilute to 1,000 mL with demineralized water.

5.3 *Mercury* standard solution II, 1.00 mL = 1.00 μg Hg: Dilute 10.0 mL mercury standard solution I, 5 mL concentrated HNO_3,

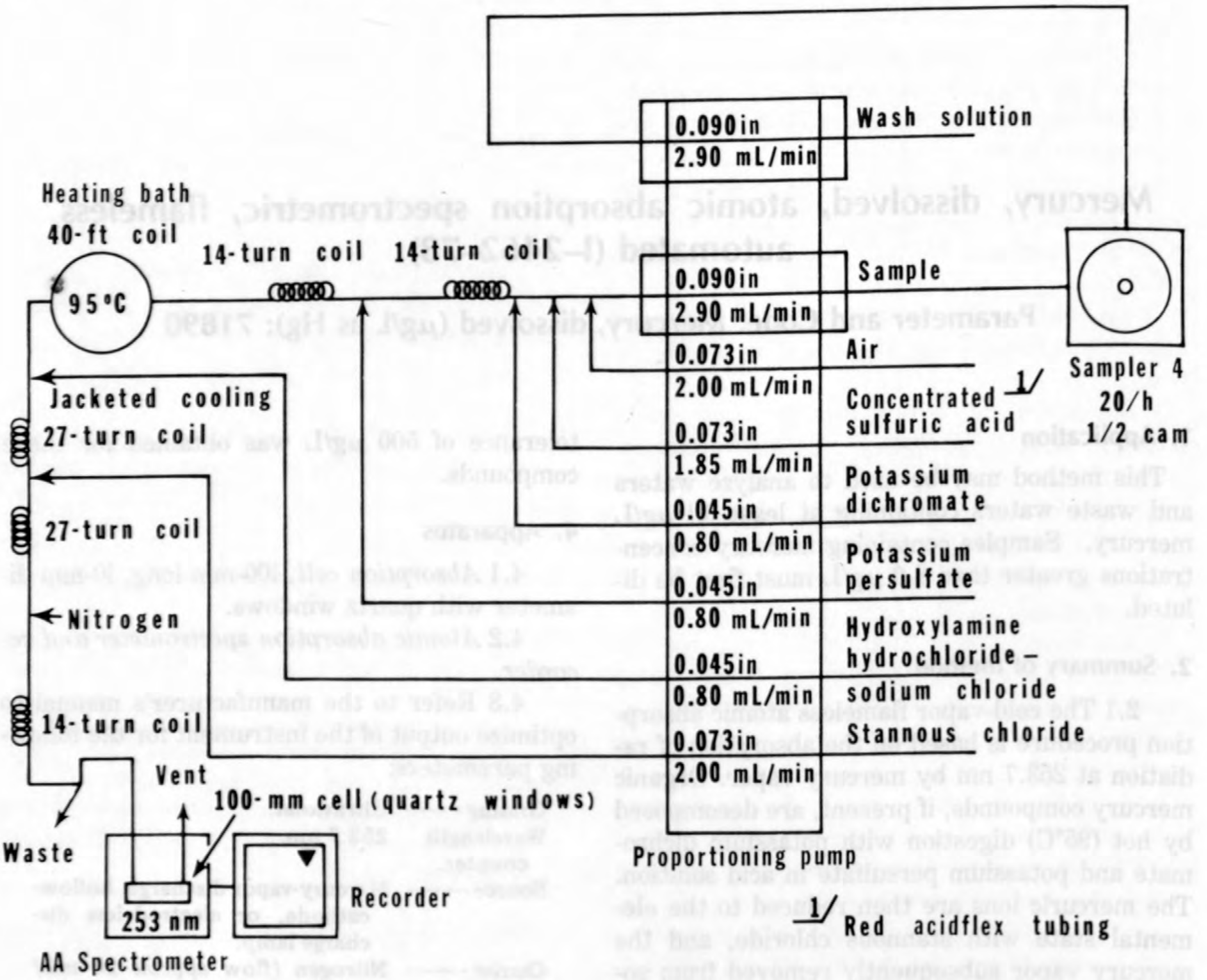


FIGURE 18.—Mercury manifold.

and 25 mL potassium dichromate solution to 1,000 mL with demineralized water.

5.4 *Mercury* standard solution III, 1.00 mL = 0.100 μg Hg: Dilute 100.0 mL mercury standard solution II, 5 mL concentrated HNO_3, and 25 mL potassium dichromate solution to 1,000 mL with demineralized water. Use this solution to prepare working standards. The working standards should also contain 5 mL/L of concentrated HNO_3 and 25 mL/L of potassium dichromate solution. The working standards are stable for at least 3 weeks.

5.5 *Nitric acid*, concentrated (sp gr 1.41), with low mercury content. Both du Pont and Baker reagent grade acids have been found to be satisfactory.

5.6 *Nitric acid* (1 + 99) wash solution. Dilute 10 mL of concentrated HNO_3 (sp gr 1.41) to 1 L with demineralized water.

5.7 *Potassium dichromate* solution, 20 g/L: Dissolve 20 g $K_2Cr_2O_7$ in demineralized water and dilute to 1 L.

5.8 *Potassium persulfate* solution, 40 g/L: Dissolve 40 g $K_2S_2O_8$ in demineralized water and dilute to 1 L. Prepare fresh each week.

5.9 *Stannous chloride* solution, 84 g/L: Dissolve 100 g $SnCl \cdot 2H_2O$ in 100 mL concentrated hydrochloric acid and dilute to 1 L with demineralized water.

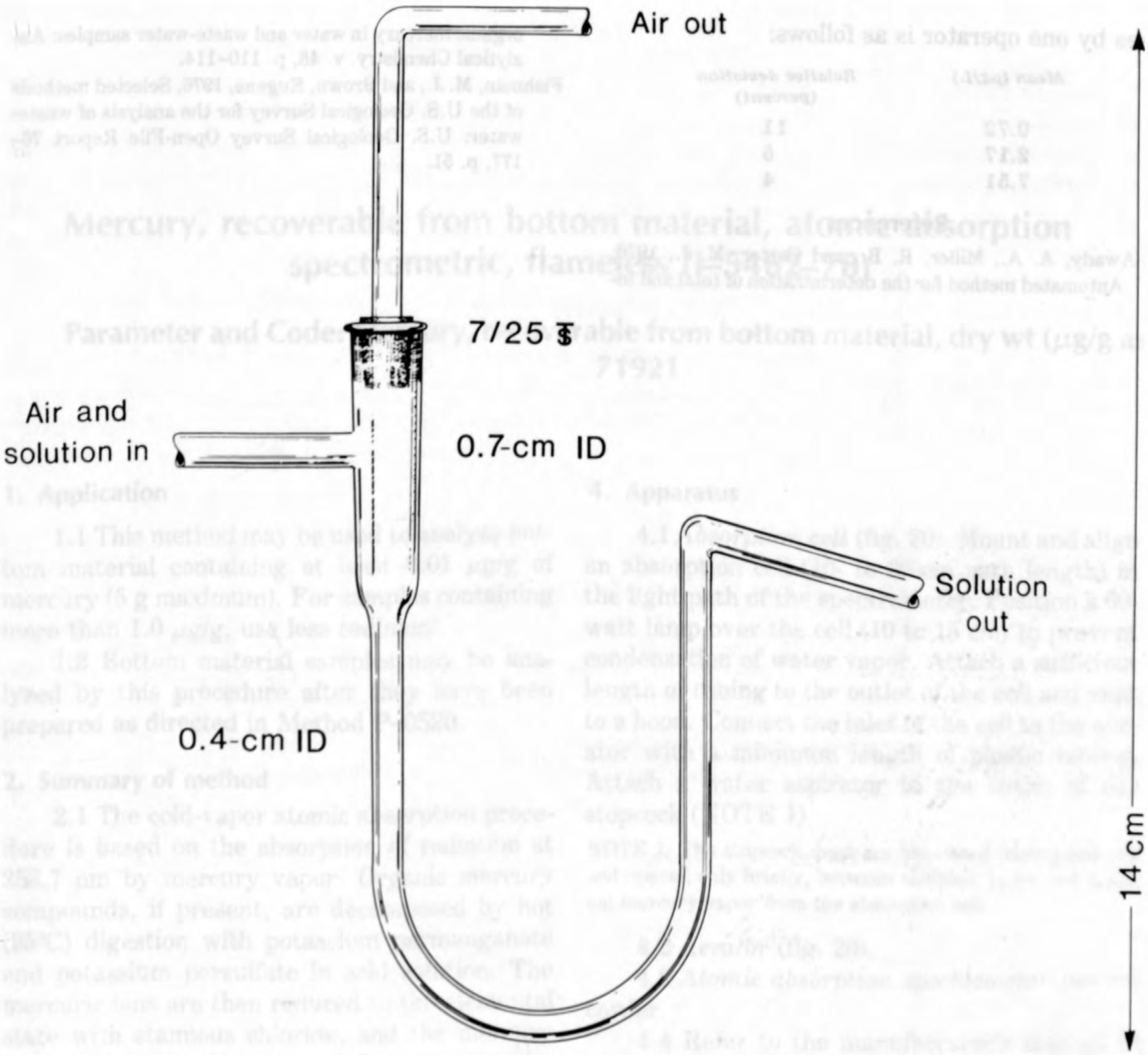
5.10 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 Set up manifold (fig. 18).

6.2 Prepare a blank of demineralized water and sufficient standards up to 8.0 μg/L by appropriate dilutions of mercury standard solution III.

6.3 Feed all reagents through the system



using the nitric acid wash solution in the sample line. Allow the heating bath to warm to 95°C.

6.4 Beginning with the most concentrated standard, place a complete set of standards in the first positions of the first sample tray. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.5 Remove the sample line from the nitric acid wash solution when the baseline stabilizes and begin analysis.

7. Calculations

7.1 Prepare an analytical curve by plotting the absorbances of standards.

7.2 Compute the concentration of mercury in each sample by comparing its absorbance to the analytical curve. Any baseline drift that may occur must be taken into account when computing the absorbance of a sample or standard.

8. Report

Report mercury, dissolved (71890), concentrations as follows: less than 10 μg/L, nearest 0.1 μg/L; 10 μg/L and above, two significant figures.

9. Precision

Precision expressed in terms of relative deviation (coefficient of variation) for replicate analyses by one operator is as follows:

Mean (µg/L)	*Relative deviation (percent)*
0.72	11
2.17	5
7.51	4

References

El-Awady, A. A., Miller, R. B., and Carter, M. J., 1976, Automated method for the determination of total and inorganic mercury in water and waste-water samples: Analytical Chemistry, v. 48, p. 110–114.

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewater: U.S. Geological Survey Open-File Report 76–177, p. 51.

Mercury, recoverable from bottom material, atomic absorption spectrometric, flameless (I–5462–78)

Parameter and Code: Mercury, recoverable from bottom material, dry wt (μg/g as Hg): 71921

1. Application

1.1 This method may be used to analyze bottom material containing at least 0.01 μg/g of mercury (5 g maximum). For samples containing more than 1.0 μg/g, use less sediment.

1.2 Bottom material samples may be analyzed by this procedure after they have been prepared as directed in Method P–0520.

2. Summary of method

2.1 The cold-vapor atomic absorption procedure is based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds, if present, are decomposed by hot (95°C) digestion with potassium permanganate and potassium persulfate in acid solution. The mercuric ions are then reduced to the elemental state with stannous chloride, and the mercury vapor subsequently removed from solution by aeration and passed through a cell positioned in the light path of an atomic absorption spectrometer.

2.2 This method is based on a procedure described by Hatch and Ott (1968) and is similar in substance to the flameless atomic absorption method in "Methods for Chemical Analysis of Water and Wastes," published by the Water Quality Office of the Environmental Protection Agency (1974).

3. Interferences

Some samples may contain volatile organic compounds that absorb radiation at 253.7 nm and that may be swept from the solution along with the mercury vapor. These constitute a positive interference and the possibility of their presence must not be overlooked.

4. Apparatus

4.1 *Absorption cell* (fig. 20). Mount and align an absorption cell (10- to 20-cm path length) in the light path of the spectrometer. Position a 60-watt lamp over the cell (10 to 15 cm) to prevent condensation of water vapor. Attach a sufficient length of tubing to the outlet of the cell and vent to a hood. Connect the inlet of the cell to the aerator with a minimum length of plastic tubing. Attach a water aspirator to the outlet of the stopcock (NOTE 1).

NOTE 1. The stopcock must remain closed during analysis and opened only briefly, between samples, to remove residual mercury vapor from the absorption cell.

4.2 *Aerator* (fig. 20).

4.3 *Atomic absorption spectrometer* and recorder.

4.4 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating -------	Ultraviolet.
Wavelength counter.	253.7 nm.
Source -------	Mercury-vapor discharge, hollow-cathode, or electrodeless discharge lamp.

4.5 *BOD bottle*, 300-mL capacity.

4.6 *Water bath*, 95°C.

5. Reagents

5.1 *Hydroxylamine hydrochloride-sodium chloride* solution: Dissolve 10 g $NH_2OH \cdot HCl$ and 12 g NaCl in demineralized water and dilute to 100 mL (NOTE 2). Prepare fresh daily. Alternatively 12 g hydroxylamine sulfate may be used instead of the hydroxylamine hydrochloride.

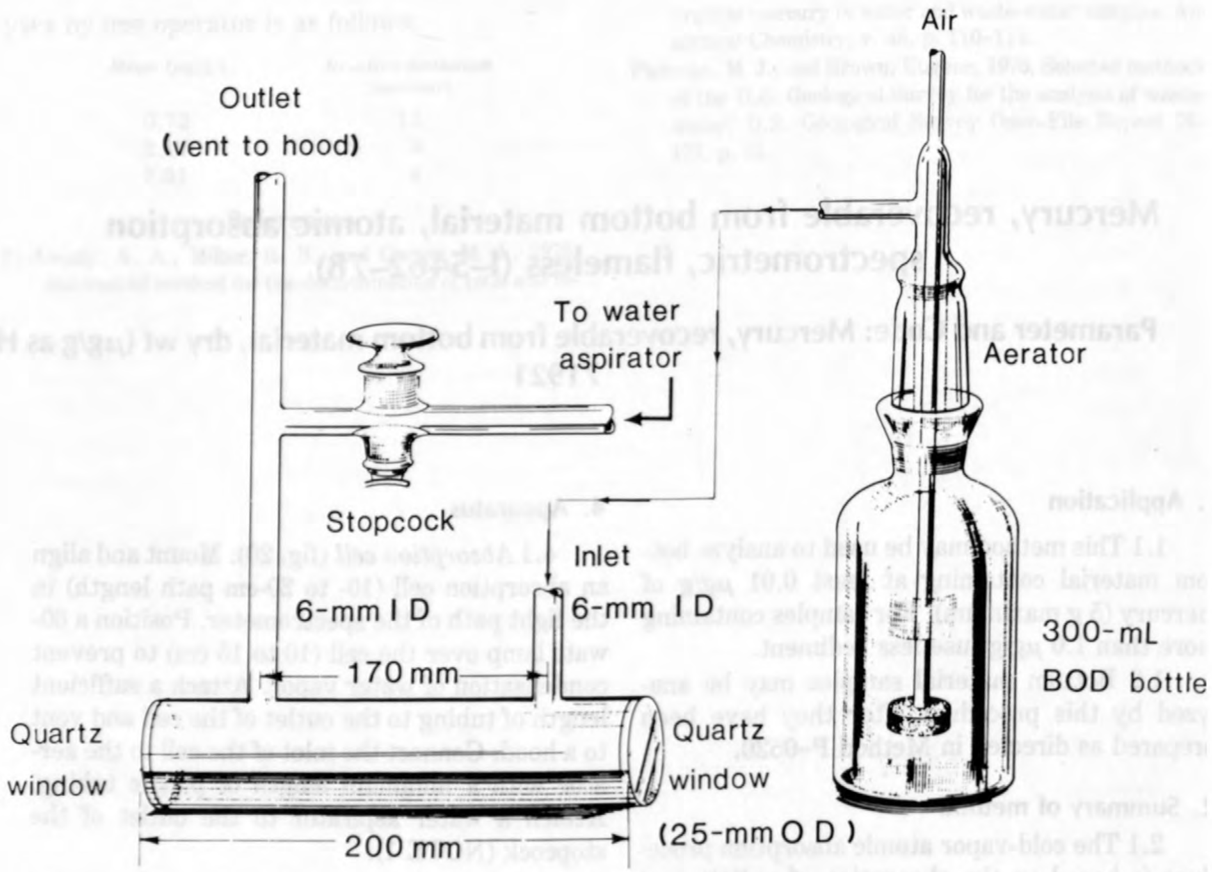


FIGURE 20.—Absorption cell and aerator.

NOTE 2. A larger volume of this reagent can be prepared and stored if it is kept refrigerated.

5.2 *Mercury* standard solution I, 1.00 mL = 100 μg Hg: Dissolve 0.1712 g $Hg(NO_3)_2 \cdot H_2O$ in demineralized water. Add 1.5 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.3 *Mercury* standard solution II, 1.00 mL = 1.00 μg Hg: Dilute 5.00 mL mercury standard solution I and 1.5 mL concentrated HNO_3 to 500 mL with demineralized water. This and the following mercury standard solutions must be prepared fresh daily.

5.4 *Mercury* standard solution III, 1.00 mL = 0.050 μg Hg: Dilute 10.0 mL mercury standard solution II and 1.5 mL concentrated HNO_3 to 200 mL with demineralized water (NOTE 3). Use this solution to prepare working standards at the time of analysis.

NOTE 3. Mercury standard solution III, 1.00 mL = 0.01 μg Hg has also been found useful. Dilute 5.0 mL mercury standard solution II and 4.0 mL concentrated HNO_3 to 500 mL with demineralized water.

5.5 *Nitric acid*, concentrated (sp gr 1.41), with low mercury content: du Pont reagent grade acid has been found to be satisfactory.

5.6 *Potassium permanganate* solution, 50 g/L: Dissolve 5 g $KMnO_4$ in demineralized water and dilute to 100 mL. Prepared fresh weekly. Store in brown glass bottle.

5.7 *Potassium persulfate* solution, 50 g/L: Dissolve 5 g $K_2S_2O_8$ in demineralized water and dilute to 100 mL.

5.8 *Stannous chloride* solution, 74 g/L: Add 22 g $SnCl_2 \cdot 2H_2O$ to 250 mL 0.25*M* H_2SO_4. Prepare fresh daily.

5.9 *Sulfuric acid*, concentrated (sp gr 1.84).

5.10 *Sulfuric acid*, 0.25*M*: *Cautiously* add 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

Immediately before each use, clean all glassware used in this determination by rinsing, first with warm, dilute HNO_3 (1 + 4), and then with demineralized water.

6.1 Place a weighed portion of sample containing less than 1.0 μg Hg (5 g maximum) into a 300-mL capacity BOD bottle and add approx 100 mL demineralized water.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.3 Add 5 mL concentrated H_2SO_4 and 2.5 mL concentrated HNO_3, mixing after each addition.

6.4 Add 15 mL $KMnO_4$ solution and shake. Add additional small portions of $KMnO_4$ solution, if necessary, until the purple color persists for at least 15 min.

6.5 Add 8 mL $K_2S_2O_8$ solution, mix, and heat for 2 h in a boiling-water bath or for 3 h in an oven at 95°C.

6.6 Remove from water bath, cool, and add $NH_2OH \cdot HCl$–NaCl solution in 2-mL increments to reduce the excess permanganate, as evidenced by the disappearance of the permanganate color.

6.7 Add 5 mL $SnCl_2$ solution to one sample and immediately attach the bottle to the aerator (NOTE 4). Record the maximum absorbance. After maximum absorbance has been recorded, remove the BOD bottle and open the stopcock to the vacuum. Momentarily pinch off the vent tube in order to remove residual mercury vapor from the absorption cell. Treat each succeeding sample, blank, and standard in a like manner.

NOTE 4. Use the atomic absorption compressed-air supply or a peristaltic pump to aerate the sample. Adjust the rate of air flow to approx 2 L/min.

7. Calculations

7.1 Determine the micrograms of mercury in the sample from a plot of absorbances of standards. Exact reproducibility is not obtained, and an analytical curve must be prepared with each set of samples.

7.2 Determine the concentration of mercury in micrograms per gram of air-dried bottom material sample as follows:

$$\text{Hg } (\mu g/g) = \frac{\mu g \text{ Hg in sample}}{\text{sample weight (g)}}$$

8. Report

Report mercury, recoverable from bottom material (71921), concentrations as follows: less than 1.00 μg/g, nearest 0.01 g/g; 1.0 g/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 46 percent in the lower portion of the analytical range and greater than 18 percent in the mid-portion of the analytical range.

References

Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 116–126.

Hatch, W. R., and Ott, W. L., 1968, Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry: Analytical Chemistry, v. 40, p. 2085–2087.

Mercury, total recoverable, atomic absorption spectrometric, flameless (I–3462–78)

Parameter and Code: Mercury, total recoverable (μg/L as Hg): 71900

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 0.5 μg/L of mercury. Samples containing mercury concentrations greater than 10 μg/L must first be diluted. Industrial and sewage effluents may be analyzed, as well as samples of fresh and saline water.

1.2 Water-suspended sediment mixtures may be analyzed by this procedure after each sample has been thoroughly mixed by vigorous shaking and a suitable sample portion has been rapidly withdrawn from the mixture.

2. Summary of method

2.1 The cold-vapor atomic absorption procedure is based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds, if present, are decomposed by hot (95°C) digestion with potassium permanganate and potassium persulfate in acid solution. The mercuric ions are then reduced to the elemental state with stannous chloride, and the mercury vapor subsequently removed from solution by aeration and passed through a cell positioned in the light path of an atomic absorption spectrometer.

2.2 This method is based on a procedure described by Hatch and Ott (1968) and is similar in substance to the flameless atomic absorption method in "Methods for Chemical Analysis of Water and Wastes," published by the Water Quality Office of the Environmental Protection Agency (1974).

3. Interferences

Some samples may contain volatile organic compounds that absorb radiation at 253.7 nm and that may be swept from the solution along with the mercury vapor. These constitute a positive interference and the possibility of their presence must not be overlooked.

4. Apparatus

4.1 *Absorption cell* (fig. 21). Mount and align an absorption cell (10– to 20-cm path length) in the light path of the spectrometer. Position a 60-watt lamp over the cell (10 to 15 cm) to prevent condensation of water vapor. Attach a sufficient length of tubing to the outlet of the cell and vent to a hood. Connect the inlet of the cell to the aerator with a minimum length of plastic tubing. Attach a water aspirator to the outlet of the stopcock (NOTE 1).

NOTE 1. The stopcock must remain closed during analysis and opened only briefly, between samples, to remove residual mercury vapor from the absorption cell.

4.2 *Aerator* (fig. 21).

4.3 *Atomic absorption spectrometer* and recorder.

4.4 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating -------- **Ultraviolet.**
Wavelength--- **253.7 nm.**
Source --------- **Mercury-vapor discharge, hollow-cathode, or electrodeless discharge lamp.**

4.5 *BOD bottle*, 300-mL capacity.

4.6 *Water bath*, 95°C.

5. Reagents

5.1 *Hydroxylamine hydrochloride-sodium chloride* solution: Dissolve 10 g $NH_2OH \cdot HCl$ and 12 g NaCl in demineralized water and dilute to 100 mL (NOTE 2). Prepare fresh daily. Alternatively 12 g hydroxylamine sulfate may be used instead of the hydroxylamine hydrochloride.

NOTE 2. A larger volume of this reagent can be prepared and stored if it is kept refrigerated.

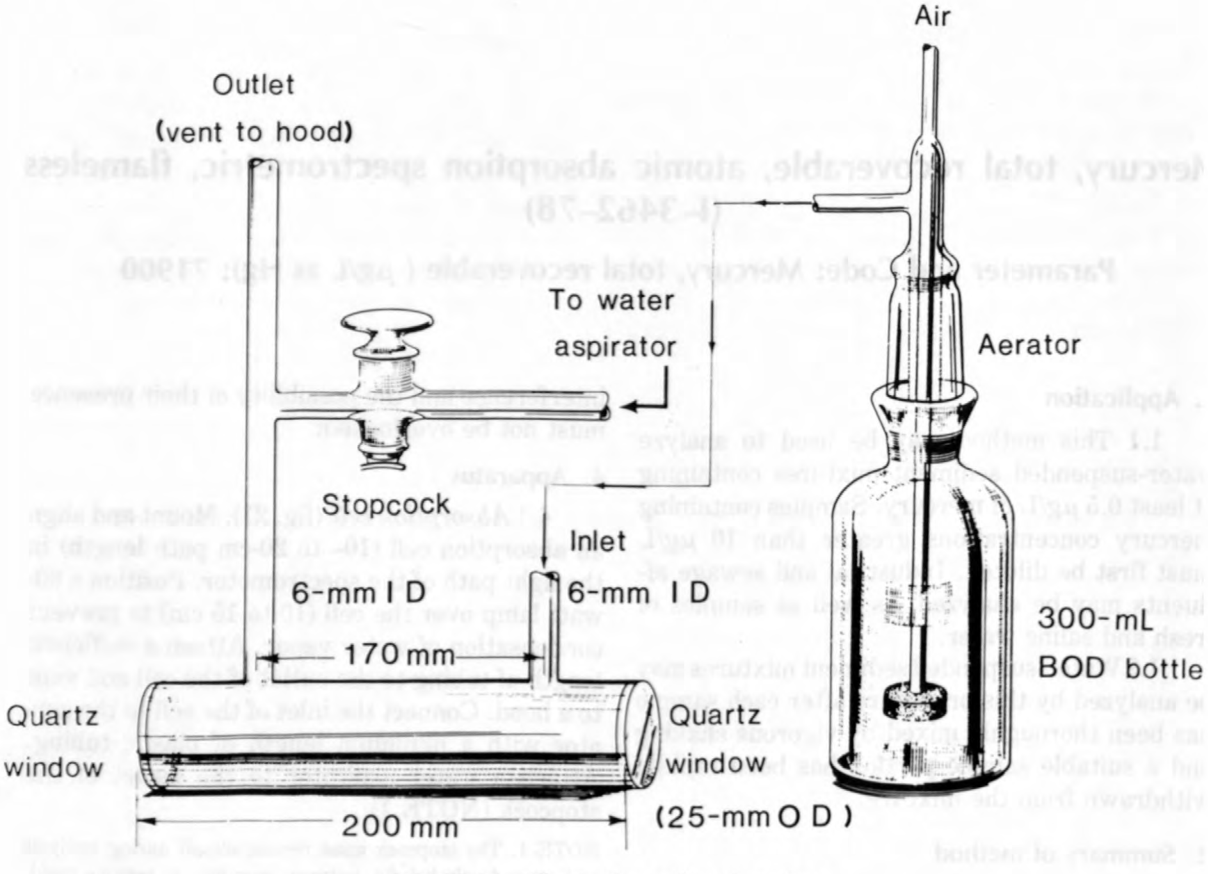


FIGURE 21.—Absorption cell and aerator.

5.2 *Mercury* standard solution I, 1.00 mL = 100 μg Hg: Dissolve 0.1712 g $Hg(NO_3)_2 \cdot H_2O$ in demineralized water. Add 1.5mL concentrated HNO_3 and dilute to 1,000 mL with demineralized water.

5.3 *Mercury* standard solution II, 1.00 mL = 1.00 μg Hg: Dilute 5.00 mL mercury standard solution I and 1.5 mL concentrated HNO_3 to 500 mL with demineralized water. This and the following mercury standard solutions must be prepared fresh daily.

5.4 *Mercury* standard solution III, 1.00 mL = 0.050 μg Hg: Dilute 10.0 mL mercury standard solution II and 1.5 mL concentrated HNO_3 to 200 mL with demineralized water (NOTE 3). Use this solution to prepare working standards at the time of analysis.

NOTE 3. Mercury standard solution III, 1.00 mL = 0.01 μg Hg has also been found useful. Dilute 5.0 mL mercury standard solution II and 4.0 mL concentrated HNO_3 to 500 mL with demineralized water.

5.5 *Nitric acid*, concentrated (sp gr 1.41), with low mercury content: du Pont reagent grade acid has been found to be satisfactory.

5.6 *Potassium permanganate* solution, 50 g/L: Dissolve 5 g $KMnO_4$ in demineralized water and dilute to 100 mL. Prepare fresh weekly. Store in brown glass bottle.

5.7 *Potassium persulfate* solution, 50 g/L: Dissolve 5 g $K_2S_2O_8$ in demineralized water and dilute to 100 mL.

5.8 *Stannous chloride* solution, 74 g/L: Add 22 g $SnCl_2 \cdot 2H_2O$ to 250 mL 0.25*M* H_2SO_4. Prepare fresh daily.

5.9 *Sulfuric acid*, concentrated (sp gr 1.84).

5.10 *Sulfuric acid*, 0.25*M*: *Cautiously* add 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

Immediately before each use, clean all glassware used in this determination by rinsing, first with warm, dilute HNO_3 (1 + 4), and then with demineralized water.

6.1 Pipet a volume of sample containing less than 1.0 μg Hg (100 mL maximum) into a 300-mL capacity BOD bottle and adjust the volume to approx 100 mL.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.3 Add 5 mL concentrated H_2SO_4 and 2.5 mL concentrated HNO_3, mixing after each addition.

6.4 Add 15 mL $KMnO_4$ solution and shake. Add additional small portions of $KMnO_4$ solution, if necessary, until the purple color persists for at least 15 min.

6.5 Add 8 mL $K_2S_2O_8$ solution, mix, and heat for 2 h in a boiling-water bath or for 3 h in an oven at 95°C.

6.6 Remove from water bath, cool, and add $NH_2OH \cdot HCl\text{–}NaCl$ solution in 2-mL increments to reduce the excess permanganate, as evidenced by the disappearance of the permanganate color.

6.7 Add 5 mL $SnCl_2$ solution to *one* sample and immediately attach the bottle to the aerator (NOTE 4). Record the maximum absorbance. After maximum absorbance has been recorded, remove the BOD bottle and open the stopcock to the vacuum. Momentarily pinch off the vent tube in order to remove residual mercury vapor from the absorption cell. Treat each succeeding sample, blank, and standard in a like manner.

NOTE 4. Use the atomic absorption compressed-air supply or a peristaltic pump to aerate the sample. Adjust the rate of air flow to approx 2 L/min.

7. Calculations

7.1 Determine the micrograms of mercury in the sample from a plot of absorbances of standards. Exact reproducibility is not obtained, and an analytical curve must be prepared with each set of samples.

7.2 Compute the concentration of mercury in the sample as follows:

$$\text{Hg } (\mu g/L) = \mu g \text{ Hg} \times \frac{1{,}000}{\text{mL sample aliquot}}$$

8. Report

Report mercury, total recoverable (71900), concentrations as follows: less than 10 $\mu g/L$ and greater than or equal to 0.5 $\mu g/L$, nearest 0.1 $\mu g/L$; 10 $\mu g/L$ and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 46 percent at 0.60 $\mu g/L$ and greater than 18 percent at 6.54 $\mu g/L$.

References

Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 118–126.

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177. p. 51.

Hatch, W. R., and Ott, W. L., 1968, Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry: Analytical Chemistry, v. 40, p. 2085–2087.

Molybdenum, dissolved, atomic absorption spectrometric, chelation-extraction (I–1490–78)

Parameter and Code: Molybdenum, dissolved ($\mu g/L$ as Mo): 01060

1. Application

This method may be used to analyze waters containing from 1 to 50 $\mu g/L$ of molybdenum.

2. Summary of method

Molybdenum is determined by atomic absorption spectrometry following chelation with 8-hydroxyquinoline and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into a nitrous oxide-acetylene flame of the spectrometer (Chau and Lum-Shue-Chan, 1969).

3. Interferences

The method is free from interference from most elements commonly found in fresh water. Vanadium(V) and iron(III) enhance the absorption, while chromium(VI) and tungsten(VI) suppress it. With the addition of ascorbic acid, up to 50,000 $\mu g/L$ of iron(III), 1,000 $\mu g/L$ of vanadium(V), and 10,000 $\mu g/L$ of chromium(VI) or tungsten(VI) can be tolerated (Chau and Lum-Shue-Chan, 1969).

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength counter	**313.3 nm.**
Source (hollow-cathode lamp).	**Molybdenum.**
Oxidant	**Nitrous oxide.**
Fuel	**Acetylene.**
Type of flame	**Fuel-rich.**

4.3 Different nitrous-oxide burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ascorbic acid* solution, 1 g/100 mL: Dissolve 1 g ascorbic acid in 100 mL demineralized water.

5.2 *Bromophenol blue indicator* solution, 0.1 g/100 mL: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.

5.3 *Hydrochloric acid,* 0.3*M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.4 *8-Hydroxyquinoline-methyl isobutyl ketone (MIBK)* solution, 1 g/100 mL: Dissolve 1 g 8-hydroxyquinoline in 100 mL methyl isobutyl ketone. Prepare fresh daily.

5.5 *Methyl isobutyl ketone (MIBK).*

5.6 *Molybdenum* standard solution I, 1.0 mL = 100 μg Mo: Dissolve 0.1500 g reagent-grade MoO_3 in 10 mL 0.1*M* NaOH (warm if necessary). Make just acid with 0.1*M* HCl and dilute to 1,000 mL with demineralized water.

5.7 *Molybdenum*standard solution II, 1.00 mL = 1.0 μg Mo: Dilute 10.0 mL molybdenum standard solution I to 1,000 mL with demineralized water.

5.8 *Molybdenum* standard solution III, 1.0 mL = 0.10 μg Mo: Immediately before use, dilute 10.0 mL molybdenum standard solution II to 100 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.9 *Sodium hydroxide* solution, 2.5*M*: Dissolve 100 g NaOH in demineralized water and dilute to 1 L.

6. Procedure

Clean all glassware used in this determination with warm, dilute HNO_3 (1 + 9), and rinse with demineralized water immediately before use.

6.1 Pipet a volume of sample containing less than 5.0 µg Mo (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.2 Prepare a demineralized-water blank with 1.5 mL conc. HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.3 Add 5 mL ascorbic acid solution and mix.

6.4 Add 2 drops bromophenol blue indicator solution and mix.

6.5 Adjust the pH by addition of 2.5*M* NaOH until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears; then add 2.0 mL 0.3*M* HCl in excess. The pH at this point should be 2.3.

6.6 Add 5.0 mL 8-hydroxyquinoline-MIBK solution and shake vigorously for 15 min.

6.7 Allow the layers to separate; then add demineralized water until the ketone layer is completely in the neck of the flask.

6.8 While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentrations of the standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of molybdenum in each sample from the digital display or printer output. Dilute those samples whose molybdenum concentrations exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

8. Report

Report molybdenum, dissolved (01060), concentrations as follows: less than 100 µg/L, nearest microgram per liter; 100 µ/L and above, two significant figures.

9. Precision

9.1 The precision of this method within its designated range may be expressed as follows (American Society for Testing and Materials, 1976):

$$S_T = 0.072X + 0.447$$

where

S_T = overall precision, micrograms per liter and,

X = concentration of molybdenum, micrograms per liter

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (µg/L)*	*Relative deviation (percent)*
5	2.0	36
4	29.7	11

References

American Society for Testing and Materials, 1976, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 357.

Chau, Y. K., and Lum-Shue-Chan, K., 1969, Atomic absorption determination of microgram quantities of molybdenum in lake waters: Analytical Chemical Acta, v. 48, p. 205–212.

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S Geological Survey for the analysis of wastewater: U.S. Geological Survey Open-File Report 76–177, p. 61.

Molybdenum, recoverable from bottom material, atomic absorption spectrometric, chelation-extraction (I–5490–78)

Parameter and Code: Molybdenum, recoverable from bottom material, dry wt (μg/g as Mo): 01063

1. Application

1.1 This method may be used to analyze bottom material containing at least 0.25 μg/g of molybdenum. Prepared sample solutions (Method I–5485) containing more than 50 μg/L of molybdenum must first be diluted.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure. Concentrations of iron greater than 50 mg/L in prepared solutions interfere.

2. Summary of method

Molybdenum is determined by atomic absorption spectrometry following chelation with 8-hydroxyquinoline and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into a nitrous oxide-acetylene flame of the spectrometer (Chau and Lum-Shue-Chan, 1969).

3. Interferences

The method is free from interference from most elements commonly found in fresh water. Vanadium(V) and iron(III) enhance the absorption while chromium(VI) and tungsten(VI) suppress it. With the addition of ascorbic acid, up to 50,000 μg/L of iron(III), 1,000 μg/L of vanadium(V), and 10,000 μg/L of chromium(VI) or tungsten(VI) can be tolerated (Chau and Lum-Shue-Chan, 1969).

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength counter	313.3 nm.
Source (hollow-cathode lamp).	Molybdenum.
Burner	Nitrous oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

4.3 Different nitrous-oxide burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ascorbic acid* solution 1 g/100 mL: Dissolve 1 g ascorbic acid in 100 mL demineralized water.

5.2 *Bromophenol blue indicator* solution, 0.1 g/100 mL: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.

5.3 *Hydrochloric acid*, 0.3*M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.4 *8-Hydroxyquinoline-methyl isobutyl ketone (MIBK)* solution, 1 g/100 mL: Dissolve 1 g 8-hydroxyquinoline in 100 mL methyl isobutyl ketone. Prepare fresh daily.

5.5 *Methyl isobutyl ketone (MIBK)*.

5.6 *Molybdenum* standard solution I, 1.0 mL = 100 μg Mo: Dissolve 0.1500 g reagent-grade MoO_3 in 10 mL 0.1*M* NaOH (warm if necessary). Make just acid with 0.1*M* HCl and dilute to 1,000 mL with demineralized water.

5.7 *Molybdenum* standard solution II, 1.00 mL = 1.0 μg Mo: Dilute 10.0 mL molybdenum standard solution I to 1,000 mL with demineralized water.

5.8 *Molybdenum* standard solution III, 1.00 mL = 0.10 μg Mo: Immediately before use, dilute 10.0 mL molybdenum standard solution II to 100 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.9 *Sodium hydroxide* solution, 2.5*M*: Dissolve 100 g NaOH in demineralized water and dilute to 1L.

6. Procedure

Clean all glassware used in this determination with warm, dilute HNO_3 (1 + 9), and rinse with demineralized water immediately before use.

6.1 Pipet a volume of prepared sample solution containing less than 5.0μg Mo (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.2 Prepare a demineralized-water blank with 1.5 mL conc. HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.3 Add 5 mL ascorbic acid solution and mix.

6.4 Add 2 drops bromophenol blue indicator solution and mix.

6.5 Adjust the pH by addition of 2.5*M* NaOH until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears then add 2.0 mL 0.3*M* HCl in excess. The pH at this point should be 2.3.

6.6 Add 5.0 mL 8-hydroxyquinoline-MIBK solution and shake vigorously for 15 min.

6.7 Allow the layers to separate; then add demineralized water until the ketone layer is completely in the neck of the flask.

6.8 While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentration of the standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of molybdenum in each sample from the digital or printer output. Dilute those samples whose molybdenum concentrations exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

7.2 To determine micrograms per gram of molybdenum in bottom material samples, first determine the micrograms per liter of molybdenum as in 7.1, then

$$\text{Mo } (\mu\text{g/g}) = \frac{\mu\text{g/L Mo} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report molybdenum, recoverable from bottom material (01063), concentrations as follows: less than 10 μg/g, nearest 0.1 μg/g; 10 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 36 percent in the lower portion of the analytical range and greater than 11 percent in the mid portion of the analytical range.

Reference

Chau, Y. K., and Lum-Shue-Chan, K., 1969, Atomic absorption determination of microgram quantities of molybdenum in lake waters: Analytical Chemical Acta, v. 48, p. 205–212.

Molybdenum, total recoverable, atomic absorption spectrometric, chelation-extraction (I–3490–78)

Parameter and Code: Molybdenum, total recoverable (μg/L as Mo): 01062

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing from 1 to 50 μg/L of molybdenum.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure. Concentrations of iron greater than 50 μg/L interfere.

2. Summary of method

Molybdenum is determined by atomic absorption spectrometry following chelation with 8-hydroxyquinoline and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into a nitrous oxide-acetylene flame of the spectrometer (Chau and Lum-Shue-Chan, 1969).

3. Interferences

The method is free from interference from most elements commonly found in fresh water. Vanadium(V) and iron(III) enhance the absorption while chromium(VI) and tungsten(VI) suppress it. With the addition of ascorbic acid, up to 50,000 μg/L of iron(III), 1,000 g/L of vanadium(V), and 10,000 μg/L of chromium(VI) or tungsten(VI) can be tolerated (Chau and Lum-Shue-Chan, 1969).

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	313.3 nm.
Source (hollow-cathode lamp)	Molybdenum.
Burner	Nitrous oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

4.3 Different nitrous-oxide burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ascorbic acid* solution, 1 g/100 mL: Dissolve 1 g ascorbic acid in 100 mL demineralized water.

5.2 *Bromophenol blue indicator* solution, 0.1 g/100 mL: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.

5.3 *Hydrochloric acid* 0.3*M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.4 *8-Hydroxyquinoline-methyl isobutyl ketone* (*MIBK*) solution, 1 g/100 mL: Dissolve 1 g 8-hydroxyquinoline in 100 mL methyl isobutyl ketone. Prepare fresh daily.

5.5 *Methyl isobutyl ketone* (*MIBK*).

5.6 *Molybdenum* standard solution I, 1.0 mL = 100 μg Mo: Dissolve 0.1500 g reagent-grade MoO_3 in 10 mL 0.1*M* NaOH (warm if necessary). Make just acid with 0.1*M* HCl and dilute to 1,000 mL with demineralized water.

5.7 *Molybdenum* standard solution II, 1.00 mL = 1.0 μg Mo: Dilute 10.0 mL molybdenum standard solution I to 1,000 mL with demineralized water.

5.8 *Molybdenum* standard solution III, 1.00 mL = 0.10 μg Mo: Immediately before use, dilute 10.0 mL molybdenum standard solution II to 100 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.9 *Sodium hydroxide* solution, 2.5*M*: Dissolve 100 g NaOH in demineralized water and dilute to 1 L.

6. Procedure

Clean all glassware used in this determination with warm, dilute HNO_3 (1 + 9), and rinse with demineralized water immediately before use.

6.1 Pipet a volume of prepared sample solution (Method I–3485) containing less than 5.0 μg Mo (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.2 Prepare a demineralized-water blank with 1.5 mL conc. HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.3 Add 5 mL ascorbic acid solution and mix.

6.4 Add 2 drops bromophenol blue indicator solution and mix.

6.5 Adjust the pH by addition of 2.5*M* NaOH until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears, then add 2.0 mL 0.3*M* HCl in excess. The pH at this point should be 2.3.

6.6 Add 5.0 mL 8-hydroxyquinoline-MIBK solution and shake vigorously for 15 min.

6.7 Allow the layers to separate; then add demineralized water until the ketone layer is completely in the neck of the flask.

6.8 While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentrations of the standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of molybdenum in each sample from the digital display or printer output. Dilute those samples whose molybdenum concentrations exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

8. Report

Report molybdenum, total recoverable (01062), concentrations as follows: less than 100 μg/L, nearest microgram per liter; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 30 percent at 2.0 μg/L and greater than 11 percent at 29.7 μg/L.

References

Chau, Y. K., and Lum-Shue-Chan, K., 1969, Atomic absorption determination of microgram quantities of molybdenum in lake waters: Analytical Chemical Acta, v. 48, p. 205–212.

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76-177, p. 61.

Nickel, dissolved, atomic absorption spectrometric, chelation-extraction (I–1500–78)

Parameter and Code: Nickel, dissolved (μg/L as Ni): 01065

1. Application

1.1 This method may be used to analyze waters and brines containing from 1 to 100 μg/L of nickel, although dilution prior to chelation-extraction is required for samples containing more than 25 μg/L nickel. Water samples containing more than 100 μg/L may be either diluted prior to chelation-extraction or analyzed by Method I–1499.

1.2 If the iron concentration of the sample exceeds 25,000 μg/L, determine nickel by direct atomic absorption (Method I–1499).

2. Summary of method

2.1 Nickel is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer (Fishman and Midgett, 1968).

2.2 Two procedures are given (6A and 6B), differing only in the manner of adjusting the pH of the sample solution prior to chelation and extraction of the nickel. Both methods are believed to be equally reliable, and the choice of method is left to the analyst.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the nickel absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	232.0 nm (NOTES (1 and 2).
Source (hollow-cathode lamp)	Nickel.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

NOTE 1. Setting the proper wavelength for nickel is critical because of presence of an ion line at 231.6 nm. By aspirating a standard that gives approximately 50 percent absorbance, the 232.0 nm-absorption line can be easily set.

NOTE 2. The 352.4-nm wavelength is less susceptible to nonautomatic absorbance and may be used. The analytical curve is more nearly linear; however, there is some loss of sensitivity.

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate (APDC)* solution, 1 g/100 mL: Dissolve 1.0 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 1 g/L: Dissolve 1 g bromophenol blue in 1 L 50-percent ethanol.

5.3 *Citric acid-sodium citrate buffer* solution: Dissolve 252 g citric acid monohydrate and 88.2 g of sodium citrate dihydrate in demineralized water. Add 100 mL bromophenol blue indicator solution and dilute to 1 L with demineralized water. (Procedure A only.)

5.4 *Hydrochloric acid*, 0.3*M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L. (Procedure B only.)

5.5 *Methyl isobutyl ketone (MIBK)*.

5.6 *Nickel* standard solution I, 1.00 mL = 200 μg Ni: Dissolve 0.9906 g $Ni(NO_3)_2 \cdot 6H_2O$ in a minimum volume of concentrated HNO_3 (sp gr

1.41) and dilute to 1,000 mL with demineralized water.

5.7 *Nickel* standard solution II, 1.00 mL = 2.00 μg Ni: Dilute 10.0 mL nickel standard solution I and 1 mL concentrated HNO_3 to 1,000 mL with demineralized water. This solution is used to prepare working standards at the time of analysis.

5.8 *Sodium hydroxide* 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 mL (NOTE 3). (Procedure B only.)

NOTE 3. Some batches of NaOH may contain traces of nickel. If this is suspected, use 2.5*M* NH_4OH rather than 2.5*M* NaOH. Prepare the NH_4OH solution by thoroughly mixing 20 mL concentrated NH_4OH (sp gr 0.90) with 100 mL demineralized water.

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.A Procedure A.

6.A.1 Pipet a volume of sample containing less than 2.5 μg Ni (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.A.2 Prepare a blank with 1.5 mL conc. HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.A.3 Add 10 mL buffer solution and mix (NOTE 4).

NOTE 4. If the proper amount of acid is present, the color will be a greenish yellow. If the color is yellow, add buffer solution dropwise until the proper color is obtained. If the color is green or greenish blue, add concentrated nitric acid dropwise until the proper color is obtained.

6.A.4 Add 2.5 mL APDC solution and shake for 3 min.

6.A.5 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.A.6 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.A.7 Aspirate the ketone layer within 1 h. While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

6.B Procedure B

6.B.1 Pipet a volume of sample containing less than 2.5 μg Ni (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.B.2 Prepare a blank with 1.5 mL conc. HNO_3 per liter demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.B.3 Add 2 drops bromophenol blue indicator solution to each sample and standard.

6.B.4 Adjust the pH of each by addition of either 2.5*M* NaOH or 2.5*M* NH_4OH by drops until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears. Then add 2.0 mL 0.3*M* HCl in excess. The pH at this point should be 2.3 (NOTE 5). Return to step 6.A.4 and proceed through step 6.A.7.

NOTE 5. The pH adjustment in steps 6.B.3 and 6.B.4 may be made with a pH meter instead of using indicator.

7. Calculations

Determine the micrograms per liter of nickel in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose nickel concentrations exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

8. Report

Report nickel, dissolved (01065), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 3.0 to 25 μg/L may be expressed as follows:

$$S_T = 0.187X + 1.45$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of nickel, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
8	5.9	37
4	12.2	31
13	23.2	23

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapters A1, p. 115.

Fishman, M. J., and Midgett, M. R., 1968, Extraction techniques for the determination of cobalt, nickel, and lead in fresh water by atomic absorption, *in* Trace inorganics in water: American Chemical Society Advances in Chemistry Series, no. 73, p. 230.

Nickel, dissolved, atomic absorption spectrometric, direct (I–1499–78)

Parameter and Code: Nickel, dissolved (µg/L as Ni): 01065

1. Application

This method may be used to analyze waters containing at least 100 µg/L of nickel. Sample solutions containing more than 1,000 µg/L must either be diluted or less scale expansion used. Sample solutions containing less than 100 µg/L, in the absence of interferences, and brines must be analyzed by Method I–1500.

2. Summary of method

Nickel is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment.

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), and cadmium, lead, copper, zinc, cobalt, and chromium (10,000 µg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**232.0 nm (NOTES 1 and 2).**
Source (hollow-cathode lamp).	**Nickel.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

NOTE 1. Setting the proper wavelength for nickel is critical because of presence of an ion line at 231.6 nm. By aspirating a standard that gives approx 50 percent absorbance, the 232.0 nm-absorption line can be easily set.

NOTE 2. The 352.4-nm wavelength is less susceptible to nonatomic absorbance and may be used. The analytical curve is more nearly linear; however, there is some loss of sensitivity.

5. Reagents

5.1 *Nickel* standard solution I, 1,000 mL = 200 µg Ni: Dissolve 0.9906 g $Ni(NO_3)_2\cdot 6H_20$ in a minimum volume of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2*Nickel* standard solution II, 1.00 mL = 20 µg Ni: Dilute 100 mL nickel standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.3 *Nickel* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 µg/L of nickel by appropriate dilution of nickel standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set the instrument digital display to read zero concentration. While aspirating standards use auto concentration to set instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of nickel in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose nickel concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report nickel, dissolved (01065), concentrations to the nearest 100 μg/L.

9. Precision

Precision data are not available for this method.

Reference

American Society for Testing and Materials, 1975, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 345.

Nickel, recoverable from bottom material, atomic absorption spectrometric, direct (I–5499–78)

Parameter and Code: Nickel, recoverable from bottom material, dry wt (μg/g as Ni): 01068

1. Application

1.1 This method may be used to analyze bottom material containing at least 2.5 μg/g of nickel. Prepared sample solutions (Method I–5485) containing more than 1,000 μg/L must either be diluted or less scale expansion used.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

Nickel is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–5485) into an air-acetylene flame.

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), and cadmium, lead, copper, zinc, cobalt, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	232.0 nm (NOTES 1 and 2).
Source (hollow-cathode lamp).	Nickel.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

NOTE 1. Setting the proper wavelength for nickel is critical because of presence of an ion line at 231.6 nm. By aspirating a standard that gives approx 50 percent absorbance, the 232.0 nm-absorption line can be easily set.

NOTE 2. The 352.4-nm wavelength is less susceptible to nonatomic absorbance and may be used. The analytical curve is more nearly linear; however, there is some loss of sensitivity.

5. Reagents

5.1 *Nickel* standard solution I, 1.00 mL = 200 μg Ni: Dissolve 0.9906 g $Ni(NO_3)_2 \cdot 6H_2O$ in a minimum volume of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Nickel* standard solution II, 1.00 mL = 20 μg Ni: Dilute 100 mL nickel standard solution I and 1 mL concentrated HNO_3 to 1,000 mL with demineralized water.

5.3 *Nickel* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 μg/L of nickel by appropriate dilution of nickel standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set the instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of nickel in each prepared sample solution (Method I–5485) from the digital display or printer output while aspirating each sample. Dilute those samples whose nickel concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per gram of nickel in bottom material samples, first determine the micrograms per liter of nickel as in 7.1, then

$$\text{Ni } (\mu g/g) = \frac{\mu g/L \text{ Ni} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report nickel, recoverable from bottom material (01068), concentrations as follows: less than 100 μg/g, nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

Precision data are not available for this method.

Reference

American Society for Testing and Materials, 1975, Annual book of ASTM standards, part 3l, water: Philadelphia, American Society for Testing and Materials, p. 345.

Nickel, total recoverable, atomic absorption spectrometric, chelation-extraction (I–3500–78)

Parameter and Code: Nickel, total recoverable (μg/L as Ni): 01067

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing from 1 to 100 μg/L of nickel, although dilution prior to chelation-extraction is required for samples containing more than 25 μg/L nickel. Sample solutions containing more than 100 μg/L may be either diluted prior to chelation-extraction or analyzed by Method I–3499.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

1.3 If the iron concentration of the sample exceeds 25,000 μg/L, determine nickel by direct atomic absorption (Method I–3499).

2. Summary of method

2.1 Nickel is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer (Fishman and Midgett, 1968).

2.2 Two procedures are given (6A and 6B), differing only in the manner of adjusting the pH of the sample solution prior to chelation and extraction of the nickel. Both methods are believed to be equally reliable, and the choice of method is left to the analyst.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the nickel absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	232.0 nm (NOTES 1 and 2).
Source (hollow-cathode lamp).	Nickel.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

NOTE 1. Setting the proper wavelength for nickel is critical because of presence of an ion line at 231.6 nm. By aspirating a standard that gives approx 50 percent absorbance, the 232.0-nm absorption line can be easily set.

NOTE 2. The 352.4-nm wavelength is less susceptible to nonatomic absorbance and may be used. The analytical curve is more nearly linear; however, there is some loss of sensitivity.

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate (APDC)* solution, 1 g/100 mL: Dissolve 1.0 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 1 g/L: Dissolve 1 g bromophenol blue in 1 L 50-percent ethanol.

5.3 *Sodium citrate buffer* solution: Dissolve 450 g sodium citrate dihydrate in demineralized water. Add 100 mL bromophenol blue indicator solution and dilute to 1 L with demineralized water. (Procedure A only.)

5.4 *Hydrochloric acid* 0.3*M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L. (Procedure B only.)

5.5 *Methyl isobutyl ketone (MIBK).*

5.6 *Nickel* standard solution I, 1.00 mL = 200 μg Ni: Dissolve 0.9906 g $Ni(NO_3)_2 \cdot 6H_2O$ in a than 37 percent at 5.9 μg/L and greater than 23 percent at 23.2 μg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 115.

Fishman, M. J., and Midgett, M. R., 1968, Extraction techniques for the determination of cobalt, nickel, and lead in fresh water by atomic absorption, *in* Trace inorganics in water: American Chemical Society, Advances in Chemistry Series no. 73, p. 230.

minimum volume of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.7 *Nickel* standard solution II, 1.00 mL = 2.00 μg Ni: Dilute 10.0 mL nickel standard solution I and 1 mL concentrated HNO_3 to 1,000 mL with demineralized water. This solution is used to prepare working standards at the time of analysis.

5.8 *Sodium hydroxide* 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 mL (NOTE 3). (Procedure B only.)

NOTE 3. Some batches of NaOH may contain traces of nickel. If this is suspected, use 2.5*M* NH_4OH rather than 2.5*M* NaOH. Prepare the NH_4OH solution by thoroughly mixing 20 mL concentrated NH_4OH (sp gr 0.90) with 100 mL demineralized water.

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.A Procedure A

6.A.1 Pipet a volume of prepared sample solution (Method I–3485) containing less than 2.5 μg Ni (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL (NOTE 4).

NOTE 4. If the samples must be diluted prior to chelation-extraction, a specially prepared dilution water must be used. It is prepared as follows: Mix 25 mL conc. HCl with demineralized water and dilute to 1 L.

6.A.2 Prepare a blank and at least six standards, and adjust the volume of each to approx 100 mL with the specially prepared dilution water in NOTE 4.

6.A.3 Add 10 mL buffer solution and mix (NOTE 5).

NOTE 5. If the proper amount of acid is present, the color will be greenish yellow. If the color is yellow, add buffer solution dropwise until the proper color is obtained. If the color is green or greenish blue, add concentrated nitric acid dropwise until the proper color is obtained.

6.A.4 Add 2.5 mL APDC solution and shake for 3 min.

6.A.5 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.A.6 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.A.7 Aspirate the ketone layer within 1 h. While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

6.B Procedure B

6.B.1 Pipet a volume of prepared sample solution (Method I–3485) containing less than 2.5 μg Ni (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.B.2 Prepare a blank with 1.5 mL concentrated HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.B.3 Add 2 drops bromophenol blue indicator solution to each sample and standard.

6.B.4 Adjust the pH of each by addition of either 2.5*M* NaOH or 2.5*M* NH_4OH by drops until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears. Then add 2.0 mL 0.3*M* HCl in excess. The pH at this point should be 2.3 (NOTE 6). Return to step 6.A.4 and proceed through step 6.A.7.

NOTE 6. The pH adjustment in steps 6.B.3 and 6.B.4 may be made with a pH meter instead of using indicator.

7. Calculations

Determine the micrograms per liter of nickel in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose nickel concentrations exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

8. Report

Report nickel, total recoverable (01067), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 37 percent at 5.9 μg/L and greater than 23 percent at 23.2 μg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 115.

Fishman, M. J., and Midgett, M. R., 1968, Extraction techniques for the determination of cobalt, nickel, and lead in fresh water by atomic absorption, *in* Trace inorganics in water: American Chemical Society, Advances in Chemistry Series no. 73, p. 230.

Nickel, total recoverable, atomic absorption spectrometric, direct (I–3499–78)

Parameter and Code: Nickel, total recoverable (μg/L as Ni):01067

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 100 μg/L of nickel. Sample solutions containing more than 1,000 μg/L must either be diluted or less scale expansion used. Sample solutions containing less than 100 μg/L, in the absence of interferences, must be analyzed by Method I–3500–74.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

Nickel is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–3485) into an air-acetylene flame.

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), and cadmium, lead, copper, zinc, cobalt, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**232.0 nm (NOTES 1 and 2).**
Source (hollow-cathode lamp).	**Nickel.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

NOTE 1. Setting the proper wavelength for nickel is critical because of the presence of an ion line at 231.6 nm. By aspirating a standard that gives approx 0.5 absorbance, the 232.0-nm absorption line can be easily set.

NOTE 2. The 352.4-nm wavelength is less susceptible to non-atomic absorbance and may be used. The analytical curve is more nearly linear; however, there is some loss of sensitivity.

5. Reagents

5.1 *Nickel* standard solution I, 1.00 mL = 200 μg Ni: Dissolve 0.9906 g $Ni(NO_3)_2 \cdot 6H_2O$ in a minimum volume of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Nickel* standard solution II, 1.00 mL = 20 μg Ni: Dilute 100 mL nickel standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.3 *Nickel* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 1,000 μg/L of nickel by appropriate dilution of nickel standard solution II. Prepare fresh daily.

6. Procedure

While aspirating the blank use auto zero to set the instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of nickel in each prepared sample solution (Method I–3485) from the digital display or printer output while aspirating each sample. Dilute those samples whose nickel concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report nickel, total recoverable (01067), concentrations to the nearest 100 μg/L.

9. Precision

Precision data are not available for this method.

Reference

American Society for Testing and Materials, 1975, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing Materials, p. 345.

Potassium, dissolved, atomic absorption spectrometric, direct (I–1630–78)

Parameter and Code:Potassium, dissolved (mg/L as K):00935

1. Application

This method may be used to analyze waters and brines containing from 0.1 to 2,000 mg/L of potassium. Samples whose potassium concentrations exceed 100 mg/L must first be diluted.

2. Summary of method

2.1 Potassium is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment of the sample (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 Of the substances commonly occurring in water, only sodium has been found to interfere, and its interference is greatly minimized if a reducing flame is used and the burner is raised to approximately 0.05 cm below the optical light path. The following data are indicative of the magnitude of sodium interference under these conditions:

Potassium added (mg/L)	*Sodium added (mg/L)*	*Potassium found (mg/L)*
1.00	0.0	1.00
1.00	100	1.03
1.00	500	1.05
1.00	1,000	1.07

3.2 Alternatively, an excess of sodium may be added to all samples and standards. Such additions essentially eliminate the effects of the then comparatively minor contributions of sodium present in the samples.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Visible.
Wavelength	766.5 nm.
Source (hollow-cathode lamp).	Potassium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Slightly reducing.

4.3 The 50-mm (2-in.) flathead single slot burner allows a working range of 0.1 to 10 mg/L. If the burner is rotated 90°, the range may be extended to 100 mg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Potassium* standard solution I, 1.00 mL = 0.100 mg K: Dissolve 0.1907 g KCl, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Potassium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0.00 to 10.0 mg/L of potassium by appropriate dilution of potassium standard solution I.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the milligrams per liter of potassium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose potassium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report potassium, dissolved (00935), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 0.5 to 8 mg/L may be expressed as follows:

insert equation

where

S_T = overall precision, milligrams per liter, and

X = concentration of potassium, milligrams per liter.

9.2 The precision results may also be expressed in terms of relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
15	0.8	14
32	5.2	11

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 134.

Fishman, M. J., and Downs, S. C., 1966, Method for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 36.

Potassium, recoverable from bottom material, atomic absorption spectrometric, direct (I–5630–78)

Parameter and Code: Potassium, recoverable from bottom material, dry wt (mg/kg as K):00938

1. Application

1.1 This method may be used to analyze bottom material containing at least 10 mg/kg of potassium. Prepared sample solutions (Method I–5485) containing more than 100 mg/L must be diluted.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

2.1 Potassium is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–5485) into an air-acetylene flame (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 Of the substances commonly occurring in water, only sodium has been found to interfere, and its interference is greatly minimized if a reducing flame is used and the burner is raised to approximately 0.05 cm below the optical light path. The following data are indicative of the magnitude of sodium interference under these conditions:

Potassium added (mg/L)	*Sodium added (mg/L)*	*Potassium found (mg/L)*
1.00	0.0	1.00
1.00	100	1.03
1.00	500	1.05
1.00	1,000	1.07

3.2 Alternatively, an excess of sodium may be added to all samples and standards. Such additions essentially eliminate the effects of the then comparatively minor contributions of sodium present in the samples.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Visible.
Wavelength	766.5 nm.
Source (hollow-cathode lamp).	Potassium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Slightly reducing.

4.3 The 50-mm (2-in.) flathead single slot burner allows a working range of 0.1 to 10 mg/L. If the burner is rotated 90°, the range may be extended to 100 mg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Potassium* standard solution I, 1.00 mL = 0.100 mg K: Dissolve 0.1907 g KCl, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Potassium* standard working solution: Prepare a series of at least six standard working solutions containing from 0 to 10 mg/L of potassium by appropriate dilution of potassium standard solution I.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the milligrams per liter of potassium in each prepared sample solution (Method I–5485) from the digital display or printer output while aspirating each sample. Dilute those samples whose potassium concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine milligrams per kilogram concentration of potassium in bottom material samples, first determine the milligrams per liter of potassium as in 7.1, then

$$\text{K (mg/kg)} = \frac{\text{mg/L K} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}.$$

8. Report

Report potassium, recoverable from bottom material (00938), concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 14 percent in the lower portion of the analytical range.

Reference

Fishman, M. J., and Downs, S. C., 1966, Method for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 36.

Potassium, total recoverable, atomic absorption spectrometric, direct (I–3630–78)

Parameter and Code: Potassium, total recoverable (mg/L as K):none assigned

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing from 0.1 to 2,000 mg/L of potassium. Samples whose concentrations of potassium exceed 100 mg/L must first be reduced by dilution.

1.2 Water-suspended mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

2.1 Potassium is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–3485) into an air-acetylene flame (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 Of the substances commonly occurring in water, only sodium has been found to interfere, and its interference is greatly minimized if a reducing flame is used and the burner is raised to approximately 0.05 cm below the optical light path. The following data are indicative of the magnitude of sodium interference under these conditions:

Potassium added (mg/L)	*Sodium added (mg/L)*	*Potassium found (mg/L)*
1.00	0.0	1.00
1.00	100	1.03
1.00	500	1.05
1.00	1,000	1.07

3.2 Alternatively, an excess of sodium may be added to all samples and standards. Such additions essentially eliminate the effects of the then comparatively minor contributions of sodium present in the samples.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Visible.
Wavelength	766.5 nm.
Source (hollow-cathode lamp).	Potassium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Slightly reducing.

4.3 The 50-mm (2-in.) flathead single slot burner allows a working range of 0.1 to 10 mg/L. If the burner is rotated 90°, the range may be extended to 100 mg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Potassium* standard solution I, 1.00 mL = 0.100 mg K: Dissolve 0.1907 g KCl, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Potassium* standard working solution: Prepare a series of at least six standard working solutions containing from 0 to 10 mg/L of potassium by appropriate dilution of potassium standard solution I.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the milligrams per liter of potassium in each prepared sample solution (Method I–3485) from the digital display or printer output while aspirating each sample. Dilute those samples whose potassium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report potassium, total recoverable concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 14 percent at 0.8 mg/L and greater than 11 percent at 5.2 mg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 134.

Fishman, M. J., and Downs, S. C., 1966, Method for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 36.

Potassium, total recoverable, atomic absorption spectrometric, direct-EPA (I–3631–78)

Parameter and Code: Potassium, total recoverable (mg/L as K):00937

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing from 0.1 to 2,000 mg/L of potassium. Samples whose potassium concentrations exceed 100 mg/L must first be diluted.

1.2 For ambient waters, analysis may be made on a portion of the acidified water-suspended sediment sample.

1.3 For all other waters, including domestic and industrial effluents, the atomic absorption procedure must be preceded by a digestion-solubilization as specified below. In cases where the analyst is uncertain about the type of sample, the digestion-solubilization procedure must be used.

2. Summary of method

2.1 Potassium is determined by atomic absorption spectrometry by direct aspiration of the filtered or digested and filtered sample into an air-acetylene flame (Fishman and Downs, 1966).

2.2 Effluent samples must undergo a preliminary nitric acid digestion followed by a hydrochloric acid solubilization.

2.3 This atomic absorption procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 Of the substances commonly occurring in water, only sodium has been found to interfere, and its interference is greatly minimized if a reducing flame is used and the burner is raised to approximately 0.05 cm below the optical light path. The following data are indicative of the magnitude of sodium interference under these conditions:

Potassium added (mg/L)	*Sodium added (mg/L)*	*Potassium found (mg/L)*
1.00	0.0	1.00
1.00	100	1.03
1.00	500	1.05
1.00	1,000	1.07

3.2 Alternatively, an excess of sodium may be added to all samples and standards. Such additions essentially eliminate the effects of the then comparatively minor contributions of sodium present in the samples.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Visible.**
Wavelength	**766.5 nm.**
Source (hollow-cathode lamp).	**Potassium.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Slightly reducing.**

4.3 The 50-mm (2-in.) flathead single slot burner allows a working range of 0.1 to 10 mg/L. If the burner is rotated 90°, the range may be extended to 100 mg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Hydrochloric acid*, 6*M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.2 *Hydrochloric acid*, 0.3*M*: Dilute 25 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.3 *Nitric acid*, concentrated HNO_3 (sp gr 1.41).

5.4 *Potassium* standard solution I, 1.00 mL = 0.100 mg K: Dissolve 0.1907 g KCl, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.5 *Potassium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 10 mg/L of potassium by appropriate dilution of potassium standard solution I.

6. Procedure

6.1 Transfer the entire sample to a beaker.

6.2 Rinse the sample bottle with 3 mL concentrated HNO_3 for each 100 mL of sample and add to the beaker. Prepare a blank using 3 mL concentrated HNO_3 per 100 mL demineralized water.

6.3 Evaporate samples and blank to dryness on a hot plate, making sure the samples do not boil.

6.4 Cool and add an additional 3 mL concentrated HNO_3 to each beaker. Cover with a watch glass, return to the hot plate, and gently reflux the samples.

6.5 Continue heating, adding additional acid as necessary, until the digestion is complete (indicated by a light-colored residue). Evaporate just to dryness.

6.6 Add 6 mL 6*M* HCl solution per 100 mL original sample and warm the beaker to dissolve the residue.

6.7 Wash the watch glass and beaker with demineralized water and filter the sample (Whatman No. 41 or equivalent), rinsing the filter with hot 0.3*M* HCl. Dilute to the original volume with demineralized water.

6.8 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the milligrams per liter of potassium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose potassium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report potassium, total recoverable (00937), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 14 percent at 0.8 mg/L and greater than 11 percent at 5.2 mg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 134.

Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 82–83, 143–144.

Fishman, M. J., and Downs, S. C., 1966, Method for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 36.

Selenium, dissolved, atomic absorption spectrometric, hydride (I–1667–78)

Parameter and Code: Selenium, dissolved (μg/L as Se): 01145

1. Application

This method may be used to analyze waters containing at least 1 μg/L of selenium. Samples containing more than 20 μg/L must first be diluted.

2. Summary of method

Organic selenium compounds, if present, are first decomposed by digestion with potassium permanganate in hot acid solution. The solution is then made basic and evaporated to dryness in the presence of calcium chloride to prevent loss of selenate during the evaporation. Hydrochloric acid is added to the residue to reduce the selenate to selenite. To obtain quantitative reduction without loss of selenium, the temperature, time, and acid concentration must be controlled. All selenium must be in the selenite form prior to its final reduction with stannous chloride in 6*M* hydrochloric acid solution. The selenium hydride so formed is subsequently removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame where it is determined by atomic absorption at 196.0 nm (Freeman and Uthe, 1974, and Lansford and others, 1974).

3. Interferences

3.1 Arsenic interferes by suppressing the selenium absorption if an excess of stannous chloride is used. This interference can be avoided by carefully controlling the amount of stannous chloride added. If 42 mg stannous chloride is added, as much as 150 μg/L of arsenic can be tolerated. At least this amount must be added, however, to ensure efficient reduction of selenite to the hydride.

3.2 Mercury interferes when its concentration exceeds 25 μg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer.*

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	196.0 nm.
Source (electrodeless discharge lamp).	Selenium.
Burner	Three-slot.
Fuel	Hydrogen.
Diluent	Nitrogen.
Carrier	Nitrogen.

4.3 *Selenium hydride vapor analyzer* (fig. 22) consisting of—

4.3.1 *Fleaker*, 300-mL capacity, or beaker, berzelius, 200-mL capacity.

4.3.2 *Gas dispersion tube*, coarse frit (Scientific Glass Apparatus Co. No. JG–8500 has been found to be satisfactory).

4.3.3 *Medicine dropper*, 2-mL capacity, minimum.

5. Reagents

5.1 *Ammonium chloride* solution, 250 g/L: Dissolve 250 g NH_4Cl in demineralized water and dilute to 1 L.

5.2 *Calcium chloride* solution, 22.6 g/L: Dissolve 30 g $CaCl_2 \cdot 2H_2O$ in demineralized water and dilute to 1 L.

5.3 *Hydrochloric acid*, concentrated (sp gr 1.19).

5.4 *Hydrochloric acid*, 6*M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.5 *Hydrochloric acid*, 0.1*M*: Dilute 8 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.6 *Methyl orange indicator solution*, 50 mg/100 mL: Dissolve 50 mg methyl orange in 100 mL demineralized water.

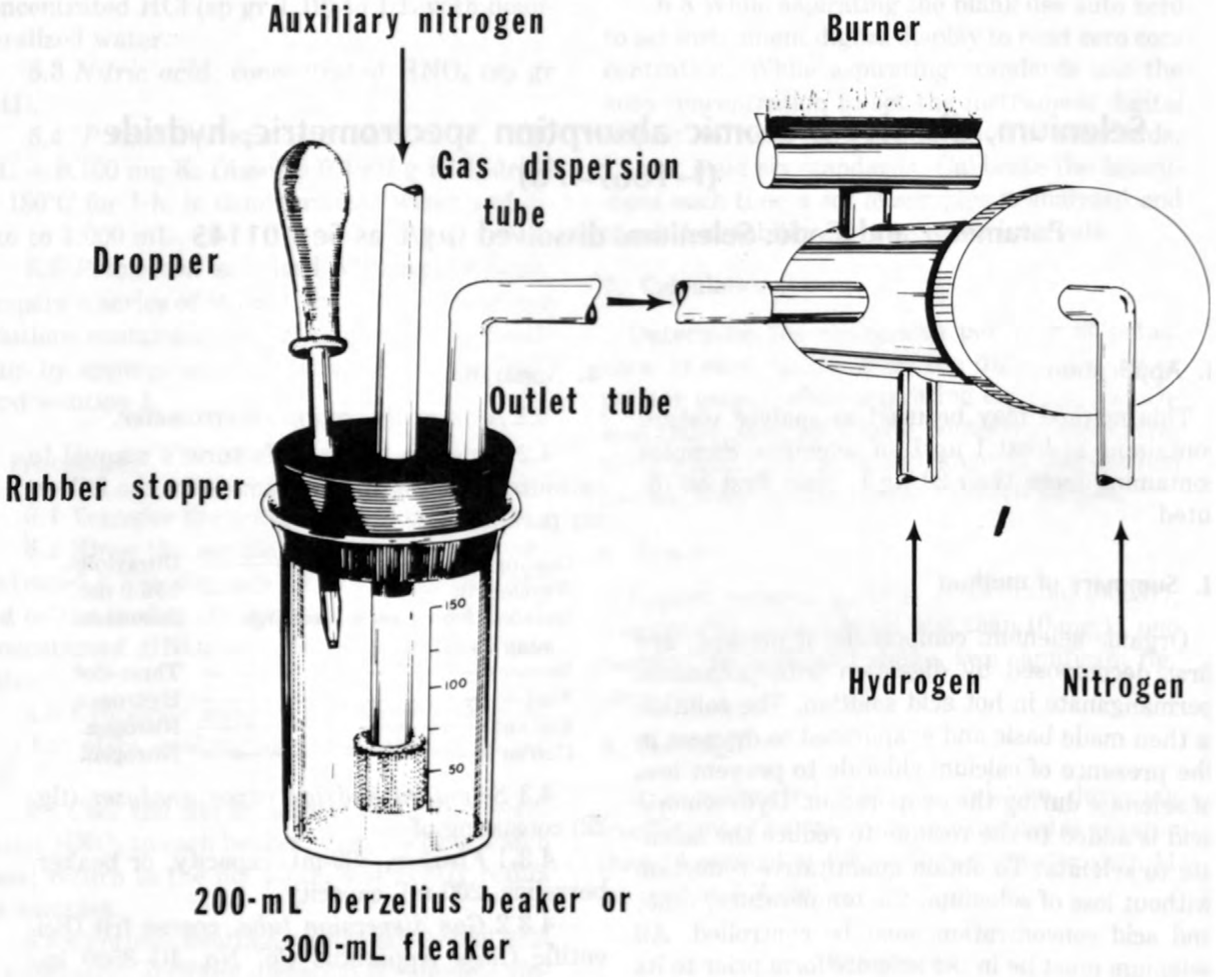


FIGURE 22.—Selenium hydride vapor analyzer .

5.7 *Potassium permanganate* solution, 0.3 g/L: Dissolve 0.3 g $KMnO_4$ in 1 L demineralized water.

5.8 *Selenium* standard solution I: Place an accurately weighed pellet of metallic selenium (approx 50 mg) into a small beaker. Add 5 mL concentrated HNO_3 (sp gr 1.41). Warm until reaction is complete and cautiously evaporate just to dryness. Dilute to 1,000 mL with demineralized water. (This solution should contain about 50 mg/L of selenium.)

5.9 *Selenium* standard solution II: 1.00 mL = 1.00 µg Se: From a buret, measure an appropriate amount of selenium standard solution I and dilute to 1,000 mL with demineralized water.

5.10 *Selenium* standard solution III: 1.00 mL = 0.100 µg Se: Dilute 20.0 mL selenium standard solution II to 200 mL with demineralized water. Prepare fresh before each use.

5.11 *Sodium hydroxide* solution, 0.1*M*: Dissolve 4 g NaOH in demineralized water and dilute to 1 L.

5.12 *Stannous chloride* solution, 4.2 g per 100 mL concentrated HCl: Dissolve 5 g $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl (sp gr 1.19). This solution is stable if a few small pieces of mossy tin are added to prevent oxidation.

6. Procedure

6.1 Pipet a volume of sample containing less than 2.0 µg Se (100 mL maximum) into a 300-mL fleaker and dilute to 100 mL.

6.2 Prepare, in 300-mL fleakers, a blank and sufficient standards containing from 0.0 to 2.0 µg

Se by diluting 0.0- to 20.0-mL portions of selenium standard solution III. Dilute each to approx 100 mL.

6.3 To each fleaker add 1 drop methyl orange, 0.5 mL $CaCl_2$ solution, and a boiling chip or several glass beads.

6.4 To the fleakers containing the blank and standards, add 0.5 mL 0.1*M* HCl.

6.5 To the fleakers containing the samples, titrate with 0.1*M* HCl until the indicator shows a distinct red color and then add 0.5 mL excess (NOTE 1).

NOTE 1. If the samples have been acidified either at the time of collection or in the laboratory, titrate with 2*M* NaOH until the indicator shows a distinct yellow-orange color and then continue with step 6.5. When the presence of interferences makes it impossible to adjust the pH with use of methyl orange, use a pH meter for this adjustment.

6.6 Add 3 drops $KMnO_4$ solution to each fleaker and heat to boiling on a hot plate, adding $KMnO_4$ as required to maintain a purple tint. If a precipitate of MnO_2 forms at this point, it will have no adverse effect.

6.7 After the volume has been reduced to approx 50 mL, add 2 mL 0.1*M* NaOH; evaporate to dryness and allow the fleakers to cool. Avoid prolonged heating of the residue.

6.8 Add 5 mL concentrated HCl and 10 mL NH_4Cl solution. Heat in a boiling-water bath or steam bath for 20 ± 0.5 min (NOTE 2).

NOTE 2. Samples can be heated on a hot plate at low temperature if boiling can be prevented.

6.9 Dilute each sample, blank, and standard to approx 100 mL with 6*M* HCl.

6.10 Attach one fleaker at a time to the rubber stopper containing the gas dispersion tube.

6.11 Fill the medicine dropper with 1 mL $SnCl_2$ solution and insert into hole in rubber stopper.

6.12 Add the $SnCl_2$ solution to the sample solution. After the absorbance has reached a maximum and has returned to the baseline remove the fleaker. Rinse the gas dispersion tube in demineralized water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

7. Calculations

7.1 Determine the micrograms of selenium in each sample aliquot from a plot of absorbances of standards. Exact reproducibility is not obtained, and an analytical curve must be prepared with each set of samples.

7.2 Compute the concentration of selenium in each sample as follows:

$$\text{Se } (\mu\text{g/L}) = \frac{1{,}000}{\text{mL sample}} \times \mu\text{g Se in sample.}$$

8. Report

Report selenium, dissolved (01145), concentrations as follows: less than 100 μg/L, nearest microgram per liter; 100 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 2 to 10 μg/L may be expressed as follows:

$$S_T = 0.275X - 0.134$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of selenium, micrograms per liter.

9.2 The precision may also be expressed in terms of relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
6	3.5	29
6	8.5	27
5	18.6	47

References

Freeman, H. C., and Uthe, J. F., 1974, An improved hydride generation apparatus for determining arsenic and selenium byatomic absorption spectrometry: Atomic Absorption News-letter, v. 13, p. 75.

Lansford, Myra, McPherson, E. M., and Fishman, M. J., 1974, Determination of selenium in water: Atomic Absorption Newsletter, v. 13, p. 103.

Selenium, total in bottom material, atomic absorption spectrometric, hydride (I–5667–78)

Parameter and Code: Selenium, total in bottom material, dry wt (μg/g as Se):01148

1. Application

1.1 This method may be used to analyze bottom material containing at least 1 μg/g of selenium. Ordinarily a 100-mg sample of prepared bottom material (Method P–0520) is taken for analysis. However, if the sample contains more than 20 μg/g of selenium, a smaller sample must be used.

1.2 Bottom-material samples must be prepared for analysis as directed in Method P–0520.

2. Summary of method

Organic selenium compounds, if present, are first decomposed by digestion with potassium permanganate in hot acid solution. The solution is then made basic and the solution evaporated to dryness in the presence of calcium chloride to prevent loss of selenate during the evaporation. Hydrochloric acid is added to the residue to reduce the selenate to selenite. To obtain quantitative reduction without loss of selenium, the temperature, time, and acid concentration must be controlled. All selenium must be in the selenite form prior to its final reduction with stannous chloride in 6*M* hydrochloric acid solution. The selenium hydride so formed is subsequently removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame where it is determined by atomic absorption at 196.0 nm (Lansford and others, 1974).

3. Interferences

3.1 Arsenic interferes by suppressing the selenium absorption if an excess of stannous chloride is used. This interference can be avoided by carefully controlling the amount of stannous chloride added. If 42 mg stannous chloride is added, as much as 150 μg/L of arsenic can be tolerated. At least this amount must be added, however, to ensure efficient reduction of selenite to the hydride.

3.2 Mercury interferes when its concentration exceeds 25 μg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer.*

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	196.0 nm.
Source (electrodeless discharge lamp).	Selenium.
Burner	Three-slot.
Fuel	Hydrogen.
Diluent	Nitrogen.
Carrier	Nitrogen.

4.3 *Selenium hydride vapor analyzer* (fig. 23) consisting of—

4.3.1 *Fleaker*, 300-mL capacity, or beaker, berzelius, 200-mL capacity.

4.3.2 *Gas dispersion tube*, coarse frit (Scientific Glass Apparatus Co. No. JG–8500 has been found to be satisfactory).

4.3.3 *Medicine dropper*, 2-mL capacity, minimum.

5. Reagents

5.1 *Ammonium chloride* solution, 250 g/L: Dissolve 250 g NH_4Cl in demineralized water and dilute to 1 L.

5.2 *Calcium chloride* solution, 22.6 g/L: Dissolve 30 g $CaCl_2 \cdot 2H_2O$ in demineralized water and dilute to 1 L.

5.3 *Hydrochloric acid*, concentrated (sp gr 1.19).

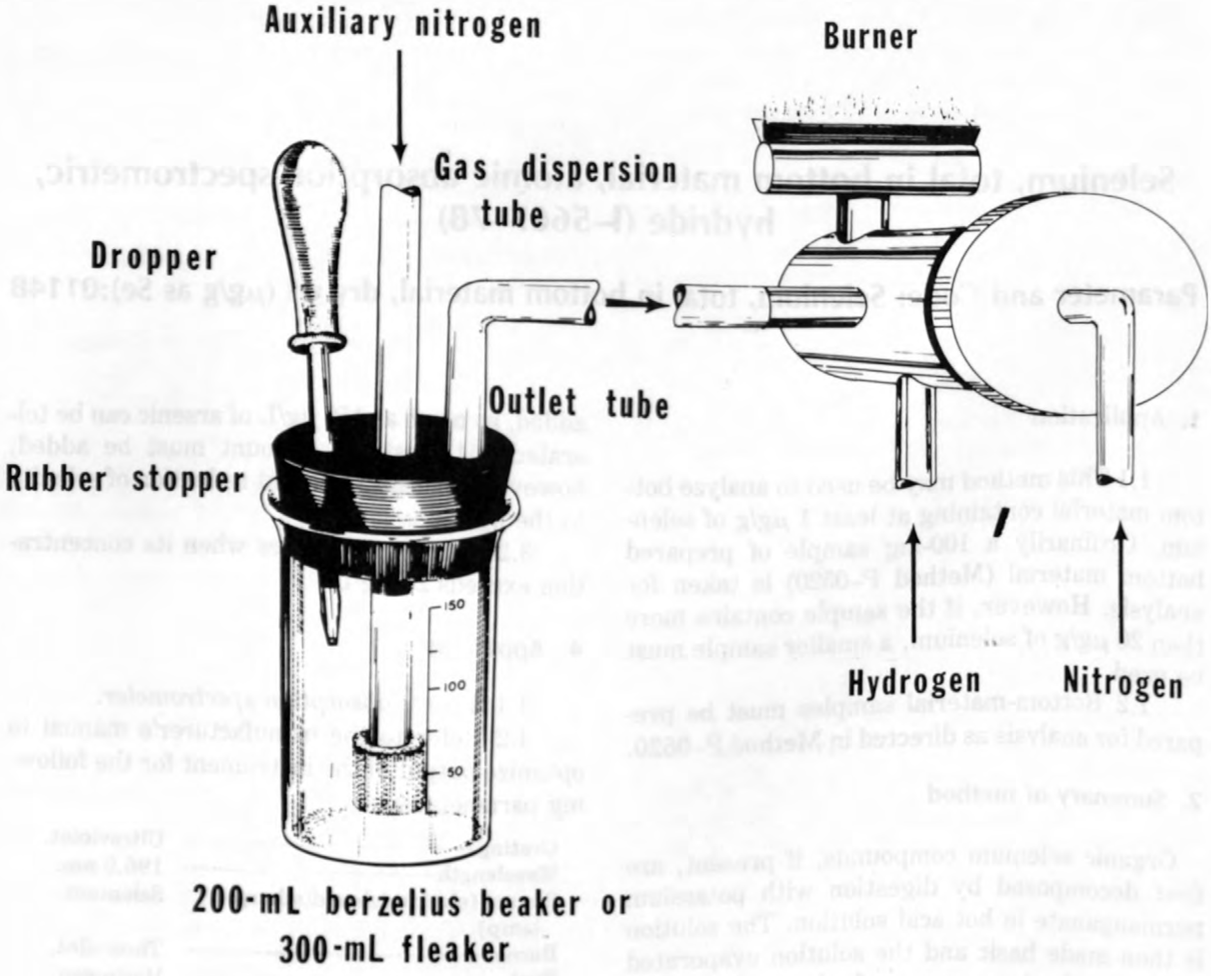


FIGURE 23.—Selenium hydride vapor analyzer.

5.4 *Hydrochloric acid,* 6*M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.5 *Hydrochloric acid,* 0.1*M*: Dilute 8 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.6 *Methyl orange indicator* solution, 50 mg/100 mL: Dissolve 50 mg methyl orange in 100 mL demineralized water.

5.7 *Potassium permanganate* solution, 0.3 g/L: Dissolve 0.3 g $KMnO_4$ in 1 L demineralized water.

5.8 *Selenium* standard solution I: Place an accurately weighed pellet of metallic selenium (approx 50 mg) into a small beaker. Add 5 mL concentrated HNO_3 (sp gr 1.41). Warm until reaction is complete and cautiously evaporate just to dryness. Dilute to 1,000 mL with demineralized water. (This solution should contain about 50 mg/L of selenium.)

5.9 *Selenium* standard solution II: 1.00 mL = 1.00 μg Se: From a buret, measure an appropriate amount of selenium standard solution I and dilute to 1,000 mL with demineralized water.

5.10 *Selenium* standard solution III: 1.00 mL = 0.100 μg Se: Dilute 20.0 mL selenium standard solution II to 200 mL with demineralized water. Prepare fresh before each use.

5.11 *Sodium hydroxide* solution, 0.1*M*: Dissolve 4 g NaOH in demineralized water and dilute to 1 L.

5.12 *Stannous chloride* solution, 4.2 g per 100 mL concentrated HCl: Dissolve 5 g $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl (sp gr 1.19). This solution is stable if a few small pieces of mossy tin are added to prevent oxidation.

6. Procedure

6.1 Place a weighed portion of sample containing less than 2.0 μg Se (100 mg maximum) into a 300-mL fleaker and add 100 mL demineralized water (NOTE 1). Stir to mix thoroughly and allow to settle.

NOTE 1. Do not use more than 100 mg of bottom material, or severe bumping and loss of selenium may occur during the subsequent digestion of the sample.

6.2 Prepare, in 300-mL fleakers, a blank and sufficient standards containing from 0.0 to 2.0 μg Se by diluting 0.0- to 20.0-mL portions of selenium standard solution III. Dilute each to approx 100 mL.

6.3 To each fleaker add 1 drop methyl orange, 0.5 mL $CaCl_2$ solution, and a boiling chip or several glass beads.

6.4 To the fleakers containing the blank and standards, add 0.5 mL 0.1*M* HCl.

6.5 To the fleakers containing the samples, titrate with 0.1*M* HCl until the indicator shows a distinct red color and then add 0.5 mL excess.

6.6 Add 3 drops $KMnO_4$ solution to each fleaker and heat to boiling on a hot plate, adding $KMnO_4$ as required to maintain a purple tint. If a precipitate of MnO_2 forms at this point, it will have no adverse effect.

6.7 After the volume has been reduced to approx 50 mL, add 2 mL 0.1*M* NaOH; evaporate to dryness and allow the fleakers to cool. Avoid prolonged heating of the residue.

6.8 Add 5 mL concentrated HCl and 10 mL NH_4Cl solution. Heat in a boiling-water bath or steam bath for 20 + t0.5 min (NOTE 2).

NOTE 2. Samples can be heated on a hot plate at low temperature if boiling can be prevented.

6.9 Dilute each sample, blank, and standard to approx 100 mL with 6*M* HCl.

6.10 Attach one fleaker at a time to the rubber stopper containing the gas dispersion tube.

6.11 Fill the medicine dropper with 1 mL $SnCl_2$ solution and insert into hole in rubber stopper.

6.12 Add the $SnCl_2$ solution to the sample solution. After the absorbance has reached a maximum and has returned to the baseline remove the fleaker. Rinse the gas dispersion tube in demineralized water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

7. Calculations

7.1 Determine the micrograms of selenium in each sample from a plot of absorbances of standards. Exact reproducibility is not obtained, and an analytical curve must be prepared with each set of samples.

7.2 Determine the concentration of selenium in micrograms per gram of air-dried sample as follows:

$$\text{Se } (\mu g/g) = \frac{\mu g \text{ Se in sample}}{\text{sample weight (g)}}$$

8. Report

Report selenium, total in bottom material (01148), concentrations as follows: less than 100 μg/g, to the nearest microgram per gram; 100 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 27 percent in the lower portion of the analytical range.

Reference

Lansford, Myra, McPherson, E. M., and Fishman, M. J., 1974, Determination of selenium in water: Atomic Absorption Newsletter, v. 13, p. 103.

Selenium, total, atomic absorption spectrometric, hydride (I–3667–78)

Parameter and Code: Selenium, total (μg/L as Se): 01147

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 1 μg/L of selenium. Sample solutions containing more than 20 μg/L must first be diluted.

1.2 Water-suspended sediment mixtures may be analyzed by this procedure after each sample has been thoroughly mixed by vigorous shaking and a suitable aliquot has been rapidly withdrawn from the mixture.

2. Summary of method

Organic selenium compounds, if present, are first decomposed by digestion with potassium permanganate in hot acid solution. The solution is then made basic and the solution evaporated to dryness in the presence of calcium chloride to prevent loss of selenate during the evaporation. Hydrochloric acid is added to the residue to reduce the selenate to selenite. To obtain quantitative reduction without loss of selenium, the temperature, time, and acid concentration must be controlled. All selenium must be in the selenite form prior to its final reduction with stannous chloride in 6*M* hydrochloric acid solution. The selenium hydride so formed is subsequently removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame where it is determined by atomic absorption at 196.0 nm (Freeman and Uthe, 1974, and Lansford and others, 1974).

3. Interferences

3.1 Arsenic interferes by suppressing the selenium absorption if an excess of stannous chloride is used. This interference can be avoided by carefully controlling the amount of stannous chloride added. If 42 mg stannous chloride is added, as much as 150 μg/L of arsenic can be tolerated. At least this amount must be added, however, to ensure efficient reduction of selenite to the hydride.

3.2 Mercury interferes when its concentration exceeds 25 μg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer.*

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	196.0 nm.
Source (electrodeless discharge lamp).	Selenium.
Burner	Three-slot.
Fuel	Hydrogen.
Diluent	Nitrogen.
Carrier	Nitrogen.

4.3 *Selenium hydride vapor analyzer* (fig. 24) consisting of—

4.3.1 *Fleaker*, 300-mL capacity, or beaker, berzelius, 200-mL capacity.

4.3.2 *Gas dispersion tube*, coarse frit (Scientific Glass Apparatus Co. No. JG–8500 has been found to be satisfactory).

4.3.3 *Medicine dropper*, 2-mL capacity, minimum.

5. Reagents

5.1 *Ammonium chloride* solution, 250 g/L: Dissolve 250 g NH_4Cl in demineralized water and dilute to 1 L.

5.2 *Calcium chloride* solution, 22.6 g/L: Dissolve 30 g $CaCl_2 \cdot 2H_2O$ in demineralized water and dilute to 1 L.

5.3 *Hydrochloric acid*, concentrated (sp gr 1.19).

5.4 *Hydrochloric acid*, 6*M*: Dilute 500 mL

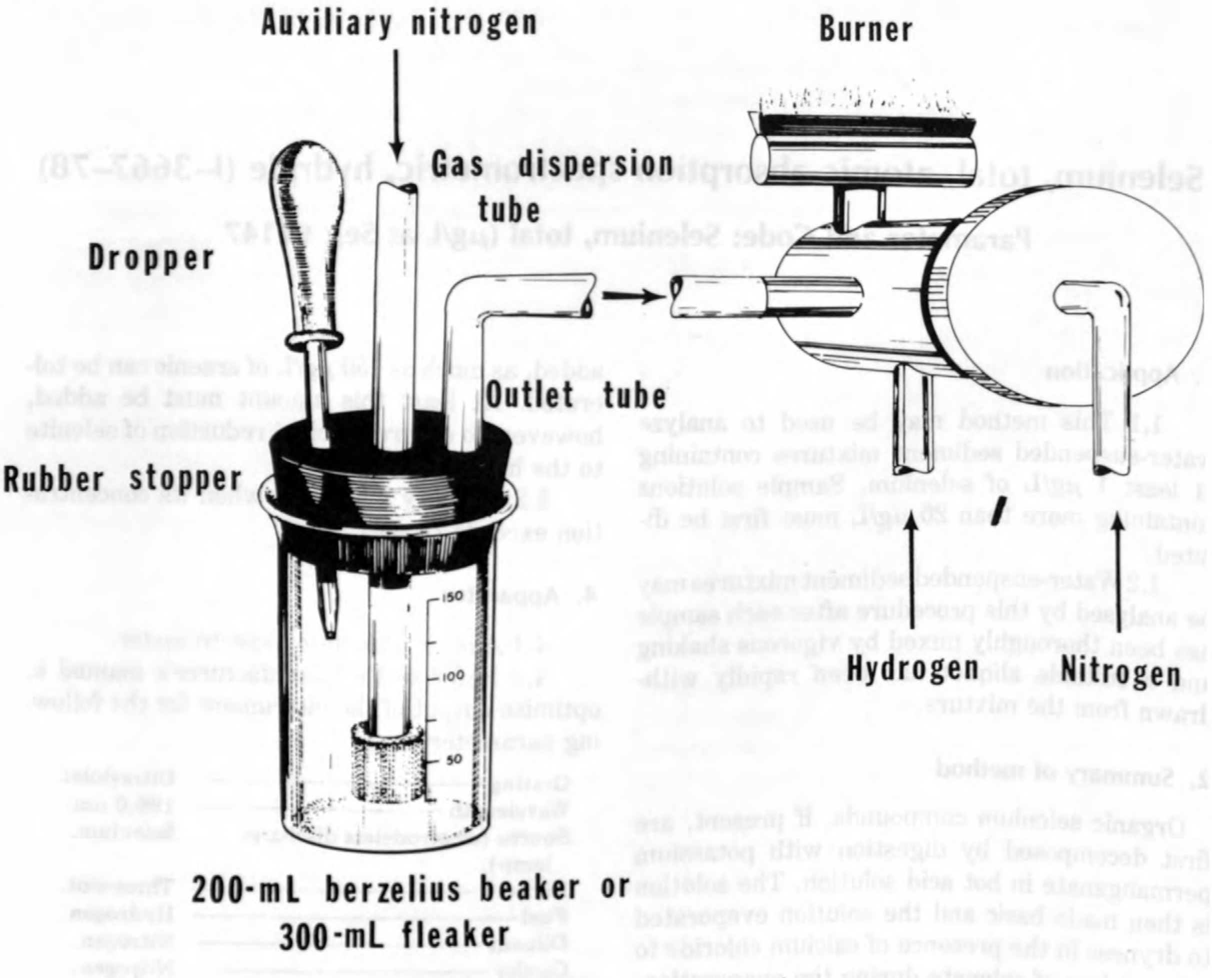


FIGURE 24.—Selenium hydride vapor analyzer.

concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.5 *Hydrochloric acid*, 0.1*M*: Dilute 8 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.6 *Methyl orange indicator* solution, 50 mg/100 mL. Dissolve 50 mg methyl orange in 100 mL demineralized water.

5.7 *Potassium permanganate* solution, 0.3 g/L: Dissolve 0.3 g $KMnO_4$ in 1 L demineralized water.

5.8 *Selenium* standard solution I: Place an accurately weighed pellet of metallic selenium (approx 50 mg) into a small beaker. Add 5 mL concentrated HNO_3 (sp gr 1.41). Warm until reaction is complete and cautiously evaporate just to dryness. Dilute to 1,000 mL with demineralized water. (This solution should contain about 50 mg/L of selenium.)

5.9 *Selenium* standard solution II: 1.00 mL = 1.00 μg Se: From a buret, measure an appropriate amount of selenium standard solution I and dilute to 1,000 mL with demineralized water.

5.10 *Selenium* standard solution III: 1.00 mL = 0.100 μg Se: Dilute 20.0 mL selenium standard solution II to 200 mL with demineralized water. Prepare fresh before each use.

5.11 *Sodium hydroxide* solution, 0.1*M*: Dissolve 4 g NaOH in demineralized water and dilute to 1 L.

5.12 *Stannous chloride* solution, 4.2 g per 100 mL concentrated HCl: Dissolve 5 g $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl (sp gr 1.19). This solution is stable if a few small pieces of mossy tin are added to prevent oxidation.

6. Procedure

6.1 Pipet a volume of sample containing less than 2.0 μg Se (100 mL maximum) into a 300-mL fleaker and dilute to 100 mL.

6.2 Prepare, in 300-mL fleakers, a blank and sufficient standards containing from 0.0 to 2.0 μg Se by diluting 0.0- to 20.0-mL portions of selenium standard solution III. Dilute each to approximately 100 mL.

6.3 To each fleaker add 1 drop methyl orange, 0.5 mL $CaCl_2$ solution, and a boiling chip or several glass beads.

6.4 To the fleakers containing the blank and standards, add 0.5 mL 0.1*M* HCl.

6.5 To the fleakers containing the samples, titrate with 0.1*M* HCl until the indicator shows a distinct red color and then add 0.5 mL excess (NOTE 1).

NOTE 1. If the samples are acidified at time of collection or in the laboratory, titrate with 2*M* NaOH until the indicator shows a distinct yellow-orange color and then continue with step 6.5. When the presence of interferences makes it impossible to adjust the pH using methyl orange, use a pH meter for this adjustment.

6.6 Add 3 drops $KMnO_4$ solution to each fleaker and heat to boiling on a hot plate, adding $KMnO_4$ as required to maintain a purple tint. If a precipitate of MnO_2 forms at this point, it will have no adverse effect.

6.7 After the volume has been reduced to approx 50 mL, add 2 mL 0.1*M* NaOH; evaporate to dryness and allow the fleakers to cool. Avoid prolonged heating of the residue.

6.8 Add 5mL concentrated HCl and 10 mL NH_4Cl solution. Heat in a boiling-water bath or steam bath for 20 + 0.5 min (NOTE 2).

NOTE 2. Samples can be heated on a hot plate at low temperature if boiling can be prevented.

6.9 Dilute each sample, blank, and standard to approx 100 mL with 6*M* HCl.

6.10 Attach one fleaker at a time to the rubber stopper containing the gas dispersion tube.

6.11 Fill the medicine dropper with 1 mL $SnCl_2$ solution and insert into hole in rubber stopper.

6.12 Add the $SnCl_2$ solution to the sample solution. After the absorbance has reached a maximum and has returned to the baseline remove the fleaker. Rinse the gas dispersion tube in demineralized water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

7. Calculations

7.1 Determine the micrograms of selenium in each sample aliquot from a plot of absorbances of standards. Exact reproducibility is not obtained, and an analytical curve must be prepared with each set of samples.

7.2 Compute the concentration of selenium in each sample as follows:

$$\text{Se } (\mu g/L) = \frac{1{,}000}{\text{mL sample}} \times \mu g \text{ Se in sample.}$$

8. Report

Report selenium, total (01147), concentrations as follows: less than 100 μg/L, nearest microgram per liter; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 24 percent at 3.5 μg/L and greater than 47 percent at 18.6 μg/L.

References

Freeman, H. C., and Uthe, J. F., 1974, An improved hydride generation apparatus for determining arsenic and selenium byatomic absorption spectrometry: Atomic Absorption Newsletter, v. 13, p. 75.

Lansford, Myra, McPherson, E. M., and Fishman, M. J., 1974, Determination of selenium in water: Atomic Absorption Newsletter, v. 13, p. 103.

Silica, dissolved, atomic absorption spectrometric, direct (I–1702–78)

Parameter and Code: Silica, dissolved (mg/L as SiO_2):00955

1. Application

This method may be used to analyze water containing at least 0.5 mg/L of silica. Samples containing more than 35 mg/L must either be diluted or less scale expansion used. The sensitivity of the determination is dependent on the amount of acetylene remaining in the cylinder. When a full cylinder is used (290 psi), a sensitivity of about 0.40 mg SiO_2 per scale division may be expected. However, when a near-empty cylinder is used (for example, 50 psi), a sensitivity of only about 0.55 mg SiO_2 per scale division is observed. The significant amount of acetone vapor present in the last acetylene to be withdrawn from a cylinder decreases the sensitivity for silica in the nitrous-oxide-acetylene flame.

2. Summary of method

Silica is determined by atomic absorption spectrometry by direct aspiration of the sample into a nitrous oxide-acetylene flame without preconcentration or pretreatment of the sample.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	251.6 nm.
Source (hollow-cathode lamp).	Silica.
Burner	Nitrous-oxide.
Oxidant	Nitrous oxide.
Fuel	Acetylene.
Type of flame	Fuel-rich.

5. Reagents

5.1 *Silica* standard solution I, 1.00 mL = 0.500 mg SiO_2: Dissolve 2.366 g sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$) in demineralized water and dilute to 1,000 mL. The concentration of this solution must be verified by standard gravimetric analysis. Store in a plastic bottle.

5.2 *Silica* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 25 mg/L of silica by appropriate dilution of silica standard solution I. Store in plastic bottles.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use auto concentration to set the instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the milligrams per liter of silica (as SiO_2) in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose concentrations of silica exceed the working range of the method. Repeat those analyses and multiply by the proper dilution factors.

8. Report

Report silica, dissolved (00955), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
4	3.90	22
5	11.0	9
4	16.5	4

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 140.

Silver, dissolved, atomic absorption spectrometric, chelation-extraction (I–1720–78)

Parameter and Code: Silver, dissolved (μg/L as Ag): 01075

1. Application

This method may be used to analyze waters and brines containing from 1 to 10 μg/L of silver. Higher concentrations must either be reduced by dilution or less scale expansion used.

2. Summary of method

Silver is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the silver absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**328.1 nm.**
Source (hollow-cathode lamp)	**Silver.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate (APDC)* solution, 1 g/100 mL: Dissolve 1.0 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 0.1 g/100 mL: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.

5.3 *Hydrochloric acid,* 0.3*M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.4 *Methyl isobutyl ketone (MIBK).*

5.5 *Silver* standard solution I, 1.00 mL = 100 μg Ag: Crush approx 2 g of $AgNO_3$ crystals and dry to constant mass at 40°C. Dissolve 0.1575 g $AgNO_3$ in demineralized water and dilute to 1,000 mL. Store in amber bottle.

5.6 *Silver* standard solution II, 1.00 mL = 1.00 μg Ag. Dilute 10.0 mL silver standard solution I and 1.0 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This solution is used to prepare working standards at the time of analysis. Store in amber bottle.

5.7 *Sodium hydroxide,* 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 mL.

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.1 Pipet a volume of sample containing less than 1.0 μg Ag (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.2 Prepare a blank of demineralized water with 1.5 mL concentrated HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.3 Add 2 drops bromophenol blue indicator solution.

6.4 Adjust the pH of each by addition of 2.5*M* NaOH by drops until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears. Then add 2.0 mL 0.3*M* HCl in excess. The pH at this point should be approx 2.4 (NOTE 1).

NOTE 1. The pH adjustment in steps 6.3 and 6.4 may be made with a pH meter instead of using indicator.

6.5 Add 2.5 mL APDC solution and shake for 3 min.

6.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.8 While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentrations of the standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of silver in each sample from the digital display or printer output. Dilute those samples whose silver concentrations exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

8. Report

Report silver, dissolved (01075), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 2 to 10 μg/L may be expressed as follows:

$$S_T = 0.172X - 0.182$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of silver, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
5	3.2	14
6	6.4	14
6	10.0	14

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 142.

Silver, total recoverable, atomic absorption spectrometric, chelation-extraction (I–3720–78)

Parameter and Code: Silver, total recoverable (μg/L as Ag): 01077

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing from 1 to 10 μg/L of silver. Samples containing higher concentrations of silver must either be diluted or less scale expansion used.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

Silver is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the silver absorption.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**328.1 nm.**
Source (hollow-cathode lamp)	**Silver.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution, 1 g/100 mL: Dissolve 1.0 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Bromophenol blue indicator* solution, 0.1 g/100 mL: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.

5.3 *Hydrochloric acid, 0.3M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.4 *Methyl isobutyl ketone* (MIBK).

5.5 *Silver* standard solution I, 1.00 mL = 100 μg Ag: Crush approx 2 g of $AgNO_3$ crystals and dry to constant mass at 40°C. Dissolve 0.1575 g $AgNO_3$ in demineralized water and dilute to 1,000 mL. Store in amber bottle.

5.6 *Silver* standard solution II, 1.00 mL = 1.00 μg Ag. Dilute 10.0 mL silver standard solution I and 1.0 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This solution is used to prepare working standards at the time of analysis. Store in amber bottle.

5.7 *Sodium hydroxide*, 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 mL.

6. Procedure

Clean all glassware used in this determination with warm, dilute nitric acid (1 + 9) and rinse with demineralized water immediately before use.

6.1 Pipet a volume of prepared sample solution (Method I–3485) containing less than 1.0 μg Ag (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.2 Prepare a blank of demineralized water with 1.5 mL concentrated HNO_3 per liter demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.3 Add 2 drops bromophenol blue indicator solution.

6.4 Adjust the pH of each by addition of 2.5*M* NaOH by drops until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears. Then add 2.0 mL 0.3*M* HCl in excess. The pH at this point should be approx 2.3 (NOTE 1).

NOTE 1. The pH adjustment in steps 6.3 and 6.4 may be made with a pH meter instead of using indicator.

6.5 Add 2.5 mL APDC solution and shake for 3 min.

6.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.8 While aspirating the ketone layer of the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentrations of the standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of silver in each sample from the digital display or printer output. Dilute those samples whose silver concentrations exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

8. Report

Report silver, total recoverable (01077), concentrations as follows: less than 10 μg/L, nearest micrograms per liter; 10 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method will be greater than 14 percent within the analytical range.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 142.

Sodium, dissolved, atomic absorption spectrometric, direct (I–1735–78)

Parameter and Code: Sodium, dissolved (mg/L as Na): 00930

1. Application

This method may be used to analyze samples of water and brines containing at least 0.1 mg/L of sodium. If the sodium concentration exceeds 80 mg/L, the sample solution must first be diluted. The method is very sensitive and can be extended to much lower sodium concentrations.

2. Summary of method

2.1 Sodium is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment of the sample (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Visible.
Wavelength	588.8 nm.
Source (hollow-cathode lamp).	Sodium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The 50-mm (2-in.) flathead single slot burner rotated 90° allows a working range of 0.1 to 80 mg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Sodium* standard solution I, 1.00 mL = 1.00 mg Na: Dissolve 2.542 g NaCl in demineralized water and dilute to 1,000 mL.

5.2 *Sodium* standard working solutions: Prepare a series of at least six standard solutions containing from 0 to 80 mg/L of sodium by appropriate dilutions of sodium standard solution I. The preparation of an intermediate standard solution is desirable when preparing working solutions of extreme dilution.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the milligrams per liter of sodium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose sodium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report sodium, dissolved (00930), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 3 to 80 mg/L may be expressed as follows:

$$S_T = 0.039X + 0.448$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of sodium, milligrams per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (µg/L)*	*Relative deviation (percent)*
26	3.44	9
19	43.7	4
23	78.8	4

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 143.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 38–41.

Sodium, recoverable from bottom material, atomic absorption spectrometric, direct (I–5735–78)

Parameter and Code: Sodium, recoverable from bottom material, dry wt (mg/kg as Na): 00934

1. Application

1.1 This method may be used to analyze samples of bottom material containing at least 10 mg/kg of sodium. If the sodium concentration of the prepared sample solution (Method I–5485) exceeds 80 mg/L, the sample solution must first be diluted. The method is very sensitive and can be extended to much lower sodium concentrations.

1.2 Bottom material must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

2.1 Sodium is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–5485) into an air-acetylene flame (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

None of the substances commonly occurring in natural water interfere with this method.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Visible.**
Wavelength	**588.8 nm.**
Source (hollow-cathode lamp)	**Sodium.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

4.3 The 50-mm (2-in.) flathead single slot burner rotated 90° allows a working range of 0.1 to 80 mg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Sodium* standard solution I, 1.00 mL = 1.00 mg Na: Dissolve 2.542 g NaCl in demineralized water and dilute to 1,000 mL.

