Book 5
Ch. A1

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U. S. DEPARTMENT OF THE INTERIOR
March 3, 1849

Techniques of Water-Resources Investigations of the United States Geological Survey

METHODS FOR COLLECTION AND ANALYSIS OF WATER SAMPLES FOR DISSOLVED MINERALS AND GASES

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METHODS FOR COLLECTION AND ANALYSIS OF WATER SAMPLES FOR DISSOLVED MINERALS AND GASES

By Eugene Brown, M. W. Skougstad, and M. J. Fishman

Book 5

LABORATORY ANALYSIS

UNITED STATES DEPARTMENT OF THE INTERIOR
WALTER J. HICKEL, Secretary

GEOLOGICAL SURVEY
William T. Pecora, Director

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1970

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 — Price $2

PREFACE

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 the several Interior agencies, the U.S. Geological Survey's 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 groundwater 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 a large part of 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 was prepared to provide accurate and precise procedures for the collection and analysis of water samples required for these needs.

The series of manuals on techniques describes procedures for planning and executing specialized work in water-resources investigations. The material is grouped under major subject headings called books and further subdivided into sections and chapters; Section A of Book 5 is on water analysis. The chapter on dissolved minerals and gases is the first in this series of chapters on laboratory methods for water-quality analysis.

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.

Provisional drafts of chapters are distributed to field offices of the U.S. Geological Survey for their use. These drafts are subject to revision because of experience in use or because of advancement in knowledge, techniques, or equipment. After the technique described in a chapter is sufficiently developed, the chapter is published and is for sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

CONTENTS

Page

Part IV. Analytical procedures—Continued

Page

Part IV. Analytical procedures—Continued

Page

Part IV. Analytical procedures—Continued

Page

Part IV. Analytical procedures—Continued

FIGURES

TABLES

Methods for collection and analysis of water samples for dissolved minerals and gases

By Eugene Brown, Marvin W. Skougstad, and M. J. Fishman

Abstract

Chapter A1 of the manual contains methods used by the U.S. Geological Survey to collect, preserve, and analyze water samples for their content of dissolved minerals and gases. Among the topics discussed are selection of sampling sites, frequency of sampling, sampling equipment, sample preservation, laboratory equipment and instrumental techniques, accuracy and precision of analysis, and reporting of results. Seventy-six analytical procedures are given for determining 55 water properties. Listed below are the water properties for which analytical procedures are given, and the principal procedure for the determination of each.

Classical chemical method

Acidity
Alkalinity
Aluminum
Arsenic
Boron
Bromide
Carbon dioxide
Chloride
Chlorine, residual
Color
Cyanide
Density
Hardness, all forms
Iodide
Molybdenum
Nitrogen, all forms
Oxygen demand
Oxygen, dissolved
pH
Phosphorus, all forms
Selenium
Solids, all forms
Specific conductance
Sulfate
Sulfide
Turbidity
Vanadium

Atomic-absorption flame spectrophotometric method

Barium
Beryllium
Cadmium
Calcium
Chromium, all forms
Cobalt
Copper
Iron, all forms
Lead
Lithium
Magnesium
Manganese
Nickel
Potassium
Silica
Silver
Sodium
Strontium
Zinc

Ion-specific electrode method

Fluoride

Introduction

Purpose.—The purpose of this manual is to record and disseminate methods of collection and analysis of water samples used by the Geological Survey in making water-quality investigations. The manual is an updating and enlargement of Geological Survey Water-Supply Paper 1454, "Methods for Collection and Analysis of Water Samples," by Rainwater and Thatcher, published in 1960.

Although excellent and authoritative manuals on water analysis are available, most of them emphasize primarily either municipal, industrial, or agricultural water utilization, and generally consider only briefly problems related to sample collection. 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.

Rapid changes in technology are constantly providing new and improved methods for the study of water-quality parameters. It is, therefore, necessary that methods manuals now be revised more frequently than previously in order to gain the advantages of improved technology and obtain water-quality data in the most efficient manner possible and with a high degree of quality control to assure uniformity and standardization of data, nationally.

Scope.—This manual includes techniques and procedures found to be suitable for the collection and analysis of representative water samples. For convenience, the analytical procedures are grouped into the following categories:

- Dissolved minerals and gases
- Organic substances
- Microbiota
- Minor elements by emission spectroscopy
- Radionuclides.

Because of specialized techniques and instrumentation, as well as the volume of material represented, methods in each of the above categories will be compiled and published separately. The form of publication will be as Chapters A1 through A5 of Book 5, Laboratory Analysis, in the manual series, "Techniques of Water-Resources Investigations of the U.S. Geological Survey."

Methods for the determination of concentrations and loads of suspended sediment are not included in this manual, but are given in Book 5, Section C. However, a method for turbidity is included. Similarly, methods for the analysis of rock and soil materials related to water-quality investigations are published as Book 5, Section B.

Application.—The methods of analysis given in this manual chapter are intended for application to a wide range of waters—from those having trace concentrations of dissolved minerals or gases to those having very high concentrations, such as are found in sea water and brines. However, it is the policy to specify in each procedure the type of water or range in concentration to which the method is principally applicable. In general, only the preferred method is given for a specific application. Although other methods may yield equally valid results, the method presented is believed preferable for the application stated.

Interferences.—Interferences plague practically all analytical methods. Indeed, it is rare that a method is free from all interferences at all concentration levels. Nevertheless, most methods will yield reliable results with very little interference when followed as presented.

Analytical procedures are usually designed either to give the total amount of element present or to give the amount of a certain definite solute species. Interferences which may affect either type of result are a serious potential source of error against which the analyst must always exercise due caution.

Analytical procedures are usually designed for solutions in commonly encountered ranges of concentration. Waters of high dissolved-solids content, or having high or low pH or high concentrations of unusual constituents, commonly require modification of methods given in this or other manuals.

Not all the possible interferences have been or can be described in this manual. Where upper limits are given for interfering substances, a simple dilution of the sample to bring it within the prescribed limit is not always an adequate way of eliminating the interference. To be satisfactory, a method must have a high sensitivity and a high degree of specificity for the element sought. Only in cases of very high sensitivity for a given ion in relation to interfering substances can dilution of a sample eliminate the effects of interferences. Wherever possible, the methods in this manual indicate corrective action to overcome or eliminate the effects of interfering substances.

Reliability of methods.—The objectives of all methods of analysis are to yield results that are accurate, precise, sensitive, and free of interferences. In practice, very few meet all of these objectives. Thus, nearly all methods represent some degree of compromise. Nevertheless, continued research has upgraded methodology, and especially instrumentation, to the point where today's methods bear little resemblance to those of 30 years ago. In fact, many of the accepted methods of only 10 years ago are now obsolete.

Accuracy, in the absolute sense, is almost impossible to attain in the laboratory. The concept of accuracy includes both precision and bias. It is a measure of the degree of conformity of a value obtained by a specific procedure to the true value. The methods in this manual do not include sections on accuracy.

Precision is the degree to which repeated measurements of a constituent of a single sample deviate from the mean of these measurements. Precision can be expressed in statistical terms. Insofar as possible, a section on precision is included for each method.

The sensitivity, or detection limit, of a method is the smallest concentration that can be measured with certainty. Its numerical value cannot be less than the precision.

Analytical reference testing.—The Geological Survey requires participation of all of its water laboratories in a program of analytical reference testing. Several times each year water samples of known composition are distributed to the laboratories for analysis. Results are analyzed statistically so that each laboratory can evaluate its work comparatively with other laboratories for the specified parameters. Followup is made to correct deficiencies. This practice is applied to all existing methods on a routine basis, and to each new or proposed method prior to its acceptance as an official method.

Sources of methods.—The development of methods of analysis for water samples is a continuing activity not only by chemists in the Geological Survey but by chemists in the technical community, both in and out of government. In general, methods selected for use in this manual represent the original or revised published papers of individual chemists or groups of chemists. Some methods have been developed or revised by Geological Survey chemists. Others have appeared in manuals published by technical associations. For all methods, appropriate references are made to source material.

References.—In addition to specific sources of data cited throughout this manual, listed below are additional general references for the topics indicated:

For chemistry of individual constituents and techniques of interpretation of analysis,

Hem, J. D., 1970, Study and interpretation of the chemical characteristics of natural water—Revised edition: U.S. Geol. Survey Water-Supply Paper 1473, 363 p.

For solubility data and calculations,

Sillén, L. G., and Martell, A. E., 1964, Stability constants of metal-ion complexes: Chem. Soc. [London] Spec. Pub. 17, 754 p.

Garrels, R. M., and Christ, C. L., 1964, Solutions, minerals and equilibria: New York, Harper and Row, 450 p.

For water-quality standards and tolerances,

[U.S.] Federal Water Pollution Control Administration, 1968, Report of the committee on water-quality criteria: Washington, U.S. Govt. Printing Office, 234 p.

Part I. Sampling

Water samples are collected and analyzed to determine the chemical and physical composition of a water body, and its suitability for domestic, industrial, and agricultural uses. Water samples are also analyzed to aid in understanding geochemical and hydrologic relationships in natural systems and to evaluate the influence of man's activities on these systems. Interpretation of the analytical reports from a systematic sampling and analysis program may also indicate the nature, source, and variability of both dissolved and suspended matter present in the water body. If, in the course of such studies, samples are obtained which are not truly representative of the entire water body, an error will be introduced which may be the most significant one in the entire data-gathering process. The extent to which a single small sample may be considered representative of the large water mass will depend on several factors, among which might be included: (1) The homogeneity of the water body being sampled, (2) the number of points sampled, (3) the size of the individual samples, and (4) the manner in which the samples are collected.

Most water bodies are not completely homogeneous, and obtaining a truly representative sample will depend on the sampling technique employed, as well as the size and number of samples collected. A more representative sample can usually be obtained by collecting several small samples from different parts of the water body, than by collecting one large sample at a single point. The larger the individual samples, and the larger the number of points sampled, the more nearly will the composite sample represent the water body.

Most natural-water bodies are subject to forces which promote homogeneity, such as turbulence and wind action, but they are also affected by chemical, physical, and biological processes which promote nonhomogeneous conditions.

Some sampling error, especially that connected with sampling frequency, can now be reduced substantially through the use of modern automatic and continuous sensing and recording devices. No device, however, has yet been developed which completely eliminates sampling error, or which materially reduces the importance of proper sample collection in a data acquisition program.

Site selection

Of first importance in the selection of any water-quality sampling site is the extent to which the proposed location complements the overall program of which it is a part. Water-quality data-collection programs have historically developed to meet specific and often unique requirements of water utilization or development in a particular area. Such programs have developed with some degree of uniformity within a given area, but these activities have been difficult to correlate in terms of a national program for assessment of water quality in a broad sense. Wherever possible, the location of sampling stations should be selected to provide data of benefit to basin, regional, and national network programs.

Surface water

Rivers and streams

A program designed to obtain proper samples from flowing water bodies must consider first the need for the samples taken to represent the entire flow of the stream at that point and at that time. Sampling stations should not be established at locations where mixing is incomplete, or where significant differences in water composition exist in the stream cross section. A sample typical of the entire flow of the stream is usually necessary. For some purposes, however, only the composition of the water at a fixed intake point is desired. Where the water composition at such a fixed intake point differs significantly from that of the entire stream, this fact should be noted in order not to mislead users of the published water data.

The homogeneity of a stream throughout a given cross section is determined by such physical factors as turbulence and distance from large inflows. At and immediately below the confluence of tributary streams there is frequently a distinct physical separation between the waters of the tributary and the main stream. This effect is more pronounced, and may persist for many miles downstream, if the composition of the two waters differs significantly with regard to temperature, and (or) to dissolved and suspended solids. Theoretically, a sample representing the overall composition of a stream can be obtained by compositing several depth-integrated samples of equal volume taken at places with equal flow across the cross section. Due to the large number of samples required, it is highly desirable to find a stream section in which the water composition is uniform with depth and cross section. Such sections can usually be located on small- and medium-size streams, but are frequently impossible to find on large rivers. Where uniform sections can be found, however, the sampling procedure may often be simplified to the extent that a single "grab" sample may be obtained that is entirely representative of the stream composition.

Local differences in water composition are most likely to occur in small or slowly moving streams and are due to poor vertical or lateral mixing. The differences in composition may be due to nearby ground- or surface-water inflows or to biological activity.

In addition to the above factors, certain operational aspects must also be considered in selecting sampling sites. Among these are: access to the sampling site, availability of reliable sample collectors or electric power if needed for operation of sensing devices, and availability of streamflow records.

Locating a water-quality station at a stream-gaging station has decided advantages because adequate water-discharge data are essential for computing the dissolved load carried by the stream. However, the site conditions for a good stream-gaging station may be unsatisfactory for a water-quality station. Rather than consider the presence of a stream-gaging station as a prerequisite for a chemical-quality station, the chemist may explore the possibility of obtaining water-discharge data at the chemical-quality station by direct or indirect means.

Each sampling station should be selected, so far as possible, to fit into a comprehensive network of sampling stations to cover a State or drainage basin. Even though an individual station is established to meet a specific need for information, the possibility of placing and operating it to supply data for other studies of chemical quality should not be overlooked. If two or more sites will give about equally usable information for the immediate needs, preference should be given to the one that most nearly fits the following criteria:

1. Best fits an overall plan for evaluating chemical quality on a broad basis.
2. Gives information that can be correlated with periodic information obtained at other sites or that can supplement such periodic information.
3. Gives the total of dissolved material discharged from an area.
4. Is at a transition from the surface outcrop of one geologic formation to another.
5. Is at a place where future water-resources development or changes in waste-disposal practices can be foreseen.

Lakes and reservoirs

The selection of sites for sampling lakes and reservoirs depends on the degree of accuracy required in determining the composition and on the degree of mixing. Water circulation and movement caused by wind, temperature changes, and currents between points of inflow and outflow cause mixing. Other factors such as irregularity in shape of the body of water, difference in composition of inflow and stored water, thermal stratification, evaporation, solution or evolution of gases at the air-water interface, and activity of aquatic plant and animal life all tend to bring about heterogeneous quality. A thorough study of water composition can be made by sampling along a three-dimensional grid pattern; samples can be collected at different depths at each grid intersection. A more economical and conservative approach might be to sample at different depths along selected cross sections in the body of water. The adequacy of such a sampling program depends on the judicious selection of the cross sections and sampling points. When only one sample is collected to define the average character of the lake or reservoir it should be collected near the center of the water mass. A single sample is completely inadequate for a study of a lake of any size and, at best, provides only an approximation of average water quality. In order to evaluate quality of reservoir water for the user downstream, the sampling site or station should be located at or near the point of discharge.

Ground water

A ground-water reservoir is analogous to a surface-water reservoir in that most usable ground water is in motion, although the rate of ground-water movement may be very slow and the reservoir may have poorly defined boundaries. A well can be considered as a sampling point in a large body of slowly moving water, which differs in chemical composition vertically as well as areally. Most of the forces which cause mixing in bodies of surface water are absent or much weaker in ground-water reservoirs. Turbulence is virtually nonexistent. The major forces that tend to mix ground water are probably the differences in velocities as the water moves through material of heterogeneous permeability, pressure differentials, and, to a lesser extent, ionic diffusion. The movement induced by pumpage and natural discharge may influence the composition of stored water. Commonly, differences in mineral composition of rocks within the ground-water reservoir, and variations in rate and chemical composition of recharge from precipitation and streamflow, cause differences in composition of water from place to place in a ground-water reservoir. Differences in samples collected at different times from the same source may also be observed.

Sampling programs are planned to determine the mineral content of ground water throughout the aquifer, although a completely comprehensive program is not always practical. Efficient collection of water-quality data and intelligent selection of the ground-water sampling site generally require more judicious consideration than the selection of a surface-water sampling site because the elements influencing water quality are not as easily observed. The composition of water obtained from a well is likely to be influenced by details of well construction, development, and pump operation, and these need to be taken into account in the sampling program.