5.2 *Sodium* standard working solutions: Prepare a series of at least six standard solutions containing from 0 to 80 mg/L of sodium by appropriate dilutions of sodium standard solution I. The preparation of an intermediate standard solution is desirable when preparing working solutions of extreme dilution.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the milligrams per liter of sodium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose sodium concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine milligrams per kilogram of sodium in bottom material samples, first determine the milligrams per liter of sodium as in 7.1, then

$$\text{Na (mg/kg)} = \frac{\text{mg/L Na} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report sodium, recoverable from bottom material (00934), concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 9 percent in the lower portion of the analytical range and greater than 4 percent in the upper portion of the analytical range.

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 38–41.

Sodium, total recoverable, atomic absorption spectrometric, direct (I–3735–78)

Parameter and Code: Sodium, total recoverable (mg/L as Na): none assigned

1. Application

1.1 This method may be used to analyze samples of water-suspended sediment mixtures containing at least 0.1 mg/L of sodium. If the sodium concentration exceeds 80 mg/L, the sample solution must first be diluted. The method is very sensitive and can be extended to much lower sodium concentrations.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

2.1 Sodium is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–3485) into an air-acetylene flame (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Visible.
Wavelength	588.8 nm.
Source (hollow-cathode lamp).	Sodium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The 50-mm (2-in.) flathead single slot burner rotated 90° allows a working range of 0.1 to 80 mg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Sodium* standard solution I, 1.00 mL = 1.00 mg Na: Dissolve 2.542 g NaCl in demineralized water and dilute to 1,000 mL.

5.2 *Sodium* standard working solutions: Prepare a series of at least six standard solutions containing from 0 to 80 mg/L sodium by appropiate dilutions of sodium standard solution I. The preparation of an intermediate standard solution is desirable when preparing working solutions of extreme dilution.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the milligrams per liter of sodium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose sodium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report sodium, total recoverable, concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 9 percent at 3.44 mg/L and greater than 4 percent at 78.8 mg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 143.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 38–41.

Sodium, total recoverable, atomic absorption spectrometric, direct-EPA (I–3736–78)

Parameter and Code: Sodium, total recoverable (mg/L as Na): 00929

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 0.1 mg/L of sodium. If the sodium concentration exceeds 80 mg/L, the sample solution must first be diluted. The method is very sensitive and can be extended to much lower sodium concentrations.

1.2 For ambient waters, analysis may be made on an aliquot of the acidified water-suspended sediment sample.

1.3 For all other waters, including domestic and industrial effluents, the atomic absorption procedure must be preceded by a digestion-solubilization as specified below. In cases where the analyst is uncertain of the type of sample, this procedure must be followed.

2. Summary of method

2.1 Sodium is determined by atomic absorption spectrometry by direct aspiration of the filtered or digested and filtered sample into an air-acetylene flame (Fishman and Downs, 1966).

2.2 Effluent samples must undergo a preliminary nitric acid digestion followed by a hydrochloric acid solubilization.

2.3 This atomic absorption procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

None of the substances commonly occurring in natural water interfere with this method.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Visible.**
Wavelength	**588.8 nm.**
Source (hollow-cathode lamp)	**Sodium.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

4.3 The 50-mm (2-in.) flathead single slot burner rotated 90° allows a range of 0.0 to 80 mg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Hydrochloric acid 6M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.2 *Hydrochloric acid*, *0.3M*: Dilute 25 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.3 *Nitric acid*, concentrated HNO_3 (sp gr 1.41).

5.4 *Sodium* standard solution I, 1.00 mL = 1.00 mg Na: Dissolve 2.542 g NaCl in demineralized water and dilute to 1,000 mL.

5.5 *Sodium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 80 mg/L sodium by appropriate dilutions of sodium standard solution I. The preparation of an intermediate standard solution is desirable when preparing working solutions of extreme dilution.

6. Procedure

When analyzing samples of ambient waters, begin the analysis at step 6.8.

6.1 Transfer the entire sample to a beaker.

6.2 Rinse the sample bottle with 3 mL concentrated HNO_3 for each 100 mL of sample and add to the beaker. Prepare a blank using 3 mL concentrated HNO_3 per 100 mL demineralized water.

6.3 Evaporate samples and blank to dryness on a hot plate, making sure the samples do not boil.

6.4 Cool and add an additional 3 mL concentrated HNO_3 to the beaker. Cover with a watch glass, return to the hot plate and gently reflux the samples.

6.5 Continue heating, adding additional acid as necessary, until the digestion is complete (indicated by a light colored residue). Evaporate just to dryness.

6.6 Add 6 mL 6*M* HCl solution per 100 mL original sample and warm the beaker to dissolve the residue.

6.7 Wash the watch glass and beaker with demineralized water and filter the sample (Whatman No. 41 or equivalent), rinsing the filter with hot 0.3*M* HCl. Dilute to the original volume with demineralized water.

6.8 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the milligrams per liter of sodium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose sodium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report sodium, total recoverable (00929), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 9 percent at 3.44 mg/L and greater than 4 percent at 78.8 mg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 143.

Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 82–83, 147–148.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 38–41.

Strontium, dissolved, atomic absorption spectrometric, direct (I–1800–78)

Parameter and Code: Strontium, dissolved (μg/L as Sr): 01080

1. Application

1.1 This method may be used to analyze waters and brines containing more than 10 μg/L of strontium. Samples whose strontium concentrations exceed 5,000 μg/L must first be diluted.

1.2 Samples containing more than 2,500 mg/L of total solutes must first be diluted. If the strontium concentration in the diluted sample is below detection, the undiluted sample may be analyzed by the standard-addition method.

2. Summary of method

2.1 Strontium is determined by atomic absorption spectrometry. Lanthanum chloride and excess potassium chloride are added to mask interferences and control ionization of strontium in the flame (Fishman and Downs, 1966).

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer. (See Metals, I–2470.)

3. Interferences

3.1 Sodium and potassium decrease the strontium ionization in the flame. To control the ionization, 1,000 mg/L of potassium are added to both standards and samples.

3.2 Aluminum, phosphate, and silica interfere but are masked by the addition of lanthanum.

3.3 Nitrate interferes, but in the presence of lanthanum chloride-potassium chloride solution at least 2,000 mg/L can be tolerated. The addition of nitric acid in the field to preserve the sample causes no problem in the following procedure.

3.4 Low strontium values result even in the presence of potassium and lanthanum if the dissolved solids concentration exceeds 2,500 mg/L. For this reason brines and highly mineralized waters must either be diluted or analyzed by the standard-addition method. When using standard addition, the dissolved solids content of the samples must be reduced to less than 20,000 mg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Visible.**
Wavelength	**460.7 nm.**
Source (hollow-cathode lamp).	**Strontium.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Slightly reducing.**

4.3 The 100-mm (4-in.) single slot burner allows a working range of 10 to 5,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Lanthanum chloride-potassium chloride* solution: Dissolve 117.3 g La_2O_3 in a minimum amount of dilute HCl. Add 19.1 g KCl, and dilute to 1 L with demineralized water.

5.2 *Strontium* standard solution I, 1.00 mL = 100 μg Sr: Dissolve 0.1684 g $SrCO_3$ in a minimum amount of dilute HCl, and dilute to 1,000 mL.

5.3 *Strontium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 5,000 μg/L of Sr by appropriate dilutions of strontium standard solution I. Add 1.0 mL of $LaCl_3$–KCl solution to each 10 mL of the working standards prepared. For example, to 500 mL of a working standard, add 50 mL $LaCl_3$–KCl solution.

6. Procedure

6.1 Add 1.0 mL $LaCl_3$–KCl solution to 10.0 mL of prepared sample solution (Method I–3485).

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of strontium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose strontium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report strontium, dissolved (01080), concentrations as follows: less than 100 µg/L, nearest 10 µg/L; 100 µg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 82 to 1,400 µg/L may be expressed as follows:

$$S_T = 0.104X + 15.4$$

where

S_T = overall precision, micrograms per liter, and

X = concentration strontium, micrograms per liter.

9.2 The precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (µg/L)*	*Relative deviation (percent)*
17	82	34
8	1,400	9

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 150.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 41.

Strontium, recoverable from bottom material, atomic absorption spectrometric direct (I–5800–78)

Parameter and Code: Strontium, recoverable from bottom material, dry wt (μg/g as Sr): 01083

1. Application

1.1 This method may be used to analyze bottom material containing at least 1.0 μg/g of strontium. If the prepared sample solution (Method I–5485) contains more than 5,000 μg/L of strontium, it must first be diluted.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

1.3 Prepared sample solutions (Method I–5485) containing more than 2,500 mg/L total solutes must first be diluted. If the strontium concentration in the diluted sample is below detection, the undiluted sample may be analyzed by the standard-addition method.

2. Summary of method

2.1 Strontium is determined by atomic absorption spectrometry. Lanthanum chloride and excess potassium chloride are added to mask interferences and control ionization of strontium in the flame (Fishman and Downs, 1966).

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 Both sodium and potassium decrease strontium ionization in the flame. To control the ionization, 1,000 mg/L of potassium is added to both standards and samples.

3.2 Aluminum, phosphate, and silica interfere but are masked by the addition of lanthanum.

3.3 Nitrate interferes, but in the presence of lanthanum chloride-potassium chloride solution at least 2,000 mg/L can be tolerated. The addition of nitric acid to the sample as a preservative at the time of collection causes no problem in the following procedure.

3.4 Low strontium values result, even in the presence of potassium and lanthanum, if the dissolved solids concentration of the prepared sample solution (Method I–5485) exceeds 2,500 mg/L. Such samples must be either diluted or analyzed by the standard-addition method. When using standard addition, the dissolved solids content of the samples must not exceed 20,000 mg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameter:

Grating	Visible.
Wavelength	460.7 nm.
Source (hollow-cathode lamp).	Strontium.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Slightly reducing.

4.3 The 100-mm (4-in.) single slot burner allows a working range of 10 to 5,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Lanthanum chloride-potassium chloride* solution: Dissolve 117.3 g La_2O_3 in a minimum amount of dilute HCl. Add 19.1 g KCl, and dilute to 1,000 mL with demineralized water.

5.2 *Strontium* standard solution I, 1.00 mL = 0.10 mg Sr: Dissolve 0.1684 g $SrCO_3$ in a minimum amount of dilute HCl and dilute to 1,000 mL.

5.3 *Strontium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 5,000 μg/L of Sr by appropriate dilutions of strontium standard solution I. Add 1.0 mL of $LaCl_3$–KCl solution to each 10 mL of the working standards prepared. For example, to 500 mL of a working standard, add 50 mL $LaCl_3$–KCl solution.

6. Procedure

6.1 Add 1.0 mL $LaCl_3$–KCl solution to 10.0 mL of sample solution prepared as directed in Method I–5485.

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of strontium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose strontium concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per gram of strontium in bottom material samples, first determine the micrograms per liter of strontium as in 7.1, then

$$\text{Sr } (\mu g/g) = \frac{\mu g/L \text{ Sr} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report strontium, recoverable from bottom material (01083), concentrations as follows: less than 10 μg/g, nearest microgram per gram; 10 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 34 percent in the lower portion of the analytical range and greater than 9 percent in the upper portion of the analytical range.

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 41.

Strontium, total recoverable, atomic absorption spectrometric, direct (I–3800–78)

Parameter and Code: Strontium, total recoverable (μg/L as Sr):01082

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing more than 10 μg/L of strontium. Samples whose strontium concentrations exceed 5,000 μg/L must first be diluted.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion–solubilization by Method I–3485 before analysis by this procedure.

1.3 Samples containing more than 2,500 mg/L of total solutes must first be diluted. If the strontium concentration in the diluted sample is below detection, the undiluted sample may be analyzed by the standard-addition method.

2. Summary of method

2.1 Strontium is determined by atomic absorption spectrometry. Lanthanum chloride and excess potassium chloride are added to mask interferences and control ionization of strontium in the flame (Fishman and Downs, 1966).

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and a strip-chart recorder, or a printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 Sodium and potassium decrease the strontium ionization in the flame. To control the ionization, 1,000 mg/L of potassium are added to both standards and samples.

3.2 Aluminum, phosphate and silica interfere but are masked by the addition of lanthanum.

3.3 Nitrate interferes, but in the presence of lanthanum chloride-potassium chloride solution at least 2,000 mg/L can be tolerated. The addition of nitric acid in the field to preserve the sample causes no problem in the following procedure.

3.4 Low strontium values result even in the presence of potassium and lanthanum if the dissolved solids concentration exceeds 2,500 mg/L. For this reason brines and highly mineralized waters must be either diluted or analyzed by the standard-addition method. When using standard addition, the dissolved solids content of the samples must be reduced to less than 20,000 mg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Visible.**
Wavelength	**460.7 nm.**
Source (hollow-cathode lamp).	**Strontium.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Slightly reducing.**

4.3 The 100-mm (4-in.) single slot burner allows a working range of 10 to 5,000 μg/L. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Lanthanum chloride—potassium chloride* solution: Dissolve 117.3 g La_2O_3 in a minimum amount of dilute HCl. Add 19.1 g KCl, and dilute to 1,000 mL with demineralized water.

5.2 *Strontium* standard solution I, 1.00 mL = 100μg Sr: Dissolve 0.1684 g $SrCO_3$ in a minimum amount of dilute HCl, and dilute to 1,000 mL.

5.3 *Strontium* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 5,000 μg/L of Sr by appropriate dilutions of strontium standard solution I. Add 1.0 mL of $LaCl_3$–KCl solution to each 10 mL of the working standards prepared. For example, to 500 mL of a working standard, add 50 mL $LaCl_3$–KCl solution.

6. Procedure

6.1 Add 1.0 mL $LaCl_3$–KCl solution to 10.0 mL of prepared sample solution (Method I–3485).

6.2 While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of strontium in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose strontium concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report strontium, total recoverable (01082), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 34 percent at 82 μg/L and greater than 9 percent at 1,400 μg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 150.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 41.

Tin, dissolved, atomic absorption spectrometric, direct (I–1850–78)

Parameter and Code: Tin, dissolved (μg/L as Sn): 01100

1. Application

This method may be used to analyze water containing at least 100 μg/L of tin. Up to 10,000 μg/L can be determined by this method.

2. Summary of method

Tin is determined by atomic absorption spectrometry by direct aspiration of the sample into an air–acetylene flame without preconcentration or pretreatment of the sample.

3. Interferences

3.1 Samples must be preserved with hydrochloric acid (1 mL of concentrated hydrochloric acid per 100 mL of sample).

3.2 There are no known interferences.

4. Apparatus

4.1 *Atomic absorption spectrometer* with strip-chart recorder.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	224.6 nm.
Source (hollow-cathode lamp or electrodeless discharge lamp).	Tin.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Reducing.

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Tin* standard solution I, 1.00 mL = 1,000 μg Sn: Dissolve 1,000 g tin metal in 100 mL concentrated HCl and dilute to 1,000 mL with demineralized water.

5.2 *Tin* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 10,000 μg/L tin by appropriate dilution of tin standard solution I. These standards must contain 10 mL of concentrated HCl (sp gr 1.19) in every 100 mL of standard working solution. Prepare fresh daily.

6. Procedure

6.1 While aspirating the blank, set the chart recorder to zero concentration (NOTE 1). Aspirate a series of at least six standards. Calibrate the instrument in this manner each time a set of samples is analyzed and check for stability at reasonable intervals.

NOTE 1. Although a digital readout may be used, the high level of instrument noise makes using a chart recorder preferable.

6.2 Aspirate a portion of each sample and record its absorbance on the strip-chart recorder.

7. Calculations

Determine the micrograms per liter of tin in each sample from a plot of absorbances of standards. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report tin, dissolved (01100), concentrations as follows: less than 1,000 μg/L, nearest 100 μg/L; 1,000 μg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

Reference

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 65.

Tin, total recoverable, atomic absorption spectrometric, direct (I–3850–78)

Parameter and Code: Tin, total recoverable (μg/L as Sn):01102

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 100 μg/L of tin. Up to 10,000 μg/L can be determined by this method.

1.2 Samples must undergo a preliminary digestion by Method I–3485 before analysis by this procedure.

2. Summary of method

Tin is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–3485) into an air–acetylene flame without further preconcentration or pretreatment of the sample.

3. Interferences

3.1 Samples must be preserved with hydrochloric acid (1 mL of concentrated hydrochloric acid per 100 mL of sample).

3.2 There are no known interferences.

4. Apparatus

4.1 *Atomic absorption spectrometer* with strip-chart recorder.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	224.6 nm.
Source (hollow-cathode lamp or electrodeless discharge lamp).	Tin.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Reducing.

4.3 Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Tin* standard solution I, 1.00 mL = 1,000 μg Sn: Dissolve 1,000 g tin metal in 100 mL concentrated HCl and dilute to 1,000 mL with demineralized water.

5.2 *Tin* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 10,000 μg/L tin by appropriate dilution of tin standard solution I. These standards must contain 10 mL concentrated HCl (sp gr 1.19) in every 100 mL of standard working solution. Prepare fresh daily.

6. Procedure

6.1 While aspirating the blank, set the chart recorder to zero concentration (NOTE 1). Then aspirate a series of at least six standards. Calibrate the instrument in this manner each time a set of samples is analyzed and check for stability at reasonable intervals.

NOTE 1. Although a digital readout may be used, the high level of instrument noise makes using a chart recorder preferable.

6.2 Aspirate a portion of each prepared sample solution (Method I–3485) and record its absorbance on the strip-chart recorder.

7. Calculations

Determine the micrograms per liter of tin in each sample from a plot of absorbances of standards. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report tin, total recoverable (01102), concentrations as follows: less than 1,000 μg/L, nearest

100 μg/L; 1,000 μg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

Reference

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 65.

Zinc, dissolved, atomic absorption spectrometric, direct (I–1900–78)

Parameter and Code: Zinc, dissolved (μg/L as Zn): 01090

1. Application

This method may be used to analyze waters containing at least 10 μg of zinc. Sample solutions containing more than 500 μg/L must either be diluted or less scale expansion must be used.

2. Summary of method

2.1 Zinc is determined by atomic absorption spectrometry by direct aspiration of the sample into an air–acetylene flame without preconcentration or pretreatment of the sample.

2.2 The procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 Magnesium at concentrations greater than 100 mg/L interferes unless other cations, such as sodium, are present in the sample.

3.2 Individual concentrations of sodium, potassium, sulfate, and chloride (9,000 mg/L each), calcium (4,500 mg/L), nitrate (2,000 mg/L), iron ($4 \times 10^6 \mu$g/L), and cadmium, nickel, copper, lead, cobalt, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

3.3 Samples containing 100 mg/L of silica cause no interference; however, zinc recovery is approximately 10 percent low in samples containing 200 mg/L of silica.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	213.8 nm.
Source (hollow-cathode lamp)	Zinc.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The 50-mm (2-in.) and 100-mm (4-in.) flathead single slot burners allow a working range from 10 to 2,000 μg/L zinc. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Zinc* standard solution I, 1.00 mL = 100 μg Zn: Dissolve 0.100 g reagent grade zinc (30-mesh) in a slight excess of HCl, and dilute to 1,000 mL with demineralized water.

5.2 *Zinc* standard solution II, 1.00 mL = 1.0 μg Zn: Dilute 10.0 mL zinc standard solution I to 1,000 mL with demineralized water containing 1 mL concentrated HNO_3 (sp gr 1.41).

5.3 *Zinc* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 200 μg/L of zinc by appropriate dilutions of zinc standard solution II.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set instrument digital display to read the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of zinc in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose zinc concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report zinc, dissolved (01090), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 35 to 450 μg/L may be expressed as follows:

$$S_T = 0.034X + 16.6$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of zinc, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
35	41	35
23	253	14
27	437	7

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water- Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 159.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540–C, p. 43.

Zinc, recoverable from bottom material, atomic absorption spectrometric, direct (I–5900–78)

Parameter and Code: Zinc, recoverable from bottom material, dry wt (μg/g as Zn): 01093

1. Application

1.1 This method may be used to analyze bottom material containing at least 1.0 μg/g of zinc. Prepared sample solutions (Method I–5485) containing more than 500 μg/L of zinc must either be diluted or less scale expansion must be used.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

2.1 Zinc is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–5485) into an air-acetylene flame.

2.2 The procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 Magnesium concentrations greater than 100 mg/L interfere unless other cations, such as sodium, are present in the sample.

3.2 Individual concentrations of sodium, potassium, sulfate, chloride (9,000 mg/L each), calcium (4,500 mg/L), nitrate (2,000 mg/L), iron (4×10^6 μg/L), and cadmium, nickel, copper, lead, cobalt, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

3.3 Samples containing 100 mg/L of silica cause no interference; however, zinc recovery is approx 10 percent low in samples containing 200 mg/L of silica.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	Ultraviolet.
Wavelength	213.8 nm.
Source (hollow-cathode lamp)	Zinc.
Oxidant	Air.
Fuel	Acetylene.
Type of flame	Oxidizing.

4.3 The 50-mm (2-in.) and 100-mm (4-in.) flathead single slot burners allow a working range from 10 to 2,000 μg/L zinc. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Zinc* standard solution I, 1.00 mL = 100 μg Zn: Dissolve 0.100 g reagent grade zinc (30-mesh) in a slight excess of HCl, and dilute to 1,000 mL with demineralized water.

5.2 *Zinc* standard solution II, 1.00 mL = 1.0 μg Zn: Dilute 10.0 zinc standard solution I to 1,000 mL with demineralized water containing 1 mL concentrated HNO_3.

5.3 *Zinc* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 200 μg/L of zinc by appropriate dilutions of zinc standard solution II.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of zinc in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose zinc concentrations exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per gram of zinc in bottom material samples, first determine the micrograms per liter of zinc as in 7.1, then

$$\text{Zn } (\mu g/g) = \frac{\mu g/L \text{ Zn} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report zinc, recoverable from bottom material (01093), concentrations as follows: less than 10 $\mu g/g$, nearest microgram per gram; 10 $\mu g/g$ and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 55 percent in the lower portion of the analytical range and greater than 7 percent in the upper portion of the analytical range.

Zinc, total recoverable, atomic absorption spectrometric, direct (I–3900–78)

Parameter and Code: Zinc, total recoverable (μg/L as Zn):01092

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 10 μg/L of zinc. Sample solutions containing more than 500 μg/L must either be diluted or less scale expansion must be used.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

2.1 Zinc is determined by atomic absorption spectrometry by direct aspiration of the prepared sample solution (Method I–3485) into an air-acetylene flame.

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer, or both. (See Metals, I–2470.)

3. Interferences

3.1 Magnesium at concentrations greater than 100 mg/L interferes unless other cations, such as sodium, are present in the sample.

3.2 Individual concentrations of sodium, potassium, sulfate, chloride (9,000 mg/L each), calcium (4,500 mg/L), nitrate (2,000 mg/L), iron ($4 \times 10^6 \mu$g/L), and cadmium, nickel, copper, lead, cobalt, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

3.3 Samples containing 100 mg/L of silica cause no interference; however, zinc recovery is approx 10 percent low in samples containing 200 mg/L of silica.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero, and automatic concentration control.

4.2 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating	**Ultraviolet.**
Wavelength	**213.8 nm.**
Source (hollow-cathode lamp)	**Zinc.**
Oxidant	**Air.**
Fuel	**Acetylene.**
Type of flame	**Oxidizing.**

4.3 The 50-mm (2-in.) and 100-mm (4-in.) flathead single slot burners allow a working range from 10 to 2,000 μg/L zinc. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Zinc* standard solution I, 1.00 mL = 100 μg Zn: Dissolve 0.100 g reagent grade zinc (30-mesh) in a slight excess of concentrated HCl, and dilute to 1,000 mL with demineralized water.

5.2 *Zinc* standard solution II, 1.00 mL = 1.0 μg Zn: Dilute 10.0 mL zinc standard solution I to 1,000 mL with demineralized water containing 1 mL concentrated HNO_3 (sp gr 1.41).

5.3 *Zinc* standard working solutions: Prepare a series of at least six standard working solutions containing from 0 to 200 μg/L of zinc by appropriate dilutions of zinc standard solution II.

6. Procedure

While aspirating the blank use auto zero to set instrument digital display to read zero concentration. While aspirating standards use the auto concentration to set the instrument digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check for stability at reasonable intervals.

7. Calculations

Determine the micrograms per liter of zinc in each sample from the digital display or printer output while aspirating each sample. Dilute those samples whose zinc concentrations exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report zinc, total recoverable (01092), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, to two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 35 percent at 41 μg/L and greater than 7 percent at 437 μg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 159.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: United States Geological Survey Water-Supply Paper 1540–C, p. 43.

CALCULATION METHODS

Carbon dioxide, dissolved, calculation (I–1160–78)

Parameter and Code: Carbon dioxide, dissolved (mg/L as CO_2):00405

1. Application

This method may be applied to any sample for which measured values of pH and bicarbonate ion are available.

2. Summary of method

2.1 Carbon dioxide concentration is calculated from measured values of pH and bicarbonate ion. The pH is determined instrumentally (Method I–1586), and the bicarbonate ion by electrometric titration.

2.2 Gaseous carbon dioxide hydrolyzes slightly

$$CO_2\,(aq) + H_2O \rightarrow H_2CO_3 \qquad (1)$$

for which the hydrolysis constant expression is

$$K_{\mathrm{hydr}} = \frac{[H_2\,CO_3]}{[CO_2]} = 2.6 \times 10^{-3}. \qquad (2)$$

The square brackets denote concentrations in moles per liter.

Carbonic acid is a weak acid and dissociates by steps

$$H_2CO_3 \rightleftharpoons H^{+1} + HCO_3^{-1} \qquad (3)$$

$$HCO_3^{-1} \rightleftharpoons H^{+1} + CO_3^{-2}. \qquad (4)$$

Only the two equilibria represented by equations (1) and (3), however, are ordinarily of significance in determining CO_2 concentrations. When the pH of a water is sufficiently high to permit the existence of CO_3^{-2}, the concentration of free CO_2 which can coexist is negligibly small. The CO_2 concentrations can, therefore, be calculated within experimental accuracy from equations (1) and (3) and their corresponding equilibrium-constant expressions as follows:

$$K_{\mathrm{hydr}} = \frac{[H_2\,CO_3]}{[CO_2]} = 2.6 \times 10^{-3} \qquad (5)$$

$$K_1 = \frac{[H^{+1}]\,[HCO_3^{-1}]}{[H_2CO_3]} = 1.7 \times 10^{-4}. \qquad (6)$$

Multiply equations (5) and (6):

$$K_{\mathrm{hydr}}K_1 = \frac{[H^{+1}]\,[HCO_3^{-1}]}{[CO_2]} = 4.4 \times 10^{-7}; \qquad (7)$$

and solving for $[CO_2]$

$$[CO_2] = \frac{[H^{+1}]\,[HCO_3^{-1}]}{4.4 \times 10^{-7}}. \qquad (8)$$

This equation can then be used to determine the CO_2 concentration when $[HCO_3^{-1}]$ and $[H^{+1}]$, or pH, of the sample have been determined. Equation (8) can be rearranged to simplify the calculation, since both CO_2 and bicarbonate $[HCO_3^{-1}]$ concentrations are usually expressed in units of milligrams per liter rather than moles per liter, and hydrogen-ion concentrations normally as pH units:

$$\mathrm{mg}\ CO_2/\mathrm{L} = 1.60 \times 10^{(6.0-\mathrm{pH})} \times \mathrm{mg}\ HCO_3^{-1}/\mathrm{L}. \qquad (9)$$

For convenience in making the calculations, the values of $1.60 \times 10^{(6.0-\mathrm{pH})}$ may be tabulated for a range of pH values (table 4).

2.3 For additional information on the theory

TABLE 4.—Values of $1.60 \times 10^{(6.0-\mathrm{pH})}$

pH	$1.60 \times 10^{(6.0-\mathrm{pH})}$	pH	$1.60 \times 10^{(6.0-\mathrm{pH})}$
6.0	1.60	7.6	0.040
6.2	1.00	7.8	.025
6.4	.633	8.0	.016
6.6	.399	8.2	.010
6.8	.252	8.4	.006
7.0	.160	8.6	.004
7.2	.100	8.8	.003
7.4	.063	9.0	.002

of this method see De Martini (1938), Langelier (1936), Larson and Buswell (1942), and Moore (1939).

3. Interferences

3.1 The values of the constants K_{hydr} and K_1 vary with temperature and with both the concentration and nature of the dissolved solutes. Therefore, the accuracy of the calculation depends on the reliability of values of K_{hydr} and K_1 for a particular sample. For practical purposes and for most samples containing less than 800 mg/L of solutes, a value for ($K_{\mathrm{hydr}} \times K_1$) of 4.54×10^{-7} has been recommended and was used in calculating the constant factor of equation (9).

3.2 Carbon dioxide is easily lost from solution, and precautions must be taken to prevent or minimize such losses when collecting the sample. The pH and bicarbonate must be determined in the field at the time of collection.

7. Calculations

7.1 Calculate mg/L CO_2 as follows:

$$\mathrm{mg/L}\ CO_2 = 1.60 \times 10^{(6.0-\mathrm{pH})} \times \mathrm{mg/L}\ HCO_3^{-1}$$

7.2 The calculated values of the variable $1.60 \times 10^{(6.0-\mathrm{pH})}$ are shown in table 4.

8. Report

Report carbon dioxide, dissolved, calculated (00405), concentrations as follows: less than 10 mg/L, one decimal; from 10 to 99 mg/L, whole numbers; 100 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 68.

De Martini, F. E., 1938, Corrosion and the Langelier calcium carbonate saturation index: American Water Works Association Journal, v. 30, p.85.

Langelier, W. F., 1936, The analytical control of anti-corrosion water treatment: American Water Works Association Journal, v. 28, p. 1500.

Larson, T. E., and Buswell, A. N., 1942, Calcium carbonate saturation and alkalinity interpretations: American Water Works Association Journal, v. 34, p. 1667.

Moore, E. W., 1939, Graphic determination of carbon dioxide and three forms of alkalinity: American Water Works Association Journal, v. 31, p. 51.

Hardness, calculation (I–1340–78)

Parameter and Code: Hardness, dissolved (mg/L as $CaCO_3$): 00900

1. Application

This method may be used to calculate hardness for any sample for which determined values for barium, calcium, strontium, and magnesium are available.

2. Summary of method

Hardness is computed from the individual determinations of the alkaline earths. This is best accomplished by summing the milliequivalents per liter for calcium, magnesium, strontium, and barium. In many cases the contributions of strontium and barium are insignificant compared to those of calcium and magnesium and can be safely ignored.

7. Calculations

Hardness as mg/L $CaCO_3$

$$= \sum \text{me/L} \, (\text{Ca} + \text{Mg} + \text{Ba} + \text{Sr}) \times 50.05.$$

8. Report

Report hardness, dissolved, calculated (00900) concentrations as follows: less than 10 mg/L, whole numbers, 10 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method, but reproducibility should be comparable to the individual determinations.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 97.

Hardness, noncarbonate, calculation (I–1344–78)

Parameter and Code: Hardness, noncarbonate (mg/L as $CaCO_3$):00902

1. Application

This method may be used to compute noncarbonate hardness for any water for which determined values are available for hardness and alkalinity.

2. Summary of method

Noncarbonate hardness is computed from the hardness and alkalinity determinations (Methods I–1340 and I–1030 or I–2030). No negative values are reported. However, "negative noncarbonate hardness" will counteract "positive noncarbonate hardness" in a mixture of two or more waters. Hence, in all calculations of averages concerned with a mixture of waters for which two or more analyses are available, noncarbonate hardness of the resulting mixture must be computed from the average hardness and average alkalinity and not by averaging the noncarbonate hardness of the individual samples.

7. Calculations

Hardness, noncarbonate, as mg/L $CaCO_3$

$$= (\text{me/L hardness} - \text{me/L alkalinity}) \times 50.05.$$

8. Report

Report hardness, noncarbonate, calculated (00902), concentrations as follows: less than 10 mg/L, whole numbers; 10 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method, but reproducibility should be comparable to that of the individual determinations.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 98.

Sodium adsorption ratio, calculation (I-1738-78)

Parameter and Code: Sodium adsorption ratio: 00931

1. Application

This method may be applied to any sample for which measured values for sodium, calcium, and magnesium are available.

2. Summary of method

The sodium adsorption ratio (SAR) is computed from the individual determination of sodium, calcium, and magnesium after conversion of each to milliequivalents per liter (me/L).

7. Calculations

$$\text{SAR} = \frac{\text{me/L Na}}{\sqrt{\dfrac{\text{me/L Ca} + \text{me/L Mg}}{2}}}$$

8. Report

Report sodium adsorption ratio, calculated (00931) as follows: less than 1.0, one decimal; 1.0 and above, whole numbers.

9. Precision

Precision data are not available for this method, but reproducibility should be comparable to the individual determinations.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 143.

Sodium, percent, calculation (I–1740–78)

Parameter and Code: Sodium, percent: 00932

1. Application

This method may be applied to any sample for which measured values for sodium, potassium, calcium, and magnesium are available.

2. Summary of method

Percent sodium is computed from the milliequivalents per liter (me/L) of sodium, potassium, calcium, and magnesium.

7. Calculations

Sodium (percent)

$$= \frac{\text{me/L Na}}{\sum \text{me/L (Na + K + Ca + Mg)}} \times 100.$$

8. Report

Report sodium, percent, calculated (00932), as follows: whole numbers.

9. Precision

Precision data are not available for this method, but reproducibility should be comparable to the individual determinations.

Solids, sum of constituents, dissolved, calculation (I–1751–78)

Parameter and Code: Solids, dissolved (mg/L): 70301

1. Application

The calculation method is applicable only to those analyses that include determinations for all major constituents. Such analyses are considered to be complete for all practical purposes. The chemist can never be certain of the completeness of the analysis, but for most alkaline waters other than brines, the determination of silica, calcium, magnesium, sodium, potassium, alkalinity, sulfate, chloride, and nitrate is sufficient. The wide range of metals possible in acid water precludes assumptions as to the completeness of the analysis.

2. Summary of method

2.1 The concentrations of all determined constituents are converted mathematically into the forms in which they would normally exist in an anhydrous residue. These quantities are then added. If the water is grossly polluted, it is usually necessary to determine the nitrogen components. Concentration of carbonaceous material can be estimated by redissolving the residue on evaporation and treating it with several successive portions of hydrogen peroxide. The difference in weight between the nonoxidized residue and the oxidized residue is an indication of the carbonaceous solids. The estimated carbonaceous solids are not included in the calculated dissolved solids, but are one measure of the differences to be expected between dissolved solids determined by residue on evaporation and by calculation (Howard, 1933).

2.2 The conversion of the constituents in the analysis to the forms in which they would normally exist in an anhydrous residue involves many variables that are not known. Consequently, when summarizing the constituents, all material is arbitrarily assumed to be present in the theoretical anhydrous residue in the same form as reported in the analysis, with the exception of bicarbonate. It is assumed that all bicarbonate in solution will exist as carbonate in the residue:

$$2HCO_3^{-1} \rightarrow CO_3^{-2} + CO_2 + H_2O.$$

Therefore, the bicarbonate in solution is mathematically converted to its equivalent weight as carbonate in the residue.

2.3 The accuracy of the result is dependent on the completeness of the analysis and on the validity of each reported constituent concentration.

7. Calculations

7.1.A If a field bicarbonate determination was made, convert bicarbonate concentration to carbonate concentration as follows:

$$\text{mg/L } CO_3^{-2} = \frac{\text{mg/L } HCO_3^{-1}}{2.03}.$$

7.1.B Alternatively, convert alkalinity concentration reported as mg/L $CaCO_3$ to carbonate concentration:

$$\text{mg/L } CO_3^{-2} = \text{mg/L } CaCO_3 \times 0.60.$$

7.2 Add all determined dissolved constituents reported in the analytical statement. The following constituents must be included: calcium, magnesium, sodium, potassium, alkalinity, chloride, sulfate, and silica.

8. Report

Report solids, dissolved, calculated (70301), concentrations as follows: less than 100 mg/L, whole numbers; 100 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 146.

Howard, C. S., 1933, Determination of total dissolved solids in water analysis: Industrial Engineering Chemistry, Analytical Edition, v. 5, p. 4.

Colorimetry

Instrumental principles

Spectrometry may be regarded as the instrumental measurement of the absorption of radiant energy by a solution at a given wavelength. In order to accomplish this, all spectrometers contain the following essential components:

1. **Source of radiant energy.**—Usually, ordinary tungsten-filament incandescent lamps are used for the visible region; hydrogen or deuterium discharge lamps are usually for the ultraviolet region.
2. **Monochromator.**—A device for isolating a narrow band of radiant energy from the source.
3. **Cells or containers.**—To hold the solution being analyzed.
4. **Receiver or detector.**—A device to receive and measure the radiant energy passed through the solution.

A detailed discussion of these components, including various commercial instruments available, is given by Willard, Merritt, and Dean (1974). This and other standard texts contain excellent presentations of the basic principles governing the transmission and measurement of radiant energy and its absorption by substances in solution. Therefore, no extensive treatment of either theory or instrumentation will be given in this manual.

In the practical application of spectrometric analysis, only two terms need to be considered in detail. These are the fundamental term "transmittance" and the term "absorbance," which is derived from it. Transmittance is defined by the equation

$$T = \frac{I_2}{I_1}$$

where

T = transmittance,
I_1 = radiant energy incident upon the first surface of the sample, and
I_2 = radiant energy leaving the sample.

It should be noted that the transmittance relation is correct only if the reflection and absorption losses at the cell windows are insignificant and identical in sample and solvent cells. These conditions are met in normal applications of ultraviolet and visible-light spectrometry in water analysis.

The second term of importance and the one most generally used is "absorbance," which is defined as the negative logarithm of the transmittance:

$$A = -\log_{10} T = \log_{10} \frac{1}{T}.$$

In the preparation of curves of light-intensity ratio plotted against concentration, it is preferable to use absorbance as the basis of the plot. Under these conditions, a system that conforms to Beer's law gives a straight-line plot, and the commonly used colorimetric systems that do not conform usually show only moderate curvature. Extreme curvature is sometimes a sign that the system is not sufficiently stable for analytical purposes. Semicolloidal suspensions of colored substances often give extreme curvatures. When transmittance data are used for plotting, a curve is always obtained unless semilogarithmic coordinates are used. Modern spectrometers have an absorbance calibration as well as the conventional "percent transmittance," and it is increasingly prevalent practice to use the absorbance scale. The relations between transmittance and absorbance plots for potassium permanganate solutions at three wavelengths are illustrated by Mellon (1950).

Several other terms for light absorption are given in the literature and are still found on the printed scales of some photometers. "Optical density" is often used and it is the same as absorbance.

Sensitivity

In spectrometric determinations in water analysis, it is desirable to attain maximum sensitivity. This provides several advantages besides the obvious one of extending the determination to the lower concentration ranges: The interferences of other ions can be minimized, the effect of natural color and turbidity in the water sample can often be made insignificant, and a small volume of sample can be used.

Sensitivity is a word that is used loosely, and it is important to identify the type of sensitivity under consideration. The detection limit of a method is the smallest concentration that can be detected by the method and depends on both the chemical phase of the determination and the instrumental phase. Generally, the chemical phase provides the major differentiation of the constituent sought against the "background," although the instrument used to analyze and measure the system also contributes. To improve sensitivity requires an improvement of the absorbance of the constituent sought relative to the background absorbance, of interfering ions, natural color, and turbidity.

Interferences

In spectrometric determinations, interferences result generally from the presence in the sample of dissolved or suspended foreign material that either absorbs radiant energy or reacts with the color reagent to form a complex that absorbs radiant energy or that scatters the light. In either case, the absorbance of the sample will be increased. Where the interference results from the formation of an absorbing complex by ions in solution, dilution of the sample may eliminate the interference if the sensitivity of the color reagent for the element sought is sufficiently greater than for the interfering ions. Where this is not the case, other means must be taken to increase the selectivity of the method. Among such means might be listed: (l) pH adjustment: where pH is an important factor in complex ion formation, its adjustment may favor the formation of the complex of the element desired instead of the interfering ions. (2) Masking: compounds such as EDTA (ethylenediamine tetraacetic acid) may often be added to the sample to form a stable complex with interfering ions, thus preventing their reaction with the color reagent. (3) Solvent extraction: preferential solubility of some ions or ion complexes in organic solvents often permits the removal of interfering ions.

Another common source of interference in spectrometry is the use of color reagents that absorb at the wavelength at which the complex of the element desired is measured. Such interference may usually be reduced or eliminated by the use of a reagent blank.

In a large number of samples a significant source of interference results from the presence of natural color. The natural color in many water samples shows an appreciable absorbance at the wavelengths used in a number of determinations, and this effect requires either compensation or elimination. In some cases it is possible to select a spectrometric reagent of such high sensitivity that the absorbance of the constituent sought will exceed the absorbance of the natural color by a very large factor. If this factor is as high as 50 for a particular determination, the error introduced by the natural color will be only 2 percent, and in routine work no compensation would be required. Several of the spectrometric determinations described in this manual, notably the chromate and phosphate determinations, will normally give an absorbance reading considerably higher than 50 times the absorbance of the natural coloring matter in the water sample. In other procedures, such as the aluminum determination, the absorbance of the color may be as high as that contributed by the analytical system. Thus, correction for color and turbidity is very rarely required for chromate and phosphate, but correction is frequently required for aluminum. A knowledge of the relative sensitivity for the constituent sought as compared to the natural color in the sample is necessary to the application of spectrometric methods. Where this relative sensitivity is not known, or when there is any doubt as to the effect of color on the absorbance of the element sought, it is desirable to remove or compensate for the color present by one of the following methods:

1. Subtraction of natural-color absorbance

Determine absorbance of the test sample, A_{ts}, against the blank specified for the procedure. Determine absorbance of the natural-color sample, A_{ncs}, against distilled water, using the same spectrometric conditions as for the test sample. The difference is the corrected absorbance, A_s. Use A_s to obtain concentration values.

The test sample is the water sample with color developed as outlined in the analytical procedure.

The natural-color sample can be prepared in two ways. The most general method is to take the same volume of sample water as was used for the test sample. Treat it exactly as the test sample with one exception: do not add the indicator reagent. Instead, add an equal volume of indicator solvent, usually dilution water. The second method uses color- and turbidity-correction solutions, which are simply shortcuts of the general procedure above. These solutions combine the significant reagents into one solution, so that a single addition of reagent suffices. The color-correction solutions are not applicable in every case. The full procedure is usually a little more reliable.

The subtraction method is the most generally applicable correction method. It can be applied to turbidity corrections as well as to natural-color corrections. The method fails where the indicator reagent reacts with or affects the natural color or turbidity in the water sample or where the effects of the other reagent on the test sample and natural-color sample are not essentially identical. The latter qualification relates more to turbidity than color, and filtration of excessively turbid samples may be required.

2. Direct compensation

All reagents except the indicator are added to the sample. The sample is placed in the spectrometer and the absorbance is set at zero by adjusting the slit width. This step eliminates the natural absorbance of the water. The indicator reagent is then added. The color is developed and the correct absorbance is read directly from the scale. This procedure is not of general utility and can be applied only under special conditions. One requirement is that the absorbance curve should have only a shallow slope in the operating region.

3. Bleaching

If the indicator reagent reacts with the material that gives the sample its natural color, the resulting color must be removed by bleaching. One example of such a reaction is the periodate determination of manganese. Periodate oxidizes manganese to permanganate, developing the familiar pink color. Periodate also partially oxidizes the organic coloring matter in the water and changes the natural color. Therefore, compensation by means of a natural-color sample will not be correct. In the permanganate test the procedure is to develop the color in the test sample and determine the absorbance. A few crystals of sodium nitrite are then added to the sample. This destroys the permanganate color immediately but does not affect the organic matter. The color contribution of the organic matter can now be directly measured. It is subtracted from the absorbance of the test sample to obtain the corrected absorbance.

4. Removal of color material

The color material is sometimes removed with conventional activated-carbon or alumina treatments. The method is mentioned only to cite its limitations. Gross contamination from impurities in activated carbon is an ever-present possibility. Furthermore, the carbon will absorb trace metals and can completely change the content of trace metals in the sample. Alumina is less likely to be a source of contamination, but it will take up trace metals just as avidly as activated carbon. These two methods cannot be used for sensitive analyses. The acceptable procedures for removing color are chemical oxidations with nitric acid, hydrogen peroxide, and similar agents. Care must be taken to remove all remaining traces of hydrogen peroxide to prevent its reacting with the indicator reagent.

Since color removal through the use of activated carbon or alumina will alter the trace metal content of the sample, it is recommended that when trace metal analyses are required on samples with natural water color, atomic absorption spectrometric procedures should be used whenever possible.

Since most photometric procedures are carried out on filtered samples, interference due to turbidity is not of major concern. When unfiltered samples are analyzed by spectrometric procedures, however, the presence of turbidity may increase absorbance appreciably because of light absorption and scattering. Although the previously described procedure for color compensation may often be used to correct for small amounts of turbidity, its removal is usually desirable. To date only one generally acceptable method for removing such turbidity has been found; this is filtration through a 0.45 μm membrane filter. Centrifuging is often useful, but it is less efficient than membrane filters for fine particles. Good results can sometimes be obtained by filtering the sample through a fine filter paper, such as Whatman No. 42, that will remove a large part of the turbidity. The residual turbidity in the sample is then corrected for by the same methods as for color.

Automated analyses

The popularity of automated, continuous-flow analyzers has increased greatly in recent years because of their ability to analyze samples at a much faster rate than is possible using manual procedures. Consequently, this instrumentation now plays an important role in U.S. Geological Survey and many other water-quality laboratories. The most commonly used automated system is composed of individual sampler, proportioning pump, cartridge manifold, filter-photometer, recorder, and printer modules.

Solutions are introduced into the analytical system by the sampler. The sampler solutions are poured into small cups that are placed in a rotating turntable. The turntable advances at preset times and the sample solution is aspirated from each cup. A wash solution is aspirated for a timed interval between samples. It is necessary to carefully control both the sampling rate and the sample-to-wash ratio in order to accurately analyze samples with a minimum amount of sample carryover and, at the same time, maintain a satisfactory rate of analysis.

The proportioning pump works on a peristaltic principle and meters samples, reagents, and air bubbles into the flow system through various sizes of flow-calibrated pump tubing. The air bubbles are introduced to minimize carryover from one sample to another by providing scrubbing action between segments and also to act as a diffusion barrier between samples.

The arrangement of reagent additions, mixing coils, delay coils, and heating bath, if needed to make a reaction proceed at an acceptable rate, make up the cartridge manifold. These vary in complexity and detail for each determination. The pump tubing and manifold arrangements are usually depicted in a "flow diagram" that is included for each automated procedure.

The colorimeter normally used for automated analyses is a two-photocell photometer. The solution stream is debubbled before it enters the flow cell, and the output of the colorimeter is measured on a recorder and possibly a printer. The basic principles of colorimetry discussed previously in this section apply as well to these colorimetric, automated procedures.

Two flow cells are provided in each photometer; therefore, color can sometimes be compensated for by passing an additional stream containing the sample and all reagents except the indicator reagent through the reference channel of the photometer. The points at which the reagent solutions are added and the mixing schemes must be identical for the two streams, and they must be phased so that the sample solutions arrive at both cells simultaneously. The absorbance due to the natural color of the sample is thereby subtracted from the total absorbance of the stream to produce the absorbance due to the color-forming reaction.

The recorder measures the output from the photometer. An analytical curve can be constructed after a sufficient number of standard solutions have been analyzed. The concentration values of the samples are obtained from this curve. Alternatively, a printer can be used which receives a signal from the recorder by way of a retransmitting potentiometer. The results are usually read directly in concentration.

A brief discussion of the principles and techniques of automatic chemical analysis may be found in the text by Willard, Merritt, and Dean (1974).

References

Mellon, M. G., 1950, Analytical absorption spectroscopy: New York, John Wiley & Sons, p. 95, figs. 2, 3.

Willard, H. H., Merritt, L. L., Jr., and Dean, J. A., 1974, Instrumental methods of analysis [5th ed.]: New York, D. Van Nostrand.

COLORIMETRIC METHODS

Aluminum, dissolved, colorimetric, ferron-orthophenanthroline (I–1050–78)

Parameter and Code: Aluminum, dissolved (μg/L as Al): 01106

1. Application

This method may be used to analyze samples containing from 100 to 3,000 μg/L of aluminum. Smaller concentrations are detectable but are not considered accurately measurable. Samples containing more than 3,000 μg/L must be diluted.

2. Summary of method

Ferron (8-hydroxy-7-iodo-5-quinoline sulfonic acid) reacts with aluminum to give a soluble, intensely colored complex. Color development is complete immediately. Normal temperature variations do not affect the reaction.

3. Interferences

3.1 The method is subject to significant interference from iron, but this effect can be greatly minimized by adding an iron-complexing agent. Orthophenanthroline is ideal for the purpose and has the additional advantage that iron may be simultaneously determined. A correction for iron must still be made, but it is comparatively small.

3.2 Several other metals and anions show small interference effects, but only manganese, lead, cobalt, and fluoride show sufficiently pronounced effects to require correction. Beryllium minimizes the interference of fluoride. The relative interfering effects of certain constituents are indicated by the following results obtained in solutions containing 1,000 μg of aluminum per liter:

Constituent	*Concentration (mg/L)*	*Al found (μg/L)*
Mg	40	1,040
Mg	80	1,090
Zn	5	1,050
Mn	5	1,170
Mn	10	1,280
F	1	940
F	2	900
F	5	800

The corrections indicated by the data above are illustrative only; each laboratory should prepare its own set of corrections to be applied for the interference by these and other constituents. Orthophosphate up to 5 mg/L and residual chlorine up to 5 mg/L do not interfere. Natural color interferes in the aluminum determination, and a correction is usually required.

3.3 Interferences are relatively rare in the associated orthophenanthroline determination of iron, since the reagent is generally considered specific for iron. Copper may interfere if the pH goes above 6, but this will not happen if the pH buffer is in good condition.

3.4 In the analytical sequence, the constituents listed in the above table should be determined before aluminum so that the necessary corrections can be applied. These corrections are derived from the data in the preceding list of interferences, and they apply strictly only at an aluminum concentration of 1,000 μg/L. However, the indicated corrections are usually satisfactory for general analytical purposes. If an accurate aluminum determination is desired in waters containing high concentrations of interfering ions, it is suggested that empirical corrections be made by adding similar concentrations of the interfering ions to an appropriate aluminum standard and by measuring the resulting absorbance change.

3.5 Additional information on the determination is given by Davenport (1949) and Smith and Richter (1944).

4. Apparatus

4.1 *Spectrophotometer*, for use at 370 and 520 nm; Beckman Model B, or equivalent.

4.2 With this instrument the following operating conditions are recommended:

	Al	Fe
Wavelength	370 nm	520 nm.
Cells	40 mm	40 mm.
Phototube	Blue-sensitive	Blue-sensitive.
Filter	Blue	None.
Blank	Demineralized water plus reagent.	Demineralized water plus reagent.
Initial sensitivity setting.		
Slit width (approx).	1.0 mm	0.1 mm.

4.3 The following absorbances have been observed for iron and aluminum:

Fe			Al	
Amount (μg)	*Absorbance (370 nm)*	*(520 nm)*	*Amount (μg)*	*Absorbance (370 nm)*
25	0.07	0.51	25	0.64
50	.125	1.02	50	1.14
75	.185	1.53	75	1.60
100	.25	1.95		
125	.305	2.33		

5. Reagents

5.1 *Aluminum* standard solution I, 1.00 mL = 100 μg Al: Dissolve 1.758 g $AlK(SO_4)_2 \cdot 12H_2O$ in demineralized water, add 1 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL with demineralized water.

5.2 *Aluminum* standard solution II, 1.00 mL = 10.0 μg Al: Dilute 25.0 mL aluminum standard solution I to 250.0 mL with demineralized water.

5.3 *Ferron-orthophenanthroline* reagent: Add 0.5 g ferron and 1.0 g orthophenanthroline to 1 L demineralized water. Stir for several hours until the maximum solution is obtained. The ferron may not dissolve completely. Allow any solids to settle out and decant the clear supernatant solution for use.

5.4 *Hydroxylamine-hydrochloric acid* reagent: Dissolve 100 g $NH_2OH \cdot HCl$ in demineralized water. Add 40 mL concentrated HCl (sp gr 1.19). Add 1 g $BeSO_4 \cdot 2H_2O$. Dilute to 1 L with demineralized water. (CAUTION: Beryllium compounds are toxic and should be handled with care.)

5.5 *Iron* standard solution I, 1.00 mL = 400 μg Fe: Weigh out 0.400 g analytical grade iron wire which has been cleaned in dilute HCl, rinsed, and dried. Dissolve in a minimum of dilute HCl and dilute to 1,000 mL with demineralized water.

5.6 *Iron* standard solution II, 1.00 mL = 4.0 μg Fe: Dilute 10.0 mL iron standard solution I to 1,000 mL with demineralized water, containing 1 or 2 drops concentrated HCl (sp gr 1.19).

5.7 *Sodium acetate* solution, 350 g/L: Dissolve 350 g anhydrous $NaC_2H_3O_2$ in demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 75 μg Al and 100 μg Fe (25.0 mL maximum) into a 50-mL beaker, and adjust the volume to 25.0 mL.

6.2 Prepare a demineralized-water blank and sufficient standards, and adjust the volume of each to 25.0 mL.

6.3 Add 2.0 mL $NH_2OH \cdot HCl$ reagent and let stand 30 min to permit complete reduction of the iron to ferrous iron. If precipitated iron is present, the standing time must be prolonged until all iron is in solution (overnight standing is a good practice).

6.4 Add 5.0 mL ferron-orthophenanthroline reagent and stir.

6.5 Add 2.0 mL $NaC_2H_3O_2$. Stir and let stand at least 10 min but not more than 30 min.

6.6 Determine the absorbance of the sample and standards against the blank at 370 nm and 520 nm and, when necessary, make corrections for water color.

7. Calculations

7.1 Determine the micrograms of iron in the sample from a plot of absorbances of standards at 520 nm.

7.2 Determine the iron concentration in micrograms per liter as follows:

$$\text{Fe } (\mu g/L) = \frac{1{,}000}{\text{mL sample}} \times \mu g \text{ Fe in sample.}$$

7.3 Determine the apparent micrograms of Al in the sample from a plot of absorbances of standards at 370 nm.

7.4 Determine the apparent aluminum concentration in micrograms per liter as follows:

$$\text{Apparent Al } (\mu g/L) = \frac{1{,}000}{\text{mL sample}} \times \text{apparent } \mu g \text{ Al in sample.}$$

7.5 Determine the aluminum concentration in micrograms per liter as follows:

$$\text{Al } (\mu g/L) = \text{apparent } \mu g/L \text{ Al} - (0.12 \times \mu g/L \text{ Fe}) - (0.04 \times \mu g/L \text{ Mn}) + (0.05 \times \mu g/L \text{ F}).$$

8. Report

Report aluminum, dissolved (01106), concentrations as follows: less than 1,000 μg/L, one significant figure; 1,000 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 200 to 600 μg/L aluminum may be expressed as follows:

$$S_T = 0.077X + 27.33$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of aluminum, micrograms per liter.

9.2 The statistical results may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
9	402	15
14	607	12

9.3 Precision data for Fe by this method are not available.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 44.

Davenport, W. H., 1949, Determination of aluminum in presence of iron: Analytical Chemistry, v. 21, p. 710.

Smith, G. F., and Richter, F. P., 1944, Phenanthroline and substituted phenanthroline indicators: Columbus, Ohio, G. F. Smith Chemical Company.

Arsenic, dissolved, colorimetric, silver diethyldithiocarbamate (I–1060–78)

Parameter and Code: Arsenic, dissolved (μg/L as As): 01000

1. Application

1.1 This method may be used to analyze water samples containing from 5 to 200 μg/L of arsenic. Samples containing more than 200 μg/L must be diluted.

1.2 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the strong-acid digestion, paragraphs 6.3 and 6.4 of the procedure.

2. Summary of method

2.1 Organic compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the samples to fumes of sulfur trioxide. The arsenic(V) so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsenic(III) by potassium iodide and stannous chloride, and finally to gaseous arsine by zinc in hydrochloric acid solution. The resultant mixture of gases is passed through a scrubber consisting of borosilicate glass wool impregnated with lead acetate solution and into a gas absorber containing silver diethyldithiocarbamate (AgDDC) dissolved in pyridine. Arsine reacts with AgDDC to form a soluble red complex having maximum absorbance at about 535 nm. The absorbance of the solution is measured spectrophotometrically, and arsenic determined by reference to an analytical curve prepared from standards.

2.2 Additional information on the determination is given by Liederman, Bowen, and Milner (1959); by Ballinger, Lishka, and Gales (1962); by Stratton and Whitehead (1962); and by Fresenius and Schneider (1964).

3. Interferences

3.1 Ordinarily, ground- and surface-water samples are relatively free of interferences. Occasionally samples may contain hydrogen sulfide; however, commonly encountered quantities are effectively removed by a lead acetate scrubber. Several metals—cobalt, nickel, mercury, silver, platinum, copper, chromium, and molybdenum—interfere with the evolution of arsine. Where such interferences exist, they can be minimized or eliminated by pretreatment of the sample (Liederman and others, 1959). Antimony salts, under the reducing conditions in the generator, form stibine, which passes into the absorber and causes high results.

3.2 The blank and standards fade slowly on standing, but not enough to influence results significantly during the first 20 min.

4. Apparatus

4.1 *Arsine generator, scrubber, and absorber* (fig. 25).

4.2 *Spectrophotometer*, for use at 535 nm; Beckman Model B, or equivalent.

4.3 With this instrument the following operating conditions have been found satisfactory:

Wavelength	535 nm.
Cells	10 mm.
Phototube	Blue-sensitive.
Initial sensitivity setting	2.
Slit width (approx)	0.2 mm.

4.4 Under these conditions the following absorbances have been observed:

Amount of arsenic (μg)	*Absorbance* (μg)
5.0	0.325
10	.650
15	.970
20	1.305

5. Reagents

5.1 *Arsenic* standard solution I, 1.00 mL = 1.00 mg As: Dissolve 1.320 g As_2O_3, dried for 1 h

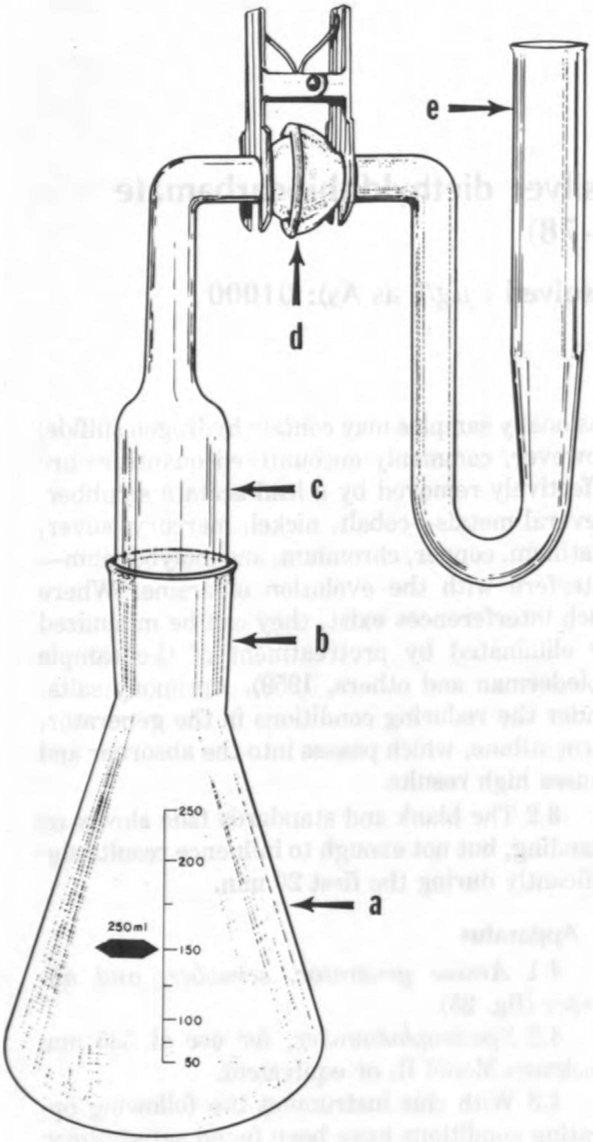


FIGURE 25.—Arsine generator, scrubber, and absorber. (a) Generator, 250-mL erlenmeyer flask. (b) Standard taper neck. (c) Scrubber, lead acetate on glass wool. (d) Ground glass ball-and-socket joint. (e) Absorber, contains silver diethyl dithiocarbamate.

at 110°C, in 10 mL $10M$ NaOH and dilute to 1,000 mL with demineralized water. This solution is stable.

5.2 *Arsenic* standard solution II, 1.00 mL = 10.0 µg As: Dilute 5.00 mL arsenic standard solution I to 500.0 mL with demineralized water. This solution is stable.

5.3 *Arsenic* standard solution III, 1.00 mL = 1.00 µg As: Dilute 10.0 mL arsenic standard solution II to 100.0 mL with demineralized water. Prepare fresh before each use.

5.4 *Hydrochloric acid,* concentrated (sp gr 1.19): Use analytical-grade acid with arsenic content not greater than 1×10^{-6} percent.

5.5 *Lead acetate* solution, 8.6 g/100 mL: Dissolve 10 g $(CH_3COO)_2Pb \cdot 3H_2O$ in 100 mL demineralized water. Keep tightly stoppered.

5.6 *Nitric acid,* concentrated (sp gr 1.41): Use analytical-grade acid with arsenic content not greater than 5×10^{-7} percent.

5.7 *Potassium iodide* solution, 15 g/100 mL: Dissolve 15 g KI in 100 mL demineralized water. This solution is stable when stored in an amber bottle.

5.8 *Silver diethyldithiocarbamate* (AgDDC) solution, 0.5 g/100 mL: Dissolve 1 g $(C_2H_5)_2NCSSAg$ in 200 mL pyridine. This solution is stable when stored in an amber bottle.

5.9 *Stannous chloride* solution, 33.6 g/100 mL concentrated HCl: Dissolve 40 g arsenic-free $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl. This solution is stable if a few small pieces of mossy tin are added to the bottle to prevent oxidation.

5.10 *Sulfuric acid, 9M: Cautiously,* and with constant stirring and cooling, add 250 mL concentrated H_2SO_4 (sp gr 1.84) to 250 mL demineralized water.

5.11 *Zinc:* Granular zinc, about 20 mesh, with arsenic content not greater than 1×10^{-6} percent.

6. Procedure

Clean all glassware used in this determination with warm, dilute HNO_3 (1 + 4) and rinse with demineralized water immediately before each use. The absorbers must also be rinsed with acetone and air dried or briefly oven dried.

6.1 Pipet a volume of sample containing less than 20 µg As (100 mL maximum) into the flask of an arsine generator and dilute to 100 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.3 To each flask, add 7 mL $9M$ H_2SO_4 and 5 mL concentrated HNO_3. Add a small boiling chip and carefully evaporate to fumes of SO_3. Cool, add 25 mL demineralized water, and again evaporate to fumes of SO_3 to expel oxides of nitrogen. Maintain an excess of HNO_3 until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of arsenic.

6.4 Cool, and adjust the volume to approx 100 mL. (NOTE 1.)

NOTE 1. If only inorganic arsenic is to be determined, omit steps 6.3 and 6.4.

6.5 To each flask add successively, with thorough mixing after each addition, 10 mL concentrated HCl, 4 mL KI solution, and 1 mL $SnCl_2$ solution. Allow about 15 min for reduction of the arsenic to the tervalent state.

6.6 Place in each scrubber a plug of borosilicate glass wool that has been impregnated with lead acetate solution. Assemble the generator, scrubber, and absorber, making certain that all parts fit and are correctly adjusted. Add 3.00 mL silver diethyldithiocarbamate-pyridine solution to each absorber. Add glass beads to the absorbers until the liquid just covers them.

6.7 Disconnect each generator, add 6 g granular zinc, and reconnect immediately.

6.8 Allow 30 min for complete evolution of the arsine. Warm the generator flasks for a few minutes to make sure that all the arsine is released, and then pour the solutions from the absorbers directly into the spectrophotometer cells. Determine the absorbances of the standards and samples against the blank without unnecessary delay, as the color developed is not permanent.

7. Calculations

7.1 Determine the micrograms of As in the sample from a plot of absorbances of standards.

7.2 Determine the arsenic concentration in micrograms per liter as follows:

$$\text{As} \ (\mu\text{g/L}) = \mu\text{g As in sample} \times \frac{1{,}000}{\text{mL sample}}$$

8. Report

Report arsenic, dissolved (01000), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within its designated range may be expressed as follows:

$$S_T = 0.230X + 2.11$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of arsenic, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (µg/L)*	*Relative deviation (percent)*
12	9.8	42
16	109	24

References

Ballinger, D. G., Lishka, R. J., and Gales, M. E., 1962, Application of the silver diethyldithiocarbamate method to the determination of arsenic: American Water Works Association Journal, v. 54, p. 1424–1428.

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 31.

Fresenius, W., and Schneider, W., 1964, Determination of slight amounts of arsenic with silver diethyldithiocarbamate in water analysis: Journal of Analytical Chemistry, v. 203, p. 417–422.

Liederman, D., Bowen, J. E., and Milner, O. I., 1959, Determination of arsenic in petroleum stocks and catalysts by evolution of arsine: Analytical Chemistry, v. 31, p. 2052.

Stratton, G., and Whitehead, H. E., 1962, Colorimetric determination of arsenic in water with silver diethyldithiocarbamate: American Water Works Association Journal, v. 54, p. 861.

Arsenic, total in bottom material, colorimetric, silver diethyldithiocarbamate (I–5060–78)

Parameter and Code: Arsenic, total in bottom material, dry wt (μg/g as As): 01003

1. Application

1.1 This method may be used to analyze bottom material samples containing 5 to 200 μg/g of arsenic. For samples containing more than 200 μg/g a smaller subsample is used in the analysis.

1.2 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the strong-acid digestion, paragraphs 6.3 and 6.4 of the procedure.

1.3 Bottom material samples may be analyzed by this procedure after they have been prepared as directed in Method P–0520.

2. Summary of method

2.1 Organic compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the samples to fumes of sulfur trioxide. The arsenic(V) so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsenic(III) by potassium iodide and stannous chloride, and finally to gaseous arsine by zinc in hydrochloric acid solution. The resultant mixture of gases is passed through a scrubber consisting of borosilicate glass wool impregnated with lead acetate solution, and into a gas absorber containing silver diethyldithiocarbamate (AgDDC) dissolved in pyridine. Arsine reacts with AgDDC to form a soluble red complex having maximum absorbance at about 535 nm. The absorbance of the solution is measured spectrophotometrically, and arsenic determined by reference to an analytical curve prepared from standards.

2.2 Additional information on the determination is given by Liederman, Bowen, and Milner (1959); by Ballinger, Lishka, and Gales (1962); by Stratton and Whitehead (1962); and Fresenius and Schneider (1964).

3. Interferences

3.1 Some samples may contain sulfides; however, small quantities are effectively removed by a lead acetate scrubber. Several metals—cobalt, nickel, mercury, silver, platinum, copper, chromium, and molybdenum—interfere with the evolution of arsine. Antimony salts, under the reducing conditions in the generator, form stibine, which passes into the absorber and causes high results.

3.2 The blank and standards fade slowly on standing, but not enough to influence results significantly during the first 20 minutes.

4. Apparatus

4.1 *Arsine generator, scrubber, and absorber* (fig. 26).

4.2 *Spectrophotometer*, for use at 535 nm.

4.3 Refer to the manufacturer's manual to optimize output of the instrument for the following parameter:

Wavelength .... 535 nm.

5. Reagents

5.1 *Arsenic* standard solution I, 1.00 mL = 1.00 mg As: Dissolve 1.320 g As_2O_3, dried for 1 h at 110°C, in 10 mL 10*M* NaOH and dilute to 1,000 mL with demineralized water. This solution is stable.

5.2 *Arsenic* standard solution II, 1.00 mL = 10.0 μg As: Dilute 5.00 mL arsenic standard solution I to 500.0 mL with demineralized water. This solution is stable.

5.3 *Arsenic* standard solution III, 1.00 mL = 1.00 μg As: Dilute 10.0 mL arsenic standard solution II to 100.0 mL with demineralized water. Prepare fresh before each use.

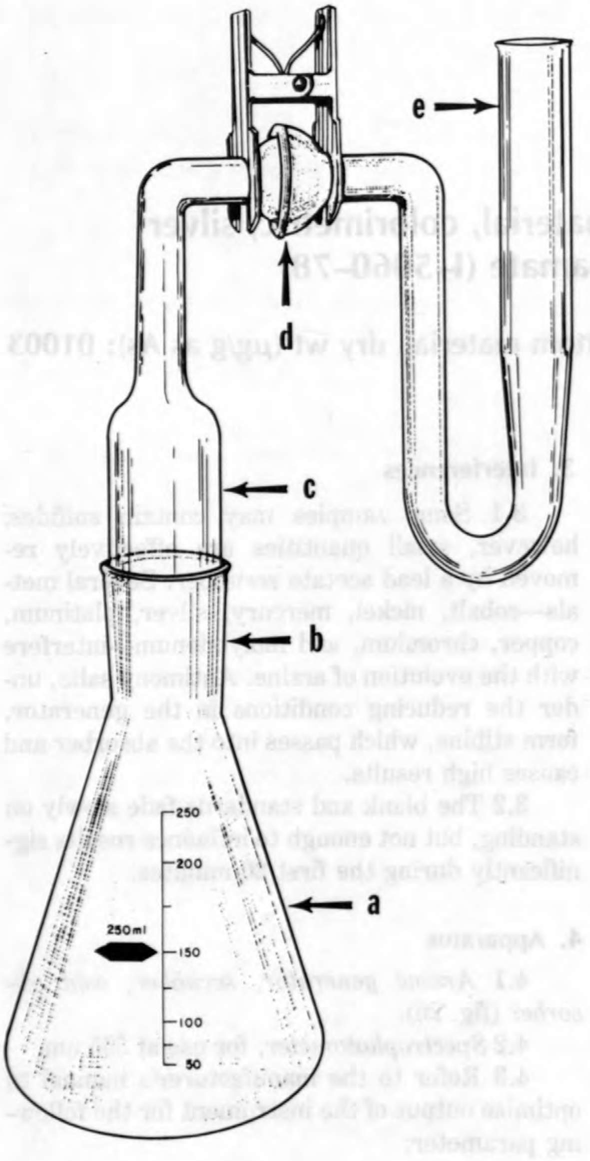


FIGURE 26.—Arsine generator, scrubber, and absorber. (a) Generator, 250-mL erlenmeyer flask. (b) Standard taper neck. (c) Scrubber, lead acetate on glass wool. (d) Ground glass ball-and-socket joint. (e) Absorber, contains silver diethyl dithiocarbamate.

5.4 *Hydrochloric acid,* concentrated (sp gr 1.19): Use analytical grade with arsenic content not greater than 1×10^{-6} percent.

5.5 *Lead acetate* solution, 8.6 g/100 mL: Dissolve 10 g $(CH_3COO)_2Pb \cdot 3H_2O$ in 100 mL demineralized water. Keep tightly stoppered.

5.6 *Nitric acid,* concentrated (sp gr 1.41): Use analytical-grade acid with arsenic content not greater than 5×10^{-7} percent.

5.7 *Potassium iodide* solution, 15 g/100 mL: Dissolve 15 g KI in 100 mL demineralized water. This solution is stable when stored in an amber bottle.

5.8 *Silver diethyldithiocarbamate* (AgDDC) solution, 0.5 g/100 mL: Dissolve 1 g $(C_2H_5)_2NCSSAg$ in 200 mL pyridine. This solution is stable when stored in an amber bottle.

5.9 *Stannous chloride* solution, 33.6 g/100 mL concentrated HCl: Dissolve 40 g arsenic-free $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl. This solution is stable if a few small pieces of mossy tin are added to the bottle to prevent oxidation.

5.10 *Sulfuric acid, 9M: Cautiously,* and with constant stirring and cooling, add 250 mL concentrated H_2SO_4 (sp gr 1.84) to 250 mL demineralized water.

5.11 *Zinc:* Granular zinc, about 20 mesh, with arsenic content not greater than 1×10^{-6} percent.

6. Procedure

Clean all glassware used in this determination with warm, dilute HNO_3 (1 + 4) and rinse with demineralized water immediately before each use. The absorbers must also be rinsed with acetone and air dried or briefly oven dried.

6.1 Weigh a portion (NOTE 1) of prepared bottom material sample (Method P–0520) containing less than 20 μg As and transfer to the flask of an arsine generator.

NOTE 1: The sample weight must not exceed 100 mg; otherwise severe bumping and loss of arsenic may occur.

6.2 Prepare a blank and sufficient standards (20 μg As maximum), and adjust the volume of each to approx 100 mL with demineralized water.

6.3 To each flask, add 7 mL 9*M* H_2SO_4 and 5 mL concentrated HNO_3. Add a small boiling chip and carefully evaporate to fumes of SO_3. Cool, add 25 mL demineralized water, and again evaporate to fumes of SO_3 to expel oxides of nitrogen. Maintain an excess of HNO_3 until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of arsenic.

6.4 Cool, and adjust the volume to approx 100 mL. (NOTE 2.)

NOTE 2. If only inorganic arsenic is to be determined, omit steps 6.3 and 6.4.

6.5 To each flask add successively, with thorough mixing after each addition, 10 mL concentrated HCl, 4 mL KI solution, and 1 mL $SnCl_2$ solution. Allow about 15 min for reduction of the arsenic to the tervalent state.

6.6 Place in each scrubber a plug of borosilicate glass wool that has been impregnated with lead acetate solution. Assemble the generator, scrubber, and absorber, making certain that all parts fit and are correctly adjusted. Add 3.00 mL silver diethyldithiocarbamate-pyridine solution to each absorber. Add glass beads to the absorbers until the liquid just covers them.

6.7 Disconnect each generator, add 6 g granular zinc, and reconnect immediately.

6.8 Allow 30 min for complete evolution of the arsine. Warm the generator flasks for a few minutes to make sure that all the arsine is released, and then pour the solutions from the absorbers directly into the spectrophotometer cells. Determine the absorbances of the standards and samples against the blank without unnecessary delay, as the color developed is not permanent.

7. Calculations

7.1 Determine the micrograms total arsenic in the sample from a plot of absorbances of standards.

7.2 Determine the concentration of arsenic in micrograms per gram of air-dried sample as follows:

$$\text{As } (\mu\text{g/g}) = \frac{\mu\text{g As per sample}}{\text{sample weight (g)}}$$

8. Report

Report arsenic, total in bottom material (01003), concentrations as follows: less than 100 μg/g, to the nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of the method is greater than 42 percent in the lower portion of the analytical range.

References

Ballinger, D. G., Lishka, R. J., and Gales, M. E., 1962, Application of the silver diethyldithiocarbamate method to the determination of arsenic: American Water Works Association Journal, v. 54, p. 1424–1428.

Fresenius, W., and Schneider, W., 1964, Determination of slight amounts of arsenic with silver diethyldithiocarbamate in water analysis: Journal of Analytical Chemistry, v. 203, p. 417–422.

Liederman, D., Bowen, J. E., and Milner, O. I., 1959, Determination of arsenic in petroleum stocks and catalysts by evolution of arsine: Analytical Chemistry, v. 31, p. 2052.

Stratton, G., and Whitehead, H. E., 1962, Colorimetric determination of arsenic in water with silver diethyldithiocarbamate: American Water Works Association Journal, v. 54, p. 861.

Arsenic, total, colorimetric, silver diethyldithiocarbamate (I–3060–78)

Parameter and Code: Arsenic, total (μg/L as As): 01002

1. Application

1.1 This method may be used to analyze samples of water-suspended sediment mixtures containing 5 to 200 μg/L of arsenic. Samples containing more than 200 μg/L must be diluted.

1.2 Water-suspended sediment mixtures may be analyzed by this procedure after each sample has been thoroughly mixed by vigorous shaking and a suitable sample portion has been rapidly withdrawn from the mixture.

2. Summary of method

2.1 Organic compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the samples to fumes of sulfur trioxide. The arsenic(V) so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsenic(III) by potassium iodide and stannous chloride, and finally to gaseous arsine by zinc in hydrochloric acid solution. The resultant mixture of gases is passed through a scrubber consisting of borosilicate glass wool impregnated with lead acetate solution and into a gas absorber containing silver diethyldithiocarbamate (AgDDC) dissolved in pyridine. Arsine reacts with AgDDC to form a soluble red complex having maximum absorbance at about 535 nm. The absorbance of the solution is measured spectrometrically, and arsenic determined by reference to an analytical curve prepared from standards.

2.2 Additional information on the determination is given by Liederman, Bowen, and Milner (1959); by Ballinger, Lishka, and Gales (1962); by Stratton and Whitehead (1962); and by Fresenius and Schneider (1964).

3. Interferences

3.1 Ordinarily, ground- and surface-water samples are relatively free of interferences. Occasionally samples may contain hydrogen sulfide; however, commonly encountered quantities are effectively removed by a lead acetate scrubber. Several metals—cobalt, nickel, mercury, silver, platinum, copper, chromium, and molybdenum—interfere with the evolution of arsine. Where such interferences exist, they can be minimized or eliminated by pretreatment of the sample (Liederman and others, 1959). Antimony salts, under the reducing conditions in the generator, form stibine, which passes into the absorber and causes high results.

3.2 The blank and standards fade slowly on standing, but not enough to influence results significantly during the first 20 min.

4. Apparatus

4.1 *Arsine generator, scrubber, and absorber* (fig. 27).

4.2 *Spectrometer*, for use at 535 nm; Beckman Model B, or equivalent.

4.3 With this instrument the following operating conditions have been found satisfactory:

Wavelength	535 nm.
Cells	10 mm.
Phototube	Blue-sensitive.
Initial sensitivity setting	2.
Slit width (approx)	0.2 mm.

4.4 Under these conditions the following absorbances have been observed:

Amount of arsenic (μg)	*Absorbance*
5	0.325
10	.650
15	.970
20	1.305

5. Reagents

5.1 *Arsenic* standard solution I, 1.00 mL = 1.00 mg As: Dissolve 1.320 g As_2O_3, dried for 1 h at 110°C, in 10 mL 10*M* NaOH and dilute to 1,000 mL with demineralized water. This solution is stable.

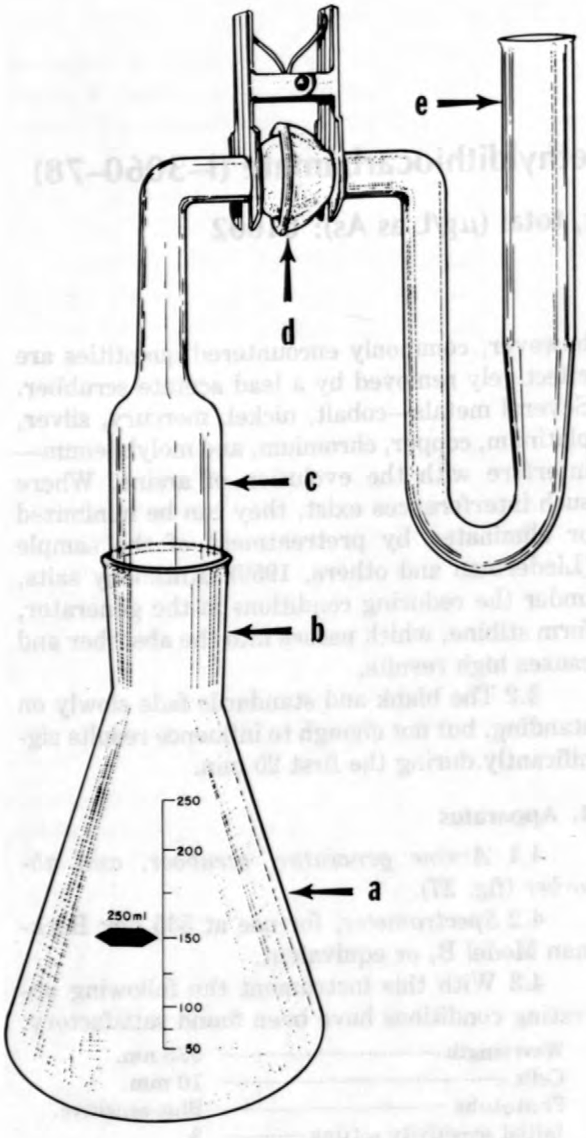


FIGURE 27.—Arsine generator, scrubber, and absorber. (a) Generator, 250-mL erlenmeyer flask. (b) Standard taper neck. (c) Scrubber, lead acetate on glass wool. (d) Ground glass ball-and-socket joint. (e) Absorber, contains silver diethyl dithiocarbamate.

5.2 *Arsenic* standard solution II, 1.00 mL = 10.0 μg As: Dilute 5.00 mL arsenic standard solution I to 500.0 mL with demineralized water. This solution is stable.

5.3 *Arsenic* standard solution III, 1.00 mL = 1.00 μg As: Dilute 10.0 mL arsenic standard solution II to 100.0 mL with demineralized water. Prepare fresh before each use.

5.4 *Hydrochloric acid,* concentrated (sp gr 1.19): Use analytical-grade acid with arsenic content not greater than 1×10^{-6} percent.

5.5 *Lead acetate* solution, 8.6 g/100 mL: Dissolve 10 g $(CH_3COO)_2Pb \cdot 3H_2O$ in 100 mL demineralized water. Keep tightly stoppered.

5.6 *Nitric acid,* concentrated (sp gr 1.41): Use analytical-grade acid with arsenic content not greater than 5×10^{-7} percent.

5.7 *Potassium iodide* solution, 15 g/100 mL: Dissolve 15 g KI in 100 mL demineralized water. This solution is stable when stored in an amber bottle.

5.8 *Silver diethyldithiocarbamate* (AgDDC) solution, 0.5 g/100 mL: Dissolve 1 g $(C_2H_5)_2NCSSAg$ in 200 mL pyridine. This solution is stable when stored in an amber bottle.

5.9 *Stannous chloride* solution, 33.6 g/100 mL concentrated HCl: Dissolve 40 g arsenic-free $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl. This solution is stable if a few small pieces of mossy tin are added to the bottle to prevent oxidation.

5.10 *Sulfuric acid, 9M: Cautiously,* and with constant stirring and cooling, add 250 mL concentrated H_2SO_4 (sp gr 1.84) to 250 mL demineralized water.

5.11 *Zinc:* Granular zinc, about 20 mesh, with arsenic content not greater than 1×10^{-6} percent.

6. Procedure

Clean all glassware used in this determination with warm, dilute HNO_3 (1 + 4) and rinse with demineralized water immediately before each use. The absorbers must also be rinsed with acetone and then air dried or briefly oven dried.

6.1 Pipet a volume of well mixed sample containing less than 20 μg As (100 mL maximum) into the flask of an arsine generator. Rinse the pipet with demineralized water to remove adhering particles and combine with the sample. Dilute the sample to approx 100 mL if less than 100 mL is used.

6.2 Prepare a blank and sufficient standards and adjust the volume of each to approx 100 mL with demineralized water.

6.3 To each flask, add 7 mL 9*M* H_2SO_4 and 5 mL concentrated HNO_3. Add a small boiling chip and carefully evaporate to fumes of SO_3. Cool, add 25 mL demineralized water and again evaporate to fumes of SO_3 to expel oxides of nitrogen. Maintain an excess of HNO_3 until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of arsenic.

6.4 Cool, and adjust the volume to approx mL (NOTE 1).

NOTE 1. If only inorganic arsenic is to be determined, omit steps 6.3 and 6.4.

6.5 To each flask add successively, with thorough mixing after each addition, 10 mL concentrated HCl, 4 mL KI solution, and 1 mL $SnCl_2$ solution. Allow about 15 min for reduction of the arsenic to the tervalent state.

6.6 Place in each scrubber a plug of borosilicate glass wool that has been impregnated with lead acetate solution. Assemble the generator, scrubber, and absorber, making certain that all parts fit and are correctly adjusted. Add 3.00 mL silver diethyldithiocarbamate-pyridine solution to each absorber. Add glass beads to the absorbers until the liquid just covers them.

6.7 Disconnect each generator, add 6 g granular zinc, and reconnect immediately.

6.8 Allow 30 min for complete evolution of the arsine. Warm the generator flasks for a few minutes to make sure that all the arsine is released, and then pour the solutions from the absorbers directly into the spectrometer cells. Determine the absorbances of the standards and samples against the blank without unnecessary delay, as the color developed is not permanent.

7. Calculations

7.1 Determine the micrograms total arsenic in the sample from a plot of absorbances of standards.

7.2 Determine the total arsenic concentration in micrograms per liter as follows:

$$\text{As total } (\mu\text{g/L}) = \mu\text{g As in sample} \times \frac{1{,}000}{\text{mL sample}} .$$

8. Report

Report arsenic, total (01002), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of the method is greater than 42 percent at 9.8 μg/L and greater than 24 percent at 109 μg/L.

References

Ballinger, D. G., Lishka, R. J., and Gales, M. E., 1962, Application of the silver diethyldithiocarbamate method to the determination of arsenic: American Water Works Association Journal, v. 54, p. 1424–1428.

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewater: U.S. Geological Survey Open-File Report 76–177, p. 31.

Fresenius, W., and Schneider, W., 1964, Determination of slight amounts of arsenic with silver diethyldithiocarbamate in water analysis: Journal of Analytical Chemistry, v. 203, p. 417–422.

Liederman, D., Bowen, J. E., and Milner, O. I., 1959, Determination of arsenic in petroleum stocks and catalysts by evolution of arsine: Analytical Chemistry, v. 31, p. 2052.

Stratton, G., and Whitehead, H. E., 1962, Colorimetric determination of arsenic in water with silver diethyldithiocarbamate: American Water Works Association Journal, v. 54, p. 861.

Boron, dissolved, colorimetric, carminic acid (I–1111–78)

Parameter and Code: Boron, dissolved (μg/L as B): 01020

1. Application

This method may be used to analyze fresh waters and seawaters containing more than 500 μg/L of boron. The optimum range for the method on undiluted or unconcentrated samples is 500 to 10,000 μg/L. Samples containing less than 500 μg/L must first be concentrated by evaporation in strong alkaline solution to prevent loss of volatile boric acid.

2. Summary of method

2.1 In acid solution, boron forms a colored complex with carmine. The color change is from red to blue. Maximum color development requires approximately 1 h, but the color intensity decreases thereafter. The fading is proportional to the boron content and is therefore of little consequence if standards are analyzed simultaneously with the sample. Fading is rather rapid, however, with approximately 25 percent or more reduction in intensity between 1 and 2 h.

2.2 Additional information on the principle of the determination is given by Hatcher and Wilcox (1950).

3. Interferences

Strong ammonia fumes affect the reagent. Silica interferes, but the interference is independent of the silica concentration and dependent on the boron concentration. With 500 μg/L of boron the determined value may be about 20 percent high in the presence of up to 30 mg/L of silica. At lower boron levels, the effect is variable. Fluoride, nitrate, and phosphate contribute some interference, but to a lesser degree.

4. Apparatus

4.1 *Steam bath.*

4.2 *Spectrometer.*

4.3 Refer to manufacturer's manual for optimizing instrumental parameters.

Wavelength .... 600 nm.

Using a 10-mm cell, the following data have been obtained:

Amount of boron (μg)	*Absorbance*
10	0.098
20	.195
30	.301

5. Reagents

5.1 *Boron* standard solution I, 100 mL = 100 μg B: Dissolve approx 10 g $Na_2B_4O_7\cdot 10H_2O$ in demineralized water at 50°C to 60°C. Recrystallize by placing in a refrigerator for several hours. Dry by removing water with suction and washing with alcohol followed by ether. Do not dry in oven. Dissolve 0.8820 g in demineralized water and dilute to 1,000 mL. Store in plastic bottle.

5.2 *Boron* standard solution II, 1.00 mL = 10.0 μg B: Dilute 100.0 mL boron standard solution I to 1,000 mL with demineralized water. Store in plastic bottle.

5.3 *Carmine* solution, 0.5 g/L concentrated H_2SO_4. Suspend 0.50 g carmine in 1 L concentrated H_2SO_4 (sp gr 1.84) and mix with a mechanical stirrer until solution is complete. The stain certified by the Biological Stain Commission of the American Chemical Society has been used satisfactorily.

5.4 *Hydrochloric acid*, concentrated (sp gr 1.19).

5.5 *Hydrochloric acid*, 0.6*M*: Mix 50 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.6 *Sodium hydroxide*, 0.5*M*: Dissolve 2 g NaOH in demineralized water and dilute to 100 mL.

5.7 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 Pipet a volume of sample containing between 1.0 and 20 μg B (2.00 mL maximum) into a 150-mL flask. If the sample contains less than 500 μg/L B, pipet a 2.00-mL aliquot of sample concentrated as follows:

a. Pipet an accurately measured volume of sample (100 mL maximum) into an evaporating dish. Include a blank with every group of samples.

b. Add 1 mL 0.5*M* NaOH.

c. Evaporate to dryness on a steam bath.

d. Take up the residue, triturate in 5.00 mL 0.6*M* HCl with a rubber policeman, and centrifuge to obtain a clear solution.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 2.0 mL.

6.3 Add 2 drops concentrated HCl, 12 mL concentrated H_2SO_4, mix, and allow to cool for at least 30 min.

6.4 Add 10 mL carmine solution, mix, and allow the solution to stand approx 1 h.

6.5 Determine the absorbances of the samples and standards against the blank and when necessary make corrections for water color.

7. Calculations

7.1 Determine the micrograms of boron in the sample from a plot of absorbances of standards.

7.2 Determine the boron concentration in micrograms per liter as follows:

$$\text{B} (\mu\text{g/L}) = \frac{1{,}000}{\text{mL sample}} \times \mu\text{g B in sample.}$$

7.3 If the concentration procedure described in 6.1a through 6.1d was followed, the result obtained in 7.2 must be divided by the concentration factor.

8. Report

Report boron, dissolved (01020), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 50 to 550 μg/L may be expressed as follows:

$$S_T = 0.463X + 20.2$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of boron, micrograms per liter.

9.2 The statistical results may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
9	72	78
5	522	14

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 56.

Hatcher, J. T., and Wilcox, L. V., 1950, Colorimetric determination of boron using carmine: Analytical Chemistry, v. 22, p. 567.

Boron, dissolved, colorimetric, curcumin (I–1112–78)

Parameter and Code: Boron, dissolved (μg/L as B): 01020

1. Application

This method may be used to analyze waters containing more than 100 μg/L of boron. The optimum range for the method on undiluted or unconcentrated samples is 100 to 1,000 μg/L.

2. Summary of method

2.1 When a sample of water containing boron is acidified and evaporated in the presence of curcumin, a red-colored product called rosocyanine is formed. The rosocyanine is extracted into a suitable solvent and the red color, which has a maximum absorbance at 540 nm, is measured spectrometrically.

2.2 The method is identical to that found in "Standard Methods for the Examination of Water and Wastewater" (1976).

3. Interferences

3.1 Nitrate-nitrogen concentrations greater than 20 mg/L interfere.

3.2 Significantly high results are possible when the total of calcium and magnesium hardness exceeds 100 mg/L as $CaCO_3$. Moderate hardness levels also can cause a considerable percentage error in the low boron range. The interference results from the insolubility of the hardness salts in 95-percent ethanol and consequent turbidity in the final solution. Filter the final solution or pass the original sample through a column of strongly acid cation-exchange resin in the hydrogen form to remove the interfering cations. The latter procedure enables application of the method to waters and effluents of high hardness or solids content.

4. Apparatus

4.1 *Evaporating dish*, 100- to 150-mL capacity, of Vycor glass, platinum, or other suitable material.

4.2 *Ion-exchange column*, 50-cm long by 1.3-cm diameter.

4.3 *Spectrometer*, for use at 540 nm, and cells with a minimum light path of 1 cm.

4.4 Refer to manufacturer's manual for optimizing instrumental parameters.

4.5 *Water bath*, 55°C ± 2°C.

5. Reagents

5.1 *Boron* standard solution I, 1.00 mL = 100 μg B: Dissolve approx 10 g $Na_2B_4O_7 \cdot 10H_2O$ in demineralized water at 50°C to 60°C. Recrystallize by placing in a refrigerator for several hours. Dry by removing water with suction and washing with alcohol followed by ether. Do not dry in oven. Dissolve 0.8820 g in demineralized water and dilute to 1,000 mL. Store in a plastic bottle.

5.2 *Boron* standard solution II, 1.00 mL = 1.00 μg B: Dilute 10.00 mL boron standard solution I to 1,000 mL with demineralized water. Store in a plastic bottle.

5.3 *Cation-exchange resin:* Load the column with a strongly acidic cation-exchange resin. Backwash the column with distilled water to remove the entrained air bubbles. Henceforth, make certain the resin remains covered with liquid at all times. Pass 50 mL 2*M* HCl through the column at a rate of 0.2 mL/min of acid per milliliter of resin in column, and then wash it free of acid with distilled water. The frequency of regeneration depends on the mineral content of the samples.

5.4 *Curcumin* reagent: Dissolve 40 mg finely ground curcumin (Eastman No. 1179 or equivalent) and 5.0 g oxalic acid in 80 mL 95-percent ethanol. Add 4.2 mL concentrated hydrochloric acid (sp gr 1.19) and dilute to 100 mL with ethanol. The reagent is stable for several days if stored in a refrigerator.

5.5 *Ethanol*, 95 percent.

5.6 *Hydrochloric acid, 2M*: Mix 166 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

6. Procedure

Precautions: Exercise close control of such variables as volumes and concentrations of samples, standards, and reagents as well as time and temperature of drying. Use evaporating dishes identical in shape, size, and composition to insure equal evaporation time. Increasing the time of evaporation results in intensification of the resulting color.

6.1 For samples containing high hardness (100 mg/L $CaCO_3$ or more) proceed as follows (NOTE 1): Pipet 25 mL sample, or a smaller sample of known high boron content diluted to 25 mL, onto the resin column. Adjust the rate of flow through the column to about 2 drops per second and collect the effluent in a 50-mL volumetric flask. Wash the column with small portions of distilled water until the flask is full to the mark and mix.

NOTE 1. For samples containing less than 100 mg/L hardness as $CaCO_3$, start with paragraph 6.2.

6.2 Pipet 1.00 mL of sample containing less than 1.0 μg B into an evaporating dish (NOTE 2).

NOTE 2. If the sample contains more than 1.00 mg/L boron, make an appropriate dilution with boron-free distilled water, so that a 1.00-mL portion contains approx 0.50 μg boron.

6.3 Prepare in evaporating dishes a blank and sufficient standards (1.0 μg B max) and adjust the volume of each to exactly 1.0 mL with demineralized water.

6.4 Add 4.0 mL curcumin reagent to each and swirl each dish gently to mix contents thoroughly.

6.5 Float the dishes on a water bath set at 55°C ± 2°C and let them remain for 80 min, a time usually sufficient for complete drying and removal of HCl. Keep drying time constant for standards and samples.

6.6 After the dishes cool to room temperature, add 10.0 mL 95-percent ethanol to each dish, stirring gently with a polyethylene rod to insure complete dissolution of the red-colored product.

6.7 Wash the contents of each dish into a 25-mL volumetric flask using 95-percent ethanol and adjust to volume with ethanol. Mix thoroughly by repeated inversion (NOTE 3).

NOTE 3. If the final sample solution is turbid, filter through No. 30 Whatman filter paper or equivalent.

6.8 Determine the absorbance of each sample and standard against the blank. Complete all absorbance readings within 1 h of drying the samples.

7. Calculations

7.1 Determine the micrograms boron in each sample from a plot of absorbances of standards.

7.2 Determine the boron concentration in micrograms per liter as follows:

$$B\ (\mu g/L) = 1{,}000 \times \mu g\ B \text{ in sample.}$$

7.3 If the sample was diluted prior to analysis (see NOTE 2), multiply the concentration of boron found in paragraph 7.2 by the dilution factor.

8. Report

Report boron, dissolved (01020), concentrations as follows: less than 1,000 μg/L, nearest 100 μg/L; 1,000 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 50 to 600 μg/L may be expressed as follows:

$$S_T = 0.034X + 42.4$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of boron, micrograms pe liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
3	87	68
5	386	13

References

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater [14th ed.]: Washington, D.C., American Public Health Association, p. 287.

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Washington, U.S. Government Printing Office, p. 13.

Boron, dissolved, colorimetric, dianthrimide (I–1110–78)

Parameter and Code: Boron, dissolved (μg/L as B): 01020

1. Application

1.1 This method may be used to analyze waters containing between 20 and 1,000 μg/L of boron. Samples containing more than 1,000 μg/L must first be diluted.

1.2 This method is not suitable for waters containing high concentrations of oxidizing or reducing materials or dissolved organic matter. However, it is not affected by buffering solutions or high concentrations of total salts.

2. Summary of method

Boron, when heated with 1,1′-dianthrimide in concentrated sulfuric acid, gives a colored complex (Ellis and others, 1949; Rainwater, 1959). The color change ranges from greenish yellow to blue. The reaction producing the blue color depends on the temperature and the duration of heating and on the concentrations of reagent and of boron. Maximum color development is achieved after the reaction has proceeded for 3 h at 90°C.

3. Interferences

3.1 Traces of moisture will precipitate the reagent and interfere in the determination; therefore, precautionary measures given in the procedure must be followed explicitly. Nitrate and bicarbonate interfere with color development and must be removed by volatilization as nitric acid and carbon dioxide in the presence of sulfuric acid. Organic matter in high concentrations chars and causes a discoloration of the complex, but this interference is easily recognized; small quantities of organic material cause no trouble. Some success in removal of the organic-material interference has been obtained by heating the sample in the presence of hydrogen peroxide for 1 to 2 h, but it is essential that all nascent oxygen be volatilized before the dianthrimide is added to the sample. When peroxide digestion is used, the final color complex should be compared with standard boron solutions similarly treated. Oxidizing and reducing constituents also interfere. Do not use glassware cleaned with chromic-sulfuric acid.

3.2 Some boric acid is probably volatilized during evaporation of the sample in the presence of sulfuric acid. Prolonged heating or temperatures higher than that recommended volatilizes an excessive amount of boron and decreases the sensitivity of the test. The loss of boron is proportional to the boron content of the sample or standard; hence, such loss in no way affects the linearity of the color development if the heating is uniform. Nonlinearity of the concentration-versus-absorbance curve can result from weak reagents. The standards in step 6.2 of the procedure act as a check on linearity of the reaction and suitability of the working reagent.

4. Apparatus

4.1 *Oven*, 90°C: Uniformity of temperature throughout the oven is imperative.

4.2 *Spectrometer*.

4.3 Refer to manufacturer's manual for optimizing instrumental parameters.

Wavelength .... 620 nm.

Using a Beckman Model B unit with 23-mm cells, the following data have been obtained:

Amount of boron *(μg)*	*Absorbance*
1.0	0.26
2.0	.52
3.0	1.30

Using a Coleman Model 55 unit with a 10-mm flow-through cell, the following data have been obtained:

Amount of boron *(μg)*	*Absorbance*
2.0	0.100
5.0	.250
10.0	.500
20.0	.950

5. Reagents

5.1 *Boron* standard solution I, 1.00 mL = 100 µg B: Dissolve 10 g $Na_2B_4O_7 \cdot 10H_2O$ in 50 mL demineralized water at 50°C to 60°C. Recrystallize by placing in refrigerator for several hours. Dry by removing the water with suction and washing with alcohol followed by ether. Do not dry in oven. Dissolve 0.8820 g in demineralized water and dilute to 1,000 mL. Store in plastic bottle.

5.2 *Boron* Standard solution II, 1.00 mL = 1.0 µg B: Dilute 10.0 mL boron standard solution I to 1,000 mL with demineralized water. Store in plastic bottle.

5.3 *1,1′-Dianthrimide* (or 1,1′-iminodianthraquinone) solution I, 200 mg per 50 mL concentrated H_2SO_4: Dissolve 200 mg 1,1′-dianthrimide in 50 mL concentrated H_2SO_4 (sp gr 1.84). The reagent is stable for a long period if the container is sealed and refrigerated. Store in teflon bottle.

5.4 1,1′-*Dianthrimide* solution II, (1 + 19): Dilute 1 volume of 1,1′-dianthrimide solution I with 19 volumes of concentrated H_2SO_4 (sp gr 1.84). The reagent is stable for a long period if the container is sealed and refrigerated. Store in teflon bottle.

5.5 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 Pipet a volume of sample containing less than 5.0 µg B (5.00 mL max) into an absorption cell or pyrex test tube and adjust volume to 5.0 mL.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each 5.0 mL.

6.3 Cautiously add 1.0 mL concentrated H_2SO_4 and mix thoroughly by swirling the contents of the cell. Use of a test tube vibrating mixer is helpful.

6.4 Evaporate for at least 40 h in oven at 90°C. At the end of the evaporation, the solution volume should be between 1.0 and 0.5 mL.

6.5 Add 5.0 mL 1,1′-dianthrimide solution II and mix well by swirling.

6.6 Heat in oven for 3 h at 90°C.

6.7 Immediately after cooling, and with caution, add 10.0 mL concentrated H_2SO_4. Mix thoroughly but carefully with a stirring rod or test tube mixer. The contents must not be separated on the upper walls of the cell.

6.8 Remove all traces of acid, reagent, and fingerprints from the exterior surface of the cell, and determine the absorbance of each sample and standard against the blank. Alternatively, transfer contents of test tube into the 10-mm flow-through cell.

7. Calculations

7.1 Determine the micrograms boron in each sample from a plot of absorbances of standards.

7.2 Determine the boron concentration in micrograms per liter as follows:

$$\mathrm{B}\ (\mu g/L) = \frac{1{,}000}{\text{mL sample}} \times \mu g \text{ B in sample.}$$

8. Report

Report boron, dissolved (01020), concentrations as follows: less than 100 µg/L, nearest 10 µg/L; 100 µg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 20 to 550 µg/L may be expressed as follows:

$$S_T = 0.079X + 17.11$$

where

S_T = overall precision, micrograms per liter, and
X = concentration of boron, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (µg/L)*	*Relative deviation (percent)*
4	40	68
4	530	12

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 54.

Ellis, G. H., Zook, E. G., and Baudisch, Oskar, 1949, Colorimetric determination of boron using 1,1′-dianthrimide: Analytical Chemistry, v. 21, p. 1345.

Rainwater, F. H., 1959, Determination of boron with 1,1′-dianthrimide: American Water Works Association Journal, v. 51. p. 1046.

Boron, recoverable from bottom material, colorimetric, carminic acid (I–5111–78)

Parameter and Code: Boron, recoverable from bottom material, dry wt ($\mu g/g$ as B): 01023

1. Application

1.1 This method may be used to analyze bottom material containing at least 10 $\mu g/g$ of boron. If the sample solution prepared for analysis (Method I–5485) contains more than 2,500 μg boron, the aliquot taken for analysis must first be diluted. Prepared sample solutions containing less than 400 $\mu g/L$ boron must first be concentrated by evaporation from a strongly alkaline solution to prevent the loss of volatile boric acid, or a larger portion of bottom material sample must be digested.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

2.1 In acid solution, boron forms a colored complex with carmine. The color change is from red to blue. Maximum color development requires approximately 1 h, but the color intensity decreases thereafter. The fading is proportional to the boron content and is therefore of little consequence if standards are run simultaneously with the sample. Fading is rather rapid, however, with approximately 25 percent or more reduction in intensity between 1.0 and 2.0 h.

2.2 Additional information on the principle of the determination is given by Hatcher and Wilcox (1950).

3. Interferences

Strong ammonia fumes affect the reagent. Silica interferes, but the interference is independent of the silica concentration and dependent on the boron concentration. With 500 $\mu g/L$ of boron the determined value may be about 20 percent high in the presence of up to 30 mg/L of silica. At lower boron levels, the effect is variable. Fluoride, nitrate, and phosphate contribute some interference, but to a lesser degree.

4. Apparatus

4.1 *Steam bath.*

4.2 *Spectrometer.*

4.3 Refer to manufacturer's manual for optimizing instrumental parameters:

Wavelength -- 600 nm.

Using a 10-mm cell, the following data have been obtained:

Amount of boron (μg)	*Absorbance*
10	0.098
20	.195
30	.301

5. Reagents

5.1 *Boron* standard solution I, 1.00 mL = 100 μg B: Dissolve approx 10 g $Na_2B_4O_7 \cdot 10H_2O$ in demineralized water at 50°C to 60°C. Recrystallize by placing in a refrigerator for several hours. Dry by removing water with suction and washing with alcohol followed by ether. Do not dry in oven. Dissolve 0.8820 g in demineralized water and dilute to 1,000 mL. Store in plastic bottle.

5.2 *Boron* standard solution II, 1.00 mL = 10.0 μg B: Dilute 100.0 mL boron standard solution I to 1,000 mL with demineralized water. Store in plastic bottle.

5.3 *Carmine* solution, 0.5 g/L in concentrated H_2SO_4. Suspend 0.50 g carmine in 1 L concentrated H_2SO_4 (sp gr 1.84) and mix with a mechanical stirrer until solution is complete. The stain certified by the Biological Stain Commission of the American Chemical Society has been used satisfactorily.

5.4 *Hydrochloric acid,* concentrated (sp gr 1.19).

5.5 *Hydrochloric acid,* 0.6*M*: Mix 50 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.6 *Sodium hydroxide,* 0.5*M*: Dissolve 2 g NaOH in demineralized water and dilute to 100 mL.

5.7 *Sulfuric acid,* concentrated (sp gr 1.84).

6. Procedure

6.1 Pipet a volume of prepared sample solution (Method I–5485) containing between 0.8 and 20 μg B (2.00 mL maximum) into a 150-mL flask. If the prepared sample solution (Method I–5485) contains less than 400 μg/L B, pipet a 20-mL aliquot of sample concentrated as follows:

a. Pipet an accurately measured volume of prepared sample solution (Method I–5485) (100 mL maximum) into an evaporating dish. Include a blank with every group of samples.

b. Add 1 mL 0.5*M* NaOH.

c. Evaporate to dryness on a steam bath. Inasmuch as total boron is being determined, follow the evaporation with an ignition at 500°C to 550°C for 30 min to destroy organic matter.

d. Take up the residue, triturate in 5.00 mL 0.6*M* HCl with a rubber policeman, and centrifuge to obtain a clear solution.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 2.0 mL.

6.3 Add 2 drops concentrated HCl, 12 mL concentrated H_2SO_4, mix and allow to cool for at least 30 min.

6.4 Add 10 mL carmine solution, mix, and allow the solution to stand approx 1 h.

6.5 Determine the absorbances of the sample and standards against the blank and when necessary make corrections for water color.

7. Calculations

7.1 Determine the micrograms boron in the sample solution from a plot of absorbances of standards.

7.2 Determine the boron concentration in micrograms per gram in bottom material as follows:

$$B\ (\mu g/g) = \frac{\mu g\ B \text{ in sample} \times \text{mL of original digest}}{\text{wt sample in grams} \times \text{mL sample}}$$

7.3 When the concentration procedure described in 6.1a through 6.1d is followed, the value determined in 7.2 must be divided by the concentration factor.

8. Report

Report boron, recoverable from bottom material (01023), concentrations as follows: less than 100 μg/g, nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of the method is greater than 14 percent.

Reference

Hatcher, J. T., and Wilcox, L. V., 1950, Colorimetric determination of boron using carmine: Analytical Chemistry, v. 22, p. 567.

Boron, recoverable from bottom material, colorimetric, dianthrimide (I–5110–78)

Parameter and Code: Boron, recoverable from bottom material, dry wt (μg/g as B): 01023

1. Application

1.1 This method may be used to analyze samples of bottom material containing at least 10 μg/g of boron. If the sample solution prepared for analysis (Method I–5485) contains more than 250 μg boron, a portion of it must be diluted before analysis.

1.2 Bottom material samples must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

1.3 This method is not suitable for bottom material samples containing high concentrations of oxidizing or reducing materials or organic matter. However, it is not affected by buffering materials.

2. Summary of method

Boron, when heated with 1.1′-dianthrimide in concentrated sulfuric acid, gives a colored complex (Ellis and others, 1949; Rainwater, 1959). The color change ranges from greenish yellow to blue. The reaction producing the blue color depends on the temperature and duration of heating and the concentrations of reagent and of boron. Maximum color development is achieved after the reaction has proceeded for 3 h at 90°C.

3. Interferences

3.1 Traces of moisture will precipitate the reagent and interfere in the determination; therefore, precautionary measures given in the procedure must be followed explicitly. Nitrate and bicarbonate interfere with color development and must be removed by volatilization as nitric acid and carbon dioxide in the presence of sulfuric acid. Organic matter in high concentrations chars and causes a discoloration of the complex, but this interference is easily recognized; small quantities of organic material cause no trouble. Some success in removal of the organic-material interference has been obtained by heating the sample in the presence of hydrogen peroxide for 1 to 2 h, but it is essential that all nascent oxygen be volatilized before the dianthrimide is added to the sample. When peroxide digestion is used, the final color complex should be compared with standard boron solutions similarly treated. Oxidizing and reducing constituents also interfere. Do not use glassware cleaned with chromic-sulfuric acid.

3.2 Some boric acid is probably volatilized during evaporation of the sample in the presence of sulfuric acid. Prolonged heating or temperatures higher than that recommended volatilizes an excessive amount of boron and decreases the sensitivity of the test. The loss of boron is proportional to the boron content of the sample or standard; hence, such loss in no way affects the linearity of the color development if the heating is uniform. Nonlinearity of the concentration-versus-absorbance curve can result from weak reagents. The standards in step 6.2 of the procedure act as a check on linearity of the reaction and suitability of the working reagent.

4. Apparatus

4.1 *Oven*, 90°C: Uniformity of temperature throughout the oven is imperative.

4.2 *Spectrometer*.

4.3 Refer to manufacturer's manual for optimizing instrumental parameters:

Wavelength	**620 nm.**

Using a Beckman Model B unit with 23-mm cells, the following data have been obtained:

Amount of boron (*µg*)	*Absorbance*
1.0	0.26
2.0	.52
5.0	1.30

Using a Coleman Model 55 unit with a 10-mm flow-through cell, the following data have been obtained:

Amount of boron (*µg*)	*Absorbance*
2.0	0.100
5.0	.250
10.0	.500
20.0	.950

5. Reagents

5.1 *Boron* standard solution I, 1.00 mL = 100 µg B: Dissolve 10 g $Na_2B_4O_7 \cdot 10H_2O$ in 50 mL demineralized water at 50°C to 60°C. Recrystallize by placing in refrigerator for several hours. Dry by removing the water with suction and washing with alcohol followed by ether. Do not dry in oven. Dissolve 0.8820 g in demineralized water and dilute to 1,000 mL. Store in plastic bottle.

5.2 *Boron* standard solution II, 1.00 mL = 1.0 µg B: Dilute 10.0 mL boron standard solution I to 1,000 mL with demineralized water. Store in plastic bottle.

5.3 *1.1′-Dianthrimide* (or 1.1′-iminodianthraquinone) solution I, 200 mg per 50 mL concentrated H_2SO_4: Dissolve 200 mg 1,1′-dianthrimide in 50 mL concentrated H_2SO_4 (sp gr 1.84). The reagent is stable for a long period if the container is sealed and refrigerated. Store in telfon bottle.

5.4 *1.1′-Dianthrimide* solution II, (1 + 19): Dilute 1 volume of 1,1′-dianthrimide solution I with 19 volumes concentrated H_2SO_4 (sp gr 1.84). The reagent is stable for a long period if the container is sealed and refrigerated. Store in teflon bottle.

5.5 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 Pipet a volume of prepared sample solution (Method I–5485) containing less than 5.0 µg B (5.00 mL maximum) into an absorption cell, and adjust volume to 5.0 mL.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to 5.0 mL.

6.3 Cautiously add 1.0 mL concentrated H_2SO_4 and mix thoroughly by swirling the contents of the cell. Use of a test tube vibrating mixer is helpful.

6.4 Evaporate for at least 40 h in an oven at 90°C. At the end of the evaporation, the solution volume should be between 1.0 and 0.5 mL.

6.5 Add 5.0 mL 1,1′-dianthrimide solution II and mix well by swirling.

6.6 Heat in oven for 3 h at 90°C.

6.7 Immediately after cooling, and with caution, add 10.0 mL concentrated H_2SO_4. Mix thoroughly but carefully with a stirring rod or test tube mixer. The contents must not be spattered on the upper walls of the cell.

6.8 Remove all traces of acid, reagent, and fingerprints from the exterior surface of the cell, and determine the absorbance of each sample and standard against the blank.

7. Calculations

7.1 Determine micrograms boron in each sample solution from a plot of absorbances of standards.

7.2 Determine the boron concentrations in micrograms per gram in bottom material as follows:

$$\text{B } (\mu g/g) = \frac{\mu g \text{ B in sample} \times \text{mL of original digest}}{\text{wt sample (g)} \times \text{mL sample}}$$

8. Report

Report boron, recoverable from bottom material (01023), concentrations as follows: less than 100 µg/g, nearest 10 µg/g; 100 µg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of the method is greater than 68 percent in the lower portion of the analytical range and greater than 12 percent in the middle portion of the analytical range.

References

Ellis, G. H., Zook, E. G., and Baudisch, Oskar, 1949, Colorimetric determination of boron using 1.1′-dianthrimide: Analytical Chemistry, v. 21, p. 1345.

Rainwater, F. H., 1959, Determination of boron with 1.1′-dianthrimide: American Water Works Association Journal, v. 51, p. 1046.

Boron, total in bottom material, colorimetric, fusion, dianthrimide (I–5114–78)

Parameter and Code: Boron, total in bottom material, dry wt (µg/g as B): none assigned

1. Application

This method may be used to analyze samples of bottom material containing at least 10 µg/g of boron. If the sample solution prepared for analysis contains more than 5 µg boron, it must first be diluted.

2. Summary of method

2.1 A sample of sieved (2.0-mm) air-dried bottom material, ground to pass a 0.16-mm (100-mesh) sieve, is fused with a 1:1 mixture of potassium and sodium carbonates. The cooled melt is dissolved in dilute sulfuric acid and diluted to volume, and an aliquot of the resulting solution is analyzed by the dianthrimide colorimetric method (Method I–1110). Fusion of the sample with carbonate flux ensures conversion of all boron-containing compounds to soluble forms.

2.2 This method is essentially the same as that given by Berger and Truo (1944), Dible and others (1954), and Jackson (1958).

3. Interferences

3.1 See Method I–1110.

3.2 Silica, when present in concentrations exceeding 500 mg/L in the final solution prepared for analysis (paragraph 6.7), interferes with the dianthrimide colorimetric method for determining boron. When this is the case, a further dilution of the solution is necessary, or a smaller portion of the sample must be taken for analysis.

4. Apparatus

4.1 *Ball mill.*

4.2 *Burner*, meeker type, or equivalent.

4.3 *Crucible*, platinum, 20-mL capacity.

4.4 *Tongs*, crucible, platinum-tipped.

4.5 See Method I–1110 for additional items of equipment required for this determination.

5. Reagents

5.1 K_2CO_3/Na_2CO_3 flux, (1 + 1): Thoroughly mix 50 g of dry K_2CO_3 with an equal weight of dry Na_2CO_3.

5.2 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 Weigh, to the nearest milligram, 0.1 g of sample and transfer to a platinum crucible.

6.2 Add 1.5 g dry K_2CO_3/Na_2CO_3 flux to the crucible and mix sample and flux thoroughly with a polyethylene rod.

6.3 Heat the mixture over a meeker burner until completely molten. Continue heating at a full red heat for 10 min.

6.4 Remove the crucible containing the melt from the burner with a pair of tongs, and while the melt cools, rotate the crucible to spread the melt in a thin layer around the inside of the crucible.

6.5 When cool, invert the crucible and tap the melt into a 250-mL beaker. If any melt remains in the crucible, carefully police it into the beaker.

6.6 Add 50 mL demineralized water to the melt in the beaker; add concentrated H_2SO_4 drop by drop until the melt has completely dissolved. Use a minimum amount of H_2SO_4—usually 5 mL is sufficient to effect complete solution of the melt.

6.7 Quantitatively transfer the dissolved melt to a 100-mL volumetric flask and dilute to the mark with demineralized water.

6.8 Analyze this sample solution according to Method I–1110, beginning with paragraph 6.1.

7. Calculations

7.1 Determine micrograms of boron in the sample solution from a plot of absorbances of standards.

7.2 Determine the boron concentration in micrograms per gram in bottom material as follows:

$$B\ (\mu g/g) = \frac{\mu g\ B \text{ in sample} \times 100}{\text{wt sample (g)} \times \text{mL sample}}$$

8. Report

Report boron, total in bottom material, concentrations as follows: less than 100 μg/g, nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of the method is greater than 68 percent in the lower portion of the analytical range and greater than 12 percent in the middle portion of the analytical range.

References

Berger, K. C., and Truog, Emil, 1944, Boron tests and determination for soils and plants: Soil Science, v. 57, p. 25–36.

Dible, W. T., Truog, Emil, and Berger, K. C., 1954, Boron determination in soils and plants; simplified curcumin procedure: Analytical Chemistry, v. 26, p. 418–421.

Jackson, M. L., 1958, Soil chemical analysis: New York, Prentice-Hall, p. 384–385.

Boron, total recoverable, colorimetric, carminic acid (I–3111–78)

Parameter and Code: Boron, total recoverable (μg/L as B): 01022

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 500 μg/L of boron. The optimum range for the method on undiluted or unconcentrated samples is from 500 to 10,000 μg/L. Samples containing less than 500 μg/L must first be concentrated by evaporation from strongly alkaline solution to prevent the loss of volatile boric acid.

1.2 Samples must first undergo a preliminary digestion-solubilization by Method I–3485.

2. Summary of method

2.1 In acid solution, boron forms a colored complex with carmine. The color change is from red to blue. Maximum color development requires approximately 1 h, but the color intensity decreases thereafter. The fading is proportional to the boron content and is therefore of little consequence if standards are run simultaneously with the sample. Fading is rather rapid, however, with approx 25 percent or more reduction in intensity between 1.0 and 2.0 h.

2.2 Additional information on the principle of the determination is given by Hatcher and Wilcox (1950).

3. Interferences

Strong ammonia fumes affect the reagent. Silica interferes, but the interference is independent of the silica concentration and dependent on the boron concentration. With 500 μg/L of boron the determined value may be about 20 percent high in the presence of up to 30 mg/L of silica. At lower boron levels, the effect is variable. Fluoride, nitrate, and phosphate contribute some interference, but to a lesser degree.

4. Apparatus

4.1 *Steam bath.*

4.2 *Spectrometer,* for use at 600 nm.

4.3 Refer to the manufacturer's manual to optimize output of the instrument for the following parameter:

Wavelength -- 600 nm.

4.4 Using a 10-mm cell, the following data have been obtained:

Amount of boron (μg)	*Absorbance*
10	0.098
20	.195
30	.301

5. Reagents

5.1 *Boron* standard solution I, 1.00 mL = 100 μg B: Dissolve approx 10 g $Na_2B_4O_7 \cdot 10H_2O$ in demineralized water at 50°C to 60°C. Recrystallize by placing in a refrigerator for several hours. Dry by removing water with suction and washing with alcohol followed by ether. Do not dry in oven. Dissolve 0.8820 g in demineralized water and dilute to 1,000 mL. Store in a plastic bottle.

5.2 *Boron* standard solution II, 1.00 mL = 10.0 μg B: Dilute 100.0 mL boron standard solution I to 1,000 mL with demineralized water. Store in a plastic bottle.

5.3 *Carmine* solution, 0.5 g/L in concentrated H_2SO_4: Suspend 0.50 g carmine in 1 L concentrated H_2SO_4 (sp gr 1.84) and mix with a mechanical stirrer until solution is complete. The stain certified by the Biological Stain Commission of the American Chemical Society has been used satisfactorily.

5.4 *Hydrochloric acid,* concentrated (sp gr 1.19).

5.5 *Hydrochloric acid,* 0.6*M*: Mix 50 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.6 *Sodium hydroxide,* 0.5*M*: Dissolve 2 g NaOH in demineralized water and dilute to 100 mL.

5.7 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 Pipet a volume of sample containing between 1.0 and 10 μg B (2.00 mL maximum) into a 150-mL flask. If the sample contains less than 500 g/L B, take a 2.00-mL aliquot of sample concentrated as follows:

a. Pipet an accurately measured volume of sample (100 mL maximum) into an evaporating dish. Pipet 100 mL of distilled water into a separate evaporating dish as a blank.

b. Add 1 mL 0.5*M* NaOH to sample and blank.

c. Evaporate to dryness on a steam bath.

d. Follow evaporation with an ignition at 500°C to 550°C for 0.5 h in order to destroy organic matter.

e. Take up the residue, triturate in 5.00 mL 0.6*M* HCl with a rubber policeman, and centrifuge to obtain a clear solution.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 2.0 mL.

6.3 Add 2 drops concentrated HCl and 12 mL concentrated H_2SO_4, mix, and allow to cool for at least 30 min.

6.4 Add 10 mL carmine solution, mix, and allow the solution to stand approx 1 h.

6.5 Determine the absorbances of the sample and standards against the blank and when necessary make corrections for water color.

7. Calculations

7.1 Determine the micrograms boron in the sample from a plot of absorbances of standards.

7.2 Determine the boron concentration in micrograms per liter as follows:

$$B\ (\mu g/L) = \frac{1{,}000}{\text{mL sample}} \times \mu g\ B \text{ in sample.}$$

8. Report

7.3 When the concentration procedure described in 6.1a through 6.1e is followed, the value determined in 7.2 must be divided by the concentration factor.

Report boron, total recoverable (01022), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of the method is greater than 78 percent at 72 μg/L and greater than 14 percent at 522 μg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigation of the United States Geological Survey, book 5, chapter A1, p. 56.

Hatcher, J. T., and Wilcox, L. V., 1950. Colorimetric determination of boron using carmine: Analytical Chemistry, V. 22, p. 567.

Boron, total recoverable, colorimetric, curcumin (I–3112–78)

Parameter and Code: Boron, total recoverable (μg/L as B): 01022

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing at least 100 μg/L of boron. The optimum range for the method on undiluted or unconcentrated samples is from 100 to 1,000 μg/L.

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of method

2.1 When a sample of water containing boron is acidified and evaporated in the presence of curcumin, a red-colored product called rosocyanine is formed. The rosocyanine is extracted into a suitable solvent and the red color, which has a maximum absorbance at 540 nm, is measured spectrometrically.

2.2 The method is identical to that found in "Standard Methods for the Examination of Water and Wastewater" (1976).

3. Interferences

3.1 Nitrate-nitrogen concentrations greater than 20 mg/L interfere.

3.2 Significantly high results are possible when the total of calcium and magnesium hardness exceeds 100 mg/L as $CaCO_3$. Moderate hardness levels also can cause a considerable percentage error in the low boron range. The interference arises from the insolubility of the hardness salts in 95-percent ethanol and consequent turbidity in the final solution. Filter the final solution or pass the original sample through a column of strongly acidic cation-exchange resin in the hydrogen form to remove the interfering cations. The latter procedure enables application of the method to waters and effluents of high hardness or solids content.

4. Apparatus

4.1 *Evaporating dish*, 100- to 150-mL capacity, of Vycor glass, platinum, or other suitable material.

4.2 *Ion-exchange column*, 50-cm long by 1.3-cm diameter.

4.3 *Spectrometer*, for use at 540 nm, and cells with a minimum light path length of 1 cm.

4.4 Refer to manufacturer's manual for optimizing instrumental parameters.

4.5 *Water bath*, 55°C ± 2°C.

5. Reagents

5.1 *Boron* standard solution I, 1.00 mL = 100 μg B: Dissolve approx 10 g $Na_2B_4O_7 \cdot 10H_2O$ in demineralized water at 50°C to 60°C. Recrystallize by placing in a refrigerator for several hours. Dry by removing water with suction and washing with alcohol followed by ether. Do not dry in oven. Dissolve 0.8820 g in demineralized water and dilute to 1,000 mL. Store in a plastic bottle.

5.2 *Boron* standard solution II, 1.00 L = 1.00 μg B: Dilute 10.00 mL boron standard solution I to 1,000 mL with demineralized water. Store in a plastic bottle.

5.3 *Cation-exchange resin:* Load the column with a strongly acidic cation-exchange resin. Backwash the column with distilled water to remove entrained air bubbles. Henceforth, make certain the resin remains covered with liquid at all times. Pass 50 mL 2*M* HCl through the column at a rate of 0.2 mL/min of acid per milliliter of resin in column and then wash it free of acid with distilled water. The frequency of regeneration depends on the mineral content of the samples.

5.4 *Curcumin* reagent: Dissolve 40 mg finely ground curcumin (Eastman No. 1179 or equivalent) and 5.0 g oxalic acid in 80 mL 95-percent ethanol. Add 4.2 mL concentrated hydrochloric acid (sp gr 1.19) and dilute to 100 mL with ethanol. The reagent is stable for several days if stored in a refrigerator.

5.5 *Ethanol*, 95 percent.

5.6 *Hydrochloric acid, 2M*: Mix 166 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

6. Procedure

Precautions: Exercise close control of such variables as volumes and concentrations of samples, standard and reagents as well as time and temperature of drying. Use evaporating dishes identical in shape, size, and composition to insure equal evaporation time. Increasing the time of evaporation results in intensification of the resulting color.

6.1 For samples containing high hardness (100 mg/L $CaCO_3$ or more) proceed as follows (NOTE 1): Pipet 25 mL of a well-mixed sample, or a smaller sample of known high boron content diluted to 25 mL, onto the resin column. Adjust the rate of flow through the column to about 2 drops per second and collect the effluent in a 50-mL volumetric flask. Wash the column with small portions of distilled water until the flask is full to the mark and mix.

NOTE 1. For samples containing less than 100 mg/L hardness as $CaCO_3$, start with paragraph 6.2.

6.2 Pipet 1.00 mL of a well mixed sample containing less than 1.0 μg B into an evaporating dish (NOTE 2).

NOTE 2. If the sample contains more than 1,000 μg/L boron, make an appropriate dilution with boron-free distilled water, so that a 1.00-mL portion contains approx 0.50 μg boron.

6.3 Prepare in evaporating dishes a blank and sufficient standards (1.0 μg B maximum) and adjust the volume of each to exactly 1.0 mL with demineralized water.

6.4 Add 4.0 mL curcumin reagent to each and swirl each dish gently to mix contents thoroughly.

6.5 Float the dishes on a water bath set at 55°C ± 2°C and let them remain for 80 min, a time usually sufficient for complete drying and removal of HCl. Keep drying time constant for standards and samples.

6.6 After the dishes cool to room temperature, add 10.0 mL 95-percent ethanol to each dish, stirring gently with a polyethylene rod to insure complete dissolution of the red-colored product.

6.7 Wash the contents of each dish into a 25-mL volumetric flask using 95 percent ethanol and adjust to volume with ethanol. Mix thoroughly by repeated inversion (NOTE 3).

NOTE 3. If the final sample solution is turbid, filter through No. 30 Whatman filter paper or equivalent.

6.8 Determine the absorbance of the sample and standards against the blank. Complete all absorbance readings within 1 h of drying the samples.

7. Calculations

7.1 Determine the micrograms boron in the sample from a plot of absorbances of standards.

7.2 Determine the boron concentration in micrograms per liter as follows:

$$B\ (\mu g/L) = 1{,}000 \times \mu g\ B \text{ in sample.}$$

7.3 If the sample was diluted prior to analysis (see 6.2), multiply the concentration of boron found in paragraph 7.2 by the dilution factor.

8. Report

Report boron, total recoverable (01022), concentrations as follows: less than 1,000 μg/L, nearest 100 μg/L; 1,000 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of the method is greater than 68 percent at 87 μg/L and greater than 13 percent at 386 μg/L.

References

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater [14th ed.]: Washington, D.C., American Public Health Association, p. 287.

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 13.

Boron, total recoverable, colorimetric, dianthrimide (I–3110–78)

Parameter and Code: Boron, total recoverable: (μg/L as B): 01022

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing between 20 and 1,000 μg/L of boron. Sample solutions containing more than 1,000 μg/L must first be diluted.

1.2 Water-suspended sediment mixtures may be analyzed by this method after preliminary digestion-solubilization by Method I–3485.

1.3 This method is not suitable for waters containing high concentrations of oxidizing or reducing materials or dissolved organic matter. However, it is not affected by buffering solutions or high concentrations of total salts.

2. Summary of method

Boron, when heated with 1,1′-dianthrimide in concentrated sulfuric acid, gives a colored complex (Ellis and others; 1949; Rainwater, 1959). The color change ranges from greenish yellow to blue. The reaction producing the blue color depends on the temperature and duration of heating and the concentrations of reagent and of boron. Maximum color development is achieved after the reaction has proceeded for 3 h at 90°C.

3. Interferences

3.1 Traces of moisture will precipitate the reagent and interfere in the determination; therefore, precautionary measures given in the procedure must be followed explicitly. Nitrate and bicarbonate interfere with color development, and must be removed by volatilization as nitric acid and carbon dioxide in the presence of sulfuric acid. Organic matter in high concentrations chars and causes a discoloration of the complex, but this interference is easily recognized; small quantities of organic material cause no trouble. Some success in removal of the organic-material interference has been obtained by heating the sample in the presence of hydrogen peroxide for 1 to 2 h, but it is essential that all nascent oxygen be volatilized before the dianthrimide is added to the sample. When peroxide digestion is used, the final color complex should be compared with standard boron solutions similarly treated. Oxidizing and reducing constituents also interfere. Do not use glassware cleaned with chromic-sulfuric acid.

3.2 Some boric acid is probably volatilized during evaporation of the sample in the presence of sulfuric acid. Prolonged heating or temperatures higher than that recommended volatilize an excessive amount of boron and decrease the sensitivity of the test. The loss of boron is proportional to the boron content of the sample or standard; hence, such loss in no way affects the linearity of the color development if the heating is uniform. Nonlinearity of the concentration-versus-absorbance curve can result from weak reagents. The standards in step 6.2 of the procedure act as a check on linearity of the reaction and suitability of the working reagent.

4. Apparatus

4.1 *Oven*, 90°C: Uniformity of temperature throughout the oven is imperative.

4.2 *Spectrometer*.

4.3 Refer to manufacturer's manual for optimizing instrumental parameters:

Wavelength ---------------------------------- 620 nm.

Using a Beckman Model B unit with 23-mm cells, the following data have been obtained:

Amount of boron (μg)	*Absorbance*
1.0	0.26
2.0	.52
5.0	1.30

Using a Coleman Model 55 unit with a 10-mm flow-through cell, the following data have been obtained:

Amount of boron (μg)	*Absorbance*
2.0	0.100
5.0	.250
10.0	.500
20.0	.950

5. Reagents

5.1 *Boron* standard solution I, 1.00 mL = 100 μg B: Dissolve 10 g $Na_2B_4O_7 \cdot 10H_2O$ in 50 mL demineralized water at 50°C to 60°C. Recrystallize by placing in refrigerator for several hours. Dry by removing the water with suction and washing with alcohol followed by ether. Do not dry in oven. Dissolve 0.8820 g in demineralized water and dilute to 1,000 mL. Store in plastic bottle.

5.2 *Boron* standard solution II, 1.00 mL = 1.0 μg B: Dilute 10.0 mL boron standard solution I to 1,000 mL with demineralized water. Store in plastic bottle.

5.3 *1,1′-Dianthrimide* (or 1,1′-iminodianthraquinone) solution I, 200 mg per 50 mL concentrated H_2SO_4: Dissolve 200 mg 1,1′-dianthrimide in 50 mL concentrated H_2SO_4 (sp gr 1.84). The reagent is stable for a long period if the container is sealed and refrigerated. Store in teflon bottle.

5.4 *1,1′-Dianthrimide* solution II, (1 + 19): Dilute 1 volume of 1,1′-dianthrimide solution I with 19 volumes of concentrated H_2SO_4 (sp gr 1.84). The reagent is stable for a long period if the container is sealed and refrigerated. Store in teflon bottle.

5.5 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 Pipet a volume of sample containing less than 5.0 μg B (5.00 mL max) into an absorption cell or pyrex test tube, and adjust volume to 5.0 mL.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to 5.0 mL.

6.3 Cautiously add 1.0 mL concentrated H_2SO_4 and mix thoroughly by swirling the contents of the cell. Use of a test tube vibrating mixer is helpful.

6.4 Evaporate for at least 40 h in an oven at 90°C. At the end of the evaporation, the solution volume should be between 1.0 and 0.5 mL.

6.5 Add 5.0 mL 1,1′-dianthrimide solution II and mix well by swirling.

6.6 Heat in oven for 3 h at 90°C.

6.7 Immediately after cooling, and with caution, add 10.0 mL concentrated H_2SO_4. Mix thoroughly but carefully with a stirring rod or test tube mixer. The contents must not be spattered on the upper walls of the cell.

6.8 Remove all traces of acid, reagent, and fingerprints from the exterior surface of the cell, and determine the absorbance of each sample and standard against the blank. Alternatively, transfer contents of test tube into the 10-mm flow-through cell.

7. Calculations

7.1 Determine the micrograms boron in each sample from a plot of absorbances of standards.

7.2 Determine the boron concentration in micrograms per liter as follows:

$$\text{B } (\mu\text{g/L}) = \frac{1{,}000}{\text{mL sample}} \times \mu\text{g B in sample.}$$

8. Report

Report boron, total recoverable (01022), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of the method is greater than 68 percent at 40 μg/L and greater than 12 percent at 530 μg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 54.

Ellis, G. H., Zook, E. G., and Baudisch, Oskar, 1949, Colorimetric determination of boron using 1,1′-dianthrimide: Analytical Chemistry, v. 21, p. 1345.

Rainwater, F. H., 1959, Determination of boron with 1,1′-dianthrimide: American Water Works Association Journal, v. 51, p. 1046.

Bromide, dissolved, colorimetric, catalytic oxidation (I–1127–78)

Parameter and Code: Bromide, dissolved (mg/L as Br): 71870

1. Application

This method is applicable to natural waters containing from 0.01 to 0.10 mg/L of bromide. Samples containing more than 0.10 mg/L must first be diluted. Samples containing more than 1.0 mg/L should be analyzed by the hypochlorite oxidation titrimetric method (Method I–1125).

2. Summary of method

2.1 The method is based on the catalytic effect of bromide on the oxidation of iodide or iodine to iodate by potassium permanganate in acid solution. Consecutive reactions occur: (1) rapid oxidation of iodide to iodine and (2) slow oxidation of iodine to iodate. Traces of bromide catalytically promote the latter reaction, and at a given temperature and for a given reaction time, the extent of oxidation is directly proportional to the concentration of bromide. The reaction is stopped by extracting the unreacted iodine with carbon tetrachloride. Bromide concentration is then determined indirectly by measuring the absorbance of the carbon tetrachloride extract (Fishman and Skougstad, 1963; Shiota and others, 1959).

2.2 This method is similar to that published by the American Society for Testing and Materials (1976).

3. Interferences

Interference occurs if the following concentrations are exceeded: iodide, 10 mg/L; silver, 500 μg/L; zinc, 1,000 μg/L; manganese, 1,000 μg/L; or ferric iron, 500 μg/L. Chlorine, when present, must be removed by boiling. Other ions commonly occurring in water do not interfere.

4. Apparatus

4.1 *Separatory funnels*, 125-mL capacity with teflon stopcocks. These must be thoroughly rinsed with dilute HCl before each use.

4.2 *Spectrometer*.

4.3 Refer to manufacturer's manual for optimizing instrumental parameters:

Wavelength .... 515 nm.

Using a Beckman Model B unit with 10-mm cells, the following data have been obtained:

Bromide (mg)	*Ratio of sample absorbance to control absorbance*
0.0000	1.000
.0002	.593
.0004	.381
.0006	.272
.0008	.190
.0010	.140

Using a Coleman Model 55 Unit with a 10-mm flow-through cell, the following data have been obtained:

Bromide (mg)	*Ratio of sample absorbance to control absorbance*
0.0000	1.000
.0005	.332
.0010	.141
.0020	.035

5. Reagents

5.1 *Bromide* standard solution I, 1.00 mL = 0.100 mg Br^{-1}: Dissolve 0.149 g KBr, dried overnight over concentrated H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.2 *Bromide* standard solution II, 1.00 mL = 0.0001 mg Br^{-1}: Dilute 1.00 mL bromide standard solution I to 1,000 mL with demineralized water.

5.3 *Carbon tetrachloride*, reagent-grade.

5.4 *Potassium iodide* solution, 1.31 g/L: Dissolve 1.31 g KI dried overnight over concentrated H_2SO_4, in demineralized water and add 350 mL concentrated H_2SO_4. Dilute to 1,000 mL with demineralized water. Store in a dark bottle. Once iodine crystals begin to form, a fresh solution must be prepared.

5.5 *Potassium permanganate* solution, 0.04*M*: Dissolve 6.32 g $KMnO_4$ in demineralized water and dilute to 1 L. Allow to stand several days and decant if necessary. Store in a dark bottle.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.0010 mg bromide (10.0 mL max) into a 125-mL separatory funnel, and adjust the volume to 10.0 mL with demineralized water.

6.2 Prepare a demineralized-water blank to be used as a control, and sufficient standards containing less than 0.0010 mg bromide, and adjust the volume of each to 10.0 mL with demineralized water.

6.3 Add 1.0 mL potassium iodide solution.

6.4 Place all separatory funnels in an ice bath. Temperature control within the range 0.0°C to 0.2°C is imperative. Allow 30 to 45 min for samples to reach temperature equilibrium.

6.5 At zero time add 1.0 mL 0.04*M* potassium permanganate solution (temperature equilibrated) and mix thoroughly. Return separatory funnels to the ice bath immediately.

6.6 After exactly 10 min add 5.0 mL carbon tetrachloride. Shake for 10 to 15 sec. Withdraw the carbon tetrachloride layer into a 10-mm absorption cell.

6.7 Measure the absorbance at 515 nm, using carbon tetrachloride as a reference.

7. Calculations

7.1 Construct an analytical curve by plotting the ratio A_s/A_c against milligrams of Br^{-1} on semilog paper; A_s = absorbance of standard, and A_c = absorbance of control.

7.2 From the curve, determine the milligrams of Br^{-1} corresponding to the absorbance ratio obtained for each sample.

7.3 Determine the bromide concentration in milligrams per liter as follows:

$$Br^{-1}\ (mg/L) = \frac{1{,}000}{mL\ sample} \times mg\ Br^{-1}\ in\ sample.$$

8. Report

Report bromide, dissolved (71870), concentrations as follows: less than 0.1 mg/L, two decimals; 0.1 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
2 (65 replicates)	0.267	30
1 (single operator)	.020	4
1 (single operator)	.050	2
1 (single operator)	.100	3

References

American Society for Testing and Materials, 1976, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 326.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 60.

Fishman, M. J., and Skougstad, M. W., 1963, Indirect spectrophotometric determination of traces of bromide in water: Analytical Chemistry, v. 35, p. 146.

Shiota, M., Tusumi, S., and Iwasaki, I., 1959, Determination of bromide by its catalytic action: Nippon Kagaku Zasshi, v. 80, p. 753–757; Chemical Abstracts, v. 54, no. 19278d.

Chloride, dissolved, colorimetric, ferric thiocyanate (I–1187–78)

Parameter and Code: Chloride, dissolved: 00940

1. Application

1.1 This method may be used to determine dissolved chloride in samples containing from 0.1 to 10 mg/L of chloride ion. It is particularly useful for the analysis of low-dissolved-solids-content waters when low chloride concentrations must be determined accurately.

1.2 It is suitable for the analysis of acidic as well as fresh-water samples.

2. Summary of method

2.1 Chloride is determined by measurement of the color developed by the displacement of the thiocyanate ion from mercuric thiocyanate by chloride ion in the presence of ferric ion; an intensely colored ferric thiocyanate complex is formed:

$$2Cl^{-1} + Hg(SCN)_2 + 2Fe^{+3} \rightarrow HgCl_2 + 2Fe(SCN)^{+2}.$$

2.2 The color is stable for at least 2 h and is proportional to the chloride-ion concentration. The color has a maximum absorbance at 460 nm and is not extractable by organic solvents (ether or ethanol).

2.3 For additional information see American Society for Testing and Materials (ASTM) Method D 512–67, "Standard Methods of Testing for Chloride Ion in Water" (ASTM, 1976).

3. Interferences

Bromide, iodide, cyanide, thiosulfate, and nitrite interfere. Color, depending upon its spectral absorbance, may interfere with the photometric measurement.

4. Apparatus

4.1 *Spectrometer* for use at 460 nm; Beckman Model B, or equivalent.

With this instrument the following operating conditions have been used:

Wavelength	460 nm.
Cells	40 mm.
Phototube	Blue-sensitive.
Initial sensitivity setting	1.
Slit width (approx)	0.1 mm.

4.2 With these operating conditions the following absorbances have been observed:

Chloride (*mg*)	*Absorbance*
0.000	0.000
.050	.184
.100	.324
.150	.428
.200	.508
.250	.585

5. Reagents

5.1 *Chloride* standard solution I, 1.00 mL = 1.00 mg Cl^{-1}: Dissolve 1.648 g primary standard NaCl crystals, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Chloride* standard solution II, 1.00 mL = 0.010 mg Cl^{-1}: Dilute 5.0 mL of chloride standard solution I to 500.0 mL with demineralized water.

5.3 *Ferric ammonium sulfate* solution, 22.8 g/L: Dissolve 41.4 g of reagent-grade $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 570 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1 L with demineralized water.

5.4 *Mercuric thiocyanate* solution, 3 g/L: Dissolve 3 g reagent-grade mercuric thiocyanate in 1 L 95-percent ethanol (denatured alcohol formula No. 3A is also satisfactory). Stir for 1 h to saturate the solvent; allow undissolved thiocyanate to settle, then filter through a pyrex-wool plug or a 0.45 μm membrane filter. Store the colorless filtrate in a pyrex, No-Sol-Vit, or other good quality bottle.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.250 mg of Cl^{-1} (25.0 mL max) into a 50-mL beaker and adjust the volume to 25.0 mL with demineralized water.

6.2 Prepare a demineralized-water blank and at least five standards containing from 0.000 to 0.250 mg Cl^{-1} and adjust the volume of each to 25.0 mL.

6.3 Add 2.0 mL $FeNH_4(SO_4)_2$ solution and stir. The samples will be essentially colorless at this point.

6.4 Add 2.0 mL $Hg(SCN)_2$ solution and stir.

6.5 After at least 10 min, but within 2 h, read the absorbance of each standard and sample against the blank at 460 nm, and when necessary, make corrections for water color.

7. Calculations

7.1 Determine the milligrams chloride from a plot of absorbances of standards containing known amounts of Cl^{-1}.

7.2 Determine the chloride concentration in milligrams per liter as follows:

$$Cl^{-1}\ (\text{mg/L}) = \frac{1{,}000}{\text{mL sample}} \times \text{mg } Cl^{-1}.$$

8. Report

Report chloride, dissolved (00940), concentrations of less than 10 mg/L to the nearest 0.1 mg/L.

9. Precision

9.1 Data published by the American Society for Testing and Materials (1976) indicate the overall precision of the method to be

$$S_T = 0.056X - 0.002$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of Cl^{-1}, milligrams per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
6	1.4	33

References

American Society for Testing and Materials, 1976, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 274–275.

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 46.

Chloride, dissolved, colorimetric, ferric thiocyanate, automated (I–2187–78)

Parameter and Code: Chloride, dissolved (mg/L as Cl): 00940

1. Application

This method may be used to determine concentrations of chloride in surface, domestic, and industrial waters in the range of 10 to 100 mg/L or 0.1 to 10.0 mg/L. The latter range can be accomplished by interchanging the sample and diluent pump tubes.

2. Summary of method

This method is based on the displacement of thiocyanate from mercuric thiocyanate by chloride, and the subsequent reaction of the liberated thiocyanate ion with ferric ion to form the intensely colored complex $[Fe(SCN)]^{+2}$. The absorbance of this complex is then measured colorimetrically (O'Brien, 1962; Zall and others, 1956).

$$Hg(SCN)_2 + 2Cl^{-1} \rightarrow HgCl_2 + 2SCN^{-1},$$

$$SCN^{-1} + Fe^{+3} \rightarrow [Fe(SCN)]^{+2}.$$

3. Interferences

Bromide, iodide, cyanide, thiosulfate, and nitrite interfere.

4. Apparatus

Technicon AutoAnalyzer II, consisting of a sampler, proportioning pump, cartridge manifold, colorimeter, voltage stabilizer, recorder, and printer.

With this equipment the following operating conditions have been found satisfactory for the ranges from 10 to 100 mg/L and from 0.0 to 10.0 mg/L:

Absorption cell	15 mm.
Wavelength	480 nm.
Cam	60/h (6/1).

5. Reagents

5.1 *Chloride* standard solution I, 1.00 mL = 0.50 mg Cl^{-1}: Dissolve 0.8242 g primary standard NaCl crystals, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Chloride* working standards; Prepare a blank and 500 mL each of a series of chloride working standards by appropriate quantitative dilution of the chloride standard solution I, as follows:

Chloride standard solution (mL)	*Chloride concentration (mg/L)*
0.0	0.0
5.0	5.0
10.0	10.0
20.0	20.0
30.0	30.0
50.0	50.0
60.0	60.0
80.0	80.0
100.0	100.0

5.3 *Ferric nitrate* stock solution, 121 g/L: Dissolve 202 g $Fe(NO_3)_3 \cdot 9H_2O$ in approx 500 mL demineralized water. Add 225 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1 L. Filter and store in an amber-colored container.

5.4 *Mercuric thiocyanate* stock solution, 4.17 g/L in methanol: Dissolve 4.17 g $Hg(SCN)_2$ in 500 mL methanol, dilute to 1 L with methanol, and filter.

5.5 *Chloride* color reagent: Add 150 mL of ferric nitrate stock solution and 150 mL of mercuric thiocyanate stock solution to demineralized water and dilute to 1 L. Add 1 mL/L of Brij-35 solution. Use amber bottle for storage.

6. Procedure

6.1 Set up manifold (fig. 28).

6.2 Allow colorimeter and recorder to warm up for at least 30 min. Adjust baseline to read

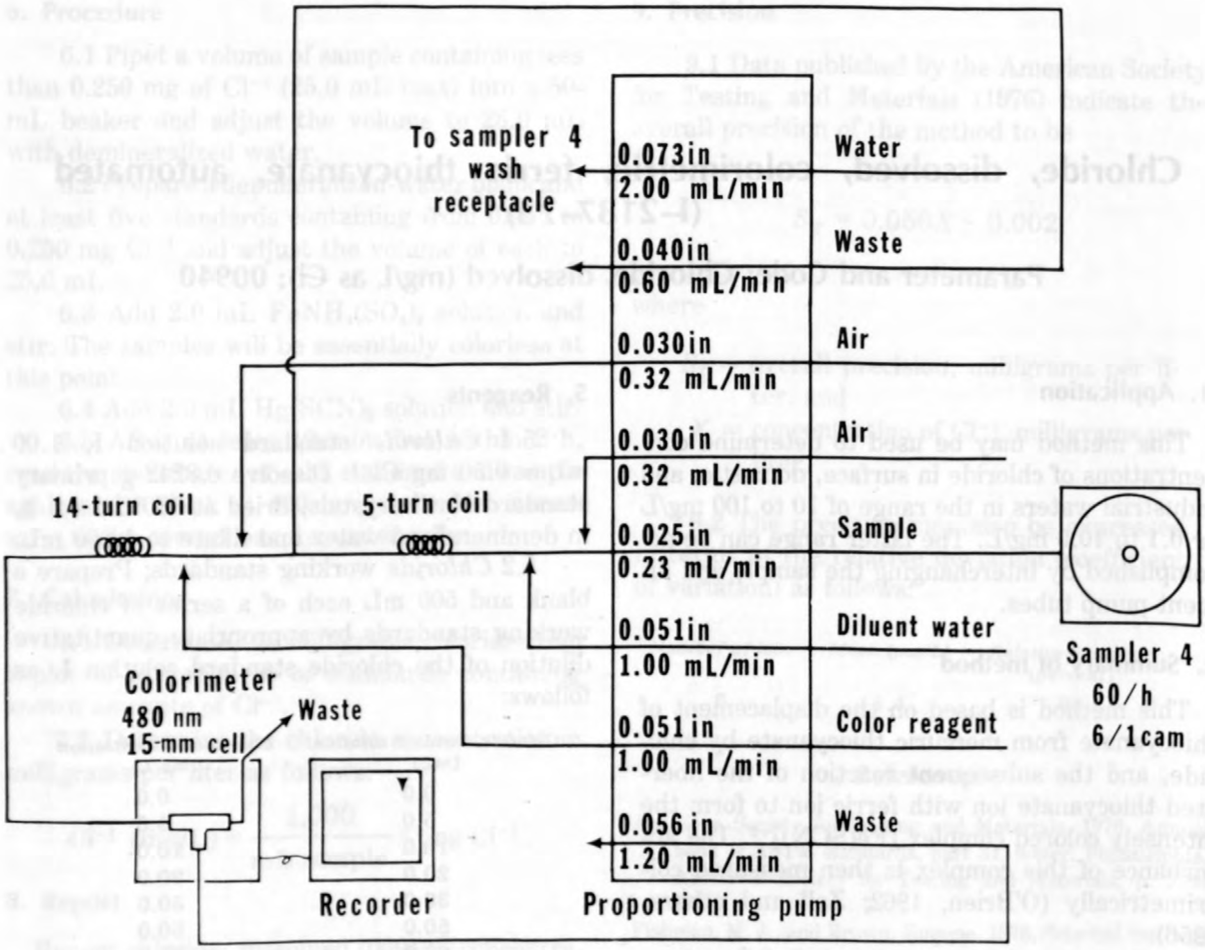


FIGURE 28.—Chloride manifold.

zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.3 Beginning with the most concentrated standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples (NOTE 1).

NOTE 1. The sample cups should remain sealed in their packages until just prior to use to avoid contamination. Handle cups carefully to avoid contamination from perspiration on hands.

6.4 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL Control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective chloride concentration.

7.2 Compute the chloride-ion concentration of each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report chloride, dissolved (00940), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 1.0 to 100 mg/L may be expressed as follows:

$$S_T = 0.057X - 0.25$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of chloride, milligrams per liter.

9.2 The statistical results may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
7	1.7	16
7	48	5

References

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 46.

O'Brien, J. E., 1962, Automatic analysis of chlorides in sewage: Wastes Engineering, v. 33, p. 67–672.

Zall, D. M., Fisher, D., and Garner, M. Q., 1956, Photometric determination of chlorides in water: Analytical Chemistry, v. 28, p. 1665–1668.

Chromium, dissolved, colorimetric, permanganate azide (I–1237–78)

Parameter and Code: Chromium, dissolved (μg/L as Cr): 01030

1. Application

1.1 This method may be used to analyze most natural waters containing from 50 to 4,000 μg/L of hexavalent plus tervalent chromium. Higher concentrations must be reduced by dilution.

2. Summary of method

2.1 All ionic forms of chromium are determined by oxidizing tervalent chromium to the hexavalent state with potassium permanganate prior to diphenylcarbazide color development. The excess oxidant is destroyed with sodium azide.

2.2 In acid solution, diphenylcarbazide and hexavalent chromium form a soluble red-violet product that absorbs light at 540 nm. The formula for the colored substance is not known. The pH of the reaction is not particularly critical; solutions differing in pH from 0.7 to 1.3 give identical colors. The color of the chromium-diphenylcarbazide product changes slightly with time, but for practical purposes it can be considered to be stable.

2.3 Attention must be given to the glassware used, because scratched glassware may absorb chromium. Any glassware cleaned with chromic acid cleaning solution should be rinsed with hydrochloric acid to remove the last traces of chromium.

2.4 Additional information on the principle of the determination is given by Saltzman (1952), Lieber (1956), and Sandell (1950).

3. Interferences

For all practical purposes the reaction is specific for chromium; metallic interference almost never occurs. Iron, mercury, and molybdenum in concentrations as high as 100,000 μg/L show only a small effect. Vanadium should not be present in concentrations exceeding 4,000 μg/L. The effect of water color is small, and color up to 50 Pt-Co units can be tolerated. The chromium color develops almost instantly and is stable, whereas vanadium color develops almost instantly and then fades rapidly. If the original vanadium concentration is less than 4,000 μg/L, no vanadium color persists after 10 min.

4. Apparatus

4.1 *Spectrometer* for use at 540 nm; Beckman Model B, or equivalent.

4.2 With this instrument the following operating conditions have been used:

Wavelength	**540 nm.**
Cells	**10 mm.**
Phototube	**Blue-sensitive.**
Initial sensitivity setting	**1.**
Slit width (approx)	**0.1 mm.**

4.3 With these operating conditions the following absorbances have been observed:

Amount of chromium (*μg*)	*Absorbance*
0	0.00
10	.70
20	1.2
30	1.7
45	2.5

5. Reagents

5.1 *Ammonium hydroxide*, 7.5*M*: Mix 50 mL concentrated NH_4OH (sp gr 0.900) with demineralized water and dilute to 100 mL.

5.2 *Chromium* standard solution I, 1.00 mL = 100 μg Cr^{+6}: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.3 *Chromium* standard solution II, 1.00 mL = 2.00 μg Cr^{+3}: Pipet 5.00 mL of chromium standard solution I into a 25-mL erlenmeyer flask. Add approx 15 mg Na_2SO_3 and 0.5 mL concentrated HNO_3 (sp gr 1.41). Gently evaporate to dryness; strong heating reoxidizes the Cr^{+3}.

Add 0.5 mL concentrated HNO_3 and again evaporate to dryness to destroy any excess sulfite. Dissolve in 1 mL concentrated HNO_3 with warming, and dilute to 250.0 mL with demineralized water.

5.4 *Diphenylcarbazide reagent:* Dissolve 0.2 g diphenylcarbazide and 1.0 g phthalic anhydride in 200 mL ethanol. This reagent is stable for several weeks; slight discoloration may be noted, but this does not impair the usefulness of the reagent.

5.5 *Potassium permanganate* solution, 0.32 g/100 mL: Dissolve 0.32 g $KMnO_4$ in 100 mL demineralized water. Allow to stand several days and decant if necessary.

5.6 *Sodium azide* solution, 5 g/100 mL: Dissolve 5 g NaN_3 in 100 mL demineralized water.

5.7 *Sulfuric acid*, 1.2*M*: Slowly add 6.5 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 100 mL.

5.8 *Sulfuric acid*, 0.25*M*: Slowly add 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 400 µg Cr (50.0 mL max) into a 250-mL erlenmeyer flask, and adjust the volume to approx 50 mL.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approx 50 mL with demineralized water.

6.3 Add 10 mL 0.25*M* H_2SO_4 and mix.

6.4 Add approx 0.5 mL $KMnO_4$ solution.

6.5 Heat on steam bath for 20 min. If color disappears, add $KMnO_4$ by drops to maintain a slight excess.

6.6 While still on the steam bath, add sodium azide solution by drops until the $KMnO_4$ color just disappears. Heat for about 2 min between each addition and avoid adding any excess. Continue heating for 5 min after adding the last drop of sodium azide solution.

6.7 Promptly cool to room temperature in a cold-water bath.

6.8 Add 0.75 mL 7.5*M* NH_4OH and dilute to 100.0 mL.

6.9 Pipet a 10.0-mL aliquot into a 50-mL beaker.

6.10 Add 1.0 mL 1.2*M* H_2SO_4 and mix.

6.11 Add 0.5 mL diphenylcarbazide reagent and mix.

6.12 Allow to stand 10 min.

6.13 Determine the absorbance of the sample and standards against the blank. No color correction is necessary.

7. Calculations

7.1 Determine the micrograms hexavalent plus tervalent chromium in the aliquot from a plot of absorbances of standards.

7.2 Determine the concentration of hexavalent plus tervalent chromium as follows:

$$\text{Cr }(\mu g/L) = \frac{1{,}000}{\text{mL sample}} \times \frac{100}{\text{mL aliquot}} \times \mu g \text{ Cr in aliquot}$$

8. Report

Report chromium, dissolved hexavalent plus tervalent (01030), concentrations as follows: 50 to 100 µg/L, nearest 10 µg/L; 100 µg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (µg/L)*	*Relative deviation (percent)*
3	27	78
4	31	86

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 77.

Lieber, Maxim, 1956, Permanganate-azide test for total chromium in water: American Water Works Association Journal, v. 48, p. 295.

Saltzman, B., 1952, Microdetermination of chromium with diphenylcarbazide by permanganate oxidation: Analytical Chemistry, v. 24, p. 1016.

Sandell, E. B., 1950, Colorimetric determination of traces of metals 2d ed.: New York, Interscience Publishers, p. 260.

Chromium, hexavalent, dissolved, colorimetric, diphenylcarbazide (I–1230–78)

Parameter and Code: Chromium, hexavalent, dissolved (μg/L as Cr^{+6}): 01032

1. Application

This method may be used to analyze most natural waters containing from 50 to 4,000 μg/L hexavalent chromium. Samples containing higher concentrations must first be diluted.

2. Summary of method

2.1 This method determines only hexavalent chromium in solution.

2.2 In acid solution, diphenylcarbazide and hexavalent chromium form a soluble red-violet product that absorbs light at 540 nm. The formula for the colored substance is not known. The pH of the reaction is not particularly critical; solutions differing in pH from 0.7 to 1.3 give identical colors. The color of the chromium-diphenylcarbazide product changes slightly with time, but for practical purposes it can be considered stable.

2.3 Additional information on the principle of the determination is given by Sandell (1950).

3. Interferences

For all practical purposes the reaction is specific for chromium; metallic interference almost never occurs. Iron, mercury, and molybdenum in concentrations as high as 100,000 μg/L show only a small effect. Vanadium should not be present in concentrations exceeding 4,000 μg/L. The effect of water color is small, and color up to 50 can be tolerated. The chromium color develops almost instantly and is stable, whereas vanadium color develops instantly and then fades rapidly. If the original vanadium concentration is less than 4,000 μg/L, no vanadium color persists after 10 min.

4. Apparatus

4.1 *Spectrometer* for use at 540 nm; Beckman Model B, or equivalent.

4.2 With this instrument the following operating conditions have been used:

Wavelength	**540 nm.**
Cells	**10 mm.**
Phototube	**Blue-sensitive.**
Initial sensitivity setting	**1.**
Slit width (approx)	**0.1 mm.**

4.3 With these operating conditions the following absorbances have been observed:

Amount of chromium (*μg*)	*Absorbance*
0	0.00
10	.70
20	1.2
30	1.7
45	2.5

5. Reagents

5.1 *Chromium* standard solution, 1.00 mL = 100 μg Cr^{+6}: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.2 *Diphenylcarbazide* reagent: Dissolve 0.2 g diphenylcarbazide and 1.0 g phthalic anhydride in 200 mL ethanol. This reagent is stable for several weeks; slight discoloration may be noted, but this does not impair the usefulness of the reagent.

5.3 *Sulfuric acid*, 1.2*M*: Slowly add 6.5 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 100 mL.

6. Procedure

6.1 Pipet a volume of sample containing less than 40 μg Cr^{+6} (10.0 mL max) into a 50-mL beaker, and adjust the volume to 10.0 mL with demineralized water.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to 10.0 mL with demineralized water.

6.3 Add 1.0 mL 1.2*M* H_2SO_4 and mix.

6.4 Add 0.5 mL diphenylcarbazide reagent and mix.

6.5 Allow to stand 10 min.

6.6 Determine the absorbance of the sample and standards against the blank, and when necessary make a correction for water color.

7. Calculations

7.1 Determine micrograms hexavalent chromium in the sample from a plot of absorbances of standards.

7.2 Determine the hexavalent chromium concentration in micrograms per liter as follows:

$$Cr^{+6}\ (\mu g/L) = \frac{1{,}000}{\text{mL sample}} \times \mu g\ Cr^{+6} \text{ in sample.}$$

8. Report

Report chromium, dissolved hexavalent (01032), concentrations as follows: 50 to 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (μg/L)*	*Relative deviation (percent)*
5	810	5

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 75.

Sandell, E. B., 1950, Colorimetric determination of traces of metals [2d ed.]: New York, Interscience Publishers, p. 260.

Cyanide, dissolved, colorimetric, barbituric acid, automated (I–2302–78)

Parameter and Code: Cyanide, dissolved (mg/L as CN): 00723

1. Application

This method may be used to analyze waters containing from 0.01 to 0.30 mg/L cyanide. Samples containing more than 0.30 mg/L must first be diluted.

2. Summary of method

This method is based on the chlorination of cyanide with chloramine-T and the subsequent reaction with a pyridine-barbituric acid reagent (Goulden and others, 1972). This method detects simple cyanides only; therefore, it is first necessary to break down any complex cyanides by passing the acidified sample solution through an ultraviolet digestion-distillation procedure. The distillation step also removes certain interferences.

3. Interferences

3.1 Chloride interferes if its concentration exceeds 3,000 mg/L.

3.2 Oxidizing agents may interfere.

3.3 Glycine and urea at the 10-mg/L level do not interfere.

3.4 A concentration of 10 mg/L sulfide increases the apparent cyanide concentration by approx 0.02 mg/L. Concentrations of sulfide greater than 10 mg/L interfere considerably.

3.5 Thiocyanate is broken down to cyanide and sulfide by this procedure and therefore interferes on an equimolar basis.

3.6 Sulfate concentrations of 4,000 mg/L do not interfere. Higher concentrations were not tested.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold with ultraviolet digestor, proportioning pump, heating bath with distillation head, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 0.30 mg/L CN:

Absorption cell	15 mm.
Wavelength	570 nm.
Cam	20/h (6/1).
Heating bath temperature	155°C.

5. Reagents

5.1 *Chloramine-T* solution, 4.0 g/L: Dissolve 2.0 g chloramine-T in demineralized water and dilute to 500 mL.

5.2 *Cyanide* standard solution I, 1.00 mL = 0.100 mg CN: Dissolve 0.2500 g KCN (NOTE 1) in 0.1*M* NaOH and dilute to 1,000 mL with 0.1*M* NaOH.

NOTE 1. CAUTION—POISON: May be fatal if swallowed or inhaled. Contact with acid liberates poisonous gas. Contact with KCN may burn eyes and irritate skin.

5.3 *Cyanide* standard solution II, 1.00 mL = 0.002 mg CN: Add 20 mL cyanide standard solution I to 800 mL 0.1 *M* NaOH and dilute to 1,000 mL with 0.1 *M* NaOH.

5.4 *Cyanide* working standards: Prepare a blank and 100 mL each of a series of cyanide working standards by appropriate quantitative dilution of cyanide standard solution II as follows:

Cyanide standard solution II (mL)	*Cyanide concentration (mg/L)*
2.0	0.040
5.0	.100
10.0	.200
15.0	.300

5.5 *Phosphate* buffer solution: Dissolve 13.6 g KH_2PO_4 and 0.28 g Na_2HPO_4 in demineralized water and dilute to 1 L. Add 0.5 mL Brij-35 solution and mix.

5.6 *Phosphoric acid-hypophosphorous acid* distillation reagent: Carefully add 250 mL concentrated phosphoric acid (sp gr 1.69) and 50 mL hypophosphorous acid to approx 700 mL demineralized water. Dilute to 1 L with demineralized water.

5.7 *Pyridine-barbituric acid* solution: Place 15 g barbituric acid in a 1-L beaker and add enough demineralized water (about 100 mL) to wash the sides of the beaker and wet the barbituric acid. Add 75 mL pyridine and mix. Add 15 mL concentrated HCl (sp gr 1.19) and mix. Dilute to about 900 mL with demineralized water and mix until all the barbituric acid has dissolved. Transfer the solution to a 1,000-mL volumetric flask and dilute to volume with demineralized water.

6. Procedure

6.1 Set up manifold (fig. 29).

6.2 Allow the colorimeter, recorder, and heating bath to warm up for 30 min or until the

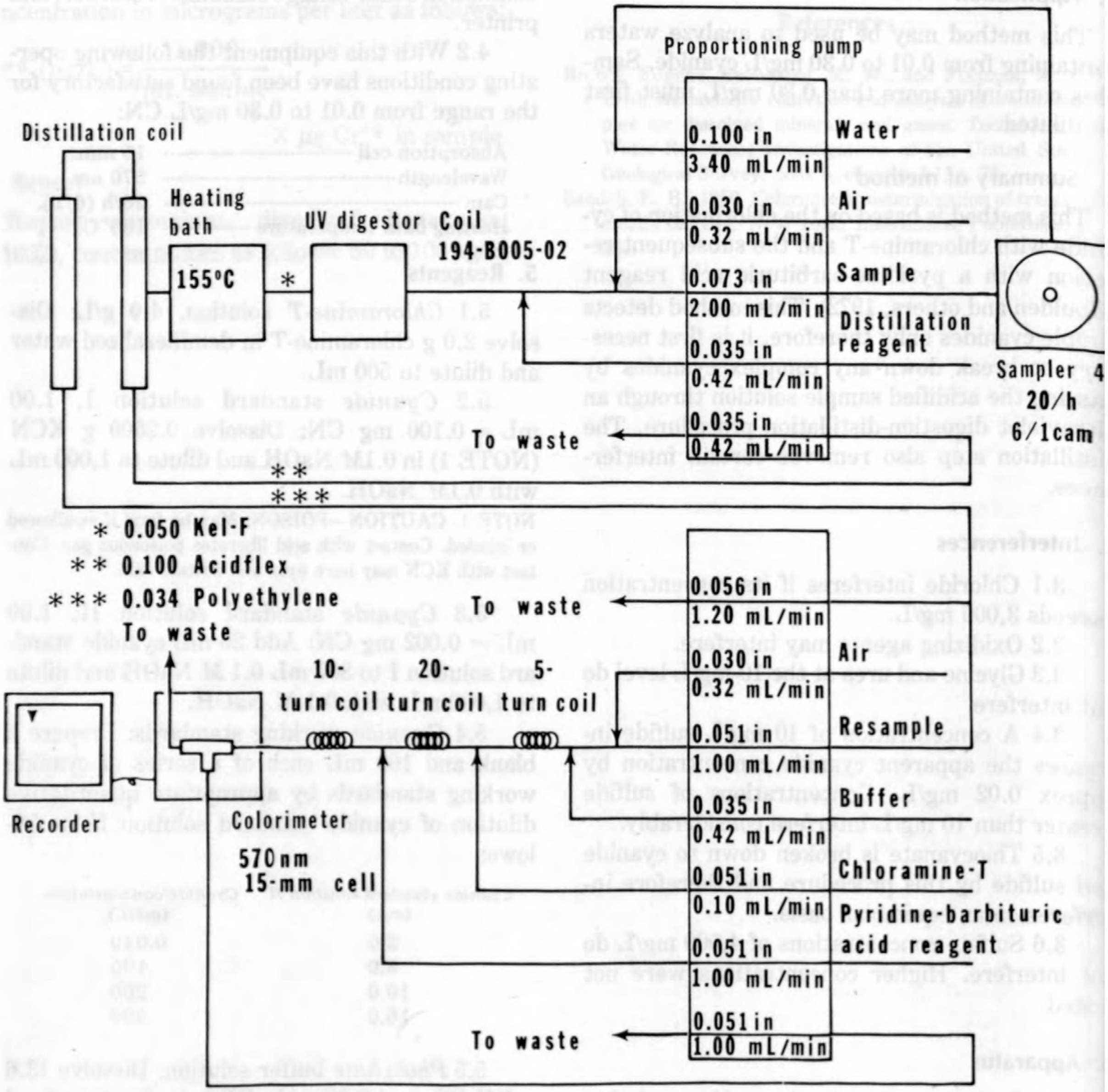


FIGURE 29.—Cyanide manifold.

heating bath temperature has stabilized at 155°C. Cold water must be flowing through the condensing jacket of the distillation head when heating bath is operating. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample tube.

6.3 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray. Place individual standards of differing concentrations in every eighth position of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective cyanide concentration.

7.2 Compute the concentration of cyanide in milligrams per liter by comparing each sample peak height with the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report cyanide, dissolved (00723), concentrations as follows: less than 1.00 mg/L, nearest 0.01 mg/L; 1.00 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the relative deviation (coefficient of variation) for replicate analysis by a single operator is as follows:

Mean (μg/L)	*Relative deviation (percent)*
0.041	2
.125	1
.224	1

References

Goulden, P. D., Afghan, B. K., and Brooksbank, Peter, 1972, Determination of nanogram quantities of simple and complex cyanides in water: Analytical Chemistry, v. 44, p. 1845–1849.

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 40.

Cyanide, dissolved, colorimetric, pyridine-pyrazolone (I–1300–78)

Parameter and Code: Cyanide, dissolved (mg/L as CN): 00723

1. Application

This method may be used to determine cyanide in water and brines containing at least 0.01 mg/L of cyanide.

2. Summary of method

This method is based on the chlorination of cyanide and the subsequent reaction of the product with a mixed solution of pyridine-pyrazolone to form a stable complex dye. The method detects only simple cyanides, and it is therefore necessary to break down any complex cyanides present. The decompositon of complex cyanides is accomplished by an acid reflux and distillation prior to the colorimetric procedure. The distillation also removes certain interferences. The distillation may be omitted if these interferences, as well as complex cyanides, are known to be absent. The distillation and colorimetric procedures given are essentially the same as in American Society for Testing and Materials, 1976, Method A, p. 500–505.

3. Interferences

3.1 Common interferences include sulfide, heavy-metal ions, fatty acids, steam-distillable organic compounds, cyanate, thiocyanate, glycine, urea, oxidizing agents, and substances which may contribute color or turbidity to the sample.

3.2 These interferences may be removed or their effect minimized as follows:

3.2.1 *Sulfide* is removed as lead sulfide by adding a slight excess of lead carbonate to 400 mL of the alkaline (pH 11.0 or above) sample. Filter the sample immediately, wash the precipitate with demineralized water, and add the washings to the filtrate.

3.2.2 *Fatty acids* are removed by acidifying 400 mL of sample with acetic acid to a pH of between 6 and 7 and extracting with 80 mL of either isooctane or hexane. A single extraction is usually sufficient.

3.2.3 *Oxidizing agents* are removed by adding sodium sulfite solution to 400 mL of sample until a negative test with starch-iodide paper is obtained.

3.2.4 *Most remaining interferences* are removed by the distillation.

4. Apparatus

4.1 *Distillation train*, fig. 30. An efficient gas washer is essential to the proper operation of the distillation assembly. The Fisher-Milligan unit has been found satisfactory.

4.2 *Heating element* for Claisen flask.

4.3 *Spectrometer*.

4.4 Refer to the manufacturer's manual for optimizing instrumental parameters:

Wavelength ------------------------------------ 620 nm.

5. Reagents

5.1 *Acetic acid*, 3*M*: Mix 172 mL glacial $HC_2H_3O_2$ (sp gr 1.06) with demineralized water and dilute to 1 L.

5.2 *Chloramine-T* solution, 1 g/100 mL: Dissolve 0.25 g chloramine-T in 25 mL demineralized water. This solution is unstable and must be prepared immediately before use. When a blank and standards are used, the chloramine-T solution may be used over a period of several hours, but each succeeding use results in lower absorbance readings for the same concentration of cyanide.

5.3 *Cyanide* standard solution I, 1.00 mL = 1.000 mg CN: Dissolve 2.50 g KCN in 1 L demineralized water (NOTE 1). Standardize with silver nitrate standard solution, 1.00 mL = 1.00 mg CN, as follows: Adjust the pH of 5.0 mL cyanide standard solution I to 11.0 or above,

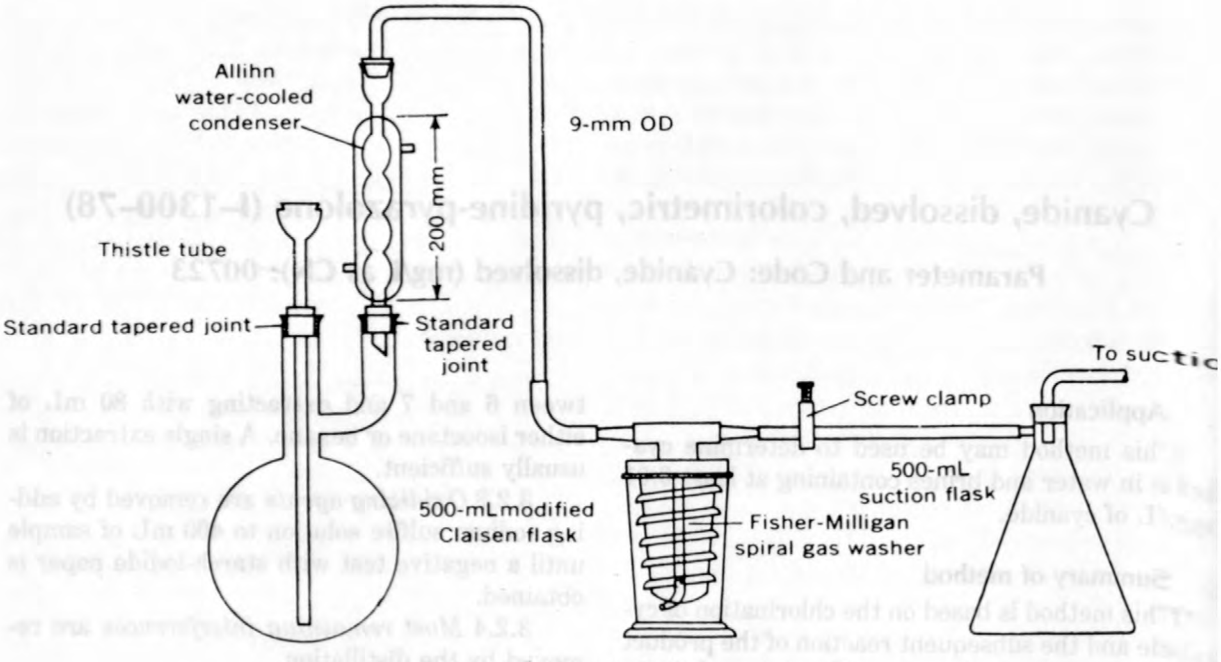


FIGURE 30.—Cyanide distillation train.

and dilute to 250 mL with demineralized water. Add 0.5 to 1.0 mL 5-(*p*-dimethylaminobenzylidene)rhodamine indicator solution and titrate with standard silver nitrate solution to the first color change from canary yellow to salmon. Subtract the blank obtained by titrating an identical volume of water, alkali, and indicator. The cyanide solution is unstable and must be either restandardized weekly or prepared fresh when needed.

NOTE 1. CAUTION—POISON: May be fatal if swallowed or inhaled. Contact with acid liberates poisonous gas. Contact with KCN may burn eyes and irritate skin.

5.4 *Cyanide* standard solution II, 1.00 mL = 0.010 mg CN: Add 10.0 mL cyanide standard solution I to demineralized water and dilute to 1,000 mL. This solution must be prepared fresh before use.

5.5 *Cyanide* standard solution III, 1.00 mL = 0.001 mg CN: Add 10.0 mL cyanide standard solution II to demineralized water and dilute to 100 mL. This solution must be prepared fresh before use.

5.6 *Magnesium chloride* solution, 24 g/100 mL: Dissolve 51 g $MgCl_2 \cdot 6H_2O$ in 100 mL demineralized water.

5.7 *5-(*p*-Dimethylaminobenzylidene)rhodamine indicator* solution, 0.02 g/100 mL: Dissolve 0.02 g 5-(*p*-dimethylaminobenzylidene)rhodamine in 100 mL acetone. Eastman Kodak 2748 has been found satisfactory.

5.8 *Pyrazolone* solution I: Add 0.8 g phenyl-3-methyl-5-pyrazolone to 150 mL demineralized water at 75°C. Cool to room temperature, with stirring; filter. Eastman Kodak 1397 has been found satisfactory.

5.9 *Pyrazolone* solution II: Dissolve 0.025 bis-pyrazolone in 25 mL pyridine and filter. Several minutes of mixing are usually required to effect solution. Eastman Kodak No. 6969 has been found satisfactory.

5.10 *Pyridine-pyrazolone* reagent: Mix mL pyrazolone solution I with 25 mL pyrazolone solution II. The mixed reagent develops a color on standings which does not affect color development. Prepare this reagent fresh daily before each use.

5.11 *Pyridine*.

5.12 ***Silver nitrate*** standard solution, 1.00 mL ≎ 1.00 mg CN: Crush approx 5 g $AgNO_3$ crystals and dry to constant mass at 40°C. Dissolve 3.2647 g $AgNO_3$ in demineralized water and dilute to 1 L. This solution is needed only to standardize the cyanide standard solution I.

5.13 *Sodium hydroxide*, 1*M*: Dissolve NaOH in 100 mL demineralized water.

5.14 *Sulfuric acid*, concentrated (sp gr 1

6. Procedure

6.1 *Distillation*

6.1.1 Assemble the distillation train, consisting of Claisen flask, thistle tube, condenser, gas washer, screw clamp, suction flask, and aspirator. Add 400 mL sample (or smaller aliquot diluted to 400 mL) to the boiling flask. Add *exactly* 50 mL 1*M* NaOH and 100 mL demineralized water to the gas washer. Connect train and adjust suction so that 1 to 2 bubbles per second enter the boiling flask through the air inlet. Do not increase airflow beyond 2 bubbles per second.

6.1.2 Add 10 mL $MgCl_2$ solution through the thistle tube, and allow the airflow to mix for 3 min. Rinse air tube with demineralized water, then slowly add 20 mL concentrated H_2SO_4. Rinse the tube again.

6.1.3 Heat at a rate which provides rapid boiling, but not enough to flood the condenser inlet or permit the vapors to rise more than halfway into the condenser. Reflux for 1 h. Turn off heat, but permit airflow to continue for 15 min.

6.1.4 Transfer gas washer contents to a 200-mL volumetric flask. Wash tube, from condenser to gas washer, and the gas washer with small amounts of demineralized water and add to contents of flask. Dilute contents of volumetric flask to 200 mL.

6.1.5 Refill the gas washer with NaOH and demineralized water, as in 6.1.1, and repeat reflux procedure. If only readily hydrolyzed cyanides are present, the absorber liquid from the first reflux period will contain all the available cyanide. If stable complex cyanides are present, a measurable yield will appear in the absorber liquid during the second and succeeding reflux periods, depending on the degree of stability of the compounds.

6.2 *Colorimetric procedure:* The standards and many of the reagents used in this procedure are unstable and must be prepared immediately before use if maximum color development is to be obtained. The color development is also dependent on there being approximately equal total salt concentrations in both sample and standards. If the final distillate volume is 200 mL, it will be about 0.25*M* in NaOH. For this reason 0.25*M* NaOH must be used for dilutions and for the blank. Any substantial deviation in the quantity of 3*M* acetic acid required to neutralize blank and standards will require additional manipulation to bring these volumes into approximate agreement. The variation should be less than 0.3 mL.

6.2.1 Prepare a blank by pipetting 15 mL 0.25*M* NaOH into a 23-mm absorption cell fitted with a rubber stopper. Prepare standards containing 0.5 μg and 1.0 μg CN, each diluted to 15 mL with 0.25*M* NaOH in similar containers.

6.2.2 Take 15-mL aliquots (or smaller volumes diluted to 15 mL with 0.25*M* NaOH) of the distillates from the purification procedure and place in 23-mm stoppered absorption cells.

6.2.3 Neutralize samples, blank, and standards with 3*M* acetic acid, using phenolphthalein indicator solution.

6.2.4 To samples, blank, and standards add 4 drops chloramine-T solution, stopper, and shake. Allow 2 min for the reaction.

6.2.5 Add 5.0 mL mixed pyridine–pyrazolone solution and mix well. Allow 20 min for color development.

6.2.6 Read absorbances at 620 nm. The color is stable for 30 min. Concentrations of 0.0 to 80 μg/L have been shown to obey Beer's law. The absorbance decreases slowly over a period of 3 h, and can probably be read between 30 min and 3 h with some decrease in accuracy.

7. Calculations

7.1

$$F = \frac{\text{mL distillate}}{\text{mL original sample volume}} \times \frac{\text{mg standard}}{\text{mL aliquot volume}} \times \frac{1{,}000}{A_{\text{std}}}$$

where

F = factor.
A_{std} = absorbance of standard.

7.2 Determine the cyanide concentration in milligrams per liter as follows:

$$\text{CN (mg/L)} = F \times A_{\text{sample}}$$

where

A_{sample} = absorbance of sample.

8. Report

Report cyanide, dissolved (00723), concentrations as follows: less than 1.0 mg/L, nearest 0.01 mg/L; 1.0 mg/L and above, two significant figures.

9. Precision

Data published by the American Society for Testing and Materials (1976) indicate the overall precision obtained on a mixed cyanide solution, to be:

$$S_T = 0.115X + 0.031$$

where

S_T = overall precision, milligrams per liter and

X = concentration of cyanide, milligrams pe liter.

References

American Society for Testing and Materials, 1976, Annu book of ASTM standards, part 31, water: Philadelphi American Society for Testing and Materials, p. 500 505.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J 1970, Methods for collection and analysis of water san ples for dissolved minerals and gases: Techniques Water-Resources Investigations of the United State Geological Survey, book 5, chapter A1, p. 85.

Cyanide, total in bottom material, colorimetric, pyridine-pyrazolone (I–5300–78)

Parameter and Code: Cyanide, total in bottom material, dry wt (mg/kg as CN): 00721

1. Application

This method may be used to determine cyanide in bottom material containing at least 0.5 mg/kg.

2. Summary of method

This method is based on the chlorination of cyanide and the subsequent reaction of the product with a mixed solution of pyridine-pyrazolone to form a stable complex dye. The method detects only simple cyanides, and it is therefore necessary to break down any complex cyanides present. The decomposition of complex cyanides is accomplished by an acid reflux and distillation prior to the colorimetric procedure. The distillation also removes certain interferences. The distillation and colorimetric procedures given are essentially the same as in American Society for Testing and Materials, 1976, Method A, p. 500–505, and in American Public Health Association and others (1976).

3. Interferences

3.1 Common interferences include sulfide, heavy-metal ions, fatty acids, steam-distillable organic compounds, cyanate, thiocyanate, glycine, urea, oxidizing agents, and substances which may contribute color or turbidity to the sample.

3.2 This method includes no provisions for removing these interferences or for minimizing their effects. The analyst must be aware of the fact that when such interfering substances are present, the analytical result obtained may be in error, although distillation of the cyanide certainly separates it from some of the interfering substances.

4. Apparatus

4.1 *Distillation train* (fig. 31). An efficient gas washer is essential to the proper operation of the distillation assembly. The Fisher-Milligan unit has been found satisfactory.

4.2 *Heating element* for Claisen flask.

4.3 *Spectrometer*.

4.4 Refer to manufacturer's manual for optimizing instrumental parameters:

Wavelength -- 620 nm.

5. Reagents

5.1 *Acetic acid*, 3*M*: Mix 172 mL glacial $HC_2H_3O_2$ (sp gr 1.06) with demineralized water and dilute to 1 L.

5.2 *Chloramine-T* solution, 1 g/100 mL: Dissolve 0.25 g chloramine-T in 25 mL demineralized water. This solution is unstable and must be prepared immediately before use. When a blank and standards are used, the chloramine-T solution may be used over a period of several hours, but each succeeding use results in lower absorbance readings for the same concentration of cyanide.

5.3 *Cyanide* standard solution I, 1.00 mL = 1.000 mg CN: Dissolve 2.50 g KCN in 1 L demineralized water (NOTE 1). Standardize with silver nitrate standard solution, 1.00 mL ≎ 1.00 mg CN, as follows: Adjust the pH of 5.0 mL cyanide standard solution I to 11.0 or above, and dilute to 250 mL with demineralized water. Add 0.5 to 1.0 mL 5-(*p*-dimethylaminobenzylidene)rhodamine indicator solution and titrate with standard silver nitrate solution to the first color change from canary yellow to salmon. Subtract the blank obtained by titrating an identical volume of water, alkali, and indicator. The cyanide solution is unstable and must be

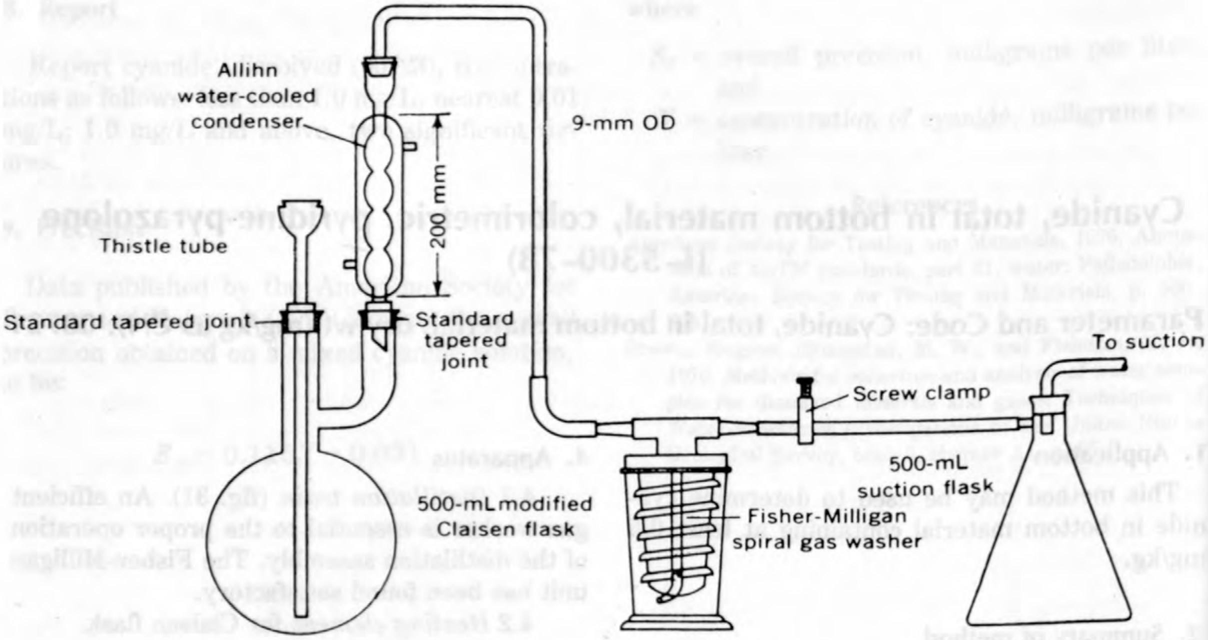


FIGURE 31.—Cyanide distillation train.

either restandardized weekly or prepared fresh when needed.

NOTE 1. CAUTION—POISON: May be fatal if swallowed or inhaled. Contact with acid liberates poisonous gas. Contact with KCN may burn eyes and irritate skin.

5.4 *Cyanide* standard solution II, 1.00 mL = 0.010 mg CN: Add 10.0 mL cyanide standard solution I to demineralized water and dilute to 1,000 mL. This solution must be prepared fresh before each use.

5.5 Cyanide standard solution III, 1.00 mL = 0.001 mg CN: Add 10.0 mL cyanide standard solution II to demineralized water and dilute to 100 mL. This solution must be prepared fresh before each use.

5.6 *Magnesium chloride* solution, 24 g/100 mL: Dissolve 51 g $MgCl_2 \cdot 6H_2O$ in 100 mL demineralized water.

5.7 *5-(p-Dimethylaminobenzylidene)rhodamine indicator* solution, 0.02 g/100 mL: Dissolve 0.02 g 5-(*p*-demethylaminobenzylidene) rhodamine in 100 mL acetone. Eastman Kodak No. 2748 has been found satisfactory.

5.8 *Pyrazolone* solution I: Add 0.8 g 1-phenyl-3-methyl-5-pyrazolone to 150 mL demineralized water at 75°C. Cool to room temperature, with stirring; filter. Eastman Kodak No. 1397 has been found satisfactory.

5.9 *Pyrazolone* solution II: Dissolve 0.025 g bis-pyrazolone in 25 mL pyridine and filter. Several minutes of mixing are usually required to effect solution. Eastman Kodak No. 6969 has been found satisfactory.

5.10 *Pyridine-pyrazolone* reagent: Mix 125 mL pyrazolone solution I with 25 mL pyrazolone solution II. The mixed reagent develops a pink color on standing, which does not affect color development. Prepare this reagent fresh daily or before each use.

5.11 *Pyridine*.

5.12 *Silver nitrate* standard solution, 1.00 mL ≎ 1.00 mg CN: Crush approx 5 g of $AgNO_3$ crystals and dry to constant mass at 40°C. Dissolve 3.2647 g $AgNO_3$ in demineralized water and dilute to 1,000 mL. This solution is needed only to standardize cyanide standard solution I.

5.13 *Sodium hydroxide*, 1*M*: Dissolve 4 g NaOH in 100 mL demineralized water.

5.14 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 *Distillation*

6.1.1 Assemble the distillation train, consisting of Claisen flask, thistle tube, condenser, gas washer, screw clamp, suction flask, and aspirator. Add a weighed portion (5 to 10 g) of sample and 250 to 500 mL demineralized water to the boiling flask. Add *exactly* 50 mL $1M$ NaOH and 100 mL demineralized water to the gas washer. Connect train and adjust suction so that 1 to 2 bubbles per second enter the boiling flask through the air inlet. Do not increase airflow beyond 2 bubbles per second.

6.1.2 Add 10 mL $MgCl_2$ solution through the thistle tube, and allow the airflow to mix for 3 min. Rinse air tube with demineralized water, then slowly add 20 mL concentrated H_2SO_4. Rinse the tube again

6.1.3 Heat at a rate which provides rapid boiling, but not enough to flood the condenser inlet or permit the vapors to rise more than halfway into the condenser. Reflux for 1 h. Turn off heat, but permit airflow to continue for 15 min.

6.1.4 Transfer gas washer contents to a 200-mL volumetric flask. Wash tube from condenser to gas washer, and the gas washer, with small amounts of demineralized water and add to contents of flask. Dilute contents of volumetric flask to 200 mL.

6.1.5 Refill the gas washer with NaOH and demineralized water, as in 6.1.1, and repeat reflux procedure. If only readily hydrolyzed cyanides are present, the absorber liquid from the first reflux period will contain all the available cyanide. If stable complex cyanides are present, a measurable yield will appear in the absorber liquid during the second and succeeding reflux periods, depending on the degree of stability of the compounds.

6.2 *Colorimetric procedure:* The standards and many of the reagents used in this procedure are unstable and must be prepared immediately before use if maximum color development is to be obtained. The color development is also dependent on there being approximately equal total salt concentrations in both samples and standards. If the final distillate volume is 200 mL, it will be about $0.25M$ in NaOH. For this reason 0.25M NaOH must be used for dilutions and for the blank. Any substantial deviation in the quantity of $3M$ acetic acid required to neutralize blank and standards will require additional manipulation to bring these volumes into approximate agreement. The variation should be less than 0.3 mL.

6.2.1 Prepare a blank by pipetting 15 mL of $0.25M$ NaOH into a 23-mm absorption cell fitted with a rubber stopper. Prepare standards containing 0.5 μg and 1.0 μg CN, each diluted to 15 mL with $0.25M$ NaOH in similar containers.

6.2.2 Take 15-mL aliquots (or smaller volumes diluted to 15 mL with $0.25M$ NaOH) of the distillates from the purification procedure and place in 23-mm stoppered absorption cells.

6.2.3 Neutralize each sample, blank, and standard with $3M$ acetic acid, using phenolphthalein indicator solution.

6.2.4 To each sample, blank, and standard add 4 drops chloramine-T solution, stopper, and shake. Allow 2 min for the reaction to proceed.

6.2.5 Add 5.0 mL pyridine-pyrazolone reagent and mix well. Allow 20 min for color development.

6.2.6 Read absorbances at 620 nm. The color is stable for 30 min. Concentrations of from 0.0 to 80 μg/L have been shown to obey Beer's law. The absorbance decreases slowly over a period of 3 h, and can probably be read during this period with some decrease in accuracy.

7. Calculations

Compute cyanide concentrations in bottom material as follows:

$$\text{CN (mg/kg)} = \frac{1{,}000}{\text{wt sample (g)}} \times \frac{\text{vol. distillate (mL)}}{\text{vol. aliquot (mL)}} \times \text{(mg standard)} \times \frac{A_{\text{sample}}}{A_{\text{std}}}$$

where

A_{sample} = absorbance of sample
A_{std} = absorbance of standard

8. Report

Report cyanide, total in bottom material (00721), concentration as follows: less than 10 mg/kg, nearest 0.1 mg/kg; 10 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater, 14th ed. : Washington, D.C., American Public Health Association, p. 367.

American Society for Testing and Materials, 1976, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing Materials, p. 500.

Cyanide, total, colorimetric, barbituric acid, automated (I–4302–78)

Parameter and Code: Cyanide, total recoverable (mg/L as CN): 00720

1. Application

This method may be used to analyze unfiltered water samples containing from 0.01 to 0.30 mg/L cyanide. Water samples containing more than 0.30 mg/L must first be diluted.

2. Summary of method

This method is based on the chlorination of cyanide with chloramine-T and the subsequent reaction with a pyridine-barbituric acid reagent (Goulden, Afghan, and Brooksbank, 1972). This method detects simple cyanides only; therefore, it is first necessary to break down any complex cyanides by passing the acidified sample solution through an ultraviolet digestion-distillation procedure. The distillation also removes certain interferences.

3. Interferences

3.1 Chloride interferes if its concentration exceeds 3,000 mg/L.

3.2 Oxidizing agents may interfere.

3.3 Glycine and urea at the 10-mg/L level do not interfere.

3.4 A concentration of 10 mg/L sulfide increases the apparent cyanide concentration by approximately 20 μg/L. Concentrations greater than 10 mg/L interfere severely.

3.5 Thiocyanate is broken down to cyanide and sulfide by this procedure and therefore interferes on an equimolar basis.

3.6 Sulfate concentrations of 4,000 mg/L do not interfere. Higher concentrations were not tested.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler with mixer, cartridge manifold with ultraviolet digestor, proportioning pump, heating bath with distillation head, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 0.30 mg/L CN:

Absorption cell	15 mm.
Wavelength	570 nm.
Cam	20/h (6/1).
Heating bath temperature	155°C.

5. Reagents

5.1 *Chloramine-T* solution, 4.0 g/L: Dissolve 2.0 g chloramine-T in demineralized water and dilute to 500 mL.

5.2 *Cyanide* standard solution I, 1.00 mL = 0.100 mg CN: Dissolve 0.2500 g KCN (NOTE 1) in 0.1*M* NaOH and dilute to 1,000 mL with 0.1*M* NaOH.

NOTE 1. CAUTION—POISON: May be fatal if swallowed or inhaled. Contact with acid liberates poisonous gas. Contact with KCN may burn eyes and irritate skin.

5.3 *Cyanide* standard solution II, 1.00 mL = 0.002 mg CN: Add 20 mL cyanide standard solution I to 800 mL 0.1*M* NaOH and dilute to 1,000 mL with 0.1*M* NaOH.

5.4 *Cyanide* working standards: Prepare a blank and 100 mL each of a series of cyanide working standards by appropriate quantitative dilution of cyanide standard solution II as follows:

Cyanide standard solution II (mL)	*Cyanide concentration (mg/L)*
2.0	0.040
5.0	.100
10.0	.200
15.0	.300

5.5 *Phosphate* buffer solution: Dissolve 13.6 g KH_2PO_4 and 0.28 g Na_2HPO_4 in demineralized water and dilute to 1 L. Add 0.5 mL Brij–35 solution and mix.

5.6 *Phosphoric acid-hypophosphorous acid* distillation reagent: Carefully add 250 mL concentrated phosphoric acid (sp gr 1.69) and 50 mL hypophosphorous acid to approx 700 mL demineralized water. Dilute to 1 L with demineralized water.

5.7 *Pyridine-barbituric acid* solution: Place 15 g barbituric acid in a 1-L beaker and add enough demineralized water (about 100 mL) to wash the sides of the beaker and wet the barbituric acid. Add 75 mL pyridine and mix. Add 15 mL concentrated HCl (sp gr 1.19) and mix. Dilute to about 900 mL with demineralized water and mix until all the barbituric acid has dissolved. Transfer the solution to a 1,000-mL volumetric flask and dilute to volume with demineralized water.

6. Procedure

6.1 Set up manifold (fig. 32).

6.2 Allow the colorimeter, recorder, and heating bath to warm up for 30 min or until the heating bath temperature has stabilized at 155°C. Cold water must be flowing through the condensing jacket of the distillation head when heating bath is operating. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample tube.

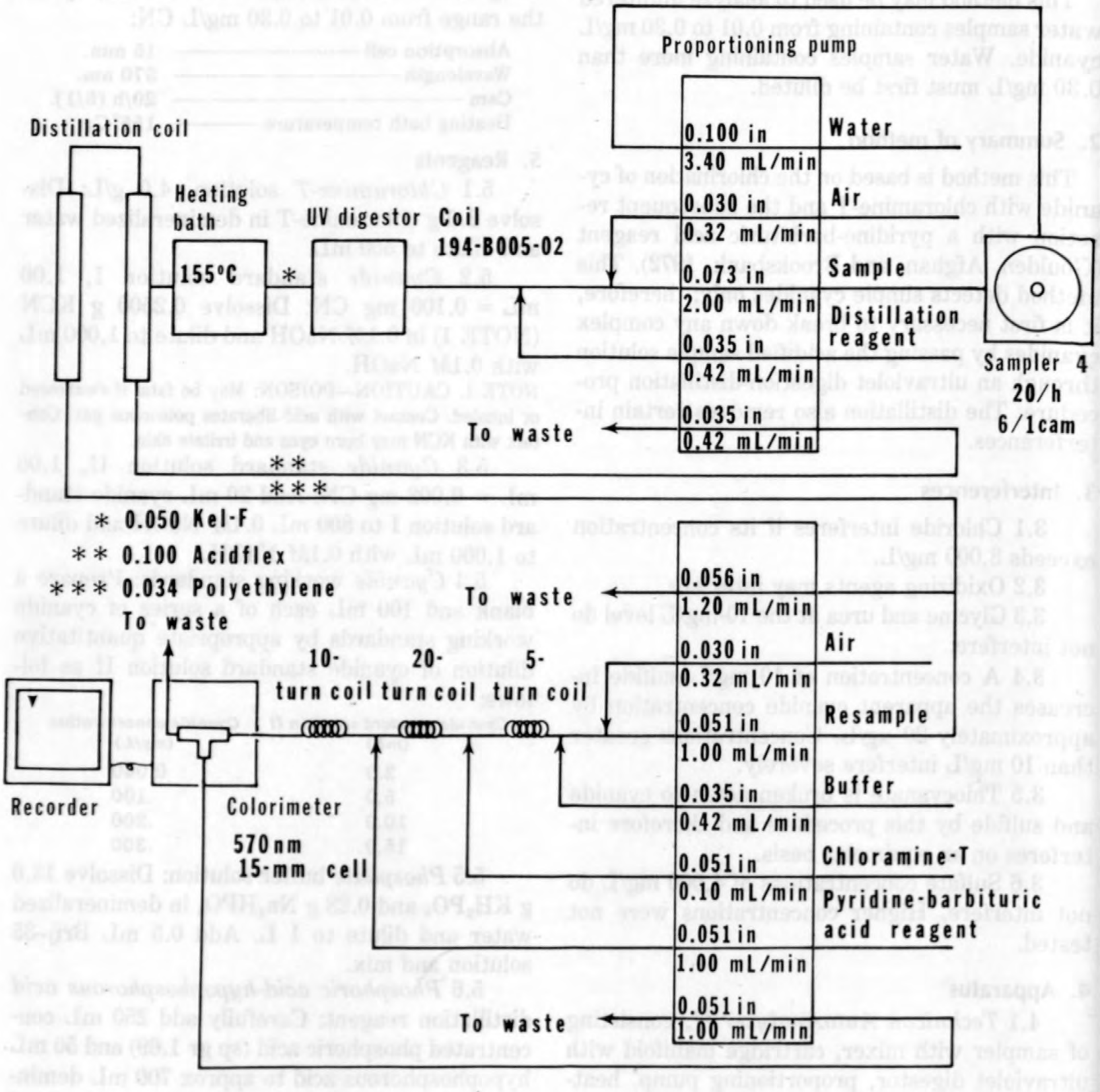


FIGURE 32.—Cyanide manifold.

6.3 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the sample tray. Place individual standards of differing concentrations in every eighth position of this and subsequent sample trays. Fill remainder of each tray with unknown samples. Each sample must be well mixed by vigorous shaking before transferring a portion to a sample cup.

6.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective cyanide concentration.

7.2 Compute the concentration of cyanide in milligrams per liter by comparing each sample peak height with the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report cyanide, total (00720), concentrations as follows: less than 1.00 mg/L, nearest 0.01 mg/L; 1.00 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method for a single operator is greater than 2 percent at 0.041 mg/L and greater than 1 percent at 0.224 mg/L.

References

Goulden, P. D., Afghan, B. K., and Brooksbank, Peter, 1972, Determination of nanogram quantities of simple and complex cyanides in water: Analytical Chemistry, v. 44, p. 1845–1849.

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 40.

Cyanide, total, colorimetric, pyridine-pyrazolone (I–3300–78)

Parameter and Code: Cyanide, total (mg/L as CN): 00720

1. Application

1.1 The method may be used to determine cyanide in water-suspended sediment mixtures containing at least 0.01 mg/L of cyanide.

1.2 Water-suspended sediment mixtures may be analyzed by this method if each sample is shaken vigorously and a suitable aliquot of well mixed sample withdrawn.

2. Summary of method

This method is based on the chlorination of cyanide and the subsequent reaction of the product with a mixed solution of pyridine-pyrazolone to form a stable complex dye. The method detects only simple cyanides, and it is therefore necessary to break down any complex cyanides present. The decomposition of complex cyanides is accomplished by an acid reflux and distillation prior to the colorimetric procedure. The distillation also removes certain interferences. The distillation and colorimetric procedures given are essentially the same as in American Society for Testing and Materials, 1976, Method A, p. 500–505, and in American Public Health Association and others (1976).

3. Interferences

3.1 Common interferences include sulfide, heavy-metal ions, fatty acids, steam-distillable organic compounds, cyanate, thiocyanate, glycine, urea, oxidizing agents, and substances that contribute color or turbidity to the sample.

3.2 This method includes no provisions for removing these interferences or for minimizing their effects. The analyst must be aware of the fact that when such interfering substances are present, the analytical result obtained may be in error, although distillation of the cyanide certainly separates it from some of the interfering substances.

4. Apparatus

4.1 *Distillation train*, (fig. 33). An efficient gas washer is essential to the proper operation of the distillation assembly. The Fisher-Mulligan unit has been found satisfactory.

4.2 *Heating element* for Claisen flask.

4.3 *Spectrometer*.

4.4 Refer to manufacturer's manual for optimizing instrumental parameters:

Wavelength -- 620 nm.

5. Reagents

5.1 *Acetic acid*, 3*M*: Mix 172 mL glacial $HC_2H_3O_2$ (sp gr 1.06) with demineralized water and dilute to 1 L.

5.2 *Chloramine-T* solution, 1 g/100 mL: Dissolve 0.25 g chloramine-T in 25 mL demineralized water. This solution is unstable and must be prepared immediately before use. When a blank and standards are used, the chloramine-T solution may be used over a period of several hours, but each succeeding use results in lower absorbance readings for the same concentration of cyanide.

5.3 *Cyanide* standard solution I, 1.00 mL = 1.000 mg CN: Dissolve 2.50 g KCN (NOTE 1) in 1 L demineralized water. Standardize with silver nitrate standard solution, 1.00 mL $\Leftrightarrow$ 1.00 mg CN, as follows: Adjust the pH of 5.0 mL cyanide standard solution I to 11.0 or above, and dilute to 250 mL with demineralized water. Add 0.5 to 1.0 mL 5-(*p*-dimethylaminobenzylidene) rhodamine indicator solution and titrate with standard silver nitrate solution to the first color change from canary yellow to salmon. Subtract the blank obtained by titrating an identical volume of water, alkali, and indicator. The cyanide solution is unstable and must either be restandardized weekly or prepared fresh when needed.

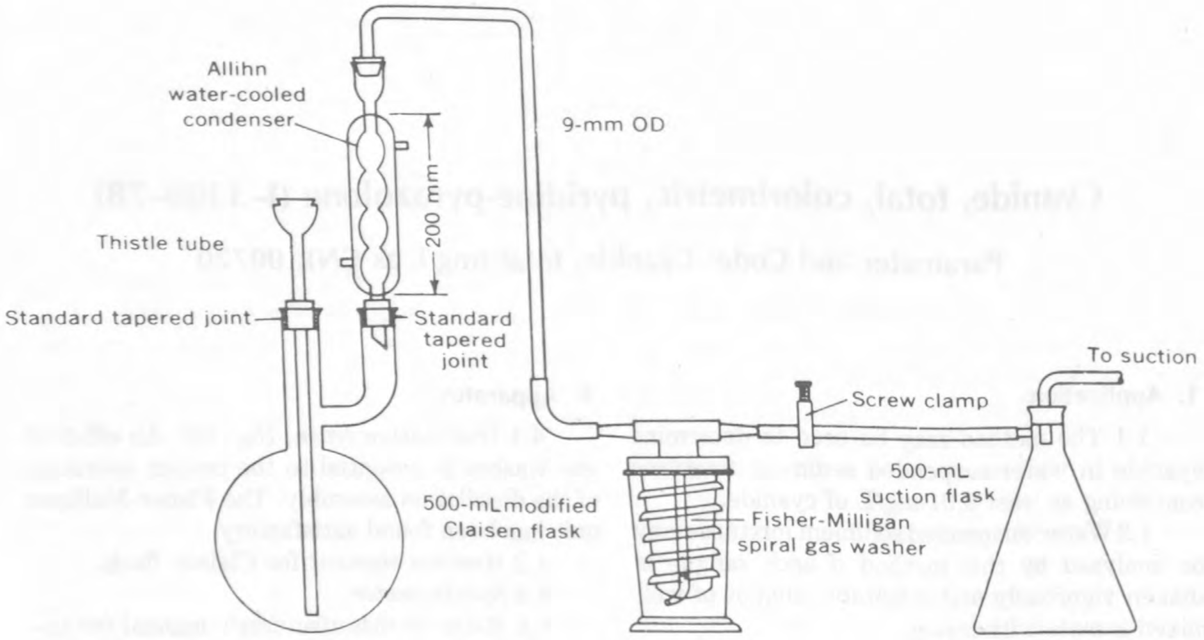


FIGURE 33.—Cyanide distillation train.

NOTE 1. CAUTION—POISON: May be fatal if swallowed or inhaled. Contact with acid liberates poisonous gas. Contact with KCN may burn eyes and irritate skin.

5.4 *Cyanide* standard solution II, 1.00 mL = 0.010 mg CN: Add 10.0 mL cyanide standard solution I to demineralized water and dilute to 1,000 mL. This solution must be prepared fresh before each use.

5.5 *Cyanide* standard solution III, 1.00 mL = 0.001 mg CN: Add 10.0 mL cyanide standard solution II to demineralized water and dilute to 100 mL. This solution must be prepared fresh before each use.

5.6 *Magnesium chloride* solution, 24 g/100 mL: Dissolve 51 g $MgCl_2 \cdot 6H_2O$ in 100 mL demineralized water.

5.7 *5-(*p*-dimethylaminobenzylidene)rhodamine indicator* solution, 0.02 g/100 mL: Dissolve 0.02 g 5-(*p*-dimethylaminobenzylidene)rhodamine in 100 mL acetone. Eastman Kodak No. 2748 has been found satisfactory.

5.8 *Pyrazolone* solution I: Add 0.8 g 1-phenyl-3-methyl-5-pyrazolone to 150 mL demineralized water at 75°C. Cool to room temperature, with stirring; filter. Eastman Kodak No. 1397 has been found satisfactory.

5.9 *Pyrazolone* solution II: Dissolve 0.025 g bis-pyrazolone in 25 mL pyridine and filter. Several minutes of mixing are usually required to effect solution. Eastman Kodak No. 6969 has been found satisfactory.

5.10 *Pyridine-pyrazolone* reagent: Mix 125 mL pyrazolone solution I with 25 mL pyrazolone solution II. The mixed reagent develops a pink color on standing, which does not affect color development. Prepare this reagent fresh daily or before each use.

5.11 *Pyridine*.

5.12 *Silver* nitrate standard solution, 1.00 mL ≎ 1.00 mg CN: Crush approx 5 g of $AgNO_3$ crystals and dry to constant mass at 40°C. Dissolve 3.2647 g $AgNO_3$ in demineralized water and dilute to 1,000 mL. This solution is needed only to standardize cyanide standard solution I.

5.13 *Sodium hydroxide,* 1*M*: Dissolve 4 g NaOH in 100 mL demineralized water.

5.14 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 *Distillation*

6.1.1 Assemble the distillation train, consisting of Claisen flask, thistle tube, condenser, gas washer, screw clamp, suction flask, and aspirator. Add 400 mL sample (or smaller aliquot diluted to 400 mL) to the boiling flask. Add *exactly* 50 mL 1*M* NaOH and 100 mL demineralized water to the gas washer. Connect train and adjust suction so that 1 to 2 bubbles per second enter the boiling flask through the air inlet. Do not increase airflow beyond 2 bubbles per second.

6.1.2 Add 10 mL $MgCl_2$ solution through the thistle tube, and allow the airflow to mix for 3 min. Rinse air tube with demineralized water, then slowly add 20 mL concentrated H_2SO_4. Rinse the tube again.

6.1.3 Heat at a rate which provides rapid boiling, but not enough to flood the condenser inlet or permit the vapors to rise more than halfway into the condenser. Reflux for 1 h. Turn off heat, but permit airflow to continue for 15 min.

6.1.4 Transfer gas washer contents to a 200-mL volumetric flask. Wash tube from condenser to gas washer, and the gas washer, with small amounts of demineralized water and add to contents of flask. Dilute contents of volumetric flask to 200 mL.

6.1.5 Refill the gas washer with NaOH and demineralized water, as in 6.1.1, and repeat reflux procedure. If only readily hydrolyzed cyanides are present, the absorber liquid from the first reflux period will contain all the available cyanide. If stable complex cyanides are present, a measurable yield will appear in the absorber liquid during the second and succeeding reflux periods, depending on the degree of stability of the compounds.

6.2 *Colorimetric procedure:* The standards and many of the reagents used in this procedure are unstable and must be prepared immediately before use if maximum color development is to be obtained. The color development is also dependent on there being approximately equal total salt concentrations in both samples and standards. If the final distillate volume is 200 mL, it will be about 0.25*M* in NaOH. For this reason 0.25*M* NaOH must be used for dilutions and for the blank. Any substantial deviation in the quantity of 3*M* acetic acid required to neutralize blank and standards will require additional manipulation to bring these volumes into approximate agreement. The variation should be less than 0.3 mL.

6.2.1 Prepare a blank by pipetting 15 mL of 0.25*M* NaOH into a 23-mm absorption cell fitted with a rubber stopper. Prepare standards containing 0.5 μg and 1.0 μg CN, each diluted to 15 mL with 0.25*M* NaOH in similar containers.

6.2.2 Pipet 15-mL aliquots (or smaller volumes diluted to 15 mL 0.25*M* NaOH) of the distillates from the purification procedure and place in 23-mm stoppered absorption cells.

6.2.3 Neutralize each sample, blank, and standard with 3*M* acetic acid, using phenolphthalein indicator solution.

6.2.4 To each sample, blank and standard add 4 drops chloramine-T solution, stopper, and shake. Allow 2 min for the reaction to proceed.

6.2.5 Add 5.0 mL mixed pyridine-pyrazolone reagent and mix well. Allow 20 min for color development.

6.2.6 Read absorbances at 620 nm. The color is stable for 30 min. Concentrations of from 0.0 to 80 μg/L have been shown to obey Beer's law. The absorbance decreases slowly over a period of 3 h, and can probably be read during this period with some decrease in accuracy.

7. Calculations

7.1

$$F = \frac{\text{mL distillate}}{\text{mL original sample volume}} \times \frac{\text{mg standard}}{\text{mL aliquot volume}} \times \frac{1{,}000}{A_{\text{std}}}$$

where

F = factor

A_{std} = absorbance of standard.

7.2 Determine the cyanide concentration in milligrams per liter as follows:

$$\text{CN in (mg/L)} = F \times A_{\text{sample}}$$

where

A_{sample} = absorbance of sample.

8. Report

Report cyanide, total (00720), concentrations as follows: less than 1.0 mg/L, nearest 0.01 mg/L; 1.0 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 27 percent at 0.2 mg/L.

References

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater [14th ed.]: Washington, D.C., American Public Health Association, p. 367.

American Society for Testing and Materials, 1976, Annual book of ASTM standards, water: Philadelphia, American Society for Testing and Materials, p. 500–505.

Brown, Eugene, Skougstad, M. W. and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 85.

Fluoride, dissolved, colorimetric, zirconium-eriochrome cyanine R (I–1325–78)

Parameter and Code: Fluoride, dissolved (mg/L as F): 00950

1. Application

This method may be used to analyze water and brines containing from 0.1 to 3.0 mg/L of fluoride. Higher concentrations must be reduced by dilution. If the fluoride concentration exceeds 30 mg/L, determine fluoride by the ion-selective electrode method (I–1327).

2. Summary of method

2.1 The zirconium-eriochrome cyanine R method given here is a modified version of the procedure of Megregian (1954).

2.2 In acid solution, zirconium reacts with eriochrome cyanine R to form a red complex ion. Fluoride forms a more stable complex with zirconium (ZrF_6^{-2}) and withdraws zirconium from the organic complex to produce a bleaching effect. Eriochrome cyanine R shows a decided specificity to zirconium.

2.3 The quality of eriochrome cyanine R from different sources differs significantly, and it is necessary to test the reagent each time it is prepared. The individual absorbance curves show corresponding differences, and the sensitivity of fluoride between reagents may differ by 20 percent.

2.4 The method includes a distillation step for the elimination of interferences noted below. Samples that contain a high concentration of dissolved solids must undergo the distillation step. A fixed volume of sample is added to a sulfuric acid solution having a specific boiling point and is distilled until an identical volume is recovered (Bellack, 1958). The fluoride is distilled as fluosilicic acid.

3. Interferences

3.1 Under the experimental conditions the dye does not give a color with titanium or beryllium, two metals which react with many other zirconium agents. Aluminum decreases the apparent fluoride concentration. This interference is eliminated by allowing the solution to stand for at least 2 h before making the absorbance measurement. Up to 10,000 μg/L of aluminum can be tolerated.

3.2 Analytical conditions are not overly critical. The pH is controlled at a highly acid level by the addition of 1.7 mL of concentrated hydrochloric acid to each sample. This assures that high concentrations of bicarbonate or other alkaline ions will not affect the pH significantly. Sulfate interferes but is removed by precipitation as barium sulfate. Overnight standing is usually required to assure complete settling of barium sulfate before making color comparison. The clarification of the sample can be accelerated by centrifuging, if immediate results are required. Filtration should not be used because of loss of color by absorption on the filter medium.

3.3 Residual chlorine, chromate, and probably other strong oxidants attack the dye. Stannous chloride is used to eliminate chromate and chlorine interference. Chromium, cadmium, and nickel, in concentrations of less than 5,000 μg/L, do not interfere. When the fluoride concentration exceeds 1.0 mg/L, larger quantities of these metals can be tolerated. Ten milligrams per liter cyanide and phosphate and 10,000 μg/L iron, zinc, and lead cause no appreciable interference if the sample is allowed to stand overnight.

3.4 The determination shows "salt effect"; the sensitivity is depressed by 5 to 10 percent at a dissolved-solids concentration of 10,000 mg/L. The effect of the usual type of color is not serious. A color of 70 on the platinum-cobalt scale is equivalent to an absorbance error of only 0.005 in the spectrophotometric measurement. Thus, it appears that color correction will not often be necessary. Highly colored or highly mineralized samples should be subjected to the distillation procedure given below.

3.5 The method has rather good tolerance for temperature differences. For most purposes, operating at room temperature without other precautions is satisfactory.

4. Apparatus

4.1 *Distillation assembly*, consisting of a round-bottom distilling flask, adapter, connecting tube, condenser, receiving flask, and thermometer, 250°C (fig. 34).

4.2 *Spectrometer*.

4.3 Refer to manufacturer's manual for optimizing instrumental parameters:

Wavelength .... 540 nm.

5. Reagents

5.1 *Eriochrome cyanine R* solution, 0.90 g/100 mL: Dissolve 1.80 g tested eriochrome cyanine R in water and dilute to 200 mL. The National Aniline Co. product labeled "alizarol cyanine RC" has been used successfully. A precipitate sometimes forms when the indicator solution is prepared, but the indicator may be filtered prior to use.

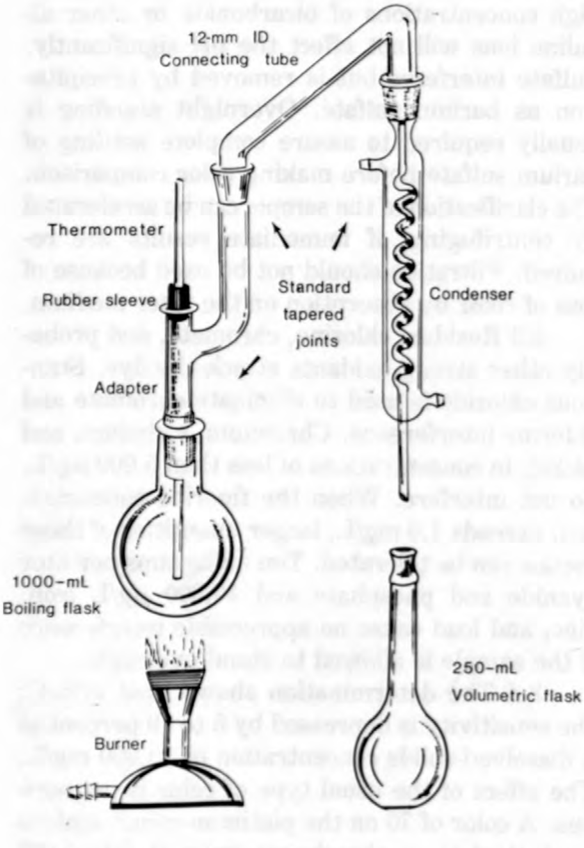


FIGURE 34.—Fluoride distillation assembly.