Because of the diversified purposes of ground-water investigations, it is impractical to attempt specific direction for the selection of sampling sites. Nevertheless, some general suggestions can be given. If the objective is the general evaluation of quality of a ground-water resource, there are perhaps two equally satisfactory approaches, both of which employ comprehensive and partial analyses. One approach utilizes the determination of key constituents (one or several) in a large number of samples collected over the entire area. By this means an areal water-quality pattern is developed that is of value in selecting the sites for collection of samples for comprehensive analysis. In some investigations the identity of the key constituents may be unknown at the beginning of the investigation. Then, the reverse approach may be required, and comprehensive analyses may be made early in the study, and these data augmented by partial and additional comprehensive analyses of samples collected at other sites to complete the water-quality picture. Either method requires great care in the selection of sampling points.

In selecting a site for repeated sampling to detect water-quality changes or stability, the controlling variables should be considered. If the hydrologic regimen is modified near the site during the investigation, the results may reflect the change so strongly that all other effects are obscured. For example, if irrigation is begun in the vicinity of a well selected as a sampling site, any variations in quality resulting from natural-recharge patterns will be blotted out.

Although some ground-water studies may be concerned only with surveying the chemical characteristics of the water, the data are often used in conjunction with other geologic and hydrologic information. Consequently, the value of the water analysis is usually directly proportional to the facts known about the source of the sample. One general observation is pertinent: The most useful samples are collected from wells for which good well schedules and other data are available.

Frequency

Samples of surface and ground water that will best serve the objectives of the data user or of a specific study should be obtained at intervals such that no important change in quality could pass unnoticed between sampling times. This requisite immediately gives rise to two additional questions: What magnitude of change is important, and what are the physical and economic factors that must be considered in obtaining the record? By necessity the sampling schedule adopted is usually a compromise between the accuracy and detail desired in the water-quality record and the funds and personnel available for the work.

For each sampling site, determining the proper frequency of measurement will depend on the variability in concentration of each parameter and how accurately one needs to describe this variability. If the variability in values is large throughout the year, many measurements, perhaps even continuous sensing, may be needed to adequately describe a parameter. If variability is small, frequency could be altered seasonally to achieve desired accuracy. If values are negligible or do not constitute an immediate or forseeable problem, measurements could be omitted except for periodic checks to see whether the values remain negligible.

Surface water

For some streams, especially those where flow is completely controlled by large storage reservoirs, or is maintained at a nearly steady rate by large constant ground-water inflows, a single sample or observation may suffice to characterize the quality for many days or even weeks. Normally, however, one sample cannot be safely extrapolated for more than a day or two and for some streams not more than a few hours.

Streams are constantly subjected to forces and changing environment which bring about variations in the chemical character of the waters. These variations may be relatively small in areas subjected to intensive weathering for long periods of time, such as the Piedmont province near the Atlantic coastal region. Younger, incompletely leached rocks and scattered, infrequent, and often intense rainfall in the arid and semiarid Western States constitute an environment conducive to erratic and often extreme changes in water quality. Since the beginning of water-resources investigations in this country, the chemical-quality hydrologist has been confronted with the problem of the frequency of sampling required to detect adequately the changes in the chemical composition of a stream. On the basis of water-quality studies of a large number of streams and the practical economics of sampling-station operation, the U.S. Geological Survey has long followed a practice of collecting samples once daily, as this appeared to be the minimum frequency necessary to define adequately the water quality for the majority of water uses. Once-daily sampling has been considered as standard for the usual comprehensive chemical-quality investigation. Less frequent sampling schedules are often used, however, and the value of weekly or monthly samples in reconnaissance or unit basin studies should not be minimized.

In recent years, equipment has been developed which can be installed on a streambank or bridge, to record measurements of various water-quality parameters every few minutes or to transmit the data to a central point. Developments in this field have been rapid, and it is now possible to provide much more detailed information than could be obtained by the old sampling methods.

As automated or continuous recording equipment for conductivity and other variables comes into wider use, the number of complete chemical analyses required can be decreased. Various combinations of continuous recording equipment, supplemented with periodic sampling, are now in use, and they are particularly useful in streams with large actual or potential inflows of waste, as well as streams influenced by tidal inflow. Some limitations of sampling remain, however, as the water on which measurements are made has to be brought to the instrument through a fixed intake. The location of the intake represents a fixed sampling point, and the results of such measurements must be interpreted in terms of stream homogeneity at that sampling point.

Ground water

The chemical quality of ground water at the sampling point may vary in response to changes in rate of water movement, to pumpage, or to differences in rate and chemical composition of recharge from precipitation and from the surrounding area. Although concentrations of dissolved constituents in ground water from any one well may vary widely, sometimes severalfold, in general the changes take place much slower than those commonly associated with surface water. Until disproved, it is safer to assume that the quality of water from a well fluctuates rather than that it is uniform for long periods of time. Changes in groundwater quality usually can be described satisfactorily by monthly, seasonal, or annual sampling schedules.

Equipment

The water analyst has a wide variety of sampling equipment from which to choose. Only those items that have been used satisfactorily by the Geological Survey are discussed here. This does not imply that omitted items are unsatisfactory.

Containers

Factors that are pertinent in selecting containers used to collect and store water samples are resistance to solution and breakage, efficiency of closure, size, shape, weight, availability, and cost. Preferences for one type of container over another are varied, and selection is guided largely by experience, cost, effect of the container on the water sample, and use of containers in the individual laboratories. Although a great number of glass bottles are still in use, the current trend in Geological Survey laboratories is toward the polyethylene, teflon, or other plastic containers.

Hard rubber, polyethylene, teflon and other plastics, and some types of borosilicate glass are suitable on the basis of experience within the Survey and the reports of others in water chemistry. A limited investigation, conducted by the Survey, of the relative merits of four common types of bottles showed that storage in Pyrex and polyethylene did not significantly alter the silica, sodium, total alkalinity, chloride, and boron content, or the specific conductance, pH, or hardness of the water during a storage period of about 5 months. Glass bottles marketed under the name "No-Sol-Vit" added boron to the samples but were otherwise satisfactory. The increase in silica content of water stored in soft-glass bottles (citrate of magnesia type) was significant after 2 or 3 weeks. Prolonged storage in these bottles also increased decidedly the sodium content and the hardness of the water. The chemical type and concentration of the stored water apparently has a definite influence on the rate and nature of materials dissolved from the container. Comparative tests conducted by Wickers, Finn, and Clabaugh (1941) of four brands of chemical glassware showed that the relative resistance to attack depended on the reagent tested. Hubbard and Hamilton (1941) have shown that American Ceramic Bottle No. 1 glass is more resistant to attack by alkaline solutions at pH 11–12 than Pyrex glass.

Before use, all new bottles must be thoroughly cleansed, filled with water, and allowed to soak several days. The soaking removes much of the water-soluble material from the container surface. Old beverage bottles or other containers of this type should not be used for the collection or storage of water samples.

For a more detailed discussion of sample containers, the chemist is referred to Rainwater and Thatcher (1960).

Shipping cases

Sample shipping cases commonly used by the Geological Survey are shown in figure 1. Where cork or rubber stoppers are used as bottle closures instead of plastic or other screw-type caps, the lid of the case should exert pressure on the stopper to prevent its loosening during shipment.