5.2 *Fluoride* standard solution I, 1.00 mL = 0.10 mg F^{-1}: Dissolve 0.2210 g NaF in demineralized water and dilute to 1,000 mL.

5.3 *Fluoride* standard solution II, 1.00 mL = 0.01 mg F^{-1}: Dilute 100 mL fluoride standard solution I to 1,000 mL with demineralized water.

5.4 *Hydrochloric acid, 6M*: Mix 50 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 100 mL.

5.5 *Mixed indicator* solution: To about 300 mL demineralized water add 20.0 mL eriochrome cyanine R solution and 10.0 mL $ZrO(NO_3)_2 \cdot 2H_2O$ solution. Add 70 mL concentrated HCl (sp gr 1.19) and 4 g $BaCl_2$. Dissolve and dilute to 1 L with demineralized water (NOTE 1, NOTE 2).

NOTE 1. It is practical to prepare more than 1 L of mixed indicator solution at a time. Eighteen liters contained in a 5-gallon reagent bottle seem to be a practical volume. If this is done, the component solutions must be prepared in correspondingly larger volumes.

NOTE 2. Once prepared, the mixed indicator solution should be allowed to stand for about 1 week in order to permit any precipitate to settle to the bottom of the bottle. The reagent is then used without disturbing the precipitate.

5.6 *Silver sulfate*, powder.

5.7 *Stannous chloride* solution, 1.7 g/100 mL: Dissolve 1.0 g $SnCl_2 \cdot 2H_2O$ in 10 mL concentrated HCl (sp gr 1.19) and dilute to 50 mL with demineralized water.

5.8 *Sulfuric acid*, concentrated (sp gr 1.84).

5.9 *Zirconyl nitrate* solution, 0.21 g/100 mL: Dissolve 0.49 g $ZrO(NO_2)_2 \cdot 2H_2O$ in 200 mL 6*M* HCl.

6. Procedure

6.1 *Distillation:* In the absence of color or other interfering substances the distillation may be omitted.

6.1.1 Place 400 mL demineralized water in a 1-L distilling flask containing a few glass beads. *Cautiously*, and with constant swirling, add 200 mL concentrated sulfuric acid. Connect the flask to the condenser assembly and distill until the temperature of the acid mixture reaches 180°C.

At this point the proper acid concentration has been reached. The acid need not be replaced until the accumulation of nonvolatile material is sufficient to cause interference. An occasional recovery check with a standard fluoride sample will indicate the need for replacement.

6.1.2 Cool to room temperature.

6.1.3 *Cautiously,* and with constant swirling, add 250 mL sample to the acid mixture in the distillation flask.

6.1.4 Distill until 250 mL of distillate has been collected, and the temperature of the acid mixture is again 180°C. When the temperature of the acid mixture at the completion of the distillation exceeds 183°C, add 50 mL distilled water and distill the mixture until the temperature again reaches 180°C. After distilling a high-fluoride sample (3 mg/L or more), clean the apparatus by distilling 150 mL of water. This prevents a carryover of fluoride in subsequent samples. When samples with high-chloride content are to be distilled, silver sulfate should be added to the distilling flask in proportion of 5 mg per milligram of chloride.

6.2 *Colorimetric procedure:*

6.2.1 Pipet a volume of sample or a volume of the cooled distillate (step 6.1.4) containing less than 0.03 mg F^{-1} (10.0 mL maximum) into a 50-mL centrifuge tube or test tube.

6.2.2 Prepare a blank and sufficient standards, and adjust the volume of each to 10.0 mL.

6.2.3 If chromate, residual chlorine, or other strong oxidizing agents are present in the sample, add 0.1 mL $SnCl_2$ solution and let the solution stand for 10 min.

6.2.4 Add 25.0 mL mixed indicator solution.

6.2.5 Allow the solution to stand overnight for barium sulfate to settle.

6.2.6 Decant approx 25 mL clear supernatant solution, taking care not to disturb the precipitate.

6.2.7 Determine the absorbance of each sample and standard against the blank which is set at an absorbance of 1.50 (NOTE 3); when necessary make correction for water color.

NOTE 3. Alternatively, measurement of transmittance may allow some instruments to be calibrated so that concentration can be read out directly.

7. Calculations

7.1 Determine milligrams of fluoride in each sample from a plot of absorbances of standards.

7.2 Determine the fluoride concentration in milligrams per liter as follows:

$$\text{F (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times \text{mg F in sample.}$$

8. Report

Report fluoride, dissolved (00950), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 0.1 to 2.0 mg/L may be expressed as follows:

$$S_T = 0.109X + 0.014$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of fluoride, milligrams per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
9	0.30	16
4	1.15	11
17	1.97	19

References

Bellack, Ervin, 1958, Simplified fluoride distillation method: American Water Works Association Journal, v. 50, p. 530.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 90.

Megregian, Stephen, 1954, Rapid spectrophotometric determination of fluoride with zirconium-eriochrome cyanine R lake: Analytical Chemistry, v. 26, p. 1161.

Fluoride, total, colorimetric, zirconium-eriochrome cyanine R (I–3325–78)

Parameter and Code: Fluoride, total (mg/L as F): 00951

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing from 0.1 to 3.0 mg/L of fluoride. Higher concentrations must be reduced by dilution. If the fluoride concentration exceeds 30 mg/L, determine fluoride by the ion-selective electrode method (I–1327).

1.2 Water-suspended sediment mixtures may be analyzed by this method if each sample is shaken vigorously and a suitable aliquot of well mixed sample is rapidly withdrawn. All water-suspended sediment mixtures must undergo the distillation step.

2. Summary of method

2.1 The zirconium-eriochrome cyanine R method given here is a modified version of the procedure of Megregian (1954).

2.2 In acid solution, zirconium reacts with eriochrome cyanine R to form a red complex ion. Fluoride forms a more stable complex with zirconium (ZrF_6^{-2}) and withdraws zirconium from the organic complex to produce a bleaching effect. Eriochrome cyanine R shows a decided specificity to zirconium.

2.3 The quality of the eriochrome cyanine R from different sources differs significantly, and it is necessary to test the reagent each time it is prepared. The individual curves show corresponding differences, and the sensitivity of fluoride between reagents may differ by 20 percent.

2.4 The method includes a distillation step to decompose organic fluoride compounds and attack minerals such as fluorspar. It also eliminates interferences noted below. A fixed volume of sample is added to a sulfuric acid solution having a specific boiling point and is distilled until an identical volume is recovered (Bellack, 1958). The fluoride is distilled as fluosilicic acid.

3. Interferences

3.1 Under the experimental conditions the dye does not give a color with titanium or beryllium, two metals which react with many other zirconium agents. Aluminum decreases the apparent fluoride concentration. This interference is eliminated by allowing the solution to stand for at least 2 h before making the absorbance measurement. Up to 10,000 μg/L of aluminum can be tolerated.

3.2 Analytical conditions are not overly critical. The pH is controlled at a highly acid level by the addition of 1.7 mL of concentrated hydrochloric acid to each sample. This assures that high concentrations of bicarbonate or other alkaline ions will not affect the pH significantly. Sulfate interferes but is removed by precipitation as barium sulfate. Overnight standing is usually required to assure complete settling of barium sulfate before making color comparison. The clarification of the sample can be accelerated by centrifuging, if immediate results are required. Filtration should not be used because of loss of color by adsorption on the filter medium.

3.3 Residual chlorine, chromate, and probably other strong oxidants attack the dye. Stannous chloride is used to eliminate chromate and chlorine interference. Chromium, cadmium, and nickel, in concentrations of less than 5 mg/L, do not interfere. When the fluoride concentration exceeds 1.0 mg/L, larger quantities of these metals can be tolerated. Ten mg/L of cyanide and phosphate and 10,000 μg/L of iron, zinc, and lead cause no appreciable interference if the sample is allowed to stand overnight.

3.4 The determination shows "salt effect"; the sensitivity is depressed by 5 to 10 percent at a dissolved-solids concentration of 10,000 mg/L. The effect of the usual type of color is not serious. A color of 70 on the platinum-cobalt scale is equivalent to an absorbance error of only 0.005 in the spectrophotometric measurement. Thus, it appears that color correction will not often be necessary. Highly colored or highly mineralized samples should be subjected to the distillation procedure given below.

3.5 The method has rather good tolerance for temperature differences. For most purposes, operating at room temperature without other precautions is satisfactory.

4. Apparatus

4.1 *Distillation assembly* consisting of a round-bottom distilling flask, adapter, connecting tube, condenser, receiving flask, and thermometer, 250°C (fig. 35).

4.2 *Spectrometer.*

4.3 Refer to manufacturer's manual for optimizing instrumental parameters:

Wavelength .... 540 nm.

5. Reagents

5.1 *Eriochrome cyanine R* solution, 0.90 g/100 mL: Dissolve 1.80 g tested eriochrome cyanine R in water and dilute to 200 mL. The National Aniline Co. product labeled "alizarol cyanine RC" has been used successfully. A precipitate sometimes forms when the indicator solution is prepared, but the indicator may be filtered prior to use.

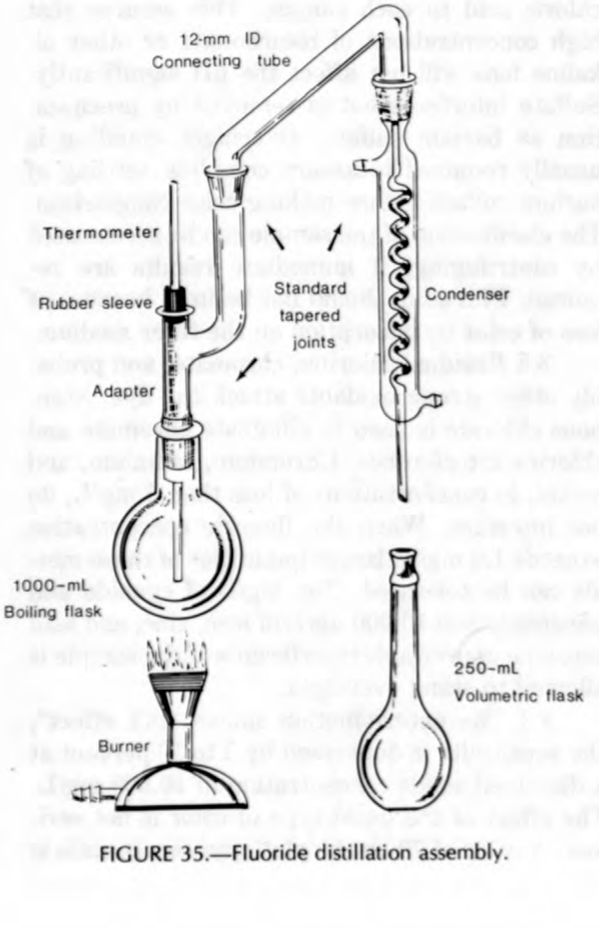


FIGURE 35.—Fluoride distillation assembly.

5.2 *Fluoride* standard solution I, 1.00 mL = 0.10 mg F^{-1}: Dissolve 0.2210 g NaF in demineralized water and dilute to 1,000 mL.

5.3 *Fluoride* standard solution II, 1.00 mL = 0.01 mg F^{-1}: Dilute 100 mL fluoride standard solution I to 1,000 mL with demineralized water.

5.4 *Hydrochloric acid,* 6*M*: Mix 50 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 100 mL.

5.5 *Mixed indicator* solution: To about 300 mL demineralized water add 20.0 mL eriochrome cyanine R solution and 10.0 mL $ZrO(NO_3)_2 \cdot 2H_2O$ solution. Add 70 mL concentrated HCl (sp gr 1.19) and 4 g $BaCl_2$. Dissolve and dilute to 1,000 mL with demineralized water.

NOTE 1. It is practical to prepare more than 1 L of mixed indicator solution at a time. Eighteen liters contained in a 5-gallon reagent bottle seem to be a practical volume. If this is done, the component solutions must be prepared in correspondingly larger volumes.

NOTE 2. Once prepared, the mixed indicator solution should be allowed to stand for about 1 week in order to permit any precipitate to settle to the bottom of the bottle. The reagent is then used without disturbing the precipitate.

5.6 *Silver sulfate,* powder.

5.7 *Stannous chloride* solution, 1.7 g/100 mL: Dissolve 1.0 g $SnCl_2 \cdot 2H_2O$ in 10 mL concentrated HCl (sp gr 1.19) and dilute to 50 mL with demineralized water.

5.8 *Sulfuric acid,* concentrated (sp gr 1.84).

5.9 *Zirconyl nitrate* solution, 0.21 g/100 mL: Dissolve 0.49 g $ZrO(NO_2)_2 \cdot 2H_2O$ in 200 mL 6*M* HCl.

6. Procedure

6.1 *Distillation:*

6.1.1 Place 400 mL demineralized water in a 1-L distilling flask containing a few glass beads. *Cautiously,* and with constant swirling, add 200 mL concentrated sulfuric acid. Connect the flask to the condenser assembly and distill until the temperature of the acid mixture reaches 180°C. At this point the proper acid concentration has been reached. The acid need not be replaced until the accumulation of nonvolatile material is sufficient to cause interference. An occasional recovery check with a standard fluoride sample will indicate the need for replacement.

6.1.2 Cool to room temperature.

6.1.3 *Cautiously,* and with constant swirling, add 250 mL well mixed sample to the acid mixture in the distillation flask.

6.1.4 Distill until 250 mL of distillate has been collected, and the temperature of the acid mixture is again 180°C. When the temperature of the acid mixture at the completion of the distillation exceeds 183°C, add 50 mL distilled water and distill the mixture until the temperature again reaches 180°C. After distilling a high-fluoride sample (3 mg/L or more), clean the apparatus by distilling 250 mL of water. This prevents a carryover of fluoride in subsequent samples. When samples with high-chloride content are to be distilled, silver sulfate should be added to the distilling flask in proportion of 5 mg per milligram of chloride.

6.2 *Colorimetric procedure:*

6.2.1 Pipet a volume of sample or a volume of the cooled distillate (step 6.1.4) containing less than 0.03 mg F^{-1} (10.0 mL maximum) into a 50-mL centrifuge tube or test tube.

6.2.2 Prepare a blank and sufficient standards, and adjust the volume of each to 10.0 mL.

6.2.3 If chromate, residual chlorine, or other strong oxidizing agents are present in the sample, add 0.1 mL $SnCl_2$ solution and let the solution stand for 10 minutes.

6.2.4 Add 25.0 mL mixed indicator solution.

6.2.5 Allow the solution to stand overnight for barium sulfate to settle.

6.2.6 Decant approximately 25 mL clear supernatant solution, taking care not to disturb the precipitate.

6.2.7 Determine the absorbance of each sample and standard against the blank, which is set at an absorbance of 1.50 (NOTE 3); when necessary make correction for water color.

NOTE 3. Alternatively, measurement of transmittance may allow some instruments to be calibrated so that concentration can be read out directly.

7. Calculations

7.1 Determine milligrams of fluoride in each sample from a plot of absorbances of standards.

7.2 Determine the fluoride concentration in milligrams per liter as follows:

$$F\ (\text{mg/L}) = \frac{1{,}000}{\text{mL sample}} \times \text{mg F in sample.}$$

8. Report

Report fluoride, total (00951), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 16 percent at 0.3 mg/L and greater than 11 percent at 1.15 mg/L.

References

Bellack, Ervin, 1958, Simplified fluoride distillation method: American Water Works Association Journal, v. 50, p. 530.

Brown, Eugene, Skougstad, M. W. and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 90.

Megregian, Stephen, 1954, Rapid spectrophotometric determination of fluoride with zirconium-eriochrome cyanine R lake: Analytical Chemistry, v. 26, p. 1161.

Iodide, dissolved, colorimetric, ceric-arsenious oxidation (I–1371–78)

Parameter and Code: Iodine, dissolved (mg/L as I): 71865

1. Application

This method may be used to determine iodide in fresh waters and brines containing from 0.001 to 0.060 mg/L of iodide. Higher concentrations must be reduced by dilution; however, samples containing concentrations greater than 1 mg/L should be analyzed by the bromine oxidation method (Method I–1370).

2. Summary of method

This method is based on the catalytic effect of iodide on the ceric-arsenious oxidation reaction in acid solution. In the presence of a small amount of iodide, the reaction follows first-order reaction-rate kinetics—and at a given temperature and for a given reaction time, the extent of reduction of ceric ion is directly proportional to the iodide concentration. The reaction may be stopped completely at any time by the addition of silver ion. Photometric measurement of the absorbance of the solution permits evaluation of the extent of the reaction (Mitchell, 1966).

3. Interferences

3.1 Most substances normally present in natural water do not interfere.

3.2 Low values for iodide may result if the reaction test tubes are not thoroughly clean. Rinsing each sample tube with HCl followed by deionized water immediately before use removes possible contaminants.

3.3 Bromide ion does not interfere, and any substance which oxidizes iodide to iodine has no effect on the reaction.

3.4 Certain phosphate compounds used in water treatment, such as Calgon, have an inhibiting effect on the reaction. This effect can be eliminated by adding 3 drops concentrated nitric acid at step 6.1 in the procedure. The nitric acid should be aerated to remove nitrogen oxides.

4. Apparatus

4.1 *Stirring rods*, glass.

4.2 *Water bath*, constant temperature (30°C ± 0.5°C).

4.3 *Spectrometer*.

4.4 Refer to manufacturer's manual for optimizing instrumental parameters:

Wavelength .... 450 nm.

5. Reagents

5.1 *Arsenious acid* standard solution, 0.3*N* H_3AsO_3: Add 14.84 g primary standard As_2O_3 to 500 mL demineralized water in a 1,000-mL beaker. Next, add slowly 28 mL concentrated H_2SO_4 (sp gr 1.84); stir and warm the mixture until the As_2O_3 is dissolved. Cool, transfer to a 1,000-mL volumetric flask, and dilute to volume with demineralized water. Add a small piece of metallic arsenic to stabilize the solution.

5.2 *Ceric sulfate* standard solution, 0.1*N* $Ce(HSO_4)_4$: Dissolve 52.80 g anhydrous $Ce(HSO_4)_4$ in 600 mL 2.5*M* H_2SO_4 contained in a 1-L volumetric flask. Warm the mixture and stir occasionally until a clear solution is obtained (1 h). When cool, dilute to volume with 2.5*M* H_2SO_4.

5.3 *Iodide* standard solution I, 1.00 mL = 0.01 mg I^{-1}: Dissolve 0.0131 g KI crystals, dried overnight in a sulfuric acid desiccator, in demineralized water and dilute to 1,000 mL.

5.4 *Iodide* standard solution II, 1.00 mL = 0.0001 mg I^{-1}: Dilute 10.0 mL iodide standard solution I to 1,000 mL with demineralized water.

5.5 *Silver nitrate* solution 0.10 g/L: Dissolve 0.10 g $AgNO_3$ in 1 L demineralized water. Store in a dark bottle.

5.6 *Sulfuric acid*, 2.5*M*: Cautiously add 139 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.0012 mg I^{-1} (20.0 mL maximum) into a 23-mm absorption cell.

6.2 Prepare a demineralized water blank to be used as a control and sufficient standards containing less than 0.0012 mg I^{-1}, in 23-mm absorption cells.

6.3 Dilute each sample, blank, and standard to 20.0 mL; add 0.5 mL concentrated H_2SO_4 to each and mix.

6.4 Add 1.0 mL H_3AsO_3 standard solution to each absorption cell and mix.

6.5 Place all absorption cells in a constant temperature bath at 30°C. Allow 30 to 45 min for the contents to reach temperature equilibrium.

6.6 At zero time add 1.0 mL ceric sulfate standard solution (temperature equilibrated) and mix thoroughly.

6.7 After exactly 10 min add, with stirring, 1 drop (0.05 mL) $AgNO_3$ solution (NOTE 1).

NOTE 1. The addition of $AgNO_3$ solution may be omitted if the ceric sulfate solution is added at intervals of 30 sec or longer and the absorbance of each sample, blank, and standard measured exactly 10.0 min after the addition of the ceric sulfate solution.

6.8 Measure the absorbance of each blank, standard, and sample at 450 nm, using demineralized water as a reference.

7. Calculations

7.1 Construct an analytical curve by plotting the ratio A_s/A_c, against milligrams of iodide on semilog paper (A_s = absorbance of standard and A_c = absorbance of control).

7.2 From the curve, determine the milligrams of iodide corresponding to the absorbance ratio obtained for each sample.

7.3 Determine the iodide concentration in milligrams per liter as follows:

$$\text{I (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times \text{mg I in sample.}$$

8. Report

Report iodide, dissolved (71865), concentrations as follows: less than 0.1 mg/L, three decimals; 0.1 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
3	0.34	88

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 100.

Mitchell, C. G., 1966, Semimicroanalytical method for the determination of iodide in water: U.S. Geological Survey Water-Supply Paper 1822, p. 77.

Iodide, dissolved, colorimetric, ceric-arsenious oxidation, automated (I–2371–78)

Parameter and Code: Iodide, dissolved (mg/L as I): 71865

1. Application

This method may be used to determine iodide in fresh waters and brines containing from 0.001 to 0.060 mg/L of iodide. Higher concentrations must be reduced by dilution; however, samples containing concentrations greater than 1 mg/L should be analyzed by the bromine oxidation method (Method I–1370).

2. Summary of method

The method is based on the catalytic effect of iodide on the ceric-arsenious oxidation reaction in acid solution. In the presence of a small amount of iodide, the reaction follows first-order reaction-rate kinetics—and at a given temperature and for a given reaction time, the extent of reduction of ceric ion is directly proportional to the iodide concentration. Photometric measurement of the absorbance of the solution permits evaluation of the extent of the reaction (Mitchell, 1966).

3. Interferences

3.1 Most substances normally present in natural water do not interfere.

3.2 Bromide ion does not interfere.

3.3 Low iodide values will be obtained if the pH of the water samples is less than 3 or if the iron concentration exceeds 500 μg/L.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of a sampler proportioning pump, cartridge manifold, colorimeter, voltage stabilizer, recorder, printer, and heating bath.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.001 to 0.060 mg/L:

Absorption cell	15 mm.
Wavelength	410 nm.
Cam	30/h (2/1).

5. Reagents

5.1 *Arsenious acid* solution, 2.782 g/L: Add 2.782 g primary standard As_2O_3 to approx 500 mL demineralized water in a 1,000-mL volumetric flask. Slowly add 3 mL concentrated H_2SO_4 (sp gr 1.84). Warm the mixture in a steam bath and stir frequently until the As_2O_3 is dissolved. Cool and dilute to 1,000 mL with demineralized water. Add a small piece of metallic arsenic to stabilize the solution.

5.2 *Ceric sulfate* solution, 1.584 g/L: Add 600 mL 2.5*M* H_2SO_4 and 1.584 g anhydrous $Ce(HSO_4)_4$ to a 1,000-mL volumetric flask. Warm the mixture and stir occasionally until a clear solution is obtained. Cool and dilute to volume with 2.5*M* H_2SO_4.

5.3 *Iodide* standard solution I, 1.00 mL = 0.01 mg I^{-1}: Dissolve 0.0131 g KI crystals, dried overnight in a sulfuric acid desiccator, in demineralized water and dilute to 1,000 mL.

5.4 *Iodide* standard solution II, 1.00 mL = 0.0005 mg I^{-1}: Dilute 50.0 mL iodide standard solution I to 1,000 mL with demineralized water.

5.5 *Iodide* working standards: Prepare a blank and 500 mL each of a series of iodide working standards by appropriate quantitative dilution of the iodide standard solution II as follows:

Iodide standard solution II (mL)	*Iodide concentration (mg/L)*
0.0	0.000
2.0	.002
5.0	.005
10.0	.010

Iodide standard solution II (mL)	*Iodide concentration (mg/L)*
20.0	.020
40.0	.040
60.0	.060

5.6 *Sulfuric acid*, 2.5*M*: Cautiously add 139 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Set up manifold (fig. 36).

6.2 Allow colorimeter and recorder to warm up for at least 30 min. Adjust the baseline to read zero scale division on the recorder with all reagents, but with demineralized water in the sample tube.

6.3 Beginning with the most concentrated standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each peak versus its respective iodide concentration.

7.2 Compute the iodide concentration of each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report iodide, dissolved (71865), concentrations as follows: less than 0.1 mg/L, three decimals; 0.1 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 100.

Mitchell, C. G., 1966, Semimicroanalytical method for the determination of iodide in water: U.S. Geological Survey Water-Supply Paper 1822, p. 77.

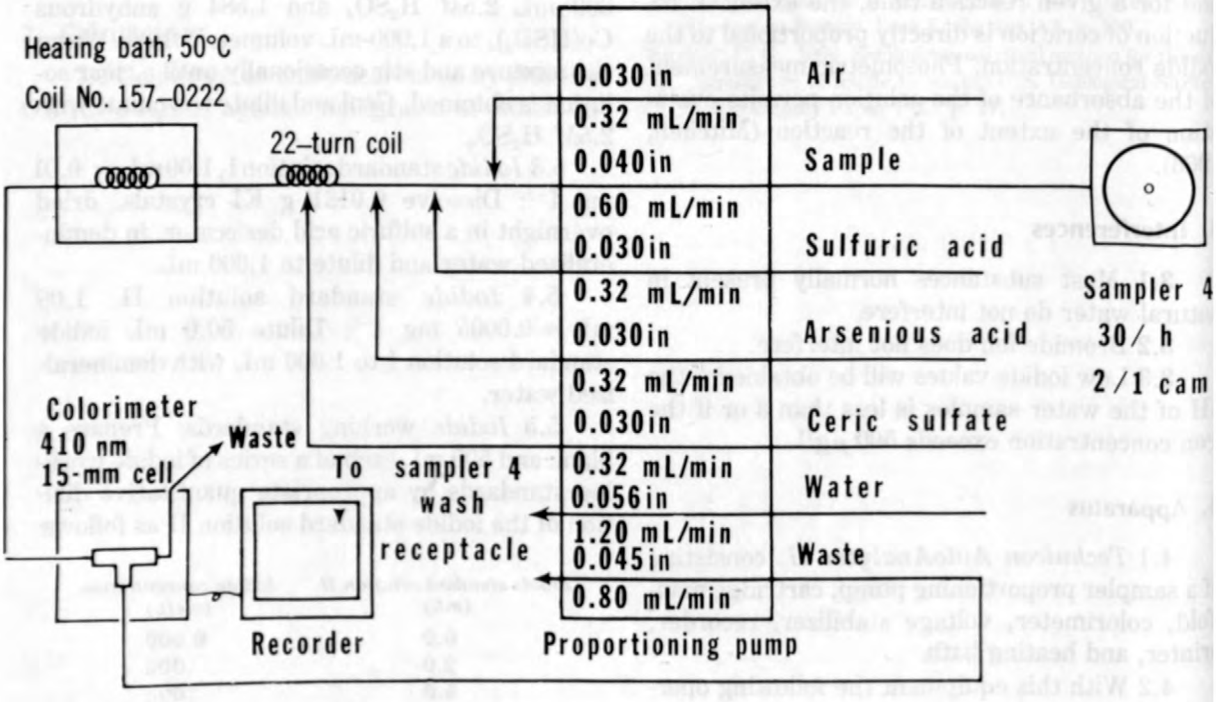


FIGURE 36.—Iodide manifold.

Iron, dissolved, colorimetric, bipyridine (I–1379–78)

Parameter and Code: Iron, dissolved (μg/L as Fe): 01046

1. Application

This method may be used to analyze samples containing between 10 and 4,000 μg/L of iron. Samples containing more than 4,000 μg/L must first be diluted.

2. Summary of method

This method is based on the reaction between ferrous iron and 2,2′-bipyridine that yields a red complex (Moss and Mellon, 1942). Hydroxylamine hydrochloride reduces ferric iron to ferrous iron. The color develops immediately and is stable for several hours. The color intensity is independent of pH in the range of 3 to 10.

3. Interferences

3.1 Copper reacts with bipyridine at pH values greater than 6, but the method embodies pH adjustment to about 5.5 where copper does not show appreciable interference. Silver, antimony, zinc, and bismuth must be absent. The procedure can be used with undiluted samples for analysis of water having metal concentrations as high as:

	μg/L		μg/L
Cd	50,000	Hg	5,000
Cr	15,000	Ni	10,000
Co	20,000	Zn	5,000
Cu	5,000		

3.2 Interfering anions must be limited to the following concentrations:

	mg/L		mg/L
CN	10	P_2O_7 (as P)	5
Cr_2O_7	100	WO_4	7
PO_4 (as P)	50		

3.3 At 520 nm, the wavelength used in the determination, the natural color of the water may contribute a measurable absorbance and a correction must be made if the color exceeds about 50 platinum-cobalt units. This applies only to the "normal" type of yellow color found in water.

4. Apparatus

4.1 *Spectrometer* for use at 520 nm; Beckman Model B, or equivalent.

4.2 With this instrument the following operating conditions have been used.

Wavelength	520 nm.
Cells	40 mm.
Phototube	Blue-sensitive.
Initial sensitivity setting	1.
Slit width	0.1 mm.

4.3 With these operating conditions the following readings have been observed:

Amount of Fe (μg)	*Absorbance*
0.0	0.000
12.5	.265
25.0	.540
50.0	1.070
100	2.140

5. Reagents

5.1 *Bipyridine solution,* 2.0 g/L: Dissolve 1.0 g 2,2′-bipyridine in demineralized water and dilute to 500 mL.

5.2 *Hydroxylamine-hydrochloric acid* reagent: Dissolve 100 g $NH_2OH \cdot HCl$ in demineralized water. Add 40 mL concentrated HCl (sp gr 1.19) and dilute to 1 L with demineralized water.

5.3 *Iron* standard solution I, 1.00 mL = 400 μg Fe: Weigh 0.400 g analytical grade iron wire which has been cleaned in dilute HCl, rinsed and dried. Dissolve in a minimum of dilute HCl and dilute to 1,000 mL with demineralized water.

5.4 *Iron* standard solution II, 1.00 mL = 4.00 μg Fe: Dilute 10.0 mL iron standard solution I to 1,000 mL with demineralized water containing 1 mL concentrated HCl (sp gr 1.19).

5.5 *Sodium acetate* solution, 350 g/L: Dissolve 350 g CH_3COONa in demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 100 µg Fe (25.0 mL maximum) into a 50-mL beaker, and adjust the volume to 25.0 mL with demineralized water.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to 25.0 mL.

6.3 Add 1.0 mL bipyridine solution. Color development at this stage indicates the presence of ferrous iron.

6.4 Add 2.0 mL hydroxylamine-hydrochloric acid reagent, mix, and allow the solution to stand 30 min.

6.5 Add 2.0 mL CH_3COONa solution and mix.

6.6 Determine the absorbance of each sample and standard against the blank and, when necessary, correct for water color.

7. Calculations

7.1 Determine micrograms of iron in the sample from a plot of absorbances of standards.

7.2 Determine iron concentrations in milligrams per liter as follows:

$$\text{Fe } (\mu g/L) = \frac{1{,}000}{\text{mL sample}} \times \mu g \text{ Fe in sample.}$$

8. Report

Report iron, dissolved (01046), concentrations as follows: less than 100 µg/L, nearest 10 µg/L; 100 µg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 25 to 1,000 µg/L may be expressed as follows:

$$S_T = 0.019X + 9.18$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of iron, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (µg/L)*	*Relative deviation (percent)*
3	27	22
7	824	2

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 103.

Moss, M. L., and Mellon, M. G., 1942, Colorimetric determination of iron with 2,2′ bipyridyl and with 2,2′,2″-terpyridyl: Industrial Engineering Chemistry, Analytical Edition, v. 14, p. 862.

Iron, dissolved, colorimetric, bipyridine, automated (I–2379–78)

Parameter and Code: Iron, dissolved (μg/L as Fe): 01046

1. Application

This method may be used to analyze waters and brines containing between 10 and 5,000 μg/L of iron. Samples containing more than 5,000 μg/L must first be diluted. If the iron concentration exceeds 50,000 μg/L, determine iron by absorption (Method I–1381).

2. Summary of method

This method is based on the reaction between ferrous iron and 2,2′-bipyridine that yields a red complex (Moss and Mellon, 1942). Hydroxylamine hydrochloride reduces ferric iron to ferrous iron. The color develops immediately and is stable for several hours. The color intensity is independent of pH in the range of 3 to 10.

3. Interferences

3.1 Copper reacts with bipyridine at pH values greater than 6, but the method embodies pH adjustment to about 5.5, where copper does not show appreciable interference. Silver, antimony, zinc, and bismuth must be absent. The procedure can be used with undiluted samples for analysis of water having metal concentrations as high as:

	μg/L		μg/L
Cd	50,000	Hg	5,000
Cr	15,000	Ni	10,000
Co	20,000	Zn	5,000
Cu	5,000		

3.2 Interfering anions must be limited to the following concentrations:

	mg/L		mg/L
CN	10	P_2O_7 (as P)	5
Cr_2O_7	100	WO_4	7
PO_4 (as P)	50		

3.3 At 520 nm, the wavelength used in the determination, the natural color of the water may contribute a measurable absorbance and must be corrected for if the color exceeds about 50 platinum-cobalt units. This applies only to the "normal" type of yellow color found in water. It is preferable to analyze highly colored samples by atomic absorption spectrometry.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of a sampler, proportioning pump, cartridge manifold, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0 to 5,000 μg/L:

Absorption cell	**50 mm.**
Wavelength	**520 nm.**
Cam	**40/h (2/1).**

5. Reagents

5.1 *Bipyridine solution*, 0.5 g/L: Dissolve 0.5 g 2,2′-bipyridine in demineralized water and dilute to 1 L.

5.2 *Hydroxylamine-hydrochloric acid* reagent: Dissolve 25 g $NH_2OH \cdot HCl$ in demineralized water. Add 10 mL concentrated HCl (sp gr 1.19). Dilute to 1 L with demineralized water. Add 1 mL Brij–35. Refrigerate if possible.

5.3 *Iron* standard solution I, 1.00 mL = 500 μg Fe: Dissolve 0.500 g analytical-grade iron wire (cleaned in dilute HCl, rinsed and dried) in 3 to 5 mL concentrated HNO_3 (sp gr 1.19). Dilute to 1,000 mL with demineralized water.

5.4 *Iron* standard solution II, 1.00 mL = 50 μg Fe: Dilute 100.0 mL iron standard solution I to 1,000 mL with demineralized water containing 2 or 3 drops concentrated HNO_3 (sp gr 1.19).

5.5 *Iron* working standards: Prepare a blank and 500 mL each of a series of iron working standards by appropriate quantitative dilution of iron standard solution II as follows: Add 0.5 mL concentrated HNO_3 (sp gr 1.19) to each standard before diluting to 500.0 mL.

Iron standard solution II (mg)	*Iron concentration* (µg/L)
0.0	0
1.0	100
2.0	200
5.0	500
10.0	1,000
20.0	2,000
30.0	3,000
40.0	4,000
50.0	5,000

5.6 *Sodium acetate* solution, 150 g/L: Dissolve 150 g CH_3COONa in demineralized water and dilute to 1 L for the filtered acidified samples. Add 1 mL Brij–35 solution.

6. Procedure

6.1 Set up manifold (fig. 37).

6.2 Allow colorimeter and recorder to warm up for at least 30 min. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample tube.

6.3 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective iron concentration.

7.2 Compute the concentration of iron in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report iron, dissolved (01046), concentrations as follows: less than 100 µg/L, nearest 10 µg/L; 100 µg/L and above, two significant figures.

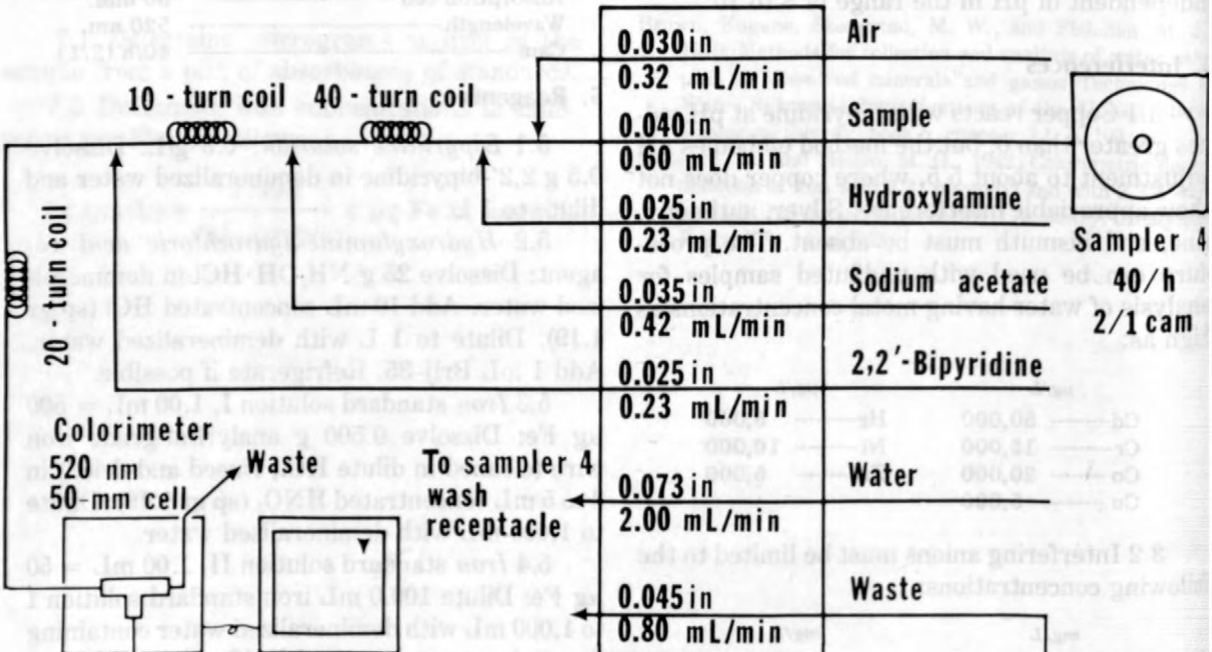


FIGURE 37.—Iron manifold.

9. Precision

The precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean* (*µg/L*)	*Relative deviation* (*percent*)
2 (40 replicates)	118	13
2 (39 replicates)	991	6

References

Brown, Eugene, Skougstad, M. W. and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 103.

Moss, M. L., and Mellon, M. G., 1942, Colorimetric determination of iron with 2,2'-bipyridyl and with 2,2',2"-terpyridyl: Industrial Engineering Chemistry, Analytical Edition, v. 14, p. 862.

Iron, recoverable from bottom material, colorimetric, bipyridine automated (I–6379–78)

Parameter and Code: Iron, recoverable from bottom material, dry wt (μg/g as Fe): 01170

1. Application

1.1 This method may be used to analyze bottom material containing at least 1 μg/g of total iron. Prepared sample solutions (Method I–5485) containing more than 5,000 μg/L must first be diluted. If the iron concentration exceeds 50,000 μg/L, determine iron by atomic absorption (Method I–5381).

1.2 Bottom material must undergo a preliminary digestion-solubilization by Method I–5485 before analysis by this procedure.

2. Summary of method

This method is based on the reaction between ferrous iron and 2,2′-bipyridine that yields a red complex (Moss and Mellon, 1942). Hydroxylamine hydrochloride reduces ferric iron to ferrous iron. The color develops immediately and is stable for several hours. The color intensity is independent of pH in the range 3 to 10.

3. Interferences

3.1 Copper reacts with bipyridine at pH values greater than 6, but the method embodies pH adjustment to about 5.5, where copper does not show appreciable interference. Silver, antimony, zinc, and bismuth must be absent. The procedure can be used with undiluted samples for analysis of water having metal concentrations as high as:

	μg/L		μg/L
Cd	50,000	Hg	5,000
Cr	15,000	Ni	10,000
Co	20,000	Zn	5,000
Cu	5,000		

3.2 Interfering anions must be limited to the following concentrations:

	mg/L		mg/L
CN	10	P_2O_7 (as P)	5
Cr_2O_7	100	WO_4	7
PO_4 (as P)	50		

3.3 At 520 nm, the wavelength used in the determination, the natural color of the water may contribute a measurable absorbance and must be corrected for if the color exceeds about 50 platinum-cobalt units. This applies only to the "normal" type of yellow color found in water. Highly colored samples must be analyzed by atomic absorption spectrometry.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of a sampler, proportioning pump, cartridge manifold, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 10 to 5,000 μg/L:

Absorption cell	50 mm.
Wavelength	520 nm.
Cam	40/h (2/1).

5. Reagents

5.1 *Bipyridine solution*, 0.5 g/L: Dissolve 0.5 g 2,2′-bipyridine in demineralized water and dilute to 1 L.

5.2 *Hydroxylamine-hydrochloric acid* reagent: Dissolve 25 g $NH_2OH \cdot HCl$ in demineralized water. Add 10 mL concentrated HCl (sp gr 1.19). Dilute to 1 L with demineralized water. Add 1 mL Brij–35 solution. Refrigerate if possible.

5.3 *Iron* standard solution I, 1.00 mL = 500 μg Fe: Dissolve 0.500 g analytical-grade iron wire (cleaned in dilute HCl, rinsed and dried) in 3 to 5 mL concentrated HNO_3 (sp gr 1.19). Dilute to 1,000 mL with demineralized water.

5.4 *Iron* standard solution II, 1.00 mL = 50 μg Fe: Dilute 100.0 mL iron standard solution I to 1,000 mL with demineralized water containing 2 or 3 drops concentrated HNO_3 (sp gr 1.19).

5.5 *Iron* working standards: Prepare a blank and 500 mL each of a series of iron working standards by appropriate quantitative dilution of iron standard solution II as follows: Add 0.5 mL concentrated HNO_3 (sp gr 1.19) to each standard before diluting to 500.0 mL.

Iron standard solution II (mL)	*Iron concentration (μg/L)*
0.0	0
1.0	100
2.0	200
5.0	500
10.0	1,000
20.0	2,000
30.0	3,000
40.0	4,000
50.0	5,000

5.6 *Sodium Acetate* solution, 350 g/L: Dissolve 350 g CH_3COONa in demineralized water and dilute to 1 L for the digested samples. Add 1 mL Brij–35.

6. Procedure

6.1 Set up manifold (fig. 38).

6.2 Allow colorimeter and recorder to warm up for at least 30 min. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample tube.

6.3 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

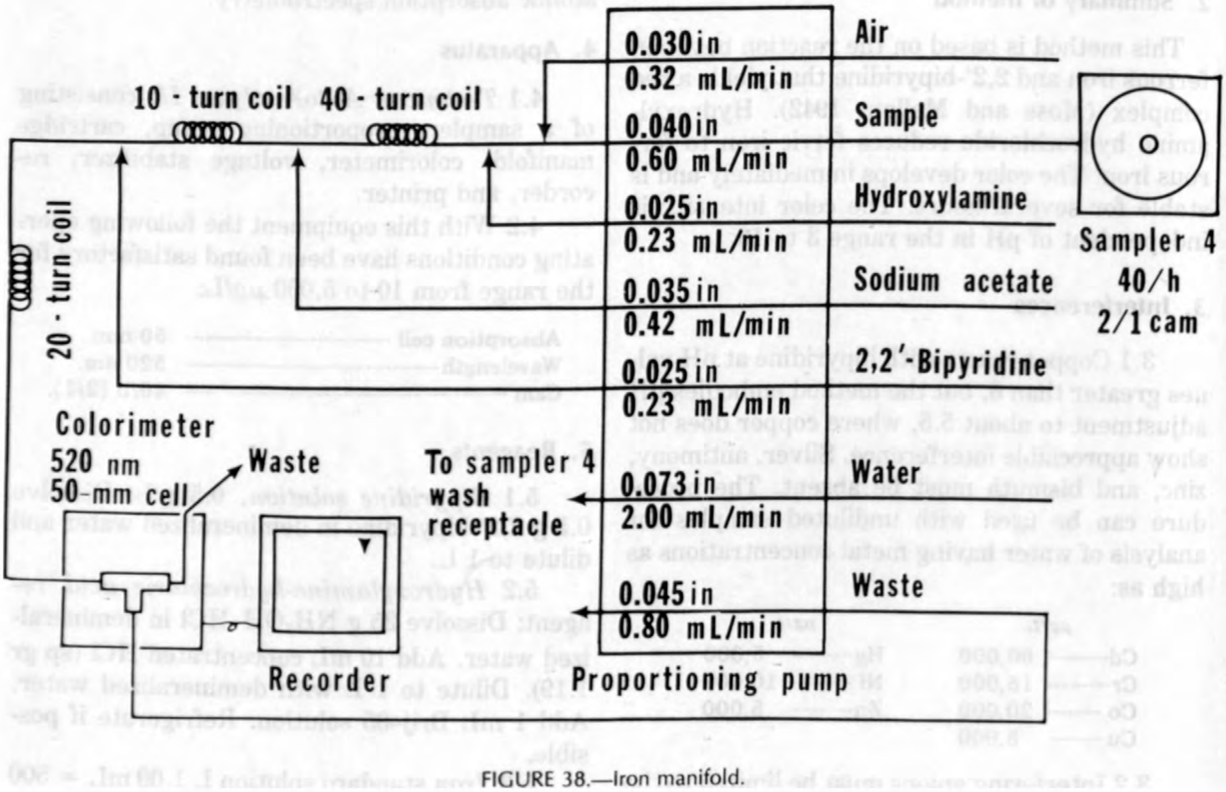


FIGURE 38.—Iron manifold.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective iron concentration.

7.2 Compute the concentration of iron in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 Compute the concentration of iron, total in bottom material as follows:

$$\text{Fe } (\mu g/g) = \frac{\mu g/L \text{ Fe} \times \dfrac{\text{mL of original digest}}{1{,}000}}{\text{wt of sample (g)}}$$

8. Report

Report iron, recoverable from bottom material (01170), concentrations as follows: less than 100 µg/g, nearest 1 µg/g; 100 µg/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method will be greater than 13 percent in the lower portion of the analytical range.

Reference

Moss, M. L., and Mellon, M. G., 1942, Colorimetric determination of iron with 2,2′-bipyridyl and with 2,2,2″-terpyridyl: Industrial Engineering Chemistry, Analytical Edition, v. 14, p. 862.

Iron, total recoverable, colorimetric, bipyridine, automated (I–4379–78)

Parameter and Code: Iron, total recoverable (μg/L as Fe): 01045

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing between 10 and 5,000 μg/L of iron. Prepared sample solutions (Method I–3485) containing more than 5,000 μg/L must first be diluted. If the iron concentration exceeds 50,000 μg/L determine iron by atomic absorption (Method I–1381).

1.2 Water-suspended sediment mixtures must undergo a preliminary digestion-solubilization by Method I–3485 before analysis by this procedure.

2. Summary of Method

This method is based on the reaction between ferrous iron and 2,2′-bipyridine that yields a red complex (Moss and Mellon, 1942). Hydroxylamine hydrochloride reduces ferric iron to ferrous iron. The color develops immediately and is stable for several hours. The color intensity is independent of pH in the range 3 to 10.

3. Interferences

3.1 Copper reacts with bipyridine at pH values greater than 6, but the method embodies pH adjustment to about 5.5, where copper does not show appreciable interference. Silver, antimony, zinc, and bismuth must be absent. The procedure can be used with undiluted samples for analysis of water having metal concentrations as high as:

	μg/L		μg/L
Cd	50,000	Hg	5,000
Cr	15,000	Ni	10,000
Co	20,000	Zn	5,000
Cu	5,000		

3.2 Interfering anions must be limited to the following concentrations:

	mg/L		mg/L
CN	10	P_2O_7 (as P)	5
Cr_2O_7	100	WO_4	7
PO_4 (as P)	50		

3.3 At 520 nm, the wavelength used in the determination, the natural color of the water may contribute a measurable absorbance and must be corrected for if the color exceeds about 50 platinum–cobalt units. This applies only to the "normal" type of yellow color found in water. Highly colored samples must be analyzed by atomic absorption spectrometry.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of a sampler, proportioning pump, cartridge manifold, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 10 to 5,000 μg/L:

Absorption cell	50 mm.
Wavelength	520 nm.
Cam	40/h (2/1).

5. Reagents

5.1 *Bipyridine* solution, 0.5 g/L: Dissolve 0.5 g 2,2′-bipyridine in demineralized water and dilute to 1 L.

5.2 *Hydroxylamine-hydrochloric acid* reagent: Dissolve 25 g $NH_2OH \cdot HCl$ in demineralized water. Add 10 mL concentrated HCl (sp gr 1.19). Dilute to 1 L with demineralized water. Add 1 mL Brij–35 solution. Refrigerate if possible.

5.3 *Iron* standard solution I, 1.00 mL = 500 μg Fe: Dissolve 0.500 g analytical-grade iron wire (cleaned in dilute HCl, rinsed, and dried) in 3 to 5 mL concentrated HNO_3 (sp gr 1.19). Dilute to 1,000 mL with demineralized water.

5.4 *Iron* standard solution II, 1.00 mL = 50 μg Fe: Dilute 100.0 mL iron standard solution I to 1,000 mL with demineralized water containing 2 or 3 drops concentrated HNO_3 (sp gr 1.19).

5.5 *Iron* working standards: Prepare a blank and 500 mL each of a series of iron working standards by appropriate quantitative dilution of iron standard solution II as follows: Add 0.5 mL concentrated HNO_3 (sp gr 1.19) to each standard before diluting to 500.0 mL.

Iron standard solution II (mL)	*Iron concentration (μg/L)*
0.0	0
1.0	100
2.0	200
5.0	500
10.0	1,000
20.0	2,000
30.0	3,000
40.0	4,000
50.0	5,000

5.6 *Sodium acetate* solution, 350 g/L: Dissolve 350 g CH_3COONa in demineralized water and dilute to 1 L for the digested samples. Add 1 mL Brij–35.

6. Procedure

6.1 Set up manifold (fig. 39).

6.2 Allow colorimeter and recorder to warm up for at least 30 min. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample tube.

6.3 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

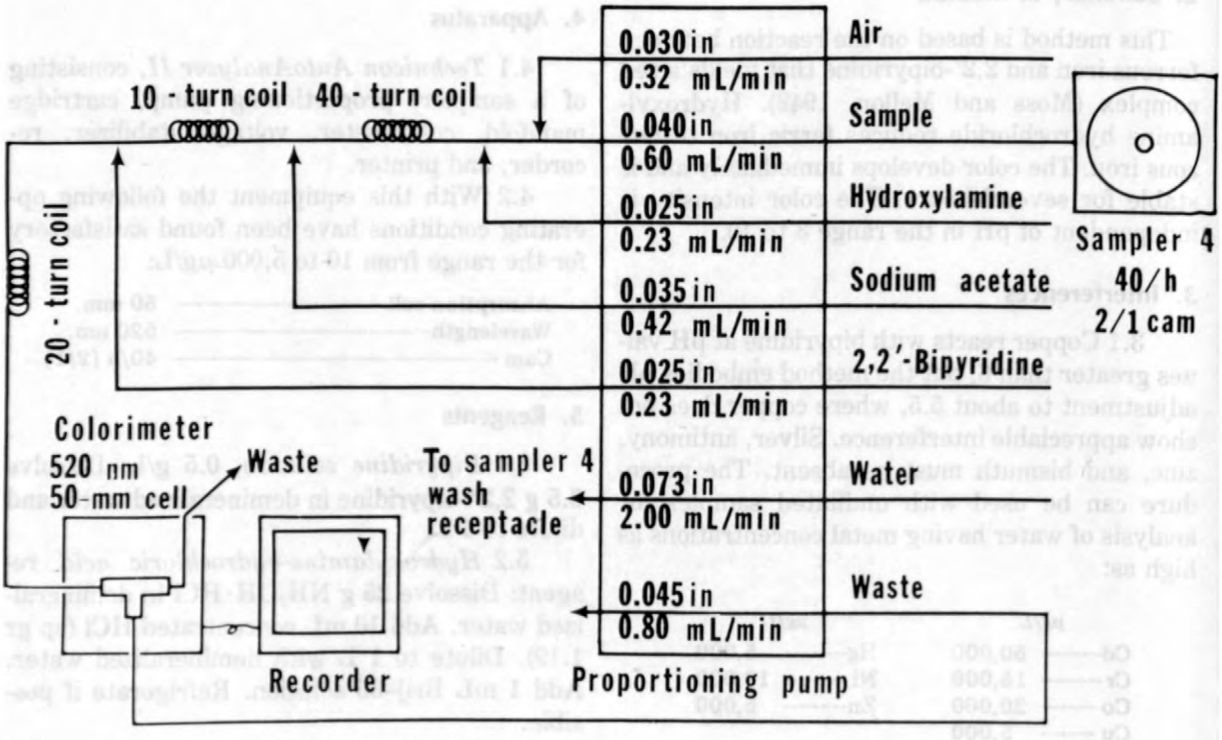


FIGURE 39.—Iron manifold.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective iron concentration.

7.2 Compute the concentration of iron in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report iron, total recoverable (01045), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 13 percent at 118 μg/L and greater than 6 percent at 991 μg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 103.

Moss, M. L., and Mellon, M. G., 1942, Colorimetric determination of iron with 2,2′-bipyridyl and with 2,2′,2″-terpyridyl: Industrial Engineering Chemistry, Analytical Edition, v. 14, p. 862.

Iron, ferrous, dissolved, colorimetric, bipyridine (I–1388–78)

Parameter and Code: Iron, ferrous, dissolved (μg/L as Fe):01047

1. Application

This method may be used to analyze samples containing between 10 and 4,000 μg/L of ferrous iron (NOTE 1). Samples containing more than 4,000 μg/L must first be diluted.

NOTE 1. Results obtained with this method may be meaningless unless the analysis is performed in the field immediately on collecting the sample.

2. Summary of method

2.1 This method is identical to the colorimetric bipyridine method for determining iron (Method I–1379), except that no reductant is added to reduce ferric iron in solution.

2.2 The method is based on the reaction between ferrous iron and 2,2′-bipyridine that yields a red complex (Moss and Mellon, 1942). The color develops immediately and is stable for several hours. The color intensity is independent of pH in the range 3 to 10.

3. Interferences

3.1 Copper reacts with bipyridine at pH values greater than 6, but the method embodies pH adjustment to about 5.5, where copper does not show appreciable interference. Silver, antimony, zinc, and bismuth must be absent. The procedure can be used with undiluted samples for analysis of water having metal concentrations as high as:

	μg/L		*μg/L*
Cd	50,000	Hg	5,000
Cr	15,000	Ni	10,000
Co	20,000	Zn	5,000
Cu	5,000		

3.2 Interfering anions must be limited to the following concentrations:

	μg/L		*μg/L*
CN	10	P_2O_7 (as P)	5
Cr_2O_7	100	WO_4	7
PO_4 (as P)	50		

3.3 At 520 nm, the wavelength used in the determination, the natural color of the water may contribute a measurable absorbance and must be corrected for if the color exceeds about 50 platinum–cobalt units. This applies only to the "normal" type of yellow color found in water.

4. Apparatus

4.1 *Spectrometer* for use at 520 nm; Beckman Model B, or equivalent.

4.2 With this instrument the following operating conditions have been used:

Wavelength	520 nm.
Cells	40 mm.
Phototube	Blue-sensitive.
Initial sensitivity setting	1.
Slit width	0.1 mm.

4.3 With these operating conditions the following readings have been observed:

Amount of Fe (μg)	*Absorbance*
0.0	0.000
12.5	265
25.0	540
50.0	1.070
100	2.140

5. Reagents

5.1 *Bipyridine* solution, 2.0 g/L: Dissolve 1.0 g 2,2′-bipyridine in demineralized water and dilute to 500 mL.

5.2 *Hydroxylamine—hydrochloric acid* reagent: Dissolve 100 g $NH_2OH \cdot HCl$ in demineralized water. Add 40 mL concentrated HCl (sp gr 1.19) and dilute to 1 L with demineralized water.

5.3 *Iron* standard solution I, 1.00 mL = 400 μg Fe: Dissolve 0.400 g analytical grade iron wire (cleaned in dilute HCl, rinsed, and dried) in a minimum of dilute HCl and dilute to 1,000 mL with demineralized water.

5.4 *Iron* standard solution II, 1.00 mL = 4.00 μg Fe: Dilute 10.0 mL iron standard solution I to 1,000 mL with demineralized water containing 1 mL concentrated HCl (sp gr 1.19).

5.5 *Sodium acetate* solution, 350 g/L: Dissolve 350 g CH_3COONa in demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 100 μg Fe (25.0 mL max) into a 50-mL beaker, and adjust the volume to 25.0 mL with demineralized water.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to 25.0 mL.

6.3 Add 1.0 mL bipyridine solution to samples, standards, and blank.

6.4 Add 2.0 mL hydroxylamine-hydrochloric acid reagent to the blank and standards *only*. Mix and allow the solutions to stand 30 min.

6.5 Add 2.0 mL CH_3COONa solution to samples, standards, and blank and mix.

6.6 Determine the absorbances of the sample and standards against the blank, and when necessary, make correction for water color.

7. Calculations

7.1 Determine micrograms of ferrous iron in each sample from a plot of absorbances of standards.

7.2 Determine the ferrous iron concentration in micrograms per liter as follows:

$$Fe^{+2}\ (\mu g/L) = \frac{1{,}000}{\text{mL sample}} \times \mu g\ Fe^{+2} \text{ in sample.}$$

8. Report

Report iron, ferrous, dissolved (01047), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

It is estimated that the precision is the same as has been obtained for Method I–1379.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 104.

Moss, M. L., and Mellon, M. G., 1942, Colorimetric determination of iron with 2,2′-bipyridyl and with 2,2′,2″-terpyridyl: Industrial Engineering Chemistry, Analytical Edition, v. 14, p. 862.

Nitrogen, ammonia plus organic, dissolved, colorimetric, block digestoralicylate-hypochlorite, automated (I–2552–78)

Parameter and Code: Nitrogen, ammonia plus organic, dissolved (mg/L as N): 00623

1. Application

Concentrations of 0.1 to 10 mg/L nitrogen (ammonia plus organic) can be determined by this method. Concentrations greater than 10 mg/L must be reduced by dilution.

2. Summary of method

Organic nitrogen compounds are reduced to the ammonium ion by digestion in a block digestor with sulfuric acid in the presence of mercuric sulfate, which acts as a catalyst, and potassium sulfate. The ammonium ion produced by this digestion, as well as the ammonium ion originally present, is determined by reaction with sodium salicylate, sodium nitroprusside, and sodium hypochlorite in an alkaline medium. The resulting color is directly proportional to the concentration of ammonia present.

3. Interferences

3.1 A comparison study of results obtained by this method with those from the colorimetric, digestion-distillation-nesslerization and colorimetric, digestion-distillation-indophenol, automated, methods (Methods I–1550 and I–2551, respectively,) indicated the absence of interferences.

3.2 The samples are easily contaminated by ammonia in the laboratory atmosphere. The digestion process should be performed in a fume hood that is operating properly and that is located in an ammonia-free area of the laboratory. Other laboratory procedures may be performed outside or near this hood only if there is no possibility of ammonia contamination.

4. Apparatus

4.1 *Technicon block digestor*, Model BD–40 with 75-mL digestion tubes.

4.2 With this equipment, the following operating conditions have been found satisfactory:

Modeswitch	Automatic.
Low temperature regulator	160° C.
High temperature regulator	370° C.
Low temperature timer	1.5 h.
Total cycle time	3.5 h.

4.3 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating, bath, colorimeter, voltage stabilizer, recorder, and printer.

4.4 With this equipment, the following operating conditions have been found satisfactory (NOTE 1):

Absorption cell	15 mm.
Wavelength	660 nm.
Cam	60/h (6/1).
Water bath temperature	37° C.

NOTE 1. Two concentration ranges of 0 to 3 mg/L and 2 to 10 mg/L N are obtained by using different STD CAL settings.

5. Reagents

5.1 *Ammonium chloride* standard solution I, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonium chloride* standard solution II, 1.00 mL = 0.010 mg NH_3-N: Dilute 10.00 mL NH_4Cl standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Buffer* stock solution, 71 g/L: Dissolve 71 g anhydrous Na_2HPO_4 in approx 800 mL demineralized water. Add 100 mL $5M$ NaOH, dilute to 1 L with ammonia-free water, and mix thoroughly.

5.4 *Buffer* working solution: Add, with stirring, 250 mL stock potassium sodium tartrate solution to 200 mL stock buffer solution. Slowly, with stirring, add 120 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water, add 1 mL Brij–35 solution, and mix thoroughly.

5.5 *Mercuric sulfate* solution, 11 g/100 mL: Dissolve 8 g red HgO in 50 mL 3.6*M* H_2SO_4 and dilute to 100 mL with ammonia-free water.

5.6 *Potassium sodium tartrate* solution, 149 g/L: Dissolve 200 g $NaKC_4H_4O_6 \cdot 4H_2O$ in approx 600 mL ammonia-free water. Dilute to 1 L.

5.7 *Sodium hydroxide* solution 5*M*: Add, with cooling and stirring, 200 g NaOH to approx 800 mL ammonia-free water. Cool and dilute to 1 L.

5.8 *Sodium hypochlorite* solution: Dilute 6.0 mL sodium hypochlorite solution (a commercial bleach solution containing 5.25 percent available chlorine is satisfactory) to 100 mL with ammonia-free water. Add 0.1 mL Brij–35 solution. Prepare fresh daily.

5.9 *Sodium salicylate-sodium nitroprusside* solution: Dissolve 150 g sodium salicylate and 0.30 g sodium nitroprusside [$Na_2Fe(CN)_5NO \cdot 2H_2O$] in approx 600 mL ammonia-free water. Filter through Whatman 41 filter paper, or equivalent, and dilute to 1 L. Add 1.0 mL Brij–35 solution and store in a light-resistant container.

5.10 *Sulfuric acid,* concentrated (sp gr 1.84).

5.11 *Sulfuric acid,* 0.20*M*: *Cautiously* add 11 mL concentrated H_2SO_4 (sp gr 1.84) to ammonia-free water and dilute to 1 L.

5.1? *Sulfuric acid,* 3.6*M*: *Cautiously* add 200 mL concentrated H_2SO_4 (sp gr 1.84) to approx 700 mL ammonia-free water. Cool and dilute to 1 L with ammonia-free water.

5.13 *Sulfuric acid-mercuric sulfate-potassium sulfate* solution: Dissolve 267 g K_2SO_4 in approx 1,300 mL ammonia-free water. *Cautiously* add 400 mL concentrated H_2SO_4 (sp gr 1.84) and 50 mL mercuric sulfate solution (paragraph 5.5). Cool and dilute to 2 L with ammonia-free water.

6. Procedure

Rinse all glassware with ammonia-free water before each use.

6.1 Pipet a volume of sample containing less than 0.2 mg ammonia plus organic nitrogen (as N) into a digestor tube (20.0 mL max) and adjust the volume to 20 mL with ammonia-free water.

6.2 Prepare an ammonia-free water blank and at least five standards containing either from 0.00 to 0.06 or 0.00 to 0.20 mg ammonia-nitrogen, depending upon use of 0- to 3-mg/L or 2- to 10-mg/L concentration range of interest. The standards and blank must also undergo the digestion process.

6.3 Add 4.0 mL sulfuric acid–mercuric sulfate–potassium sulfate solution (paragraph 5.13) and two boiling chips. Mix well before placing in digestor (NOTES 2 and 3).

NOTE 2. Protective eyeglasses and clothing are mandatory for this procedure because the use of sulfuric acid and high temperature solutions is very hazardous.

NOTE 3. Teflon boiling chips, available from Cole-Parmer Instrument Co., are preferable. Before use they should be soaked in dilute HCl (approx 6*M*), rinsed several times in ammonia-free water, and dried at 180°C. In order to avoid contamination by laboratory fumes, they should then be stored in a tightly stoppered container in an ammonia-free area of the laboratory.

6.4 Digest under a hood for 3½ h using the listed conditions. It is imperative that the heating block cool to 150°C before subsequent batches of samples are placed in the digestor. Extreme spattering will occur if this direction is not followed.

6.5 Cautiously remove tubes from the digestor and allow to cool for approx 15 min in a hood. Quickly add approx 50 mL ammonia-free water to each tube with vigorous agitation and extreme caution (NOTE 4). Allow to cool briefly before making the final dilution to the calibration mark. Stopper the tubes and invert several times until well mixed (NOTE 5). If it is necessary to dilute a portion of this solution to remain within the designated concentration range, this dilution must be made with 0.20*M* H_2SO_4.

NOTE 4. The precipitation of salts is minimized by this procedure. A vortex mixer is useful for agitating the water–acid mixture.

NOTE 5. Allow any precipitate that has formed or any boiling chip flakes to settle before filling the sample cups in paragraph 6.8.

6.6 Set up manifold (fig. 40). If the laboratory air is contaminated with ammonia, it must be passed through a scrubber containing 2.5*M* H_2SO_4 before it enters the air-manifold tube.

6.7 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with 0.20*M* H_2SO_4 in the sample line. The solution remaining

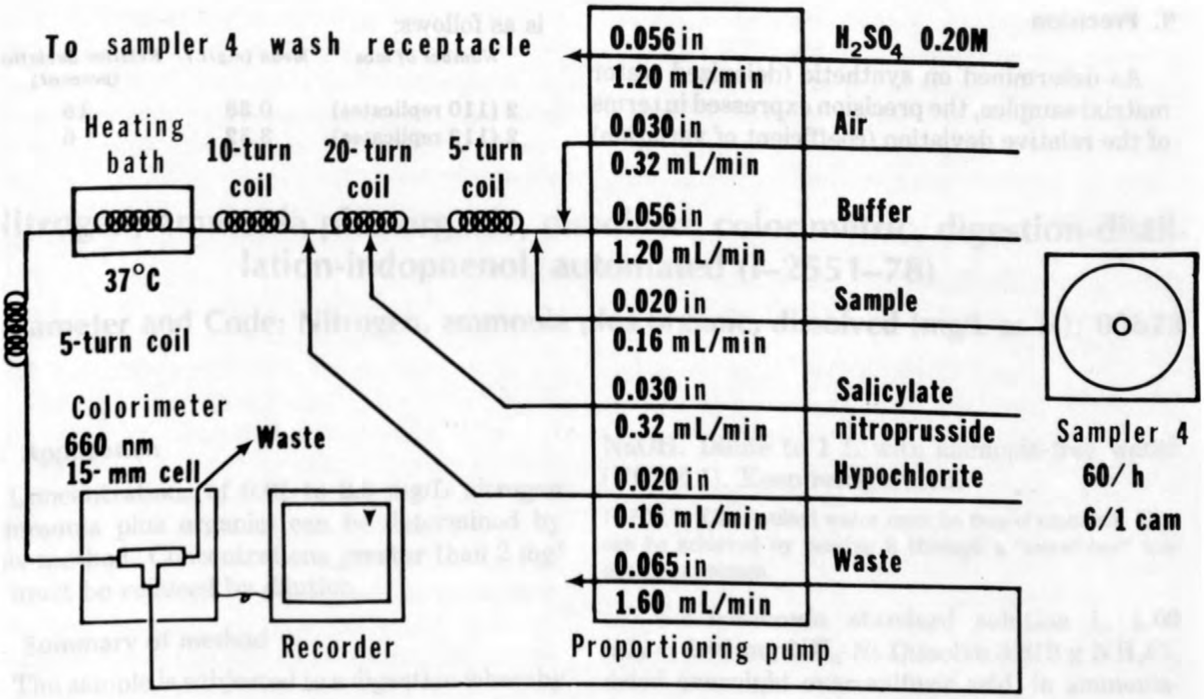


FIGURE 40.—Nitrogen, ammonia plus organic, salicylate-hypochlorite manifold.

in the wash reservoir from previous analyses may have become contaminated; therefore this reservoir should be emptied and rinsed and filled with fresh wash solution before proceeding. Place each reagent line except salicylate into its respective container; allow at least 5 min for the introduction of these reagents, and then place the salicylate line into its reagent container. If a precipitate forms after the addition of the salicylate, the pH of the solution stream is too low.

6.8 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray (NOTE 6). Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill the remainder of each sample tray with unknown samples.

NOTE 6. To avoid possible contamination of the sample cups, do not open their sealed package until just prior to use. Rinse each sample cup with sample prior to filling.

6.9 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective nitrogen concentration.

7.2 Compute the concentration of NH_3-N (mg/L) in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak. Likewise, the amount of NH_3-N present from the addition of H_2SO_4, as indicated by the concentration of NH_3-N in the blank, must be subtracted from the total concentration of NH_3-N in each sample.

7.3 Dissolved ammonia plus organic nitrogen is equal to NH_3-N (mg/L) as determined in paragraph 7.2.

8. Report

Report nitrogen, ammonia plus organic, total (00623) concentrations as follows: less than 1.0 mg/L, one decimal; 1.0 mg/L and above, two significant figures.

9. Precision

As determined on synthetic (deionized water matrix) samples, the precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
2 (110 replicates)	0.38	18
2 (112 replicates)	3.32	6

Nitrogen, ammonia plus organic, dissolved, colorimetric, digestion-distillation-indophenol, automated (I–2551–78)

Parameter and Code: Nitrogen, ammonia plus organic, dissolved (mg/L as N): 00623

1. Application

Concentrations of 0.01 to 2.0 mg/L nitrogen (ammonia plus organic) can be determined by this method. Concentrations greater than 2 mg/L must be reduced by dilution.

2. Summary of method

The sample is subjected to a digestion whereby all organic nitrogen-containing compounds are converted to ammonium salts. The resulting mixture is then made strongly alkaline, and the ammonia so formed is distilled from the mixture into a solution of boric acid and subsequently determined by an automated indophenol colorimetric reaction.

3. Interferences

There are no known interferences with this method.

4. Apparatus

4.1 *Kjeldahl distillation apparatus* including 800-mL capacity kjeldahl flasks.

4.2 *Technicon AutoAnalyzer II* consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment, the following operating conditions have been found satisfactory:

Absorption cell	15 mm.
Wavelength	630 nm.
Cam	60/h (6/1).
Heating bath temperature	50°C.

5. Reagents

5.1 *Alkaline phenol* solution: Mix 89 mL liquid phenol (approx 90 percent) in 50 mL ammonia-free water. Cautiously add, while cooling, in small increments with agitation, 180 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water (NOTE 1). Keep refrigerated.

NOTE 1. The distilled water must be free of ammonia. This can be achieved by passing it through a "mixed-bed" ion-exchange column.

5.2 *Ammonia* standard solution I, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.3 *Ammonia* standard solution II, 1.00 mL = 0.025 mg NH_3-N: Dilute 25.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh weekly.

5.4 *Ammonia* working standards: Prepare a blank and 500 mL each of a series of ammonia working standards by appropriate quantitative dilution of ammonia standard solution II as follows:

Ammonia standard solution II (mL)	*Ammonia-nitrogen concentration (mg/L)*
0.0	0.00
.5	.025
1.0	.05
2.0	.10
5.0	.25
10.0	.50
20.0	1.0
40.0	2.0

Prepare fresh weekly.

5.5 *Boric acid* solution, 20 g/L: Dissolve 20 g H_3BO_3 crystals in 800 mL ammonia-free water and dilute to 1 L.

5.6 *Brij–35* solution: 30 percent aqueous (Baker Cat. No. C706, or equivalent).

5.7 *Kel-Pak* powder No. 3.

5.8 *Sodium hydroxide* solution, 5*M*: *Cautiously* dissolve 200 g NaOH in ammonia-free water. Cool and dilute to 1 L. Store in a plastic container.

5.9 *Potassium sodium tartrate—sodium citrate* solution: Dissolve 33 g $KNaC_4H_4O_6 \cdot 4H_2O$ and 24 g sodium citrate in 950 mL ammonia-free water. Adjust the pH of this solution to 5.0 with concentrated H_2SO_4 (sp gr 1.84) and dilute to 1 L with ammonia-free water. Add 0.5 mL of Brij–35 solution.

5.10 *Sodium hydroxide-thiosulfate* solution: *Cautiously* dissolve 500 g NaOH in 600 mL ammonia-free water. Add 80 g $Na_2S_2O_3 \cdot 5H_2O$ and dilute to 1 L.

5.11 *Sodium hypochlorite* stock solution: Chlorox or any other good commercial household bleach having approx 5 percent available chlorine.

5.12 *Sodium hypochlorite* working solution: Dilute 200 mL sodium hypochlorite stock solution to 1 L with ammonia-free water.

5.13 *Sodium nitroprusside* solution, 0.45 g/L: Dissolve 0.5 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ in ammonia-free water and dilute to 1 L. This reagent is stable for approx 1 month.

5.14 *Sodium thiosulfate* crystals, $Na_2S_2O_3 \cdot 5H_2O$.

5.15 *Sulfuric acid*, concentrated, (sp gr 1.84).

6. Procedure

6.1 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent (CAUTION: deadly poison) (see Method I–1520).

6.2 Pipet 200 mL of a well-mixed sample into a 800-mL capacity digestion flask.

6.3 In the same manner prepare a blank and standard (2.0 mg/L).

6.4 With care, add 25 mL concentrated H_2SO_4 (sp gr 1.84) and swirl the contents of the flask under a hood until thoroughly mixed.

6.5 Add one Kel-Pak and mix well. Add a few glass beads and begin the digestion. Digest until copious fumes are given off and continue the digestion until a clear solution is obtained, and then continue fuming 1 h.

6.6 Cool the flask until crystals appear. (Do not cool completely.) Add 150 mL ammonia-free water; mix and allow to cool.

6.7 Add 100 mL NaOH–$Na_2S_2O_3$ solution. Immediately connect the flask to the distillation apparatus and cautiously mix the contents by swirling.

6.8 Distill at a rate of not more than 10 nor less than 6 mL/min; collect the distillate in a 200-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.9 Collect approx 150 mL of distillate, dilute to 200 mL with ammonia-free water, and mix.

6.10 Set up manifold (fig. 41). If the laboratory air is contaminated with ammonia, it must be passed through a scrubber containing 2.5*M* H_2SO_4 before it enters the air-manifold tube.

6.11 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min or until the temperature of the heating bath reaches 50°C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with ammonia-free water in the sample line.

6.12 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray (NOTE 2). Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with the distilled blank, standards and unknown samples.

NOTE 2. To avoid possible contamination of the sample cups, they should remain sealed in their packages until just prior to use. Rinse each sample cup with sample prior to filling.

6.13 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective nitrogen concentration.

7.2 Compute the concentration of NH_3-N (mg/L) in each sample by comparing its peak height to the analytical curve and subtracting the concentration of any nitrogen in the blank. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report nitrogen, ammonia plus organic, dissolved (00623), concentrations as follows: less

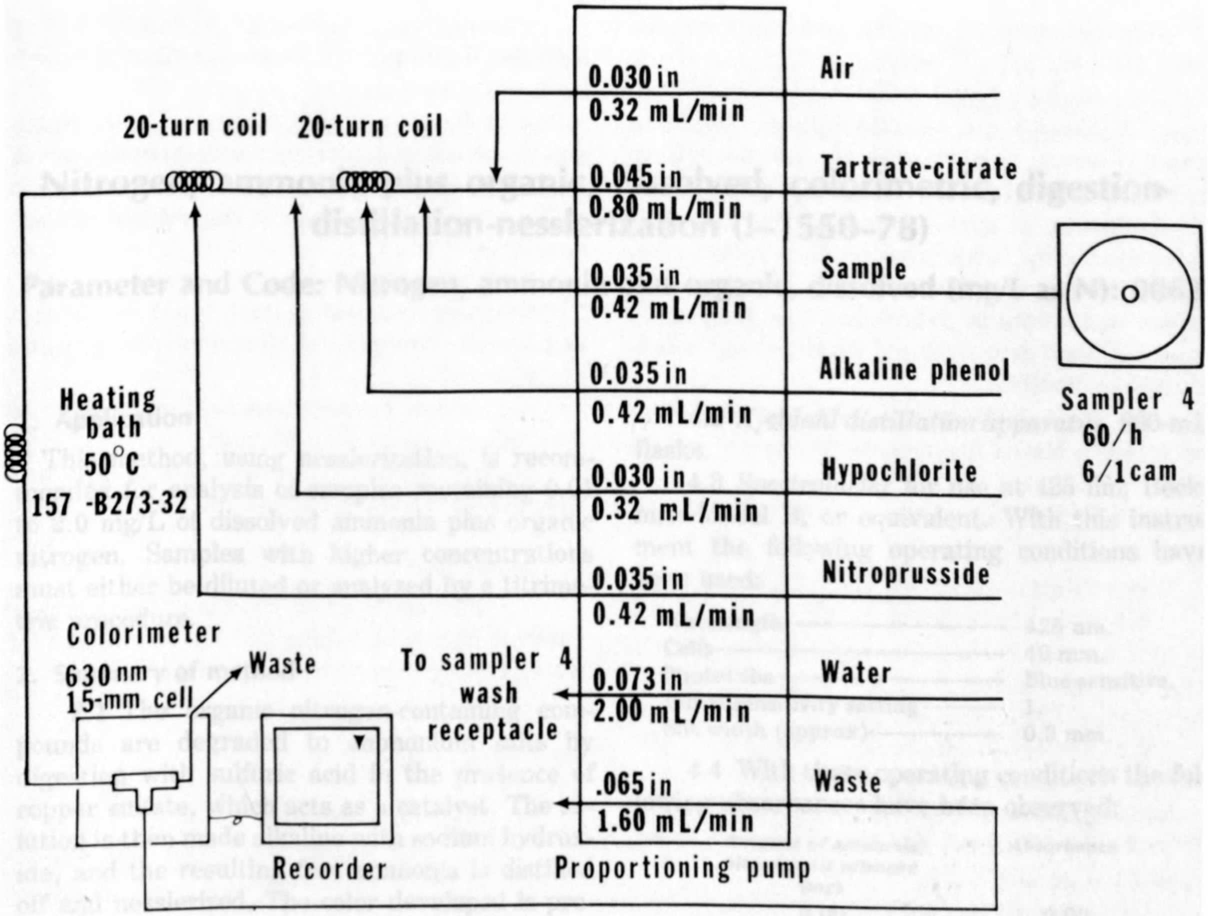


FIGURE 41.—Nitrogen, ammonia plus organic, manifold.

1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

Reference

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, [U.S.] Environmental Protection Agency, p. 190.

Nitrogen, ammonia plus organic, dissolved, colorimetric, digestion-distillation-nesslerization (I-1550-78)

Parameter and Code: Nitrogen, ammonia plus organic, dissolved (mg/L as N): 00623

1. Application

This method, using nesslerization, is recommended for analysis of samples containing 0.01 to 2.0 mg/L of dissolved ammonia plus organic nitrogen. Samples with higher concentrations must either be diluted or analyzed by a titrimetric procedure.

2. Summary of method

2.1 The organic nitrogen-containing compounds are degraded to ammonium salts by digestion with sulfuric acid in the presence of copper sulfate, which acts as a catalyst. The solution is then made alkaline with sodium hydroxide, and the resulting free ammonia is distilled off and nesslerized. The color developed is proportional to the ammonia plus organic nitrogen content of the sample.

2.2 Additional information on the principle of the determination is given by Kolthoff and others (1969).

3. Interferences

3.1 Nitrate and nitrite do not interfere.

3.2 Calcium, magnesium, iron, and sulfide interfere with the nesslerization, but the interference of the metals is eliminated by the distillation and sulfides are completely destroyed during the digestion.

3.3 Some organic compounds may distill over with the ammonia and form colors with nessler reagent which cannot be satisfactorily read with the spectrophotometer. Under such conditions, the sample should be titrated with standard sulfuric acid solution.

4. Apparatus

4.1 Cylinder, graduated, mixing, with ground-glass stopper, 50-mL capacity (Corning No. 3002, or equivalent).

4.2 *Kjeldahl distillation apparatus*, 800-mL flasks.

4.3 *Spectrometer* for use at 425 nm; Beckman Model B, or equivalent. With this instrument the following operating conditions have been used:

Wavelength	**425 nm.**
Cells	**40 mm.**
Phototube	**Blue-sensitive.**
Initial sensitivity setting	**1.**
Slit width (approx)	**0.3 mm.**

4.4 With these operating conditions the following absorbances have been observed:

Amount of ammonia plus organic nitrogen (mg)	*Absorbance*
0.00	0.00
.02	.24
.04	.47
.06	.70
.10	1.16

5. Reagents

5.1 *Ammonium chloride* standard solution I, 1.00 mL = 1.00 mg N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonium chloride* standard solution II, 1.00 mL = 0.010 mg N: Dilute 10.00 mL NH_4Cl standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Borate* buffer solution: Dissolve 9.54 g $Na_2B_4O_7 \cdot 10H_2O$ in ammonia-free water. Adjust the pH to 9.5 with 1*M* NaOH (approx 15 mL), and dilute to 1 L with ammonia-free water.

5.4 *Boric acid* solution, 20 g/L: Dissolve 20 g H_3BO_3 in ammonia-free water and dilute to 1 L.

5.5 *Copper sulfate* solution, 6.5 g/100 mL: Dissolve 6.5 g $CuSO_4$ (anhydrous) in ammonia-free water and dilute to 100 mL.

5.6 *Methyl red indicator* solution 0.1 g/100 mL: Dissolve 0.1 g methyl red indicator in 100 mL 95-percent ethanol.

5.7 *Nessler* reagent (CAUTION: HgI_2 is a deadly poison, and the reagent must be so marked): Dissolve 100 g HgI_2 and 70 g KI in a small volume of ammonia-free water. Add this mixture slowly, with stirring, to a cooled solution of 160 g NaOH in 500 mL ammonia-free water and dilute to 1 L. Allow the reagent to stand at least overnight and filter through a fritted-glass crucible.

5.8 *Sodium hydroxide* solution, 10*M*: Dissolve 400 g NaOH in ammonia-free water and dilute to 1 L.

5.9 Sulfuric acid, concentrated (sp gr 1.84).

6. Procedure

Rinse all glassware with ammonia-free water.

6.1 Free the kjeldahl distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent (CAUTION: deadly poison).

6.2 *Ammonia plus organic nitrogen:* To determine ammonia plus organic nitrogen, pipet a volume of sample containing less than 1.0 mg nitrogen (250 mL max) and transfer to a 800-mL kjeldahl digestion flask.

6.3 Add 5.0 mL concentrated H_2SO_4 and 0.5 mL $CuSO_4$ solution, and mix.

6.4 Digest under a hood until copious fumes are given off. Continue heating until the fumes have subsided and the liquid becomes colorless or pale yellow. Continue digestion an additional 30 min.

6.5 Cool and dilute to approx 150 mL with ammonia-free water.

6.6 Add 25 mL 10*M* NaOH cautiously down the side of the flask.

6.7 Immediately connect the flask to the distillation apparatus, and cautiously mix the contents by gently swirling.

6.8 Distill at a rate of no more than 10 nor less than 6 mL/min; collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.9 Collect approx 150 mL distillate, dilute to the mark with ammonia-free water, and mix.

6.10 Pipet an aliquot of distillate containing less than 0.1 mg ammonia-nitrogen (50.0 mL max) into a glass-stoppered, graduated mixing cylinder, and adjust the volume to 50.0 mL with ammonia-free water.

6.11 Prepare a blank of ammonia-free water and a series of standards in glass-stoppered, graduated mixing cylinders. Add 5 mL boric acid solution to each, and adjust the volume of each to 50.0 mL.

6.12 Add 1.0 mL nessler reagent (CAUTION: deadly poison) to each blank, standard, and sample. Stopper and invert several times to mix thoroughly.

6.13 Allow the solutions to stand at least 10 min, but not more than 30 min.

6.14 Determine the absorbance of each test sample and standard against the blank.

7. Calculations

7.1 Determine a reagent blank for each new batch of H_2SO_4 by taking 250 mL ammonia-free water through the entire procedure:

$$\text{mg reagent blank} = \left(\begin{array}{c}\text{mg ammonia}\\ \text{plus organic N}\\ \text{per 5.0 mL H}_2\text{SO}_4\end{array}\right) \times \frac{\text{mL aliquot}}{\text{mL distillate}}$$

7.2 Determine the milligrams of ammonia plus organic nitrogen in each sample aliquot from a plot of absorbances of standards.

7.3 Determine the ammonia plus organic nitrogen concentration in milligrams per liter as follows:

$$\text{Ammonia plus organic nitrogen, mg/L} = \frac{1{,}000}{\text{mL sample}} \times \frac{250}{\text{mL aliquot}} \times [(\text{mg ammonia plus organic N in aliquot}) - (\text{mg reagent blank})].$$

8. Report

Report nitrogen, ammonia plus organic, dissolved (00623) concentrations as follows: less than 1.0 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 122.

Kolthoff, I. M., Sandell, E. B., Meehen, E. J., and Bruckenstein, S., 1969, Quantitative chemical analysis [4th ed.]: New York, Macmillan, 1199 p.

Nitrogen, ammonia plus organic, total in bottom material, colorimetric, block digestor-salicylate-hypochlorite, automated (I–6552–78)

Parameter and Code: Nitrogen, ammonia plus organic, total in bottom material, dry wt (mg/kg as N): 00626

1. Application

This method may be used to analyze samples of bottom material containing at least 10 mg/kg nitrogen (ammonia plus organic). Concentration ranges for determining 10 to 120 and 80 to 400 mg/kg of nitrogen are used.

2. Summary of method

2.1 An accurately weighed portion of wet sample is mixed with ammonia-free water and digested with sulfuric acid, mercuric sulfate, and potassium sulfate in a block digestor. The resulting ammonium ion is then determined by an automated indophenol salicylate-hypochlorite colorimetric reaction.

2.2 See also Nitrogen, ammonia plus organic, dissolved (Method I–2552).

3. Interferences

A comparison study of results obtained by this method with those from the colorimetric digestion-distillation-nesslerization and colorimetric, digestion-distillation-indophenol, automated, methods (Methods I–1550 and I–2551) indicated the absence of interferences.

4. Apparatus

See Nitrogen, ammonia plus organic, dissolved (Method I–2552).

5. Reagents

See Nitrogen, ammonia plus organic, dissolved (Method I–2552).

6. Procedure

Rinse all glassware with ammonia-free water before each use.

6.1 Weigh, to the nearest milligram, an amount of wet sample (500 mg max) containing less than 0.2 mg total ammonia plus organic nitrogen.

6.2 Quantitatively transfer the weighed sample to a 75-mL digestion tube, rinsing the weighing container with ammonia-free water as needed. Add additional ammonia-free water as necessary to bring the liquid volume in the digestion tube to approximately 20 mL.

6.3 Proceed as directed in Nitrogen, ammonia plus organic, dissolved (Method I–2552), beginning with paragraph 6.2.

6.4 Determine the percent of moisture in the wet sample by placing a representative portion (0.5 to 1.0 g) into a tared weighing bottle. Place the weighed bottle containing the accurately weighed sample in a drying oven and heat for 2 h at 110°C. Cool in a desiccator for 30 min and immediately weigh.

6.5 Compute the loss in weight in grams, of the sample, on heating at 110°C.

6.6 Compute the percent moisture in the sample as follows:

$$\text{Percent moisture} = \frac{\text{Loss in wt (g)}}{\text{Wet sample wt (g)}} \times 100$$

Sample dry wt (g)

$$= \frac{\text{Wet sample wt } (100 - \text{percent moisture})}{100}.$$

7. Calculations

7.1 Total ammonia plus organic nitrogen is equal to ammonia nitrogen as determined in paragraph 7.2, Method I–2552.

7.2 Convert to dry weight concentrations as follows:

Total ammonia plus organic nitrogen (mg/kg) =

$$\frac{\text{mg } NH_3\text{-N in sample}}{\text{Sample dry wt (g)}} \times 1000.$$

8. Report

Report nitrogen, ammonia plus organic, total in bottom material (00626) in milligrams per kilogram of dry weight sample as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 18 percent in the lower portion of the analytical range.

Nitrogen, ammonia plus organic, total in bottom material, colorimetric, digestion-distillation-indophenol, automated (I–6551–78)

Parameter and Code: Nitrogen, ammonia plus organic, total in bottom material, dry wt (mg/kg as N):00626

1. Application

This method may be used to determine the nitrogen concentration (ammonia plus organic) in samples of bottom material containing at least 1 mg/kg of nitrogen. Only that portion of bottom material that passes a 2-mm sieve is taken for analysis.

2. Summary of method

The sample is subjected to digestion whereby all organic nitrogen-containing compounds are converted to ammonium salts. The resulting mixture is then made strongly alkaline and the ammonia so formed is distilled from the mixture into a solution of boric acid and subsequently determined by an automated indophenol colorimetric reaction.

3. Interferences

There are no known interferences with this method.

4. Apparatus

4.1 *Kjeldahl distillation apparatus*, including 800-mL capacity kjeldahl flasks.

4.2 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge, manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment, the following operating conditions have been found satisfactory:

Absorption cell	**15 mm.**
Wavelength	**630 nm.**
Cam	**60/h (6/1).**
Heating bath temperature	**50° C.**

5. Reagents

5.1 *Alkaline phenol* solution: Mix 89 mL liquid phenol (approx 90 percent) in 50 mL ammonia-free water. Cautiously add, while cooling, in small increments with agitation, 180 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water (NOTE 1). Keep refrigerated.

NOTE 1. The distilled water must be free of ammonia. This can be achieved by passing it through a "mixed-bed" ion-exchange column.

5.2 *Ammonia* standard solution I, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.3 *Ammonia* standard solution II, 1.00 mL = 0.025 mg NH_3-N: Dilute 25.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh weekly.

5.4 *Ammonia* working standards: Prepare a blank and 500 mL each of a series of ammonia working standards by appropriate quantitative dilution of ammonia standard solution II as follows:

Ammonia standard solution II (mL)	*Ammonia-nitrogen concentration (mg/L)*
0.0	0.00
.5	.025
1.0	.05
2.0	.10
5.0	.25
10.0	.50
20.0	1.0
40.0	2.0

Prepare fresh weekly.

5.5 *Boric acid* solution, 20 g/L: Dissolve 20 g H_3BO_3 crystals in 800 mL ammonia-free water and dilute to 1 L.

5.6 *Brij–35* solution: 30 percent aqueous (Baker Cat. No. C706, or equivalent).

5.7 *Kel-Pak powder No. 3.*

5.8 *Sodium hydroxide* solution, 5*M*: *Cautiously* dissolve 200 g NaOH in ammonia-free water. Cool and dilute to 1 L. Store in a plastic container.

5.9 *Potassium sodium tartrate-sodium citrate* solution: Dissolve 33 g $KNaC_4H_4O_6 \cdot 4H_2O$ and 24 g sodium citrate in 950 mL ammonia-free water. Adjust the pH of this solution to 5.0 with concentrated H_2SO_4 (sp gr 1.84) and dilute to 1 L with ammonia-free water. Add 0.5 mL of Brij–35 solution.

5.10 *Sodium hydroxide-thiosulfate* solution: *Cautiously* dissolve 500 g NaOH in 600 mL ammonia-free water. Add 80 g $Na_2S_2O_3 \cdot 5H_2O$ and dilute to 1 L.

5.11 *Sodium hypochlorite* stock solution: Chlorox or any other good commercial household bleach having approx 5 percent available chlorine.

5.12 *Sodium hypochlorite* working solution: Dilute 200 mL sodium hypochlorite stock solution to 1 L with ammonia-free water.

5.13 *Sodium nitroprusside* solution, 0.45 g/L: Dissolve 0.5 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ in ammonia-free water and dilute to 1 L. This reagent is stable for approx 1 month.

5.14 *Sodium thiosulfate*, crystals, $Na_2S_2O_3 \cdot 5H_2O$.

5.15 *Sucrose*.

5.16 *Sulfuric acid*, concentrated, sp gr 1.84.

6. Procedure

6.1 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent (CAUTION: deadly poison).(See Method I–1520.)

6.2 Weigh, to the nearest milligram, 3 g of sample, prepared as directed in Method P–0810, and transfer to a 800-mL capacity digestion flask.

6.3 In the same manner prepare a blank and standard (2.0 mg/L), using 2.0 g sucrose for the blank and 0.5 mg NH_3-N (20.0 mL ammonia standard solution II) plus 2.0 g sucrose for the standard.

6.4 With care, add 25 mL concentrated H_2SO_4 (sp gr 1.84) and swirl the contents of the flask under a hood until thoroughly mixed.

6.5 Add one Kel-Pak and mix well. Add a few glass beads and begin the digestion. Continue the digestion until a clear solution is obtained, and then continue fuming 1 h.

6.6 Cool the flask until crystals appear. (Do not cool completely.) Add 150 mL ammonia-free water; mix and allow to cool.

6.7 Add 100 mL NaOH–$Na_2S_2O_3$ solution. Immediately connect the flask to the distillation apparatus and cautiously mix the contents by swirling.

6.8 Distill at a rate of not more than 10 nor less than 6 mL/min; collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.9 Collect approx 200 mL of distillate, dilute to 250 mL with ammonia-free water, and mix.

6.10 Set up manifold (fig. 42). If the laboratory air is contaminated with ammonia, it must be passed through a scrubber containing 2.5*M* H_2SO_4 before it enters the air-manifold tube.

6.11 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min or until the temperature of the heating bath reaches 50°C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with ammonia-free water in the sample line.

6.12 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray (NOTE 2). Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill the remainder of each sample tray with the distilled blank, standards and unknown samples.

NOTE 2. To avoid possible contamination of the sample cups, they should remain sealed in their packages until just prior to use. Rinse each sample cup with sample prior to filling.

6.13 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective nitrogen concentration.

7.2 Compute the concentration of NH_3-N (mg/L) in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

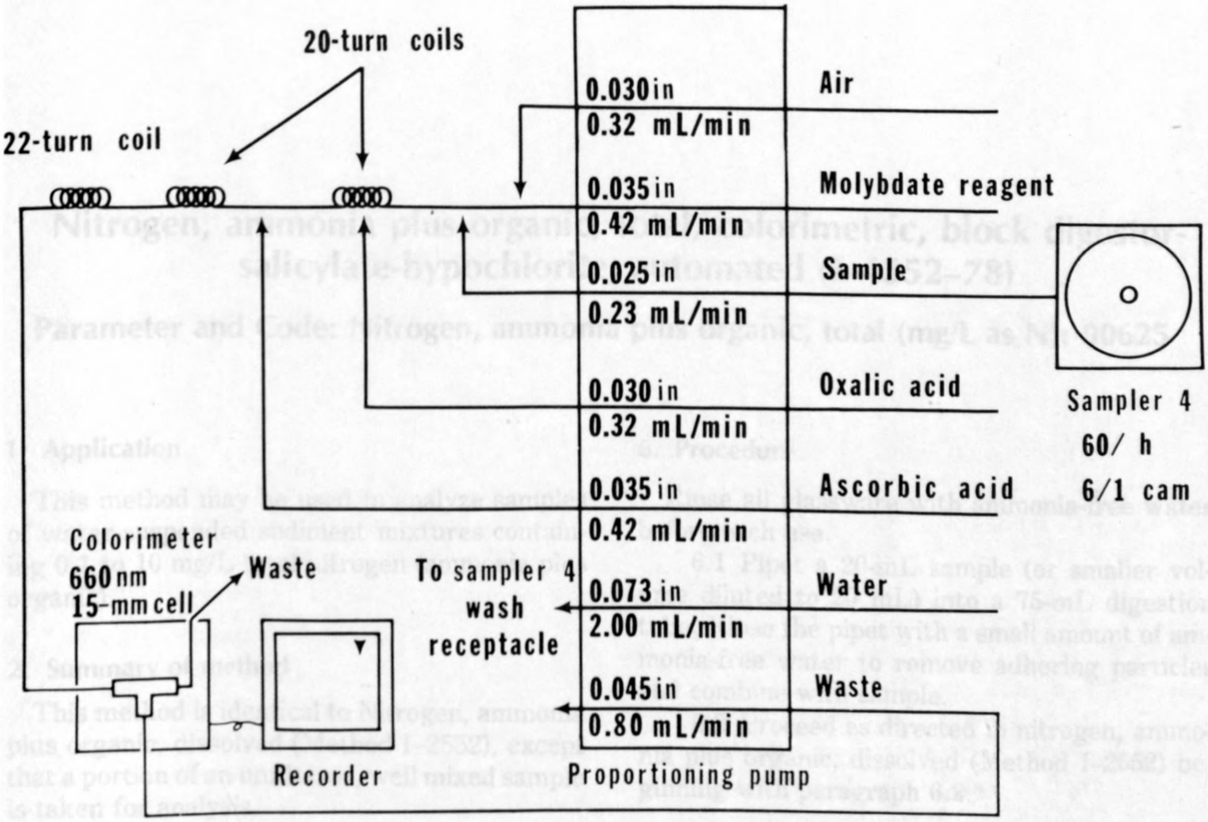


FIGURE 42.—Nitrogen, ammonia plus organic, manifold.

7.3 Determine the ammonia plus organic nitrogen concentration in milligrams per kilogram as follows:

$$\text{Ammonia plus organic nitrogen (mg/kg)} = \frac{\text{mg/L NH}_3\text{-N in sample} - \text{mg/L NH}_3\text{-N in blank}}{\text{wt of sample (g)}} \times 250$$

8. Report

Report nitrogen, ammonia plus organic, total in bottom material (00626), in milligrams per kilogram, as follows: less than 100 mg/kg, nearest milligram per kilogram; 100 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.

Nitrogen, ammonia plus organic, total, colorimetric, block digestor-salicylate-hypochlorite, automated (I–4552–78)

Parameter and Code: Nitrogen, ammonia plus organic, total (mg/L as N): 00625

1. Application

This method may be used to analyze samples of water-suspended sediment mixtures containing 0.1 to 10 mg/L total nitrogen (ammonia plus organic).

2. Summary of method

This method is identical to Nitrogen, ammonia plus organic, dissolved (Method I–2552), except that a portion of an unfiltered, well mixed sample is taken for analysis.

3. Interferences

A comparison study of results obtained by this method with those from the colorimetric digestion-distillation-nesslerization and colorimetric, digestion-distillation-indophenol automated, methods (Methods I–1550 and I–2551, respectively) indicated the absence of interferences.

4. Apparatus

For additional items of required apparatus, see Nitrogen, ammonia plus organic, dissolved (Method I–2552).

5. Reagents

See Nitrogen, ammonia plus organic, dissolved (Method I–2552).

6. Procedure

Rinse all glassware with ammonia-free water before each use.

6.1 Pipet a 20-mL sample (or smaller volume diluted to 20 mL) into a 75-mL digestion tube. Rinse the pipet with a small amount of ammonia-free water to remove adhering particles and combine with sample.

6.2 Proceed as directed in nitrogen, ammonia plus organic, dissolved (Method I–2552) beginning with paragraph 6.2.

7. Calculations

Total ammonia plus organic nitrogen is equal to ammonia-nitrogen as determined in paragraph 7.2, Method I–2552.

8. Report

Report nitrogen, ammonia plus organic, total (00625), concentrations as follows: less than 1.0 mg/L, one decimal; 1.0 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 18 percent at 0.88 mg/L and greater than 6 percent at 3.3 mg/L.

Nitrogen, ammonia plus organic, total, colorimetric, digestion-distillation-indophenol, automated (I–4551–78)

Parameter and Code: Nitrogen, ammonia plus organic, total (mg/L as N): 00625

1. Application

Concentrations of 0.01 to 2.0 mg/L nitrogen (ammonia plus organic) can be determined by this method. Samples with concentrations greater than 2 mg/L must be diluted.

2. Summary of method

The sample is subjected to digestion whereby all organic nitrogen-containing compounds are converted to ammonium salts. The resulting mixture is then made strongly alkaline and the ammonia so formed is distilled from the mixture into a solution of boric acid and subsequently determined by an automated indophenol colorimetric reaction.

3. Interferences

There are no known interferences with this method.

4. Apparatus

4.1 *Kjeldahl distillation apparatus*, including 800-mL capacity kjeldahl flasks.

4.2 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment the following operating conditions have been found satisfactory:

Absorption cell	15 mm.
Wavelength	630 nm.
Cam	60/h (6/1).
Heating bath temperature	50° C.

5. Reagents

5.1 *Alkaline phenol* solution: Mix 89 mL liquid phenol (approx 90 percent) in 50 mL ammonia-free water. Cautiously add, while cooling, in small increments with agitation, 180 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water (NOTE 1). Keep refrigerated.

NOTE 1. The distilled water must be free of ammonia. This can be achieved by passing it through a "mixed-bed" ion-exchange column.

5.2 *Ammonia* standard solution I, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.3 *Ammonia* standard solution II, 1.00 mL = 0.025 mg NH_3-N: Dilute 25.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh weekly.

5.4 *Ammonia* working standards: Prepare a blank and 500 mL each of a series of ammonia working standards by appropriate quantitative dilution of ammonia standard solution II as follows:

Ammonia standard solution II (mL)	*Ammonia-nitrogen (mg/L)*
0.0	0.00
.5	.025
1.0	.05
2.0	.10
5.0	.25
10.0	.50
20.0	1.0
40.0	2.0

Prepare fresh weekly.

5.5 *Boric acid* solution, 20 g/L: Dissolve 20 g H_3BO_3 crystals in 800 mL ammonia-free water and dilute to 1 L.

5.6 *Brij–35* solution: 30 percent aqueous (Baker Cat. No. C706, or equivalent).

5.7 *Kel-Pak powder No. 3.*

5.8 *Sodium hydroxide* solution, 5*M*: *Cautiously* dissolve 200 g NaOH in ammonia-free water. Cool and dilute to 1 L. Store in a plastic container.

5.9 *Potassium sodium tartrate-sodium citrate* solution: Dissolve 33 g $KNaC_4H_4O_6 \cdot 4H_2O$ and 24 g sodium citrate in 950 mL ammonia-free water. Adjust the pH of this solution to 5.0 with concentrated H_2SO_4 (sp gr 1.84) and dilute to 1 L with ammonia-free water. Add 0.5 mL of Brij–35 solution.

5.10 *Sodium hydroxide-thiosulfate* solution: *Cautiously* dissolve 500 g NaOH in 600 mL ammonia-free water. Add 80 g $Na_2S_2O_3 \cdot 5H_2O$ and dilute to 1 L.

5.11 *Sodium hypochlorite* stock solution: Chlorox or any other good commercial household bleach having approx 5 percent available chlorine.

5.12 *Sodium hypochlorite* working solution: Dilute 200 mL sodium hypochlorite stock solution to 1 L with ammonia-free water.

5.13 *Sodium nitroprusside* solution, 0.45 g/L: Dissolve 0.5 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ in ammonia-free water and dilute to 1 L. This reagent is stable for approx 1 month.

5.14 *Sodium thiosulfate* crystals, $Na_2S_2O_3 \cdot 5H_2O$.

6. Procedure

6.1 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent (CAUTION: deadly poison). (See Method I–1520.)

6.2 Pipet 200 mL of a well mixed sample into a 800-mL capacity digestion flask.

6.3 In the same manner prepare a blank and standard (2.0 mg/L).

6.4 With care, add 25 mL concentrated H_2SO_4 (sp gr 1.84) and swirl the contents of the flask under a hood until thoroughly mixed.

6.5 Add one Kel-Pak and mix well. Add a few glass beads and begin the digestion. Digest until copious fumes are given off and continue the digestion until a clear solution is obtained, and then continue fuming 1 h.

6.6 Cool the flask until crystals appear (do not cool completely). Add 150 mL ammonia-free water; mix and allow to cool.

6.7 Add 100 mL $NaOH–Na_2S_2O_3$ solution. Immediately connect the flask to the distillation apparatus and cautiously mix the contents by swirling.

6.8 Distill at a rate of not more than 10 mL nor less than 6 mL/min; collect the distillate in a 200-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.9 Collect approx 150 mL of distillate, dilute to 200 mL with ammonia-free water, and mix.

6.10 Set up manifold (fig. 43). If the laboratory air is contaminated with ammonia, it must be passed through a scrubber containing 2.5*M* H_2SO_4 before it enters the air-manifold tube.

6.11 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min or until the temperature of the heating bath reaches 50°C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with ammonia-free water in the sample line.

6.12 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray (NOTE 2). Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with the distilled blank, standards and unknown samples.

NOTE 2. To avoid possible contamination of the sample cups, they should remain sealed in their packages until just prior to use. Rinse each sample cup with sample before filling.

6.13 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective nitrogen concentration.

7.2 Compute the concentration of NH_3-N (mg/L) in each sample by comparing its peak height to the analytical curve and subtracting the concentration of any nitrogen in the blank. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report nitrogen, ammonia plus organic, total (00625), concentrations as follows: less than 1.0

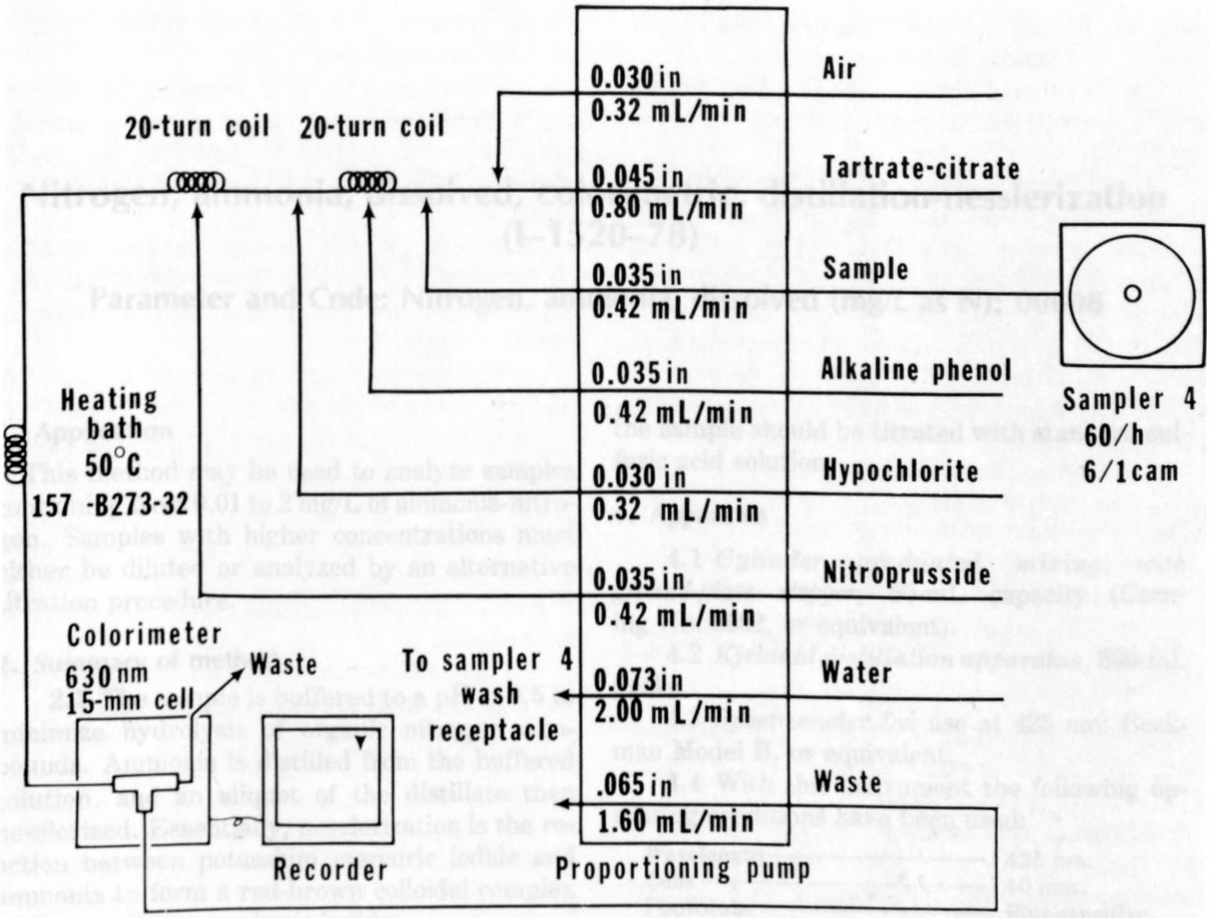


FIGURE 43.—Nitrogen, ammonia plus organic, manifold.

mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

Reference

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 182.

Nitrogen, ammonia, dissolved, colorimetric, distillation-nesslerization (I–1520–78)

Parameter and Code: Nitrogen, ammonia, dissolved (mg/L as N): 00608

1. Application

This method may be used to analyze samples containing from 0.01 to 2 mg/L of ammonia-nitrogen. Samples with higher concentrations must either be diluted or analyzed by an alternative titration procedure.

2. Summary of method

2.1 The sample is buffered to a pH of 9.5 to minimize hydrolysis of organic nitrogen compounds. Ammonia is distilled from the buffered solution, and an aliquot of the distillate then nesslerized. Essentially, nesslerization is the reaction between potassium mercuric iodide and ammonia to form a red-brown colloidal complex of mercuric ammono-basic iodide:

$$2(HgI_2 \cdot 2KI) + 2NH_3 \rightarrow NH_2Hg_2I_3 + 4KI + NH_4I$$

Concentrations of ammonia are then determined by standard spectrometric measurements. Alternatively, the distillate may be titrated with standard sulfuric acid solution.

2.2 Additional information on the principle of the determination is given by Blaedel and Meloche (1963).

3. Interferences

3.1 Calcium, magnesium, iron, and sulfide interfere with the nesslerization, but the interference of the metals is eliminated by the distillation, and sulfide can be precipitated in the distillation flask with lead carbonate.

3.2 Some organic compounds may distill over the ammonia and form colors with nessler reagent which cannot be satisfactorily read with the spectrophotometer. Under such conditions, the sample should be titrated with standard sulfuric acid solution.

4. Apparatus

4.1 *Cylinder, graduated, mixing, with ground-glass stopper,* 50-mL capacity (Corning No. 3002, or equivalent).

4.2 *Kjeldahl distillation apparatus*, 800-mL flasks.

4.3 *Spectrometer* for use at 425 nm: Beckman Model B, or equivalent.

4.4 With this instrument the following operating conditions have been used:

Wavelength	425 nm.
Cells	40 mm.
Phototube	Blue-sensitive.
Initial sensitivity	1.
Slit width	0.3 mm.

4.5 With these operating conditions the following absorbances have been observed:

Amount of ammonia-nitrogen (mg)	*Absorbance*
0.00	0.00
.02	.24
.04	.47
.06	.70
.10	1.16

5. Reagents

5.1 *Ammonium chloride* standard solution I, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonium chloride* standard solution II, 1.00 mL = 0.010 mg NH_3-N: Dilute 10.0 mL ammonium chloride standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Borate* buffer solution: Dissolve 9.54 g $Na_2B_4O_7 \cdot 10H_2O$ in ammonia-free water. Adjust the pH to 9.5 with 1*M* NaOH (approx 15 mL) and dilute to 1 L ammonia-free water.

5.4 *Boric acid* solution, 20 g/L: Dissolve 20 g H_3BO_3 in 800 mL ammonia-free water and dilute to 1 L.

5.5 *Nessler* reagent (CAUTION: HgI_2 is a deadly poison, and the reagent must be so marked): Dissolve 100 g HgI_2 and 70 g KI in a small volume of ammonia-free water. Add this mixture slowly, with stirring, to a cooled solution of 160 g NaOH in 500 mL ammonia-free water and dilute to 1 L. Allow the reagent to stand at least overnight and filter through a fritted-glass crucible.

5.6 *Sodium hydroxide* solution, 1*M*: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 L.

6. Procedure

All glassware should first be rinsed with ammonia-free water.

6.1 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent (CAUTION: deadly poison).

6.2 Measure a volume of sample containing less than 1.0 mg ammonia-nitrogen (250 mL maximum) into a 400-mL beaker, and adjust the volume to approx 250 mL with ammonia-free water.

6.3 Add 12.5 mL borate buffer solution, and adjust the pH to 9.5 with 1*M* NaOH, if necessary.

6.4 Immediately transfer the solution to the distillation flask and distill at a rate of not more than 10 mL or less than 6 mL per min; collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.5 Collect approx 200 mL of distillate, dilute to 250 mL with ammonia-free water, and mix.

6.6 Pipet an aliquot of distillate containing less than 0.1 mg ammonia-nitrogen (50.0 mL maximum) into a glass-stoppered, graduated mixing cylinder, and adjust the volume to 50.0 mL with ammonia-free water.

6.7 Prepare a blank of ammonia-free water and a series of standards in glass-stoppered, graduated mixing cylinders. Add 5 mL boric acid solution to each, and adjust the volume of each to 50.0 mL.

6.8 Add 1.0 mL nessler reagent (CAUTION: deadly poison) to each blank, standard, and sample. Stopper and invert several times to mix thoroughly.

6.9 Allow the solutions to stand at least 10 min, but not more than 30 min.

6.10 Determine the absorbance of each test sample and standard against the blank.

7. Calculations

7.1 Determine milligrams of ammonia-nitrogen in each sample from a plot of absorbances of standards.

7.2 Determine the ammonia nitrogen concentration in milligrams per liter as follows:

Ammonia-nitrogen as N, (mg/L) =

$$\frac{1{,}000}{\text{mL sample}} \times \frac{250}{\text{mL aliquot}} \times \text{mg N in aliquot.}$$

8. Report

Report nitrogen, ammonia, dissolved (00608), concentrations as follows: less than 1.0 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

Blaedel, W. J., and Meloche, V. W., 1963, Elementary quantitative analysis: theory and practice [2d ed.]: New York, Harper and Row, 826 p.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 117.

Nitrogen, ammonia, dissolved, colorimetric, indophenol, automated (I–2523–78)

Parameter and Code: Nitrogen, ammonia, dissolved (mg/L as N): 00608

1. Application

This method may be used to determine concentrations of ammonia-nitrogen in surface, domestic, and industrial waters and brines in the range from 0.00 to 5.0 mg/L NH_3-N. The range may be extended to 10.0 mg/L NH_3-N if the nitroprusside is omitted.

2. Summary of method

Ammonia reacts with hypochlorite and alkaline phenol to form an intensely colored indophenol compound, the absorbance of which is directly proportional to the ammonia concentration. Sodium nitroprusside may be added to improve the sensitivity of this determination (Bolleter and others, 1961; O'Brien and Fiore, 1962; Tetlow and Wilson, 1964; Van Slyke and Hiller, 1933).

3. Interferences

A complexing reagent consisting of sodium potassium tartrate and sodium citrate is added to remove interferences from several metal ions, including calcium, magnesium, and iron. The color development is pH dependent; therefore, samples whose pH values lie outside of the range from 4 to 10 should be analyzed with use of standards and wash solution of approximately the same pH. Aromatic amines may interfere.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been satisfactory for the range from 0.01 to 5.0 mg/L NH_3-N:

Absorption cell	**15 mm.**
Wavelength	**630 nm.**
Cam	**60/h (6/1).**
Heating bath temperature	**50° C.**

5. Reagents

5.1 *Alkaline phenol* solution: Mix 89 mL liquid phenol (approx 90 percent) in 50 mL ammonia-free water. Cautiously add, while cooling, in small increments with agitation, 180 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water (NOTE 1). Keep refrigerated in an amber bottle.

NOTE 1. The demineralized water must be free of ammonia. This can be achieved by passing it through a "mixed-bed" ion-exchange column.

5.2 *Ammonia-nitrogen* standard solution I, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL. Refrigerate.

5.3 *Ammonia-nitrogen* standard solution II, 1.00 mL = 0.025 mg NH_3-N: Dilute 25.0 ml ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh weekly and refrigerate.

5.4 *Ammonia-nitrogen* working standards: Prepare a blank and 250 mL each of a series of ammonia-nitrogen working standards by appropriate quantitative dilution of ammonia-nitrogen standard solution II with ammonia-free water as follows:

Ammonia-nitrogen standard solution II (mL)	*Ammonia-nitrogen concentration (mg/L)*
0.0	0.00
10	1.0
20	2.0
30	3.0
40	4.0
50	5.0

Prepare fresh weekly and refrigerate.

5.5 *Brij—35* solution, 30 percent aqueous solution (Baker Cat. No. C706, or equivalent).

5.6 *Potassium sodium tartrate-sodium citrate* solution: Dissolve 33 g $KNaC_4H_4O_6 \cdot 4H_2O$ and 24 g sodium citrate in 950 mL of ammonia-free water. Adjust the pH of this solution to 5.0 with concentrated H_2SO_4 (sp gr 1.84) and dilute to 1 L with ammonia-free water. Add 0.5 mL of Brij–35 solution.

5.7 *Sodium hydroxide* solution, 5*M*: *Cautiously* dissolve 200 g NaOH in ammonia-free water. Cool and dilute to 1L. Store in a plastic container.

5.8 *Sodium hypochlorite* stock solution: Chlorox or any other good commercial household bleach having approx 5 percent available chlorine.

5.9 *Sodium hypochlorite* working solution: Dilute 200 mL sodium hypochlorite stock solution to 1 L with ammonia-free water.

5.10 *Sodium nitroprusside* solution, 0.44 g/L: Dissolve 0.5 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ in ammonia-free water and dilute to 1 L.

6. Procedure

6.1 Set up manifold (fig. 44). If the laboratory air is contaminated with ammonia, it must be passed through a scrubber containing 2.5*M* H_2SO_4 before it enters the air-manifold tube.

6.2 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min, or until the temperature of the heating bath reaches 50°C. Adjust the baseline to reach zero scale divisions on the recorder with all reagents, but with ammonia-free water in the sample line.

6.3 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray (NOTE 2). Place individual standards of differing concentrations in every eighth position of the

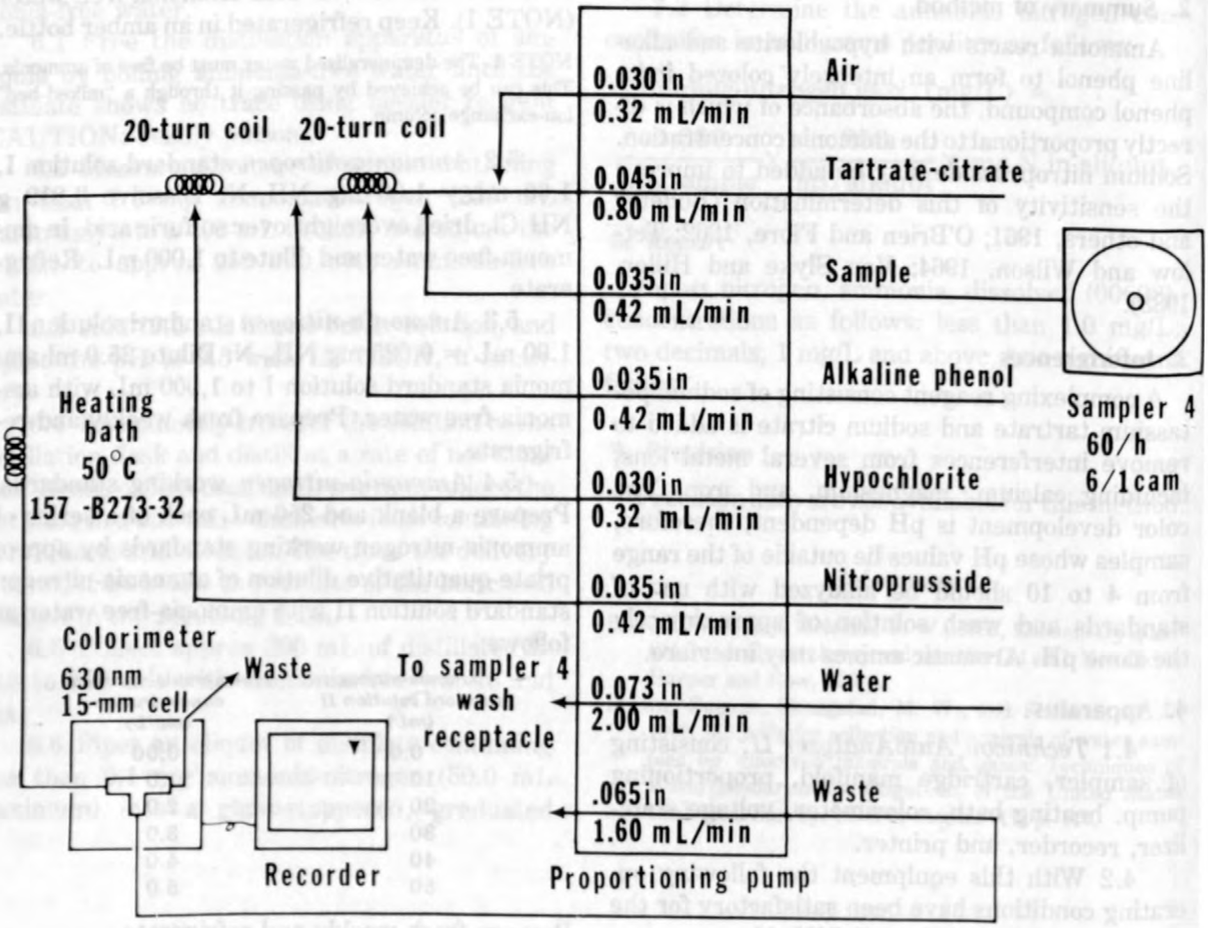


FIGURE 44.—Nitrogen, ammonia, manifold.

remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

NOTE 2. To avoid possible contamination of the sample cups, they should remain sealed in their packages until just prior to use. Rinse each sample cup with sample prior to filling.

6.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective nitrogen concentration.

7.2 Compute the concentration of NH_3-N in milligrams per liter in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report nitrogen, ammonia, dissolved (00608), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

As determined on synthetic (deionized) water matrix samples, relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
2 (99 replicates)	0.22	17
2 (103 replicates)	1.53	6

References

Bolleter, W. T., Bushman, C. J., and Tidwell, P. W., 1961, Spectrophotometric determination of ammonia as indophenol: Analytical Chemistry, v. 33, p. 592–594.

O'Brien, J. E., and Fiore, J., 1962, Ammonia determination by automatic analysis: Wastes Engineering, v. 33, p. 352–353, 377.

Tetlow, J. A., and Wilson, A. L., 1964, An absorptiometric method for determining ammonia in boiler-feed water: Analyst, v. 89, p. 453–465.

Van Slyke, D. D., and Hiller, A. J., 1933, Determination of ammonia in blood: Biological Chemistry Journal, v. 102, p. 499–504.

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 168.

Nitrogen, ammonia, total in bottom material, colorimetric, extraction-indophenol, automated (I-6523-78)

Parameter and Code: Nitrogen, ammonia, total in bottom material, dry wt (mg/kg as N): 00611

1. Application

This method may be used to determine concentrations of ammonia nitrogen in bottom material containing at least 0.2 mg/kg NH_3-N. Prepared sample solutions (paragraph 6.1.5) containing more than 5.0 mg/L NH_3-N must first be diluted. The range may be extended to 10.0 mg/L NH_3-N if the nitroprusside is omitted.

2. Summary of method

2.1 Sodium ion is a good replacement ion for ammonium in the slow exchange positions of soil minerals (Jackson, 1958). For this reason, the sample of bottom material is treated with an acidified sodium chloride solution. The resulting mixture is then centrifuged to obtain a clear supernatant solution for analysis.

2.2 Ammonia reacts with hypochlorite and alkaline phenol to form an intensely colored indophenol compound, the absorbance of which is directly proportional to the ammonia concentration. Sodium nitroprusside may be added to improve the sensitivity of this determination (Bolleter and others, 1961; O'Brien and Fiore, 1962; Tetlow and Wilson, 1964; Van Slyke and Hiller, 1933).

3. Interferences

A complexing reagent consisting of sodium potassium tartrate and sodium citrate is added to remove interferences from several metal ions, including calcium, magnesium, and iron. The color development is pH dependent; therefore, samples whose pH values lie outside of the range from 4 to 10 should be analyzed with use of standards and wash solution of approximately the same pH. Aromatic amines may interfere.

4. Apparatus

4.1 *Centrifuge*.

4.2 *Shaker*, wrist-action.

4.3 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.4 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 5.0 mg/L NH_3-N:

Absorption cell	15 mm.
Wavelength	630 nm.
Cam	60/h (6/1).
Heating bath temperature	50° C.

5. Reagents

5.1 *Alkaline phenol* solution: Mix 89 mL liquid phenol (approximately 90 percent) in 50 mL ammonia-free water. Cautiously add, while cooling, in small increments with agitation, 180 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water (NOTE 1). Keep refrigerated in an amber bottle.

NOTE 1. The demineralized water must be free of ammonia. This can be achieved by passing it through a "mixed-bed" ion-exchange column.

5.2 *Ammonia-nitrogen* standard solution I, 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL. Refrigerate.

5.3 *Ammonia-nitrogen* standard solution II, 1.00 mL = 0.025 mg NH_3-N: Dilute 25.0 mL ammonia standard solution I to 1,000 mL with sodium chloride solution (paragraph 5.8). Prepare fresh weekly and refrigerate.

5.4 *Ammonia-nitrogen* working standards: Prepare a blank and 250 mL each of a series of ammonia working standards by appropriate quantitative dilution of ammonia standard solution II with sodium chloride solution (5.8) as follows: Prepare fresh weekly and refrigerate.

Ammonia standard solution II (mL)	*Ammonia-nitrogen concentration (mg/L)*
0.0	0.00
10	1.0
20	2.0
30	3.0
40	4.0
50	5.0

5.5 *Brij–35* solution, 30 percent aqueous solution (Baker Cat. No. C706, or equivalent).

5.6 *Sodium hydroxide* solution, 5*M*: *Cautiously* dissolve 200 g NaOH in ammonia-free water. Cool and dilute to 1 L. Store in a plastic container.

5.7 *Potassium sodium tartrate-sodium citrate* solution: Dissolve 33 g $KNaC_4H_4O_6 \cdot 4H_2O$ and 24 g sodium citrate in 950 mL of ammonia-free water. Adjust the pH of this solution to 5.0 with concentrated H_2SO_4 (sp gr 1.84) and dilute to 1 L with ammonia-free water. Add 0.5 mL Brij–35 solution.

5.8 *Sodium chloride* solution, 100 g/L, acidified: Dissolve 100 g NaCl in 950 mL ammonia-free water. Acidify with concentrated HCl (sp gr 1.19) to a pH of 2.5. Dilute to 1 L.

5.9 *Sodium hypochlorite* stock solution: Chlorox or any other good commercial household bleach having approximately 5 percent available chlorine.

5.10 *Sodium hypochlorite* working solution: Dilute 200 mL of stock sodium hypochlorite to 1 L with ammonia-free water.

6. Procedure

6.1 *Extraction procedure*:

6.1.1 Weigh to the nearest milligram, approx 5 g of sample, prepared as directed in Method P–0520, and transfer to a 250-mL erlenmeyer flask.

6.1.2 Add 50 mL NaCl solution (5.8) and shake on the wrist-action shaker for 30 min.

6.1.3 Carefully transfer the entire sample, including all sediment particles, to a centrifuge tube. Centrifuge for 5 min; if the sample does not flocculate, add a drop of concentrated HCl (sp gr 1.19) and recentrifuge.

6.1.4 Transfer the supernatant solution to a 100-mL volumetric flask, taking care not to disturb the residue in the bottom of the centrifuge tube.

6.1.5 Wash the sediment in the centrifuge tube with 20 mL NaCl solution (paragraph 5.8), recentrifuge and transfer the clear wash solution to the volumetric flask. Adjust to volume with NaCl solution (5.8).

6.2 *Colorimetric procedure:*

6.2.1 Set up manifold (fig. 45). If the laboratory air is contaminated with ammonia, it must be passed through a scrubber containing 2.5*M* H_2SO_4 before it enters the air-manifold tube.

6.2.2 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min, or until the temperature of the heating bath reaches 50°C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with ammonia-free water in the sample line.

6.2.3 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray (NOTE 2). Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

NOTE 2. To avoid possible contamination of the sample cups, they should remain sealed in their packages until just prior to use. Rinse each sample cup with sample prior to filling.

6.2.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective nitrogen concentration.

7.2 Compute the concentration of NH_3-N in milligrams per liter in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 Compute ammonia nitrogen concentrations in the bottom-material sample as follows:

$$NH_3\text{-N (mg/kg)} = \frac{C_N \times 100}{\text{wt sample (g)}}$$

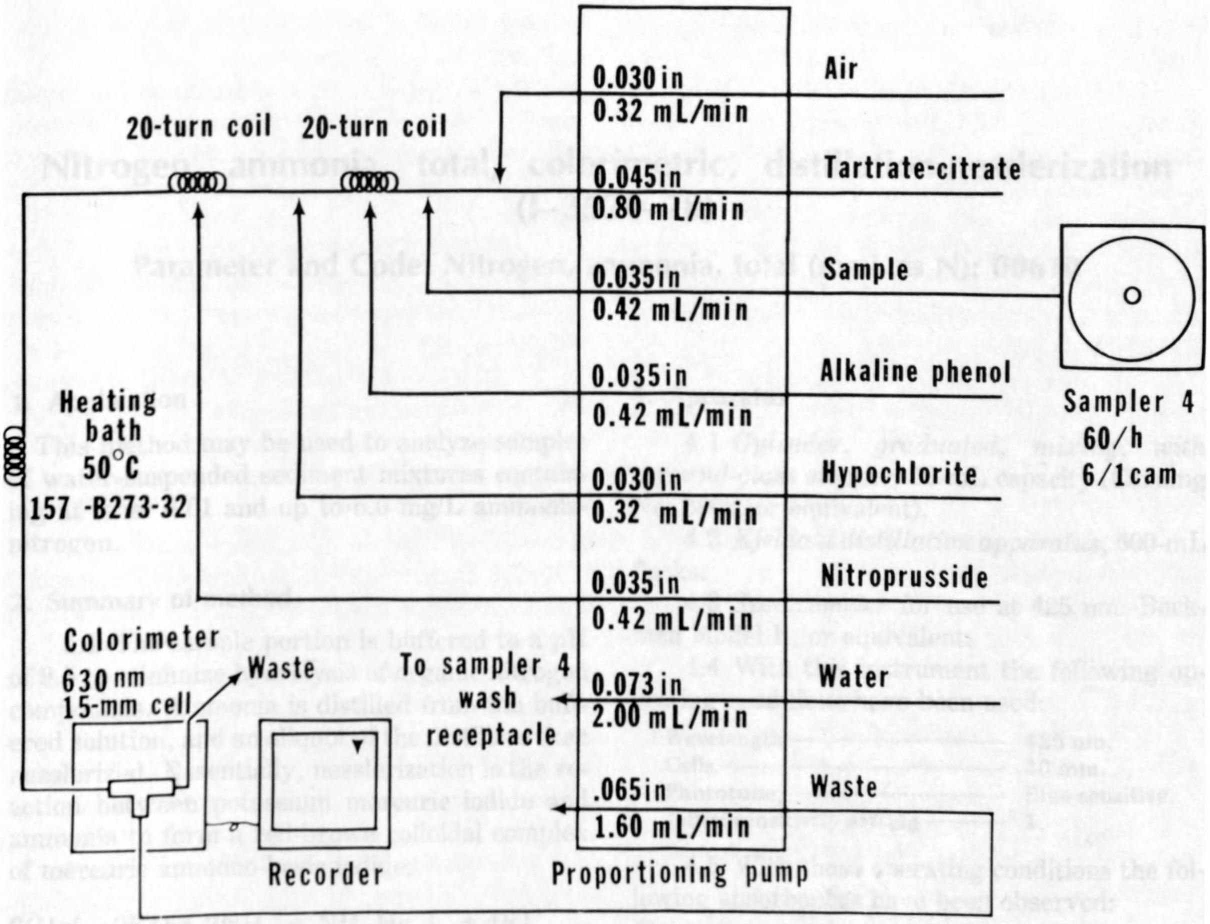


FIGURE 45.—Nitrogen, ammonia, manifold.

where

C_N = NH_3-N concentration, milligrams of NH_3-N per liter.

8. Report

Report nitrogen, ammonia, total in bottom material (00611), as follows: less than 10 mg/kg, one decimal; 10 mg/kg and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 17 percent in the lower portion of the analytical range.

References

Bolleter, W. T., Bushman, C. J., and Tidwell, P. W., 1961, Spectrophotometric determination of ammonia as indophenol: Analytical Chemistry, v. 33, p. 592–594.

Jackson, M. L., 1958, Soil chemical analysis: Englewood Cliffs, N.J., Prentice-Hall, p. 193–194.

O'Brien, J. E., and Fiore, J., 1962, Ammonia determination by automatic analysis: Wastes Engineering, v. 33. p. 352–353, 377.

Tetlow, J. A., and Wilson, A. L., 1964, An absorptiometric method for determining ammonia in boiler-feed water: Analyst, v. 89, p. 453–465.

Van Slyke, D. D., and Hiller, A. J., 1933, Determination of ammonia in blood: Biological Chemistry Journal, v. 102, p. 499–504.

Nitrogen, ammonia, total, colorimetric, distillation-nesslerization (I–3520–78)

Parameter and Code: Nitrogen, ammonia, total (mg/L as N): 00610

1. Application

This method may be used to analyze samples of water-suspended sediment mixtures containing at least 0.01 and up to 5.0 mg/L ammonia-nitrogen.

2. Summary of method

2.1 The sample portion is buffered to a pH of 9.5 to minimize hydrolysis of organic nitrogen compounds. Ammonia is distilled from the buffered solution, and an aliquot of the distillate then nesslerized. Essentially, nesslerization is the reaction between potassium mercuric iodide and ammonia to form a red-brown colloidal complex of mercuric ammono-basic iodide:

$$2(HgI_2 \cdot 2KI) + 2NH_3 \rightarrow NH_2Hg_2I_3 + 4KI + NH_4I$$

Concentrations of ammonia are then determined by standard spectrometric measurements. Alternatively, the distillate may be titrated with standard sulfuric acid solution.

2.2 Additional information on the principle of the determination is given by Blaedel and Meloche (1963).

3. Interferences

3.1 Calcium, magnesium, iron, and sulfide interfere with the nesslerization, but the interference of the metals is eliminated by the distillation, and sulfide can be precipitated in the distillation flask with lead carbonate.

3.2 Some organic compounds may distill over with the ammonia and form colors with nessler reagent which cannot be satisfactorily read with the spectrophotometer. Under such conditions, the sample should be titrated with standard sulfuric acid solution.

4. Apparatus

4.1 *Cylinder, graduated, mixing, with ground-glass stopper*, 50-mL capacity (Corning No. 3002, or equivalent).

4.2 *Kjeldahl distillation apparatus*, 500-mL flasks.

4.3 *Spectrometer* for use at 425 nm: Beckman Model B, or equivalent.

4.4 With this instrument the following operating conditions have been used:

Wavelength ---------- 425 nm.
Cells ---------- 40 mm.
Phototube ---------- Blue-sensitive.
Initial sensitivity setting ---------- 1.

4.5 With these operating conditions the following absorbances have been observed:

Amount of nitrogen (mg)	*Absorbance*
0.00	0.00
.02	.24
.04	.47
.06	.70
.10	1.16

5. Reagents

5.1 *Ammonium chloride* standard solution I, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonium chloride* standard solution II, 1.00 mL = 0.010 mg NH_3-N: Dilute 10.0 mL ammonium chloride standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Borate* buffer solution: Dissolve 9.54 g $Na_2B_4O_7 \cdot 10H_2O$ in ammonia-free water. Adjust the pH to 9.5 with 1*M* NaOH (approx 15 mL) and dilute to 1 L with ammonia-free water.

5.4 *Boric acid* solution, 20 g/L: Dissolve 20 g H_3BO_3 in 800 mL ammonia-free water and dilute to 1 L.

5.5 *Nessler* reagent (CAUTION: HgI_2 is a deadly poison, and the reagent must be so marked): Dissolve 100 g HgI_2 and 70 g KI in a small volume of ammonia-free water. Add this mixture slowly, with stirring, to a cooled solution of 160 g NaOH in 500 mL ammonia-free water and dilute to 1 L. Allow the reagent to stand at least overnight and filter through a fritted-glass crucible.

5.6 *Sodium hydroxide* solution, 1*M*: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 L.

6. Procedure

Rinse all glassware used in this determination with ammonia-free water.

6.1 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace with use of nessler reagent (CAUTION: deadly poison).

6.2 Pipet a volume of sample containing less than 1.0 mg NH_3-N (250 mL maximum) into a 400-mL beaker. Rinse the pipet with ammonia-free water to remove adhering particles and combine with sample. Dilute the sample to approx 250 mL if less than 250 mL is used.

6.3 Add 12.5 mL borate buffer solution, and adjust the pH to 9.5 with 1*M* NaOH, if necessary.

6.4 Immediately transfer the solution to the distillation flask and distill at a rate of not more than 10 mL nor less than 6 mL/min; collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.5 Collect approx 200 mL of distillate, dilute to 250 mL with ammonia-free water, and mix.

Nesslerization procedure

6.6 Pipet an aliquot of distillate containing less than 0.1 mg ammonia-nitrogen (50.0 mL maximum) into a glass-stoppered, graduated mixing cylinder, and adjust the volume to 50.0 mL with ammonia-free water.

6.7 Prepare a blank of ammonia-free water and a series of standards in glass-stoppered, graduated mixing cylinders. Add 5 mL boric acid solution to each, and adjust the volume of each to 50.0 mL.

6.8 Add 1.0 mL nessler reagent (CAUTION: deadly poison) to each blank, standard, and sample. Stopper and invert several times to mix thoroughly.

6.9 Allow the solutions to stand at least 10 min, but not more than 30 min.

6.10 Determine the absorbance of each test sample and standard against the blank.

7. Calculations

7.1 Determine the milligrams of total ammonia-nitrogen in each sample from a plot of absorbances of standards.

7.2 Determine the total ammonia-nitrogen concentration in milligrams per liter as follows:

Total ammonia-nitrogen as N (mg/L)

$$= \frac{1{,}000}{\text{mL sample}} \times \frac{250}{\text{mL aliquot}} \times \text{mg N in aliquot}$$

8. Report

Report nitrogen, ammonia, total (00610), concentrations as follows: less than 1.0 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

Blaedel, W. J., and Meloche, V. W., 1963, Elementary quantitative analysis: theory and practice [2nd ed.]: New York, Harper and Row, 826 p.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 117.

Nitrogen, ammonia, total, colorimetric, extraction-indophenol, automated (I–4523–78)

Parameter and Code: Nitrogen, ammonia, total (mg/L as N): 00610

1. Application

1.1 This method may be used to determine concentrations of ammonia-nitrogen in water-suspended sediment mixtures in the range from 0.01 to 5.0 mg/L NH_3-N. The range may be extended to 10.0 mg/L NH_3-N if the nitroprusside is omitted.

1.2 Sodium ion is a good replacement ion for ammonium in the slow exchange positions of soil minerals (Jackson, 1958). The water-suspended sediment mixture is treated and preserved in the field with mercury chloride/sodium chloride. The resulting mixture, prior to analysis in the laboratory, is either centrifuged or decanted to obtain a clear supernatant solution.

2. Summary of method

Ammonia reacts with hypochlorite and alkaline phenol to form an intensely colored indophenol compound, the absorbance of which is directly proportional to the ammonia concentration. Sodium nitroprusside may be added to improve the sensitivity of this determination (Bolleter and others, 1961; O'Brien and Fiore, 1962; Tetlow and Wilson, 1964; Van Slyke and Hiller, 1933).

3. Interferences

A complexing reagent consisting of sodium potassium tartrate and sodium citrate is added to remove interferences from several metal ions, including calcium, magnesium, and iron. The color development is pH dependent; therefore, samples whose pH values lie outside of the range from 4 to 10 must be analyzed with use of standards and wash solution of approximately the same pH. Aromatic amines may interfere.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 5.0 mg/L NH_3-N:

Absorption cell	15 mm.
Wavelength	630 nm.
Cam	60/h (6/1).
Heating bath temperature	50° C.

5. Reagents

5.1 *Alkaline phenol* solution: Mix 89 mL liquid phenol (approx 90 percent) in 50 mL ammonia-free water. Cautiously add, while cooling, in small increments with agitation, 180 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water (NOTE 1). Keep refrigerated in an amber bottle.

NOTE 1. The distilled water must be free of ammonia. This can be achieved by passing it through a "mixed-bed" ion-exchange column.

5.2 *Ammonia* standard solution I, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL. Refrigerate.

5.3 *Ammonia* standard solution II, 1.00 mL = 0.025 mg NH_3-N: Dilute 25.0 mL ammonia standard solution I to 1,000 mL with sodium chloride solution (paragraph 5.8). Prepare fresh weekly and refrigerate.

5.4 *Ammonia* working standards: Prepare a blank and 250 mL each of a series of ammonia working standards by appropriate quantitative dilution of ammonia standard solution II with sodium chloride solution (5.8) as follows:

Ammonia standard solution II (mL)	*Ammonia-nitrogen concentration (mg/L)*
0.0	0.00
10	1.0
20	2.0
30	3.0
40	4.0
50	5.0

Prepare fresh weekly and refrigerate.

5.5 *Brij–35* solution: 30 percent aqueous solution (Baker Cat. No. C706, or equivalent).

5.6 *Potassium sodium tartrate-sodium citrate* solution. Dissolve 33 g $KNaC_4H_4O_6 \cdot 4H_2O$ and 24 g sodium citrate in 950 mL ammonia-free water. Adjust the pH of this solution to 5.0 with concentrated H_2SO_4 (sp gr 1.84) and dilute to 1 L with ammonia-free water. Add 0.5 mL Brij–35 solution.

5.7 *Sodium hydroxide* solution, 5*M*: *Cautiously* dissolve 200 g NaOH in ammonia-free water. Cool and dilute to 1 L. Store in a plastic container.

5.8 *Sodium hypochlorite* stock solution: Chlorox or any other good commercial household bleach having approx 5 percent available chlorine.

5.9 *Sodium hypochlorite* working solution: Dilute 200 mL of stock sodium hypochlorite to 1 L with ammonia-free water.

5.10 *Sodium nitroprusside* solution, 0.44 g/L: Dissolve 0.5 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ in ammonia-free water and dilute to 1 L.

6. Procedure

6.1 Set up manifold (fig. 46). If the laboratory air is contaminated with ammonia, it must be passed through a scrubber containing 2.5*M* H_2SO_4 before it enters the air-manifold tube.

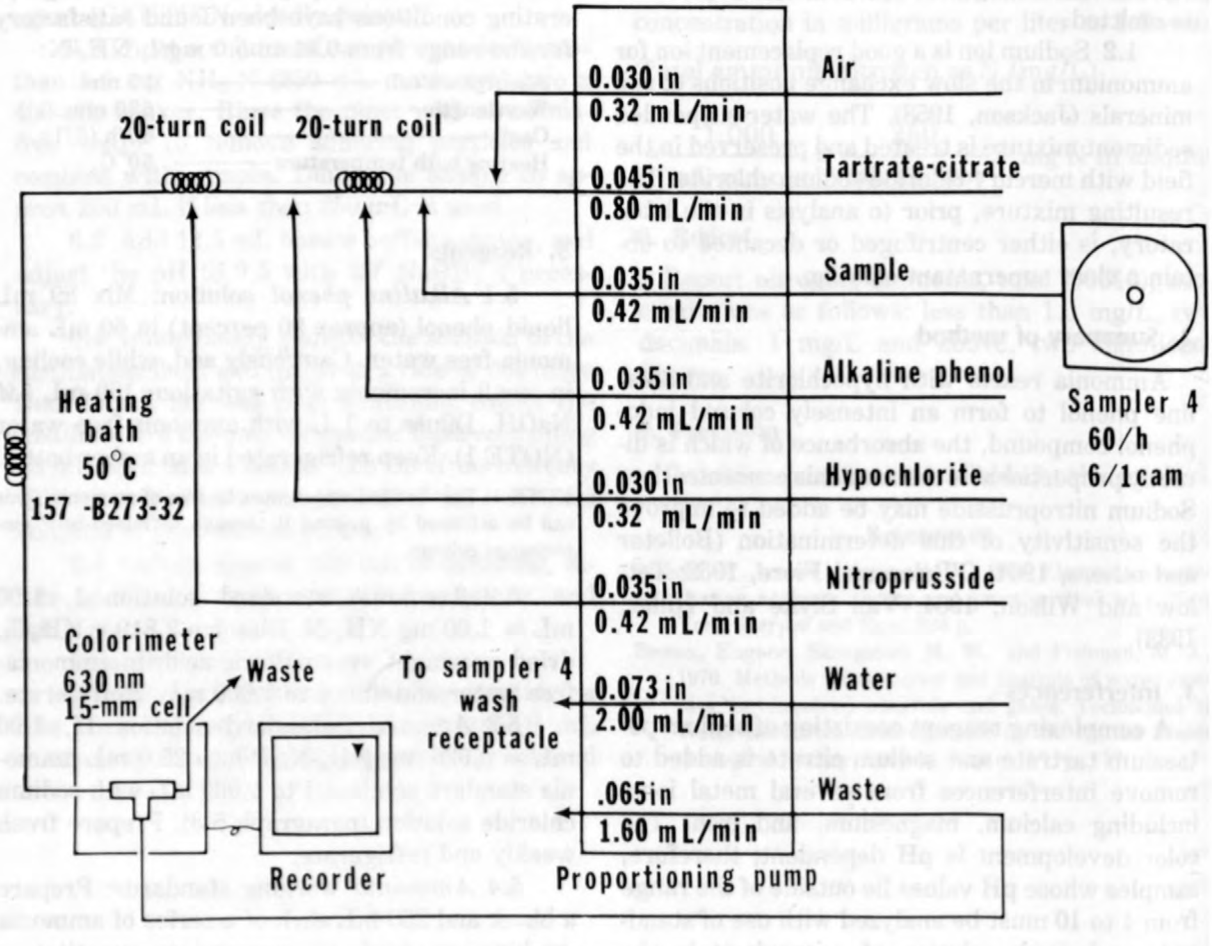


FIGURE 46.—Nitrogen, ammonia, manifold.

6.2 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min, or until the temperature of the heating bath reaches 50°C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with ammonia-free water in the sample line.

6.3 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray (NOTE 2). Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown field-acidified samples which have been either centrifuged or decanted to obtain a clear supernatant solution.

NOTE 2. To avoid possible contamination of the sample cups, they should remain sealed in their packages until just prior to use. Rinse the sample cup with the sample prior to filling.

6.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective nitrogen concentration.

7.2 Compute the concentration of NH_3-N (mg/L) in each sample by comparing its peak-height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report nitrogen, ammonia, total (00610), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 17 percent at 0.22 mg/L and greater than 6 percent at 1.53 mg/L.

References

Bolleter, W. T., Bushman, C. J., and Tidwell, P. W., 1961, Spectrophotometric determination of ammonia as indophenol: Analytical Chemistry, v. 33, p. 592–594.

Jackson, M. L., 1958, Soil chemical analysis: Englewood Cliffs, N.J., Prentice-Hall, p. 193–194.

O'Brien, J. E., and Fiore, J., 1962, Ammonia determination by automatic analysis: Wastes Engineering, v. 33, p. 352–353, 377.

Tetlow, J. A., and Wilson, A. L., 1964, An absorptiometric method for determining ammonia in boiler-feed water: Analyst, v. 89, p. 453–465.

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 168.

Van Slyke, D. D., and Hiller, A. J., 1933, Determination of ammonia in blood: Biological Chemistry Journal, v. 102, p. 499–504.

Nitrogen, nitrate, dissolved, colorimetric, brucine (I-1530-78)

Parameter and Code: Nitrogen, nitrate, dissolved (mg/L as N): 00618

1. Application

1.1 This method may be applied to essentially colorless water containing from 0.1 to 1.0 mg/L of nitrate-nitrogen. Any significant amount of color should be removed. Samples containing higher concentrations must first be diluted.

1.2 Samples containing more than 6 mg/L of NO_3-N may be analyzed by reduction using Devarda's alloy, distillation of the resulting NH_3, and titration with standard H_2SO_4 solution. Details of the procedure are given by Blaedel and Meloche (1963). For high concentrations of nitrate-nitrogen, the method yields results which are comparable in accuracy to those obtained by the brucine method.

2. Summary of method

The reaction between the alkaloid, brucine, and nitrate ion in acid medium produces a yellow color that may be measured by standard spectrometric procedures. Close attention must be given to procedural techniques if accuracy and precision are to be obtained. The procedure is similar to that of Jenkins and Medsker (1964).

3. Interferences

Organic color, nitrite ion, and all strong oxidizing and reducing agents interfere. The interference by residual chlorine up to 5 mg/L may be eliminated by addition of sodium arsenite, and interference of up to 1 mg/L of nitrite eliminated by use of sulfanilic acid. The interference by chloride is effectively masked by the addition of a large amount of chloride ion to the reaction mixture.

4. Apparatus

4.1 *Water bath,* boiling.

4.2 *Spectrometer* for use at 410 nm; Beckman Model B, or equivalent.

4.3 With this instrument the following operating conditions have been used:

Wavelength	410 nm.
Cells	23 mm.
Phototube	Blue-sensitive.
Initial sensitivity setting	2.
Slit width (approx)	0.10 mm.

4.4 With these operating conditions the following absorbances have been observed:

NO_3-N (*mg*)	*Absorbance*
0.000	0.000
.001	.100
.002	.195
.004	.390
.006	.565
.008	.730
.010	.870

5. Reagents

5.1 *Brucine-sulfanilic acid* reagent: Dissolve 1 g brucine sulfate (CAUTION: very poisonous) and 0.1 sulfanilic acid in 70 mL hot demineralized water. Add 3 mL concentrated HCl (sp gr 1.19), cool, and dilute to 100 mL. This solution is stable for several months. The pink color that develops does not affect its usefulness.

5.2 *Nitrate-nitrogen* standard solution I, 1.00 mL = 0.100 mg NO_3-N: Dissolve 0.7218 g KNO_3, dried overnight over concentrated H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.3 *Nitrate-nitrogen* standard solution II, 1.00 mL = 0.0010 mg NO_3-N: Dilute 10.0 mL nitrate-nitrogen standard solution I to 1,000 mL with demineralized water.

5.4 *Sodium chloride* solution, 300 g/L: Dissolve 300 g NaCl in 1 L demineralized water.

5.5 *Sulfuric acid,* 14.5*M*: Cautiously add 500 mL concentrated H_2SO_4 (sp gr 1.85) to 125 mL demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.01 mg NO_3-N (10.0 mL maximum) into a 23-mm absorption cell, and dilute to 10.0 mL.

6.2 Prepare a demineralized-water blank and sufficient standards, and adjust the volume of each to 10.0 mL.

6.3 Add 2.0 mL sodium chloride solution, and mix well by swirling.

6.4 Place the absorption cells into a cold-water bath (15°C to 20°C) and add 10.0 mL 14.5*M* H_2SO_4. Mix well by swirling, return to cold-water bath, and allow the contents of the tubes to cool to water-bath temperature.

6.5 Add 0.5 mL brucine-sulfanilic acid solution and mix thoroughly (NOTE 1).

NOTE 1. If a deep pink color forms immediately upon addition of the brucine-sulfanilic acid reagent, it is an indication of high nitrate concentration—exceeding the range of the method. Such sample aliquots must be discarded at this point and the samples reanalyzed, using a smaller aliquot.

6.6 Remove the absorption cells from the cold-water bath and place in a boiling-water bath for 20 min. The water bath must be sufficiently large so that boiling does not cease when the absorption cells are placed in it. This step is critical; all absorbance cells must be heated uniformly.

6.7 Remove the absorption cells from the boiling-water bath and immerse them in the cold-water bath. Allow to cool before proceeding; this inhibits any further color change. The cold-water bath must be sufficiently large to cool all absorption cells uniformly. Circulation of water in the bath is desirable.

6.8 Determine the absorbance of each sample and standard against the blank without unnecessary delay.

7. Calculations

7.1 Determine the milligrams of nitrate-nitrogen in each sample from a plot of absorbances of standards.

7.2 Determine the nitrate-nitrogen concentration in milligrams per liter as follows:

$$NO_3\text{-N (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times \text{mg } NO_3\text{-N in sample.}$$

8. Report

Report nitrate-nitrogen, dissolved (00618), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the relative deviation (coefficient and variation) is as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
11	0.20	22
8	1.01	6

References

Blaedel, W. J., and Meloche, V. W., 1963, Elementary quantitative analysis: theory and practice [2d ed.]: New York, Harper & Row, 826 p.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 119.

Jenkins, D., and Medsker, L. L., 1964, Brucine method for determination of nitrate in ocean, estuarine, and fresh waters: Analytical Chemistry, v. 36, p. 610.

Nitrogen, nitrite, dissolved, colorimetric, diazotization (I–1540–78)

Parameter and Code: Nitrogen, nitrite, dissolved (mg/L as N): 00613

1. Application

This method may be used to analyze samples containing between about 0.01 and 0.6 mg/L of nitrate-nitrogen; samples containing higher concentrations must first be diluted.

2. Summary of method

Nitrite is diazotized with sulfanilamide, and the resulting diazo compound is coupled with N-1-naphthylethylenediamine dihydrochloride to form an intensely colored red compound, which is determined spectrometrically at 540 nm. Sulfanilamide and the N-1-naphthylethylenediamine dihydrochloride are combined with a sodium acetate buffer to form a single reagent solution.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

4.1 *Spectrometer* for use at 540 nm; Beckman Model B, or equivalent.

4.2 With this instrument the following operating conditions have been used:

Wavelength	540 nm.
Cells	10 mm.
Phototube	Blue-sensitive.
Initial sensitivity	2.
Slit width	0.08 mm.

4.3 With these operating conditions the following absorbances have been observed:

NO_2N (*mg*)	*Absorbance*
0.000	0.000
.005	.310
.010	.610
.015	.910
.020	1.21
.030	1.81

5. Reagents

5.1 *Color-buffer* solution: Add 105 mL concentrated HCl (sp gr 1.19), 5.0 g sulfanilamide, and 0.5 g N-1-naphthylethylenediamine dihydrochloride to 250 mL demineralized water. Stir until dissolved. Add 136 g $CH_3COONa \cdot 3H_2O$ or 82 g CH_3COONa and stir until dissolved. Dilute to 500 mL with demineralized water. When 2 mL of this solution is added to 50 mL demineralized water, the resultant solution should have a pH of 1.8. Store the color-buffer solution in the dark and protect from nitrogen oxides that may be in the atmosphere. The solution is stable for several months.

5.2 *Nitrite-nitrogen* standard solution I, 1.00 mL = 0.50 mg NO_2-N: Dissolve 3.038 g KNO_2 in demineralized water and dilute to 1,000 mL.

5.3 *Nitrite-nitrogen* standard solution II, 1.00 mL = 0.05 mg NO_2-N: Dilute 100.0 mL nitrite-nitrogen standard solution I to 1,000 mL with demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.03 mg NO_2-N (50.0 mL maximum) into a 100-mL beaker and adjust the volume to 50 mL with demineralized water (NOTE 1).

NOTE 1. If the sample has a pH greater than 10 or less than 4 (or greater than 600 mg/L alkalinity or acidity), adjust to approx pH 6 with 3*M* HCl or 2.5*M* NaOH.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 mL.

6.3 Add 2.0 mL color-buffer solution and mix.

6.4 Allow the color to develop for at least 15 min and measure the absorbances of the sample and standards against the blank.

7. Calculations

7.1 Determine milligrams of nitrite-nitrogen in each test sample from a plot of absorbances of standards.

7.2 Determine the nitrite-nitrogen concentration in milligrams per liter as follows:

$$NO_2\text{-N (mg/L)} = \frac{1{,}000}{\text{mL aliquot}} \times \text{mg } NO_2\text{-N in sample.}$$

8. Report

Report nitrite-nitrogen, dissolved (00613), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 121.

Nitrogen, nitrite, dissolved, colorimetric, diazotization, automated (I–2540–78)

Parameter and Code: Nitrogen, nitrite, dissolved (mg/L as N): 00613

1. Application

This method may be used to determine concentrations of nitrite-nitrogen in surface, domestic, and industrial waters and brines in the range from 0.01 to 1.0 mg/L. Samples containing higher concentrations must first be diluted.

2. Summary of method

Nitrite ion reacts with sulfanilamide under acidic conditions to form a diazo compound which then couples with N-1-naphthylethylenediamine dihydrochloride to form a red-colored compound, the absorbance of which is measured colorimetrically (Kamphake and others, 1967).

3. Interferences

Oxidizing agents interfere by oxidizing nitrite to nitrate. Sulfide also interferes. No other substance commonly occurring in natural water interferes with this method.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 1.0 mg/L NO_2-N:

Absorption cell	15 mm.
Wavelength	520 nm.
Cam	40/h (4/1).

5. Reagents

5.1 *Color* reagent: Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to approx 1,500 mL demineralized water. Dissolve completely (warm if necessary). Add 1.0 g N-1-naphthylethylenediamine dihydrochloride and dissolve completely. Dilute to 2 L with demineralized water. Store in an amber bottle and refrigerate; however, the reagent must be at room temperature when it is used. The reagent is stable for approx 1 month.

5.2 *Nitrite-nitrogen* standard solution I, 1.00 mL = 0.100 mg NO_2-N: Dissolve 0.6076 g KNO_2 in demineralized water and dilute to 1,000 mL. This and the following nitrite standard solutions are not stable indefinitely; their concentrations must be checked frequently.

5.3 *Nitrite-nitrogen* standard solution II, 1.00 mL = 0.010 mg NO_2-N: Quantitatively dilute 100.0 mL nitrite standard solution I to 1,000 mL with demineralized water.

5.4 *Nitrite-nitrogen* working standards: Prepare a blank and 100 mL each of a series of nitrite-nitrogen working standards by appropriate quantitative dilution of nitrite-nitrogen standard solution II as follows:

Nitrate-nitrogen standard solution II (mL)	*Nitrate-nitrogen concentration (mg/L)*
0.0	0.00
2.0	0.2
5.0	0.5
10.0	1.0

6. Procedure

6.1 Set up manifold (fig. 47).

6.2 Allow colorimeter and recorder to warm up for at least 30 min. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample tube.

6.3 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray,

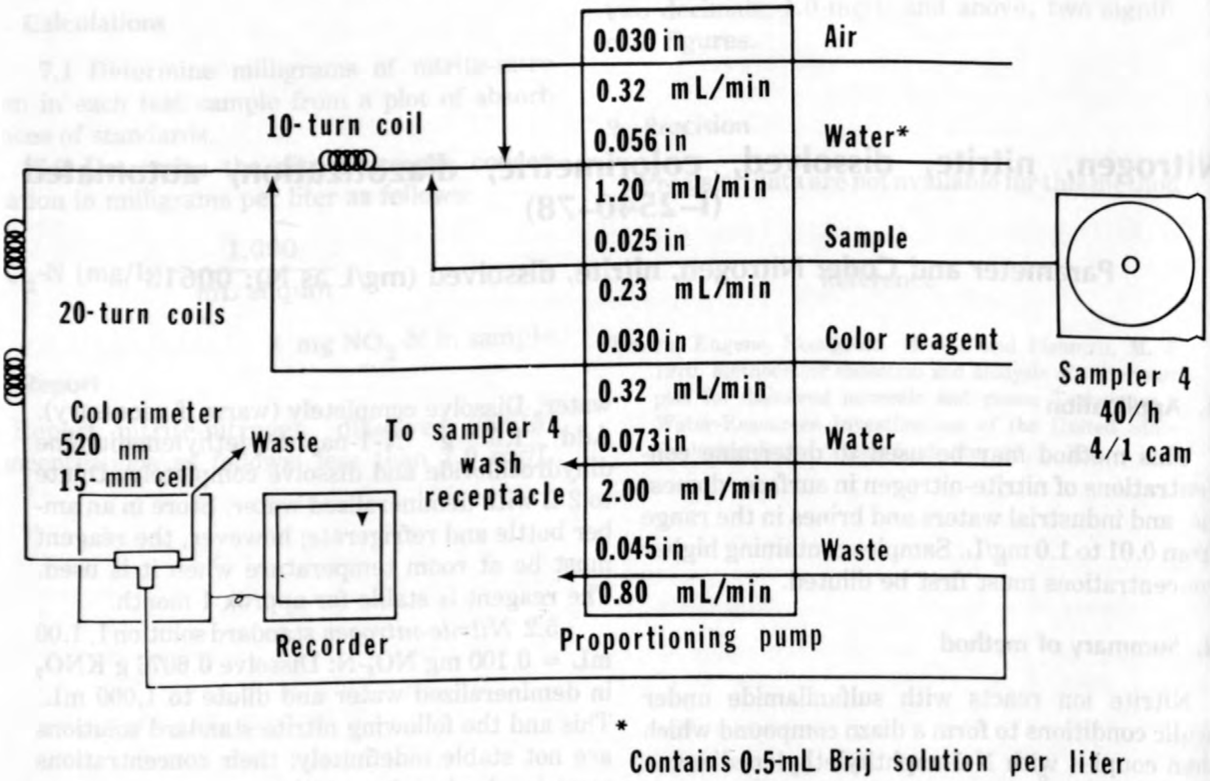


FIGURE 47.—Nitrogen, nitrite, manifold.

followed by a blank. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective nitrite-nitrogen concentration.

7.2 Compute the concentration of NO_2-N in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report nitrite-nitrogen, dissolved (00613), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 121.

Kamphake, L., Hannah, S., and Cohen, J., 1967, Automated analysis for nitrite by hydrazine reduction: Water Research, v. 1, p. 205–216.

Nitrogen, nitrite, total, colorimetric, diazotization, automated (I–4540–78)

Parameter and Code: Nitrogen, nitrite, total (mg/L as N): 00615

1. Application

1.1 This method may be used to determine concentrations of nitrite nitrogen in water-suspended sediment mixtures in the range from 0.01 to 1.0 mg/L. Samples containing higher concentrations must first be diluted.

1.2 Water-suspended sediment mixtures may be analyzed by this procedure by decanting a suitable portion from a well settled sample.

2. Summary of method

Nitrite ion reacts with sulfanilamide under acidic conditions to form a diazo compound which then couples with N-1-naphthylethylenediamine dihydrochloride to form a red-colored compound, the absorbance of which is measured colorimetrically (Kamphake and others, 1967).

3. Interferences

Oxidizing agents interfere by oxidizing nitrite to nitrate. Sulfide also interferes. No other substance commonly occurring in natural water interferes with this method.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 1.0 mg/l NO_2-N:

Absorption cell	**15 mm.**
Wavelength	**520 nm.**
Cam	**40/h (4/1).**

5. Reagents

5.1 *Color* reagent: Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to approx 1,500 mL demineralized water. Dissolve completely. (Warm if necessary.) Add 1.0 g N-1-naphthylethylenediamine dihydrochloride and dissolve completely. Dilute to 2 L with demineralized water. Store in an amber bottle and refrigerate; however, the reagent must be at room temperature when it is used. The reagent is stable for approx 1 month.

5.2 *Nitrite-nitrogen* standard solution I, 1.00 mL = 0.100 mg NO_2-N: Dissolve 0.6076 g KNO_2 in demineralized water and dilute to 1,000 mL. This and the following nitrite standard solutions are not stable indefinitely; their concentrations must be checked frequently.

5.3 *Nitrite-nitrogen* standard solution II, 1.00 mL = 0.010 mg NO_2-N: Quantitatively dilute 100.0 mL nitrite-nitrogen standard solution I to 1,000 mL with demineralized water.

5.4 *Nitrite-nitrogen* working standards: Prepare a blank and 100 mL each of a series of nitrite-nitrogen working standards by appropriate quantitative dilution of nitrite-nitrogen standard solution II as follows:

Nitrate-nitrogen standard solution II (mL)	*Nitrate-nitrogen concentration (mg/L)*
0.0	0.00
2.0	.2
5.0	.5
10.0	1.0

6. Procedure

6.1 Set up manifold (fig. 48).

6.2 Allow colorimeter and recorder to warm up for at least 30 min. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample tube.

6.3 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards

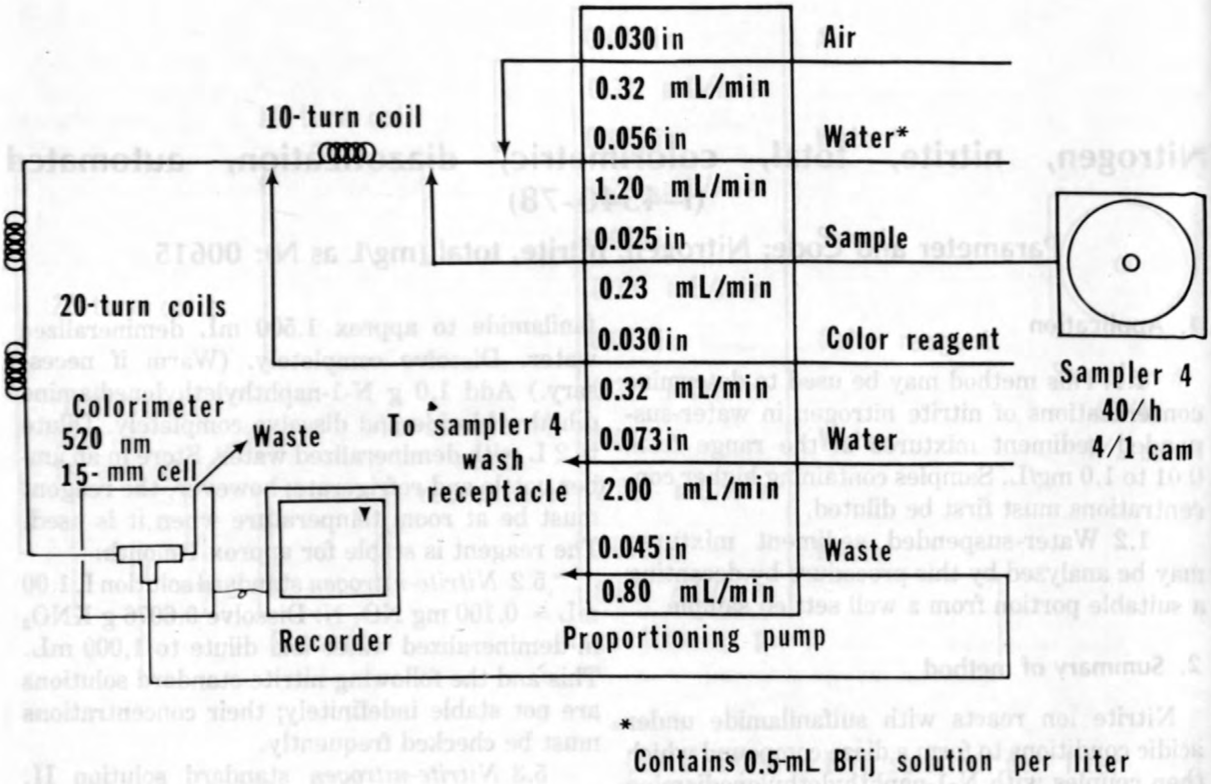


FIGURE 48.—Nitrogen, nitrite, manifold.

of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with aliquots which have been decanted from well settled samples.

6.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective nitrite-nitrogen concentration.

7.2 Compute the concentration of nitrite-nitrogen (NO_2-N) in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report nitrite-nitrogen, total (00615), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 121.

Kamphake, L., Hannah, S., and Cohen, J., 1967, Automated analysis for nitrite by hydrazine reduction: Water Research, v.1, p. 205–216.

Nitrogen, nitrite plus nitrate, dissolved, colorimetric, cadmium reduction-diazotization, automated (I–2545–78)

Parameter and Code: Nitrogen, nitrite plus nitrate, dissolved (mg/L as N): 00631

1. Application

This method may be used to determine the sum of nitrite plus nitrate nitrogen concentrations in surface, domestic, and industrial waters and brines in the range from 0.1 to 5.0 mg/L. Samples containing higher concentrations must first be diluted.

2. Summary of method

Nitrate is reduced to nitrite by a copper-cadmium column. The sample stream is then treated with sulfanilamide under acidic conditions to yield a diazo compound which couples with N-1-naphthylethylenediamine dihydrochloride to form a red-colored compound, the absorbance of which is measured colorimetrically. The final result is the sum of the nitrite originally present plus that formed by the reduction of the nitrate (Brewer and Riley, 1965; Kamphake and others, 1967; Morris and Riley, 1963; Strickland and Parsons, 1965; [U.S.] Environmental Protection Agency, 1974, p. 207–214; and G. G. Ehrlich and D. K. MacDonald, written communs., 1969).

3. Interferences

3.1 The concentrations of potentially interfering substances are seldom high enough to introduce error. High concentrations of oxidizing agents, reducing agents, and some metals, such Cu^{+2} and Hg^{+2}, interfere.

3.2 Acids destroy the cadmium column; therefore, acid-treated samples cannot be analyzed by this method.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold (including copper-cadmium reduction column), proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.1 to 5.0 mg/L ($NO_2 + NO_3$) as N:

Absorption cell	15 mm.
Wavelength	520 nm.
Cam	40/h (4/1).

5. Reagents

5.1 *Ammonium chloride* solution, 10 g/L: Dissolve 10 g NH_4Cl in alkaline water (prepared by adding NH_4OH to demineralized water to attain a pH of 8.5) and dilute to 1 L. Add 0.5 mL Brij–35 solution.

5.2 *Brij-35 solution*, 30-percent aqueous solution (Baker Cat. No. C706, or equivalent).

5.3 *Cadmium* powder, coarse (99 percent pure) (Technicon Cat. No. T11–5063, or equivalent): Wash cadmium powder with diethyl ether or 1*M* HCl followed by demineralized water. Allow to air dry. Shake the dry powder with copper sulfate solution (20 g/L). The weight of the solution should be approx 10 times that of the cadmium. Wash thoroughly with demineralized water to remove colloidal copper. A minimum of 10 washings is usually required (until no blue color remains).

5.4 *Color* reagent: Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to approx 1,500 mL demineralized water. Dissolve completely. (Warm if necessary.) Add 1.0 g N-1-naphthylethylenediamine dihydrochloride and dissolve completely. Dilute to 2 L with demineralized water. Add 1.0 mL Brij–35 solution. Store in a refrigerator; however, the reagent must be at room temperature when it is used. This reagent is stable for approx 1 month.

5.5 *Copper sulfate* solution, 20 g/L: Dissolve 20 g $CuSO_4$ (anhydrous) in demineralized water and dilute to 1 L.

5.6 *Hydrochloric acid*, 1.0*M*: Add 83.3 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.7 *Nitrate-nitrogen* standard solution I, 1.00 mL = 0.50 mg NO_3-N: Dissolve 3.609 g KNO_3, dried overnight over concentrated H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.8 *Nitrate-nitrogen* standard solution II, 1.00 mL = 0.025 mg NO_3-N: Quantitatively dilute 50.0 mL nitrate-nitrogen standard solution I to 1,000 mL with demineralized water.

5.9 *Nitrate-nitrogen* working standards: Prepare a blank and 500 mL each of a series of nitrate-nitrogen working standards by appropriate quantitative dilution of nitrate standard solution II as follows:

Nitrate-nitrogen standard solution II (mL)	*Nitrate-nitrogen concentration (mg/L)*
0.0	0.00
2.0	.10
5.0	.25
10.0	.5
20.0	1.0
30.0	1.5
40.0	2.0
60.0	3.0
80.0	4.0
100.0	5.0

6. Procedure

6.1 Set up manifold (fig. 49).

6.2 Fill the reduction column, which is a U-shaped, 36-cm length of 2.0-mm i.d. glass tubing (Technicon No. 189–0000 or equivalent), with water. This prevents entrapment of air bubbles when filling the tube with cadmium. Transfer the prepared cadmium granules to the reduction column. After the filling is completed, insert borosilicate glass wool in the exit end of the tube. Begin pumping reagents, but do not connect the reduction column to the manifold system until all

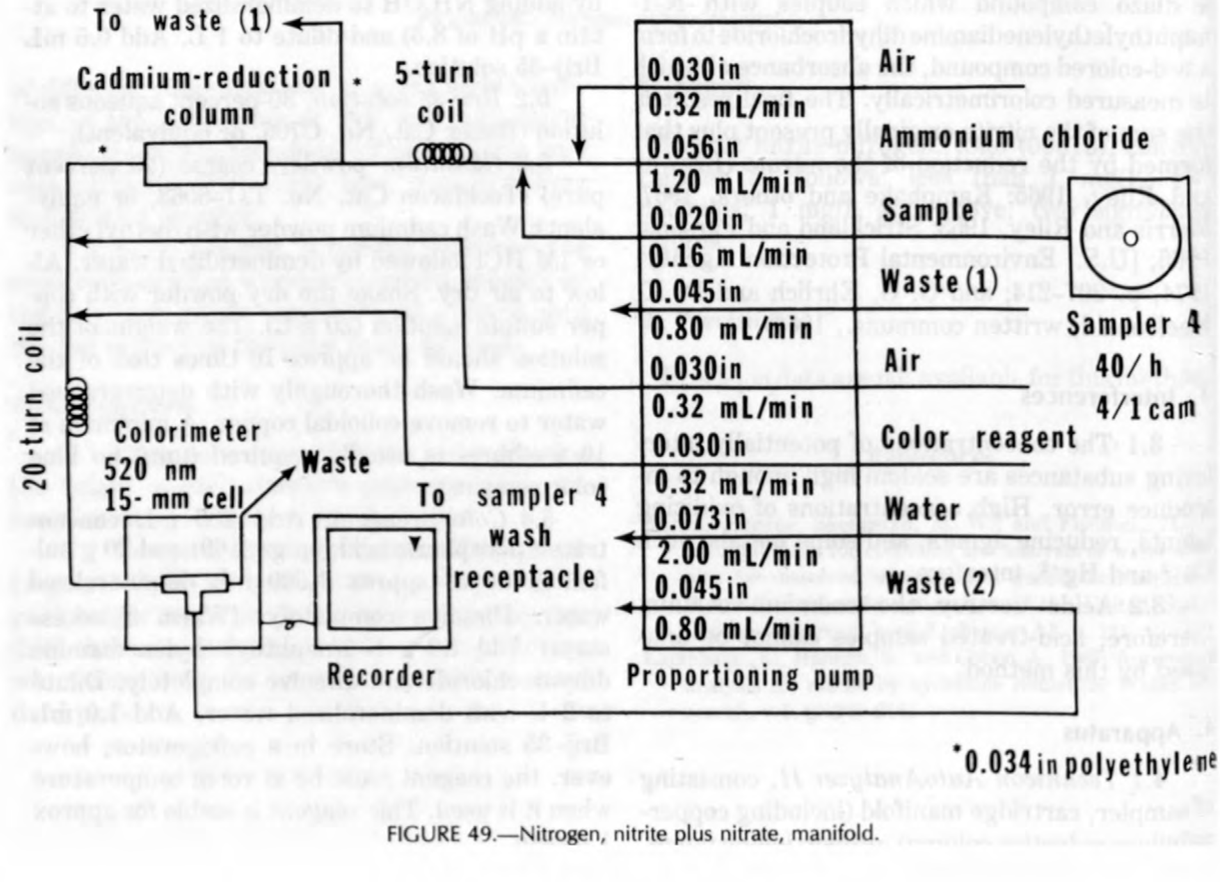


FIGURE 49.—Nitrogen, nitrite plus nitrate, manifold.

air has been pumped from the reagent and sample tubes. It's extremely important to avoid introduction of air bubbles into the reductor, because they adversely affect the flow characteristics of the system. This column should be good for several hundred samples before it needs to be refilled. Check the reduction capacity of the column by comparing the peak heights of nitrate and nitrite standards. A column must be replaced if air bubbles are introduced.

6.3 For initial activation of the reduction column, a 3.0-mg/L NO_3-N standard should be pumped through the system until a steady state is attained.

6.4 Allow colorimeter and recorder to warm up for at least 30 min. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample tube.

6.5 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray, followed by two blanks. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.6 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective nitrogen concentration.

7.2 Compute the concentration of nitrogen, nitrite plus nitrate, as N, in milligrams per liter in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report nitrogen, nitrite plus nitrate NO_2+NO_3, dissolved, as N (00631), concentrations as follows: less than 1.0 mg/L, nearest 0.1 mg/L; 1.0 mg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 0.1 to 5.0 mg/L may be expressed as follows:

$$S_T = 0.080X + 0.011$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of nitrogen, milligrams per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
15	0.46	14
10	2.85	8
19	4.88	11

References

Brewer, P. G., and Riley, J. P., 1965, The automatic determination of nitrate in sea water: Deep Sea Research, v. 12, p. 765–772.

Kamphake, L., Hannah, S., and Cohen, J., 1967, Automated analysis for nitrate by hydrazine reduction: Water Research, v. l, p. 205–216.

Morris, A. W., and Riley, J. P., 1963, The determination of nitrate in sea water: Analytica Chemica Acta, v. 29, p. 272–279.

Strickland, J. D. H., and Parsons, T. R., 1965, A manual of sea water analysis: Canada Fisheries Research Board Bull. p. 125.

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 207.

Nitrogen, nitrite plus nitrate, total in bottom material, colorimetric, cadmium reduction-diazotization, automated (I–6545–78)

Parameter and Code: Nitrogen, nitrite plus nitrate, total in bottom material, dry wt (mg/kg as N): 00633

1. Application

This method may be used to determine the sum of nitrite-plus-nitrate nitrogen concentrations in bottom material containing at least 2 mg/kg. Prepared sample solutions (sec. 6.1.5) containing more than 5.0 mg/L must first be diluted.

2. Summary of method

2.1 An acidified sodium chloride extraction procedure is used for this determination (Jackson, 1958).

2.2 Nitrate is reduced to nitrite by a copper–cadmium column. The sample stream is then treated with sulfanilamide under acidic conditions to yield a diazo compound which couples with *N*-1-naphthylethylenediamine dihydrochloride to form a red-colored compound, the absorbance of which is measured colorimetrically. The final result is the sum of the nitrite originally present plus that formed by the reduction of the nitrate (Brewer and Riley, 1965; Kamphake and others, 1967; Morris and Riley, 1963; Strickland and Parsons, 1965; [U.S.] Environmental Protection Agency, 1974, p. 207–214; and G. G. Ehrlich and D. K. MacDonald, written communs., 1969).

3. Interferences

3.1 The concentrations of potentially interfering substances are seldom high enough to introduce error. High concentrations of oxidizing agents, reducing agents, and some metals, such as Cu^{+2} and Hg^{+2}, interfere.

3.2 Acids destroy the cadmium column; therefore, acid-treated samples cannot be analyzed by this method.

4. Apparatus

4.1 *Centrifuge*.

4.2 *Shaker*, wrist-action.

4.3 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold (including copper–cadmium reduction column), proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.4 With this equipment the following operating conditions have been found satisfactory for the range from 0.1 to 5.0 mg/L NO_2+NO_3 as N:

Absorption cell	15 mm.
Wavelength	520 nm.
Cam	40/h (4/1).

5. Reagents

5.1 *Ammonium chloride* solution, 10 g/L: Dissolve 10 g NH_4Cl in alkaline water (prepared by adding NH_4OH to distilled water to attain a pH of 8.5) and dilute to 1 L. Add 0.5 mL Brij-35 solution.

5.2 *Brij–35 solution*, 30 percent aqueous (Baker Cat. No. C706, or equivalent).

5.3 *Cadmium* powder, coarse, (99 percent pure) (Technicon Cat. No. T11–5063, or equivalent): Wash cadmium powder with diethyl ether or 1*M* HCl followed by demineralized water. Allow to air dry. Shake the dry powder with copper sulfate solution (20 g/L). The weight of the solution should be approx 10 times that of the cadmium. Wash thoroughly with demineralized water to remove colloidal copper. A minimum of 10 washings is usually required (until no blue color remains).

5.4 *Color* reagent: Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to approx 1,500 mL demineralized water. Dissolve completely. (Warm if necessary.) Add 1.0 g *N*-1-naphthylethylenediamine dihydrochloride and dissolve completely. Dilute to 2 L with demineralized water. Add 1.0 mL Brij–35 solution. Store in a refrigerator; however, the reagent must be at room temperature when it is used. This reagent is stable for approx 1 month.

5.5 *Copper sulfate* solution, 20 g/L: Dissolve 20 g $CuSO_4$ (anhydrous) in demineralized water and dilute to 1 L.

5.6 *Hydrochloric acid*, 1.0*M*: Add 83.3 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.7 *Nitrate-nitrogen* standard solution I, 1.00 mL = 0.50 mg NO_3-N: Dissolve 3.609 g KNO_3, dried overnight over concentrated H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.8 *Nitrate-nitrogen* standard solution II, 1.00 mL = 0.025 mg NO_3-N: Quantitatively dilute 50.0 mL nitrate-nitrogen standard solution I to 1,000 mL with sodium chloride solution (paragraph 5.10).

5.9 *Nitrate-nitrogen* working standards: Prepare a blank and 500 mL each of a series of nitrate-nitrogen working standards by appropriate quantitative dilution of nitrate-nitrogen standard solution II with sodium chloride solution (paragraph 5.10) as follows:

Nitrate-nitrogen standard solution II (mL)	*Nitrate-nitrogen concentration (mg/L)*
0.0	0.00
2.0	.10
5.0	.25
10.0	.5
20.0	1.0
30.0	1.5
40.0	2.0
60.0	3.0
80.0	4.0
100.0	5.0

5.10 *Sodium chloride* solution, 100 g/L, acidified: Dissolve 100 g NaCl in 950 mL ammonia-free water. Acidify with concentrated HCl (sp gr 1.19) to a pH of 2.5. Dilute to 1 L.

6. Procedure

6.1 *Extraction procedure:*

6.1.1 Weigh, to the nearest milligram, approx 5 g of sample, prepared as directed in Method P–0520, and transfer to a 250-mL erlenmeyer flask.

6.1.2 Add 50 mL NaCl solution (paragraph 5.10) and shake on the wrist-action shaker for 30 min.

6.1.3 Carefully transfer the entire sample, including all sediment particles, to a centrifuge tube. Centrifuge for 5 min; if the sample does not flocculate, add a drop of concentrated HCl (sp gr 1.19) and recentrifuge.

6.1.4 Transfer the supernatant solution to a 100-mL volumetric flask, taking care not to disturb the residue in the bottom of the centrifuge tube.

6.1.5 Wash the sediment in the centrifuge tube with 20 mL NaCl solution (paragraph 5.10), recentrifuge and transfer the clear wash solution to the volumetric flask. Adjust to volume with NaCl solution (paragraph 5.10).

6.2 *Colorimetric procedure:*

6.2.1 Set up manifold (fig. 50).

6.2.2 Fill the reduction column, which is a U-shaped, 36-cm length of 2.0 mm i.d. glass tubing (Technicon No. 189–000 or equivalent) with water. This prevents entrapment of air bubbles when filling the tube with cadmium. Transfer the prepared cadmium granules to the reduction column. After the filling is completed, insert borosilicate glass wool in the exit end of the tube. Begin pumping reagents, but do not connect the reduction column to the manifold system until all air has been pumped from the reagent and sample tubes. It is extremely important to avoid introduction of air bubbles into the reductor, because they adversely affect the flow characteristics of the system. This column should be good for several hundred samples before it needs to be refilled. Check the reduction capacity of the column by comparing the peak heights of nitrate and nitrite standards. A column must be replaced if air bubbles are introduced.

6.2.3 For initial activation of the reduction column, a 3.0 mg/L NO_3-N standard should be pumped through the system for about 30 min, or until a steady state is attained.

6.2.4 Allow colorimeter and recorder to warm up for at least 30 min. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample tube.

6.2.5 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray, followed by two blanks. Place individual stand-

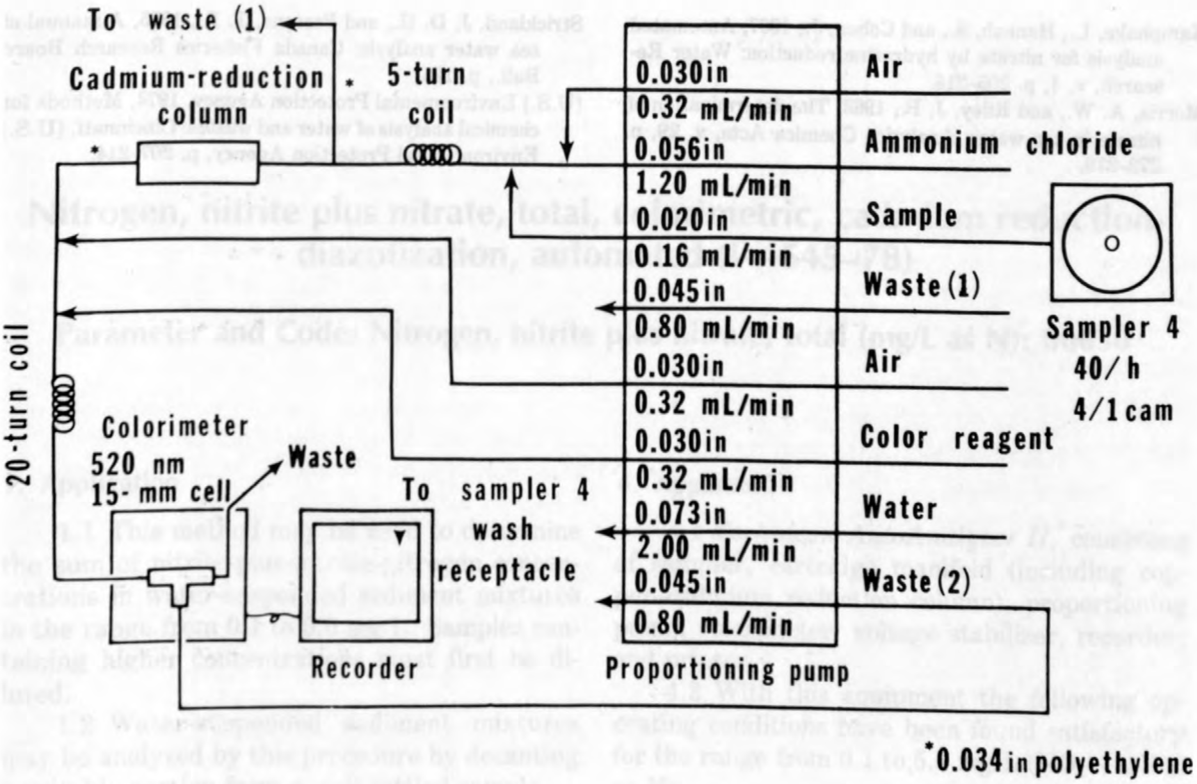


FIGURE 50.—Nitrogen, nitrite plus nitrate, manifold.

ards of differing concentrations in every eighth position of this and subsequent sample trays. Fill the remainder of each sample tray with unknown samples.

6.2.6 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective nitrogen concentration.

7.2 Compute the concentration of nitrogen, nitrite plus nitrate (NO_2+NO_3) as N in milligrams per liter in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

$$NO_3\text{-N} + NO_2\text{-N (mg/kg)} = \frac{C_N \times 100}{\text{wt sample (g)}}$$

where

C_N = NO_3-N + NO_2-N concentration, milligrams per liter.

8. Report

Report nitrite plus nitrate (NO_2+NO_3), total in bottom material as N (00633), concentrations as follows: less than 10 mg/kg, one decimal; 10 mg/kg and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 14 percent in the lower portion of the analytical range.

References

Brewer, P. G., and Riley, J. P., 1965, The automatic determination of nitrate in sea water: Deep Sea Research, v. 12, p. 765–772.

Jackson, M. L., 1958, Soil chemical analysis: Englewood Cliffs, N. J., Prentice-Hall, p. 193–194.

Kamphake, L., Hannah, S., and Cohen, J., 1967, Automated analysis for nitrate by hydrazine reduction: Water Research, v. 1, p. 205–216.

Morris, A. W., and Riley, J. P., 1963, The determination of nitrate in sea water: Analytica Chemica Acta, v. 29, p. 272–279.

Strickland, J. D. H., and Parsons, T. R., 1965, A manual of sea water analysis: Canada Fisheries Research Board Bull., p. 125.

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, [U.S.] Environmental Protection Agency, p. 207–214.

Nitrogen, nitrite plus nitrate, total, colorimetric, cadmium reduction-diazotization, automated (I–4545–78)

Parameter and Code: Nitrogen, nitrite plus nitrate, total (mg/L as N): 00630

1. Application

1.1 This method may be used to determine the sum of nitrite-plus-nitrate-nitrogen concentrations in water-suspended sediment mixtures in the range from 0.1 to 5.0 mg/L. Samples containing higher concentrations must first be diluted.

1.2 Water-suspended sediment mixtures may be analyzed by this procedure by decanting a suitable portion from a well settled sample.

2. Summary of method

Nitrate is reduced to nitrite by a copper–cadmium column. The sample stream is then treated with sulfanilamide under acidic conditions to yield a diazo compound which couples with *N*-1-naphthylethylenediamine dihydrochloride to form a red-colored compound, the absorbance of which is measured colorimetrically. The final result is the sum of the nitrite originally present plus that formed by the reduction of the nitrate (Brewer and Riley, 1965; Kamphake and others, 1967; Morris and Riley, 1963; Strickland and Parsons, 1965; [U.S.] Environmental Protection Agency, 1971, p. 175–183; and G. G. Ehrlich and D. K. MacDonald, written communs., 1969).

3. Interferences

3.1 The concentrations of potentially interfering substances are seldom high enough to introduce error. High concentrations of oxidizing agents, reducing agents, and some metals, such as Cu^{+2} and Hg^{+2}, interfere.

3.2 Acids destroy the cadmium column; therefore, acid treated samples cannot be analyzed by this method.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold (including copper–cadmium reduction column), proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.1 to 5.0 mg/L (NO_2 + NO_3) as N:

Absorption cell	15 mm.
Wavelength	520 nm.
Cam	40/h (4/1).

5. Reagents

5.1 *Ammonium chloride* solution, 10 g/L: Dissolve 10 g NH_4Cl in alkaline water (prepared by adding NH_4OH to demineralized water to attain a pH of 8.5) and dilute to 1 L. Add 0.5 mL Brij–35 solution.

5.2 *Brij–35 solution,* 30 percent aqueous (Baker Cat. No. C706, or equivalent).

5.3 *Cadmium* powder, coarse, (99 percent pure) (Technicon Cat. No. T11–5063, or equivalent): Wash cadmium powder with diethyl ether or 1*M* HCl followed by demineralized water. Allow to air dry. Shake the dry powder with copper sulfate solution (20 g/L). The weight of the solution should be approx 10 times that of the cadmium. Wash thoroughly with demineralized water to remove colloidal copper. A minimum of 10 washings is usually required (until no blue color remains).

5.4 *Color* reagent: Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to approx 1,500 mL demineralized water. Dissolve completely (warm if necessary).

Add 1.0 g *N*-1-naphthylethylenediamine dihydrochloride and dissolve completely. Dilute to 2 L with demineralized water. Add 1.0 mL Brij–35 solution. Store in a refrigerator; however, the reagent must be at room temperature when it is used. This reagent is stable for approx 1 month.

5.5 *Copper sulfate* solution, 20 g/L: Dissolve 20 g $CuSO_4$ (anhydrous) in demineralized water and dilute to 1 L.

5.6 *Hydrochloric acid*, 1.0*M*: Add 83.3 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.7 *Nitrate-nitrogen* standard solution I, 1.00 mL = 0.025 mg NO_3-N: Dissolve 3.609 g KNO_3, dried overnight over concentrated H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.8 *Nitrate-nitrogen* standard solution II, 1.00 mL = 0.025 mg NO_3-N: Quantitatively dilute 50.0 mL nitrate-nitrogen standard solution I to 1,000 mL with demineralized water.

5.9 *Nitrate-nitrogen* working standards: Prepare a blank and 500 mL each of a series of nitrate-nitrogen working standards by appropriate quantitative dilution of nitrate standard solution II as follows:

Nitrate-nitrogen standard solution II (mL)	*Nitrate-nitrogen concentration (mg/L)*
0.0	0.00
2.0	.10
5.0	.25
10.0	.5
20.0	1.0
30.0	1.5
40.0	2.0
60.0	3.0
80.0	4.0
100.0	5.0

6. Procedure

6.1 Set up manifold (fig. 51).

6.2 Fill the reduction column, which is a U-shaped, 36-cm length of 2.0-mm i.d. glass tubing (Technicon No. 189–0000, or equivalent), with water. This prevents entrapment of air bubbles when filling the tube with cadmium. Transfer the prepared cadmium granules to the reduction column. After the filling is completed, insert bo-

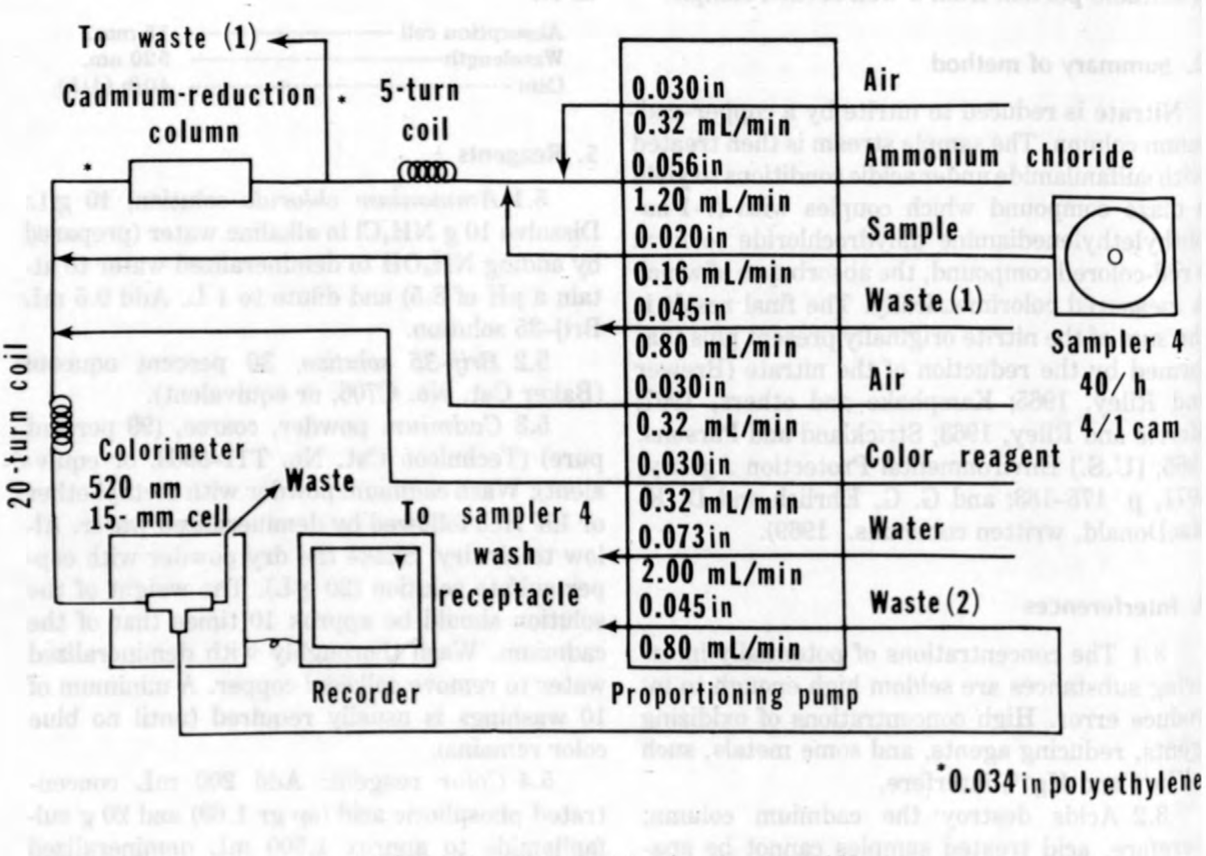


FIGURE 51.—Nitrogen, nitrite plus nitrate, manifold.

rosilicate glass wool in the exit end of the tube. Begin pumping reagents, but do not connect the reduction column to the manifold system until all air has been pumped from the reagent and sample tubes. It is extremely important to avoid introduction of air bubbles into the reductor, because they adversely affect the flow characteristics of the system. This column should be good for several hundred samples before it needs to be refilled. Check the reduction capacity of the column by comparing the peak heights of nitrate and nitrite standards. A column must be replaced if air bubbles are introduced.

6.3 For initial activation of the reduction column, a 3.0-mg/L NO_3-N standard should be pumped through the system for about 30 min or until a steady state is attained.

6.4 Allow colorimeter and recorder to warm up for at least 30 min. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample tube.

6.5 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray, followed by two blanks. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.6 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective nitrogen concentration.

7.2 Compute the concentration of nitrogen, nitrite plus nitrate (NO_2+NO_3) as N, in milligrams per liter in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report nitrite plus nitrate (NO_2+NO_3), total as N (00630), concentrations as follows: less than 1.0 mg/L, nearest 0.1 mg/L; 1.0 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 14 percent at 0.46 mg/L and greater than 11 percent at 4.88 mg/L.

References

Brewer, P. G., and Riley, J. P., 1965, The automatic determination of nitrate in sea water: Deep Sea Research, v. 12, p. 765–772.

Kamphake, L., Hannah, S., and Cohen, J., 1967, Automated analysis for nitrate by hydrazine reduction: Water Research, v. 1, p. 205–216.

Morris, A. W., and Riley, J. P., 1963, The determination of nitrate in sea water: Analytica Chemica Acta, v. 29, p. 272–279.

Strickland, J. D. H., and Parsons, T. R., 1965, A manual of sea water analysis: Canada Fisheries Research Board Bull., p. 125.

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 207.

Oxygen demand, chemical (COD), total, colorimetric, dichromate oxidation (I–3561–78)

Parameter and Code: COD, high level (mg/L): 00340

1. Application

This method may be used for analysis of water-suspended sediment mixtures containing between 10 and 500 mg/L chemical oxygen demand (COD).

2. Summary of method

2.1 Organic and other oxidizable materials are oxidized by digesting with an acid–dichromate solution in the presence of silver sulfate catalyst. The COD concentration is determined spectrometrically, after digestion, by measuring the absorbance of the Cr^{+3} that is formed.

2.2 Additional information about the principles of the method may be found in Jirka and Carter (1975).

3. Interferences

3.1 Reducing substances such as ferrous iron and chloride interfere, since they are oxidized by dichromate in acid solution. Chlorides constitute the largest and most common interference, with 1 mg/L Cl^{-1} equivalent to 0.226 mg/L COD. To eliminate chloride interference of up to 2,000 mg/L, mercuric sulfate is added to the acid–dichromate digestion solution.

3.2 Cr^{+3} interferes, with 1 mg/L Cr^{+3} equivalent to 0.719 mg/L COD. Levels high enough to have significant effect on the accuracy are unlikely in natural water samples.

3.3 Ferric iron concentrations less than 5 g/L do not interfere.

4. Apparatus

4.1 *Centrifuge*, Sorvall SS–3 Automatic Superspeed or equivalent.

4.2 *Culture tubes*, Corning No. 9825 (25 by 150 mm), with teflon-coated screwcaps.

4.3 *Spectrometer* for use at 600 nm; Beckman Model No. 24 or equivalent.

4.4 Refer to the manufacturer's manual to optimize output of the instrument:

Wavelength .... 600 nm.

5. Reagents

5.1 *Potassium acid phthalate* standard solution I, 1.0 mL = 10 mg COD: Dissolve 8.500 g potassium acid phthalate, which has been dried for 2 h at 110°C, in demineralized water and dilute to 1,000 mL.

5.2 *Potassium acid phthalate* standard solution II, 1.0 mL = 1.0 mg COD: Dilute 100 mL potassium acid phthalate standard solution I to 1,000 mL with demineralized water. This solution is used to prepare working standards at time of analysis.

5.3 *Potassium dichromate-mercuric sulfate* digestion solution: To approx 700 mL demineralized water, add 10.216 g $K_2Cr_2O_7$ and 33.0 g $HgSO_4$. Slowly (*CAUTION*) and with constant stirring, add 167 mL concentrated H_2SO_4 (sp gr 1.84). Mix until dissolved. After the solution cools, dilute to 1 L with demineralized water.

5.4 *Silver sulfate* solution: Dissolve 22 g Ag_2SO_4 in a 9-pound bottle of concentrated H_2SO_4 (sp gr 1.84).

5.5 *Sulfuric acid*, concentrated (sp gr 1.84).

5.6 *Sulfuric acid*, 3.5*M*: Add slowly (*CAUTION*) with constant stirring 200 mL concentrated H_2SO_4 to 700 mL demineralized water. After the solution cools dilute to 1 L with demineralized water.

6. Procedure

Clean the culture tubes and screwcaps with 3.5*M* sulfuric acid. Rinse with demineralized water and dry.

6.1 Pipet 10.0 mL (using a wide-mouth pipet) of a well-mixed sample into a culture tube.

6.2 Prepare a blank and sufficient standards containing from 0 to 500 mg/L COD using potassium acid phthalate standard solution II. Pipet 10.0 mL of each into a culture tube.

6.3 Add 6.0 mL potassium dichromate–mercuric sulfate digestion solution from a repipet to each culture tube (NOTE 1).

NOTE 1. Protective eyeglasses and clothing are mandatory for this entire procedure, because the use of sulfuric acid and potassium dichromate solutions at high temperatures are especially hazardous.

6.4 Add 14.0 mL silver sulfate solution from a repipet to each culture tube.

6.5 Cap the culture tubes tightly and shake vigorously.

6.6 Heat the capped culture tubes in an oven at 150°C for 2 h.

6.7 Cool the culture tubes to room temperature in a cold water bath.

6.8 Centrifuge the solutions at 5,000 rpm for 15 min.

6.9 Set the spectrophotometer at 600 nm and adjust the absorbance to 0.000 with the digested blank.

6.10 Individually transfer each standard and sample to the sample cuvette, preferably using an automated flow-through cell, and read and record each absorbance value. Care must be taken not to disturb any precipitate when pouring the sample into the cuvette (NOTE 2).

NOTE 2. A Technicon AutoAnalyzer system consisting of a sampler, proportioning pump, cartridge manifold, colorimeter, recorder, and printer may be used in place of the spectrophotometer to measure the absorbance of the digested solution (Jirka and Carter, 1975). Steps 6.1 to 6.8 remain unchanged.

7. Calculations

7.1 Prepare an analytical curve by plotting standard COD concentrations in milligrams per liter versus absorbance.

7.2 Determine the chemical oxygen demand (COD) in milligrams per liter in each sample by using the analytical curve.

8. Report

Report chemical oxygen demand (COD), total (00340), concentrations as follows: less than 10 mg/L, as <10 mg/L; 10 mg/L and above, two significant figures.

9. Precision

Using potassium acid phthalate standards, the precision for a single operator expressed in terms of the relative deviation (coefficient of variation) is as follows:

Mean (mg/L)	*Relative deviation (percent)*
50	14
400	2

Reference

Jirka, Andrea M., and Carter, Mark J., 1975, Micro semiautomated analysis of surface and wastewaters for chemical oxygen demand: Analytical Chemistry, v. 47, no. 8, p. 1397–1402.

Phosphorus, dissolved, colorimetric, phosphomolybdate (I–1600–78)

Parameter and Code: Phosphorus, dissolved (mg/L as P): 00666

1. Application

This method may be used to analyze most waters and waste waters containing between 0.02 and 0.4 mg/L of dissolved phosphorus. Higher concentrations must first be reduced by dilution.

2. Summary of method

2.1 As far as is known the phosphomolybdate method is specific for the orthophosphate form of phosphorus. Weak tests are reported with pyrophosphate and polyphosphates, but these positive tests may well result from orthophosphate contamination of the material.

2.2 Acid hydrolyzable and organic forms of phosphorus are decomposed to orthophosphate by sulfuric acid–ammonium persulfate digestion. Orthophosphate is then converted to phosphomolybdate by acidified ammonium molybdate reagent:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21H^{+1} \rightarrow$$

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4{}^{+1} + 12H_2O.$$

2.3 When phosphomolybdate is reduced with ascorbic acid in the presence of antimony (Murphy and Riley, 1962), an intense blue complex is developed that absorbs light at 882 nm. The reduction is not instantaneous, nor is the developed blue color stable. The full color develops in 6 to 10 min and fades gradually thereafter.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. Silica gives a pale-blue color that is additive to the phosphate color, and a silica correction is made when necessary. The effect of silica is somewhat dependent on the reagents; therefore, an appropriate silica correction should be determined with each batch of reagents. Nitrite interferes but can be oxidized to nitrate with hydrogen peroxide before the determination. Residual chlorine should be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples may be fortified with 85 mg/L NaCl to overcome this interference.

4. Apparatus

4.1 *Spectrometer* for use at 700 or 882 nm; Beckman Model B, or equivalent.

4.2 With this instrument the following operating conditions have been used:

Wavelength	882 or 700 nm.
Filter	Red.
Cells	50 mm.
Phototube	Red-sensitive.
Initial sensitivity setting	2.
Slit width	0.1 mm.

4.3 With these operating conditions the following values have been observed:

P	Absorbance	
(mg)	*(882 nm)*	*(700 nm)*
0.0	0.00	0.00
.001	.06	.04
.005	.29	.21
.010	.57	.43
.015	.86	.64
.020	1.14	.85

5. Reagents

5.1 *Ammonium persulfate* $(NH_4)_2S_2O_8$.

5.2 *Antimony tartrate-ammonium molybdate* solution: Dissolve 0.13 g antimony potassium tartrate, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, in about 700 mL demineralized water contained in a 1-L volumetric flask. Add 5.6 g ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and shake flask until dissolved. *Cautiously* add 70 mL concentrated H_2SO_4 (sp gr 1.84) while swirling the contents of the flask. Cool and dilute to volume. Mix thoroughly by repeated inversion and swirling. This solution is stable for at least 1 year if stored in a polyethylene bottle away from heat.

5.3 *Combined reagent* solution: Dissolve 0.50 g ascorbic acid in 100 mL antimony tartrate–ammonium molybdate solution. This reagent is stable for at least 1 week if stored at 4°C; otherwise prepare fresh daily.

5.4 *Phenolphthalein* indicator solution, 0.5 g/100 mL: Dissolve 0.5 g phenolphthalein in 100 mL 50-percent ethanol.

5.5 *Phosphate* standard solution I, 1.00 mL = 0.050 mg P: Dissolve 0.2197 g KH_2PO_4, dried overnight over H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate* standard solution II, 1.00 mL = 0.001 mg P: Dilute 20.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Sodium hydroxide*, 3*M*: Carefully, with cooling, dissolve 120 g NaOH in demineralized water and dilute to 1 L.

5.8 *Sulfuric acid*, 6*M*: Add slowly, with constant stirring, 330 mL concentrated H_2SO_4 (sp gr 1.84) to 600 mL demineralized water and dilute to 1 L.

5.9 *Sulfuric acid*, 0.25*M*: Add slowly, with constant stirring, 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.020 mg P (50.0 mL max) into a 125-mL erlenmeyer flask, and adjust the volume to 50.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 mL.

6.3 Add 1.0 mL 6*M* H_2SO_4 and 0.4 g $(NH_4)_2S_2O_8$. Boil gently on a hotplate until the volume is reduced to about 10 mL.

6.4 Cool. Add 2 drops phenolphthalein indicator solution and neutralize with 3*M* NaOH, and then add 0.25*M* H_2SO_4 carefully until the pink color just disappears. Transfer to a 50-mL volumetric flask and dilute to the mark with demineralized water.

6.5 Add 10 mL combined reagent solution to each sample, blank, and standard and mix.

6.6 After 10 min measure absorbance of each sample and standard against the blank at either 882 or 700 nm.

7. Calculations

7.1 Determine the milligrams of phosphorus in each sample from a plot of absorbances of standards.

7.2 Determine the phosphorus concentration in milligrams per liter as follows:

$$\text{P in mg/L} = \frac{1{,}000}{\text{mL sample}} \times \text{mg P in sample.}$$

8. Report

Report concentrations of dissolved phosphorus (00666) as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
11	0.06	50
12	.45	20

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 131.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31.

Phosphorus, dissolved, colorimetric, phosphomolybdate, automated (I–2600–78)

Parameter and Code: Phosphorus, dissolved (mg/L as P): 00666

1. Application

This method may be used to determine concentrations of dissolved phosphorus in most waters, wastewaters, and brines in the range from 0.01 to 2.0 mg/L P. Samples containing higher concentrations must first be diluted.

2. Summary of method

2.1 All forms of phosphorus, including organic phosphorus, are converted to orthophosphate by an acid-persulfate digestion.

2.2 Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces and intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales, Julian, and Kroner, 1966).

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. The interference from silica, which forms a pale-blue complex, is small and can usually be considered negligible. Nitrite interferes, but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples may be fortified with 85 mg/L NaCl to overcome this interference.

4. Apparatus

4.1 *Autoclave.*

4.2 *Technicon AutoAnalyzer II,* consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L P:

Absorption cell	15 mm.
Wavelength	880 or 660 nm.
Cam	40/h (5/1).
Heating bath temperature	37.5° C.

4.4 *Glass tubes with plastic caps,* disposable: 18 by 150 mm.

5. Reagents

5.1 *Ammonium molybdate* solution, 35.6 g/L: Dissolve 40 g ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] in 800 mL demineralized water and dilute to 1 L.

5.2 *Ascorbic acid* solution, 18 g/L: Dissolve 18 g of ascorbic acid ($C_6H_8O_6$) in 800 mL demineralized water and dilute to 1 L.

5.3 *Antimony potassium tartrate* solution, 3 g/L: Dissolve 3.0 g antimony potassium tartrate [$K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$] in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent:* Combine reagents together in order listed below (this reagent is stable for about 8 h):

Sulfuric acid, 2.45*M*	50 mL.
Ammonium molybdate solution	15 mL.
Ascorbic acid solution	30 mL.
Antimony potassium tartrate solution.	5 mL.

5.5 *Phosphate* standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate* standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphate* working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II. For example:

Phosphate standard solution II (mL)	*Orthophosphate phosphorus concentration (mg/L)*
0.0	0.00
5.0	.25
10	.50
20	1.00
30	1.50
40	2.00

5.8 *Potassium persulfate* solution, 4 g/L: Dissolve 4.0 g $K_2S_2O_8$ in demineralized water and dilute to 1 L.

5.9 *Sulfuric acid*, 2.45*M*: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool and dilute to 1 L with demineralized water.

5.10 *Sulfuric acid*, 0.45*M*: Slowly, and with constant stirring and cooling, add 25.2 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool and dilute to 1 L with demineralized water.

5.11 *Sulfuric acid-persulfate* reagent, (1+1): Mix equal volumes of 0.45*M* sulfuric acid and potassium persulfate solution.

5.12 *Water diluent:* Add 2.0 mL Levor IV to 1 L demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.02 mg P (10.0 mL max) into a disposable glass tube and adjust the volume to 10.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 10.0 mL.

6.3 Add 4.0 mL sulfuric acid–persulfate reagent.

6.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 psi pressure. After the samples have cooled, the caps may be pushed down.

6.5 Set up manifold (fig. 52).

6.6 Allow the colorimeter, recorder and heating bath to warm up for at least 30 min or until the temperature of the heating bath reads 37.5 °C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.7 Beginning with the most concentrated standard, place a complete set of standards in the first positions of the first sample tray, fol-

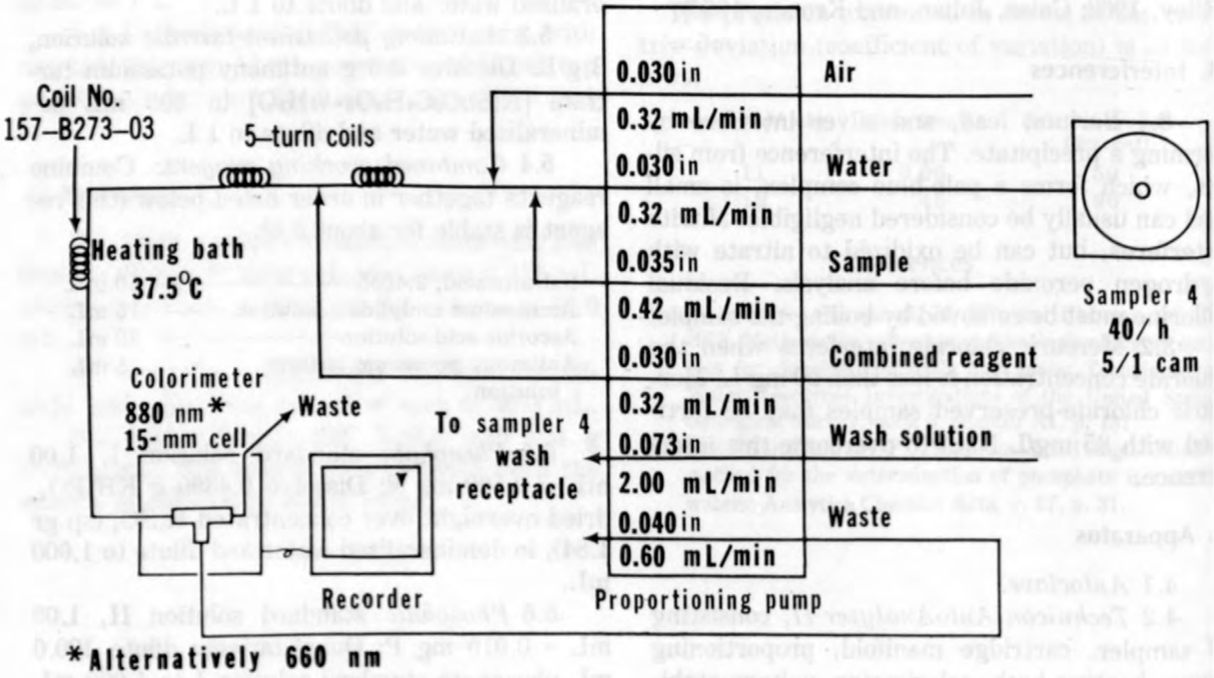


FIGURE 52.—Phosphorus manifold.

lowed by a blank. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.8 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective orthophosphate phosphorus concentration.

7.2 Compute the concentration of phosphorus in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report phosphorus, dissolved (00666), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

As determined in synthetic (deionized water matrix) samples, the precision obtained by a single laboratory during a 12 month period expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of replicates	*Mean (µg/L)*	*Relative deviation (percent)*
110	0.197	12
115	0.670	3

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 131.

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31.

Phosphorus, hydrolyzable, dissolved, colorimetric, phosphomolybdate (I–1602–78)

Parameter and Code: Phosphorus, hydrolyzable, dissolved (mg/L as P): 00672

1. Application

This method may be used to analyze most waters and waste waters containing between 0.02 and 0.4 mg/L combined acid hydrolyzable and orthophosphate-phosphorus. Higher concentrations must first be reduced by dilution.

2. Summary of method

2.1 As far as is known the phosphomolybdate method is specific for the orthophosphate form of phosphorus. Weak tests are reported with pyrophosphate and polyphosphates, but these positive tests may well result from orthophosphate contamination of the material.

2.2 Acid hydrolyzable phosphorus is decomposed to orthophosphate by sulfuric acid digestion. Orthophosphate is then converted to phosphomolybdate by acidified ammonium molybdate reagent:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21H^{+1} \rightarrow$$
$$(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^{+1} + 12H_2O.$$

2.3 When phosphomolybdate is reduced with ascorbic acid in the presence of antimony (Murphy and Riley, 1962), an intense blue complex is developed that absorbs light at 882 nm. The reduction is not instantaneous, nor is the developed blue color stable. The full color develops in 6 to 10 min and fades gradually thereafter.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. Silica gives a pale-blue color that is additive to the phosphate color, and a silica correction is made when necessary. The effect of silica is somewhat dependent on the reagents; therefore, an appropriate silica correction should be determined with each batch of reagents. Nitrite interferes but can be oxidized to nitrate with hydrogen peroxide before the determination. Residual chlorine should be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples may be fortified with 85 mg/L NaCl to overcome this interference.

4. Apparatus

4.1 *Spectrometer* for use at 700 or 882 nm; Beckman Model B, or equivalent.

4.2 With this instrument the following operating conditions have been used:

Wavelength	882 or 700 nm.
Filter	Red.
Cells	50 mm.
Phototube	Red-sensitive.
Initial sensitivity setting	2.
Slit width	0.1 mm.

4.3 With these operating conditions the following values have been observed:

P	Absorbance	
(mg)	*(882 nm)*	*(700 nm)*
0.0	0.00	0.00
.001	.06	.04
.005	.29	.21
.010	.57	.43
.015	.86	.64
.020	1.14	.85

5. Reagents

5.1 *Antimony tartrate—ammonium molybdate* solution: Dissolve 0.13 g antimony potassium tartrate, $[K(SbO)C_4H_4O_6 \cdot 1/2H_2O]$, in about 700 mL demineralized water contained in a 1-L volumetric flask. Add 5.6 g ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and shake flask until dissolved. *Cautiously* add 70 mL concentrated H_2SO_4 (sp gr 1.84) while swirling the contents of the flask. Cool and dilute to volume. Mix thoroughly by repeated inversion and swirling. This solution is stable for at least 1 year if stored in a polyethylene bottle away from heat.

5.2 *Combined reagent* solution: Dissolve 0.50 g ascorbic acid in 100 mL antimony tartrate–ammonium molybdate solution. This reagent is stable for at least 1 week if stored at 4°C; otherwise prepare fresh daily.

5.3 *Phenolphthalein* indicator solution, 0.5 g/100 mL: Dissolve 0.5 g phenolphthalein in 100 mL 50-percent ethanol.

5.4 *Phosphate* standard solution I, 1.00 mL = 0.050 mg P: Dissolve 0.2197 g KH_2PO_4, dried overnight over H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.5 *Phosphate* standard solution II, 1.00 mL = 0.001 mg P: Dilute 20.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.6 *Sodium hydroxide*, 3*M*: Carefully, with cooling, dissolve 120 g NaOH in demineralized water and dilute to 1 L.