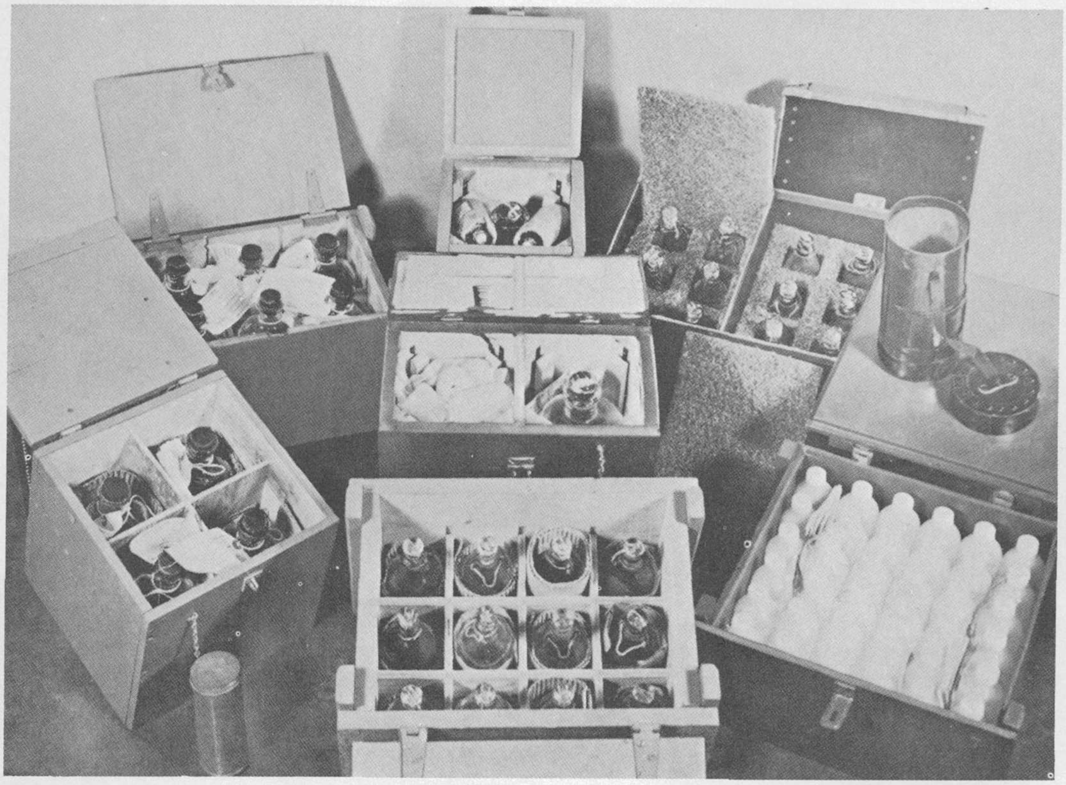


Figure 1.—Sample-bottle shipping cases.

Samplers

Depth-integrating

Depth-integrating samplers and point samplers are used to collect samples for the determination of nonvolatile constituents and those unaffected by aeration. A depth-integrating sampler consists of a mechanism for holding and submerging the bottle. When the bottle is lowered at a uniform rate, water is admitted throughout the vertical profile; hence, the sampler must be sufficiently heavy to submerge the bottle in swift water. The method of securing the bottle to the sampler should require a minimum of manipulation. Belt-and-buckle devices are generally avoided because of the difficulty in handling such items in cold weather. Some of the depth-integrating samplers used by the Survey are shown in figure 2.

Point

Point samplers are used to collect water at a specific depth and may be very simple in construction. The principal types are shown in figure 3. Sampler A is used only for collecting water samples at the bed surface of a stream or lake. The cork is tied to the suspension line in such a way that a sharp pull on the line will remove the cork and allow the bottle to fill. In operation the bottle is corked and then thrown into the water with an excess of line; when the bottle comes to rest on the bed, the suspension line is jerked, removing the cork. The bottle

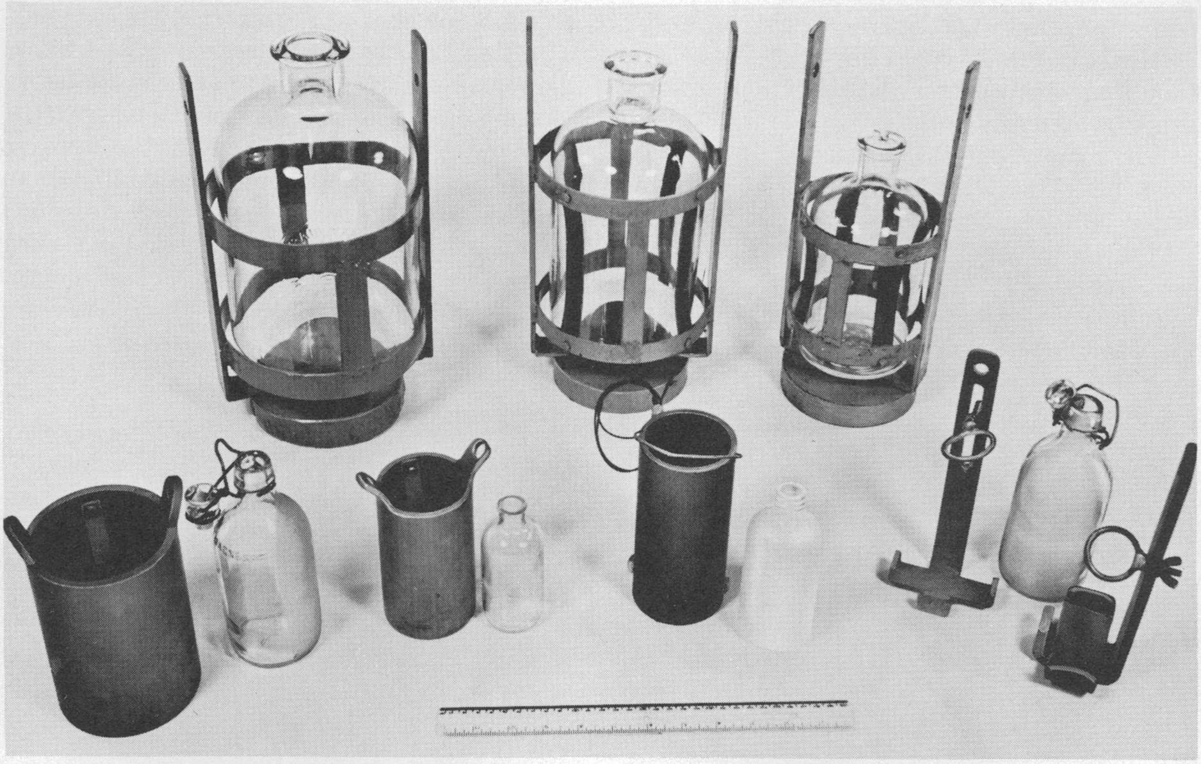


Figure 2.—Depth-integrating samplers.

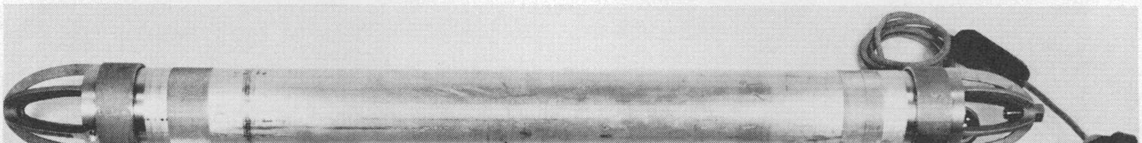


Figure 3.—Point samplers. A, Bottom sampler; B, ball-valve; C, Foerst; D, Colorado River.

is allowed to fill in place and then stoppered when it is withdrawn from the water. Sampler B is a ball-valve type and was designed for the collection of ground-water samples in wells at any desired depth. When the desired depth is reached, the sampler is filled by rapidly raising and lowering several times in succession, which opens the ball valves at either end and traps the water. The 1-gallon sampler is 3 inches in diameter and the 1-quart size about 1½ inches. Sampler C, the Foerst sampler, is used to collect surface-water samples from a given depth and has been used with some success to sample water from wells. The sampler is lowered to the desired depth in the open position; then a messenger weight, which trips the closing mechanism, is run down the suspension line. The messenger weight must meet the triggering device on the top of the sampler squarely. Hence, a set of messenger weights drilled to accommodate suspension lines of different diameters permits the use of the sampler with a wide variety of ropes and cables. The Foerst sampler is available in four sizes 400-ml (milliliter) capacity, 2 inches in diameter; 1,200-ml capacity, 2½ inches in diameter; 2,000-ml capacity, 3¼ inches in diameter; and 3,000-ml capacity, 3¾ inches in diameter. The samplers are constructed of brass and thus resist corrosion. Sampler D is used exclusively in sampling surface waters. It is lowered with stopper in place; the messenger weight then pulls the stopper, and the open bottle is raised to the surface.

Detachable weights are useful with practically all samplers. Appreciable weight is necessary in excess of that required to submerge the bottle. In moving water, inadequately weighted samplers drift with the current and tend to ride on the water surface at the end of the suspension line. Added weight also decreases the angle between the suspension line and the vertical, thereby increasing the accuracy of the depth measurement.

Special

The collection and handling of samples for the determination of dissolved-gas content and constituents susceptible to aeration require special equipment and careful technique. The sampler assembly for determining dissolved-oxygen content and biochemical oxygen demand, described by the American Public Health Association and others (1965) or a modification thereof, is generally acepted as the standard apparatus for sampling open water. This sampler provides for a threefold displacement of water in the sample bottle without aeration. Although this apparatus is efficient, satisfactory samples can be collected by other methods. A nonaerated sample collected in a Foerst sampler can be transferred by means of a tube connected to the outlet valve projecting into the bottom of the sample bottle. Twofold or threefold displacement of water in the bottle is recommended (fig. 4).