5.7 *Sulfuric acid*, 6*M*: Add slowly, with constant stirring, 330 mL concentrated H_2SO_4 (sp gr 1.84) to 600 mL demineralized water and dilute to 1 L.

5.8 *Sulfuric acid*, 0.25*M*: Add slowly, with constant stirring, 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.020 mg P (50.0 mL max) into a 125-mL erlenmeyer flask, and adjust the volume to 50.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 mL.

6.3 Add 1.0 mL 6*M* H_2SO_4. Boil gently on a hotplate until the volume is reduced to about 10 mL.

6.4 Cool. Add 2 drops phenolphthalein indicator solution and neutralize with 3*M* NaOH, and then add 0.25*M* H_2SO_4 carefully until the pink color just disappears. Transfer to a 50-mL volumetric flask and dilute to the mark with demineralized water.

6.5 Add 10 mL combined reagent to each sample, blank, and standard and mix.

6.6 After 10 min measure absorbance of each sample and standard against the blank at either 882 or 700 nm.

7. Calculations

7.1 Determine the milligrams of phosphorus in each sample from a plot of absorbances of standards.

7.2 Determine the phosphorus concentration in milligrams per liter as follows:

$$\text{P in mg/L} = \frac{1{,}000}{\text{mL sample}} \times \text{mg P in sample.}$$

7.3 P (acid hydrolyzable) in mg/L = (P as determined in sec. 7.2)−(P, ortho, as determined in Method I–1601).

8. Report

Report concentrations of dissolved acid-hydrolyzable phosphorus (00672) as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 50 percent at 0.06 mg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 131.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31.

Phosphorus, hydrolyzable, dissolved, colorimetric, phosphomolybdate, automated (I–2602–78)

Parameter and Code: Phosphorus, hydrolyzable, dissolved (mg/L as P): 00672

1. Application

1.1 This method may be used to determine concentrations of dissolved hydrolyzable phosphorus in most waters, wastewaters, and brines in the range from 0.01 to 2.0 mg/L combined hydrolyzable and orthophosphate-phosphorus. Samples containing higher concentrations must first be diluted.

1.2 Orthophosphate-phosphorus (Method I–2601) also must be determined in order to determine the hydrolyzable phosphorus.

2. Summary of method

2.1 Polyphosphates [$(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.] and a few organic phosphorus compounds are converted to orthophosphate by an acid hydrolysis.

2.2 Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales, Julian, and Kroner, 1966).

2.3 The concentration of orthophosphate-phosphorus (Method I–2601) is subtracted from the concentration of hydrolyzable plus orthophosphate-phosphorus determined by this method to obtain the concentration of hydrolyzable phosphorus.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. The interference from silica, which forms a pale blue complex, is small and can usually be considered negligible. Nitrite interferes but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples may be fortified with 85 mg/L NaCl to overcome this interference.

4. Apparatus

4.1 *Autoclave.*

4.2 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L combined hydrolyzable and orthophosphate phosphorus:

Absorption cell	15 mm.
Wavelength	880 or 660 nm.
Cam	40/h (5/1).
Heating bath temperature	37.5° C.

4.4 *Glass tubes with plastic caps*, disposable: 18 by 150 mm.

5. Reagents

5.1 *Ammonium molybdate* solution, 35.6 g/L: Dissolve 40 g ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] in 800 mL demineralized water and dilute to 1 L.

5.2 *Ascorbic acid* solution, 18 g/L: Dissolve 18 g ascorbic acid ($C_6H_8O_6$) in 800 mL demineralized water and dilute to 1 L.

5.3 *Antimony potassium tartrate* solution, 3 g/L: Dissolve 3.0 g antimony potassium tartrate [$K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$] in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent:* Combine reagents in order listed below (this reagent is stable for about 8 h):

Sulfuric acid, 2.45*M*	50 mL.
Ammonium molybdate solution	15 mL.

Ascorbic acid solution	30 mL.
Antimony potassium tartrate solution.	5 mL.

5.5 *Phosphate* standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate* standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphate* working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II. For example:

Phosphate standard solution II (mL)	*Orthophosphate phosphorus concentration (mg/L)*
0.0	0.00
5	.25
10	.50
20	1.00
30	1.50
40	1.50

5.8 *Sulfuric acid*, 2.45*M*: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool and dilute to 1 L with demineralized water.

5.9 *Sulfuric acid*,. 0.45*M*: Slowly, and with constant stirring and cooling, add 25.2 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water.

5.10 *Water diluent*: Add 2.0 mL Levor IV to 1 L demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.02 mg combined hydrolyzable and orthophosphate-phosphorus (10.0 mzl max) into a disposable glass tube and adjust the volume to 10.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 10.0 mL.

6.3 Add 2.0 mL 0.45*M* sulfuric acid.

6.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 psi pressure. After the samples have cooled, the caps may be pushed down.

6.5 Set up manifold (fig. 53).

6.6 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min

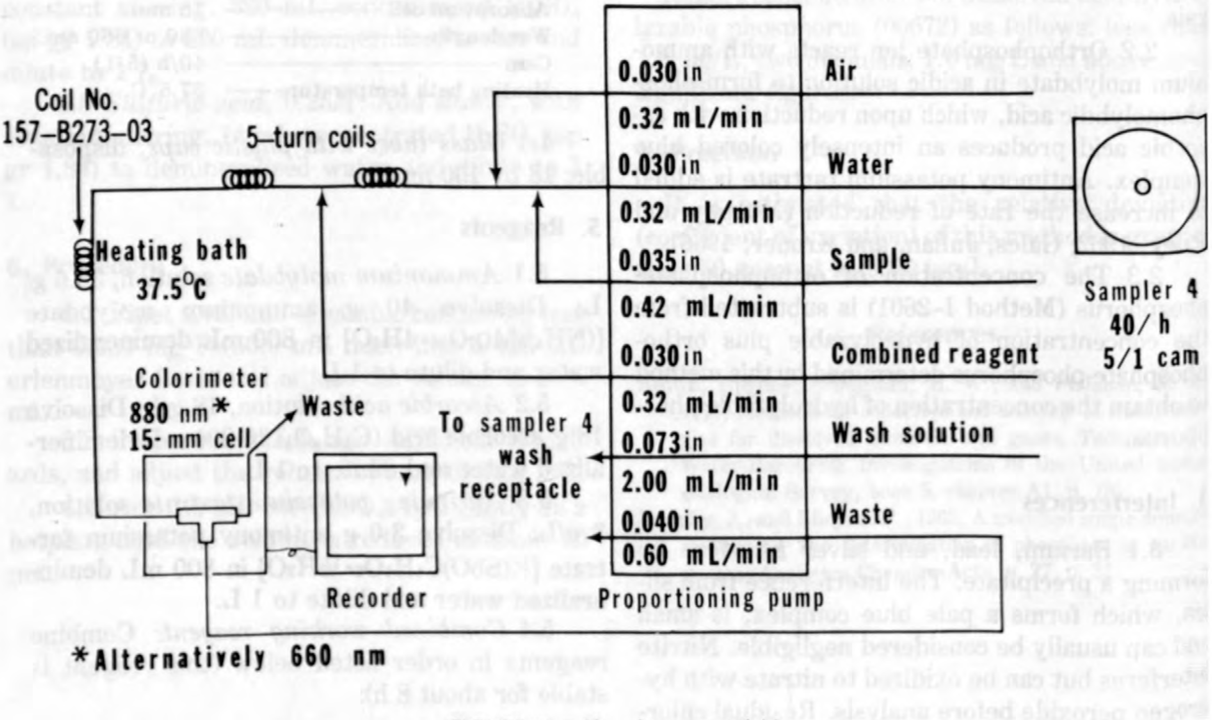


FIGURE 53.—Phosphorus manifold.

or until the temperature of the heating bath reaches 37.5°C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.7 Beginning with the most concentrated standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in approx every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.8 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective orthophosphate-phosphorus concentration.

7.2 Compute the concentration of phosphorus in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 Subtract the concentration of orthophosphate-phosphorus (Method I-2601) from the value obtained to determine the concentration of hydrolyzable phosphorus.

8. Report

Report phosphorus, dissolved hydrolyzable (00672), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 12 percent at 0.20 mg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 131.

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31.

Phosphorus, hydrolyzable, total, colorimetric, phosphomolybdate, automated (I–4602–78)

Parameter and Code: Phosphorus, hydrolyzable, total (mg/L as P): 00669

1. Application

1.1 This method may be used to determine concentrations of total hydrolyzable phosphorus in water-suspended sediment mixtures in the range from 0.01 to 2.0 mg/L combined acid hydrolyzable and orthophosphate - phosphorus. Samples containing higher concentrations must first be diluted.

1.2 Total orthophosphate-phosphorus (Method I–4601) also must be determined in order to determine the total hydrolyzable phosphorus.

2. Summary of method

2.1 Polyphosphates $[(P_2O_7)^{-4}, (P_3O_{10})^{-5}$, etc.] and a few organic phosphorus compounds are converted to orthophosphate by an acid hydrolysis.

2.2 Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales, Julian, and Kroner, 1966).

2.3 The concentration of total orthophosphate-phosphorus (Method I–4601) is subtracted from the concentration of total hydrolyzable plus orthophosphate-phosphorus determined by this method to obtain the concentration of total hydrolyzable phosphorus.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. The interference from silica, which forms a pale blue complex, is small and can usually be considered negligible. Nitrite interferes, but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples may be fortified with 85 mg/L NaCl to overcome this interference.

4. Apparatus

4.1 *Autoclave.*

4.2 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L combined total hydrolyzable and orthophosphate-phosphorus:

Absorption cell ---------------------- 15 mm.
Wavelength------------------------------ 880 or 660 nm.
Cam -------------------------------------- 40/h (5/1).
Heating bath temperature ------ 37.5°C.

4.4 *Glass tubes with plastic caps*, disposable: 18 mm by 150 mm.

5. Reagents

5.1 *Ammonium molybdate* solution, 35.6 g/L: Dissolve 40 g ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in 800 mL demineralized water and dilute to 1 L.

5.2 *Ascorbic acid* solution, 18 g/L: Dissolve 18 g ascorbic acid $(C_6H_8O_6)$ in 800 mL demineralized water and dilute to 1 L.

5.3 *Antimony potassium tartrate* solution, 3 g/L: Dissolve 3.0 g antimony potassium tartrate $[K(SbO)C_4H_4O_6 \cdot ½H_2O]$ in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent:* Combine reagents in order listed below (this reagent is stable for about 8 h):

Sulfuric acid, 2.45*M*	50 mL.
Ammonium molybdate solution	15 mL.
Ascorbic acid solution	30 mL.
Antimony potassium tartrate solution.	5 mL.

5.5 *Phosphate* standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate* standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphate* working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II. For example:

Phosphate standard solution II (mL)	*Orthophosphate-phosphorus concentration (mg/L)*
0.0	0.00
5.0	.25
10	.50
20	1.00
30	1.50
40	2.00

5.8 *Sulfuric acid,* 2.45*M*: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool and dilute to 1 L with demineralized water.

5.9 *Sulfuric acid,* 0.45*M*: Slowly, and with constant stirring and cooling, add 25.2 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool and dilute to 1 L with demineralized water.

6. Procedure

6.1 Mix each sample and immediately pipet a volume containing less than 0.02 mg combined total hydrolyzable and orthophosphate phosphorus (10.0 mL max) into a disposable glass tube, and adjust the volume to 10.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 10.0 mL.

6.3 Add 2.0 mL 0.45*M* sulfuric acid.

6.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 psi pressure. After the samples have cooled, the caps may be pushed down.

6.5 Set up manifold (fig. 54).

6.6 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min or until the temperature in the heating bath reaches

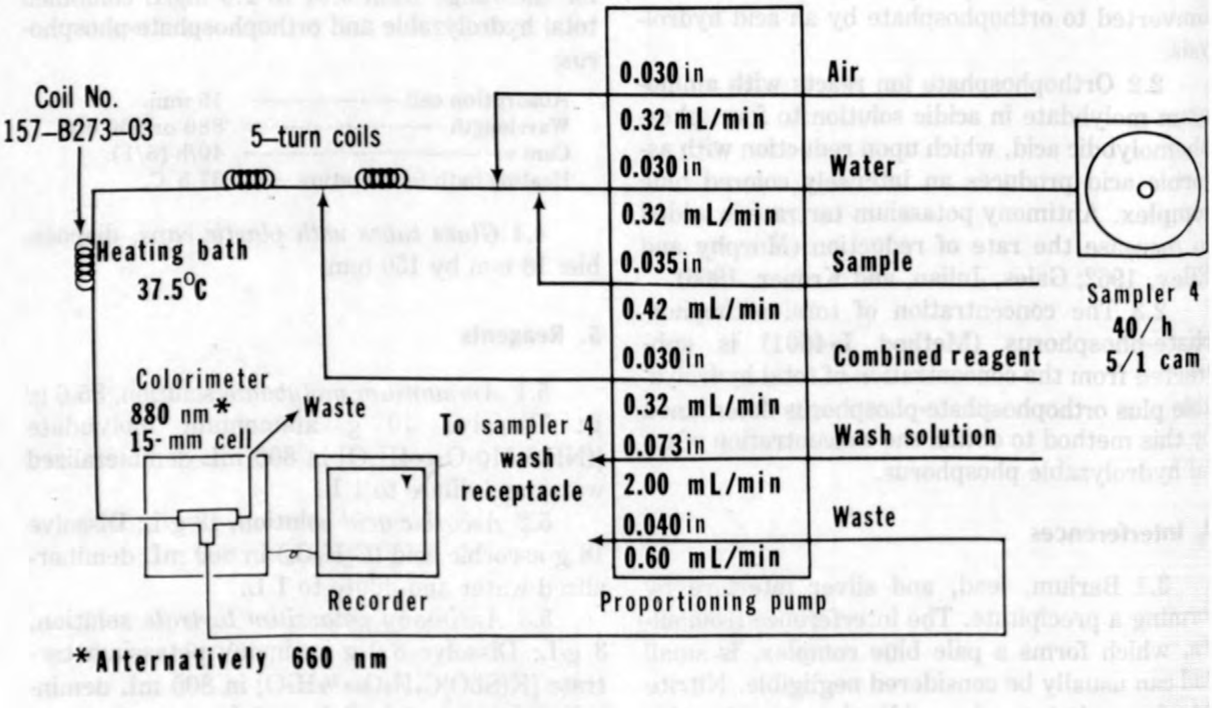


FIGURE 54.—Phosphorus manifold.

37.5 °C. Adjust the baseline to read zero scale division on the recorder with all reagents, but with demineralized water in the sample line.

6.7 Beginning with the most concentrated standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples (NOTE 1).

NOTE 1. When filling each sample cup, take care not to introduce any residue or particulate matter present in the autoclaved and cooled sample.

6.8 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective orthophosphate-phosphorus concentration.

7.2 Compute the concentration of phosphorus in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 Subtract the concentration of total orthophosphate-phosphorus (Method I-4601) from the value obtained to determine the concentration of hydrolyzable phosphate.

8. Report

Report phosphorus, total hydrolyzable (00669), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 12 percent at 0.20 mg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 131.

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31.

Phosphorus, organic, dissolved, colorimetric, calculation, (I–2603–78)

Parameter and Code: Phosphorus, dissolved organic (mg/L as P): 00673

1. Application

This method may be used to analyze most waters and waste waters containing between 0.01 and 2.0 mg/L combined hydrolyzable, organic, and orthophosphate-phosphorus. Samples with higher concentrations must first be diluted.

2. Summary of method

2.1 As far as is known the phosphomolybdate method is specific for the orthophosphate form of phosphorus. Weak tests are reported with pyrophosphate and polyphosphates, but these positive tests may well result from orthophosphate contamination of the material.

2.2 Acid-hydrolyzable and organic forms of phosphorus are decomposed to orthophosphate by sulfuric acid–ammonium persulfate digestion. Orthophosphate is then converted to phosphomolybdate by acidified ammonium molybdate reagent:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21H^{+1} \rightarrow$$

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^{+1} + 12H_2O.$$

2.3 When phosphomolybdate is reduced with ascorbic acid in the presence of antimony (Murphy and Riley, 1962) an intense blue complex is developed that absorbs light at 882 nm. The reduction is not instantaneous, nor is the developed blue color stable. The full color develops in 6 to 10 min and fades gradually thereafter.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. The interference from silica, which forms a pale-blue complex, is small and can usually be considered negligible. Nitrite interferes but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples may be fortified with 85 mg/L NaCl to overcome this interference.

4. Apparatus

4.1 *Autoclave.*

4.2 *Technicon AutoAnalyzer II,* consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment the following operating conditions have been found satisfactory for the range from 0.1 to 2.0 mg/L combined hydrolyzable, organic and orthophosphate-phosphorus:

Absorption cell	**15 mm.**
Wavelength	**880 nm or 550 nm.**
Cam	**40/h (5/1).**
Heating bath temperature.	**37.5° C.**

4.4 *Glass tubes with plastic caps,* disposable: 18 mm by 150 mm.

5. Reagents

5.1 *Ammonium molybdate* solution, 35.6 g/L: Dissolve 40 g ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in 800 mL demineralized water and dilute to 1 L.

5.2 *Ascorbic acid* solution, 18 g/L: Dissolve 18 g ascorbic acid ($C_6H_8O_6$) in 800 mL demineralized water and dilute to 1 L.

5.3 *Antimony potassium tartrate* solution, 3 g/L: Dissolve 3.0 g antimony potassium tartrate $[K(SbO)C_4H_4O_6 \cdot ½H_2O]$ in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent:* Combine reagents in order listed below (this reagent is stable for about 8 h.)

Sulfuric acid, 2.45*M*	50 mL.
Ammonium molybdate solution	15 mL.
Ascorbic acid solution	30 mL.
Antimony potassium tartrate solution	5 mL.

5.5 *Phosphate* standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate* standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphate* working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II. For example:

Phosphate standard solution II (mL)	*Orthophosphate-phosphorus concentration (mg/L)*
0.0	0.00
5.0	.25
10	.50
20	1.00
30	1.50
40	2.00

5.8 *Potassium persulfate* solution, 4 g/L: Dissolve 4.0 g $K_2S_2O_8$ in demineralized water and dilute to 1 L.

5.9 *Sulfuric acid*, 2.45*M*: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool, and dilute to 1 L with demineralized water.

5.10 *Sulfuric acid*, 0.45*M*: Slowly, and with constant stirring and cooling, add 25.2 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool, and dilute to 1 L with demineralized water.

5.11 *Sulfuric acid-persulfate* reagent (1 + 1): Mix equal volumes of 0.45*M* sulfuric acid and potassium persulfate solution.

5.12 *Water diluent:* Add 2.0 mL Levor IV to 1 L demineralized water.

6. Procedure

6.1 Mix each sample and pipet a volume containing less than 0.02 mg total P (10.0 mL maximum) into a disposable glass tube, and adjust the volume to 10.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 10.0 mL.

6.3 Add 4.0 mL acid-persulfate reagent.

6.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 psi pressure. After the samples have cooled, the caps may be pushed down.

6.5 Set up manifold (fig. 55)

6.6 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min, or until the temperature of the heating bath reaches 37.5°C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.7 Beginning with the most concentrated standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.8 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective orthophosphate-phosphorus concentration.

7.2 Compute the concentration of phosphorus in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 P (organic dissolved) in mg/L = (P as determined in sec. 7.2) − P, acid hydrolyzable, as determined in Method I–2602) − (P, ortho, as determined in Method I–2601).

8. Report

Report concentrations of dissolved organic phosphorus (00673) as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

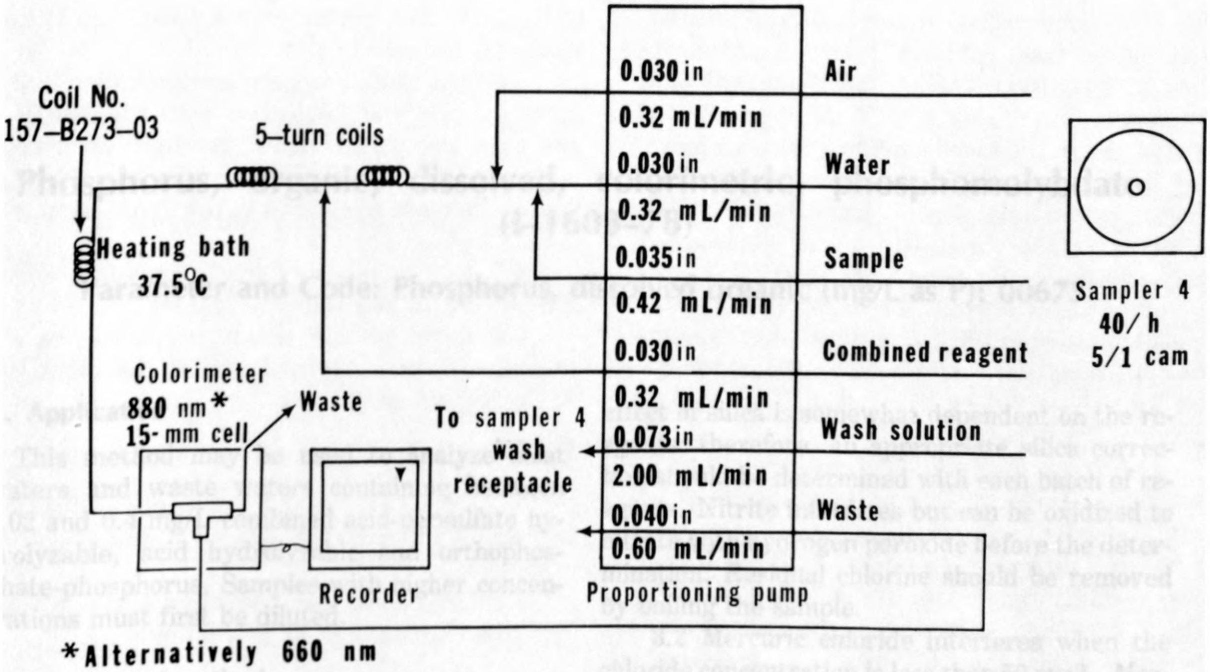


FIGURE 55.—Phosphorus manifold.

References

Brown, Eugene, Skougstad, M. W., and Fishman M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 131.

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31.

Phosphorus, organic, dissolved, colorimetric, phosphomolybdate (I–1603–78)

Parameter and Code: Phosphorus, dissolved organic (mg/L as P): 00673

1. Application

This method may be used to analyze most waters and waste waters containing between 0.02 and 0.4 mg/L combined acid-persulfate hydrolyzable, acid hydrolyzable and orthophosphate-phosphorus. Samples with higher concentrations must first be diluted.

2. Summary of method

2.1 As far as is known the phosphomolybdate method is specific for the orthophosphate form of phosphorus. Weak tests are reported with pyrophosphate and polyphosphates, but these positive tests may well result from orthophosphate contamination of the material.

2.2 Acid hydrolyzable and organic forms of phosphorus are decomposed to orthophosphate by sulfuric acid-ammonium persulfate digestion. Orthophosphate is then converted to phosphomolybdate by acidified ammonium molybdate reagent:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21H^{+1} \rightarrow$$

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^{+1} + 12H_2O.$$

2.3 When phosphomolybdate is reduced with ascorbic acid in the presence of antimony (Murphy and Riley, 1962), an intense blue complex is developed that absorbs light at 882 nm. The reduction is not instantaneous, nor is the developed blue color stable. The full color develops to 6 to 10 min and fades gradually thereafter.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. Silica gives a pale-blue color that is additive to the phosphate color, and a silica correction is made when necessary. The effect of silica is somewhat dependent on the reagents; therefore, an appropriate silica correction should be determined with each batch of reagents. Nitrite interferes but can be oxidized to nitrate with hydrogen peroxide before the determination. Residual chlorine should be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples may be fortified with 85 mg/L Na to overcome this interference.

4. Apparatus

4.1 *Spectrometer* for use at 700 or 882 nm: Beckman Model B, or equivalent.

4.2 With this instrument the following operating conditions have been used:

Wavelength	882 nm or 700 nm.
Filter	Red.
Cells	50 mm.
Phototube	Red-sensitive.
Initial sensitivity setting	2.
Slit width	0.1 mm.

4.3 With these operating conditions the following values have been observed:

P *(mg)*	*Absorbance* *882 nm*	 *700 nm*
0.00	0.00	0.00
.001	.06	.04
.005	.29	.21
.010	.57	.43
.015	.86	.64
.020	1.14	.85

5. Reagents

5.1 *Ammonium persulfate* $(NH_4)_2S_2O_8$.

5.2 *Antimony tartrate-ammonium molybdate* solution: Dissolve 0.13 g antimony potassium tartrate, $[K(SbO)C_4H_4O_2 \cdot \frac{1}{2}H_2O]$, in about

700 mL demineralized water contained in a 1-L volumetric flask. Add 5.6 g ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and shake flask until dissolved. *Cautiously* add 70 mL concentrated H_2SO_4 (sp gr 1.84) while swirling the contents of the flask. Cool and dilute to volume. Mix thoroughly by repeated inversion and swirling. This solution is stable for at least 1 year if stored in a polyethylene bottle away from heat.

5.3 *Combined reagent* solution: Dissolve 0.50 g ascorbic acid in 100 mL antimony tartrate-ammonium molybdate solution. This reagent is stable for at least 1 week if stored at 4°C; otherwise prepare fresh daily.

5.4 *Phenolphthalein indicator* solution, 0.5 g/100 mL: Dissolve 0.5 g phenolphthalein in 100 mL 50-percent ethanol.

5.5 *Phosphate* standard solution I, 1.00 mL = 0.050 mg P: Dissolve 0.2197 g KH_2PO_4, dried overnight over H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate* standard solution II, 1.00 mL = 0.001 mg P: Dilute 20.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Sodium hydroxide*, 3*M*: Carefully, with cooling, dissolve 120 g NaOH in demineralized water and dilute to 1 L.

5.8 *Sulfuric acid*, 6*M*: Add slowly, with constant stirring, 310 mL concentrated H_2SO_4 (sp gr 1.84) to 600 mL demineralized water and dilute to 1 L.

5.9 *Sulfuric acid*, 0.25*M*: Add slowly, with constant stirring, 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.020 mg P (50.0 mL maximum) into a 125-mL erlenmeyer flask, and adjust the volume to 50.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 mL.

6.3 Add 1.0 mL 6*M* H_2SO_4 and 0.4 g $(NH_4)_2S_2O_8$. Boil gently on a hotplate until the volume is reduced to about 10 mL.

6.4 Cool. Add 2 drops phenolphthalein indicator solution and neutralize with 3*M* NaOH, and then add 0.25*M* H_2SO_4 carefully until the pink color just disappears. Transfer to a 50-mL volumetric flask and dilute to the mark with demineralized water.

6.5 Add 10 mL combined reagent to each sample, blank, and standard and mix.

6.6 After 10 min measure absorbance of each sample and standard against the blank at either 882 nm or 700 nm.

7. Calculations

7.1 Determine the milligrams of phosphorus in each sample from a plot of absorbances of standards.

7.2 Determine the phosphorus concentration in milligrams per liter as follows:

$$P\ (\text{mg/L}) = \frac{1{,}000}{\text{mL sample}} \times \text{mg P in sample.}$$

7.3 P (organic dissolved) in mg/L = (P as determined in sec. 7.2) − (P, acid hydrolyzable, as determined in Method I–1602) − (P, ortho, as determined in Method I–1601).

8. Report

Report concentrations of dissolved organic phosphorus (00673) as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 131.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31.

Phosphorus, organic, total, colorimetric, calculation, (I–4603–78)

Parameter and Code: Phosphorus, organic, total (mg/L as P): 00670

1. Application

This method may be used to analyze most waters and waste waters containing between 0.01 and 2.0 mg/L combined hydrolyzable, organic, and orthophosphate-phosphorus. Samples with higher concentrations must first be diluted.

2. Summary of method

2.1 As far as is known the phosphomolybdate method is specific for the orthophosphate form of phosphorus. Weak tests are reported with pyrophosphate and polyphosphates, but these positive tests may well result from orthophosphate contamination of the material.

2.2 Acid hydrolyzable and organic forms of phosphorus are decomposed to orthophosphate by sulfuric acid-ammonium persulfate digestion. Orthophosphate is then converted to phosphomolybdate by acidified ammonium molybdate reagent:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21H^{+1}$$

$$\rightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^{+1} + 12H_2O.$$

2.3 When phosphomolybdate is reduced with ascorbic acid in the presence of antimony (Murphy and Riley, 1962), an intense blue complex is developed that absorbs light at 882 nm. The reduction is not instantaneous, nor is the developed blue color stable. The full color develops in 6 to 10 min and fades gradually thereafter.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. The interference from silica, which forms a pale blue complex, is small and can usually be considered negligible. Nitrite interferes but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples may be fortified with 85 mg/L NaCl to overcome this interference.

4. Apparatus

4.1 *Autoclave.*

4.2 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L combined hydrolyzable, organic and orthophosphate-phosphorus:

Absorption cell	15 mm.
Wavelength	880 nm or 660 nm.
Cam	40/h (5/1)
Heating bath temperature.	37.5° C.

4.4 *Glass tubes with plastic caps*, disposable: 18 mm by 150 mm.

5. Reagents

5.1 *Ammonium molybdate* solution, 35.6 g/L: Dissolve 40 g ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in 800 mL demineralized water and dilute to 1 L.

5.2 *Ascorbic acid* solution, 18 g/L: Dissolve 18 g ascorbic acid $(C_6H_8O_6)$ in 800 mL demineralized water and dilute to 1 L.

5.3 *Antimony potassium tartrate* solution, 3 g/L: Dissolve 3.0 g antimony potassium tartrate $[K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O]$ in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent:* Combine reagents together in order listed below (This reagent is stable for about 8 h).

Sulfuric acid, 2.45*M*	50 mL.
Ammonium molybdate solution	15 mL.
Ascorbic acid solution	30 mL.
Antimony potassium tartrate solution	5 mL.

5.5 *Phosphate* standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate* standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphate* working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II. For example:

Phosphate standard solution II (mL)	*Orthophosphate-phosphorus concentration (mg/L)*
0.0	0.00
5.0	.25
10	.50
20	1.00
30	1.50
40	2.00

5.8 *Potassium persulfate* solution, 4 g/L: Dissolve 4.0 g $K_2S_2O_8$ in demineralized water and dilute to 1 L.

5.9 *Sulfuric acid*, 2.45*M*: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool, and dilute to 1 L with demineralized water.

5.10 *Sulfuric acid*, 0.45*M*: Slowly, and with constant stirring and cooling, add 25.2 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool, and dilute to 1 L with demineralized water.

5.11 *Sulfuric acid-persulfate* reagent, (1 + 1): Mix equal volumes of 0.45*M* sulfuric acid and potassium persulfate solution.

5.12 *Water diluent:* Add 2.0 mL Levor IV to 1 L demineralized water.

6. Procedure

6.1 Mix each sample and pipet a volume containing less than 0.02 mg total P (10.0 mL maximum) into a disposable glass tube, and adjust the volume to 10.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 10.0 mL.

6.3 Add 4.0 mL acid-persulfate reagent.

6.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 psi pressure. After the samples have cooled, the caps may be pushed down.

6.5 Set up manifold (fig. 56)

6.6 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min or until the temperature of the heating bath reaches 37.5°C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.7 Beginning with the most concentrated standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.8 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective orthophosphate-phosphorus concentration.

7.2 Compute the concentration of phosphorus in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 P (organic, total) in mg/L = (P, as determined in sec. 7.2) − (P, acid hydrolyzable, as determined in Method I–4602) − (P, ortho, as determined in Method I–4601).

8. Report

Report concentrations of dissolved organic phosphorus (00670) as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

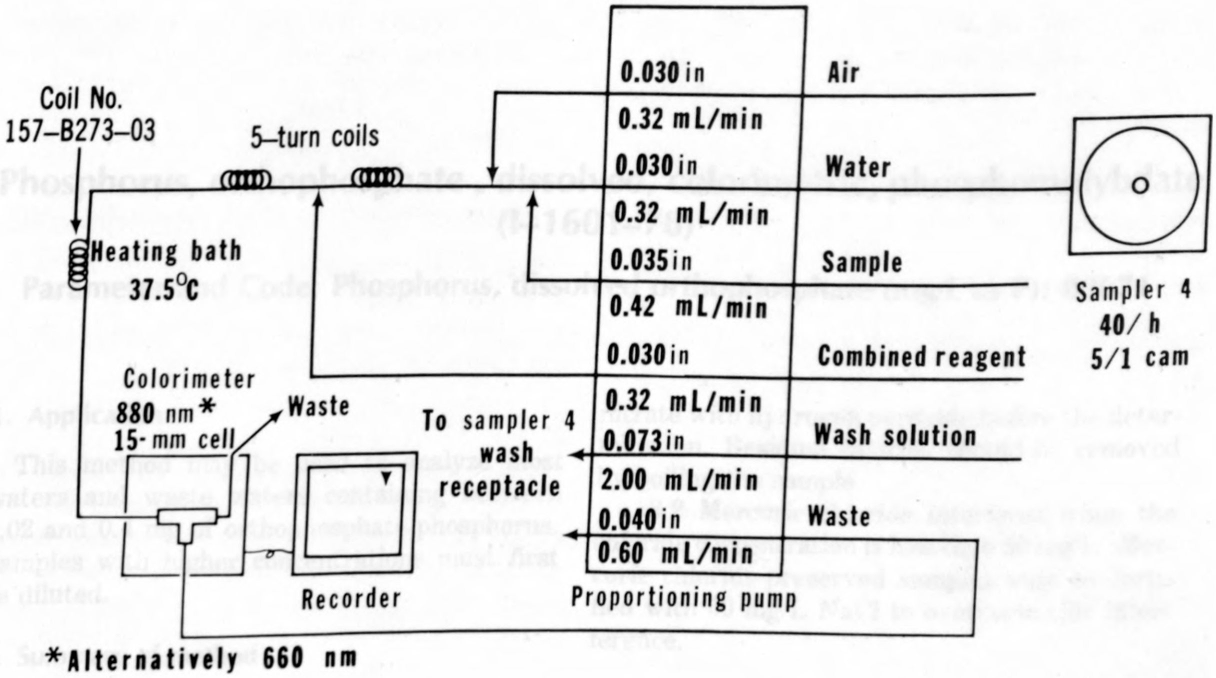


FIGURE 56.—Phosphorus manifold.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 131.

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31.

Phosphorus, orthophosphate , dissolved, colorimetric, phosphomolybdate (I–1601–78)

Parameter and Code: Phosphorus, dissolved orthophosphate (mg/L as P): 00671

1. Application

This method may be used to analyze most waters and waste waters containing between 0.02 and 0.4 mg of orthophosphate-phosphorus. Samples with higher concentrations must first be diluted.

2. Summary of method

2.1 As far as is known the phosphomolybdate method is specific for the orthophosphate form of phosphorus. Weak tests are reported with pyrophosphate and polyphosphates, but these positive tests may well result from orthophosphate contamination of the material.

2.2 Orthophosphate is converted to phosphomolybdate by acidified ammonium molybdate reagent:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21H^{+1}$$

$$\rightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^{+1} + 12H_2O.$$

2.3 When phosphomolybdate is reduced with ascorbic acid in the presence of antimony (Murphy and Riley, 1962), an intense blue complex is developed that absorbs light at 882 nm. The reduction is not instantaneous, nor is the developed blue color stable. The full color develops in 6 to 10 min and fades gradually thereafter.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. Silica gives a pale-blue color that is additive to the phosphate color, and a silica correction is made when necessary. The effect of silica is somewhat dependent on the reagents; therefore, an appropriate silica correction should be determined with each batch of reagents. Nitrite interferes but can be oxidized to nitrate with hydrogen peroxide before the determination. Residual chlorine should be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples may be fortified with 50 mg/L NaCl to overcome this interference.

4. Apparatus

4.1 *Spectrometer* for use at 700 or 882 nm; Beckman Model B, or equivalent.

4.2 With this instrument the following operating conditions have been used:

Wavelength	882 nm or 700 nm.
Filter	Red.
Cells	50 mm.
Phototube	Red-sensitive.
Initial sensitivity setting	2.
Slit width	0.1 mm.

4.3 With these operating conditions the following values have been observed:

P	Absorbance	
(mg)	*882 nm*	*700 nm*
0.00	0.00	0.00
.001	.06	.04
.005	.29	.21
.010	.57	.43
.015	.86	.64
.020	1.14	.85

5. Reagents

5.1 *Antimony tartrate-ammonium molybdate* solution: Dissolve 0.13 g antimony potassium tartrate [$K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$] in about 700 mL demineralized water contained in a 1-L volumetric flask. Add 5.6 g ammonium molybdate, $(NH_4)_6MO_7O_{24} \cdot 4H_2O$, and shake flask until dissolved. *Cautiously* add 70 mL concentrated H_2SO_4 (sp gr 1.84) while swirling the contents of the flask. Cool and dilute to volume. Mix thoroughly by repeated inversion and swirling. This solution is stable for at least 1 year if stored in a polyethylene bottle away from heat.

5.2 *Combined reagent* solution: Dissolve 0.50 g ascorbic acid in 100 mL antimony tartrate-ammonium molybdate solution. This reagent is stable for at least 1 week if stored at 4°C; otherwise prepare fresh daily.

5.3 *Phosphate* standard solution I, 1.00 mL = 0.050 mg P: Dissolve 0.2197 g KH_2PO_4, dried overnight over H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.4 *Phosphate* standard solution II, 1.00 mL = 0.001 mg P: Dilute 20.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.020 mg P (50.0 mL maximum) into a 100-mL beaker, and adjust the volume to 50.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 mL.

6.3 Add 10 mL combined reagent solution to each sample, blank, and standard and mix.

6.4 After 10 but before 30 min measure absorbance of each sample and standard against the blank at either 882 or 700 nm.

7. Calculations

7.1 Determine the milligrams of phosphorus in each sample from a plot of absorbances of standards.

7.2 Determine the phosphorus concentration in milligrams per liter as follows:

$$P\ (\text{mg/L}) = \frac{1{,}000}{\text{mL sample}} \times \text{mg P in sample.}$$

8. Report

Report concentrations of orthophosphate-phosphorus (PO_4-P), dissolved (00671), as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

Data reported by the American Society for Testing and Materials (1916) indicate that the precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Mean (mg/L)	*Relative deviation (percent)*
0.036	22
.326	6

References

American Society for Testing and Materials, 1975, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 956.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 131.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31.

Phosphorus, orthophosphate, dissolved, colorimetric, phosphomolybdate, automated (I–2601–78)

Parameter and Code: Phosphorus, orthophosphate, dissolved (mg/L as P): 00671

1. Application

This method may be used to determine concentrations of orthophosphate-phosphorus in most waters, wastewaters, and brines in the range from 0.01 to 2.0 mg/L P. Samples containing higher concentrations must first be diluted.

2. Summary of method

Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales, Julian, and Kroner, 1966).

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. The interference from silica, which forms a pale-blue complex, is small and can usually be considered negligible. Nitrite interferes, but can be oxidized to nitrate with hydrogen peroxide prior to analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples may be fortified with 85 mg/L NaCl to overcome this interference.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L P:

Absorption cell	15 mm.
Wavelength	880 nm or 660 nm.
Cam	40/h (5/1)
Heating bath temperature.	37.5° C.

5. Reagents

5.1 *Ammonium molybdate* solution, 38 g/L: Dissolve 40 g ammonium molybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$)] in 800 mL demineralized water and dilute to 1 L.

5.2 *Ascorbic acid* solution, 18 g/L: Dissolve 18 g ascorbic acid ($C_6H_8O_6$) in 800 mL demineralized water and dilute to 1 L.

5.3 *Antimony potassium tartrate* solution, 2.9 g/L: Dissolve 3.0 g antimony potassium tartrate [$K(SbO)C_4H_4O_6\cdot \frac{1}{2}H_2O$] in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent:* Combine reagents together in order listed below (this reagent is stable for about 8 h):

Sulfuric acid, 2.45*M*	50 mL.
Ammonium molybdate solution	15 mL.
Ascorbic acid solution	30 mL.
Antimony potassium tartrate solution	5 mL.

5.5 *Phosphate* standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate* standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphate* working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II as follows:

Phosphate standard solution II (mL)	*Orthophosphate-phosphorus concentration (mg/L)*
0.0	0.00
5.0	.25
10	.50
20	1.00
30	1.50
40	2.00

5.8 *Sulfuric acid*, 2.45*M*: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool and dilute to 1 L with demineralized water.

5.9 *Water diluent* solution: To demineralized water add 2.0 mL/L of Levor IV.

6. Procedure

6.1 Set up manifold (fig. 57).

6.2 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min or until the temperature of the heating bath reaches 37.5°C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.3 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

7. Calculation

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective orthophosphate-phosphorus concentration.

7.2 Compute the concentration of dissolved orthophosphate-phosphorus (PO_4-P) in each sample by comparing its peak-height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report orthophosphate-phosphorus (PO_4-P), dissolved (00671), concentrations as follows: less

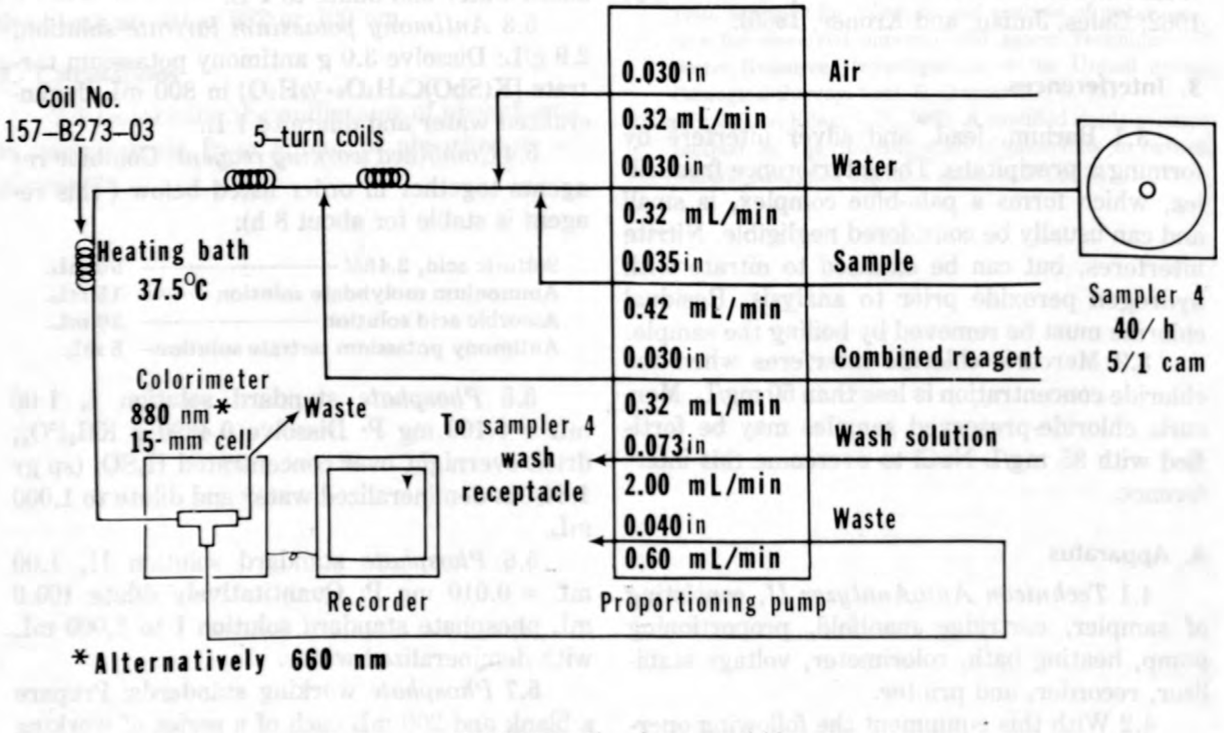


FIGURE 57.—Phosphorus manifold.

than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

As determined on synthetic (deionized water matrix) samples, the precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
2 (44 replicates)	0.050	20
2 (50 replicates)	.168	16

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 131.

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31.

Phosphorus, orthophosphate, total, colorimetric, phosphomolybdate automated (I–4601–78)

Parameter and Code: Phosphorus, total orthophosphate (mg/L as P): 70507

1. Application

1.1 This method may be used to determine concentrations of total orthophosphate-phosphorus in water-suspended sediment mixtures in the range of 0.01 to 2.0 mg/L P. Samples containing higher concentrations must first be diluted.

1.2 The suspended sediment in an unfiltered, unacidified sample is allowed to settle in the sample bottle and a portion of the clear supernatant solution is decanted for analysis.

2. Summary of method

Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales, Julian, and Kroner, 1966).

3. Interferences

3.1 Inasmuch as phosphorus is easily adsorbed on sediment, the orthophosphate recovered from the supernatant solution above a water-suspended sediment mixture after some time has elapsed may be less than that which would have been determined in the filtrate from a sample that was filtered at the time of collection. The amount recovered may also depend on the type of sediment (clay, sand, etc.).

3.2 Barium, lead, and silver interfere by forming a precipitate. The interference from silica, which forms a pale-blue complex, is small and can usually be considered negligible. Nitrite interferes, but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.3 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples may be fortified with 85 mg/L NaCl to overcome this interference.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L P:

Absorption cell	15 mm.
Wavelength	880 nm or 550 nm.
Cam	40/h (5/1)
Heating bath temperature.	37.5° C.

5. Reagents

5.1 *Ammonium molybdate* solution, 35.6 g/L: Dissolve 40 g ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in 800 mL demineralized water and dilute to 1 L.

5.2 *Ascorbic acid* solution, 18 g/L: Dissolve 18 g ascorbic acid ($C_6H_8O_6$) in 800 mL demineralized water and dilute to 1 L.

5.3 *Antimony potassium tartrate* solution, 3 g/L: Dissolve 3.0 g antimony potassium tartrate $[K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O]$ in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent:* Combine reagents together in order listed below. (this reagent is stable for about 8 h):

Sulfuric acid, 2.45*M*	50 mL.
Ammonium molybdate solution	15 mL.
Ascorbic acid solution	30 mL.
Antimony potassium tartrate solution	5 mL.

5.5 *Phosphate* standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate* standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphate* working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II. For example:

Phosphate standard solution II (mL)	*Orthophosphate-phosphorus concentration (mg/L)*
0.0	0.00
5.0	.25
10	.50
20	1.00
30	1.50
40	2.00

5.8 *Sulfuric acid*, 2.45*M*: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool and dilute to 1 L with demineralized water.

5.9 *Water diluent:* Add 2.0 mL Levor IV to 1 L demineralized water.

6. Procedure

6.1 Set up manifold (fig. 58).

6.2 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min or until the temperature of the heating bath reaches 37.5°C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.3 Beginning with the most concentrated standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples (NOTE 1).

NOTE 1. Decant a portion of the clear supernatant solution from a settled sample for analysis. Avoid transfer of any particulate matter to the sample cups.

6.4 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

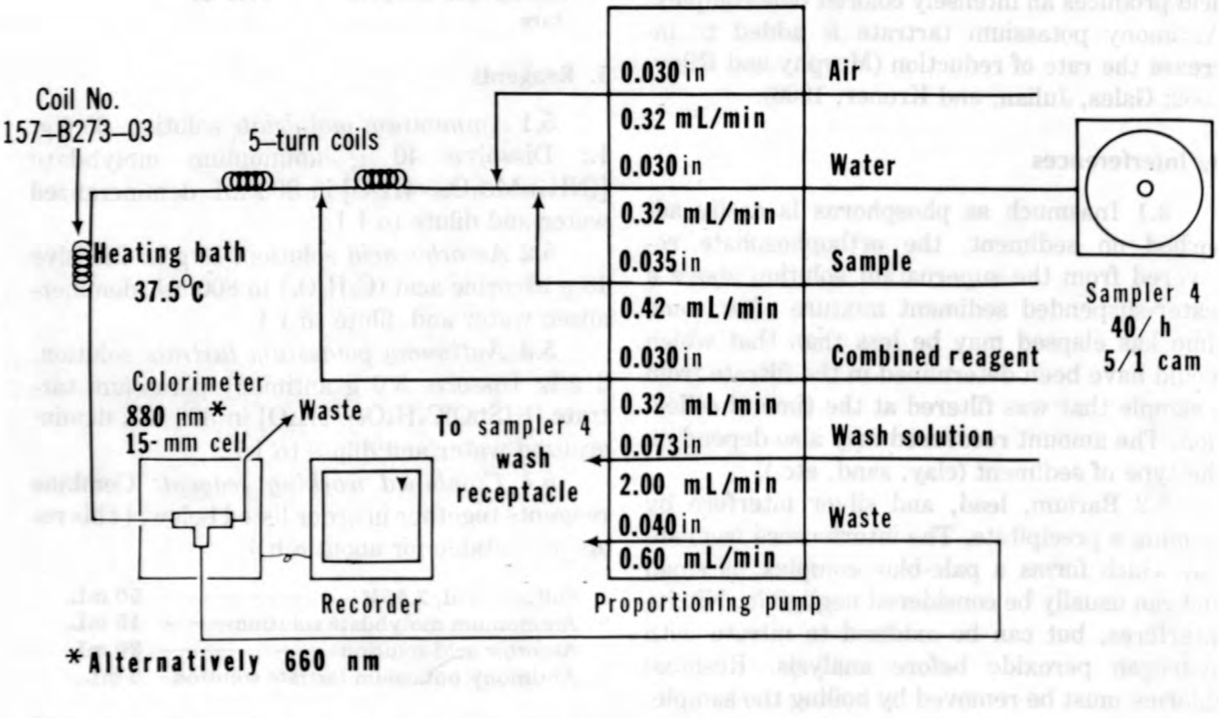


FIGURE 58.—Phosphorus manifold.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective orthophosphate-phosphorus concentration.

7.2 Compute the concentration of orthophosphate-phosphorus in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report phosphorus, total orthophosphate (70507), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 20 percent at 0.050 mg/L and greater than 16 percent at 0.168 mg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 131.

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31.

Phosphorus, total in bottom material, colorimetric, phosphomolybdate, automated (I–6600–78)

Parameter and Code: Phosphorus, total in bottom material, dry wt (mg/kg as P): 00668

1. Application

1.1 This method may be used to determine concentrations of total phosphorus in bottom material containing from 40 to 8,000 mg/kg P.

1.2 The range may be extended to 80,000 mg/kg P by using a 0.1 g subsample rather than the 1 g subsample specified.

2. Summary of method

2.1 All forms of phosphorus, including organic phosphorus, are converted to orthophosphate by an acid persulfate digestion.

2.2 The digested and centrifuged sample is diluted to reduce the acid and phosphorus concentrations before final analysis.

2.3 Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales, Julian, and Kroner, 1966).

3. Interferences

3.1 The color of the molybdate blue complex is strongly affected by pH. The method incorporates a dilution step to reduce both the phosphorus and the hydrogen ion concentrations of all samples and standards. If a further dilution is thought necessary to bring the phosphorus concentration of samples into a readable range, it is important that the standards be equally diluted, inasmuch as the standards must contain concentrations of acid equivalent to the samples.

3.2 Barium, lead, and silver interfere by forming a precipitate. The interference from silica, which forms a pale-blue complex, is small and can usually be considered negligible. Nitrite interferes, but can be oxidized to nitrite with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

4. Apparatus

4.1 *Autoclave.*

4.2 *Centrifuge.*

4.3 *Centrifuge tubes*, 50-mL capacity.

4.4 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.5 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L P in the diluted digestate:

Absorption cell	15 mm.
Wavelength	880 nm or 660 nm.
Cam	40/h (5/1)
Heating bath temperature.	37.5°C.

5. Reagents

5.1 *Ammonium molybdate* solution, 35.6 g/L: Dissolve 40 g ammonium molybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] in 800 mL demineralized water and dilute to 1 L.

5.2 *Ascorbic acid* solution, 18 g/L: Dissolve 18 g ascorbic acid ($C_6H_8O_6$) in 800 mL demineralized water and dilute to 1 L.

5.3 *Antimony potassium tartrate* solution, 3 g/L: Dissolve 3.0 g antimony potassium tartrate [$K(SbO)C_4H_4O_6\cdot \frac{1}{2}H_2O$] in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent:* Combine reagents together in order listed below (This reagent is stable for about 8 h):

Sulfuric acid, 2.45*M*	50 mL.
Ammonium molybdate solution	15 mL.
Ascorbic acid solution	30 mL.
Antimony potassium tartrate solution	5 mL.

5.5 *Phosphate* standard solution I, 1.00

mL = 2.00 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate* standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphate* working standards: Prepare a blank and 200 mL of each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II. For example:

Phosphate standard solution II (mL)	*Orthophosphate-phosphorus concentration (mg/L)*
0.0	0.00
5.0	.25
10	.50
20	1.00
30	1.50
40	2.00

5.8 *Potassium persulfate*, crystals.

5.9 *Sulfuric acid*, concentrated (sp gr 1.84).

5.10 *Sulfuric acid*, 2.45*M*: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool, and dilute to 1 L with demineralized water.

5.11 *Water diluent:* Add 2.0 mL Levor IV to 1 L demineralized water.

6. Procedure

6.1 Accurately weigh a portion of as-received sample having a dry weight of approx 1 g. The sample must first be prepared as directed in Method P–0810. Transfer the weighed sample to a 50-mL centrifuge tube and add 10 mL demineralized water.

6.2 On a separate portion, determine the dry weight of the sample (Method P–0590).

6.3 Pipet 10 mL each of a blank and working standards into 50-mL centrifuge tubes.

6.4 Add 1.0 mL concentrated H_2SO_4 and 1.0 g potassium persulfate to each centrifuge tube.

6.5 Autoclave for 30 min at 15 psi pressure.

6.6 Centrifuge for 5 to 10 min at 5,000 rpm.

6.7 Transfer the supernatant solution to a 200-mL volumetric flask, taking care not to disturb the residue in the bottom of the centrifuge tube.

6.8 Wash the residue several times with demineralized water, adding the washings to the volumetric flask. Dilute to 200 mL with demineralized water.

6.9 Pipet 5.0 mL of sample, standards, and blank into 100-mL volumetric flasks and dilute each to volume with demineralized water.

6.10 Set up manifold (fig. 59).

6.11 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min or until the temperature of the heating bath reaches 37.5 °C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.12 Beginning with the most concentrated standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.13 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective orthophosphate-phosphorus concentration.

7.2 Compute the concentration of total phosphorus in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 Calculate the concentration of total phosphorus in each bottom material sample as follows:

$$\text{Phosphorus (mg/kg)} = \frac{P}{W} \times \frac{20}{5} \times 1{,}000$$

or

$$\text{Phosphorus (mg/kg)} = \frac{P}{W} \times 4{,}000.$$

where:

P = concentration of phosphorus, milligrams per liter, (mg/L) in the sample, and

W = dry weight, grams, of the sample

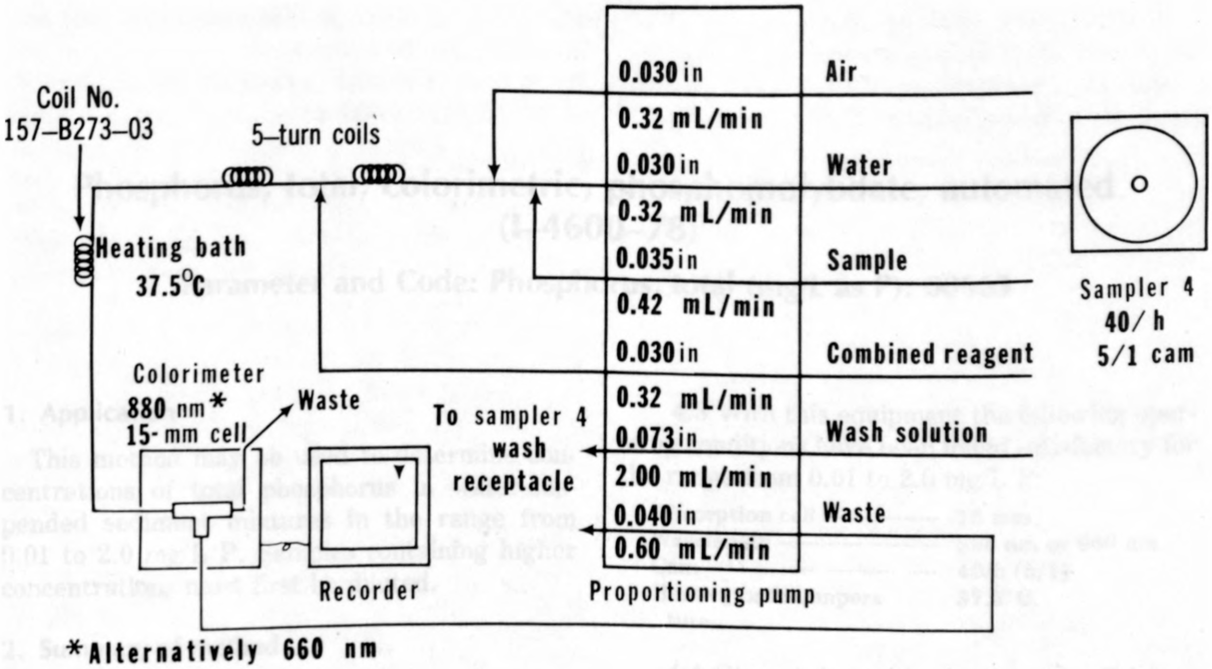


FIGURE 59.—Phosphorus manifold.

8. Report

Report phosphorus, total in bottom material (00668), in milligrams per kilogram to two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 12 percent in the lower portion of the analytical range.

References

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31.

Phosphorus, total, colorimetric, phosphomolybdate, automated (I–4600–78)

Parameter and Code: Phosphorus, total (mg/L as P): 00665

1. Application

This method may be used to determine concentrations of total phosphorus in water-suspended sediment mixtures in the range from 0.01 to 2.0 mg/L P. Samples containing higher concentrations must first be diluted.

2. Summary of method

2.1 All forms of phosphorus, including organic phosphorus, are converted to orthophosphate by an acid-persulfate digestion.

2.2 Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales, Julian, and Kroner, 1966).

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. The interference from silica, which forms a pale blue complex, is small and can usually be considered negligible. Nitrite interferes, but can be oxidixed to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chlorine interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples may be fortified with 85 mg/L NaCl to overcome this interference.

4. Apparatus

4.1 *Autoclave.*

4.2 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L P:

Absorption cell	15 mm.
Wavelength	880 nm or 660 nm.
Cam	40/h (5/1)
Heating bath temperature.	37.5°C.

4.4 *Glass tubes with plastic caps*, disposable: 18 mm by 150 mm.

5. Reagents

5.1 *Ammonium molybdate* solution, 35.6 g/L: Dissolve 40 g ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in 800 mL demineralized water and dilute to 1 L.

5.2 *Ascorbic acid* solution, 18 g/L: Dissolve 18 g ascorbic acid $(C_6H_8O_6)$ in 800 mL demineralized water and dilute to 1 L.

5.3 *Antimony potassium tartrate* solution, 3 g/L: Dissolve 3.0 g antimony potassium tartrate $[K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O]$ in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent:* Combine reagents together in order listed below (this reagent is stable for about 8 h):

Sulfuric acid, 2.45*M*	50 mL.
Ammonium molybdate solution	15 mL.
Ascorbic acid solution	30 mL.
Antimony potassium tartrate solution	5 mL.

5.5 *Phosphate* standard solution I, 1.00 mL = 2.00 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate* standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphate* working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II. For example:

Phosphate standard solution II (mL)	*Orthophosphate-phosphorus concentration (mg/L)*
0.0	0.00
5.0	.25
10	.50
20	1.00
30	1.50
40	2.00

5.8 *Potassium persulfate* solution, 4 g/L: Dissolve 4.0 g $K_2S_2O_8$ in demineralized water and dilute to 1 L.

5.9 *Sulfuric acid*, 2.45*M*: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool, and dilute to 1 L with demineralized water.

5.10 *Sulfuric acid*, 0.45*M*: Slowly, and with constant stirring and cooling, add 25.2 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool, and dilute to 1 L with demineralized water.

5.11 *Sulfuric acid-persulfate* reagent, (1 + 1): Mix equal volumes of 0.45*M* sulfuric acid and potassium persulfate solution.

5.12 *Water diluent:* Add 2.0 mL Levor IV to 1 L demineralized water.

6. Procedure

6.1 Mix each sample and pipet a volume containing less than 0.02 mg total P (10.0 mL maximum) into a disposable glass tube, and adjust the volume to 10.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 10.0 mL.

6.3 Add 4.0 mL acid-persulfate reagent.

6.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 psi pressure. After the samples have cooled, the caps may be pushed down.

6.5 Set up manifold (fig. 60)

6.6 Allow the colorimeter, recorder, and heating bath to warm up for at least 30 min or until the temperature of the heating bath reaches 37.5 °C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.7 Beginning with the most concentrated standard, place a complete set of standards in

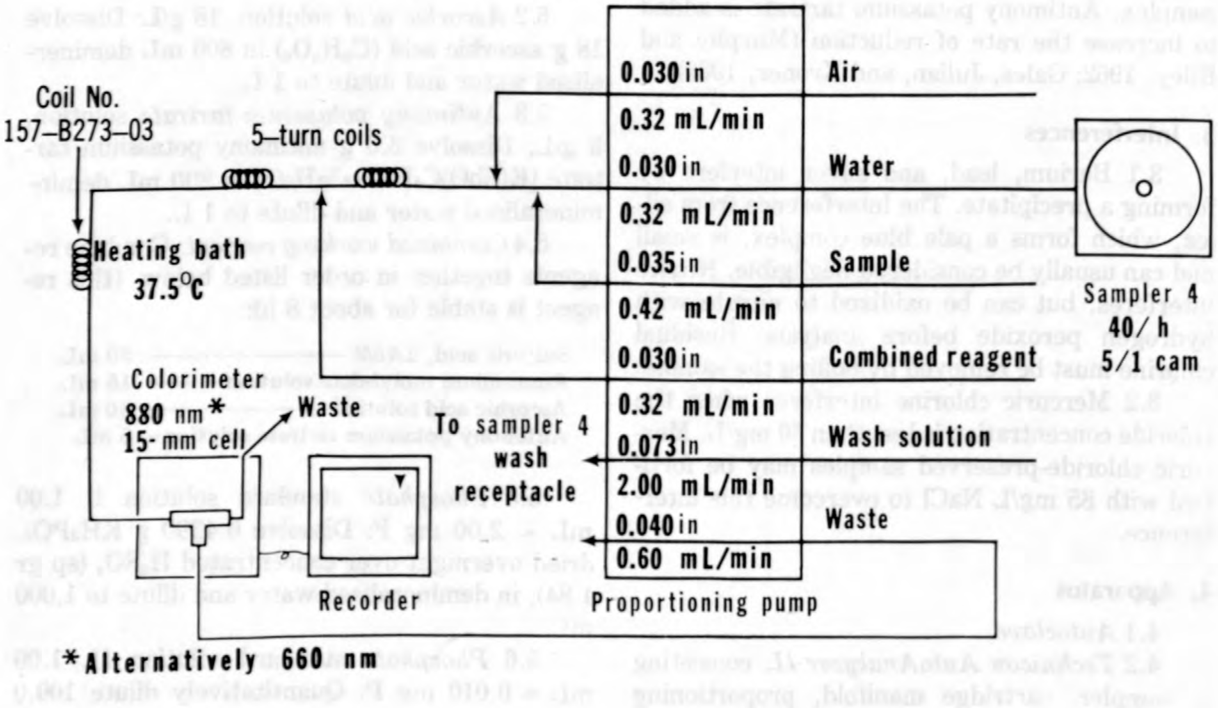


FIGURE 60.—Phosphorus manifold.

the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.8 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective orthophosphate-phosphorus concentration.

7.2 Compute the concentration of phosphorus in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report phosphorus, total (00665), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 12 percent at 0.197 mg/L and greater than 3 percent at 0.67 mg/L.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 131.

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31.

Silica, dissolved, colorimetric, molybdate blue (I–1700–78)

Parameter and Code: Silica, dissolved (mg/L as SiO_2): 00955

1. Application

This method may be used to analyze samples containing from 0.1 to 100 mg/L of silica. Samples containing more than 100 mg/L should be analyzed by standard gravimetric procedures (American Society for Testing and Materials, 1976; Kolthoff and others, 1969).

2. Summary of method

2.1 Silica in solution as silicic acid or silicate has the property of reacting with ammonium molybdate in an acid medium to form the yellow colored silicomolybdate complex. The silicomolybdate complex is then reduced by sodium sulfite to form the molybdate blue color. The silicomolybdate complex may form in water as alpha and beta polymorphs (Strickland, 1952), which have absorbance maxima at different wavelengths. In order to favor the development of the beta form, the pH of the reaction mixture is reduced below 2.5 (Govett, 1961).

2.2 The possibility of having larger concentrations of so-called unreactive silica is greater in water containing high concentrations of silica than in water with a low silica content. When significant amounts of unreactive silica are known or suspected to be present, a 1-h digestion of 50-mL sample with 5.0 mL of 1.0*M* NaOH is suggested as a means of making all the silica available for reaction with the molybdate reagent.

3. Interferences

Phosphate gives a similar molybdate complex under certain pH conditions. In the following determination, tartaric acid is added to suppress phosphate interference. There is also evidence that hydrogen sulfide and ferric and ferrous iron interfere with the determination. Hydrogen sulfide may be removed by boiling an acidified sample. The addition of disodium dihydrogen ethylenediamine tetraacetate (Na_2EDTA) eliminates the effect of high concentrations of iron, and also complexes calcium and prevents precipitation of calcium sulfite.

4. Apparatus

4.1 *Spectrometer* for use at 700 nm: Beckman Model B, or equivalent.

4.2 With this instrument the following operating conditions have been used:

Wavelength	700 nm.
Filter	Red.
Cells	10 mm or 40 mm.
Phototube	Red-sensitive.
Initial sensitivity setting	1.
Slit width	0.35 mm.

4.3 With these operating conditions the following absorbances have been observed:

SiO_2 (*mg*)	*Cell depth* (*mm*)	*Absorbance*
0.00	40	0.000
.05	40	.337
.10	40	.675
.10	10	.165
.20	10	.330
.30	10	.495
.50	10	.816

5. Reagents

5.1 *Ammonium molybdate* solution, 49 g/L: Dissolve 52 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in water, adjust the pH to between 7 and 8 with 10*M* NaOH, and dilute to 1 L with demineralized water. Filter through 0.45-μm membrane filter if necessary.

5.2 *Hydrochloric acid*, 1.0*M*: Mix 88 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.3 *Silica* standard solution I, 1.00 mL = 0.500 mg SiO_2: Dissolve 2.366 g sodium meta-silicate ($Na_2SiO_3 \cdot 9H_2O$) in demineralized water and verify by standard gravimetric analysis. Store in a plastic bottle.

5.4 *Silica* standard solution II, 1.00 mL = 0.005 mg SiO_2: Dilute 10.0 mL silica standard solution I to 1,000 mL with demineralized water. Store in a plastic bottle.

5.5 Na_2 *EDTA* solution, 10 g/L: Dissolve 10 g Na_2EDTA in demineralized water and dilute to 1 L.

5.6 *Sodium hydroxide* solution, 10*M*: Dissolve 400 g NaOH in demineralized water and dilute to 1 L.

5.7 *Sodium sulfite* solution, 170 g/L: Dissolve 170 g Na_2SO_3 in demineralized water and dilute to 1 L.

5.8 *Tartaric acid* solution, 100 g/L: Dissolve 100 g $H_2C_4H_4O_6$ in demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.5 mg SiO_2 (10.0 mL maximum) into a 50-mL beaker, and adjust the volume to 10.0 mL.

6.2 Pipet a demineralized water blank and sufficient standards into 50-mL beakers, and adjust the volume of each to 10.0 mL.

6.3 To each add, with stirring, 5.0 mL 1.0*M* HCl, 5.0 mL Na_2EDTA solution, and 5.0 mL ammonium molybdate solution.

6.4 After 5 min add 5.0 mL tartaric acid solution and mix.

6.5 Add 10.0 mL Na_2SO_3 solution and mix.

6.6 Allow to stand approx 30 min. The color is stable for several hours after this time.

6.7 Determine the absorbance of each test sample and standards against the blank.

7. Calculations

7.1 Determine milligrams of silica in each sample from a plot of absorbances of standards.

7.2 Determine the silica concentration in milligrams per liter as follows:

$$SiO_2\ (mg/L) = \frac{1{,}000}{mL\ sample} \times mg\ SiO_2\ in\ sample.$$

8. Report

Report silica, dissolved (00955), as follows: less than 10 mg/L one decimal; 10 mg/L, and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 2.0 to 40 mg/L may be expressed as follows:

$$S_T = 0.031X + 0.60$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of silica, milligrams per liter

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
12	5.87	9
19	36.5	3

References

American Society for Testing and Materials, 1976, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 401.

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Strickland, J. D. H., 1952, The preparation and properties of silicomolybdic acid; I. The properties of alpha silicomolybdic acid: American Chemical Society Journal, v. 74, p. 862–867.

Silica, dissolved, colorimetric, molybdate blue, automated (I-2700-78)

Parameter and Code: Silica, dissolved (mg/L as SiO_2): 00955

1. Application

This method may be used to determine concentrations of silica in surface, domestic, and industrial waters in the range from 0.1 to 60 mg/L.

2. Summary of method

2.1 Silica reacts with molybdate reagent in acid media to form a yellow silicomolybdate complex. This complex is reduced by ascorbic acid to form the molybdate blue color. The silicomolybdate complex may form either as an alpha or beta polymorph, or a mixture of both. Because the two polymorphic forms have absorbance maxima at different wavelengths, the pH of the mixture is kept below 2.5, a condition which favors formation of the beta polymorph (Govett, 1961; Mullen and Riley, 1955; and Strickland, 1952).

2.2 The possibility of having larger concentrations of so-called unreactive silica is greater in water containing high concentrations of silica than in water with a low silica content. When significant amounts of unreactive silica are known or suspected to be present, a 1-h digestion of a 50-mL sample with 5.0 mL of 1.0*M* NaOH is suggested as a means of making all the silica available for reaction with the molybdate reagent.

3. Interferences

Interference from phosphate, which forms a phosphomolybdate complex, is suppressed by the addition of oxalic acid. Hydrogen sulfide must be removed by boiling the acidified sample prior to analysis. Large amounts of iron interfere.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.1 to 60 mg/L:

Absorption cell ---------- 15 mm.
Wavelength ---------- 660 nm.
Cam ---------- 60/h (6/1).

5. Reagents

5.1 *Ammonium molybdate* solution, 9.4 g/L: Dissolve 10 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 0.05*M* H_2SO_4 and dilute to 1 L with 0.05*M* H_2SO_4. Filter and store in an amber plastic container.

5.2 *Ascorbic acid* solution, 17.6 g/L: Dissolve 17.6 g ascorbic acid in 500 mL demineralized water containing 50 mL acetone. Dilute to 1 L with demineralized water. Add 0.5 mL Levor IV solution. The solution is stable for 1 week if stored at 4°C.

5.3 *Levor IV* solution: Technicon No. 21-0332 or equivalent.

5.4 *Oxalic acid* solution 50 g/L: Dissolve 50 g oxalic acid in demineralized water and dilute to 1 L.

5.5 *Silica* standard solution I, 1.00 mL = 0.500 mg SiO_2: Dissolve 2.366 g sodium metasilicate $(Na_2SiO_3 \cdot 9H_2O)$ in demineralized water and dilute to 1,000 mL. The concentration of this solution must be verified by standard gravimetric analysis. Store in a plastic bottle.

5.6 *Silica* working standards: Prepare a blank and 500 mL each of a series of silica working standards by appropriate quantitative dilution of silica standard solution I as follows:

Silica standard solution I (mL)	*Silica concentration (mg/L)*
0.0	0
5.0	5
10.0	10
20.0	20
40.0	40
60.0	60

5.7 *Sulfuric acid*, 0.05*M*: *Cautiously* add

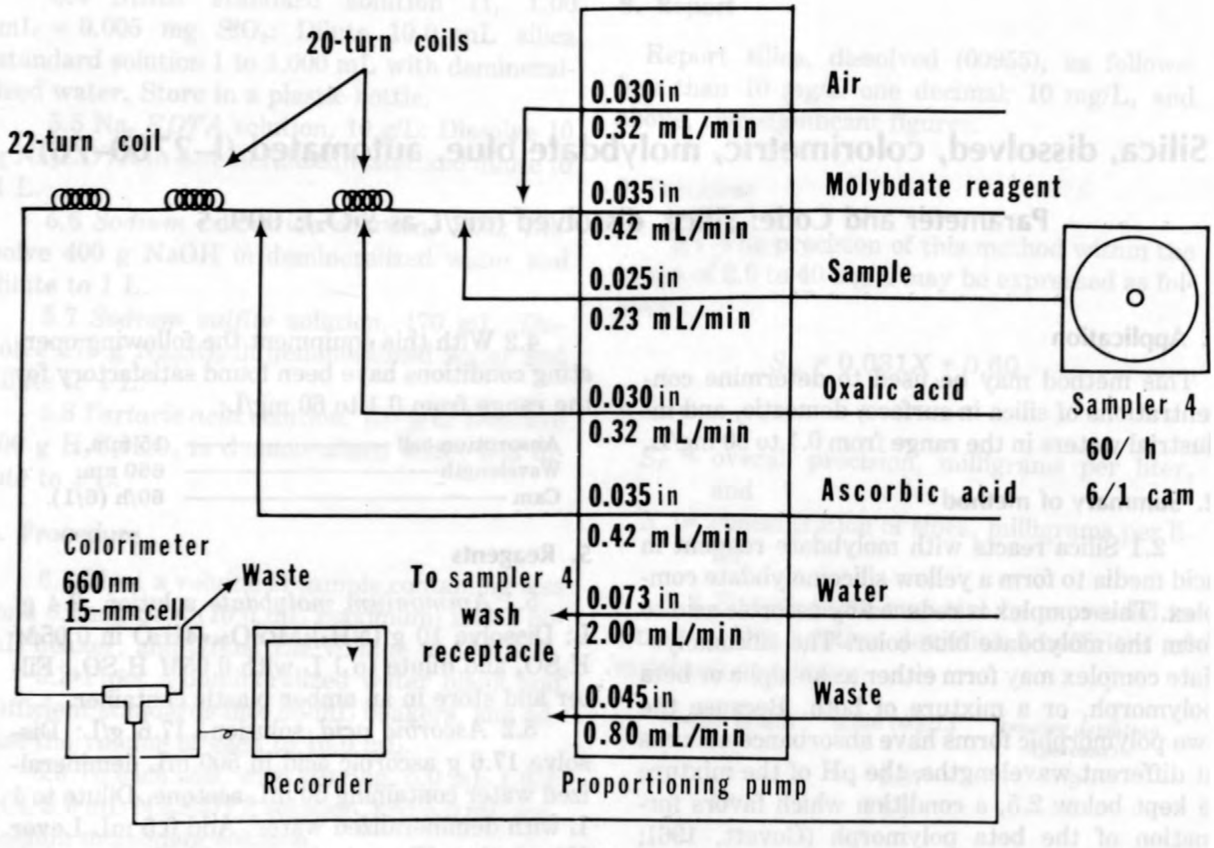


FIGURE 61.—Silica manifold.

2.8 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Set up manifold (fig. 61).

6.2 Allow colorimeter and recorder to warm up for at least 30 min. Adjust baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.3 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective silica concentration.

7.2 Compute the silica concentration of each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report silica (SiO_2), dissolved (00955), concentrations as follows: less than 10 mg/L, nearest 0.1 mg/L; 10 mg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 5.0 to 20 mg/L may be expressed as follows:

$$S_T = 0.087X - 0.148$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of silica, milligrams per liter.

9.2 The statistical results may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
7	6.51	5
5	17.4	7

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 139.

Govett, G. J. S., 1961, Critical factors in the colorimetric determination of silica: Analytica Chemica Acta, v. 25, p. 69–80.

Mullen, J. B., and Riley, J. P., 1955, The colorimetric determination of silicate with special reference to sea and natural waters: Analytica Chemica Acta, v. 12, p. 162–176.

Strickland, J. D. H., 1952, The preparation and properties of silicomolybdic acid; I. The properties of alpha silicomolybdic acid: American Chemical Society Journal, v. 74, p. 862–867.

Sulfate, dissolved, colorimetric, complexometric methylthymol blue, automated (I–2822–77)

Parameter and Code: Sulfate, dissolved (mg/L as SO_4): 00945

1. Application

This method may be used to determine concentrations of sulfate in surface, domestic, and industrial waters in the range from 5 to 100 mg/L. The range may be extended to 300 mg/L by decreasing the sample-to-water ratio. Samples containing higher concentrations must first be diluted.

2. Summary of method

The sample stream is passed through a cation-exchange column before adding an acid solution containing equimolar quantities of barium chloride and methylthymol blue (MTB). Any sulfate ion is thereby precipitated as barium sulfate. When the mixture is then made basic, the remaining barium ions form a complex with MTB, and the absorbance of the uncomplexed MTB, which is gray in color, is directly proportional to the amount of sulfate originally present (Lazarus and others, 1968).

3. Interferences

Color is the only significant interference. Interfering cations are removed by a cation-exchange column which is incorporated into the system.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the ranges from 5 to 100 mg/L and 100 to 300 mg/L:

Absorption cell	15 mm.
Wavelength	460 nm.
Cam	30/h (6/1).

5. Reagents

5.1 *Barium chloride* stock solution, 1.301 g/L: Dissolve 1.526 g $BaCl_2 \cdot 2H_2O$ (assay 99.0% minimum) in demineralized water and dilute to 1,000 mL.

5.2 *EDTA* solution: Dissolve 6.75 g NH_4Cl and 40 g disodium ethylenediaminetetraacetic acid (EDTA) in 500 mL demineralized water and 57 mL concentrated NH_4OH (sp gr 0.90). Dilute to 1 L with demineralized water.

5.3 *Hydrochloric acid, 1M*: Add 83 mL concentrated hydrochloric acid (sp gr 1.19) to demineralized water and dilute to 1 L.

5.4 *Methylthymol blue* (MTB) solution, 0.5417 g/100 mL: Dissolve 0.5417 g MTB blue (Eastman Kodak No. 8068, M. W. = 866.73) in demineralized water and dilute to 100 mL.

5.5 *MTB-barium chloride* reagent: The purity of MTB may vary from one lot to another; this variation affects the linearity of the analytical curve (Colovos and others 1976). It is therefore necessary to adjust the Ba/MTB ratio by the following calibration procedure in order to achieve a linear relationship between absorbance and sulfate concentration. Add 25.0 mL $BaCl_2 \cdot 2H_2O$ solution to each of several 500-mL volumetric flasks. Then add volumes of MTB solution ranging from 26.0 to 36.0 mL (0.96 to 0.69 Ba/MTB range), in 2.0-mL increments, to each flask. Add 4.0 mL 1*M* HCl and an appropriate volume of demineralized water to bring the total volume to 100 mL. Dilute to 500 mL with 95 percent ethanol and add 1 mL Brij–35 solution.

Analyze eight sulfate standards covering the 0-to 100-mg/L operating range (5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 75.0, and 100.0 mg/L) with reagent solutions of varying Ba/MTB molar ratios. Do not vary the instrumental parameters but adjust the baseline as necessary. Plot an analytical curve of peak height versus known sulfate concentration for each Ba/MTB ratio. Determine least-squares equation and a coefficient of correlation on a programmable calculator or computer. From the coefficient of correlation, determine the optimum Ba/MTB ratio for a particular lot of MTB. Use this ratio when preparing subsequent solutions of MTB-barium chloride reagen. Repeat this calibration procedure only when a different lot of MTB is used.

5.6 *Sodium hydroxide*, 0.18*M*: *Cautiously* dissolve 7.2 g NaOH in demineralized water and dilute to 1 L.

5.7 *Sulfate* standard solution I, 1.00 mL = 1.00 mg SO_4: Dissolve 1.4787 g Na_2SO_4, dried for 2 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.8 *Sulfate* working standards: Prepare a blank and 1,000 mL each of a series of sulfate working standards by appropriate quantitative dilution of sulfate standard solution I as follows:

Sulfate standard solution I (mL)	*Sulfate concentration (mg/L)*
0.0	0.0
5.0	5.0

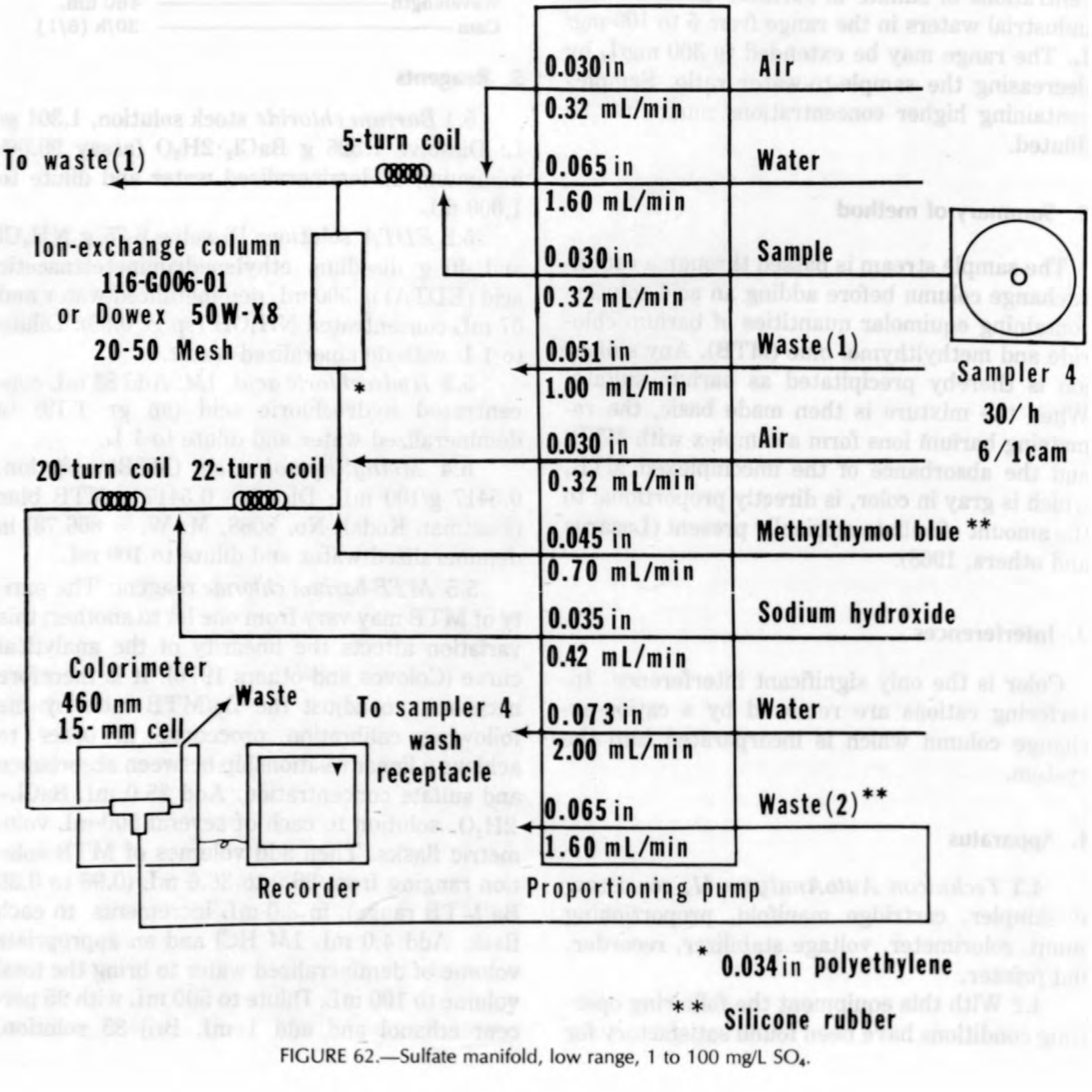


FIGURE 62.—Sulfate manifold, low range, 1 to 100 mg/L SO_4.

Sulfate standard solution I (mL)	*Sulfate conservation (mg/L)*
10.0	10.0
20.0	20
30.0	30
40.0	40
50.0	50
75.0	75
100.0	100
150.0	150
200.0	200
300.0	300

6. Procedure

6.1 Set up manifold (fig. 62 or 63) (NOTES 1 and 2).

NOTE 1. The manifold includes a cation-exchange column consisting of a 2.0-mm i.d. pyrex tube approximately 19 cm (7.5 in.) long filled with Dowex 50W–X8 (20 to 50 mesh), or equivalent, cation-exchange resin. The resin is held in place with a loose plug of glass wool on the exit end. Regenerate the resin daily with 1*M* HCl. Tygon transmission tubing, 2.0-cm (0.81-in.) i.d., may be used in place of the pyrex tube. A column must be replaced if air bubbles are introduced.

NOTE 2. At the end of each day wash the system with a solution of EDTA. This may be done by placing the MTB line and the NaOH line in water for a few minutes and then into the EDTA solution for 10 min. Wash the system with water for 15 min before shutting down.

6.2 Allow colorimeter and recorder to warm up for at least 30 min. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

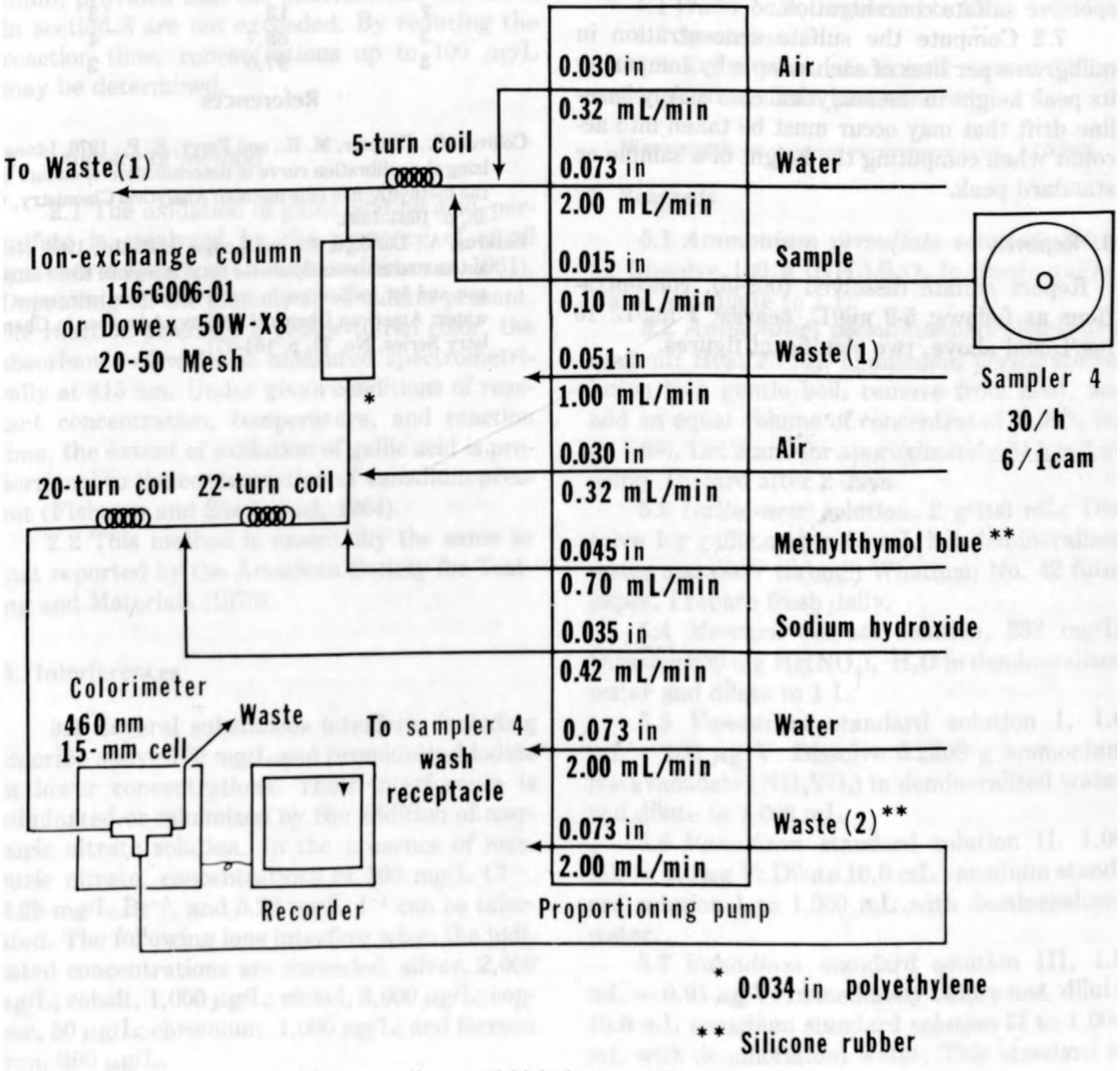


FIGURE 63.—Sulfate manifold, high range, 100 to 300 mg/L SO_4.

6.3 Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.4 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective sulfate concentration.

7.2 Compute the sulfate concentration in milligrams per liter of each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report sulfate dissolved (00945), concentrations as follows: 5-9 mg/L, nearest 1 mg/L; 10 mg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 10 to 100 mg/L may be expressed as follows:

$$S_T = 0.001X + 2.92$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of sulfate, milligrams per liter.

9.2 The precision results may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
7	13	13
3	68.7	4
3	97.0	2

References

Colovos, G., Panesar, M. R., and Parry, E. P., 1976, Linearizing the calibration curve in determination of sulfate by the methylthymol blue method: Analytical Chemistry, v. 48, p. 1693–1696.

Lazarus, A., Lorange, E., and Lodge, J. P., Jr., 1968, New automated microanalyses for total inorganic fixed nitrogen and for sulfate ion in water, *in* Trace inorganics in water: American Chemical Society, Advances in Chemistry Series, No. 73, p. 164–171.

Vanadium, dissolved, colorimetric, catalytic oxidation (I-1880-78)

Parameter and Code: Vanadium, dissolved (μg/L as V): 01085

1. Application

This method may be used to analyze most waters containing from 0.1 to 5.0 μg/L of vanadium, provided that the interferences identified in section 3 are not exceeded. By reducing the reaction time, concentrations up to 100 μg/L may be determined.

2. Summary of method

2.1 The oxidation of gallic acid by acid–persulfate is catalyzed by the presence of small amounts of vanadium (Jarabin and Szarvas, 1961). Depending on the amount of vanadium present, the reaction produces a yellow-to-red color, the absorbance of which is measured spectrometrically at 415 nm. Under given conditions of reactant concentration, temperature, and reaction time, the extent of oxidation of gallic acid is proportional to the concentration of vanadium present (Fishman and Skougstad, 1964).

2.2 This method is essentially the same as that reported by the American Society for Testing and Materials (1976).

3. Interferences

3.1 Several substances interfere, including chloride above 100 mg/L and bromide and iodide at lower concentrations. Their interference is eliminated or minimized by the addition of mercuric nitrate solution. In the presence of mercuric nitrate, concentrations of 100 mg/L Cl^{-1}, 0.25 mg/L Br^{-1}, and 0.25 mg/L I^{-1} can be tolerated. The following ions interfere when the indicated concentrations are exceeded: silver, 2,000 μg/L; cobalt, 1,000 μg/L; nickel, 3,000 μg/L; copper, 50 μg/L; chromium, 1,000 μg/L; and ferrous iron, 300 μg/L.

3.2 Nitric acid causes erratic and uncertain results.

4. Apparatus

4.1 *Water bath*, regulated to 25°C + 0.5°C.

4.2 *Spectrometer*.

4.3 Refer to manufacturer's manual for optimizing instrumental parameters:

Wavelength .... 415 nm.

5. Reagents

5.1 *Ammonium persulfate* solution, 100 g/L: Dissolve 100 g $(NH_4)_2S_2O_8$ in demineralized water and dilute to 1 L.

5.2 *Ammonium persulfate-phosphoric acid* reagent: Heat 25 mL ammonium persulfate solution to a gentle boil, remove from heat, and add an equal volume of concentrated H_3PO_4 (sp gr 1.69). Let stand for approximately 24 h before using. Discard after 2 days.

5.3 *Gallic acid* solution, 2 g/100 mL: Dissolve 1 g gallic acid in 50 mL hot demineralized water and filter through Whatman No. 42 filter paper. Prepare fresh daily.

5.4 *Mercuric nitrate* solution, 332 mg/L: Dissolve 350 mg $Hg(NO_3)_2 \cdot H_2O$ in demineralized water and dilute to 1 L.

5.5 *Vanadium* standard solution I, 1.0 mL = 100 μg V: Dissolve 0.2309 g ammonium metavanadate (NH_4VO_3) in demineralized water and dilute to 1,000 mL.

5.6 *Vanadium* standard solution II, 1.00 mL = 1.0 μg V: Dilute 10.0 mL vanadium standard solution I to 1,000 mL with demineralized water.

5.7 *Vanadium* standard solution III, 1.0 mL = 0.01 μg V: Immediately before use, dilute 10.0 mL vanadium standard solution II to 1,000 mL with demineralized water. This standard is used to prepare working standards at time of analysis.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.05 μg V (10.0 mL max) into a 23-mm absorbance cell, and adjust the volume to 10.0 mL.

6.2 Prepare a blank and sufficient standards containing from 0.00 to 0.05 μg V in 23-mm absorbance cells, and adjust the volume of each to 10.0 mL with demineralized water. (Standards must be included with each set of samples.)

6.3 Add 1.0 mL mercuric nitrate solution to each sample, standard, and blank and place all cells in a water bath (25°C). Allow 30 to 45 min for samples to reach temperature equilibrium.

6.4 Add 1.0 mL ammonium persulfate–phosphoric acid reagent (temperature equilibrated). Mix and return to water bath.

6.5 Add 1.0 mL gallic acid (temperature equilibrated). Mix thoroughly and return to water bath (NOTE 1).

NOTE 1. Since time and temperature are critical factors, the absorbance of each sample must be measured exactly 60 min after the gallic acid is added. When analyzing several samples, this is best accomplished by starting a stopwatch with the addition of gallic acid to the first sample and adding the gallic acid to subsequent samples at exactly 30-sec intervals.

6.6 After about 58 min remove from the water bath; and at exactly 60 min, measure the absorbance at 415 nm, using demineralized water as a reference (NOTE 2).

NOTE 2. All samples may be removed from the water bath 1 or 2 min before the 60-min period is up. The samples are then prepared for measurement, and the absorbance of each sample is measured exactly 60 min after the addition of the gallic acid (30-sec intervals between each measurement).

7. Calculations

7.1 Determine micrograms of vanadium in each sample from a plot of absorbances of standards.

7.2 Determine the concentration of vanadium in micrograms per liter as follows:

$$V\ (\mu g/L) = \frac{1{,}000}{\text{mL sample}} \times \mu g\ V \text{ in sample.}$$

8. Report

Report vanadium, dissolved (01085), concentrations as follows: less than 10 μg/L, 1 μg/L; 10 μg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within its designated range may be expressed as follows (American Society for Testing and Materials, 1976):

$$S_T = 0.069X + 0.422$$

where

S^T = overall precision, micrograms per liter, and
X = concentration of vanadium, micrograms per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (µg/L)*	*Relative deviation (percent)*
2 (24 replicates)	1.7	43

References

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 67.

American Society for Testing and Materials, 1976, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 446.

Fishman, M. J., and Skougstad, M. W., 1964, Catalytic determination of vanadium in water: Analytical Chemistry, v. 36, p. 1643.

Jarabin, Z., and Szarvas, P., 1961, Detection of small amounts of vanadium by catalytic reaction with the addition of gallic acid: Acta University Debrecen, v. 7, p. 131–135; Chemical Abstracts, v. 57, 9192c 1962.

Vanadium, dissolved, colorimetric, catalytic oxidation, automated (I–2880–78)

Parameter and Code: Vanadium, dissolved (μg/L as V): 01085

1. Application

This method may be used to analyze most waters containing from 1 to 10 μg/L vanadium, provided that the interferences identified in section 3 are not exceeded.

2. Summary of method

Small concentrations of vanadium catalyze the acid–persulfate oxidation of gallic acid. This reaction proceeds rapidly in the presence of vanadium but only very slowly in its absence. The amount of colored oxidation product formed by this reaction is directly proportional to the concentration of vanadium when temperature, reaction time, and concentration of reactants are carefully controlled (Fishman and Skougstad, 1964; Jarabin and Szarvas, 1961).

3. Interferences

3.1 Chloride, bromide, and iodide interfere when their concentrations exceed 100 mg/L, 10 μg/L, and 1 μg/L, respectively. Iron(II), iron(III), and copper(II) interfere when their concentrations exceed 300 μg/L, 500 μg/L, and 50 μg/L, respectively. The concentrations of other ions are rarely high enough to interfere.

3.2 Nitric acid causes erratic and uncertain results.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, proportioning pump, cartridge manifold, water bath, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 1 to 10 μg/L V:

Absorption cell	**15 mm.**
Wavelength	**410 nm.**
Cam	**20/h (1/1).**
Water-bath temperature	**60° C.**

5. Reagents

5.1 *Ammonium persulfate* solution, 100 g/L: Dissolve 100 g $(NH_4)_2S_2O_8$ in demineralized water and dilute to 1 L.

5.2 *Ammonium persulfate-phosphoric acid* reagent: Heat 25 mL ammonium persulfate solution to a gentle boil, remove from heat and add an equal volume of concentrated H_3PO_4 (sp gr 1.69). Let stand for approx 24 h before use. Before use dilute with 50 mL demineralized water. Discard after 2 days.

5.3 *Gallic acid* solution, 20 g/L: Dissolve 1 g gallic acid in 50 mL hot, demineralized water and filter through paper (Whatman No. 42, or equivalent). Prepare fresh daily. Keep the solution warm during analysis to prevent the gallic acid from precipitating.

5.4 *Mercuric nitrate* solution, 332 mg/L: Dissolve 350 mg $Hg(NO_3)_2 \cdot H_2O$ in demineralized water and dilute to 1 L.

5.5 *Vanadium* standard solution I, 1.00 mL = 100 μg V: Dissolve 0.2309 g ammonium metavanadate (NH_4VO_3) in demineralized water and dilute to 1,000 mL.

5.6 *Vanadium* standard solution II, 1.00 mL = 1.0 μg V: Dilute 10.0 mL vanadium standard solution I to 1,000 mL with demineralized water.

5.7 *Vanadium* standard solution III, 1.00 mL = 0.05 μg V: Dilute 50.0 mL vanadium standard solution II to 1,000 mL with demineralized water.

5.8 *Vanadium* working standards: Prepare a blank and 250 mL each of a series of vanadium working standards by appropriate quantitative dilution of vanadium standard solution III as follows:

Vanadium standard solution III (mL)	*Vanadium concentration (µg/L)*
0.0	0.0
5.0	1.0
10.0	2.0
20.0	4.0
30.0	6.0
40.0	8.0
50.0	10.0

6. Procedure

6.1 Set up manifold (fig. 64).

6.2 Allow colorimeter, recorder, and water bath to warm up for at least 30 min, or until the temperature of the water bath reaches 60°C. Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.3 Beginning with the most concentrated working standard, place a complete set of working standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.4 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective vanadium concentration.

7.2 Compute the concentration of vanadium in each sample by comparing its peak height to the analytical curve. Any baseline drift that may

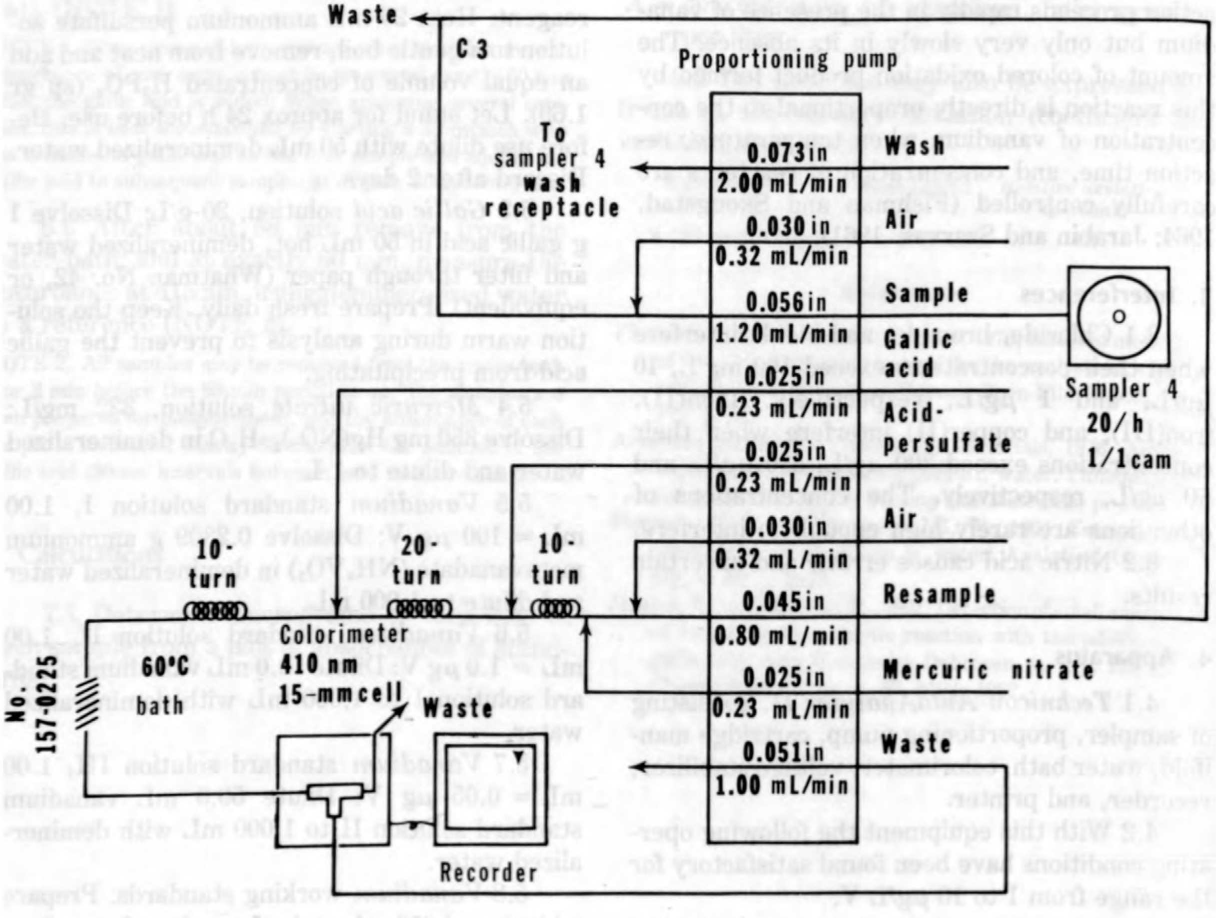


FIGURE 64.—Vanadium manifold.

occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report vanadium (V), dissolved (01085), concentrations as follows: less than 10 μg/L, nearest 1 μg/L; 10 μg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76–177, p. 67.

Fishman, M. J., and Skougstad, M. W., 1964, Catalytic determination of vanadium in water: Analytical Chemistry, v. 36, p. 1643–1646.

Jarabin, Z., and Szarvas, P., 1961, Detection of small amounts of vanadium by catalytic reaction with the addition of gallic acid: Acta University Debrecen, v. 7, p. 131–135; Chemical Abstracts, v. 57, 9192c (1962.)

Electrometry

Polarography

Principles of determination

Polarography, or voltametry, is an electrochemical method of analyzing reducible substances. The solution is placed in a glass cell containing two electrodes. One of these, the indicator electrode, is a capillary tube from which mercury is allowed to flow by drops; and the other, the reference electrode, is commonly a pool of mercury at the bottom of the cell. Other reference electrodes, such as the saturated calomel or silver–silver chloride electrode, may replace the pool of mercury, and noble metals may be used as indicator electrodes.

A voltage from −2 to 0 volts is applied to the dropping mercury electrode, and the current flow is measured. The flow of current is very small until the applied voltage is increased to a value large enough to cause the substance being determined to be reduced at the dropping mercury electrode. As the applied voltage is increased above this critical value, the current flow first increases rapidly, then gradually reaches a limiting value and remains essentially at this level as the voltage is further increased. The voltage required to cause the rapid increase in current is characteristic of the substance being reduced, and, thus, qualitatively identifies it. The limiting current attained is controlled by the rate of diffusion of the reducible substance from the body of the solution to the surface of the mercury drops, and its magnitude is proportional to the concentration of the substance present.

To determine dissolved oxygen, for example, a fixed potential of −0.6 volt is applied. At this voltage, oxygen is reduced as follows:

$$O_2 + 2H_2O + 2e \rightarrow H_2O_2 + 2OH^{-1} \text{ (neutral or alkaline solution)}$$

$$O_2 + 2H^{+1} + 2e \rightarrow H_2O_2 \text{ (acid solution).}$$

The magnitude of the current flow is a measure of the concentration of dissolved oxygen. A complete presentation of the theory and practice of polarography may be found in Kolthoff and Lingane (1952).

Commercial modifications of the basic design incorporate various combinations of electrodes, and membranes permeable mainly to O_2. When operated with care, and according to the manufacturer's directions, satisfactory determinations of dissolved oxygen may readily be obtained.

Interferences

The polarographic technique is generally less subject to interference than are other dissolved-oxygen methods, and it is satisfactory for use in wastes and polluted waters. When the dropping mercury cathode is used, cyanides and sulfides do not interfere, although high concentrations of surface-active substances which are absorbed to the mercury drop do interfere. The reduction of certain cations, such as zinc and nickel, may be a problem in some samples. Interference by substances such as chlorine, iodine, bromine, and dichromate is effectively eliminated by adding sodium arsenite or thiosulfate to the sample before determining its oxygen concentration.

Noble metal polarographic electrodes, covered with a membrane permeable to O_2, are subject to interference from the presence of other dissolved gases, such as H_2S, SO_2, and the halogens. Other dissolved substances do not normally interfere.

Specific conductance

Specific conductance is determined by using a Wheatstone bridge, in which a variable resistance is adjusted so that it is equal to the resistance of an unknown solution between two electrodes of either platinized platinum or other suitable material, such as graphite. The null point is detected by an ac (alternating current) galvanometer or a cathode ray tube. Alternating current is necessary to prevent polarization of the electrodes. Direct current produces gas bubbles on the electrodes that greatly increase the resistance and change the concentration of the electrolyte in the vicinity of the electrodes. The electrodes are coated with a thin layer of amorphous platinum, which tends to absorb gases and catalyzes their reunion, thereby minimizing polarization.

The electrode cell may be the dip, cup, or pipet type. The pipet cells are generally preferred for routine laboratory use, because they require a smaller volume of water for the determination, the water can be drawn directly from a narrow-mouth sample bottle without transferring it to another container, the total time for the determination is less, and there is less mechanical agitation of the water sample. Dip or cup type cells are preferable for fieldwork.

For many years a bridge fabricated within the Geological Survey has been used successfully for the determination of specific conductances ranging from about 25 to 35,000 μmho/cm. This bridge is used with a pipet cell (cell constant of approximately 0.3 cm^{-1}). Above about 3,000 μmho the determined specific conductances are lower than the true values by more than 3 percent, and the percentage of error increases gradually as the ionic concentration of the water increases.

Several combinations of bridges and commercially available cells have been investigated. The line-operated Serfass Model RCN 15 bridge has proved satisfactory for routine laboratory determinations when used as a resistance-measuring device and with a pipet cell having a constant of 0.3 cm^{-1}. A more detailed discussion of this instrument (and the Wheatstone bridge assembly made by the Geological Survey) is presented by Rainwater and Thatcher (1960).

Direct-reading conductivity meters are commercially available, and several such instruments investigated by the Geological Survey gave results comparable in accuracy to the resistance method. The Lab-Line Portable Lectro Mho-Meter (Cat. No. 11000–Mark IV) operates on a 9-volt battery; transistorized, solid-state circuitry makes the instrument durable for field use. Also, the Beckman Type RB3 Solu-Bridge portable conductivity meter has been found suitable for routine field and laboratory use. It is lightweight, yet rugged and durable, and provides measurements of acceptable accuracy and sensitivity.

pH

pH meters measure the electrical potential between two suitable electrodes immersed in the solution to be tested. The reference electrode assumes a constant potential, and the indicating electrode assumes a potential dependent on the hydrogen-ion activity of the solution. Electrode potential is the difference in potential between the electrode and the solution in which it is immersed. The calomel electrode, which is a widely used reference electrode in water analysis, consists of a mercury–calomel rod immersed in a saturated solution of potassium chloride; this electrode has a half-cell potential of +0.246 volt. Electrical connection with the sample is provided through porous fibers sealed into the immersion end. A hydrogen-ion-selective glass electrode is normally used as an indicating electrode. The glass electrode has several features that recommend it for pH measurements. Among the most important are that it is not affected by oxidizing or reducing substances in the sample and that it can be used to measure the pH of turbid samples and (or) colloidal suspensions. The basic design is a silver–silver chloride or mercury–mercurous chloride electrode immersed in a solution of known pH and completely sealed in glass.