Rather elaborate instructions are given by the American Society for Testing and Materials (1966) for collecting samples from closed systems, and those procedures or modifications thereof can be used. Often a sample can be collected satisfactorily by running the water through a tube to the bottom of the bottle and using twofold or threefold displacement. The water should be run in slowly to minimize agitation and the resultant excessive aeration or loss of gas.

Narrow-mouth BOD (biochemical-oxygen-demand) bottles have pointed glass stoppers to avoid entrapment of air in the sample. Unfortunately this type of stopper does not provide a seal that permits much transporting or handling of the sample, unless the container in which the sample is transported exerts pressure on the stopper. "Citrate of magnesia" bottles can be pressure sealed without entrapment of air bubbles and, consequently, are used frequently for transporting samples for the determination of dissolved gases and constituents susceptible to aeration.

Accessories

Sashcord with or without a wire core is the most common means of suspending depth-integrating samplers. When long lengths of line are required, commercially available clothesline reels (fig. 5A) are useful. These reels also have a locking device, which facilitates use with point samplers.

Figure 4.—Apparatus for sampling water that contains dissolved gases and constituents susceptible to aeration.

Figure 5B shows a versatile assembly with which the exact depth can be read from a depth indicator on the reel; different weights can be interchanged as required by the current. In use the crane is tipped forward against the bridge rail. Modified booms having similar elements can be used from boats.

Identification and records

The source of the sample and conditions under which it was collected must be recorded and attached to the bottle immediately after filling. A water analysis is of limited value if unaccompanied by detailed information on what the sample represents. Field notes are extremely valuable in project-type investigations of water quality, but they can be easily misplaced or lost. Field notes never should be relied on to take the place of detailed information accompanying the sample from point of collection to finished analysis tabulation.

The Geological Survey records the sample description in two ways. Small soft-glass bottles, of 12-ounce capacity and less, are usually etched on the outside, and the information is written directly on the etched surface with a lead pencil. Standard sample tags, which provide space for sufficient detail to describe most samples, are used for other types of containers (figs. 6 and 7). These tags should be filled out as completely as possible before affixing them to the sample bottles. The items are self-explanatory and need not be described here. A complete discussion of these tags and the items they contain may be found in Rainwater and Thatcher (1960).

Field safety and first aid

Water samples are collected under a wide range of conditions, and the work is not without some hazard. A knowledge of the hazards involved and means by which they can be minimized should be helpful in preventing accidents and in providing greater

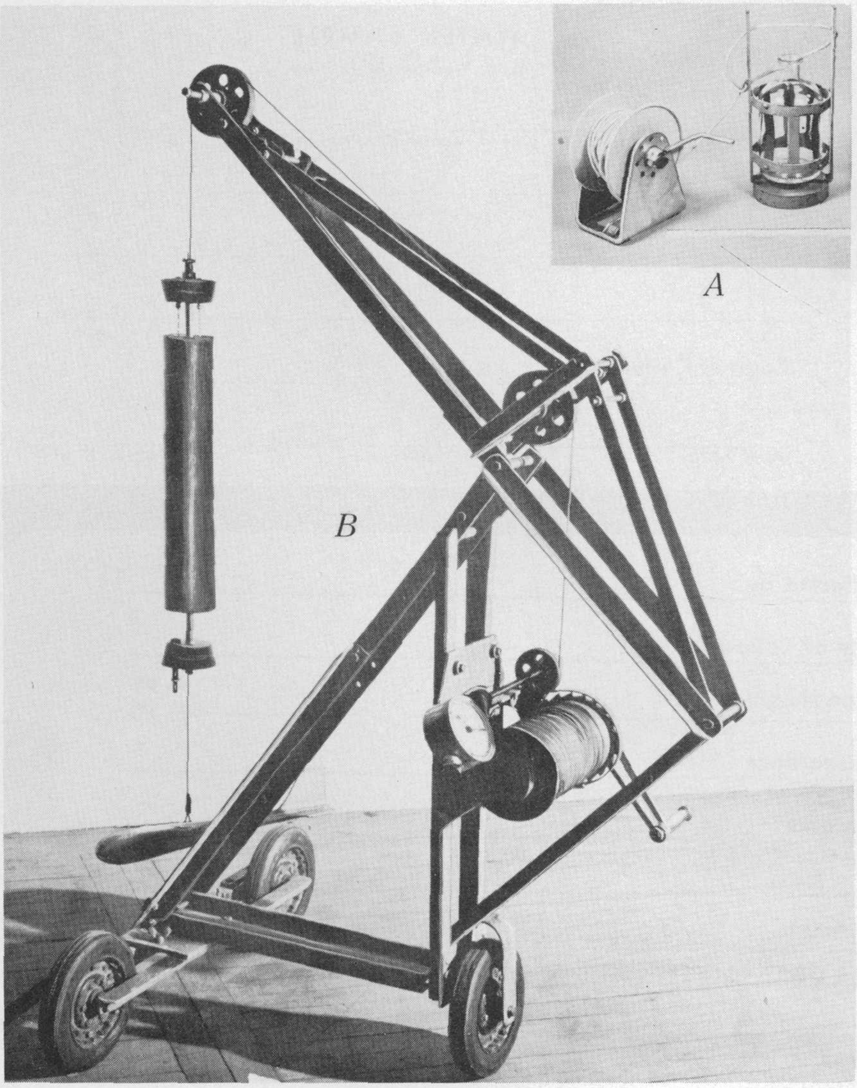
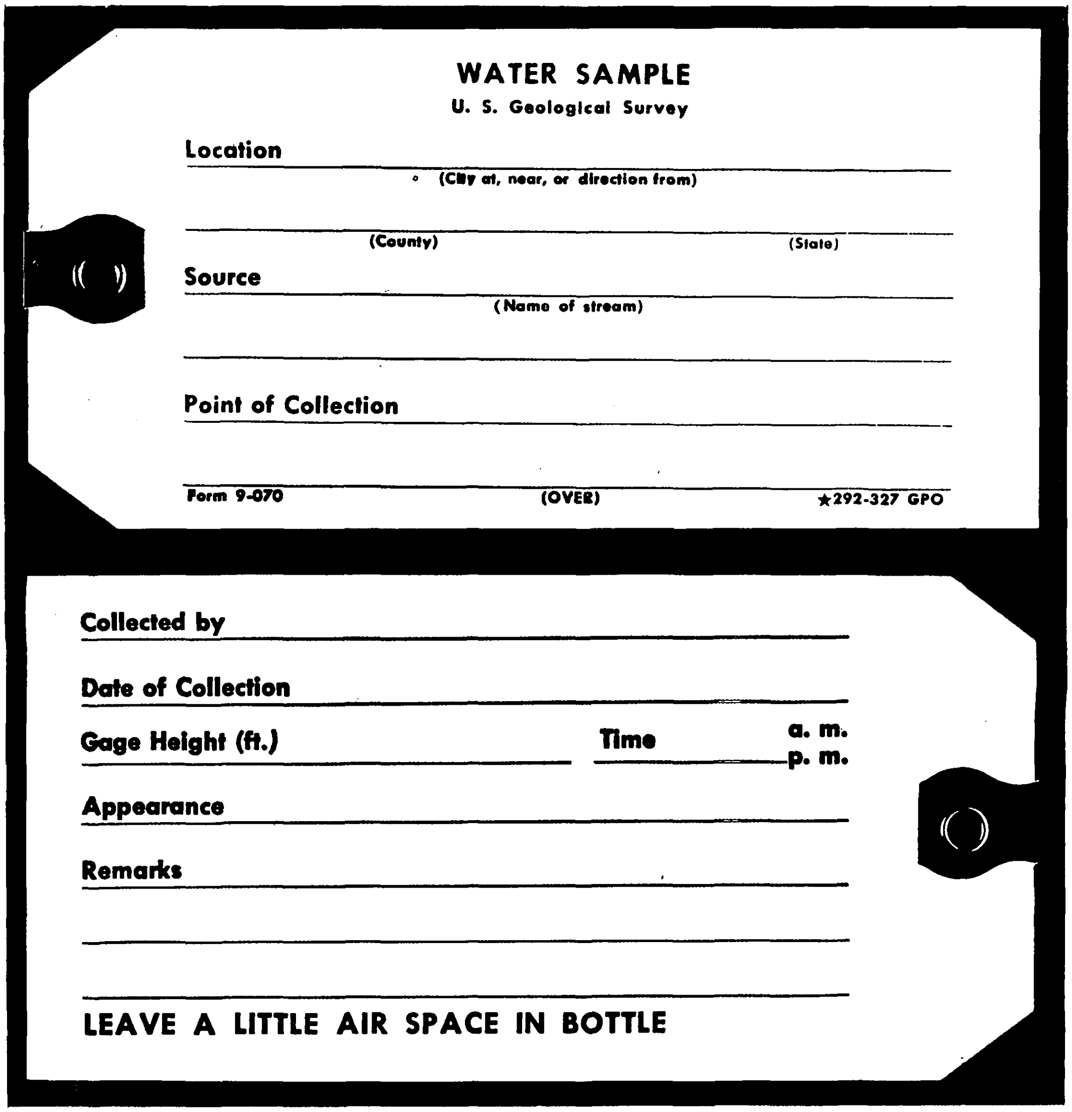


Figure 5.—Sampler suspension apparatus. A, Hand assembly for shallow water; B, crane assembly for deep water.

safety for sample collectors. Surface-water samples are collected from bridges, piers, cableways, and boats, and by wading, or through ice. Inability to swim and difficulty in freeing oneself of burdensome equipment if suddenly plunged into deep water are perhaps the most serious hazards in taking samples from streams, lakes, and reservoirs. The collection of ground-water samples has its own perils, primarily in connection with pumping equipment, snakebite, and unfriendly dogs. Dangers include loose or rotten well coverings and entanglement with belts and drive shafts. Many wells are surrounded by heavy brush which makes an attractive habitat for snakes, particularly during dry, hot months.

By definition, first aid is the immediate and temporary care of an injured or suddenly ill person until a doctor can be obtained; it is not a substitute for competent medical attention. Each field party should be supplied with a standard first-aid kit and first-aid manual as well as a kit for effective emergency treatment of snakebites. "First Aid Guide," published in 1962 as Handbook



WATER SAMPLE

U. S. Geological Survey

Location ____________________

(City at, near, or direction from)

____

(County) (State)

Source ____________________

(Name of stream)

____

Point of Collection ____________________

Form 9-070 (OVER) ★292-327 GPO

Collected by ____________________

Date of Collection ____________________

Gage Height (ft.) __________ **Time** __________ a. m. p. m.

Appearance ____________________

Remarks ____________________

____

____

LEAVE A LITTLE AIR SPACE IN BOTTLE

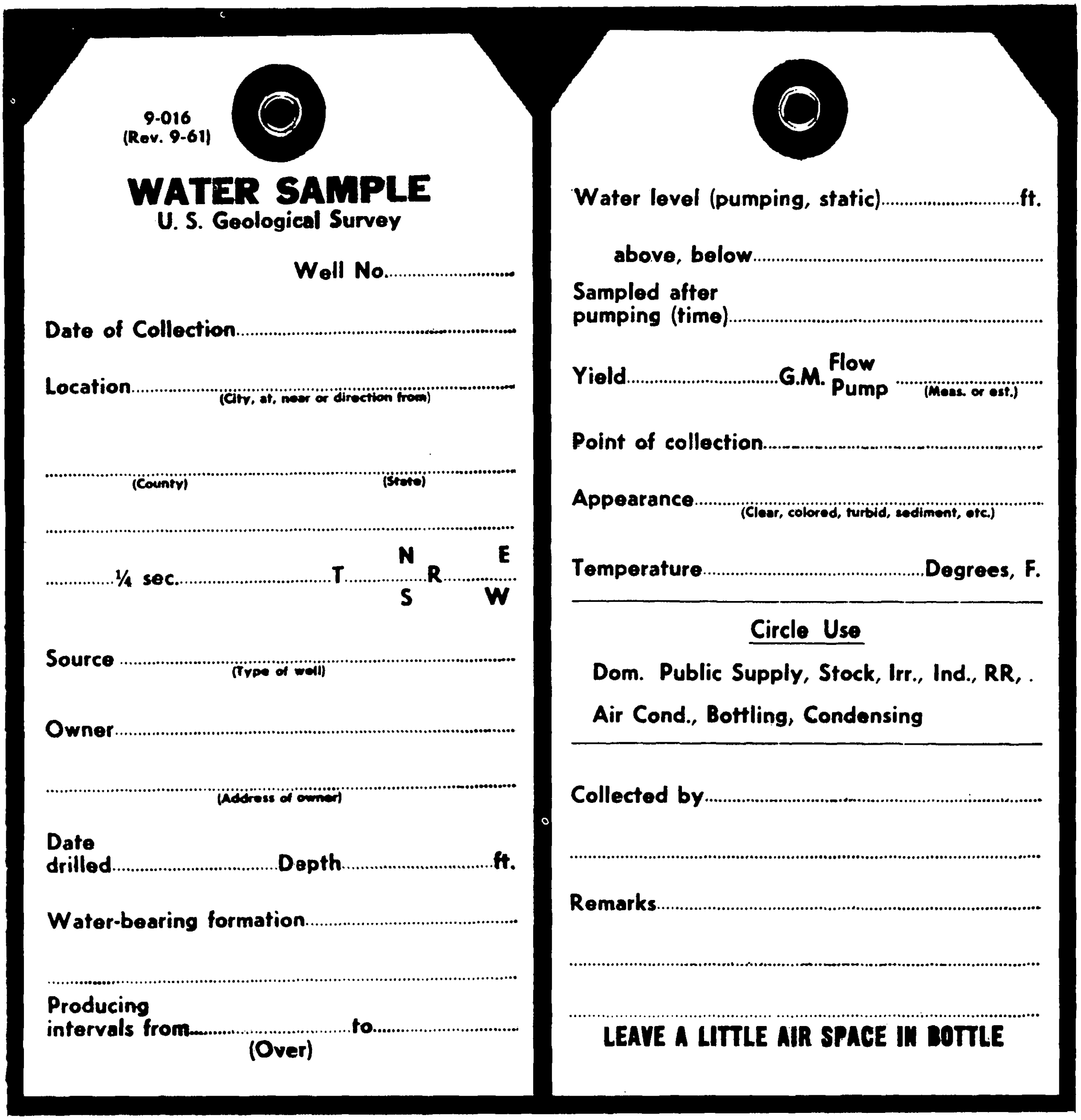
Figure 6.—Tag for surface-water sample.

227 by the U.S. Department of Agriculture (Forest Service) and sold by the U.S. Government Printing Office, is a satisfactory manual.

Sample collection and treatment

Many of the ions normally present in only trace amounts in natural waters may not remain in the water sample until it is analyzed because of such chemical and physical reactions as oxidation, reduction, precipitation, adsorption, and ion exchange. Coprecipitation may also reduce the concentrations of these constituents in solution. Iron is a particularly troublesome component in natural water because of its tendency to precipitate from solution and to coprecipitate other metal ions.

An analysis will more closely represent the water at the time of collection if separate samples are taken for determination of certain ions, or groups of ions. A classification is given below which indicates the field treatment required for the various types of samples collected for analysis by Survey laboratories, and the analytical determinations to be made on each sample type. The classification given is recommended only, and not mandatory for all data-gathering programs of the Water Resources Division.



9-016
(Rev. 9-61)

WATER SAMPLE
U. S. Geological Survey

Well No. ....

Date of Collection ....

Location .... (City, at, near or direction from)

.... (County) .... (State)

....

.... ¼ sec. .... T .... N S R .... E W

Source .... (Type of well)

Owner ....

.... (Address of owner)

Date drilled .... Depth .... ft.

Water-bearing formation ....

....

Producing intervals from .... to ....

(Over)

Water level (pumping, static) .... ft.

above, below ....

Sampled after pumping (time) ....

Yield .... G.M. Flow Pump .... (Meas. or est.)

Point of collection ....