The mechanism by which the glass membrane responds to hydrogen-ion activity involves absorption of hydrogen ions on both sides of the membrane proportionally to the activity of the hydrogen ions in solution. The cell for measuring the pH of a solution is of the following type:

$$\underbrace{\text{Ag}^0:\ \text{AgCl}\ \Big\|\ \begin{matrix}\text{Solution of}\\ \text{known pH;}\end{matrix}\ \ \begin{matrix}\text{Glass}\\ \text{membrane;}\end{matrix}}_{\text{Glass electrode}}\ \ \begin{matrix}\text{Solution of}\\ \text{unknown pH}\end{matrix}\ \Big\|\ \text{Hg}^0:\ \text{HgCl.}$$

The half-cell potential of the glass electrode is a logarithmic function of the difference in hydrogen-ion activity of the solutions on either side of the glass membrane. To measure this potential a high impedance electrometer circuit is used, because the resistance of the glass membrane is so great.

pH meters differ in their design, construction, and applicability to all phases of water analysis in which the instrument is used. Desired features in a line-operated pH meter are built-in voltage regulator, accuracy of 0.02 pH, stability of calibration, built-in temperature-compensating mechanism, durable electrodes, and a design that permits insertions of the electrodes, stirrer, and a buret into a suitable vessel for titrations. For pH determinations in the field the instrument should also be rugged, compact, and battery operated. pH meters should be carefully calibrated with two buffer solutions that bracket the pH range of the test samples, and the calibration should be checked during extended periods of operation. A third standard buffer should be used, the data of this third buffer will automatically indicate stressed or faulty electrodes by the theoretical versus actual curve being nonlinear.

Ion-selective electrodes

Analogous to the glass electrode, which is selectively sensitive to hydrogen-ion activities, a considerable number of other ion-selective electrodes based on liquid ion-exchange or solid-state principles have become available for use in water analysis and other applications. Notable among these are the fluoride-ion electrode, the ammonia electrode, and the dissolved oxygen (membrane) probe. Of some interest to the water analyst, also, is the water-hardness electrode, sensitive to calcium- and magnesium-ion activities.

The principles of measurement using these electrodes are analogous to the measurement of pH with the glass electrode. An expanded scale pH meter is necessary to measure the small potential differences resulting from small changes in the activity of the ion being measured. The electrode response is Nernstian with respect to ion activity, and often an effective concentration range several orders of magnitude may be covered, thus making the ion-selective electrode a very versatile tool. Measurements at very low concentrations, however, often take an inordinately long time to reach equilibrium. Nevertheless, such electrodes are now commonly used to determine fluoride-ion concentrations, and dissolved gases such as ammonia and oxygen.

Additional information on the theory and application of ion-selective electrodes may be found in the manufacturer's literature and in Durst (1969).

References

Durst, R. A., ed., 1969, Ion-selective electrodes: National Bureau of Standards Special Publication 314, U.S. Government Printing Office, Washington, D.C., 452 p.

Kolthoff, I. M., and Lingane, J. J., 1952, Polarography [2d ed.]: New York, Interscience Publishers, 990 p.

Rainwater, F. H., and Thatcher, L. L., 1960, Methods for collection and analysis of water samples: U.S. Geological Survey Water-Supply Paper 1454, p. 58–60.

Electrometric Methods

Acidity, electrometric titration (I–1020–78)

Parameter and Code: Acidity (mg/L as H): 71825; Acidity (mg/L as $CaCO_3$): (00435)

1. Application

This method is applicable to many acidic samples. When the sample is suspected or known to contain mostly weak acids, however, the construction of a neutralization curve is imperative, and the acidity value is then reported and interpreted in terms of the character of the curve obtained.

2. Summary of method

2.1 Acidity is determined by titrating the sample with a standard solution of a strong base to an electrometrically observed endpoint pH of 8.3. The titration is carried out at room temperature, except that the sample is heated briefly near the end of the titration to increase the rate of hydrolysis of metal ions present.

2.2 For additional information concerning the determination of acidity and for instructions for constructing an electrometric titration curve, see ASTM Method D 1067–70, Standard Methods of Test for Acidity or Alkalinity of Water (American Society for Testing and Materials, 1976).

3. Interferences

Dissolved gases which are acidic, such as CO_2 and H_2S, may be easily lost from the sample. If any substantial part of the acidity is due to gaseous solutes, special care must be taken to prevent their escape prior to and during the titration. Gases are less soluble in warm water than in cold; hence, the sample must be kept chilled until analyzed, and even then the analysis must be performed as soon as possible. Stirring and agitation of the sample cause expulsion of dissolved gases; care must be taken to avoid unnecessary agitation of the sample. A tightly capped bottle is essential for storing and transporting samples. The determination should be performed at the time of sampling for highest accuracy.

4. Apparatus

4.1 *Buret*, 50-mL capacity.

4.2 *Hotplate.*

4.3 *pH meter.*

4.4 *Stirrer*, magnetic.

5. Reagents

5.1 *Sodium hydroxide*, 2*N*: Cover approx 100 g NaOH with water until the surface coating is dissolved. Discard the supernatant liquid and immediately dissolve the remaining NaOH in approx 1 L of carbon dioxide-free water. Store in a tightly capped polyethylene bottle.

5.2 *Sodium hydroxide* standard solution, approx 0.025*N*: Dilute 12 mL 2*N* NaOH with carbon dioxide-free water to approx 1 L. Standardize the solution against primary standard potassium hydrogen phthalate ($KHC_8H_4O_4$) as follows: Lightly crush 3 g of the salt to a fineness of approx 100 mesh and dry for at least 1 h at 110°C. Dissolve about 2 g, accurately weighed to the nearest milligram, in carbon dioxide-free water and dilute to 500.0 mL. Titrate 50.0 mL of the solution with the NaOH standard solution to pH 8.6:

Normality of NaOH

$$= \frac{\text{g } KHC_8H_4O_4 \text{ in 50.0 mL} \times 4.896}{\text{mL NaOH}}$$

6. Procedure

Samples should be collected in tightly capped polyethylene bottles, with as little agitation as possible, particularly if it is suspected or known that any significant part of the acidity is due to dissolved gases. Chill or otherwise keep the sample cool during transportation to the laboratory and perform the determination as soon as possible. Do not open the sample bottle until ready to determine the acidity, and then perform the determination without delay once the bottle has been opened.

6.1 Carefully pipet an aliquot of sample containing less than 1.0 mg H^{+1} (50.0 mL maximum) into a 150-mL beaker. Avoid disturbing any sediment in the sample bottle. Do not filter.

6.2. Insert the beaker in the titration assembly and record the pH.

6.3 Titrate the sample with standard NaOH solution to pH 8.3.

6.4 Heat the solution to about 90°C (do not boil), and maintain this temperature for 2 min.

6.5 Cool to room temperature and resume the titration, titrating again to a final pH of 8.3. Record the total volume of titrant used (mL_b).

7. Calculations

7.1 Determine acidity as me/L as follows:

$$\text{Acidity, me/L} = \frac{mL_b}{mL_s} \times N_b \times 10^3 .$$

7.2 Determine acidity as hydrogen in mg/L as follows:

$$\text{Acidity, mg/L as H} = \frac{mL_b}{mL_s} \times N_b \times 1.008 \times 10^3$$

7.3 Determine acidity as $CaCO_3$ in mg/L as follows:

$$\text{Acidity, mg/L as } CaCO_3$$

$$= \frac{mL_b}{mL_s} \times N_b \times 10^3 \times 50.05$$

where

mL_b and mL_s = volumes of standard NaOH solution and sample, respectively, and

N_b = normality of standard NaOH solution.

8. Report

8.1 Report acidity values in milliequivalents per liter or milligrams per liter as H as follows: less than 10 me/L (mg/L), one decimal; 10 me/L (mg/L) and above, two significant figures.

8.2 Acidity values reported as milligrams per liter H^{+1} correspond to parameter code 71825.

8.3 Report acidity values in milligrams per liter as $CaCO_3$ (00435) as follows: less than 100 mg/L, whole numbers; 100 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

American Society for Testing and Materials, 1976, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 111.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 40.

Alkalinity, electrometric titration (I–1030–78)

Parameters and Codes: Alkalinity (mg/L as $CaCO_3$): 00410

1. Application

This method is suitable for water with any amount of alkalinity, but aliquots for analysis should be taken to avoid a titration volume of standard acid in excess of 50 mL.

2. Summary of method

2.1 Alkalinity is determined by titrating the water sample with a standard solution of strong acid. The end point of the titration is selected as pH 4.5.

2.2 For waters that contain only small quantities of dissolved mineral matter, the alkalinity determination is likely the largest single source of error in the analysis. Alkalinity is very susceptible to change between time of collection and analysis, with changes occurring more rapidly after the sample bottle is opened. The overall alkalinity value is probably somewhat more stable than the relative values of the common alkalinity components. Unless a gross error is made in the initial determination of alkalinity, it is seldom advisable to try to check the results if several days have elapsed since the bottle was first opened. The alkalinity of some samples may change appreciably in a few hours. The determination should be performed at the time of sampling for highest accuracy.

2.3 Selection of pH 4.5 as the titration end point for determining total alkalinity is arbitrary and corresponds to the true equivalence point only under ideal conditions. The equivalence point of the bicarbonate–carbonic acid titration varies with the concentration of bicarbonate present; the deviation from pH 4.5 is particularly serious at low bicarbonate-ion concentrations. When greater accuracy in the determination is needed, the titration equivalence point may be determined for each sample by adding the titrant in small increments in the vicinity of pH 4.5 and recording the pH of the solution after each measured addition. The true end point is then determined from either (a) a plot of pH versus total titrant volume, where the end point is the pH corresponding to a change in slope of the curve, or (b) a plot of

$$\frac{\Delta \mathrm{pH}}{\Delta \mathrm{mL\ titrant}} \text{ versus titrant volume,}$$

where the end point is that volume at which there occurs a maximum rate of change of pH per volume of titrant added.

There are other methods for arriving at a more reliable determination of total alkalinity. Barnes (1964) discusses the several factors involved in the accurate measurement of alkalinity, particularly under field conditions. A routine laboratory method for determining total alkalinity with improved accuracy for widely differing types of water has been described by Larson and Henley (1955) and further evaluated by Thomas and Lynch (1960). A rather complete consideration of carbonate equilibria and their analytic considerations may be found in a publication by Stumm and Morgan (1970).

3. Interferences

Salts of weak organic and inorganic acids, such as silicic, which cannot be corrected for, may yield erroneous results when present in large amounts. In addition, oils and greases, if present, may tend to foul the pH meter electrode and prevent its proper operation.

4. Apparatus

4.1 *Buret*, 50-mL capacity.
4.2 *pH meter*.
4.3 *Stirrer*, magnetic.

5. Reagents

5.1 *Sodium carbonate* standard solution, 1.0 mL ≎ 1.00 mg HCO_3^{-1}: Dry 1.0 g primary standard Na_2CO_3 at 150°C to 160°C for 2 h. Cool in a desiccator and dissolve 0.8685 g in carbon dioxide-free water; dilute to 1,000 mL.

5.2 *Sulfuric acid* standard solution, 0.01639*N*, 1.00 mL ≎ 1.00 mg HCO_3: Cautiously add 0.5 mL concentrated H_2SO_4 (sp gr 1.84) to 950 mL water. (The titrant is stable for several months if protected from ammonia fumes and is usually prepared in larger quantities.) After the solution has been thoroughly mixed, standardize it by titrating 25.00 mL Na_2CO_3 standard solution (1.00 mL ≎ 1.00 mg HCO_3) to pH 4.5. Adjust the concentration of the sulfuric acid standard solution to exactly 0.01639*N* by dilution with water or by addition of dilute acid as indicated by the first titration. Confirm the exact normality by restandardization. Although the sulfuric acid standard solution is reasonably stable, its normality should be verified at least monthly (NOTE 1).

NOTE 1. It may be found more convenient to prepare standard sulfuric acid that is not exactly 0.01639*N*. Standard sulfuric acid that is approximately 0.01639*N* (but the exact normality of which is known) can be used if the appropriate factor is applied in the calculations.

6. Procedure

Water samples for the determination of alkalinity should not be filtered, diluted, concentrated, or altered in any way. The determination should be performed without delay after the sample bottle has been opened.

6.1 From a settled, unfiltered sample, pipet a volume containing less than 40 mg alkalinity as HCO_3 (50.0 mL max) into a suitable beaker.

6.2 Insert beaker in titration assembly and record the pH.

6.3 Titrate immediately with 0.01639*N* H_2SO_4 and record the titrant volume at 4.5.

7. Calculations

Total alkalinity as $CaCO_3$ in mg/L

$$= \frac{1{,}000}{mL_s} \times 0.8202 \times (mL_a \text{ to pH } 4.5)$$

where

mL_a and mL_s = volumes of standard acid and sample, respectively.

8. Report

Report alkalinity, total (00410), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

9.1 The precision of this method within the range of 20 to 155 mg/L $CaCO_3$ may be expressed as follows:

$$S_T = 0.082X + 0.73$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of alkalinity as $CaCO_3$, milligrams per liter.

9.2 The statistical results may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L as $CaCO_3$)*	*Relative deviation (percent)*
14	20	13
19	96	8
24	154	9

References

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535–H, 17 p.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 42.

Larson, T. E., and Henley, Laurel, 1955, Determination of low alkalinity or acidity in water: Analytical Chemistry, v. 27, p. 851.

Stumm, Werner, and Morgan, J. J., 1970, Aquatic Chemistry: New York, John Wiley and Sons, 583 p.

Thomas, J. F. J., and Lynch, J. J., 1960, Determination of carbonate alkalinity in natural waters: American Water Works Association Journal, v. 52, p. 259–268.

Alkalinity, electrometric titration, automated (I–2030–78)

Parameter and Code: Alkalinity (mg/L as $CaCO_3$): 00410

1. Application

This method is suitable for analyzing water samples with any amount of alkalinity, but the sample size should be selected to avoid a titration volume of standard acid greater than 30 mL.

2. Summary of method

2.1 Alkalinity is determined by titrating the sample with a standard solution of a strong acid. The end point of the titration is selected as pH 4.5.

2.2 For additional information on the principles of the method see Alkalinity (I–1030).

3. Interferences

See Alkalinity (I–1030).

4. Apparatus

4.1 *Automatic titrator*, with potentiometric assembly.

4.2 *Combination electrode* (glass and reference). Separate glass and reference electrodes are also satisfactory.

5. Reagents

5.1 *Sodium carbonate* standard solution, 1.00 mL ≎ 1.00 mg HCO_3: Dry 1 g primary standard sodium carbonate (Na_2CO_3) at 150°C to 160°C for 2 h. Cool in a desiccator and dissolve 0.8685 g in carbon dioxide-free water; dilute to 1,000 mL.

5.2 *Sulfuric acid* standard solution, 0.01639*N*, 1.00 mL ≎ 1.00 mg HCO_3: Cautiously add 0.5 mL concentrated H_2SO_4 (sp gr 1.84) to 950 mL water. (The titrant is stable for several months if protected from ammonia fumes, and it is usually prepared in larger quantities.) After the solution has been thoroughly mixed, standardize it by titrating 25.00 mL Na_2CO_3 standard solution (1.00 mL ≎ 1.00 mg HCO_3) to pH 4.5. Adjust the concentration of the sulfuric acid standard solution to exactly 0.01639*N* by dilution with water or by addition of dilute acid as indicated by the first titration. Confirm the exact normality by restandardization. Although the sulfuric acid standard solution is reasonably stable, its normality should be verified at least monthly (NOTE 1).

NOTE 1. It may be found more convenient to prepare standard sulfuric acid that is not exactly 0.01639*N*. Standard sulfuric acid that is approximately 0.01639*N* (but the exact normality of which is known) can be used if the appropriate factor is applied in the calculations.

6. Procedure

6.1 Water samples for the determination of alkalinity should not be filtered, diluted, concentrated, or altered in any way. The determination should be performed without delay after the sample bottle has been opened.

6.2 Set up the automatic titrator according to the directions given in the instruction manual.

6.3 From a settled, unfiltered sample, transfer or pipet a volume of sample to the vessel specified by the manufacturer.

6.4 Set the end point to pH 4.5 following the instructions provided with the instrument.

6.5 Place the samples in position in the titration assembly and activate the automatic potentiometric titration, using 0.01639*N* H_2SO_4 as titrant. Continue titrations until all samples have been titrated.

7. Calculations

Total alkalinity as $CaCO_3$ (mg/L)

$$= \frac{1{,}000}{mL_s} \times 0.8202 \times (mL_a \text{ to pH } 4.5)$$

where

mL_a and mL_s = volumes of standard acid and sample, respectively.

8. Report

Report alkalinity, total (00410), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

The precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (mg/L as $CaCO_3$)*	*Relative deviation (percent)*
5	20	7
5	151	12

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 42.

Color, electrometric, visual comparison (I–1250–78)

Parameter and Code: Color (platinum–cobalt units): 00080

1. Application

This method may be used to measure the color of water samples whose colors reasonably match from 0 to 70 units of the Hazen scale and which contain no excessive amount of sediment. Samples that have a color unit greater than 70 must first be diluted.

2. Summary of method

The color of the water is compared to that of colored glass disks which have been calibrated to correspond to the platinum-cobalt scale of Hazen (1892). The unit of color is that produced by 1 mg/L of platinum. A small amount of cobalt is generally added to aid in color matching. The Hazen scale is usually satisfactory for most waters, but the hues and shades of some waters may not easily be compared with standards. If the hue of the water does not compare with that of the standard there is very little that can be done, other than to visually compare the optical densities of the sample and standard. Highly colored waters should not be diluted more than necessary because the color of the diluted sample often is not proportional to the dilution.

3. Interferences

Turbidity generally causes the observed color to be greater than the true color, but there is some disagreement as to the magnitude of the effect of turbidity. The removal of turbidity is a recurrent problem in the determination of color. Color is removed by absorption on suspended material. Filtration of samples to remove turbidity frequently removes some of the color-imparting solutes by absorption on the sediments or on the filter medium. Centrifuging is preferable to filtration, but centrifuging may not be completely effective in removing very finely divided particles. Flocculation of the dispersed particles with a strong electrolyte has been proposed (Lamar, 1949) and is sometimes effective. The process of flocculation decolorizes some waters and is, therefore, not suitable in all cases.

4. Apparatus

Color comparator, with standard color disks, covering the range 0 to 70 color units.

5. Reagents

None required.

6. Procedure

6.1 Fill one instrument tube with the sample of water, level the tube, insert the glass plug, making sure that no air bubbles are trapped, and insert the tube into the comparator.

6.2 Use demineralized water as a blank in the second tube.

6.3 The color comparison is made by revolving the disk until the colors of the two tubes match. Samples having color values greater than 70 must first be diluted.

7. Calculations

Read the color directly from the matching color standard; apply the proper dilution if required.

8. Report

Report color (00080) (platinum-cobalt units) as follows:

Color unit	*Record units to nearest—*
1-50	1
51-100	5
101-250	10
251-500	20

9. Precision

Precision data are not available for this method.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 82.

Hazen, Allen, 1892, A new color standard for natural waters: American Chemical Society Journal, v. 12, p. 427.

Lamar, W. L., 1949, Determination of color of turbid waters: Analytical Chemistry, v. 21, p., 726.

Fluoride, dissolved, electrometric, ion-selective electrode (I–1327–78)

Parameter and Code: Fluoride, dissolved, (mg/L as F): 00950

1. Application

This method is applicable to the measurement of dissolved fluoride in finished waters, natural waters, brines, and industrial waste waters. Concentrations of at least 0.1 mg/L can be determined with confidence. Samples containing more than 3 mg/L of fluoride must first be diluted.

2. Summary of method

2.1 Fluoride is determined potentiometrically in a buffered sample with use of an ion-selective (fluoride) electrode in conjunction with a standard calomel reference electrode (SCE), and a pH meter having an expanded millivolt scale (Frant and Ross, 1968).

2.2 The fluoride electrode consists of a laser-type doped lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by:

Ag/AgCl, Cl^{-1} ($0.3M$),

F^{-1} ($0.001M$)/LaF_3/test solution/SCE.

3. Interferences

3.1 The ion-selective electrode measures fluoride-ion activity, so that high concentrations of dissolved solutes (which lower the ion-activity coefficient) cause an error in the determination. Addition of the buffer solution, which contains a high concentration of dissolved solutes, effectively masks minor variations in the salt content of the samples and, therefore, minimizes this error.

3.2 The optimum pH for measurement is between 5.0 and 8.5. Below this range, HF is only slightly dissociated, and above a pH of 8.5, hydroxyl ion interferes. The addition of the buffer solution will adjust the pH of most samples to between 5.0 and 5.5.

3.3 Several polyvalent cations capable of complexing fluoride ion interfere. These include Fe^{+3}, Al^{+3}, and Si^{+4}. The extent of their interference is proportional to their concentration, so that dilution of the sample with an equal volume of buffer solution reduces the interference. The of buffer solution reduces the interference. The (1,2-cyclohexylenedinitrilo)tetraacetic acid (CDTA) in the buffer solution complexes up to 10,000 μg Fe^{+3}, 2,000 μg Al^{+3}, and 100 mg SiO_2.

3.4 Orthophosphate-phosphorus concentrations of 25 mg/L, and sulfate and chloride concentrations of 3,000 mg/L do not interfere (Harwood, 1969).

4. Apparatus

4.1 *Fluoride ion-selective electrode.*

4.2 *pH meter*, with expanded scale.

4.3 *Reference electrode*, standard calomel, sleeve-type.

4.4 *Stirrer*, magnetic, teflon-coated stirring bar.

5. Reagents

5.1 *Buffer* solution, pH 5.0 to 5.5: To approx 500 mL demineralized water in a 1-L beaker add 57 mL glacial $HC_2H_3O_2$, 58 g NaCl, and 4.5 g (1,2-cyclohexylenedinitrilo)tetraacetic acid (CDTA). Stir to dissolve and cool to room temperature. Adjust the pH of the solution to between 5.0 and 5.5 with $5M$ sodium hydroxide (about 170 mL will be required). Dilute to 1 L with demineralized water.

5.2 *Fluoride* standard solution I, 1.00 mL = 0.10 mg F^{-1}: Dissolve 0.2210 g NaF in demineralized water and dilute to 1,000 mL.

5.3 *Fluoride* standard solution II, 1.00 mL = 0.01 mg F^{-1}: Dilute 100 mL fluoride standard solution I to 1,000 mL with demineralized water.

6. Procedure

6.1 Adjust pH meter according to manufacturer's instructions.

6.2 Pipet 25.0 mL sample into 100-mL beaker.

6.3 Prepare a series of three standards containing 0.1, 1.0, and 2.0 mg/L fluoride, and pipet 25.0 mL of each into 100-mL beakers.

6.4 Add 25.0 mL buffer solution to each sample and standard.

6.5 Place beaker on magnetic stirrer, immerse electrodes, and measure potential while mixing. The electrodes must remain in the solution until reading has stabilized. This may require 5 min or more.

7. Calculations

7.1 Construct a graph of potential in millivolts (mV) versus concentration of standards (mg/L) on semilog paper, with the concentrations plotted on the logarithmic axis.

7.2 From the graph, determine the milligrams per liter of fluoride in each sample.

8. Report

Report fluoride, dissolved (00950), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
13	0.62	16
6	1.1	26
14	3.8	11

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 93.

Frant, M. S., and Ross, J. W., Jr., 1968, Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water supplies: Analytical Chemistry, v. 40, p. 1169.

Harwood, J. E., 1969, The use of an ion-selective electrode for routine fluoride analysis on water samples: Water Research, v. 3, p. 273–280.

Fluoride, dissolved, electrometric, ion-selective electrode, automated
(I-2327-78)

Parameter and Code: Fluoride, dissolved (mg/L as F): 00950

1. Application

This method may be used to analyze samples containing from 0.1 to 3.0 mg/L of fluoride and is applicable to the analysis of finished waters, natural waters, and industrial waste waters with conductivities less than 20,000 μmho/cm. Samples with higher conductivities must first be distilled by the procedure given below.

2. Summary of method

2.1 Fluoride is determined potentiometrically in a buffered sample with use of an ion-selective (fluoride) electrode in conjunction with a standard calomel reference electrode (SCE), and a pH meter having an expanded millivolt scale (Frant and Ross, 1968; Harwood, 1969; Bellack, 1958).

2.2 The fluoride electrode consists of a laser-type doped lanthanum fluoride crystal, across which a potential is developed by fluoride ions. The cell may be represented by:

Ag/AgCl, Cl^{-1} (0.3*M*),

F^{-1} (0.001*M*)/LaF$_3$/test solution/SCE.

This electrode deteriorates in time and must be replaced when results become erratic.

3. Interferences

3.1 The ion-selective electrode measures fluoride-ion activity; thus high concentrations of dissolved solutes (which lower the ion-activity coefficient) cause an error in the determination. Addition of a buffer solution that contains a high concentration of dissolved solutes effectively masks minor variations in the salt content of the samples and, therefore, minimizes this error.

3.2 The optimum pH for measurement is between 5.0 and 8.5. Below this range, HF is only slightly dissociated, and above a pH of 8.5 hydroxyl ion interferes. The addition of the buffer solution will adjust the pH of most samples to between 5.0 and 5.5.

3.3 Several polyvalent cations capable of complexing fluoride ion interfere. These include Fe^{+3}, Al^{+3}, and Si^{+4}. The extent of their interference is proportional to their concentration, so that dilution of the sample with an equal volume of buffer solution reduces the interference. The (1,2-cyclohexylenedinitrilo)tetraacetic acid (CDTA) in the buffer solution complexes up to 10,000 μg Fe^{+3}, 2,000 μg Al^{+3}, and 100 mg SiO$_2$.

3.4 Orthophosphate-phosphorus concentrations of 25 mg/L, and sulfate and chloride concentrations of 3,000 mg/L do not interfere (Harwood, 1969).

4. Apparatus

4.1 *Distillation assembly*, consisting of a round-bottom distilling flask, adapter, connecting tube, condenser, receiving flask, and thermometer (250°C) (fig. 65).

4.2 *Technicon AutoAnalyzer II*, consisting of a sampler, proportioning pump, cartridge manifold, heating bath, recorder, potentiometer, and printer.

4.3 *Fluoride ion-selective electrode*.

4.4 *Reference electrode*, standard calomel.

4.5 With this equipment a 40/h (2/1) cam has been found satisfactory for the range from 0.1 to 3.0 mg/L.

5. Reagents

5.1 *Brij-35* solution: 30 percent aqueous solution (Baker Cat. No. C 706, or equivalent).

5.2 *Buffer* solution with 0.33 mg/L fluoride, pH 5.0 to 5.5: To approx 500 mL demineralized

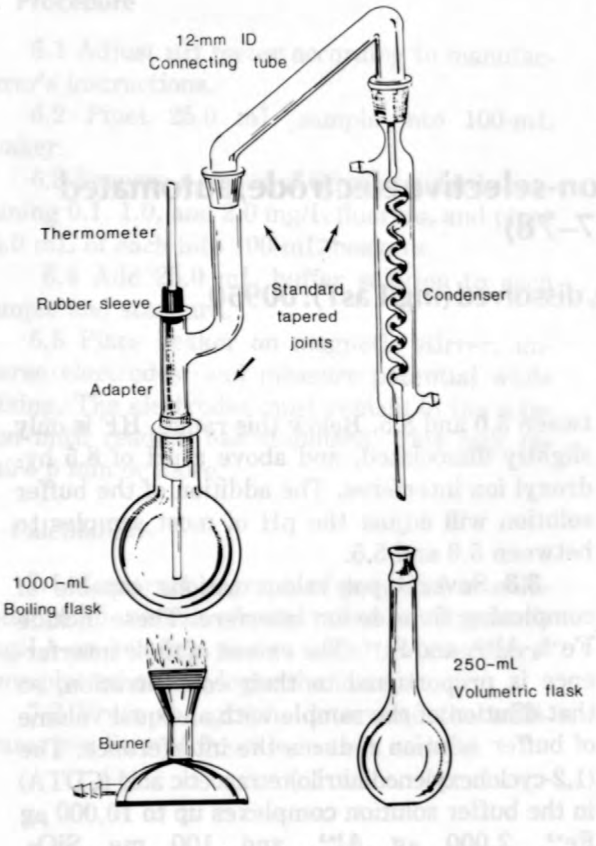


FIGURE 65.—Fluoride distillation assembly.

water in a 1-L beaker add 57 mL glacial $HC_2H_3O_2$, 58 g NaCl, and 4.5 g (1,2-cyclohexylenedinitrilo)tetraacetic acid (CDTA). Stir to dissolve and cool to room temperature. Adjust the pH of the solution to between 5.0 and 5.5 with 5*M* NaOH (about 170 mL will be required). Filter if necessary and add 33 mL of fluoride standard solution II, and 0.5 mL of Brij–35 solution. Dilute to 1,000 mL with demineralized water.

5.3 *Fluoride* standard solution I, 1.00 mL = 1.00 mg F: Dissolve 2.2101 g NaF in demineralized water and dilute to 1,000 mL.

5.4 *Fluoride* standard solution II, 1.00 mL = 0.01 mg F: Dilute 10 mL fluoride standard solution I to 1,000 mL with demineralized water.

5.5 *Fluoride* working standards: Prepare a blank and 500 mL each of a series of fluoride working standards by appropriate quantitative dilution of fluoride standard solution II as follows:

Fluoride standard solution II (mL)	*Fluoride concentration (mg/L)*
0.0	0.00
10.0	.20
25.0	.50
50.0	1.00
76.0	1.50
100.0	2.00
125.0	2.50
150.0	3.00

5.6 *Silver sulfate*, powder.

5.7 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 *Distillation procedure:* If the specific conductance of the sample is less than 20,000 µmho/cm, the distillation may be omitted.

6.1.1 Place 400 mL demineralized water in a 1-L distilling flask containing a few glass beads. *Cautiously*, and with constant swirling, add 200 mL concentrated sulfuric acid. Connect the flask to the condenser assembly and distill until the temperature of the acid mixture reaches 180°C. At this point the proper acid concentration has been reached. The acid need not be replaced until the accumulation of nonvolatile material is sufficient to cause interference. An occasional recovery check with a standard fluoride sample will indicate the need for replacement.

6.1.2 Cool to room temperature.

6.1.3 *Cautiously*, and with constant swirling, add 250 mL sample to the acid mixture in the distillation flask.

6.1.4 Distill until 250 mL distillate has been collected and the temperature of the acid mixture is again 180°C. When the temperature of the acid mixture at the completion of the distillation exceeds 183°C, add 50 mL distilled water and distill the mixture until the temperature again reaches 180°C. After distilling a high fluoride sample (3 mg/L or more), clean the apparatus by distilling 250 mL water. This prevents a carryover of fluoride in subsequent samples. When samples with high chloride content are to be distilled, silver sulfate should be added to the distilling flask in proportion of 5 mg per milligram of chloride.

6.2 *Electrometric procedure*

6.2.1 Set up manifold (fig. 66).

6.2.2 Allow potentiometer, recorder, and heating bath to warm up for at least 30 min, or until the temperature of the heating bath reaches 37°C.

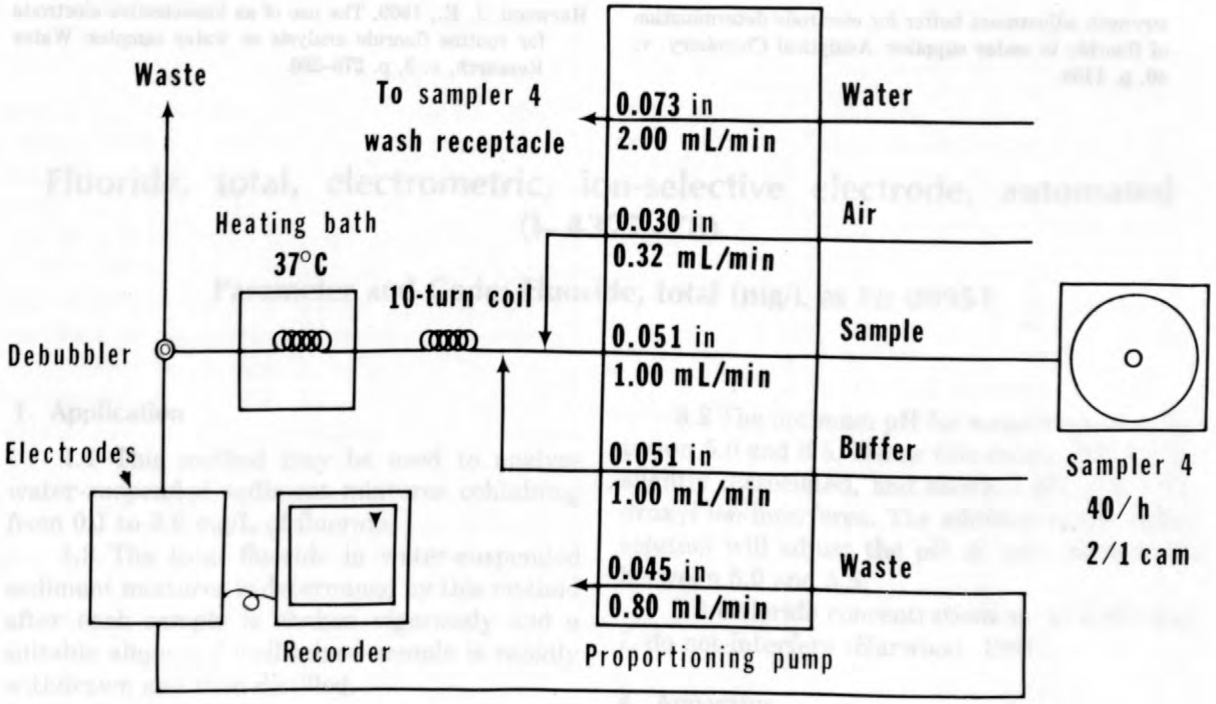


FIGURE 66.—Fluoride manifold.

6.2.3 Calibrate the potentiometer according to the manufacturer's instructions.

6.2.4 Adjust the baseline to read 10 scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.2.5 Beginning with the most concentrated working standard (the first two positions should both contain 3-mg/L standards), place a complete set of standards in the first positions of the first sample tray, followed by a blank. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.2.6 Begin analysis. When the peak from the second 3-mg/L standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads 100 scale divisions.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective fluoride concentration. This curve should be linear, or very nearly linear.

7.2 Compute the concentration of fluoride in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report fluoride, dissolved (00950), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the relative deviation (coefficient of variation) is as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
3 (112 replicates)	0.78	12
3 (107 replicates)	1.02	8

References

Bellack, Ervin, 1958, Simplified fluoride distillation method: American Water Works Association Journal, v. 50, p. 530.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 93.

Erdmann, D. E., 1975, Automated ion-selective method for determining fluoride in natural waters: Environmental Science and Technology, v. 9, p. 252.

Frant, M. S., and Ross, J. W., Jr., 1968, Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water supplies: Analytical Chemistry, v. 40, p. 1169.

Harwood, J. E., 1969, The use of an ion-selective electrode for routine fluoride analysis on water samples: Water Research, v. 3, p. 273–280.

Fluoride, total, electrometric, ion-selective electrode, automated (I–4327–78)

Parameter and Code: Fluoride, total (mg/L as F): 00951

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing from 0.1 to 3.0 mg/L of fluoride.

1.2 The total fluoride in water-suspended sediment mixtures is determined by this method after each sample is shaken vigorously and a suitable aliquot of well mixed sample is rapidly withdrawn and then distilled.

2. Summary of method

2.1 Fluoride is determined potentiometrically in a buffered sample with use of an ion-selective (fluoride) electrode in conjunction with a standard calomel reference electrode (SCE), and a pH meter having expanded millivolt scale (Frant and Ross, 1968; Harwood, 1969; Bellack, 1958).

2.2 The fluoride electrode consists of a laser-type doped lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by:

$$\mathrm{Ag/AgCl,\ Cl^{-1}\ (0.3}M\mathrm{),}$$
$$\mathrm{F^{-1}\ (0.001}M\mathrm{)/LaF_3/test\ solution/SCE.}$$

This electrode deteriorates in time and must be replaced when results become erratic.

3. Interferences

3.1 The ion-selective electrode measures fluoride-ion activity; thus high concentrations of dissolved solutes (which lower the ion-activity coefficient) cause an error in the determination. Addition of a buffer solution that contains a high concentration of dissolved solutes effectively masks minor variations in the salt content of the samples and, therefore, minimizes this error.

3.2 The optimum pH for measurement is between 5.0 and 8.5. Below this range, HF is only slightly dissociated, and above a pH of 8.5 hydroxyl ion interferes. The addition of the buffer solution will adjust the pH of most samples to between 5.0 and 5.5.

3.3 Chloride concentrations up to 3,000 mg/L do not interfere (Harwood, 1969).

4. Apparatus

4.1 *Distillation assembly*, consisting of a round-bottom distilling flask, adapter, connecting tube, condenser, receiving flask, and thermometer (250°C) (fig. 67).

4.2 *Technicon AutoAnalyzer II*, consisting of a sampler, proportioning pump, cartridge manifold, heating bath, recorder, potentiometer, and printer.

4.3 *Fluoride ion-selective electrode.*

4.4 *Reference electrode*, standard calomel.

4.5 With this equipment a 40/h (2/1) cam has been found satisfactory for the range from 0.1 to 3.0 mg/L.

5. Reagents

5.1 *Brij–35* solution: 30 percent aqueous (Baker Cat. No. C 706, or equivalent).

5.2 *Buffer* solution with 0.33 mg/L fluoride, pH 5.0 to 5.5: To approx 500 mL demineralized water in a 1-L beaker add 57 mL glacial $HC_2H_3O_2$, 58 g NaCl, and 4.5 g (1,2-cyclohexylenedinitrilo)tetraacetic acid (CDTA). Stir to dissolve and cool to room temperature. Adjust the pH of the solution to between 5.0 and 5.5 with 5*M* NaOH (about 170 mL will be required). Filter if necessary and add 33 mL of fluoride standard solution II, and 0.5 mL of Brij–35 solution. Dilute to 1,000 mL with demineralized water.

5.3 *Fluoride* standard solution I, 1.00

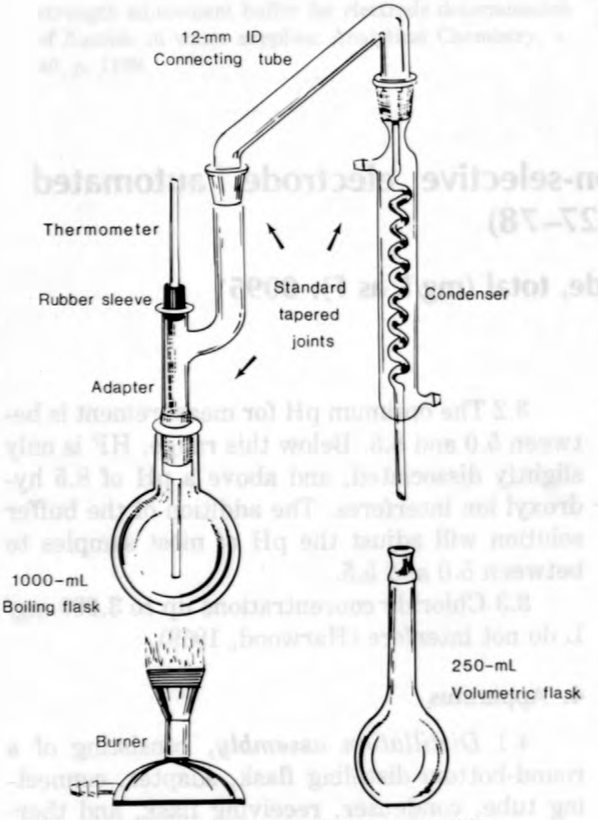


FIGURE 67.—Fluoride distillation assembly.

mL = 1.00 mg F^{-1}: Dissolve 2.2101 g NaF in demineralized water and dilute to 1,000 mL.

5.4 *Fluoride* standard solution II, 1.00 mL = 0.01 mg F^{-1}: Dilute 10 mL fluoride standard solution I to 1,000 mL with demineralized water.

5.5 *Fluoride* working standards: Prepare a blank and 500 mL each of a series of fluoride working standards by appropriate quantitative dilution of fluoride standard solution II as follows:

Fluoride standard solution II (mL)	*Fluoride concentration (mg/L)*
0.0	0.00
10.0	.20
25.0	.50
50.0	1.00
75.0	1.50
100.0	2.00
125.0	2.50
150.0	3.00

5.6 *Silver sulfate*, powder.

5.7 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 *Distillation procedure:*

6.1.1 Place 400 mL demineralized water in a 1-L distilling flask containing a few glass beads. *Cautiously*, and with constant swirling, add 200 mL concentrated sulfuric acid. Connect the flask to the condenser assembly and distill until the temperature of the acid mixture reaches 180°C. At this point the proper acid concentration has been reached. The acid need not be replaced until the accumulation of nonvolatile material is sufficient to cause interference. An occasional recovery check with a standard fluoride sample will indicate the need for replacement.

6.1.2 Cool to room temperature.

6.1.3 *Cautiously*, and with constant swirling, add 250 mL sample to the acid mixture in the distillation flask.

6.1.4 Distill until 250 mL distillate has been collected and the temperature of the acid mixture is again 180°C. When the temperature of the acid mixture at the completion of the distillation exceeds 183°C, add 50 mL distilled water and distill the mixture until the temperature again reaches 180°C. After distilling a high fluoride sample (3 mg/L or more), clean the apparatus by distilling 250 mL water. This prevents a carryover of fluoride in subsequent samples. When samples with high chloride content are to be distilled, silver sulfate should be added to the distilling flask in proportion of 5 mg per milligram of chloride.

6.2 *Electrometric procedure:*

6.2.1 Set up manifold (fig. 68).

6.2.2 Allow potentiometer, recorder, and heating bath to warm up for at least 30 min, or until the temperature of the heating bath reaches 37°C.

6.2.3 Calibrate the potentiometer according to the manufacturer's instructions.

6.2.4 Adjust the baseline to read 10 scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.2.5 Beginning with the most concentrated working standard (the first two positions should both contain 3-mg/L standards), place a complete set of standards in the first positions of the first sample tray followed by a blank. Place in-

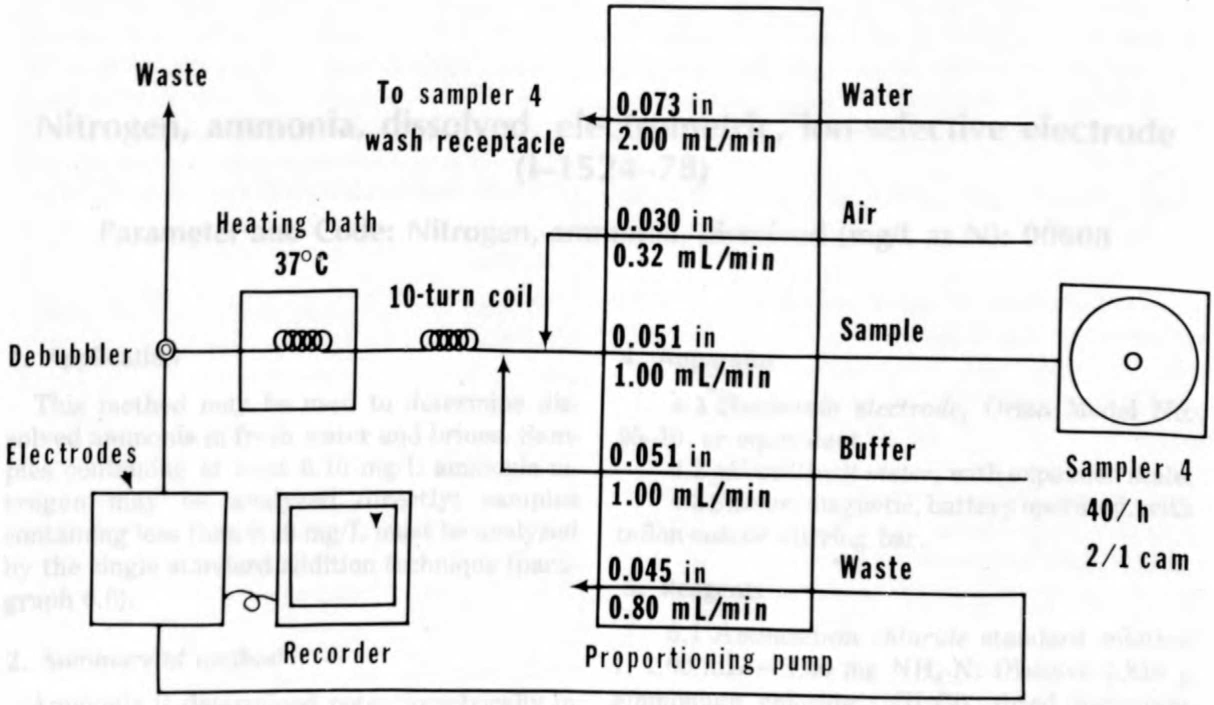


FIGURE 68.—Fluoride manifold.

dividual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.2.6 Begin analysis. When the peak from the second 3-mg/L standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads 100 scale divisions.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective fluoride concentration. This curve should be linear, or very nearly linear.

7.2 Compute the concentration of fluoride in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report fluoride, dissolved (00951), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 12 percent at 0.78 mg/L and greater than 8 percent at 1.02 mg/L.

References

Bellack, Ervin, 1958, Simplified fluoride distillation method: American Water Works Association Journal, v. 50, p. 530.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 93.

Erdmann, D. E., 1975, Automated ion-selective method for determining fluoride in natural waters: Environmental Science and Technology, v. 9, p. 252.

Frant, M. S., and Ross, J. W., Jr., 1968, Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water supplies: Analytical Chemistry, v. 40, p. 1169.

Harwood, J. E., 1969, The use of an ion-selective electrode for routine fluoride analysis on water samples: Water Research, v. 3, p. 273–280.

Nitrogen, ammonia, dissolved, electrometric, ion-selective electrode (I-1524-78)

Parameter and Code: Nitrogen, ammonia, dissolved (mg/L as N): 00608

1. Application

This method may be used to determine dissolved ammonia in fresh water and brines. Samples containing at least 0.10 mg/L ammonia-nitrogen may be analyzed directly; samples containing less than 0.10 mg/L must be analyzed by the single standard addition technique (paragraph 6.6).

2. Summary of method

Ammonia is determined potentiometrically in an alkaline medium by using an ammonia gas-detecting electrode. The internal solution of the electrode is separated from the sample solution by a gas-permeable membrane. Dissolved ammonia in the sample diffuses through the membrane until the partial pressure of ammonia is the same on both sides. The change in partial pressure is proportional to the ammonia concentration and is measured as a potential with an internal chloride-sensing reference electrode and a glass electrode.

3. Interferences

3.1 Color and turbidity do not affect the measurements. Significant quantities of inorganic cations and anions cannot penetrate the nonwettable gas-permeable membrane and do not interfere directly. However, as the salinity of the sample increases, there is an increase in the observed ammonia concentration. Samples containing dissolved substances at a total concentration greater than 1*M* should be analyzed either by standard addition, or if the ammonia concentration is sufficiently high, after appropriate dilution.

3.2 Certain other gases do present a potential interference; however, common gases such as CO_2, HCN, SO_2, and Cl_2 do not interfere (Orion Research Inc., 1971).

4. Apparatus

4.1 *Ammonia electrode,* Orion Model No. 95–10, or equivalent.

4.2 *pH/millivolt meter,* with expanded scale.

4.3 *Stirrer,* magnetic, battery operated, with teflon-coated stirring bar.

5. Reagents

5.1 *Ammonium chloride* standard solution I, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g ammonium chloride (NH_4Cl), dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonium chloride* standard solution II, 1.00 mL = 0.010 mg N: Dilute 10.0 mL of ammonium chloride standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Ammonium chloride* standard working solutions: Prepare a series of three standard solutions containing 0.1, 1.0, and 5.0 mg/L NH_3-N by appropriate dilution of either ammonium chloride standard solution I or II with ammonia-free water.

5.4 *Sodium hydroxide* solution, 10*M*. Dissolve 400 g NaOH in ammonia-free water and dilute to 1 L.

6. Procedure

Rinse all glassware with ammonia-free water before beginning this determination.

6.1 Adjust the pH/millivolt meter according to the manufacturer's instructions.

6.2 Pipet 50.0 mL each of ammonium chloride standard working solutions (0.1, 1.0, and 5.0 mg/L NH_3-N, respectively) into 100-mL beakers.

6.3 Pipet 50.0 mL of sample into a 100-mL beaker.

6.4 Place each standard and sample consecutively on a magnetic stirrer (NOTE 1), immerse the electrode, and then add 0.5 mL 10*M* NaOH solution. Start the stirrer and record the potential (mV) reading after it has stabilized (2 to 5 min). Rinse the electrode thoroughly with distilled water between samples and blot with a damp tissue.

NOTE 1. Insulate the top of the stirrer with an asbestos sheet and an air space to avoid raising the temperature of the solution.

6.5 If the millivolt reading from the analytical curve (section 7) indicates a concentration of less than 0.10 mg/L, determine NH_3-N in the sample by single standard addition (paragraph 6.6).

6.6 Add 0.5 mL ammonium chloride standard solution II to the sample (paragraph 6.4) equivalent to an increase in concentration of 0.10 mg/L NH_3-N, and record the new potential. Approx 5 min is required for the potential to stabilize.

7. Calculations

Construct an analytical curve of potential (mV) versus concentration of standards on semilog paper, with concentrations plotted on the logarithmic axis. Determine the milligrams per liter ammonia-nitrogen in each sample from the analytical curve. When standard addition is used to determine NH_3-N (paragraph 6.6), subtract 0.10 mg/L NH_3-N from the concentration obtained from the analytical curve.

8. Report

Report ammonia-nitrogen, dissolved (00608), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

Orion Research, Inc., 1971, Instruction manual, ammonia electrode, Model 95–10: Cambridge, Mass.

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environment Protection Agency, p. 165.

Nitrogen, ammonia, total, electrometric, ion-selective electrode (I–3524–78)

Parameter and Code: Nitrogen, ammonia, total (mg/L as N): 00610

1. Application

This method may be used to determine total ammonia-nitrogen in fresh water and brines. Samples containing at least 0.10 mg/L ammonia-nitrogen may be analyzed directly; samples containing less than 0.10 mg/L must be analyzed by the single standard addition technique (paragraph 6.6).

2. Summary of method

2.1 Ammonia is determined potentiometrically in an alkaline medium by using an ammonia gas-detecting electrode. The internal solution of the electrode is separated from the sample solution by a gas-permeable membrane. Dissolved ammonia in the sample diffuses through the membrane until the partial pressure of ammonia is the same on both sides. The change in partial pressure is proportional to the ammonia concentration and is measured as a potential with an internal chloride-sensing reference electrode and a glass electrode.

2.2 This method is identical to the electrometric, ion-selective electrode method for determining dissolved ammonia-nitrogen (Method I–1524), except that a suitable portion of a well mixed, unfiltered sample is taken for analysis.

3. Interferences

3.1 Color and turbidity do not affect the measurements. Significant quantities of inorganic cations and anions cannot penetrate the nonwettable gas-permeable membrane and do not interfere directly. However, as the salinity of the sample increases, there is an increase in the observed ammonia concentration. Samples containing dissolved substances at a total concentration greater than 1M should be analyzed either by standard addition, or if the ammonia concentration is sufficiently high, after appropriate dilution.

3.2 Certain other gases do present a potential interference; however, common gases such as CO_2, HCN, SO_2, and Cl_2 do not interfere (Orion Research, Inc., 1971).

4. Apparatus

4.1 *Ammonia electrode*, Orion Model No. 95–10, or equivalent.

4.2 *pH/millivolt meter*, with expanded scale.

4.3 *Stirrer*, magnetic, battery operated, with teflon-coated stirring bar.

5. Reagents

5.1 *Ammonium chloride* standard solution I, 1.00 mL = 1.00 mg N: Dissolve 3.819 g ammonium chloride (NH_4Cl), dried overnight over concentrated sulfuric acid (sp gr 1.84), in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonium chloride* standard solution II, 1.00 mL = 0.010 mg NH_3-N: Dilute 10.0 mL of ammonium chloride standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Ammonium chloride* standard working solutions: Prepare a series of three standard solutions containing 0.1, 1.0, and 5.0 mg/L NH_3-N by appropriate dilution of either ammonium chloride standard solution I or II with ammonia-free water.

5.4 *Sodium hydroxide* solution, 10*M*. Dissolve 400 g NaOH in ammonia-free water and dilute to 1 L.

6. Procedure

Rinse all glassware with ammonia-free water before beginning this determination.

6.1 Pipet 50.0 mL of well mixed sample and transfer to a 100-mL beaker.

6.2 Adjust the pH/millivolt meter according to the manufacturer's instructions.

6.3 Pipet 50.0 mL each of ammonium chloride standard working solutions (0.1, 1.0, and 5.0 mg/L NH_3-N) into 100-mL beakers.

6.4 Place each standard and sample consecutively on a magnetic stirrer (NOTE 1), immerse the electrode, and then add 0.5 mL 10*M* NaOH solution. Start the stirrer and record the potential (mV) reading after it has stabilized (2 to 5 min). Rinse the electrode thoroughly between samples with distilled water and blot with a damp tissue.

NOTE 1. Insulate the top of the stirrer with an asbestos sheet and an air space to avoid raising the temperature of the solution.

6.5 If the millivolt reading from the analytical curve (section 7) indicates a concentration of less than 0.10 mg/L, determine NH_3-N in the sample by single standard addition (paragraph 6.6).

6.6 Add 0.5 mL ammonium chloride standard solution II to the sample (paragraph 6.4) equivalent to an increase in concentration of 0.10 mg/L NH_3 and record the new potential. Approx 5 min is required for the potential to stabilize.

7. Calculations

Construct an analytical curve of potential (mV) versus concentrations of standards on semilog paper, with concentrations plotted on the logarithmic axis. Determine the milligrams per liter ammonia-nitrogen in each sample from the analytical curve. When standard addition is used to determine NH_3-N (paragraph 6.6), subtract 0.10 mg/L NH_3-N from the concentration obtained from the analytical curve.

8. Report

Report total ammonia-nitrogen (00610) concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

Orion Research, Inc., 1971, Instruction manual, ammonia electrode, Model 95–10: Cambridge, Mass.

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environment Protection Agency p. 165.

Oxygen, dissolved, electrometric, polarographic probe (I–1576–78)

Parameters and Codes: Oxygen, dissolved (mg/L): 00300; Oxygen, dissolved (percent of saturation): 00301

1. Application

This method may be used to analyze waters and wastewaters containing between 0.1 and 20 mg/L of dissolved oxygen.

2. Summary of method

2.1 Dissolved oxygen (DO) is determined by an electrode system consisting of a sensor or probe containing a gold cathode and silver anode surrounded by an electrolyte solution of potassium chloride. A thin oxygen-permeable membrane is stretched across the end of the probe to isolate the electrolyte and sensor elements from the environment. When a potential of 0.8 V is applied across the cell, oxygen is reduced at the cathode, causing current to flow in an amount proportional to the partial pressure of oxygen at the external membrane surface. Inasmuch as oxygen is consumed at the gold cathode, the oxygen pressure inside the membrane is effectively zero, and the force causing oxygen to diffuse through the membrane is therefore proportional to the absolute pressure of oxygen outside the membrane. A linear relationship exists between the cell current and external oxygen pressure or concentration of oxygen in the sample solution.

2.2 Four procedures for calibrating the oxygen meter are given. They are listed in order of preference.

3. Interferences

The membrane is permeable to gases, other than oxygen. Halogens, hydrogen sulfide, sulfur dioxide, and helium interfere. Hydrogen sulfide poisons the electrode.

4. Apparatus

4.1 *Oxygen meter*, Yellow Springs Instrument Co., Model No. 54 or No. 57, equipped with Model 5739 probe, or equivalent.

4.2 The oxygen meter selected should meet the following general requirements:

Range of dissolved oxygen: 0.1 to 20 mg/L
Accuracy: ± 1 percent of maximum range
Operating temperature range: −5°C to + 45°C
Minimum scale readability: 0.05 mg/L O_2
Temperature-compensated, portable, and rugged for field and laboratory use

4.3 *Calibration chamber*, Yellow Springs Instrument Co., Model No. 5075, or equivalent.

4.4 *Pocket altimeter-barometer*, capable of being read to at least the nearest 5 mm of mercury. USGS warehouse supply stock No. 01321, or equivalent.

5. Reagents

5.1 *Sodium sulfite* solution: Dissolve 1 g of sodium sulfite (Na_2SO_3) and a few crystals (about 1 mg) of cobalt chloride ($CoCl_2$) in 1 L of distilled water.

5.2 *Reagents for Alsterberg-Azide method:* See Method I–1575. These reagents are required when using calibration procedure 6.3.1B.

6. Procedure

6.1 Prepare oxygen meter for calibration in accordance with the manufacturer's instructions (NOTES 1, 2, 3, 4, and 5).

NOTE 1. A number of precautions should be observed when using the oxygen meter, particularly when the instrument is used for field measurements. (1) Check mechanical zero before turning meter on and adjust if necessary. (2) Turn instrument on to any operational position 1 h before use to insure stability of operation; meter should be left on until final measurement for day is completed. (3) Check REDLINE and ZERO and adjust as needed; if meter will not adjust to REDLINE recharge or replace batteries. (4) Protect instrument from temperature changes that may result from exposure to direct sunlight or contact with ice or cold wind.

NOTE 2. The DO probe requires periodic replacement of electrolyte and membrane. Follow manufacturer's directions but observe these points: (1) There should be no bubbles of air behind membrane. Electrodes with pressure compensators should have the pressure compensation membrane moved in and out with the eraser end of a pencil to insure that all bubbles are removed from pressure compensation chamber. (2) The membrane should be smooth with no wrinkles. (3) Excess membrane material should be trimmed to within 2 to 3 mm of the o-ring.

NOTE 3. Because o-rings stretch with use, they must be replaced before they become loose. A common cause of electrode malfunction is leakage of electrolyte around the o-ring seal. To check for this problem, rinse the probe unit to remove traces of electrolyte remaining from membrane replacement. Place the probe in a 250-mL beaker of distilled water; there should be no change in specific conductance of the water in the beaker after soaking for several hours.

NOTE 4. Keep DO probe in water when not in use to prevent drying out of the membrane.

NOTE 5. Periodically check the thermistor in the DO probe against a certified mercury thermometer over the normal operating temperature range of the instrument. If the two readings are not in agreement, a correction curve should be constructed, or an electronic adjustment should be made to the instrument by the manufacturer or qualified service center.

6.2 Once daily, check that the instrument will read zero in a dissolved oxygen-free solution. This may be accomplished by inserting the probe into the sodium sulfide solution and measuring the dissolved oxygen. If instrument reading exceeds 0.2 mg/L, the probe needs repair, or the membrane and electrolyte need replacement.

6.3 Calibrate the DO meter in accordance with one of the following four procedures. Procedure A is the preferred procedure. Procedures B, C, and D may be used in situations where procedure A cannot be used. These four procedures are given in order of preference.

6.3.1A *Air calibration chamber in water:* The air calibration chamber (Yellow Springs Instrument Co. No. 5075, or equivalent) permits calibration of the oxygen meter at the temperature of the water in which the DO content is to be measured, thereby minimizing errors due to temperature differences. Dip the calibration chamber into the water; pour out excess water, and then insert DO probe into the wet chamber. This insures that the air inside the chamber is saturated with water vapor. *Caution:* Be sure that no water can leak into the calibration chamber and that the membrane has no droplets of water adhering to it, since this would reduce the rate of oxygen diffusion through the membrane and would produce erroneous results.

6.3.2A Place calibration chamber in the water in which the DO content is to be measured. Allow 10 to 15 min for the temperature of the air inside the chamber to equilibrate with the water.

NOTE 6. The calibration chamber (Model 5075) design allows the membrane surface to be at ambient atmospheric pressure while in the chamber, but it does not allow sufficient room for the entire electrode, Model 5739, to fit inside. Since the pressure compensator must remain at atmospheric pressure, care must be taken to insure that the pressure compensator is not covered with water if method 6.3.1A is used.

6.3.3A Read true atmospheric pressure from pocket altimeter-barometer.

6.3.4A Recheck the REDLINE and ZERO reading on the oxygen meter and adjust if necessary.

6.3.5A Measure temperature in the calibration chamber to the nearest 0.5°C, using the thermistor in the DO probe.

6.3.6A Using oxygen saturation values from section 7.2, determine the DO saturation value at the measured water temperature and true atmospheric pressure. Apply a salinity correction if appropriate (NOTE 7).

NOTE 7. The solubility of oxygen in water decreases as salinity increases. Oxygen saturation values may be corrected for salinity, using the correction factors given in the oxygen solubility table in section 7.2. For example, the solubility of oxygen at 25°C and 760 mm of mercury in water containing 5,000 mg/L of chloride is calculated as follows:

$$\underset{\left(\begin{array}{l}\text{Saturation}\\ \text{DO at}\\ \text{0 mg/L}\\ \text{chloride}\\ \text{from sec-}\\ \text{tion 7.2}\end{array}\right)}{8.3\ \text{mg/L}} - \frac{5{,}000\ \text{mg/L Cl}}{100} \times \underset{\left(\begin{array}{l}\text{Difference}\\ \text{per 100}\\ \text{mg/L}\\ \text{chloride}\\ \text{from sec-}\\ \text{tion 7.2}\end{array}\right)}{0.008} = 7.9\ \text{mg/L}$$

The DO meter would then be adjusted to 7.9 mg/L rather than 8.3 mg/L. The YSI Model 57 DO meter has a manual salinity correction provision built into the instrument. Follow the manufacturer's instructions in its use.

6.3.7A Select the scale (0 to 10 or 0 to 20 mg/L) to be used for the DO measurement and adjust CALIBRATION control until meter reads the DO saturation value determined in 6.3.6A. Do not change scales without recalibrating meter or verifying that identical readings are obtained on both scales.

6.3.8A Remove probe from calibration chamber and place in water to be measured. Move probe through water to insure a velocity of at least 1 ft/sec past the probe (alternatively, a submersible stirrer, YSI Model 5491, or equivalent may be used) to prevent localized depletion of DO at the membrane-water interface.

6.3.9A Switch meter to TEMPERATURE; after meter reading has stabilized, record temperature to the nearest 0.5°C.

6.3.10A Switch meter to the proper DO scale; after meter reading has stabilized, record DO concentration to the nearest 0.1 mg/L.

6.3.1B *Calibration by Winkler titration:* The DO meter is calibrated with distilled or deionized water in which the DO concentration has been determined by the Winkler method.

6.3.2B Place 1 to 2 L of distilled or deionized water in a large container. The water should preferably be near saturation with respect to DO, and the water temperature should be reasonably close to the ambient temperature. These conditions should insure that the DO concentration in the distilled water remains constant.

6.3.3B Place DO probe in the distilled water. Maintain a velocity of at least 1 ft/sec past the DO probe with a magnetic stirrer or other means.

6.3.4B Check ZERO and REDLINE, and adjust if necessary.

6.3.5B Switch meter to the appropriate scale and adjust reading to the approximate DO concentration with the CALIBRATION control.

6.3.6B After DO meter has stabilized, determine the DO concentration of two aliquots of the distilled water by the Winkler titration procedure (Method I–1575). If results of the two Winkler titrations do not agree within 0.1 mg/L, the titration should be repeated.

6.3.7B Without delay recheck ZERO and REDLINE; then adjust CALIBRATION control until DO meter reads DO concentration determined in step 6.3.6B. Meter is now calibrated and ready for use.

6.3.8B Place DO probe in water to be measured. Allow sufficient time for the probe to equilibrate with the water temperature. Move probe through water at a velocity of at least 1 ft/sec (alternatively, a submersible stirrer, YSI Model 5491, or equivalent may be used) to prevent localized depletion of DO at the membrane-water interface.

6.3.9B Switch meter to TEMPERATURE; after meter has stabilized record temperature to nearest 0.5°C.

6.3.10B Switch meter to the appropriate DO scale. After meter has stabilized, record DO concentration to nearest 0.1 mg/L. The alternate salinity correction procedure (see NOTE 7) should be applied if appropriate.

6.3.1C *Calibration with air-saturated water:* The DO meter is calibrated against water which is saturated with oxygen at a known temperature and true atmospheric pressure. Obtain approximately 1 L of distilled water or water from the water body to be measured. The temperature of the water used for calibration should be close to ambient temperature so that there is no heating or cooling.

6.3.2C Place DO probe and the calibration water in a large beaker or open-mouth container and allow it to come to thermal equilibrium. Shield beaker from direct sunlight and wind to minimize temperature variations.

6.3.3C Aerate the water for 5 to 10 min. This is most readily accomplished with a small battery-operated aquarium pump or minnow bucket aerator and a short section of tubing. A gas diffusion stone should be attached to the end of the tubing and placed at the bottom of the beaker of calibration water.

NOTE 8. It is extremely important to insure that the water is exactly 100-percent saturated with oxygen. An indication of 100-percent saturation can be determined as follows. Switch DO meter to the 0 to 10-mg/L scale and adjust meter reading to approximately 8 mg/L with the CALIBRATION control. Observe meter while aerating calibration water. When no change in DO reading on meter is observed for a period of 4 to 5 min the water can be assumed to be saturated.

6.3.4C Read true atmospheric pressure from pocket altimeter-barometer.

6.3.5C Recheck the REDLINE and ZERO reading on the oxygen meter and adjust if necessary.

6.3.6C Measure temperature of the calibration water to the nearest 0.5°C.

6.3.7C Using oxygen saturation values from section 7.2 determine the DO saturation value at the measured calibration water temperature and true atmospheric pressure. Apply a salinity correction if appropriate (NOTE 7).

6.3.8C Select the scale (0 to 10 or 0 to 20 mg/L) to be used for the DO measurement. Turn off aerator and adjust CALIBRATION control until meter reads the DO saturation value determined in 6.3.7C. Do not change scales without recalibrating meter or verifying that identical readings are obtained on both scales (NOTE 9).

NOTE 9. It is essential that calibration be completed with the temperature of the calibration water at the value measured in 6.3.6C; otherwise the calibration water may be undersaturated or oversaturated with oxygen. If the temperature changes or later recalibration of the meter is necessary, the calibration procedure must be repeated beginning with step 6.3.2C.

6.3.9C Remove probe from calibration container and place in water to be measured. Move probe through water at a velocity of at least 1 ft/sec (alternatively, a submersible stirrer, YSI Model 5491, or equivalent may be used) to prevent localized depletion of DO at the membrane-water interface.

6.3.10C Switch meter to TEMPERATURE; after meter reading has stabilized record temperature to the nearest 0.5°C.

6.3.11C Switch meter to the proper DO scale; after meter reading has stabilized, record DO concentration to the nearest 0.1 mg/L.

6.3.1.D *Air calibration chamber in air:* This procedure is similar to the procedure described in 6.3.1A, except that calibration is performed with the air calibration chamber in air rather than in water. This procedure can only be used with probes that have the temperature sensing thermistor located adjacent to the membrane. The probe must be capable of automatically compensating for temperature changes. Wet the inside of the calibration chamber with water; pour out excess water and insert DO probe into the wet chamber. This insures near 100-percent humidity in the chamber. *Caution:* The calibration chamber must be shielded from direct sunlight and wind to avoid large temperature fluctuations.

6.3.2D Allow sufficient time (10 to 15 min) for DO probe and air inside calibration chamber to equilibrate.

6.3.3D Read true atmospheric pressure from pocket altimeter-barometer.

6.3.4D Recheck the REDLINE and ZERO readings on the oxygen meter and adjust if necessary.

6.3.5D Measure temperature in the calibration chamber to the nearest 0.5°C using the thermistor in the DO probe.

6.3.6D Using oxygen saturation values from section 7.2 determine the DO saturation at the measured temperature and true atmospheric pressure. Apply a salinity correction if necessary.

6.3.7D Select the scale (0 to 10 or 0 to 20 mg/L) to be used for the DO measurement and adjust CALIBRATION control until the meter reading is at the DO saturation value determined in 6.3.6D. Do not change scales without recalibrating meter or verifying that identical readings are obtained on both scales.

6.3.8D Remove probe from calibration chamber and place in water to be measured. Move probe through water at a velocity of at least 1 ft/sec (alternatively, a submersible stirrer, YSI Model 5491, or equivalent may be used) to prevent localized depletion of DO at the membrane-water interface.

6.3.9D Switch meter to TEMPERATURE; after meter reading has stabilized, record temperature to the nearest 0.5°C.

6.3.10D Switch meter to the proper DO scale; after meter reading has stabilized, record DO concentration to the nearest 0.1 mg/L.

7. Calculations

7.1 Read the concentration of dissolved oxygen in milligrams per liter directly from the meter of the instrument.

7.2 Table 5, a table of values for the solubility of oxygen in water exposed to water-saturated air, should be used to calibrate the DO meter. The table may also be used to determine dissolved oxygen as percent saturation at the measured temperature and true atmospheric pressure as follows:

$$\text{DO (percent saturation)} = \frac{\text{Measured DO (mg/L)}}{\text{Saturation DO (mg/L)}} \times 100$$

standard deviation for the determination of pH of water samples throughout the pH range may be expected to be about 0.19 pH unit.

References

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535–H, 17 p.

TABLE 5.—Solubility of oxygen in water at various temperatures and pressures

Temperature (°C)	Solubility, by atmospheric pressure (mm Hg)															Difference per 100 mg chloride
	780	770	760	750	740	730	720	710	700	690	680	670	660	650	640	
0	15.0	14.8	14.6	14.4	14.2	14.1	13.9	13.7	13.5	13.3	13.1	12.9	12.7	12.5	12.3	0.017
1	14.6	14.4	14.2	14.0	13.8	13.7	13.5	13.3	13.1	12.9	12.7	12.5	12.3	12.1	12.0	.016
2	14.2	14.0	13.3	13.6	13.5	13.3	13.1	12.9	12.7	12.5	12.4	12.2	12.0	11.8	11.6	.015
3	13.8	13.6	13.5	13.3	13.1	12.9	12.7	12.6	12.4	12.2	12.0	11.9	11.7	11.5	11.3	.015
4	13.5	13.3	13.1	12.9	12.8	12.6	12.4	12.2	12.1	11.9	11.7	11.5	11.4	11.2	11.0	.014
5	13.1	12.9	12.8	12.6	12.4	12.3	12.1	11.9	11.8	11.6	11.4	11.2	11.1	10.9	10.7	.014
6	12.8	12.6	12.5	12.3	12.1	12.0	11.8	11.6	11.5	11.3	11.1	11.0	10.8	10.6	10.5	.014
7	12.5	12.3	12.1	12.0	11.8	11.7	11.5	11.3	11.2	11.0	10.9	10.7	10.5	10.4	10.2	.013
8	12.2	12.0	11.9	11.7	11.5	11.4	11.2	11.1	10.9	10.8	10.6	10.4	10.3	10.1	10.0	.013
9	11.9	11.7	11.6	11.4	11.3	11.1	11.0	10.8	10.7	10.5	10.3	10.2	10.0	9.9	9.7	.012
10	11.6	11.5	11.3	11.2	11.0	10.9	10.7	10.6	10.4	10.3	10.1	10.0	9.8	9.7	9.5	.012
11	11.4	11.2	11.1	10.9	10.8	10.6	10.5	10.3	10.2	10.0	9.9	9.7	9.6	9.4	9.3	.011
12	11.1	11.0	10.8	10.7	10.5	10.4	10.2	10.1	9.9	9.8	9.7	9.5	9.4	9.2	9.1	.011
13	10.9	10.7	10.6	10.4	10.3	10.2	10.0	9.9	9.7	9.6	9.4	9.3	9.2	9.0	8.9	.011
14	10.6	10.5	10.4	10.2	10.1	9.9	9.8	9.7	9.5	9.4	9.2	9.1	9.0	8.8	8.7	.010
15	10.4	10.3	10.1	10.0	9.9	9.7	9.6	9.5	9.3	9.2	9.0	8.9	8.8	8.6	8.5	.010
16	10.2	10.1	9.9	9.8	9.7	9.5	9.4	9.3	9.1	9.0	8.9	8.7	8.6	8.5	8.3	.010
17	10.0	9.9	9.7	9.6	9.5	9.3	9.2	9.1	8.9	8.8	8.7	8.5	8.4	8.3	8.2	.010
18	9.8	9.7	9.5	9.4	9.3	9.1	9.0	8.9	8.8	8.6	8.5	8.4	8.2	8.1	8.0	.009
19	9.6	9.5	9.3	9.2	9.1	9.0	8.8	8.7	8.6	8.5	8.3	8.2	8.1	8.0	7.8	.009
20	9.4	9.3	9.2	9.0	8.9	8.8	8.7	8.5	8.4	8.3	8.2	8.0	7.9	7.8	7.7	.009
21	9.2	9.1	9.0	8.9	8.7	8.6	8.5	8.4	8.2	8.1	8.0	7.9	7.8	7.6	7.5	.009
22	9.0	8.9	8.8	8.7	8.6	8.4	8.3	8.2	8.1	8.0	7.9	7.7	7.6	7.5	7.4	.008
23	8.9	8.8	8.6	8.5	8.4	8.3	8.2	8.1	7.9	7.8	7.7	7.6	7.5	7.4	7.2	.008
24	8.7	8.6	8.5	8.4	8.2	8.1	8.0	7.9	7.8	7.7	7.6	7.4	7.3	7.2	7.1	.008
25	8.5	8.4	8.3	8.2	8.1	8.0	7.9	7.8	7.6	7.5	7.4	7.3	7.2	7.1	7.0	.008
26	8.4	8.3	8.2	8.1	7.9	7.8	7.7	7.6	7.5	7.4	7.3	7.2	7.1	6.9	6.8	.008
27	8.2	8.1	8.0	7.9	7.8	7.7	7.6	7.5	7.4	7.3	7.1	7.0	6.9	6.8	6.7	.008
28	8.1	8.0	7.9	7.8	7.7	7.6	7.4	7.3	7.2	7.1	7.0	6.9	6.8	6.7	6.6	.008
29	7.9	7.8	7.7	7.6	7.5	7.4	7.3	7.2	7.1	7.0	6.9	6.8	6.7	6.6	6.5	.008
30	7.8	7.7	7.6	7.5	7.4	7.3	7.2	7.1	7.0	6.9	6.8	6.7	6.6	6.4	6.3	.008

Temperature (°C)	Solubility, by atmospheric pressure (mm Hg)															Difference per 100 mg chloride
	630	620	610	600	590	580	570	560	550	540	530	520	510	500	490	
0	12.1	11.9	11.7	11.5	11.3	11.1	11.0	10.8	10.6	10.4	10.2	10.0	9.8	9.6	9.4	0.017
1	11.8	11.6	11.4	11.2	11.0	10.8	10.6	10.5	10.3	10.1	9.9	9.7	9.5	9.3	9.1	.016
2	11.4	11.3	11.1	10.9	10.7	10.5	10.3	10.2	10.0	9.8	9.6	9.4	9.2	9.1	8.9	.015
3	11.1	11.0	10.8	10.6	10.4	10.2	10.1	9.9	9.7	9.5	9.4	9.2	9.0	8.8	8.6	.015
4	10.8	10.7	10.5	10.3	10.2	10.0	9.8	9.6	9.5	9.3	9.1	8.9	8.8	8.6	8.4	.014
5	10.6	10.4	10.2	10.1	9.9	9.7	9.6	9.4	9.2	9.0	8.9	8.7	8.5	8.4	8.2	.014
6	10.3	10.1	10.0	9.8	9.6	9.5	9.3	9.1	9.0	8.8	8.6	8.5	8.3	8.2	8.0	.014
7	10.0	9.9	9.7	9.6	9.4	9.2	9.1	8.9	8.8	8.6	8.4	8.3	8.1	8.0	7.8	.013
8	9.8	9.6	9.5	9.3	9.2	9.0	8.9	8.7	8.5	8.4	8.2	8.1	7.9	7.8	7.6	.013
9	9.6	9.4	9.3	9.1	9.0	8.8	8.7	8.5	8.3	8.2	8.0	7.9	7.7	7.6	7.4	.012
10	9.4	9.2	9.1	8.9	8.8	8.6	8.4	8.3	8.1	8.0	7.8	7.7	7.5	7.4	7.2	.012
11	9.1	9.0	8.8	8.7	8.6	8.4	8.3	8.1	8.0	7.8	7.7	7.5	7.4	7.2	7.1	.011
12	8.9	8.8	8.6	8.5	8.4	8.2	8.1	7.9	7.8	7.6	7.5	7.3	7.2	7.1	6.9	.011
13	8.7	8.6	8.5	8.3	8.2	8.0	7.9	7.8	7.6	7.5	7.3	7.2	7.0	6.9	6.8	.011
14	8.6	8.4	8.3	8.1	8.0	7.9	7.7	7.6	7.4	7.3	7.2	7.0	6.9	6.8	6.6	.010
15	8.4	8.2	8.1	8.0	7.8	7.7	7.6	7.4	7.3	7.1	7.0	6.9	6.7	6.6	6.5	.010
16	8.2	8.1	7.9	7.8	7.7	7.5	7.4	7.3	7.1	7.0	6.9	6.7	6.6	6.5	6.3	.010
17	8.0	7.9	7.8	7.6	7.5	7.4	7.2	7.1	7.0	6.9	6.7	6.6	6.5	6.3	6.2	.010
18	7.9	7.7	7.6	7.5	7.3	7.2	7.1	7.0	6.8	6.7	6.6	6.5	6.3	6.2	6.1	.009
19	7.7	7.6	7.5	7.3	7.2	7.1	6.9	6.8	6.7	6.6	6.4	6.3	6.2	6.1	5.9	.009
20	7.6	7.4	7.3	7.2	7.1	6.9	6.8	6.7	6.6	6.4	6.3	6.2	6.1	5.9	5.8	.009
21	7.4	7.3	7.2	7.0	6.9	6.8	6.7	6.6	6.4	6.3	6.2	6.1	5.9	5.8	5.7	.009
22	7.3	7.1	7.0	6.9	6.8	6.7	6.5	6.4	6.3	6.2	6.1	5.9	5.8	5.7	5.6	.008
23	7.1	7.0	6.9	6.8	6.7	6.5	6.4	6.3	6.2	6.1	5.9	5.8	5.7	5.6	5.5	.008
24	7.0	6.9	6.8	6.6	6.5	6.4	6.3	6.2	6.1	5.9	5.8	5.7	5.6	5.5	5.4	.008
25	6.9	6.7	6.6	6.5	6.4	6.3	6.2	6.1	5.9	5.8	5.7	5.6	5.5	5.4	5.3	.008
26	6.7	6.6	6.5	6.4	6.3	6.2	6.1	5.9	5.8	5.7	5.6	5.5	5.4	5.3	5.2	.008
27	6.6	6.5	6.4	6.3	6.2	6.1	5.9	5.8	5.7	5.6	5.5	5.4	5.3	5.2	5.1	.008
28	6.5	6.4	6.3	6.2	6.0	5.9	5.8	5.7	5.6	5.5	5.4	5.3	5.2	5.1	5.0	.008
29	6.4	6.2	6.1	6.0	5.9	5.8	5.7	5.6	5.5	5.4	5.3	5.2	5.1	5.0	4.9	.008
30	6.2	6.1	6.0	5.9	5.8	5.7	5.6	5.5	5.4	5.3	5.2	5.1	5.0	4.9	4.8	.008

8. Report

8.1 Report dissolved oxygen concentrations to the nearest 0.1 mg/L.

8.2 Report dissolved oxygen as percent saturation to the nearest percent.

9. Precision

Precision data are not available for this method.

References

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater [14th ed.]: Washington, D.C., American Public Health Association, p. 446.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 129.

pH, electrometric, glass-electrode (I–1586–78)

Parameter and Code: pH (standard units): 00400

1. Application

This method may be used to determine the pH of any natural or treated water and any industrial or other wastewater.

2. Summary of method

See the introduction to Electrometry for the principles of pH-meter operation. See also Barnes (1964), Bates (1964), and Willard and others (1965).

3. Interferences

3.1 The determination is not affected by the presence of color or turbidity and by organic or colloidal material. Oxidizing and reducing substances do not impair the accuracy of method.

3.2 The pH measurement is temperature dependent, and a significant error results if the temperatures of the buffers and samples differ appreciably. However, a variation of less than 5°C has no significant effect except in the most exacting work.

4. Apparatus

4.1 *pH meter,* with glass and reference electrodes.

4.2 Several types of pH meters are available, including digital and expanded-scale models. Unless needed for special purposes, an ordinary laboratory line-operated pH meter capable of a reproducibility of 0.05 pH unit is adequate.

4.3 A new glass electrode or one which has been allowed to dry completely may require several hours soaking in water or buffer solution before stable, reliable readings can be obtained. The tip of the glass electrode must be kept immersed in water during the times it is not in use. Although the glass tip is reasonably durable, it can be damaged, and should never be cleaned or wiped with an abrasive or dirty tissue or cloth. A combination electrode (glass and reference) is convenient.

5. Reagents

Standard buffer solutions, pH 4.00, 7.00, and 9.00. At least three buffer solutions must be available to standardize the instrument. These should cover the range of pH of the samples to be measured. If samples of pH less than 3.5 or greater than 9.5 are to be analyzed, additional buffer solutions will be required. Ready-made buffer reagents are satisfactory.

6. Procedure

6.1 After an appropriate warmup period, standardize the instrument with the buffer solutions, bracketing the pH values of the samples. Samples and buffers must be at the same temperature.

6.2 With a minimum of aeration or agitation, measure the pH in accordance with the manufacturer's instructions.

7. Calculations

For water having an abnormally high sodium content, a correction may be necessary. This correction differs with each electrode, hence the analyst is referred to manufacturer's instructions for the computations necessary.

8. Report

Report pH values (00400) to the nearest 0.1 pH unit.

9. Precision

Analysis of two test samples by 43 and 21 laboratories resulted in means of 7.71 and 8.10 pH units and standard deviations of 0.16 and 0.22, respectively. It is believed that the average

Bates, R. G., 1964, Determination of pH—theory and practice: New York, John Wiley & Sons, 435 p.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 129.

Willard, H. H., Merritt, L. L., Jr., and Dean, J. A., 1965, Instrumental methods of analysis [4th ed.]: New York, D. Van Nostrand.

Specific conductance, electrometric, wheatstone bridge (I–1780–78)

Parameter and Code: Specific conductance, (μomho/cm at 25°C): 00095

1. Application

This method may be applied to all natural, treated, and industrial waters.

2. Summary of method

2.1 Specific conductance is determined by using a wheatstone bridge in which a variable resistance is adjusted so that it is equal to the resistance of the unknown solution between platinized electrodes of a standardized conductivity cell. The ability of a solution to conduct an electric current is a function of the concentration and charge of the ions in the solution and also depends on the rate at which the ions can move under the influence of an electrical potential. As the number of ions per unit volume of solution increases, the rate at which individual ions can move decreases, owing to interionic attraction and other effects. For this reason, a graph of total ion concentration versus specific conductance, even for solutions of a single salt, is a simple straight line only for rather dilute solutions. As specific conductance increases beyond about 5,000 μmho/cm at 25°C, the regression line curves, and beyond 50,000 μmho, the specific conductance is generally an unsatisfactory index of solute ion concentration.

2.2 The temperature of the electrolyte affects the ionic velocities and, consequently, the conductance. Conductance increases about 2 percent per degree Celsius, which is about the same as the temperature coefficient of viscosity of water.

2.3 The reported units of specific conductance are micromhos per centimeter at 25°C. The International (SI) unit of conductance is the siemen (symbol S), which is exactly equivalent to the mho. Thus, specific conductance may be reported as microsiemens per centimeter at 25°C.

2.4 In determining the specific conductance, it would be troublesome to prepare a cell having electrodes exactly 1 cm² in area and exactly 1 cm apart. Moreover, such an exacting cell is unnecessary because it is possible to determine a factor called the cell constant (C). The cell constant is determined experimentally with a standard solution of known conductance. A 0.00702N potassium chloride solution has a specific conductance of 0.001000 mho/cm at 25°C. The relation between resistance (R), cell constant (C), and specific conductance (K) is shown in the following equation, where K is known and R is determined:

$$RK = C.$$

Thus, if the resistance of the cell when filled with 0.00702N KCl is, for example, 350 ohms, the cell constant would be 0.35 for the conductivity cell used. If the conductivity cell having a cell constant of 0.35 is filled with a sample at 25°C and the observed resistance is 865 ohms, the specific conductance of the sample could be derived from the cell-constant equation:

$$\frac{C}{R} = K,$$

or by substituting values from the example,

$$\frac{0.35}{865} = 0.00405 \text{ mhos at } 25^\circ\text{C}$$

2.5 Unless a constant-temperature room or bath is available, adjustment of sample temperature (T) to exactly 25°C is difficult. For most work, specific conductance is computed from the following equation: μmho/cm = (R of 0.00702N KCl at T of sample measurement × 1,000) × (1/R of the sample).

2.6 New conductivity cells should be visually checked for cleanliness and platinum uniformity before using. Subsequently, they should be cleaned and replatinized whenever the readings become erratic or indistinct or inspection shows that any platinum black has flaked off. One platinization will usually suffice for a period of several months. To platinize the electrodes, clean them in chromic acid solution and rinse thoroughly in several changes of water. Place the electrodes in a solution of chloroplatinic acid and lead acetate (dissolve 3 g H_2PtCl_6 in 10 mL water to which 20 mg $Pb(C_2H_3O_2)_2$ is added; commercial platinizing solutions are also available). Connect the electrodes with two dry cells 1½ V each) in parallel and reverse the direction of the current once a minute for 6 min, or until the shiny platinum surface is covered. Avoid deposition of amorphous platinum on the electrodes.

Repeat the electrolytic process, using 10-percent sulfuric acid to remove chlorine. When not in use the cell should be kept immersed in distilled water.

2.7 The accuracy and reproducibility of results obtainable are dependent to a large extent on the type of bridge used, but may approach 2 percent with this equipment. Close attention to temperature is essential for reliable work.

2.8 Additional information on the theory and practice of specific conductance measurements may be found in Daniels and Alberty (1966) and in Scofield (1932).

3. Interferences

None.

4. Apparatus

4.1 *Conductivity cell:* Cells of at least two different cell constants should be available to measure a wide range of conductivities. The table below provides a general guide to the selection of an appropriate cell constant.

Specific conductance (μmho, at 25°C)	*Cell constant (cm^{-1})*
20-1,000	0.2
40-2,000	.5
100-4,000	1.0
200-10,000	2.0
400-20,000	5.0
1,000-40,000	10.0

4.2 *Conductivity meter,* wheatstone bridge type, or equivalent direct-reading meter.

4.3 *Thermometer,* 0°C to 50°C, graduated in 0.1°C. Some direct-reading conductivity meters have automatic temperature compensation built into the meter. Alternatively a thermistor device as described by Hughes (1966) provides a convenient means of directly computing the necessary temperature correction.

5. Reagents

Potassium chloride solution, 0.00702*N*: Dissolve 0.5234 g KCl, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

6. Procedure

6.1 Meters measuring resistance: The manufacturer's instructions for operation of the bridge should be followed explicitly. A constant-temperature room or 25°C bath simplifies temperature consideration. Where such facilities are not available, the sample should be brought to approximately room temperature before the determination. However, a group of samples standing in the laboratory are seldom at exactly the same temperature, because of the influence of drafts, sunlight, radiators, ovens, and open flames. Whether the conductance determination is made in the field or laboratory, the temperature of each sample should be determined at the time of measurement.

6.1.1 Prepare a graph of resistance of 0.00702*N* KCl throughout the operating temperature range.

6.1.2 Rinse the cell with sample.

6.1.3 Measure the resistance of the sample and record the temperature at the time of measurement. Record temperature to the nearest 0.1°C.

6.1.4 Determine the resistance of 0.00702*N* KCl at the temperature at which the sample resistance was measured from the graph prepared in step 6.1.1.

6.2 Direct-reading meters with built-in temperature compensators:

6.2.1 Prepare a table of conductance of 0.00702*N* KCl throughout the operating temperature range. Calculate and enter in table correction factors where measured conductance deviates from correct conductance.

6.2.2 Immerse probe-type cell in sample. (Cell will have been immersed in deionized water and blotted dry with tissue just before use.)

6.2.3 Measure conductance and temperature and record both measurements.

6.2.4 Refer to table prepared in 6.2.1 and apply appropriate correction factors to conductance measurements where necessary.

7. Calculations

Specific conductance (μmhos/cm at 25°C)

$$= \frac{R \text{ of } 0.00702N \text{ KCl}}{R \text{ of sample}} \times 1{,}000$$

where

R = resistance in ohms.

NOTE: Further calculations are unnecessary when measurements are made with a direct-reading meter with a built-in temperature compensator.

8. Report

Report specific conductance (μmho/cm at 25°C) (00095) as follows: less than 1,000 μmho/cm, to whole numbers; greater than 1,000 μmho/cm, three significant figures.

9. Precision

9.1 The precision of this method within the range of 100 to 1,600 μmho/cm can be expressed as follows:

$$S_T = 0.0197X + 2.61$$

where

S_T = overall precision, micromhos per centimeter, at 25°C, and

X = specific conductance, micromhos per centimeter,at 25°C.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (μmho/cm), at 25°C*	*Relative deviation (percent)*
30	94.4	4
29	1,250	2

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 148.

Daniels, Farrington, and Alberty, R. A., 1966, Physical chemistry [3d ed.]: New York, John Wiley & Sons, 671 p.

Hughes, L. S., 1966, Use of thermistor-thermometer in determination of specific conductance: U.S. Geological Survey Water-Supply Paper 1822, p. 66.

Scofield, C. S., 1932, Measuring the salinity of irrigation waters and of soil solutions with the wheatstone bridge: U.S. Department Agriculture Circular 232.

Turbidity, nephelometric (I–3860–78)

Parameter and Code: Turbidity (nephelometric turbidity unit): 00076

1. Application

This method is generally applicable to any sample that does not contain coarse material that settles rapidly. Samples greater than 40 nephelometric turbidity units (NTU) must be diluted prior to analysis.

2. Summary of method

2.1 The method presented below is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension under the same conditions. The greater the intensity of scattered light, the greater the turbidity. Formazin polymer, which has gained acceptance as the turbidity standard reference suspension in the brewing industry, is also used as the turbidity standard reference suspension for water. It is easy to prepare and is more reproducible in its light-scattering properties than clay or turbid, natural-water standards. The turbidity of a particular concentration of Formazin suspension is defined as 40 NTU. This same suspension of Formazin has a turbidity of approximately 40 units when measured on the Jackson candle turbidimeter; therefore turbidity units based on the Formazin preparation will closely approximate those derived from the Jackson candle turbidimeter, but may not always be identical to them.

2.2 For additional information on the turbidity measurement and its significance, see American Public Health Association and others (1976), California State Water Quality Control Board (1963), and [U.S.] Public Health Service (1962).

3. Interferences

The presence of colored solutes causes measured turbidity values to be low. Precipitation of dissolved constituents (e.g., Fe) causes measured turbidity values to be high.

4. Apparatus

Hach turbidimeter, Model No. 2100 or 2100A.

5. Reagents

5.1 *Hexamethylenetetramine* solution, 10 g/100 mL: Dissolve 10.0 g hexamethylenetetramine in demineralized water and dilute to 100.0 mL.

5.2 *Hydrazine sulfate* solution, 1 g/100 mL: Dissolve 1.000 g $(NH_2)_2 \cdot H_2SO_4$ in demineralized water and dilute to 100.0 mL.

5.3 *Turbidity* standard suspension I (Formazin): In a 100-mL volumetric flask mix 5.0 mL hydrazine sulfate solution with 5.0 mL hexamethylenetetramine solution. After 24 h standing at 25°C ± 3°C, dilute to 100.0 mL with demineralized water and mix well. Prepare fresh monthly (NOTE 1).

NOTE 1. Prepared standards of several ranges are available from the instrument manufacturer. These have a reliable shelf life of 4 to 6 months, thereby making more frequent preparation unnecessary.

5.4 *Turbidity* standard suspension II: Dilute 10.0 mL turbidity standard suspension I to 100.0 mL with demineralized water. The turbidity of this suspension is defined as 40 nephelometric turbidity units (NTU). Prepare fresh weekly. This suspension may be diluted as required to prepare more dilute turbidity standards.

6. Procedure

6.1 *Turbidimeter calibration:* The manufacturer's operating instructions should be followed. Measure the standards on the turbidimeter covering the range of 0 to 40 NTU. If the instrument is already calibrated in standard turbidity units, this procedure will check the accuracy of the calibration. At least one standard should be included for each instrument range to be used. Some instruments permit adjustment of sensitivity so that scale values will correspond to turbidities. *Reliance on a manufacturer's solid-*

scattering standard for setting overall instrument sensitivity for all ranges is not an acceptable practice unless the turbidimeter has been shown to be free of drift on all ranges. If a precalibrated scale is not supplied, then a calibration graph should be prepared for each range of the instrument.

6.2 *Turbidity less than 40 NTU:* Shake the sample to disperse the solids thoroughly. Wait until air bubbles disappear, then pour the sample into the turbidimeter tube. Read the turbidity directly from the instrument scale or from the appropriate calibration curve.

6.3 *Turbidity exceeding 40 NTU:* Dilute the sample with one or more volumes of nonturbid water until the turbidity falls below 40 NTU.

7. Calculations

$$\text{Turbidity (NTU)} \quad \text{observed turbidity} \times \frac{\text{final dilution volume}}{\text{original sample volume}}.$$

8. Report

Report turbidity (00076) as follows:

Turbidity range (NTU)	*Report to nearest*
0.0-1.0	0.05
1-10	0.1
10-40	1
40-100	5
100-400	10
400-1,000	50
> 1,000	100

9. Precision

According to data reported by the U.S. Environmental Protection Agency, the precision of a single laboratory, expressed in terms of the relative deviation (coefficient of variation) is as follows:

Mean (NTU)	Relative deviation *(percent)*
0.26	2

References

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater [14th ed.]: Washington, D.C., American Public Health Association, p. 132.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 156.

California State Water Quality Control Board, 1963, Water quality criteria: Publication 3–A, p. 290.

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environment Protection Agency, p. 207.

[U.S.] Public Health Service, 1962, Drinking water standards: Public Health Service Publication 956, p. 6.

GRAVIMETRY

Principles

Gravimetric determinations are based on the accurate measurement of the mass of a chemical compound of known composition and purity. The trend in modern analytical laboratories is away from the long, tedious, time-consuming gravimetric methods and toward faster titrimetric and instrumental techniques, particularly toward techniques that permit simultaneous determination of several constituents. Nevertheless there are some determinations that can be performed only gravimetrically. These include the determinations of the various forms of dissolved and suspended solids in a water sample.

Analytical balance

An analytical balance is an essential part of every gravimetric method. The type commonly used for this purpose is of the single-pan, direct-reading type, capable of measuring the mass of an object to within 0.1 mg. In order to maintain this sensitivity, great care must be observed in the use and maintenance of the balance. The balance must be located apart from the chemical laboratory in a room free of laboratory fumes. The room must also be free of strong drafts and the balance must be placed on a vibration-free stand, table, or shelf. Cleanliness is exceedingly important and any material spilled in the balance case must be cleaned up immediately. Objects to be weighed must not be handled with the bare hands, but only with ivory-tipped forceps or platinum-tipped tongs.

It is advisable to clean the balance thoroughly periodically and, at that time, to check its calibration. Weights conforming to Class S tolerances are satisfactory for routine water-analysis applications.

No chemicals are ever placed directly on the balance pan for weighing. At the very least a tared weighing paper or aluminum pan is used. Most commonly the material to be weighed is contained in a porcelain or platinum crucible or dish.

Accuracy

Gravimetric determinations can be among the most accurate of all quantitative determinations; they are time consuming, however. In quantitative gravimetric measurements of the solids content of water samples, the uncertainties about the composition of the material being weighed often exceed the uncertainty involved in determining its mass.

Instructions on the care and use of analytical balances and on the precautions to be observed in conducting gravimetric weighings and determinations may be found in any elementary textbook on quantitative analysis.

GRAVIMETRIC METHODS

Barium, dissolved, gravimetric (I-1080-78)

Parameter and Code: Barium, dissolved, ($\mu g/L$ as Ba): 01005

1. Application

The gravimetric method is recommended for water whose barium content is between 10,000 and about 100,000 $\mu g/L$, and for brines and industrial wastes. Samples containing more than 100,000 $\mu g/L$ must either be diluted or a smaller volume must be taken for analysis.

2. Summary of method

Barium is precipitated from an acidified sample as the sulfate, then ignited and weighed (Kolthoff and others, 1969). When the barium concentration of the sample is less than 10,000 $\mu g/L$, the quantity of barium sulfate precipitate is so small that results obtained by the gravimetric method may be in appreciable error. In such instances, determination by an atomic absorption spectrometric method is preferred.

3. Interferences

3.1 A major source of interference with the gravimetric method is the precipitation of the slightly soluble sulfates of such metals as calcium and strontium, which are often present in natural water. A second significant source of error is the possibility of coprecipitation and occlusion of other ions in the filtrate with barium sulfate. Iron, aluminum, manganese, and silica are often important contaminants in this category.

3.2 These possible interferences are particularly significant when the amount of barium is small but may usually be minimized if not eliminated if the barium determination is made on the filtrate from a gravimetric precipitation of calcium with oxalate.

4. Apparatus

4.1 *Casserole*, porcelain.

4.2 *Crucibles*, porcelain.

4.3 *Desiccator*.

4.4 *Filter paper*, Whatman No. 42, or equivalent.

4.5 *Muffle furnace*, 800°C.

4.6 *Steam bath*.

5. Reagents

5.1 *Hydrochloric acid*, concentrated (sp gr 1.19).

5.2 *Sulfuric acid*, concentrated (sp gr 1.84).

5.3 *Sulfuric acid, 1M*: *Cautiously* add 50 mL concentrated H_2SO_4 (sp gr 1.84) to 80 ml demineralized water and dilute to 1 L. Mix thoroughly.

6. Procedure

6.1 Pipet an aliquot of sample containing at least 1,000 μg Ba into a porcelain casserole.

6.2 Evaporate the aliquot to dryness and decompose any ammonium salts by gentle heating over an open flame.

6.3 Take up the residue with hot demineralized water and add 5 to 10 drops concentrated HCl.

6.4 Filter off any insoluble material through Whatman No. 42 paper and wash three times with hot demineralized water.

6.5 Combine the washings and filtrate, and dilute to 100 mL.

6.6 Heat the filtrate to boiling and add, by drops and with stirring, sufficient $1M$ H_2SO_4 to precipitate the barium and to provide a small excess. Digest the precipitate overnight on a steam bath.

6.7 Quantitatively transfer the precipitate to Whatman No. 42 filter paper. The beaker should be scrubbed at least three times with a rubber policeman.

6.8 Wash the beaker and the precipitate with hot demineralized water until a sample of the filtrate develops no turbidity with $AgNO_3$ solution.

6.9 Slowly ignite the precipitate in a tared porcelain crucible over a low, oxidizing flame until the filter paper is reduced to white ash.

6.10 Transfer the crucible to the muffle furnace and ignite at 800°C for 1 h.

6.11 Cool the crucible in a desiccator and weigh.

6.12 After weighing, add 1 drop concentrated H_2SO_4. Fume off and reweigh. The weighings in steps 6.11 and 6.12 should be identical. A discrepancy indicates probable coprecipitation of chlorides, and the weight taken in step 6.12 should be used in the calculation.

6.13 If the purity of the $BaSO_4$ with respect to calcium and strontium is questionable, dissolve the precipitate in the crucible with 5 ml hot concentrated H_2SO_4. Cool and pour into 50 mL demineralized water and dilute to 10 ml. Digest for 1 h on the steam bath, filter and wash with a little hot demineralized water, ignite, and weigh.

7. Calculations

$$\text{Ba in } \mu\text{g/L} = \frac{1{,}000}{\text{mL sample}} \times \mu\text{g BaSO}_4 \times 0.5884.$$

8. Report

Report barium, dissolved (01005), concentrations as follows: 10,000 μg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 49.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative chemical analysis [4th ed.]: New York, Macmillan, 1199 p.

Density, gravimetric (I–1312–78)

Parameter and Code: Density (g/mL at 20°C): 71820

1. Application

This method may be used to determine the density of any water from which the suspended sediment may be satisfactorily removed.

2. Summary of method

The density determination is based on the weight of a carefully measured volume of solution at a given temperature. Densities are determined at 20°C, the same temperature at which volumetric glassware is calibrated.

3. Interferences

The only significant interference with this method is suspended sediment, which may usually be removed by filtration, centrifugation, or flocculation. Precautions should be taken to minimize evaporation during removal of sediment.

4. Apparatus

4.1 *Pipet*, volumetric, calibrated to deliver 50 mL. The actual volume delivery of the pipet is determined by weighing a delivered volume of demineralized water at 20°C. The volume is obtained from relative-density tables in handbooks. Alternatively, 50-mL pycnometer can be used; it must be calibrated also.

4.2 *Water bath*, constant temperature, 20 ± 0.5°C.

4.3 *Weighing bottle*, 50-mL capacity.

5. Reagents

None required.

6. Procedure

6.1 Adjust the temperature of the sample to 20.0°C.

6.2 Using a previously calibrated 50-mL pipet, transfer the sample to a tared weighing bottle.

6.3 Stopper the bottle immediately to prevent water loss by evaporation.

6.4 Weigh the solution to the nearest 0.1 mg.

7. Calculations

7.1 Determine density as follows:

$$\text{Density} = \frac{\text{g sample}}{\text{mL sample}},$$

7.2 If a constant-temperature bath is not available, the determination can be made at the sample temperature and a correction applied for the departure from 20°C. The temperature is recorded with an accurate thermometer, and the relative density for that temperature obtained from a table. The density result is then corrected by the factor:

$$\frac{\text{Relative density } (20^\circ\text{C})}{\text{Relative density (test temperature in } ^\circ\text{C)}}$$

8. Report

Report density (71820) to three decimal places in terms of grams per millimeter at 20°C.

9. Precision

Precision data are not available for this method, but results are believed reproducible to ± 0.005 g/mL.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 89.

Solids, volatile on ignition, dissolved, gravimetric (I–1753–78)

Parameter and Code: Solids, volatile on ignition, dissolved (mg/L): 00520

1. Application

This method may be used to analyze all natural and treated waters and industrial and other wastes.

2. Summary of method

The residue obtained when determining dissolved solids (Method I–1750) is ignited at 550°C. The loss in weight of this residue on ignition is taken as a measure of dissolved volatile solids.

3. Interferences

3.1 None of the substances commonly occurring in natural waters interferes with this method.

3.2 Because of the great variability in the nature of the compounds that may be present in the sample, particularly samples of industrial and other wastes, the determination can be considered only an approximation of the amount of volatile material present. Much of the volatile material may have been driven off during the determination of total residue. Moreover, ignition at 550°C certainly volatilizes water of hydration from the hydrated salts present.

4. Apparatus

4.1 *Muffle furnace*, 550°C.

4.2 For additional items of required apparatus, see Solids, dissolved (Method I–1750).

5. Reagents

None required.

6. Procedure

6.1 Determine dissolved solids as directed in Method I–1750 beginning with paragraph 6.1.

6.2 Place the weighed evaporating dish in a muffle furnace at 550°C; heat for 1 h.

6.3 Remove and cool in a desiccator; weigh and record the weight to the nearest 0.1 mg.

7. Calculations

Solids, volatile on ignition, dissolved, mg/L

$$= \frac{1{,}000\ (ER - IR)}{V_s} \times 10^3$$

where

ER = weight of dissolved solids, grams,
IR = weight of ignited residue, grams, and
V_s = volume of sample, milliliters.

8. Report

8.1 Report solids, volatile on ignition, dissolved (00520), concentrations as follows: less than 1,000 mg/L, nearest milligram per liter; 1,000 mg/L and above, three signficant figures.

8.2 This determination is sometimes referred to as "volatile filterable solids."

9. Precision

Precision data are not available for this method.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 108.

Solids, volatile on ignition, suspended, gravimetric (I–3767–78)

Parameter and Code: Solids, volatile on ignition, suspended (mg/L): 00535

1. Application

This method may be used to analyze all natural and treated waters and industrial and other wastes.

2. Summary of method

The dry residue obtained for the determination of suspended solids (Method I 3765) is ignited at 550°C. The loss on ignition corresponds to the amount of volatile suspended solids.

3. Interferences

3.1 None of the substances commonly occurring in natural waters interferes with this method.

3.2 Because of the great variability in the nature of the compounds that may be present in the sample, particularly samples of industrial and other wastes, the determination can be considered only an approximation of the amount of volatile material present. Much of the volatile material may have been driven off during the determination of total residue. Moreover, ignition at 550°C certainly volatilizes water of hydration from the hydrated salts present.

4. Apparatus

4.1 *Muffle furnace*, 550°C.

4.2 For additional items of required apparatus, see Solids, dissolved (Method I–1750).

5. Reagents

None required.

6. Procedure

6.1 Determine suspended solids as directed in Method I–3765.

6.2 Place the weighed evaporating dish containing the dry suspended solids in a muffle furnace at 550°C; heat for 1 h.

6.3 Remove and cool in a desiccator. Weigh and record the weight to the nearest 0.1 mg.

7. Calculations

Solids, volatile on ignition, suspended, mg/L

$$= \frac{1{,}000 \times (ER - IR)}{V_s} \times 10^3$$

where

ER = weight of dry suspended solids, grams,
IR = weight of ignited suspended solids, grams, and
V_s = volume of sample, milliliters.

8. Report

8.1 Report solids, volatile on ignition, suspended (00535) concentrations as follows: less than 1,000 mg/L, nearest 1 mg/L per liter; 1,000 mg/L and above, three significant figures.

8.2 This determination is sometimes referred to as "solids, volatile nonfilterable."

9. Precision

Precision data are not available for this method.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 108.

Solids, volatile on ignition, total in bottom material, gravimetric (I–5753–78)

Parameter and Code: Solids, volatile on ignition, total in bottom material, dry wt (mg/kg): 00496

1. Application

This method may be used to analyze any sample of bottom material. Ordinarily, only that material that will pass through a 2-mm sieve is taken for analysis.

2. Summary of method

A portion of well mixed sample is dried at 110°C. A portion of the dry sample is carefully weighed and then ignited at 550°C. The loss of weight on ignition at this temperature represents the amount of volatile solids in the sample.

3. Interferences

None.

4. Apparatus

4.1 *Desiccator,* charged with indicating silica gel or other efficient desiccant.

4.2 *Muffle furnace,* 550°C.

4.3 *Oven,* 110°C.

4.4 *Platinum evaporating dishes,* 75- to 125-mL capacity, weighing less than 50 g. Platinum is recommended because the change in weight of glass or porcelain dishes may itself introduce appreciable error into the determination.

5. Reagents

None required.

6. Procedure

6.1 Spread approx 1 g of sample in the bottom of a platinum evaporating dish. Place in an oven at 110°C and heat overnight.

6.2 Place the dish containing the dry sample in a desiccator, cool, and weigh to the nearest 0.1 mg.

6.3 Ignite the weighed dry residue at 550°C for 1 h, cool in a desiccator and weigh to the nearest 0.1 mg.

7. Calculations

Solids, volatile on ignition (mg/kg)

$$= \frac{(DR - IR) \times 10^6}{DR}$$

where

IR = Weight of ignited residue, grams, and
DR = weight of dry residue, grams.

8. Report

8.1 Report solids, volatile on ignition (00496), concentrations as follows: less than 1,000 mg/kg, nearest milligram per kilogram; 1,000 mg/kg and above, three significant figures.

8.2 This determination is sometimes referred to as "solids, loss on ignition."

9. Precision

Precision data are not available for this method.

Solids, volatile on ignition, total, gravimetric (I–3753–78)

Parameter and Code: Solids, volatile on ignition, total (mg/L): 00505

1. Application

This method may be used to analyze all natural and treated waters and industrial and other wastes.

2. Summary of method

A measured volume of unfiltered, well mixed sample is evaporated to dryness and the residue dried at 110°C to determine the total solids (Method I–3750). This residue is then ignited at 550°C and reweighed, the difference in weight being termed total volatile solids.

3. Interferences

3.1 None of the substances commonly occurring in natural waters interferes with this method.

3.2 Because of the great variability in the nature of the compounds that may be present in the sample, particularly samples of industrial and other wastes, the determination can be considered only an approximation of the amount of volatile material present. Much of the volatile material may have been driven off during the determination of total residue. Moreover, ignition at 550°C certainly volatilizes water of hydration from the hydrated salts present.

4. Apparatus

4.1 *Muffle furnace*, 550°C.

4.2 For additional items of required apparatus, see Solids, dissolved (Method I–1750).

5. Reagents

None required.