Appearance .... (Clear, colored, turbid, sediment, etc.)

Temperature .... Degrees, F.

Circle Use

Dom. Public Supply, Stock, Irr., Ind., RR, .
Air Cond., Bottling, Condensing

Collected by ....

....

Remarks ....

....

....

LEAVE A LITTLE AIR SPACE IN BOTTLE

Figure 7.—Tag for ground-water sample.

The objectives of each program should determine whether a given analytical determination should be performed on a settled, filtered, or well-mixed sample.

Instructions for the treatment of samples for radiochemical and biological examination, determination of organic substances, and spectrographic analysis of minor elements are not included. Analytical procedures for these determinations are presented in separate manual chapters, which also include instructions for sample treatment.

IN SITU or ON-SITE DETERMINATIONS

Mandatory	*Recommended*
1. Temperature, °C.	1. Acidity.
2. pH.	2. Alkalinity.
3. Dissolved oxygen.	
4. Specific conductance.	

LABORATORY DETERMINATIONS
Sample 1—Field-filtered, untreated

1. Collect and immediately filter the required volume of a representative sample through a 0.45-μm (micrometer) membrane

filter. Ordinarily, 1 liter of filtrate will be sufficient. Pressure filtration using compressed nitrogen or compressed air is preferred (fig. 8).

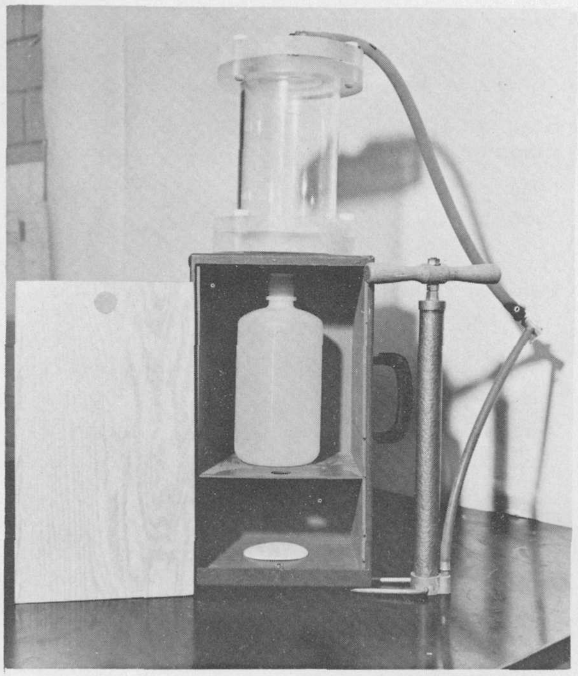


Figure 8.—Field filtration assembly

2. Store the filtrate in a tightly capped polyethylene bottle.

3. The following determinations are made on aliquots of the filtrate:

(1) Boron (B)
(2) Chloride (Cl)
(3) Fluoride (F)
(4) Hardness
(5) Lithium (Li)
(6) Nitrogen, nitrate
(7) Nitrogen, nitrite
(8) Phosphorus (all dissolved forms)
(9) Potassium (K)
(10) Selenium (Se)
(11) Silica (SiO_2)
(12) Sodium (Na)
(13) Solids, dissolved
(14) Sulfate (SO_4)

4. If a field-filtered sample cannot be provided, a laboratory-filtered sample may be substituted with slightly less confidence in the reported data. In such cases, and as an alternative, any remaining portion of sample 3 may be filtered and used for this sample.

5. The appearance of any turbidity or residue in the sample bottle when aliquots are withdrawn for analysis may be an indication of precipitation of one or more of the above constituents and should be viewed with suspicion until proved otherwise.

Sample 2—Field-filtered, acidified

1. Collect and immediately filter the required volume of a representative sample through a 0.45-μm membrane filter. Ordinarily 2 liters of filtrate will be sufficient. Pressure filtration using compressed nitrogen or compressed air is preferred (fig. 8).

2. Acidify the filtrate with double-distilled, reagent-grade HNO_3. The resultant pH must be 3.0 or less. Acidification minimizes loss of solutes by oxidation and (or) precipitation and by adsorption to the container surfaces.

3. Store the sample in a tightly capped polyethylene bottle.

4. The following determinations are made on aliquots of the acidified filtrate:

(1) Aluminum (Al)
(2) Arsenic (As)
(3) Barium (Ba)
(4) Cadmium (Cd)
(5) Calcium (Ca)
(6) Chromium (Cr)
(7) Cobalt (Co)
(8) Copper (Cu)
(9) Iron (Fe)
(10) Lead (Pb)
(11) Lithium (Li)
(12) Magnesium (Mg)
(13) Manganese (Mn)
(14) Molybdenum (Mo)
(15) Nickel (Ni)
(16) Potassium (K)
(17) Silver (Ag)
(18) Sodium (Na)
(19) Strontium (Sr)
(20) Vanadium (V)
(21) Zinc (Zn)

5. If a spectrographic analysis is to be made in addition to or in lieu of the above, either divide the sample to provide the two *identical portions,* or submit the entire sample for spectrographic analysis.

Sample 3—Unfiltered, settled

1. Collect the required volume of a representative sample. Ordinarily 1 liter will be sufficient.

2. Store in a cool place and out of bright daylight.

3. The following determinations are made on aliquots of the clear supernatant solution

after any suspended sediment has settled. The analyses must be performed immediately upon opening the sample bottle and as soon as possible after collecting the sample.

(1) Acidity
(2) Alkalinity
(3) Carbon dioxide, calculated
(4) Color
(5) pH (lab)

4. If no field-filtered sample has been provided, the sample remaining after performing the above analyses may be filtered, and any or all of the determinations specified under sample 1 then performed on aliquots of the filtrate.

NOTE.—While there may be little or no difference in the determined values for the major constituents whether a field- or laboratory-filtered sample is used, this is less likely to be so for the minor elements. When minor elements are to be determined, a field-filtered and acidified sample is much preferred and should be provided whenever possible.

Sample 4—Unfiltered, well-mixed

1. Collect the required volume of a representative sample. Store in a cool place and out of bright daylight. Analyze as soon as possible after collecting the sample. Keep the sample chilled until analysis to deter decomposition.

2. The following determinations are made on aliquots of this sample:

(1) Nitrogen, ammonia
(2) Nitrogen, organic
(3) Oxygen demand, chemical (COD)
(4) Cyanide (CN)
(5) Phosphorus
(6) Solids, suspended
(7) Solids, volatile (total)
(8) Turbidity.

3. Immediately before withdrawing each aliquot, shake the sample until all suspended material is uniformly distributed.

Additional samples—Special treatment

Collect additional representative samples and treat individually as may be required for special purposes and determinations. These may include:

(1) Nitrogen: ammonia, nitrate, and nitrite
(2) Oxygen, dissolved (Alsterberg azide)
(3) Phosphorus, organic
(4) Sulfide.

Nitrogen, ammonia.—The percentage concentrations of the various components of the nitrogen cycle may change rapidly as a result of biologic activity. Chloroform (5 ml per liter of sample) or Hg^{+2} (40 mg (milligrams) per liter of sample) (Brezouik and Lee, 1966) inactivates the organisms and fixes the nitrogen-cycle components. It is also desirable to chill or refrigerate samples preferably at 0°–4°C, until they can be analyzed. Samples should be kept in the dark until analyzed.

Nitrogen, nitrate.—See Nitrogen, ammonia (above).

Nitrogen, nitrate.—See Nitrogen, ammonia (above).

Oxygen, dissolved.—When dissolved oxygen cannot be instrumentally determined in the field, a sample must be collected for laboratory analysis. Immediately after collection, the dissolved oxygen in a sample should be converted to an equivalent amount of free iodine, which is more stable in solution than oxygen. The sample is normally collected in a 300-ml BOD bottle with a minimum of aeration. Water temperature must be taken at the time of collection if the percentage of saturation is to be computed.

Suspended solids in high concentration may adsorb appreciable quantities of iodine in acid solution and they should be removed by coagulation with aluminum sulfate (alum) as follows: Collect the sample in a 500-ml glass-stoppered bottle using the same precautions as for the BOD bottles; add 10 ml 10-percent alum solution and 1–2 ml concentrated ammonium hydroxide; mix by inversion and allow the floc and suspended material to settle; decant the supernatant into a BOD bottle until it overflows.