6. Procedure

6.1 Determine the total solids as directed in Solids, total (Method I–3750).

6.2 Place the weighed evaporating dish in a muffle furnace at 550°C; heat for 1 h.

6.3 Remove and cool in a desiccator. Weigh and record the weight to the nearest 0.1 mg.

7. Calculations

Solids, volatile on ignition, total mg/L

$$= \frac{1{,}000 \times (\mathrm{ER} - \mathrm{IR})}{V_s} \times 10^3$$

where

ER = weight of evaporated total residue, grams,

IR = weight of ignited total residue, grams, and

V_s = volume of sample, milliliters.

8. Report

Report solids, volatile on ignition, total (00505), concentrations as follows: less than 1,000 mg/L, nearest 1 mg/L 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 108.

Solids, nonvolatile on ignition, dissolved, gravimetric (I–1752–78)

Parameter and Code: Solids, nonvolatile on ignition, dissolved (mg/L): 00525

1. Application

This method may be used to calculate nonvolatile dissolved solids on any sample on which the dissolved solids (Method I–1750) and the volatile dissolved solids (Method I–1753) have been determined.

2. Summary of method

The nonvolatile solids are determined by subtracting the volatile dissolved solids (Method I–1753) from the dissolved solids (Method I–1750).

7. Calculations

Solids, nonvolatile on ignition, dissolved,

$$\text{mg/L} = \text{DS} - \text{DV}$$

where

DS = dissolved solids, milligrams per liter, and

DV = solids, volatile on ignition, dissolved, milligrams per liter.

8. Report

8.1 Report solids, nonvolatile on ignition, dissolved (00525) concentrations as follows: less than 1,000 mg/L, nearest 1 mg/L; 1,000 mg/L and above, three significant figures.

8.2 This determination is also sometimes referred to as "solids, fixed dissolved," "solids, fixed filterable," or "residue, fixed filterable."

9. Precision

Precision data are not available for this method.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 108.

Solids, nonvolatile on ignition, suspended, gravimetric (I–3766–78)

Parameter and Code: Solids, nonvolatile on ignition, suspended (mg/L): 00540

1. Application

This method may be used to calculate nonvolatile suspended solids on any sample on which the suspended solids (Method I–3765) and volatile suspended solids (Method I–3767) have been determined.

2. Summary of method

The nonvolatile suspended solids are determined by subtracting the volatile suspended solids (Method I–3767) from the suspended solids (Method I–3765).

7. Calculations

Solids, nonvolatile on ignition, suspended,

$$\text{mg/L} = SS - VS$$

where

SS = suspended solids, milligrams per liter, and

VS = solids, volatile on ignition, suspended, milligrams per liter.

8. Report

8.1 Report solids, nonvolatile on ignition, suspended (00540), concentrations as follows: less than 1,000 mg/L, nearest milligram per liter; 1,000 mg/L and above, three significant figures.

8.2 This determination is sometimes referred to as "solids, fixed nonfilterable."

9. Precision

Precision data are not available for this method.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 108.

Solids, nonvolatile on ignition, total, gravimetric (I–3752–78)

Parameter and Code: Solids, nonvolatile on ignition, total (mg/L): 00510

1. Application

This method may be used to calculate total nonvolatile solids on any sample on which the total solids (Method I–3750) and the total volatile solids (Method I–3753) have been determined.

2. Summary of method

Total nonvolatile solids are determined by subtracting the total volatile solids (I–3753) from the total solids (I–3750).

7. Calculations

Solids, nonvolatile on ignition, total, (mg/L)

$$= TS - TV$$

where

TS = total solids, milligrams per liter, and

TV = solids, volatile on ignition, total, milligrams per liter.

8. Report

8.1 Report solids, nonvolatile on ignition, total (00510), concentrations as follows: less than 1,000 mg/L, nearest 1 mg/L; 1,000 mg/L and above, three significant figures.

8.2 This determination is also sometimes referred to as "solids, total fixed," or "residue, loss on ignition, ash, total, fixed."

9. Precision

Precision data are not available for this method.

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 108.

Solids, residue on evaporation at 105°C, dissolved, gravimetric (I–1749–78)

Parameter and Code: Solids, residue at 105 °C, dissolved (mg/L): 00515

1. Application

The residue-on-evaporation method is applicable to all waters regardless of concentration, provided that the residue layer in the evaporating dish is kept sufficiently thin.

2. Summary of method

2.1 A volume of filtered sample that will yield less than 200 mg residue is evaporated just to dryness on a steam bath. The residue is dried at 105°C for 2.0 h, cooled in a desiccator, and immediately weighed.

2.2 The weight of the residue is limited to 200 mg to insure subjection of all the residue to the full effects of drying at 105°C. Voluminous residues will often seal over during the evaporation process and even entrap pockets of water that will not be completely driven off during the drying process. Massive residues also give up their water of crystallization more slowly than thin films of residue. The chemical composition of the sample has a marked effect on the dissolved-solids value obtained, but the percentage of error incurred for any given chemical type of water is independent of the total concentration if the residue film is kept thin.

2.3 Inasmuch as many of the salts in the residue are hygroscopic, it is imperative that an efficient desiccant be used. Silica gel (indicating), anyhydrous $Mg(ClO_4)_2$ or $CaSO_4$, and $Mg(ClO_4)_2 \cdot 3H_2O$ are satisfactory and can be recommended. $CaCl_2$ is not suitable. Under no circumstances should the dried residues be allowed to stand for long periods of time before weighing.

3. Interferences

There are no known interferences to this method.

4. Apparatus

4.1 *Desiccator.*

4.2 *Oven,* 105°C, uniform temperature throughout.

4.3 *Platinum evaporating dishes,* 75- to 125-mL capacity, weighing less than 50 g. Platinum is recommended for precise work because the change in weight of glass or porcelain dishes may introduce appreciable error into the determination.

4.4 *Steam bath.*

6. Procedure

6.1 Pipet a volume of filtered sample containing 10 to 200 mg dissolved solids (500 mL maximum) into a tared platinum dish.

6.2 Evaporate the sample just to dryness on a steam bath.

6.3 Dry in an oven at 105°C for 2.0 h.

6.4 Cool in a desiccator and immediately weigh. Record the weight to the nearest 0.1 mg.

7. Calculations

$$\text{Dissolved solids (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times \text{mg residue.}$$

8. Report

Report dissolved-solids (00515) concentrations as follows: less than 1,000 mg/L, nearest whole number; 1,000 mg/L and above, three significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 11 percent at 63 mg/L and greater than 5 percent at 1160 mg/L.

Reference

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater [14th ed]: Washington, D.C., American Public Health Association, p. 93.

Solids, residue at 105°C, suspended, gravimetric (I-3765-78)

Parameter and Code: Solids, residue at 105°C, suspended (mg/L): 00530

1. Application

This method may be used to analyze any natural or treated water or industrial waste.

2. Summary of method

2.1 Suspended solids are those that are retained on a glass-fiber filter. The determined value is fairly representative of the sample but does not accurately represent the suspended-sediment concentration of a stream; suspended-solids values should not be confused with sediment concentration, which is the more accurate measure of material in suspension.

2.2 The sample is mixed thoroughly and an appropriate volume is rapidly poured off into a graduated cylinder. The suspended solids are collected on a glass-fiber filter, and the insoluble material dried and weighed.

3. Interferences

Precipitation in the sample during storage, such as in the formation of iron precipitates, will give erroneously high results.

4. Apparatus

4.1 *Desiccator*, charged with indicating silica gel or other efficient desiccant.

4.2 *Filtration apparatus*, consisting of suction flask, glass-fiber filter disk, and suitable holder.

4.3 *Oven*, 105°C.

6. Procedure

6.1 Shake the sample bottle vigorously and rapidly pour off a suitable volume into a graduated cylinder. Record the volume.

6.2 Quantitatively collect the suspended material in this sample on a tared glass-fiber filter disk. A blank should be determined on every box of glass-fiber filters.

6.3 Wash the suspended material on the filter sparingly with demineralized water.

6.4 Dry the residue and filter disk overnight at 105°C.

6.5 Cool in a desiccator and weigh the filter disk containing the dry residue to the nearest 0.1 mg. Record the weight.

7. Calculations

7.1 Apply a correction for any loss shown by the blank.

7.2 Determine suspended solids in milligrams per liter as follows:

Suspended solids, mg/L

$$= \frac{1{,}000 \times Wt_r}{V_s} \times 10^3$$

where

Wt_r = weight of residue, grams, and

V_s = volume of sample, milliliters.

8. Report

8.1 Report solids, residue at 105°C, suspended (00530) concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

8.2 This determination is sometimes referred to as "solids, total nonfilterable."

9. Precision

Precision data are not available for this method.

Reference

Guy, Harold P., 1969, Laboratory theory and methods for sediment analysis: Techniques of Water-Resources Investigations of the U.S. Geological Survey, book 5, chapter C1, p. 58.

Solids, residue on evaporation at 105°C, total, gravimetric (I–3750–78)

Parameter and Code: Solids, residue on evaporation at 105°C, total (mg/L): 00500

Total residue represents the sum of both dissolved and suspended (including colloidal) material in a sample. The determination is not exact, because of the compromise that must be made in selecting the temperature at which the evaporated residue is to be dried. At temperatures sufficient to drive off water of hydration of the hydrated salts that form on evaporation, there is risk of volatilization of the more volatile materials dissolved or suspended in the sample. On the other hand, drying at a sufficiently low temperature to conserve volatiles fails to remove much of the entrapped water and ordinary water of hydration. Because of these factors, the determination must be considered as providing only an approximation of the sum of dissolved and suspended matter.

The determination is not very useful; determinations of dissolved solids (Method I–1750) and suspended solids (Method I–3765) provide more useful information.

1. Application

This method may be used to determine the total solids concentration of any sample of water or industrial or other wastes.

2. Summary of method

An appropriate portion of a well mixed sample is evaporated to dryness and the resulting residue dried at a temperature of 105°C.

3. Interferences

Care must be taken to ensure that a representative sample is provided. Ordinarily, large, floating particles are excluded from the sample.

4. Apparatus

4.1 *Desiccator*, charged with indicating silica gel, or other efficient desiccant.

4.2 *Oven*, 105°C.

4.3 *Platinum evaporating dishes*, 75- to 125-mL capacity, weighing less than 50 g. Platinum is recommended because the change in weight of glass or porcelain dishes may itself introduce appreciable error into the determination.

6. Procedure

6.1 Shake the sample vigorously and rapidly pipet a suitable aliquot.

6.2 Transfer the sample to a tared platinum evaporating dish. Record the volume.

6.3 Rinse the pipet with demineralized water to ensure transfer of all particulate matter to the evaporating dish.

6.4 Evaporate the sample just to dryness on a steam bath.

6.5 Dry in an oven at 105°C for 2.0 h.

6.6 Cool in a desiccator and immediately weigh. Record the weight to the nearest 0.1 mg.

7. Calculations

$$\text{Total solids (mg/L)} = \frac{1{,}000 \times Wt_r}{V_s} \times 10^3$$

where

Wt_r = weight of residue, grams, and
V_s = volume of sample, milliliters.

8. Report

Report solids, residue on evaporation at 105°C, total, (00500), concentrations as follows: less than

1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 11 percent at 63 mg/L and greater than 5 percent at 1160 mg/L.

Reference

[U.S.] Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environment Protection Agency, p. 270.

Solids, residue on evaporation at 180°C, dissolved, gravimetric (I–1750–78)

Parameter and Code: Solids, residue on evaporation at 180°C, dissolved (mg/L): 70300

1. Application

The residue-on-evaporation method is applicable to all waters regardless of concentration, provided that the residue layer in the evaporating dish is kept sufficiently thin.

2. Summary of method

2.1 A volume of sample that will yield less than 200 mg residue is evaporated just to dryness on a steam bath. The residue is then dried at 180°C for 2.0 h, cooled in a desiccator, and immediately weighed.

2.2 The weight of the residue is limited to 200 mg to insure subjection of all the residue to the full effects of drying at 180°C. Voluminous residues will often seal over during the evaporation process and even entrap pockets of water that will not be completely driven off during the drying process. Massive residues also give up their water of crystallization more slowly than thin films of residue. The chemical composition of the sample has a marked effect on the dissolved-solids value obtained, but the precentage of error incurred for any given chemical type of water is independent of the total concentration if the residue film is kept thin.

2.3 Bicarbonate is converted to carbonate in the evaporation and drying process. The following general observations have been reported by Howard (1933). The residues of carbonate-type water that contains considerable magnesium chloride water can be expected to lose some weight (up to 50 or 100 mg/L) during the drying process; however, such loss of weight is usually more than offset by water of crystallization tightly held by the salts. Most of the water of crystallization is driven off from sulfates of sodium and magnesium when the residue is heated at 180°C, but this temperature is insufficient to dehydrate calcium sulfate completely. Residues of water with a high nitrate content may lose as much as 30 mg/L on heating.

2.4 Inasmuch as many of the salts in the residue are hygroscopic, it is imperative that an efficient desiccant be used. Silica gel (indicating), anhydrous $Mg(ClO_4)_2$ or $CaSO_4$, and $Mg(ClO_4)_2 \cdot 3H_2O$ are satisfactory and can be recommended. $CaCl_2$ is not suitable. Under no circumstances should the dried residues be allowed to stand for long periods of time before weighing.

3. Interferences

There are no known interferences to this method.

4. Apparatus

4.1 *Desiccator.*

4.2 *Oven,* 180°C, uniform temperature throughout.

4.3 *Platinum evaporating dishes,* 75-to 125-mL capacity, weighing less than 50 g. Platinum is recommended for precise work because the change in weight of glass or porcelain dishes may introduce appreciable error into the determination.

4.4 *Steam bath.*

5. Reagents

None required.

6. Procedure

6.1 Pipet a volume of sample containing 10 to 200 mg dissolved solids (500 mL maximum) into a tared platinum dish.

6.2 Evaporate the sample just to dryness on a steam bath.

6.3 Dry in an oven at 180°C for 2.0 h.

6.4 Cool in a desiccator and immediately weigh. Record the weight to the nearest 0.1 mg.

7. Calculations

$$\text{Dissolved solids (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times \text{mg residue.}$$

8. Report

Report solids, residue on evaporation at 180°C, dissolved (70300), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

9.1 The precision of this method within the range of 60 to 1,200 mg/L may be expressed as follows:

$$S_T = 0.034X + 4.81$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of dissolved solids, milligrams per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
18	62.9	11
19	525.2	4
15	1,159	5

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 145.

Howard, C. S., 1933, Determination of total dissolved solids in water analysis: Industrial Engineering Chemistry, Analytical Edition, v. 5, p. 4.

Titrimetry

Principles

Titrimetric analytical determinations are based on the reaction of an accurately measurable volume of a solution of known concentration with an exact equivalent amount of the substance being determined. The process of adding reagent solution to react with the sample is known as titration, and the reactant added during the course of the titration is known as a standard solution. Titrimetric determinations are inherently simpler than gravimetric determinations, and hence are usually preferred where simplicity and ease and speed of analysis are important. Their sensitivity and accuracy can be made to approach that of careful gravimetric measurements.

To be suitable as a basis for a titrimetric determination, the chemical reaction involved must proceed rapidly to completion with no side reactions. The reaction between a strong acid and a strong base is a good example of an ideal reaction for a titrimetric determination. The titration of the anion of a weak acid with a strong acid does not involve an ideal reaction, but the reaction does proceed to an identifiable point of completion. Such a reaction is made use of in the determination of the alkalinity of water samples, wherein the carbonate and bicarbonate anions are titrated with standard acid to the point where poorly dissociated carbonic acid is formed.

In addition to a straightforward chemical reaction, there must be an abrupt change of some property of the solution at the equivalence point of the titration. This may be a change in hydrogen-ion concentration, a sharp increase in the concentration of one of the titrant ions, a change in the electromotive potential, or even a change in the electrical conductivity of the solution. This abrupt change may sometimes be made apparent by adding to the system a color-change indicator solution that changes color abruptly when the reaction is complete at the equivalence point. When the equivalence point is accompanied by a rapid change of pH, an indication of its occurrence may be monitored with a glass electrode. Such titrations are called electrometric titrations.

Standard solutions

The standard solution used in titrimetry must be simple to prepare and preferably stable for a comparatively long time to avoid the need for frequent restandardization. Quite commonly, the standard solution is not prepared directly, but is prepared at a concentration very close to that desired and then standardized by titrating an accurately measured amount of a primary standard. The primary standard must be of high purity, or at least of accurately known purity, must be stable, and easily dried and weighed. An example of a good primary standard substance is the sodium carbonate used to standardize the strong acid used in neutralization titrations. There are many other primary standards useful for various purposes; these are available on specification, from the usual chemical supply companies. The National Bureau of Standards supplies certified primary standard substances for the common titrimetric applications.

Factor-weight computations

The concentration of the titrant may be adjusted so that when a sample of given size is taken for analysis, the volume of titrant in milliliters is in simple proportion to the concentration of the sought constituent, for example, in milligrams per liter. Some time is involved in initial adjustment of the titrant concentration, but time is saved in the long run when many analyses are performed. Simplifying computations in this manner also minimizes arithmetic error in handling the data.

Automated titrations

Systems are available that automate the entire process of a titrimetric determination including the initial measurement of a sample aliquot into a titration vessel. Titrations involving colorimetric as well as electrometric detection of the equivalence point may be automated. The samples are placed in a revolving tray or moving platform and are sequentially moved into position for titration. As each titration is completed, a printer records the sample number and the exact volume of titrant added. Such automatic titrators speed the analytical process by freeing the analyst for other duties while the titrations are being carried out. They also have the advantage of duplicating equivalence-point conditions for all samples, avoiding individual judgment on the part of the analyst. Such automated equipment is particularly desirable when a great many routine samples are to be analyzed.

Titrimetric Methods

Bromide, dissolved, titrimetric, hypochlorite oxidation (I–1125–78)

Parameter and Code: Bromide, dissolved (mg/L as Br): 71870

1. Application

This oxidation method is generally applicable to natural waters containing at least 1.0 mg/L of bromide. Highly concentrated brines may require dilution.

2. Summary of method

2.1 The determination of bromide involves the determination of bromide and iodide collectively, and then the determination of iodide alone; bromide is calculated by difference. Bromide and iodide are oxidized to bromate and iodate, respectively, by hypochlorite, and the excess hypochlorite is subsequently decomposed with sodium formate (Kolthoff and others, 1969).

$$3OCl^{-1} + Br^{-1} \rightarrow BrO_3^{-1} + 3Cl^{-1}$$

$$3OCl^{-1} + I^{-1} \rightarrow IO_3^{-1} + 3Cl^{-1}$$

Iodine equivalent to the combined iodate and bromate is then liberated by addition of potassium iodide to an acid solution.

$$BrO_3^{-1} + 6I^{-1} + 6H^{+1} \rightarrow 3I_2 + 3H_2O + Br^{-1}$$

$$IO_3^{-1} + 5I^{-1} + 6H^{+1} \rightarrow 3I_2 + 3H_2O.$$

The liberated iodine is titrated with standard thiosulfate with use of starch as the indicator.

$$I_2 + 2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2I^{-1}$$

2.2 Iodide alone is determined by oxidation to iodate with bromine in a buffered solution. Iodine equivalent to the iodate is then liberated from added potassium iodide and titrated with thiosulfate as in the combined determination.

3. Interferences

Iron, manganese, and organic material interfere with the basic reactions of the method, but their interferences are removed by preliminary treatment with calcium oxide.

4. Apparatus

4.1 *Buret*, 10-mL capacity.

4.2 *Iodine flasks*, 250-mL capacity.

5. Reagents

5.1 *Acetic acid*, 2.2*M*: Mix 125 mL glacial $HC_2H_3O_2$ (sp gr 1.069) with demineralized water and dilute to 1 L.

5.2 *Bromine water*, saturated: Add to approx 250 mL demineralized water slightly more liquid Br_2 than will dissolve when shaken. Store in a glass-stoppered actinic-glass bottle.

5.3 *Calcium carbonate*, powder, $CaCO_3$.

5.4 *Calcium oxide*, anhydrous powder, CaO.

5.5 *Hydrochloric acid*, 6*M*: Mix 50 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 100 mL.

5.6 *Methyl red indicator* solution, 0.01 g/100 mL: Dissolve 0.01 g water-soluble methyl red in 100 mL demineralized water.

5.7 *Potassium fluoride*, crystals, $KF \cdot 2H_2O$.

5.8 *Potassium hypochlorite* solution, 4.4 g/L: Dissolve 6.2 g KOH in 100 mL demineralized water; then saturate the solution with bromine-free Cl_2 while continually cooling and stirring. Store in a glass-stoppered actinic-glass bottle. Prepare fresh daily.

5.9 *Potassium iodide*, crystals, IO_3^{-1}-free: The KI can be tested for IO_3^{-1} by dissolving about 0.1 g in 5 mL demineralized water, acidifying with 1 or 2 drops concentrated H_2SO_4 (sp gr 1.84), and adding 2 to 3 mL starch indicator solution. Immediate appearance of a blue color indicates the presence of IO_3^{-1}; slow color formation is due to atmospheric oxidation.

5.10 *Sodium acetate* solution, 165 g/L: Dissolve 273 g $NaC_2H_3O_2 \cdot 3H_2O$ in demineralized water and dilute to 1 L.

5.11 *Sodium chloride*, crystals: In addition to conforming to American Chemical Society specifications, these shall also be free from I^{-1}, IO_3^{-1}, Br^{-1}, and BrO_3^{-1}. The NaCl can be tested for IO_3^{-1} and BrO_3^{-1} by dissolving about 0.1 g in 5 mL demineralized water, acidifying with 1 or 2 drops concentrated H_2SO_4 (sp gr 1.84), and adding 2 to 3 mL starch indicator solution. Immediate appearance of a blue color indicates presence of IO_3^{-1} or BrO_3^{-1}; slow color formation is caused by atmospheric oxidation.

5.12 *Sodium formate* solution, 50 g/100 mL: Dissolve 50 g $NaHCO_2$ in hot demineralized water and dilute to 100 mL. Prepare fresh daily.

5.13 *Sodium molybdate* solution, 1.0 g/100 mL: Dissolve 1.2 g $Na_2MoO_4 \cdot 2H_2O$ in demineralized water and dilute to 100 mL.

5.14 *Sodium thiosulfate* solution, 0.10*N*: Dissolve 25.0 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free, demineralized water; add 1 g Na_2CO_3 and dilute to 1 L.

5.15 *Sodium thiosulfate* standard solution, 0.010*N*: Dilute 100.0 mL 0.10*N* sodium thiosulfate solution to 950 mL with carbon dioxide-free, demineralized water and standardize against KIO_3 as follows: Dry approx 0.5 g KIO_3 for 2 h at 180°C. Dissolve 0.3567 g in demineralized water and dilute to 1,000 mL. Pipet 25.00 mL of the KIO_3 solution into a 250-mL iodine flask, then add successively 75 mL demineralized water and 0.5 g KI crystals. After solution is complete, add 10 mL 3.6*M* H_2SO_4. Allow the stoppered flask to stand 5 min in the dark, then titrate with standard $Na_2S_2O_3$ solution with use of 2 mL starch indicator solution as the end point is approached (light straw color).

5.16 *Starch indicator* solution, stable; or "thyodene," powdered (Fisher No. T138, or equivalent).

5.17 *Sulfuric acid*, 3.6*M*: *Cautiously* add 200 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Remove soluble iron, manganese, and organic matter by adding a slight excess CaO to approx 400 mL sample; shake, let stand about 1 h, and filter through a dry, moderately retentive filter paper. Discard the first 75 mL of filtrate.

6.2 For the combined Br^{-1} and I^{-1} determination, pipet a volume of the filtrate containing less than 5.0 mg Br^{-1} and I^{-1} (100.0 mL max) into a 250-mL iodine flask, and adjust the volume to approx 100 mL.

6.3 Prepare a blank of approx 100 mL demineralized water, and carry it through the procedure along with the sample.

6.4 Add sufficient NaCl to produce a 3.0-g Cl^{-1} content.

6.5 Add a drop of methyl red indicator solution, and neutralize the solution with 6*M* HCl.

6.6 Add 10 mL KClO solution, 0.5 mL 6*M* HCl, and sufficient $CaCO_3$ to produce an excess of approx 0.1 g.

6.7 Heat the solution to boiling and maintain this temperature for about 8 min.

6.8 Reduce the excess KClO by adding 2 mL $NaHCO_2$ solution, taking precaution to wash down the sides of the flask with a small amount of hot water. Keep the solution hot for an additional 8 min.

6.9 Cool and add several drops of Na_2MoO_4 solution. If any iron precipitates at this point, add 0.5 g $KF \cdot 2H_2O$.

6.10 Add approx 1 g KI, 10 mL 3.6*M* H_2SO_4, and let stand 5 min in the dark.

6.11 Titrate the liberated I_2 with 0.010*N* $Na_2S_2O_3$ standard solution, adding 2 to 3 mL starch indicator solution as the end point is approached. Disregard the return of the blue color after the end point has been reached.

6.12 For the I^{-1} determination, pipet a volume of filtrate (step 6.1) containing less than 5.0 mg I^{-1} (100.0 mL max) into a 250-mL iodine flask, and adjust the volume to approx 100 mL.

6.13 Prepare a blank of 100.0 mL demineralized water and carry through the procedure along with the sample.

6.14 Add a drop of methyl red indicator solution, and make the solution just acid with 3.6*M* H_2SO_4.

6.15 Add 15.0 mL $NaC_2H_3O_2$ solution, 5.0 mL 2.2*M* $HC_2H_3O_2$, and sufficient bromine water to produce a light yellow color, mix, and allow to stand 5 min.

6.16 Reduce the excess Br_2 by adding $NaHCO_2$ solution drop by drop until the yellow tinge in the sample disappears, then add an excess of 1 mL.

6.17 Wash down the sides of the flask with a small amount of water and blow out Br_2 vapors with a syringe and a glass tube inserted into the mouth of the flask. If any iron precipitates at this point, add 0.5 g $KI \cdot 2H_2O$.

6.18 Add approx 1 g KI, 10 mL 3.6*M* H_2SO_4, and let stand 5 min in the dark.

6.19 Titrate the liberated I_2 with 0.010*N* $Na_2S_2O_3$ standard solution, adding 2 to 3 mL starch indicator solution as the end point is approached. Disregard any return of the blue color after the end point has been reached.

7. Calculations

7.1 Determine $Br^- + I^{-1}$ in epL as follows:

$$Br^{-1} + I^{-1}\ (\text{epL}) = \frac{1{,}000}{\text{mL sample}} \times \frac{0.01}{6} \times (\text{mL}_t - \text{mL}_b).$$

7.2 Determine I^- in epL as follows:

$$I^{-1}\ (\text{epL}) = \frac{1{,}000}{\text{mL sample}} \times \frac{0.01}{6} \times (\text{mL}_i - \text{mL}_b).$$

7.3 Determine Br^{-1} in mg/L as follows:

$$Br^{-1}\ (\text{mg/L}) = 79.90 \times [\text{epL}\ (I^{-1} + Br^{-1}) - \text{epL}\ I^{-1}].$$

where

epL = equivalents per liter,
mL_b = titrant volume for blank determination,
mL_t = titrant volume for combined determination, and
mL_i = titrant volume for I^{-1} determination.

8. Report

Report bromide (71870) concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

The single operator precision of this method (American Society for Testing and Materials, 1976) may be expressed as follows:

$$S_o = 0.0044X$$

where

S_o = single-operator precision, milligrams per liter, and
X = concentration of bromide, milligrams per liter.

References

American Society for Testing and Materials, 1976, Annual Book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, 956 p.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 58.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, quantitative chemical analysis [4th ed.]: New York, Macmillan, 1199 p.

Chloride, dissolved, titrimetric, mercurimetric (I–1184–78)

Parameter and Code: Chloride, dissolved (mg/L as Cl): 00940

1. Application

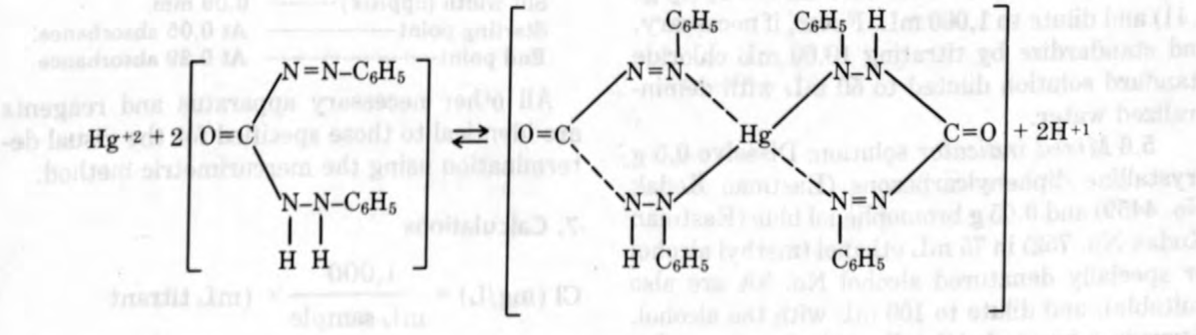
This method may be used to determine chloride in all samples containing at least 0.1 mg/L of chloride. Samples containing lower concentrations must be concentrated by evaporation.

2. Summary of method

2.1 Mercuric and chloride ions form a highly stable, soluble complex.

$$Hg^{+2} + 2Cl^{-1} \rightleftarrows HgCl_2.$$

Thus, the chloride in a sample may be titrated with a standard solution of a soluble mercuric salt such as mercuric nitrate. The equivalence point is detected by adding a small amount of diphenylcarbazone to the sample. A slight excess of mercuric ions, above that required to complex all of the chloride, reacts with this indicator to form a blue-violet complex (Dubsky and Trtilek, 1933, 1934; Clarke, 1950).



2.2 The optimum pH range for the titration is between 3.0 and 3.6. If the titration is made in a solution whose pH is less than 3.0, the results will be high, and if in a solution of pH greater than 3.6, the results are low (Clarke, 1950; Thomas, 1954). The proper pH for the titration is easily obtained by adding bromophenol blue indicator and carefully adding dilute nitric acid or sodium hydroxide to adjust the sample to the desired pH.

2.3 Two standard mercuric nitrate solutions are required. A dilute solution should be used to titrate samples containing less than 200 mg/L chloride; a more concentrated mercuric nitrate solution should be used to titrate samples containing more than 200 mg/L.

3. Interferences

The method is not subject to interference from any of the anions and cations normally found in natural waters; up to 1,000 mg/L of nitrate, sulfate, phosphate, magnesium, and calcium and 1×10^6 μg/L of aluminum do not interfere. One thousand μg/L of zinc, lead, nickel, ferrous, and chromous ions affect the colors of the solution, but not the accuracy of the titration. Nickel ion at a concentration of 1×10^5 μg/L is purple in neutral solution, green in acid solution, but gray at the chloride titration end point. Copper ion is tolerable up to 50,000 μg/L. Chromate and ferric ions, if present at concentrations exceeding 10,000 μg/L, must be reduced to their lower valence states prior to titration. The addition of dilute fresh hydroquinone solution insures reduction of these ions. Sulfite ion interferes at concentrations above 10 mg/L; the addition of a small amount of 30-percent hydrogen peroxide eliminates sulfite interference. Bromide and iodide are titrated with the chloride.

4. Apparatus

4.1 *Buret*, 5-, 10-, or 25-mL capacity.

4.2 *Fluorescent lamp*, white.

4.3 *Stirrer*, magnetic.

5. Reagents

5.1 *Chloride* standard solution, 1.00 mL = 1.00 mg Cl^{-1}: Dissolve 1.648 g primary standard NaCl crystals, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Hydrogen peroxide*, 30 percent.

5.3 *Hydroquinone* solution, 1 g/100 mL: Dissolve 1.0 g purified hydroquinone in demineralized water and dilute to 100 mL.

5.4 *Mercuric nitrate* standard solution I, 1.00 mL ≎ 1.00 mg Cl^{-1}: Dissolve 4.832 g $Hg(NO_3)_2 \cdot H_2O$ in 50 mL demineralized water acidified with 0.5 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL. Filter, if necessary, and standardize by titrating 25.00 mL chloride standard solution diluted to 50 mL with demineralized water.

5.5 *Mercuric nitrate* standard solution II, 1.00 mL ≎ 0.500 mg Cl^{-1}: Dissolve 2.416 g $Hg(NO_3)_2 \cdot H_2O$ in 25 mL demineralized water acidified with 0.25 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL. Filter, if necessary, and standardize by titrating 10.00 mL chloride standard solution diluted to 50 mL with demineralized water.

5.6 *Mixed indicator* solution: Dissolve 0.5 g crystalline diphenylcarbazone (Eastman Kodak No. 4459) and 0.05 g bromophenol blue (Eastman Kodak No. 752) in 75 mL ethanol (methyl alcohol or specially denatured alcohol No. 3A are also suitable), and dilute to 100 mL with the alcohol. Store in a brown bottle; discard after 6 months.

5.7 *Nitric acid*, 0.05*M*: Dilute 3.0 mL concentrated HNO_3 (sp gr 1.41) to 1 L with demineralized water.

5.8 *Sodium hydroxide* solution, 0.05*M*: Dissolve 2.0 g NaOH in demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing not more than 20 mg chloride (50.0 mL max) into a 125-mL erlenmeyer flask, and adjust the volume to approx 50 mL. If the sample contains less than 0.1 mg/L chloride, evaporate an appropriate volume to 50 mL.

6.2 Place the flask on a magnetic stirrer and add 10 drops mixed indicator solution.

6.3 If a blue, blue-violet, or red color develops, add nitric acid (0.05*M*) by drops until the color changes to yellow. Add 1.0 mL excess acid. If a yellow or orange color forms when the mixed indicator is added, add sodium hydroxide solution (0.05*M*) by drops until the color changes to blue violet; then add nitric acid (0.05*M*) by drops until the color changes to yellow; then add 1 mL excess.

6.4 Titrate the solution with mercuric nitrate standard solution I or II until a blue-violet color persists throughout the solution.

6.5 Determine a blank correction by similarly titrating 50 mL demineralized water.

6.6 Alternatively, the end point of the titration may be determined spectrophotometrically, with attendant improvement in precision. The following conditions have been found satisfactory:

Spectrophotometer	Beckman Model B, or equivalent
Wavelength	530 nm.
Phototube	Blue-sensitive.
Cells	100-mL beakers.
Sensitivity setting	2.
Slit width (approx)	0.09 mm.
Starting point	At 0.05 absorbance.
End point	At 0.29 absorbance.

All other necessary apparatus and reagents are identical to those specified for the visual determination using the mercurimetric method.

7. Calculations

$$\text{Cl (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times (\text{mL titrant} - \text{mL blank}) \times (\text{mg Cl per mL titrant}).$$

8. Report

Report chloride, dissolved (00940), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 1.0 to 210 mg/L may be expressed as follows:

$$S_T = 0.045X + 0.43$$

where

S_T = overall precision, milligrams per liter and

X = concentration chloride, milligrams per liter

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
14	1.51	24
15	187	7

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 71.

Clarke, F. E., 1950, Determination of chloride in water: Analytical Chemistry, v. 22, p. 553, 1458.

Dubsky, J. V., and Trtilek, J., 1933, Microvolumetric analysis using diphenylcarbazide and diphenylcarbazone as indicators (mercurimetry): Mikrochemie, v. 12, p. 315.

———1934, Mercurimetric determination of iodide using diphenylcarbazone as indicator: Mikrochemie, v. 15, p. 95.

Thomas, J. F., 1954, Mercurimetric determination of chlorides: American Water Works Association Journal, v. 46, p. 257.

Chloride, dissolved, titrimetric, Mohr (I–1183–78)

Parameter and Code: Chloride, dissolved (mg/L as Cl): 00940

1. Application

1.1 This procedure is recommended for samples whose chloride concentration is less than 2,000 mg/L and more than 10 mg/L, although it can be used satisfactorily for measuring chloride concentrations up to 5,000 mg/L.

1.2 Two titrant solutions of different concentrations are recommended. The more dilute titrant is used when the chloride concentration is less than 200 mg/L. However, the end point is not as sharp as when a more concentrated titrant is used, and the latter is recommended when the chloride concentration of the sample exceeds 200 mg/L. In high-chloride waters, the voluminous precipitate tends to mask the end point, and the maximum amount of chloride that can be titrated satisfactorily is about 50 mg. Excessive sample dilution decreases both the precision and accuracy of the determination. Sample aliquots of less than 10 mL are not recommended.

2. Summary of method

2.1 In the well-known Mohr method for determination of chloride the solution is saturated with silver chloride at the equivalence point and contains equal concentrations of silver and chloride ions. When potassium chromate is used as an indicator, a slight excess of silver precipitates as red silver chromate. The following reactions occur:

$$Ag^{+1} + Cl^{-1} \rightarrow AgCl\downarrow$$

$$2Ag^{+1} + CrO_4^{-2} \rightarrow Ag_2CrO_4\downarrow$$

The pH for the titration should be between 7.0 and 10.5. In an acid medium, the sensitivity of the method is decreased; the second ionization constant of chromic acid is small, and therefore the chromate ion reacts with hydrogen ions

$$CrO_4^{-2} + H^{+1} \leftrightarrows HCrO_4^{-1}.$$

The solution should not be too alkaline because of the limited solubility of silver hydroxide (Collins, 1928). Calcium carbonate can be used to adjust the pH of acidic waters without danger of making the solution too alkaline. Detection of the end point is facilitated by illuminating the titration with yellow light or by viewing the titration through yellow goggles or a filter.

2.2 Additional information on the principle of the determination is given by Kolthoff and others (1969).

3. Interferences

Iodide and bromide titrate stoichiometrically as chloride. Phosphate, sulfide, and cyanide interfere. Sulfide and cyanide can be removed by acidifying and boiling the sample, then adjusting the pH with calcium carbonate. Hydrogen sulfide can often be removed simply by passing pure air through the sample. Sulfite interferes but can be oxidized readily to sulfate with hydrogen peroxide.

4. Apparatus

4.1 *Buret*, 25-mL capacity.

4.2 *Yellow light* (or filter).

5. Reagents

5.1 *Chloride* standard solution, 1.00 mL = 1.00 mg Cl^{-1}: Dissolve 1.648 g of primary standard NaCl crystals, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Potassium chromate indicator* solution, 5 g/100 mL: Dissolve 5 g K_2CrO_4 in 100 mL demineralized water. Add silver standard solution

II until a small amount of red Ag_2CrO_4 precipitates. Allow to stand overnight and filter to remove the Ag_2CrO_4.

5.3 *Silver* standard solution I, 1.00 mL ≎ 5.00 mg Cl^{-1}. Pulverize approx 30 g $AgNO_3$ crystals in a clean mortar and dry at 105°C to 120°C. Discoloration of the crystals indicates decomposition caused by excessive drying temperature or impurities. Dissolve 23.96 g dried $AgNO_3$ in demineralized water and dilute to 950 mL. Standardize by titrating 25.00 mL chloride standard solution diluted to 50 mL. Store in a lightproof bottle.

5.4 *Silver* standard solution II, 1.00 mL ≎ 0.50 mg Cl^{-1}: Dilute 100 mL silver standard solution I with demineralized water to 1,000 mL. Check the titer of the reagent by titrating 10.0 mL chloride standard solution. Store in lightproof bottle.

6. Procedure

6.1 Pipet a volume of sample containing less than 50 mg Cl^{-1} (50.00 mL max) into a porcelain evaporating dish, and adjust the volume to approx 50 mL.

6.2 Add 10 drops K_2CrO_4 indicator solution.

6.3 With constant stirring, titrate with silver standard solution I or II until the pink-red Ag_2CrO_4 persists for 10 to 15 sec.

6.4 Determine a blank correction by similarly titrating 50 mL demineralized water. The normal blank correction with silver standard solution II is 0.05 or 0.10 mL. No blank correction is required with the more concentrated titrant.

7. Calculations

$$\text{Cl (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times (\text{mL titrant} - \text{mL blank}) \times (\text{mg Cl per mL titrant}).$$

8. Report

Report chloride, dissolved (00940), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 1.0 to 210 mg/L may be expressed as follows:

$$S_T = 0.034X + 0.33$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of chloride, milligrams per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
10	1.56	26
9	194	4

References

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 69.

Collins, W. D., 1928, Notes on practical water analysis: U.S. Geological Survey Water-Supply Paper 596–H, p. 235–266.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative chemical analysis [4th ed]: New York, MacMillan, 1199 p.

Hardness, titrimetric, complexometric (I–1338–78)

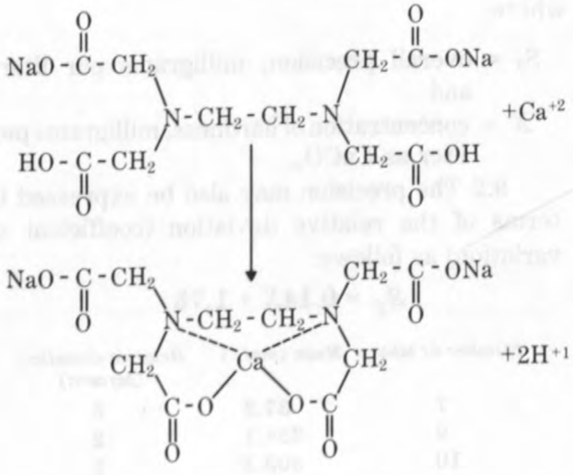
Parameter and Code: Hardness (mg/L as $CaCO_3$): 00900

1. Application

This procedure is applicable to most natural and treated waters, but the method fails conspicuously at times with acid or polluted waters that contain excessive amounts of heavy metals.

2. Summary of method

2.1 Disodium dihydrogen ethylenediaminetetraacetate (Na_2EDTA) forms a slightly ionized colorless stable complex with alkaline-earth ions. The indicator Eriochrome Black T is bright blue in the absence of alkaline earths, but with them forms a deep-red complex which has a higher ionization constant than the Na_2EDTA complex. Hence, by using Eriochrome Black T as an indicator, the alkaline earths can be titrated with Na_2EDTA. For example, with calcium, the reaction is:



2.2 All alkaline earths titrate approximately stoichiometrically. The titration should proceed immediately upon addition of the indicator, as the color of the solution fades on standing. The optimum pH of the titration is 10.4 or above.

2.3 Additional information on the principle of the determination is given by Goetz, Loomis, and Diehl (1950) and Botha and Webb (1952).

3. Interferences

3.1 The salt Na_2EDTA also forms stable complexes with iron, manganese, copper, lead, cobalt, zinc, and nickel. Heavy-metal interferences can usually be eliminated by complexing the metals with cyanide. In the presence of cyanide, the procedure can be used to analyze undiluted samples having iron, copper, zinc, or lead concentrations as high as 10 mg/L.

3.2 The higher oxidation states of manganese above Mn^{+2} react rapidly with the indicator to form discolored oxidation products. Hydroxylamine hydrochloride reagent is used to reduce manganese to the divalent state. The divalent manganese interference can be removed by addition of one or two small crystals of potassium ferrocyanide.

3.3 In the presence of high aluminum concentrations, a characteristic effect will be observed as the end point is approached. The blue color that indicates that the end point has been reached will appear and then on short standing will revert to red. The reversion should not be confused with the gradual change that normally takes place in the titrated sample several minutes after the titration has been completed.

4. Apparatus

Visual-titration assembly: Some analysts prefer to use conventional lighting and hand stirring. Others report better results by using a visual-titration assembly consisting of a motor-driven stirrer, 25-mL buret, white-porcelain-base buret holder, and shaded incandescent lamp. The sample beaker is placed near the front of the porcelain base, and the reaction is viewed diagonally downward through the side of the beaker and against the white background. Illumination is from behind the beaker.

5. Reagents

5.1 *Ammonium hydroxide*, concentrated (sp gr 0.900).

5.2 *Calcium* standard solution, 1.00 mL = 1.00 mg $CaCO_3$: Suspend 1.000 g $CaCO_3$, dried at 180°C for 1.0 h, in approx 600 mL demineralized water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 mL with demineralized water.

5.3 *Eriochrome Black T indicator* solution, 0.4 g/L: Dissolve 0.40 g Eriochrome Black T in 100 mL demineralized water and dilute to 1 L with 95-percent ethanol. This indicator is stable for at least 2 months. The Eastman Kodak Co. reagent has been found to be satisfactory.

5.4 *Hydroxylamine hydrochloride* solution, 30 g/L: Dissolve 30 g $NH_2OH \cdot HCl$ in demineralized water and dilute to 1 L.

5.5 *Potassium ferrocyanide*, crystals.

5.6 *Sodium cyanide* solution (CAUTION: NaCN is a deadly poison, and the reagent solution must be marked), 2.5 g/100 mL: Dissolve 2.5 g NaCN in demineralized water and dilute to 100 mL.

5.7 Na_2EDTA standard solution, 1.00 mL $\Bumpeq$ 1.00 mL mg $CaCO_3$: Dissolve 3.72 g $Na_2EDTA \cdot 2H_2O$, dried overnight in an H_2SO_4 desiccator, in demineralized water and dilute to 1,000 mL. The reagent is stable for several weeks and a larger volume is usually prepared. Check the titer of the reagent by titrating 25.0 mL calcium standard solution as described in the procedure for sample analysis.

6. Procedure

6.1 Pipet a volume of sample containing less than 25 mg hardness (50.0 mL max) into a 150-mL beaker, and adjust the volume to approx 50 mL.

6.2 Insert the beaker in the titration assembly and start the stirrer.

6.3 Add 1 mL $NH_2OH \cdot HCl$ solution.

6.4 Add 1 mL concentrated NH_4OH. (If not tightly stoppered, it tends to lose strength, and 1 mL of weak NH_4OH will not buffer the solution to the desired pH.)

6.5 Add 2 mL NaCN solution (CAUTION: deadly poison). The addition of NaCN may be omitted if copper, zinc, lead, cobalt, and nickel are entirely absent, and if the sample contains less than 0.25 mg Fe and 0.025 mg Mn.

6.6 If manganese is present, add one or two small crystals of $K_4Fe(CN)_6 \cdot 3H_2O$. Stir and wait at least 5 min until the $Mn_2Fe(CN)_6$ precipitates.

6.7 Add 2.0 mL Eriochrome Black T indicator solution.

6.8 Titrate with Na_2EDTA standard solution until blue or purple swirls begin to show. The end point is reached when all traces of red and purple have disappeared, and the solution is clear blue in color. The change in color occurs rapidly; so the end point of the titration must be approached cautiously.

7. Calculations

$$\text{Hardness, as } CaCO_3 \text{ (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times \text{mL titrant.}$$

8. Report

Report hardness, as $CaCO_3$ (00900), as follows: less than 10 mg/L, whole numbers; 10 mg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 10 to 300 mg/L may be expressed as follows:

$$S_T = 0.14X + 1.75$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of hardness, milligrams per liter as $CaCO_3$.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

$$S_T = 0.14X + 1.75$$

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
7	37.3	6
9	254.1	2
10	303.3	2

References

Botha, C. R., and Webb, M. M., 1952, The versenate method for the determination of calcium and magnesium in mineralized waters containing large concentrations of interfering ions: Institute of Water Engineers Journal, v. 6.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 95.

Goetz, C. A., Loomis, T. C., and Diehl, H., 1950, Total hardness in water—the stability of standard disodium dihydrogen ethylenediamine tetraacetate solutions: Analytical Chemistry, v. 22, p. 798.

Iodide, dissolved, titrimetric, bromine oxidation (I-1370-78)

Parameter and Code: Iodide, dissolved (mg/L as I): 71865

1. Application

This method may be used to analyze any natural or treated waters or brines containing at least 1.0 mg iodide per liter, and from which interfering substances have been removed.

2. Summary of method

Iodide in buffered solution is oxidized by bromine to iodate; the excess bromine is subsequently removed by adding sodium formate (Kolthoff and others, 1959):

$$I^{-1} + 3Br_2 + 3H_2O \rightarrow IO_3^{-1} + 6HBr.$$

odine equivalent to the iodate is then liberated y addition of potassium iodide to an acid soluion

$$IO_3^{-1} + 5I^{-1} + 6H^{+1} \rightarrow 3I_2 + 3H_2O.$$

inally the liberated iodine is titrated with tandard thiosulfate solution with starch used as he indicator

$$I_2 + 2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2I^{-1}.$$

. Interferences

Iron, manganese, and organic material interfere with the basic reactions of the method, but heir interferences are removed by preliminary reatment with calcium oxide.

. Apparatus

4.1 *Buret*, 10-mL capacity.

4.2 *Flasks*, 250-mL capacity.

5. Reagents

5.1 *Acetic acid*, 2.2M: Mix 125 mL glacial H_3COOH (sp gr 1.05) with demineralized water nd dilute to 1 L.

5.2 *Bromine water*, saturated: Add to prox 250 mL demineralized water slightly m liquid Br_2 than will dissolve when shaken. St in a glass-stoppered actinic-glass bottle.

5.3 *Calcium oxide*, CaO, anhydrous p der.

5.4 *Methyl red indicator solution*, 0.01 g/ mL: Dissolve 0.01 g water-soluble methyl re 100 mL demineralized water.

5.5 *Potassium fluoride*, $KF \cdot 2H_2O$, cryst

5.6 *Potassium iodide*, crystals, IO_3^{-1}-f The KI can be tested for IO_3^{-1} by dissolving g in 5 mL water, acidifying with 1 or 2 dr concentrated H_2SO_4 (sp gr 1.84), and adding 2 3 mL starch indicator. Immediate appearance a blue color indicates the presence of IO_3^{-1}; sl color formation is due to atmospheric oxidati

5.7 *Sodium acetate solution*, 165 g/L: D solve 274 g $CH_3COONa \cdot 3H_2O$ in demineraliz water and dilute to 1 L.

5.8 *Sodium formate solution*, 50 g/100 m Dissolve 50 g HCOONa in hot demineraliz water and dilute to 100 mL. Prepare fresh da

5.9 *Sodium thiosulfate solution*, 0.10N: D solve 25 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-f demineralized water. Add 1 g Na_2CO_3 and dil to 1 L.

5.10 *Sodium thiosulfate standard soluti* 0.010N: Dilute 100 mL 0.10N sodium thiosulf solution to 960 mL with carbon dioxide-free d mineralized water and standardize against KI as follows: Dry approx 0.5 g KIO_3 for 2 h 180°C. Cool and dissolve 0.3567 g in deminer ized water; dilute to 1,000 mL. Pipet 25.0 mL the KIO_3 solution into a 250-mL flask, then a successively 75 mL demineralized water and g KI crystals. After solution is complete, add mL 1.0N H_2SO_4. Allow the stoppered flask stand 5 min in the dark, then titrate with stan ard $Na_2S_2O_3$ solution with use of 2 mL starch i dicator solution as the end point is approach (light-straw color).

Iodide, dissolved, titrimetric, bromine oxidation (I–1370–78)

Parameter and Code: Iodide, dissolved (mg/L as I): 71865

1. Application

This method may be used to analyze any natural or treated waters or brines containing at least 1.0 mg iodide per liter, and from which interfering substances have been removed.

2. Summary of method

Iodide in a buffered solution is oxidized by bromine to iodate; the excess bromine is subsequently removed by adding sodium formate (Kolthoff and others, 1969):

$$I^{-1} + 3Br_2 + 3H_2O \rightarrow IO_3^{-1} + 6HBr.$$

Iodine equivalent to the iodate is then liberated by addition of potassium iodide to an acid solution

$$IO_3^{-1} + 5I^{-1} + 6H^{+1} \rightarrow 3I_2 + 3H_2O.$$

Finally the liberated iodine is titrated with standard thiosulfate solution with starch used as the indicator

$$I_2 + 2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2I^{-1}.$$

3. Interferences

Iron, manganese, and organic material interfere with the basic reactions of the method, but their interferences are removed by preliminary treatment with calcium oxide.

4. Apparatus

4.1 *Buret*, 10-mL capacity.

4.2 *Flasks*, 250-mL capacity.

5. Reagents

5.1 *Acetic acid*, 2.2*M*: Mix 125 mL glacial CH_3COOH (sp gr 1.06) with demineralized water and dilute to 1 L.

5.2 *Bromine water*, saturated: Add to approx 250 mL demineralized water slightly more liquid Br_2 than will dissolve when shaken. Store in a glass-stoppered actinic-glass bottle.

5.3 *Calcium oxide*, CaO, anhydrous powder.

5.4 *Methyl red indicator* solution, 0.01 g/100 mL: Dissolve 0.01 g water-soluble methyl red in 100 mL demineralized water.

5.5 *Potassium fluoride*, KF $2H_2O$, crystals.

5.6 ***Potassium iodide,*** crystals, IO_3^{-1}-free. The KI can be tested for IO_3^{-1} by dissolving 0.1 g in 5 mL water, acidifying with 1 or 2 drops concentrated H_2SO_4 (sp gr 1.84), and adding 2 or 3 mL starch indicator. Immediate appearance of a blue color indicates the presence of IO_3^{-1}; slow color formation is due to atmospheric oxidation.

5.7 *Sodium acetate* solution, 165 g/L: Dissolve 274 g $CH_3COONa \cdot 3H_2O$ in demineralized water and dilute to 1 L.

5.8 *Sodium formate* solution, 50 g/100 mL: Dissolve 50 g HCOONa in hot demineralized water and dilute to 100 mL. Prepare fresh daily.

5.9 *Sodium thiosulfate* solution, 0.10*N*: Dissolve 25 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free demineralized water. Add 1 g Na_2CO_3 and dilute to 1 L.

5.10 *Sodium thiosulfate* standard solution, 0.010*N*: Dilute 100 mL 0.10*N* sodium thiosulfate solution to 950 mL with carbon dioxide-free demineralized water and standardize against KIO_3 as follows: Dry approx 0.5 g KIO_3 for 2 h at 180°C. Cool and dissolve 0.3567 g in demineralized water; dilute to 1,000 mL. Pipet 25.0 mL of the KIO_3 solution into a 250-mL flask, then add successively 75 mL demineralized water and 0.5 g KI crystals. After solution is complete, add 10 mL 3.6*M* H_2SO_4. Allow the stoppered flask to stand 5 min in the dark, then titrate with standard $Na_2S_2O_3$ solution with use of 2 mL starch indicator solution as the end point is approached (light-straw color).

$$\text{Normality of } Na_2S_2O_3 = \frac{0.25}{\text{mL } Na_2S_2O_3}$$

5.11 *Starch indicator* solution, stable; or "thyodene," powdered (Fisher No. T138, or equivalent).

5.12 *Sulfuric acid*, 3.6*M*: *Cautiously* add 200 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water, cool, and dilute to 1 L.

6. Procedure

6.1 Remove dissolved iron, manganese, and organic matter by adding a slight excess CaO to approx 400 mL of sample; shake, let stand approx 1 hr, and filter through a dry, moderately retentive filter paper. Discard the first 75 mL of filtrate.

6.2 Pipet a volume of the filtrate containing less than 5.0 mg I^{-1} (100.0 mL max) into a 250-mL flask, and adjust the volume to 100 mL.

6.3 Prepare a blank of 100 mL demineralized water and carry it through the procedure along with the sample.

6.4 Add 1 drop methyl red indicator solution and make the solution just acid with 3.6*M* H_2SO_4.

6.5 Add 15.0 mL CH_3COONa solution and 5.0 mL 2.2*M* CH_3COOH.

6.6 Add sufficient Br_2 water to produce a light-yellow color, mix, and allow to stand 5 min.

6.7 Reduce the excess Br_2 by adding HCOONa solution until the yellow tinge in the sample disappears; then add 1 mL excess.

6.8 Wash down the sides of the flask with a small amount of water, and expel Br_2 vapors with a syringe and a glass tube inserted through the mouth of the flask.

6.9 If any iron precipitates at this point, add 0.5 g $KF \cdot 2H_2O$.

6.10 Add approx 1 g KI and 10 mL 3.6*M* H_2SO_4; mix and let stand 5 min in the dark.

6.11 Titrate the liberated I_2 with standard $Na_2S_2O_3$ solution, adding 2 or 3 mL starch indicator solution as the end point is approached (light-straw color). Disregard a return of the blue color after the end point has been reached.

7. Calculations

$$\text{I, mg/L} = \frac{1{,}000}{\text{mL sample}} \times 21.15$$

$$\times \left[(\text{mL titrant} - \text{mL blank}) \times N\right],$$

where

N = normality of standard thiosulfate solution, and

21.15 = equivalent weight of iodide

8. Report

Report iodide, dissolved (71865), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

The single operator precision of this method (American Society for Testing and Materials, 1976) may be expressed as follows:

$$S_o = 0.009X$$

where

S_o = single operator precision, milligrams per liter, and

X = concentration of iodide, milligrams per liter.

References

American Society for Testing and Materials, 1976, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 330.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 98.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative Chemical Analysis [4th ed.]: New York, Macmillan, 1199 p.

Nitrogen, ammonia plus organic, total in bottom material, titrimetric digestion-distillation (I–5553–78)

Parameter and Code: Nitrogen, ammonia plus organic, total in bottom material, dry wt (mg/kg as N): 00626

1. Application

This method may be used to determine the total ammonia-plus-organic nitrogen concentration in any sample of the bottom material containing at least 1 mg/kg. Only that portion of bottom material that passes a 2-mm sieve is taken for analysis.

2. Summary of method

The sample is subjected to a digestion whereby all organic nitrogen-containing compounds are converted to ammonium salts. The resulting mixture is then made strongly alkaline and the ammonia so formed is distilled from the mixture into a solution of boric acid and subsequently determined by titration with standard sulfuric acid solution.

3. Interferences

There are no known interferences with this method.

4. Apparatus

Kjeldahl distillation apparatus, including 500-mL kjeldahl flasks.

5. Reagents

5.1 *Ammonium chloride*, crystals.

5.2 *Boric acid* solution, 20 g/L: Dissolve 20 g H_3BO_3 crystals in 800 mL ammonia-free water and dilute to 1 L.

5.3 *Kel-Pak* powder No. 3.

5.4 *Mixed indicator* solution: Dissolve 20 mg methyl red and 100 mg bromocresol green in 100 mL 95-percent ethanol. Store in a well-sealed bottle.

5.5 *Sodium carbonate* solution, 0.0357*N*: Dissolve 1.892 g primary standard Na_2CO_3 in carbon dioxide-free water and dilute to 1,000 mL.

5.6 *Sodium hydroxide-thiosulfate* solution: CAUTIOUSLY dissolve 500 g NaOH in 600 mL ammonia-free water. Add 80 g $Na_2S_2O_3 \cdot 5H_2O$ and dilute to 1 L.

5.7 *Sodium thiosulfate*, crystals, $Na_2S_2O_3 \cdot 5H_2O$.

5.8 *Sucrose*.

5.9 *Sulfuric acid*, concentrated, sp gr 1.84.

5.10 *Sulfuric acid* standard solution, approx 0.036*N*: With care, add 1.0 mL concentrated H_2SO_4 (sp gr 1.84) to 800 mL ammonia-free water and dilute to 1 L. Standardize by titrating 25.0 mL 0.0357*N* Na_2CO_3 to pH 4.5. Compute normality of sulfuric acid standard solution to four decimal places.

6. Procedure

6.1 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace with use of nessler reagent (CAUTION: deadly poison). (See Method I–1520.)

6.2 Weigh to the nearest milligram, 3 g of bottom material sample, prepared as directed in Method P–0810, and transfer to the digestion flask.

6.3 In the same manner prepare a blank, using 2.0 g sucrose. Analyze the blank and each sample as directed in paragraphs 6.4 to 6.10.

6.4 With care, add 25 mL concentrated H_2SO_4 (sp gr 1.84), and under a hood, swirl the contents of the flask until thoroughly mixed.

6.5 Add one Kel-Pak and mix well. Add a few glass beads and begin the digestion. Continue the digestion until a clear solution is obtained, and then continue fuming 1 h.

6.6 Cool the flask until crystals appear (do not cool completely). Add 150 mL ammonia-free water; mix and allow to cool.

6.7 Add 100 mL NaOH-$Na_2S_2O_3$ solution. Immediately connect the flask to the distillation apparatus and cautiously mix the contents by swirling.

6.8 Distill at a rate of not more than 10 mL/min nor less than 6 mL/min; collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.9 Collect approx 200 mL of distillate, dilute to 250 mL with ammonia-free water, and mix.

6.10 To the distillate, add 3 drops mixed indicator solution, and titrate with sulfuric acid standard solution until the color of the solution changes from yellow to red.

7. Calculations

Nitrogen, total, ammonia plus organic

$$(\text{mg/Kg}) = \frac{V_a \times N_a \times 14{,}000}{Wt_s}$$

where

V_a = volume of standard H_2SO_4 used to titrate sample, milliliters, minus volume used to titrate blank, milliliters,

N_a = normality of standard H_2SO_4 solution, and

Wt_s = weight of sample, grams.

8. Report

Report nitrogen, total ammonia plus organic (00626), in bottom material as follows: less than 100 mg/kg, nearest 1 mg/kg; 100 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.

Nitrogen, total in bottom material, titrimetric, digestion–distillation (I–5554–78)

Parameter and Code: Nitrogen, total in bottom material, dry wt, (mg/kg as N): 00603

1. Application

This method may be used to determine the total nitrogen concentration of any sample of bottom material containing at least 1 mg/kg. Only that portion of bottom material that passes a 2-mm sieve is taken for analysis.

2. Summary of method

Salicylic acid in concentrated sulfuric acid is added to the sample of bottom material. The sample is then subjected to a digestion whereby all nitrogen-containing compounds are converted to ammonium salts. The resulting mixture is then made strongly alkaline and the ammonia so formed is distilled from the mixture into a solution of boric acid and subsequently determined by titration with standard sulfuric acid solution.

3. Interferences

There are no known interferences with this method.

4. Apparatus

Kjeldahl distillation apparatus, 500-mL flasks.

5. Reagents

5.1 *Ammonium chloride*, crystals.

5.2 *Boric acid* solution, 20 g/L: Dissolve 20 g H_3BO_3 crystals in 800 mL ammonia-free water and dilute to 1 L.

5.3 *Kel-Pak* powder No. 3.

5.4 *Mixed indicator* solution: Dissolve 20 mg methyl red and 100 mg bromocresol green in 100 mL 95-percent ethanol. Store in a well-sealed bottle.

5.5 *Salicylic acid*, crystals.

5.6 *Sodium carbonate* solution, 0.0357*N*: Dissolve 1.892 g primary standard Na_2CO_3 in carbon dioxide-free water and dilute to 1,000 mL.

5.7 *Sodium hydroxide-thiosulfate* solution: With care, dissolve 500 g NaOH in 600 mL ammonia-free water. Add 80 g $Na_2S_2O_3 \cdot 5H_2O$ and dilute to 1 L.

5.8 *Sodium thiosulfate*, crystals, $Na_2S_2O_3 \cdot 5H_2O$.

5.9 *Sucrose*.

5.10 *Sulfuric acid*, concentrated, sp gr 1.84.

5.11 *Sulfuric acid* standard solution, approx 0.036*N*: With care, add 1.0 mL concentrated H_2SO_4 (sp gr 1.84) to 800 mL ammonia-free water and dilute to 1 L. Standardize by titrating 25.0 mL 0.0357*N* Na_2CO_3 to pH 4.5. Compute normality of sulfuric acid standard solution to four decimal places.

6. Procedure

6.1 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent (CAUTION: deadly poison). (See Method I–1520.)

6.2 Weigh, to the nearest milligram, 3 g of bottom material sample, prepared as directed in Method P–0810, and transfer to the digestion flask.

6.3 In the same manner prepare a blank and standard, using 2.0 g sucrose for the blank and 0.1000 g NH_4Cl plus 2.0 g sucrose for the standard.

6.4 With care, add 25 mL concentrated H_2SO_4 (sp gr 1.84), and then add 1.0 g salicylic acid. Under a hood, swirl the contents of the flask until thoroughly mixed. Allow to stand for at least 30 min.

6.5 Under a hood, add 5 g $Na_2S_2O_3 \cdot 5H_2O$ and heat gently over a bunsen burner. Let stand for about 5 min or until any frothing ceases.

6.6 Add 1 Kel-Pak and mix well. Add a few glass beads and begin the digestion. Continue the digestion until a clear solution is obtained, and then continue fuming 1 h.

6.7 Cool the flask until crystals appear. (Do not cool completely.) Add 150 mL ammonia-free water; mix and allow to cool.

6.8 To avoid bumpng during the subsequent distillation, transfer the entire solution from the digestion flask to a clean kjeldahl flask. Rinse the digestion flask with a minimum of ammonia-free water and add to the contents of the clean flask.

6.9 Add 100 mL NaOH–$Na_2S_2O_3$ solution. Immediately connect the flask to the distillation apparatus and cautiously mix the contents by swirling.

6.10 Distill at a rate of not more than 10 mL/min nor less than 6 mL/min; collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.11 Collect approx 200 mL of distillate, dilute to 250 mL with ammonia-free water, and mix.

6.12 Add 3 drops mixed indicator solution to the distillate and titrate with sulfuric acid standard solution until the solution changes from yellow to red.

7. Calculations

$$\text{Nitrogen, total, mg/kg} = \frac{V_a \times N_a \times 14{,}000}{Wt_s}$$

where

V_a = volume of standard H_2SO_4 used to titrate sample, milliliters minus volume used to titrate blank, milliliters,

N_a = normality of standard H_2SO_4 solution, and

Wt_s = weight of sample, grams.

8. Report

Report total nitrogen (00603) in bottom material as follows: less than 100 mg/kg, nearest mg/kg; 100 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.

Oxygen demand, biochemical, titrimetric, 5-day at 20°C (I–1578–78)

Parameter and Code: Oxygen demand, biochemical, 5-day at 20°C (mg/L): 00310

1. Application

This method may be used to determine the oxygen requirements between the limits of 1.0 to several thousand mg/L of oxygen of wastewaters and of waters that are recipients of wastes.

2. Summary of method

The water or wastewater sample is incubated for 5 days at 20°C in the dark. The decrease in oxygen content of the sample at the end of the incubation period is a measure of the biochemical oxygen demand (BOD) of the sample.

3. Interferences

3.1 Sulfite and thiosulfate ions interfere with the modified Winkler method used to determine dissolved oxygen concentration and must be absent.

3.2 Other substances that interfere in the Winkler determination of dissolved oxygen (Method I–1575) must be considered as possible sources of error in this determination.

4. Apparatus

4.1 *Bottles*, BOD incubation.

4.2 *Buret*, 25-mL capacity.

4.3 *Incubator*, for operation at 20°C ± 1°C.

5. Reagents

See Method I–1575, Oxygen, dissolved.

6. Procedure

There are many general methods written for the determination of biochemical oxygen demand (BOD) in various types of wastewaters. An excellent discussion of the determination and an acceptable procedure to be followed may be found in "Standard Methods for the Examination of Water and Wastewater," 14th edition (1976), p. 543.

7. Calculations

See reference cited.

8. Report

Report biochemical oxygen demand (BOD), 5-day at 20°C (00310) as follows: less than 10.0 mg/L, one decimal; 10.0 mg/L and above, two significant figures.

9. Precision

Because of the varied nature of wastewaters analyzed by this method, and because of differences in analytical operations among laboratories performing BOD analyses, precision data have little meaning.

Reference

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater [14th ed.]: Washington, D.C., American Public Health Association, p. 543.

Oxygen demand, chemical, total in bottom material, titrimetric, dichromate oxidation (I–5560–78)

Parameter and Code: Oxygen demand, chemical, total in bottom material, dry wt (mg/kg): 00339

1. Application

1.1 This method may be used to analyze samples of bottom material containing more than 100 mg/kg chemical oxygen demand (COD). Samples containing less than 1,000 mg/kg COD should be analyzed as directed in paragraph 6.10.

1.2 Bottom materials may be analyzed by procedure after they have been prepared as directed in Method P–0810 or P–0811.

2. Summary of method

Organic and other oxidizable material is oxidized by refluxing with standard acid-dichromate solution in the presence of silver sulfate catalyst. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as indicator.

3. Interferences

Reducing substances such as ferrous iron, nitrites, and chlorides interfere, since they are oxidized. Chlorides constitute by far the largest and most common interference, being quantitatively oxidized by dichromate in acid solution. One mg/L of chloride is equivalent to 0.226 mg/L COD. To eliminate chloride interference, mercuric sulfate is added to the sample to form a soluble mercuric chloride complex. Nitrite interference may be eliminated by incorporating in the standard dichromate solution 10 mg of sulfamic acid for each milligram of nitrite in the reflux flask.

4. Apparatus

4.1 *Reflux* apparatus, consisting of 500-mL erlenmeyer flask and water-cooled condenser, with ground-glass joints and made of heat-resistant glass.

4.2 *Hot plate* or heating mantle.

5. Reagents

5.1 *Ferrous ammonium sulfate* standard solution I, approx 0.250*N*: Dissolve 98.0 g $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in demineralized water. Add 20 mL concentrated H_2SO_4 (sp gr 1.84), cool, and dilute to 1 L with demineralized water. To standardize: Dilute 25.0 mL standard 0.2500*N* $K_2Cr_2O_7$ solution to 250 mL. Add 20 mL concentrated H_2SO_4 (sp gr 1.84) and cool. Titrate with the ferrous ammonium sulfate solution, using 8 to 10 drops ferroin indicator. Compute normality of the ferrous ammonium sulfate standard solution to four decimal places. The solution must be standardized daily, or before use.

5.2 *Ferrous ammonium sulfate* standard solution II, 0.025*N*: Dilute 100 mL ferrous ammonium sulfate standard solution I to 1,000 mL with demineralized water. The normality of this solution is dependent upon the standardized normality of solution I.

5.3 *Mercuric sulfate*, powdered $HgSO_4$.

5.4 *Orthophenanthroline ferrous sulfate (ferroin) indicator* solution: Dissolve 1.48 g 1,10-(ortho)-phenanthroline monohydrate and 0.70 g $FeSO_4 \cdot 7H_2O$ in 100 mL water. The prepared indicator is available commercially.

5.5 *Potassium dichromate* standard solution I, 0.2500*N*: Dissolve 12.2588 g $K_2Cr_2O_7$ primary standard, dried for 2 h at 110°C, in demineralized water and dilute to 1,000 mL.

5.6 *Potassium dichromate* standard solution II, 0.0250*N*: Dilute 100 mL of potassium dichromate standard solution I to 1,000 mL with demineralized water.

5.7 *Silver sulfate*, powder, Ag_2SO_4.

5.8 *Sulfamic acid*, crystals.

5.9 *Sulfuric acid*, concentrated, sp gr 1.84.

6. Procedure

6.1 Weigh to the nearest milligram an amount of wet sample (1.0 g maximum) that will consume approx one-half of the $0.2500N$ $K_2Cr_2O_7$ solution added in paragraph 6.5.

6.2 Transfer the sample to a 500-mL reflux flask, add 50 mL demineralized water and then add slowly, over a period of 2 to 3 min, 1 g $HgSO_4$; allow to stand 5 min, swirling frequently.

6.3 Add 1 g Ag_2SO_4 and a few glass beads that have been ignited at 600°C for 1 h.

6.4 Cool in ice water and add 75 mL concentrated H_2SO_4 (sp gr 1.84) slowly enough, with mixing, to prevent appreciable solution heating.

6.5 Add 25.0 mL $0.2500N$ $K_2Cr_2O_7$ solution and mix thoroughly by swirling (NOTE 1).

NOTE 1. If contents are not well mixed, superheating may result, and the contents of the flask may be expelled from the open end of the condenser.

6.6 Attach flask to condenser, start water flow, and reflux for 2 h.

6.7 Allow flask to cool and wash down condenser with 25 mL demineralized water.

6.8 Dilute to 300 mL with demineralized water, cool to room temperature, and titrate the excess dichromate with ferrous ammonium sulfate standard solution I, using 8 to 10 drops ferroin indicator solution. The end point is a sharp change from blue green to reddish brown.

6.9 A demineralized-water blank is carried through all steps of the procedure with each group of samples.

6.10 Samples containing less than 1,000 mg/kg COD should be reanalyzed, using $0.025N$ solutions of potassium dichromate and ferrous ammonium sulfate. A sample size should be selected so that no more than half the dichromate is reduced.

7. Calculations

7.1 Compute the dry weight of sample as follows:

$$\text{Sample, dry weight (g)} = W\,\frac{(100 - M)}{100}$$

where

W = wet weight of the sample, grams, and
M = percentage moisture.

7.2 Determine the chemical oxygen demand in each sample as follows:

$$\text{COD (mg/kg)} = \frac{(A - B)N \times 8{,}000}{\text{grams of sample (dry weight)}},$$

where

COD = chemical oxygen demand from dichromate,
A = amount of ferrous ammonium sulfate for blank, milliliters,
B = amount of ferrous ammonium sulfate for sample, milliliters, and
N = normality ferrous ammonium sulfate.

8. Report

Report COD, total in bottom material, dry weight (00339) as follows: less than 10,000 mg/kg to the nearest 100 mg/kg; 10,000 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.

Oxygen demand, chemical, total, titrimetric, 0.25*N* dichromate oxidation (I–3560–78)

Parameter and Code: Oxygen demand, chemical, total, 0.25*N* dichromate (mg/L): 00340

1. Application

This method may be used to analyze natural waters and industrial wastes containing more than 50 mg/L chemical oxygen demand (COD) and less than 2,000 mg/L of chloride. Samples containing less than 50 mg/L COD should be analyzed by Method I–3562. COD values for samples containing more than 2,000 mg/L of chloride should be corrected as indicated in paragraph 6.9.

2. Summary of method

2.1 Organic and other oxidizable material is oxidized by refluxing with standard acid-dichromate solution in the presence of silver sulfate catalyst. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as indicator.

2.2 For additional information see American Society for Testing and Materials (ASTM) Method D1252–67 (1974), Standard Methods of Test for COD in Water (ASTM, 1977).

3. Interferences

Reducing substances such as ferrous iron, nitrites, and chlorides interfere, since they are oxidized. Chlorides constitute by far the largest and most common interference, being quantitatively oxidized by dichromate in acid solution. One milligram of chloride per liter is equivalent to 0.226 mg/L COD. To eliminate chloride interference, mercuric sulfate is added to the sample to form a soluble mercuric chloride complex. Nitrite interference may be eliminated by incorporating in the standard dichromate solution 10 mg of sulfamic acid for each milligram of nitrite in the reflux flask.

4. Apparatus

4.1 *Reflux* apparatus, consisting of 500-mL erlenmeyer flask and water-cooled condenser, with ground-glass joints and made of heat-resistant glass.

4.2 *Hot plate* or heating mantle.

5. Reagents

5.1 *Ferrous ammonium sulfate* standard solution, approx 0.250*N*: Dissolve 98.0 g $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in demineralized water. Add 20 mL concentrated H_2SO_4 (sp gr 1.84), cool, and dilute to 1 L with demineralized water. To standardize: Dilute 25.0 mL standard 0.2500*N* $K_2Cr_2O_7$ solution to 250 mL. Add 20 mL concentrated H_2SO_4 (sp gr 1.84) and cool. Titrate with the ferrous ammonium sulfate solution, using 8 to 10 drops ferroin indicator. Compute normality of the ferrous ammonium sulfate standard solution to four decimal places. The solution must be standardized daily, or before use.

5.2 *Ferrous ammonium sulfate* standard solution II, 0.025*N*: Dilute 100 mL of ferrous ammonium sulfate standard solution I to 1,000 mL with demineralized water. The normality of this solution is dependent upon the standardized normality of solution I.

5.3 *Mercuric sulfate*, powdered $HgSO_4$.

5.4 *Orthophenanthroline ferrous sulfate (ferroin) indicator* solution: Dissolve 1.48 g 1,10-(ortho)-phenanthroline monohydrate and 0.70 g $FeSO_4 \cdot 7H_2O$ in 100 mL water. The prepared indicator is available commercially.

5.5 *Potassium dichromate* standard solution I, 0.2500*N*: Dissolve 12.2588 g $K_2Cr_2O_7$ primary standard, dried for 2 h at 110°C, in demineralized water and dilute to 1,000 mL.

5.6 *Potassium dichromate* standard solution II, 0.0250*N*: Dilute 100 mL of potassium dichromate standard solution I to 1,000 mL with demineralized water.

5.7 *Silver sulfate*, powder, Ag_2SO_4.

5.8 *Sulfamic acid*, crystals.

5.9 *Sulfuric acid*, concentrated, sp gr 1.84.

6. Procedure

6.1 Pipet 50.0 mL of a well mixed sample, or a smaller volume diluted to 50.0 mL, into the reflux flask and add slowly, over a period of 2 to 3 min, 1 g $HgSO_4$; allow to stand 5 min, swirling frequently.

6.2 Add 1 g Ag_2SO_4 and a few glass beads that have been ignited at 600°C for 1 h.

6.3 Cool in ice water and add 75 mL concentrated H_2SO_4 (sp gr 1.84) slowly enough, with mixing, to prevent appreciable solution heating.

6.4 Add 25.0 mL 0.2500*N* $K_2Cr_2O_7$ solution and mix thoroughly by swirling (NOTE 1).

NOTE 1. If contents are not well mixed, superheating may result, and the contents of the flask may be expelled from the open end of the condenser.

6.5 Attach flask to condenser, start water flow, and reflux for 2 h.

6.6 Allow flask to cool and wash down condenser with 25 mL demineralized water.

6.7 Dilute to 300 mL with demineralized water, cool to room temperature, and titrate the excess dichromate with ferrous ammonium sulfate standard solution I, using 8 to 10 drops ferroin indicator solution. The end point is a sharp change from blue green to reddish brown.

6.8 A demineralized-water blank is carried through all steps of the procedure with each group of samples.

6.9 To determine COD on samples containing more than 2,000 mg/L of chloride, the following treatment should be used (Burns and Marshall, 1965). Add 10 mg $HgSO_4$ for each milligram of chloride ion in the sample aliquot. Prepare a series of chloride solutions containing from 2,000 to 20,000 mg/L with the concentration interval not exceeding 4,000 mg/L and add 10 mg $HgSO_4$ to each solution for each milligram of chloride ion present. Determine the COD of the sample and chloride solutions, starting with paragraph 6.2. Plot the COD values obtained versus milligrams per liter chloride. From this curve, COD values may be obtained for any desired chloride concentration. This value is subtracted as a correction factor to obtain the COD value of a sample.

7. Calculations

7.1 For samples not requiring chloride correction:

$$\text{COD (mg/L)} = \frac{(A-B)N \times 8{,}000}{\text{mL sample}};$$

7.2 For samples requiring chloride correction:

$$\text{COD (mg/L)} = \left[\frac{(A-B)N \times 8{,}000}{\text{mL sample}} - C\right] \times 1.20,$$

where

COD = chemical oxygen demand from dichromate,

A = amount of ferrous ammonium sulfate for blank, milliliters,

B = amount of ferrous ammonium sulfate for sample, milliliters,

N = normality ferrous ammonium sulfate,

C = chloride correction value from graph of chloride concentration versus COD, and

1.20 = empirical compensation factor.

8. Report

Report COD, total (00340) as follows: less than 10 mg/L, whole numbers; 10 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

American Society for Testing and Materials, 1977, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 549.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 124.

Burns, E. R., and Marshall, C., 1965, Correction for chloride interference in the chemical oxygen demand test: Water Pollution Control Federation Journal, v. 37, p. 1716.

Oxygen demand, chemical, total, titrimetric, 0.025*N* dichromate oxidation (I–3562–78)

Parameter and Code: Oxygen demand, chemical, total, 0.025*N* dichromate (mg/L): 00335

1. Application

This method may be used to analyze natural waters and industrial wastes containing between 1 and 50 mg/L chemical oxygen demand (COD) and less than 2,000 mg/L of chloride. COD values for samples containing more than 2,000 mg/L of chloride should be corrected as indicated in paragraph 6.9.

2. Summary of method

2.1 Organic and other oxidizable material is oxidized by refluxing with standard acid-dichromate solution in the presence of silver sulfate catalyst. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as indicator.

2.2 For additional information see American Society for Testing and Materials (ASTM) Method D1252–67 (1974), Standard Methods of Test for COD in Water (ASTM, 1977).

3. Interferences

Reducing substances such as ferrous iron, nitrites, and chlorides interfere, since they are oxidized. Chlorides constitute by far the largest and most common interference, being quantitatively oxidized by dichromate in acid solution. One milligram of chloride per liter is equivalent to 0.226 mg/L COD. To eliminate chloride interference, mercuric sulfate is added to the sample to form a soluble mercuric chloride complex. Nitrite interference may be eliminated by incorporating in the standard dichromate solution 10 mg of sulfamic acid for each milligram of nitrite in the reflux flask.

4. Apparatus

4.1 *Reflux* apparatus, consisting of 500-mL erlenmeyer flask and water-cooled condenser, with ground-glass joints and made of heat-resistant glass.

4.2 *Hot plate* or heating mantle.

5. Reagents

5.1 *Ferrous ammonium sulfate* standard solution I, approx 0.250*N*: Dissolve 98.0 g $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in demineralized water. Add 20 mL concentrated H_2SO_4 (sp gr 1.84), cool, and dilute to 1 L with demineralized water. To standardize: Dilute 25.0 mL standard 0.2500*N* $K_2Cr_2O_7$ solution to 250 mL. Add 20 mL concentrated H_2SO_4 (sp gr 1.84) and cool. Titrate with the ferrous ammonium sulfate solution, using 8 to 10 drops ferroin indicator. Compute normality of the ferrous ammonium sulfate standard solution to four decimal places. The solution must be standardized daily, or before use.

5.2 *Ferrous ammonium sulfate* standard solution II, 0.025*N*: Dilute 100 mL of ferrous ammonium sulfate standard solution I to 1,000 mL with demineralized water. The normality of this solution is dependent upon the standardized normality of solution I.

5.3 *Mercuric sulfate*, powdered $HgSO_4$.

5.4 *Orthophenanthroline ferrous sulfate (ferroin) indicator* solution: Dissolve 1.48 g 1,10-(ortho)-phenanthroline monohydrate and 0.70 g $FeSO_4 \cdot 7H_2O$ in 100 mL water. The prepared indicator is available commercially.

5.5 *Potassium dichromate* standard solution I, 0.2500*N*: Dissolve 12.2588 g $K_2Cr_2O_7$ primary standard, dried for 2 h at 110°C, in demineralized water and dilute to 1,000 mL (NOTE 1).

NOTE 1. This standard solution is identical to the potassium dichromate standard solution of Method I–3560, which may be used to prepare potassium dichromate standard solution II (paragraph 5.6).

5.6 *Potassium dichromate* standard solution II, 0.0250*N*: Dilute 100 mL of potassium dichromate standard solution I to 1,000 mL with demineralized water.

5.7 *Silver sulfate,* powder, Ag_2SO_4.

5.8 *Sulfamic acid,* crystals.

5.9 *Sulfuric acid,* concentrated, sp gr 1.84.

6. Procedure

6.1 Pipet 50.0 mL of a well mixed sample, or a smaller volume diluted to 50.0 mL, into the reflux flask and add slowly, over a period of 2 to 3 min, 1 g $HgSO_4$; allow to stand 5 min, swirling frequently (NOTE 2).

NOTE 2. A sample size should be selected so that no more than half the dichromate (paragraph 6.4) is reduced.

6.2 Add 1 g Ag_2SO_4 and a few glass beads that have been ignited at 600°C for 1 h.

6.3 Cool in ice water and add 75 mL concentrated H_2SO_4 (sp gr 1.84) slowly enough, with mixing, to prevent appreciable solution heating.

6.4 Add 25.0 mL 0.0250*N* $K_2Cr_2O_7$ solution and mix thoroughly by swirling (NOTE 3).

NOTE 3. If contents are not well mixed, superheating may result, and the contents of the flask may be expelled from the open end of the condenser.

6.5 Attach flask to condenser, start water flow, and reflux for 2 h.

6.6 Allow flask to cool and wash down condenser with 25 mL demineralized water.

6.7 Dilute to 300 mL with demineralized water, cool to room temperature, and titrate the excess dichromate with ferrous ammonium sulfate standard solution II, using 8 to 10 drops ferroin indicator solution. The end point is a sharp change from blue green to reddish brown.

6.8 A demineralized-water blank is carried through all steps of the procedure with each group of samples.

6.9 To determine COD on samples containing more than 2,000 mg/L of chloride, the following treatment should be used (Burns and Marshall, 1965). Add 10 mg $HgSO_4$ for each milligram of chloride ion in the sample aliquot. Prepare a series of chloride solutions containing from 2,000 to 20,000 mg/L with the concentration interval not exceeding 4,000 mg/L and add 10 mg $HgSO_4$ to each solution for each milligram of chloride ion present. Determine the COD of the sample and chloride solutions starting with paragraph 6.2. Plot the COD values obtained versus milligrams per liter chloride. From this curve, COD values may be obtained for any desired chloride concentration. This value is subtracted as a correction factor to obtain the COD value of a sample.

7. Calculations

7.1 For samples not requiring chloride correction:

$$\text{COD (mg/L)} = \frac{(A - B)N \times 8{,}000}{\text{mL sample}},$$

7.2 For samples requiring chloride correction:

$$\text{COD (mg/L)} = \left[\frac{(A - B)N \times 8{,}000}{\text{mL sample}} - C\right] \times 1.20,$$

where

COD = chemical oxygen demand from dichromate,
A = amount of ferrous ammonium sulfate for blank, milliliters,
B = amount of ferrous ammonium sulfate for sample, milliliters,
N = normality ferrous ammonium sulfate,
C = chloride correction value from graph of chloride concentration versus COD, and
1.20 = empirical compensation factor.

8. Report

Report oxygen demand, chemical, total, 0.025*N* dichromate (00335) as follows: less than 50 mg/L, whole numbers.

9. Precision

Precision data are not available for this method.

References

American Society for Testing and Materials, 1977, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 549.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 124.

Burns, E. R., and Marshall, C., 1965, Correction for chloride interference in the chemical oxygen demand test: Water Pollution Control Federation Journal, v. 37, p. 1716.

Oxygen, dissolved, titrimetric, Winkler (I-1575-78)

Parameter and Code: Oxygen, dissolved (mg/L): 00300

1. Application

This method may be used to determine between 0.1 and 20 mg/L dissolved oxygen (DO) in any sample that is not heavily polluted. It is not recommended for samples that contain more than 1,000 μg/L of ferrous iron or appreciable quantities of sulfite, thiosulfate, polythionate, hypochlorite, or free chlorine.

2. Summary of method

2.1 This method is the "Alsterberg azide modification" of the Winkler procedure for the determination of dissolved oxygen. The method depends on the formation of a precipitate of manganous hydroxide, which rapidly absorbs oxygen dissolved in the water. In so doing, a higher oxide is formed.

$$MnSO_4 + 2KOH \rightarrow Mn(OH)_2\downarrow + K_2SO_4$$

$$2Mn(OH)_2\downarrow + O_2 \rightarrow 2MnO(OH)_2\downarrow.$$

The $Mn(OH)_2$ floc acts as a "gathering" agent for dissolved gaseous oxygen.

2.2 Upon acidification in the presence of iodide, iodine is released in a quantity equivalent to the dissolved oxygen present.

$$MnO(OH)_2\downarrow + 2KI + H_2O \xrightarrow{H^{+1}} Mn(OH)_2\downarrow + I_2 + 2KOH$$

The liberated iodine is then titrated with sodium thiosulfate standard solution with use of starch indicator.

$$I_2 + 2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2I^{-1}.$$

2.3 Additional information on the principle of the determination is given in Adams, Barnett, and Keller (1943).

3. Interferences

3.1 Oxidizable organic matter consumes i dine and thereby causes low results. Its effect minimized if the titration is made immediatel after liberation of the iodine. Any readily oxidiz able or reducible constituents interfere by reac ing with either the iodine or thiosulfate. Oxidi able substances cause low results, and reducib substances, high results. The magnitude of th net effect is, of course, proportional to the abs lute and relative concentrations of the differen interferences.

3.2 In this procedure, sodium azide elim nates the interference of nitrite, and potassiu fluoride overcomes the effect of ferric salts, pr vided the ferric iron concentration does not ex ceed 200 mg/L and there is no delay in titratio The ferrous iron concentration should not excee 1,000 μg/L. High concentrations of suspende solids, which interfere, are removed by alu flocculation. Certain other substances, as note above, interfere when present in appreciab quantities.

4. Apparatus

Buret, 25-mL.

5. Reagents

5.1 *Alkaline iodide reagent*. Dissolve 50 NaOH or 70 g KOH and 13.5 g NaI or 15 g KI water, and dilute to 100 mL.

5.2 *Alkaline iodide-sodium azide solutio* Dissolve 1 g NaN_3 in 4 mL water. Add this so lution with constant stirring to 95 mL alkalin iodide reagent. The reagent should not give color with starch indicator when diluted an acidified.

5.3 *Alum solution*, 5.4 g/100 mL. Dissolv 10 g $AlK(SO_4)_2 \cdot 12H_2O$ in water and dilute to 1 mL.

Oxygen, dissolved, titrimetric, Winkler (I–1575–78)

Parameter and Code: Oxygen, dissolved (mg/L): 00300

1. Application

This method may be used to determine between 0.1 and 20 mg/L, dissolved oxygen (DO) in any sample that is not heavily polluted. It is not recommended for samples that contain more than 1,000 μg/L of ferrous iron or appreciable quantities of sulfite, thiosulfate, polythionate, hypochlorite, or free chlorine.

2. Summary of method

2.1 This method is the Alsterberg-azide modification of the Winkler procedure for the determination of dissolved oxygen. The method depends on the formation of a precipitate of manganous hydroxide, which rapidly absorbs oxygen dissolved in the water. In so doing, a higher oxide is formed.

$$MnSO_4 + 2KOH \rightarrow Mn(OH)_2\downarrow + K_2SO_4$$

$$2Mn(OH)_2\downarrow + O_2 \rightarrow 2MnO(OH)_2\downarrow .$$

The $Mn(OH)_2$ floc acts as a "gathering" agent for dissolved gaseous oxygen.

2.2 Upon acidification in the presence of iodide, iodine is released in a quantity equivalent to the dissolved oxygen present

$$MnO(OH)_2\downarrow + 2KI + H_2O \xrightarrow{H^{+1}} Mn(OH)_2\downarrow + I_2 + 2KOH$$

The liberated iodine is then titrated with sodium thiosulfate standard solution with use of starch indicator

$$I_2 + 2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2I^{-1} .$$

2.3 Additional information on the principle of the determination is given by Adams, Barnett, and Keller (1943).

3. Interferences

3.1 Oxidizable organic matter consumes iodine and thereby causes low results. Its effect is minimized if the titration is made immediately after liberation of the iodine. Any readily oxidizable or reducible constituents interfere by reacting with either the iodine or thiosulfate. Oxidizable substances cause low results, and reducible substances, high results. The magnitude of the net effect is, of course, proportional to the absolute and relative concentrations of the different interferences.

3.2 In this procedure, sodium azide eliminates the interference of nitrite, and potassium fluoride overcomes the effect of ferric salts, provided the ferric iron concentration does not exceed 200 mg/L and there is no delay in titration. The ferrous iron concentration should not exceed 1,000 μg/L. High concentrations of suspended solids, which interfere, are removed by alum flocculation. Certain other substances, as noted above, interfere when present in appreciable quantities.

4. Apparatus

Buret, 25-mL.

5. Reagents

5.1 *Alkaline iodide reagent:* Dissolve 50 g NaOH or 70 g KOH and 13.5 g NaI or 15 g KI in water, and dilute to 100 mL.

5.2 *Alkaline iodide-sodium azide* solution: Dissolve 1 g NaN_3 in 4 mL water. Add this solution with constant stirring to 95 mL alkaline iodide reagent. The reagent should not give a color with starch indicator when diluted and acidified.

5.3 *Alum* solution, 5.4 g/100 mL: Dissolve 10 g $AlK(SO_4)_2 \cdot 12H_2O$ in water and dilute to 100 mL.

5.4 *Manganous sulfate* solution, 32 g/100 mL: Dissolve 48 g $MnSO_4 \cdot 4H_2O$ or 40 g $MnSO_4 \cdot 2H_2O$ or 36 g $MnSO_4 \cdot H_2O$ in water, filter, and dilute to 100 mL.

5.5 *Potassium fluoride* solution, 24.7 g/100 mL: Dissolve 40 g $KF \cdot 2H_2O$ in water and dilute to 100 mL.

5.6 *Sodium thiosulfate* standard solution, 0.025*N* (NOTE 1): Dissolve 6.205 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free water, add 1 g Na_2CO_3, and dilute to 1,000 mL. Store the solution in a glass-stoppered bottle which has been cleaned with dichromate-sulfuric acid cleaning solution and rinsed with hot water. Standardize the $Na_2S_2O_3$ against KIO_3 as follows: Dry approx 1 g KIO_3 for 2 h at 180°C. Dissolve 0.8918 g in water and dilute to 1,000 mL. Pipet 25.00 mL of the KIO_3 standard solution into a 250-mL iodine flask, then add successively 75 mL water and 2 g KI. After solution is complete, add 10 mL 3.6*M* H_2SO_4 and mix thoroughly. Allow the stoppered flask to stand 5 min in the dark. Titrate with $Na_2S_2O_3$ solution using 2 mL starch indicator as the end point is approached.

$$\text{Normality of } Na_2S_2O_3 = \frac{\text{mL } KIO_3}{\text{mL } Na_2S_2O_3} \times 0.02500$$

NOTE 1. Phenylarsene oxide (PAO) standard solution, 0.025*N*, may be substituted for the $Na_2S_2O_3$ standard solution. The phenylarsene oxide is not subject to bacterial decomposition as is $Na_2S_2O_3$. Its solutions, therefore, are stable and require less frequent standardization. Hach Chemical Co. cat. No. 1070, Standard PAO solution, 0.025*N*, has been found to be satisfactory. The normality of the PAO solution must be checked against KIO_3 as described for $Na_2S_2O_3$.

5.7 *Starch indicator* solution, stable; or "thyodene," stable, soluble dry indicator (Fisher Scientific Co. cat. No. T–138), or equivalent.

5.8 *Sulfuric Acid*, 3.6*M*: Carefully add 200 mL concentrated H_2SO_4 (sp gr 1.84) to 750 mL water and dilute to 1 L.

6. Procedure

6.1 Add 1 mL KF solution below the liquid surface of the sample in the BOD bottle. Stopper the bottle and mix.

6.2 Add 2 mL $MnSO_4$ solution below the liquid surface of the sample, stopper the bottle, and mix.

6.3 Add 2 mL alkaline iodine-sodium azide reagent below the surface of the sample, stopper the bottle, and mix by inversion. Allow the precipitate to settle to the bottom one-third of the bottle, and then repeat the mixing and settling process.

6.4 Add 2 mL concentrated H_2SO_4 (sp gr 1.84) by allowing the acid to run down the neck of the bottle.

6.5 Mix by gentle inversion until solution is complete.

6.6 Immediately pipet an aliquot of treated sample containing less than 2.0 mg O_2 (200.0 mL maximum) and titrate the liberated I_2 with $Na_2S_2O_3$ standard solution to a pale-straw color.

6.7 Add 1 to 2 mL starch indicator and continue the titration to the first disappearance of the blue color. Subsequent recoloration should be disregarded.

7. Calculations

7.1 If the sample was treated with alum at the time of collection, correct the sample volume reacted with $MnSO_4$ as follows:

$$\text{mL sample} = (300 \times \text{mL taken for flocculation}) \times 1/(\text{mL taken for flocculation} + \text{mL } AlK(SO_4)_2 + \text{mL } NH_4OH).$$

7.2 Determine dissolved oxygen in milligrams per liter as follows:

$$O_2\,(DO)\ (\text{mg/L}) = \frac{1{,}000}{\text{mL sample}} \times \frac{(\text{mL treated aliquot} + 5)}{\text{ml treated aliquot}} \times \text{mL}_t \times N_t \times 8.$$

where

mL_t = volume of $Na_2S_2O_3$ standard solution, milliliters, and

N_t = normality of $Na_2S_2O_3$ standard solution.

8. Report

Report dissolved oxygen (00300) concentrations in milligrams per liter to one decimal.

9. Precision

Precision data are not available for this method.

References

Adams, R. C., Barnett, R. D., and Keller, D. E., Jr., 1943, Field and laboratory determination of dissolved oxygen: American Society for Testing and Materials, Proc. 43.

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater [14th ed]: Washington, D.C., American Public Health Association Incorporated, 1193 p.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 126.

Sulfate, dissolved, titrimetric, thorin (I–1820–78)

Parameter and Code: Sulfate, dissolved, (mg/L as SO_4): 00945

1. Application

This method may be used to analyze most samples containing from 0.5 to 20 mg/L of sulfate. Samples with higher concentrations must be either diluted or analyzed by the classical gravimetric method.

2. Summary of method

2.1 Thorin and barium react to form a complex which is deep red in color. The intensity of the color is dependent on pH, indicator concentration, and nature of the solvent. The color is more intense in organic than in aqueous solutions and also varies in intensity with different organic solvents. The color reaction can be utilized to titrate sulfate directly with barium chloride by adding a large volume of organic solvent to the sample and titrating in this mixed medium. When the end point is detected spectrometrically, the preferred titration medium is 80-percent alcohol maintained at pH 5 with a sodium acetate buffer.

2.2 The end point may also be detected visually by viewing the solution through a didymium glass filter. When visual detection is made, the titration medium should be 66 percent of dioxane, adjusted to a pH between 2.2 and 5. The initial yellow color of thorin in the dioxane-water medium changes to pink at the end point.

3. Interferences

Thorin reacts with many metals, including calcium; therefore, it is necessary to remove all metal ions by cation exchange prior to titration. Phosphate interferes somewhat by coprecipitation; with 100 mg/L of sulfate, 10 and 20 mg/L of phosphate give a positive error of about 2 and 3 percent, respectively. The presence of color may interfere with the spectrometric reading and require correction.

4. Apparatus

4.1 *Absorption cells*, 50-mm. The cement in some cells reacts with thorin to give a red color. Cells should be tested for thorin reaction, and those that give a red color in 10 to 15 min should be rejected. Alternatively, 100-mL beakers may be used, providing the titration assembly is designed to accept such beakers.

4.2 *Buret*, 10-mL.

4.3 *Cation-exchange column* (fig. 69). The column should be filled to within 5 to 8 cm of the

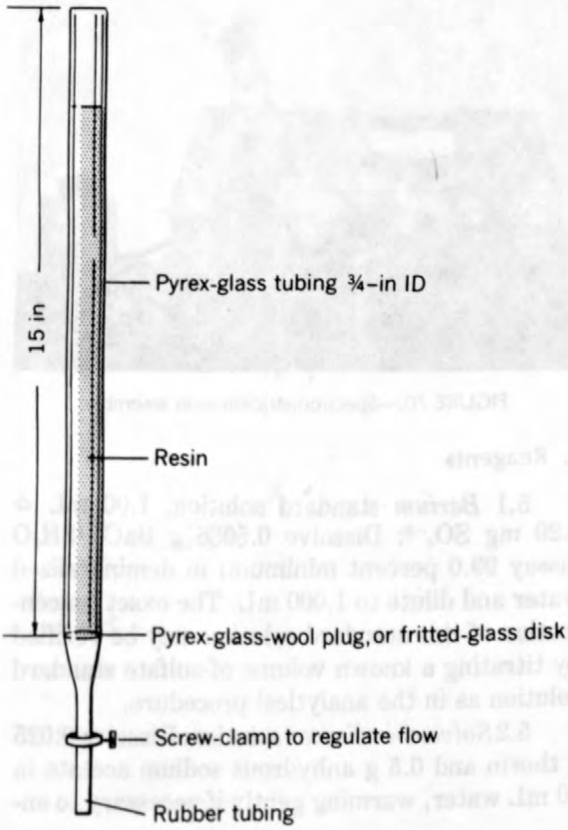


FIGURE 69.—Cation-exchange column for sulfate.

top with Amberlite IR–120, or equivalent, operating on the hydrogen cycle. The resin is regenerated with 30-percent (volume-to-volume) HCl solution. The frequency of regeneration depends on the mineral content of the samples. The need for regeneration may be determined by checking a small portion of column effluent for the presence of calcium.

4.4 *Spectrometric-titration assembly* (fig. 70).

4.5 *Spectrometer* for use at 520 nm; Beckman Model B, or equivalent.

4.6 With this instrument, the following operating conditions have been used:

Wavelength	**520 nm.**
Phototube	**Blue-sensitive.**
Initial sensitivity	**1.**
Starting point	**At 0.10 absorbance.**
End point	**At 0.20 absorbance.**

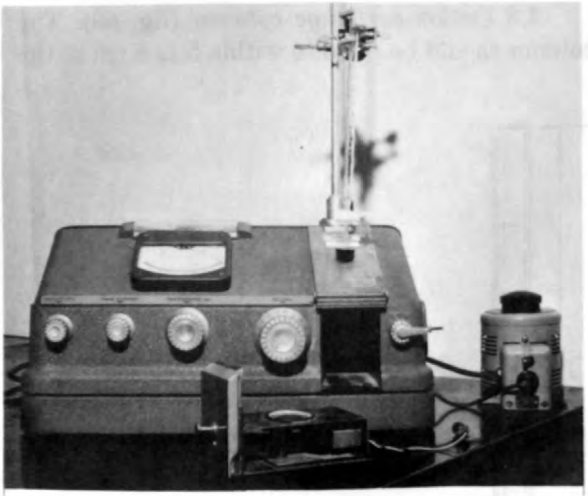


FIGURE 70.—Spectrometric-titration assembly.

5. Reagents

5.1 ***Barium*** standard solution, 1.00 mL ≎ 0.20 mg SO_4^{-2}: Dissolve 0.5086 g $BaCl_2 \cdot 2H_2O$ (assay 99.0 percent minimum) in demineralized water and dilute to 1,000 mL. The exact concentration of this standard solution may be verified by titrating a known volume of sulfate standard solution as in the analytical procedure.

5.2 *Solvent-indicator* solution: Dissolve 0.025 g thorin and 0.5 g anhydrous sodium acetate in 10 mL water, warming gently if necessary to ensure complete solution. Filter the solution through Whatman No.1 filter paper into 1 L of 95 percent ethanol and discard the filter paper without washing or rinsing. Add 12 mL glacial CH_3COOH (sp gr 1.06) and mix. Difficulty in preparing a clear solution of the indicator is probably due to poor quality thorin reagent.

5.3 *Sulfate* standard solution, 1.00 mL = 1.00 mg SO_4^{-2}: Dissolve 1.4787 g Na_2SO_4, dried for 2 h at 180°C, in demineralized water and dilute to 1,000 mL.

6. Procedure

6.1 Rinse the cation-exchange columns with 20 to 30 mL of sample and discard the rinse. (Check a portion for the presence of calcium.)

6.2 Pass sufficient sample through the exchanger to provide at least 10 mL of effluent for the determination.

6.3 Pipet a volume of sample containing less than 2 mg SO_4^{-2} and 10 mg dissolved solids (10.0 mL maximum) into a 50-mm absorption cell and adjust the volume to 10.0 mL.

6.4 Add 40 mL solvent-indicator solution.

6.5 Start the stirrer and set the absorbance at 0.100.

6.6 Titrate with $BaCl_2$ (1.00 mL ≎ 0.20 mg SO_4^{-2}) to an absorbance of 0.20. Add additional titrant if the absorbance reading does not remain at 0.20 for 30 sec.

6.7 Determine a blank correction by titrating demineralized water. The blank is constant throughout the concentration range of the method. A blank of 0.05 mL has been found. Correct for water color when necessary.

7. Calculations

$$SO_4 \text{ in mg/L} = \frac{1,000}{\text{mL sample}} \times 0.2 \times (\text{mL titrant} - \text{mL blank}).$$

8. Report

Report sulfate, dissolved (00945), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 The precision of this method within the range of 10 to 150 mg/L may be expressed as follows:

$$S_T = 0.046X + 0.575$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of sulfate, milligrams per liter.

9.2 The precision may also be expressed in terms of the relative deviation (coefficient of variation) as follows:

Number of labs	*Mean (mg/L)*	*Relative deviation (percent)*
16	21.0	6
5	104	5
16	141	6

Reference

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A1, p. 152.

Sulfide, total, titrimetric, iodometric (I–3840–78)

Parameter and Code: Sulfide, total (mg/L as S): 00745

1. Application

1.1 This method may be used to analyze water-suspended sediment mixtures containing more than 0.5 mg/L of sulfide.

1.2 Water-suspended sediment mixtures may be analyzed by this method if each sample is shaken vigorously and a suitable aliquot of well-mixed sample rapidly withdrawn.

1.3 Water containing dissolved sulfides readily loses hydrogen sulfide, particularly if the pH of the sample is low. Oxygen destroys sulfides by oxidation, particularly if the pH of the sample is high. Aeration of the sample should, therefore, be avoided. The addition of 2 g of zinc acetate per liter of water will fix the sample for several days. Acid water must be neutralized before addition of the zinc acetate.

2. Summary of method

2.1 This iodometric method does not differentiate the forms in which the sulfide exists in solution.

2.2 Sulfide is reacted with an excess of iodine in acid solution, and the remaining iodine is then determined by titration with sodium thiosulfate, using starch as an indicator (Kolthoff and others, 1969).

$$S^{-2} + I_2 \xrightarrow{H^{+1}} S + 2I^{-1}$$

$$I_2 + 2S_2O_3{}^{-2} \xrightarrow{H^{+1}} S_4O_6{}^{-2} + 2I^{-1}$$

A blank is treated with exactly the same amount of iodine and titrated with sodium thiosulfate. The sulfide concentration is calculated from the difference between the volume of thiosulfate required for the blank and the volume used for the sample.

2.3 This method is similar to that given in American Public Health Association (1976).

3. Interferences

Reducing substances such as sulfites and heavy-metal ions react with iodine and therefore contribute positive errors. Oxygen and other oxidants may react with hydriodic acid to liberate iodine and thus contribute negative errors.

4. Apparatus

Buret, 10-mL capacity.

5. Reagents

5.1 *Hydrochloric acid*, concentrated (sp gr 1.19).

5.2 *Iodine* standard solution, 0.010*N*: Dissolve 6 g iodate-free KI in approx 25 mL water. Add 1.2690 g resublimed I_2. When solution is complete, dilute to 1 L. Standardize with 0.010*N* $Na_2S_2O_3$, using starch as indicator.

$$\text{Normality of } I_2 = \frac{0.010 \times \text{mL } Na_2S_2O_3}{\text{mL } I_2}$$

Adjust the normality of the iodine standard solution, if necessary, to 0.010 by addition of small quantities of demineralized water or iodine as indicated by the first titration. Confirm the normality by restandardization.

5.3 *Potassium iodide*, crystals, iodate-free: The KI can be tested for $IO_3{}^{-1}$ by dissolving about 0.1 g in 5 mL water, acidifying with 1 or 2 drops concentrated H_2SO_4 (sp gr 1.84) and adding 2 to 3 mL starch indicator solution. Immediate appearance of blue color indicates the presence of $IO_3{}^{-1}$; slow color formation is due to atmospheric oxidation.

5.4 *Sodium thiosulfate* standard solution, 0.010*N*: Dissolve 2.482 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free water and dilute 1 L with carbon dioxide-free water. Standardize against KIO_3 as follows: Dry approx 0.5 g KIO_3 for 2 h at 180°C. Dissolve 0.3567 g in water and dilute to 1,000 mL. Pipet 25.0 mL KIO_3 solution into a 250-mL erlenmeyer flask, then add successively 75 mL deionized water and 0.5 g iodate-free KI. After solution is complete, add 10 mL HCl (sp gr 1.19). Allow the stoppered flask to stand 5 min in the dark and titrate with $Na_2S_2O_3$ solution, adding starch indicator solution as the end point is approached (light-straw color):

$$\text{Normality of } Na_2S_2O_3 = \text{mL}\,\frac{0.25}{Na_2S_2O_3}$$

Adjust the normality of the thiosulfate standard solution, if necessary, to 0.010 by addition of small quantities of demineralized water or sodium thiosulfate as indicated by the first titration. Confirm the normality by restandardization.

5.5 *Starch indicator* solution, stable (NOTE 1).

NOTE 1. A convenient substitute for starch indicator solution is the product thyodene sold by Fisher Scientific Co. It can be used in its dry form and gives an end point similar to that of starch.

6. Procedure

Samples for the determination of sulfide should be collected with a minimum of aeration and agitation.

6.1 Shake the sample vigorously to mix it thoroughly. Immediately pipet a volume of sample with ZnS in suspension containing less than 1.5 mg S^{-2} (100.0 mL maximum) into a 250-mL erlenmeyer flask, and adjust the volume to approx 100 mL.

6.2 Prepare a blank of approx 100 mL demineralized water, and carry it through the procedure along with the sample.

6.3 Add 10.0 mL 0.010*N* I_2.

6.4 Without delay add 10 mL concentrated HCl.

6.5 Immediately titrate the excess I_2 with 0.010*N* $Na_2S_2O_3$, adding 2 to 3 mL starch indicator solution as the end point is approached.

7. Calculations

$$S^{-2}\ (\text{mg/L}) = \frac{1{,}000}{\text{mL sample}} \times 0.1603$$

$$\times\ (\text{mL blank titrant} - \text{mL sample titrant}).$$

8. Report

Report sulfide, total (00745), concentrations as follows: 0.5 to 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

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