If the sample is clear, or after it has been clarified, proceed with the following treatment:

1. Add 1 ml KF solution below the liquid surface of the sample in a BOD bottle.

2. Add 2 ml $MnSO_4$ solution below the liquid surface.

3. Add 2 ml alkaline-iodine sodium azide reagent below the liquid surface.
4. Stopper and mix by inversion. Allow the precipitate to settle, and then repeat the mixing and settling proceses.
5. Add 2 ml concentrated H_2SO_4 by allowing the acid to run down the neck of the bottle.
6. Mix by gentle inversion until solution is complete.

In the absence of organic or other oxidizable matter, titration of the released iodine can be postponed for 48–72 hr if the treated sample is kept chilled or refrigerated. Instructions for preparation of reagents are given in "Part IV, Analytical procedures, Oxygen, dissolved, Alsterberg azide method."

Phosphorus, organic.—The conversion of organic phosphorus to orthophosphate is largely the result of microbiologic action. Chloroform (5 ml per liter of sample) inactivates the organisms and stabilizes the organic phosphorus–orthophosphate system.

Sulfide.—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 (grams) 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.

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Part II. Laboratory equipment and techniques

Glassware and other containers

All glass apparatus and containers used in analytical work should 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 should 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 specified by the National Bureau of Standards (1959). In addition, if such glassware is frequently used to measure strongly alkaline solutions, it should 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 micromhos/cm (centimeter), and it should 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 shall 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 strength 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 shall not be used.

Accuracy of measurement

In the instructions for making the analysis and preparing the solutions, 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 liter" 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 (H_2O) 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.

Instrumental techniques

Visible and Ultraviolet Spectrophotometry

Spectrophotometry 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 spectrophotometers contain the following essential components:

1. *Source of radiant energy.*—Usually an ordinary tungsten-filament incandescent lamp; hydrogen or deuterium discharge lamps are usually used 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 examined.
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 (1965). 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 spectrophotometric 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 spectrophotometry 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 spectrophotometric curves of light-intensity ratio plotted against concentration, it is preferable, for convenience, 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 will usually show only a moderate curvature. Extreme curvature, when the curve is plotted on the basis of absorbance data, 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. The modern spectrophotometers 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; it is the same as absorbance.

The spectrophotometer most commonly used in laboratories of the Geological Survey is the prism type, represented by the Beckman Model B. Equally good results may be obtained with other commercial instruments if the manufacturer's operating instructions are followed. Filter-type photometers are not recommended.

Sensitivity

In spectrophotometric 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 sensitivity, or "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. The type of sensitivity under consideration is that which improves the absorbance of the constituent sought relative to the background absorbance, which is made up of the absorbance of interfering ions, natural color, and turbidity. Increasing the optical path of the absorption cell does not always improve the sensitivity because the absorbance of the solvent or background is often increased proportionately. To obtain a useful improvement in the sensitivity, it is necessary to select an analytical method that will provide a greater absorbance for the constituent sought.

Interferences

In spectrophotometric 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. In either case, the absorbance of the sample will be decreased. 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: (1) 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 in organic solvents often permits the removal of interfering ions, as in the selenium procedure.

Another common source of interference in spectrophotometry 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 spectrophotometric 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 spectrophotometric 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 spectrophotometric 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 spectrophotometric

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 above general procedure. 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 the reagents except the indicator are added to the sample. The sample is placed in the spectrophotometer and the absorbance is set to 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 when conditions are right. 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 managanese. 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 adsorb 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 most photometric procedures are carried out on filtered samples, interference due to turbidity is not of major concern. When unfiltered samples are analyzed by spectrophotometric procedures, however, the presence of turbidity may increase absorbance appreciably due to light absorption and scattering. Although the above procedures 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 0.45-μm membrane filters such as that supplied by the Millipore Co. 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.

The difficulty in removing turbidity is to avoid upsetting the trace-metal ionic relations in the sample. While it is not known that any single method accomplishes this objective ideally, it is known that some methods are better than others. The methods cited above, while not ideal, are acceptable. Some methods are not acceptable because of the high possibility of gross contamination of the sample or gross change of the sample by adsorption of constituents on the filtering medium. The methods that cannot be used in spectrophotometric work are:

1. Filtration through Berkefeld tubes and similar porous porcelain or diatomaceous-earth filters.
2. Filtration with the aid of charcoal or alumina.
3. Filtration with the aid of filter pulp, unless it has been established that the pulp does not significantly adsorb the particular constituent being determined.

Filtration through fritted-glass disks is probably safe from the standpoint of adsorption losses, but it is always necessary to guard against contamination by carryover from previous filtrations with these units. Another method is the addition of large quantities of salts to the sample to neutralize the charges on the particles and cause their coagulation. What effect this procedure may have on trace metals has not been investigated, but it is obvious that contamination may occur because of the high concentration of salt that must be added.

It is impossible to specify procedures for the correction of turbidity that will fit all field conditions. Through familiarity with waters of the area, the analyst will be able to identify the appropriate method for eliminating errors resulting from turbidity. Often no correction will be necessary. In other cases, it will be possible empirically to prepare correction tables or curves for the streams. It should be necessary only occasionally to apply lengthy physical or chemical procedures.

Emission and atomic-absorption flame spectrophotometry

When a metal salt in solution is sprayed 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 spectrophotometry. The essential difference between this form of analysis and classical arc-emission spectrography is the temperature of the source used to excite the atoms. Since the gas-air and gas-oxygen flames are much cooler than the spark and arc sources used in spectrography, analysis by emission flame spectrophotometry is usually limited to the more easily excitable elements—lithium, sodium, and potassium.

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

In most respects, the instrumentation required for the two techniques is similar.

Both require the following:

1. A means of introducing the sample into a flame for vaporization.
2. A means of selecting the proper wavelength, usually a variable monochromator.
3. A means of detecting and recording the intensity of radiation emitted or absorbed.

In addition, the atomic-absorption technique requires the availability of a suitable light source, usually a hollow-cathode or vapor-discharge lamp.

For a complete discussion of these components, the analyst is referred to publications of the various manufacturers producing commercial instruments, as well as standard texts such as Dean (1960), Elwell and Gidley (1966), Robinson (1966), and Slavin (1968).

In atomic-absorption flame photometric systems, the flame functions in a fashion similar to that performed by the colored sample solution in visible and ultraviolet photometry. In both cases, radiant energy is absorbed, and the transmittance of either flame or colored solution is the ratio of the light signal reaching the detector when a sample is tested to that received when a blank is run. In either case, this may be expressed in percent. In visible photometry, the term "percent transmittance" is used, whereas in atomic-absorption photometry the complement of transmittance, or absorption, is used. Thus, a flame with a transmittance of 70 percent would have an absorption of 30 percent. In either case, Beer's law expresses a linear relationship between concentration and the logarithm of transmittance or absorption; in either case, also, the negative logarithm is called "absorbance." This relationship has been developed in "Part II, Visible and Ultraviolet Spectrophotometry," and need not be repeated here.

Analytical procedures

Direct method.—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 directly aspirated into the flame of the spectrophotometer. It is generally necessary to adjust the element concentration of the more sensitive elements by sample dilution, and it may be necessary to filter the sample to avoid clogging the atomizer-burner. 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 increase sensitivity, the percent absorption values are small, and it is unnecessary to convert percent absorption to absorbance before plotting a standard curve.

Chelation-extraction method.—In some samples, where the concentration is less than the minimum detectable amount for the particular element sought, some means of sample treatment must be resorted to. 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 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 procedure, as well as others of the extraction type included in this manual, 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 spectrophotometer.

Although APDC may be obtained commercially, a somewhat superior product may be prepared in the laboratory. The preparation is simple, rapid, requires little equipment, and the cost is considerably less than that of the commercial product. The following procedure was described by Slavin (1964).

Apparatus

Condenser, Friedrichs, with ground glass joint 24/40 (Corning No. 2600).

Flask, round-bottom, boiling, 300-ml capacity with ground glass joint 24/40 (Corning No. 4320).

Reagents

Ammonium hydroxide, 8*N*: Dilute 533 ml concentrated NH_4OH to 1,000 ml with distilled water.

Carbon disulfide, reagent grade.

Ethanol, 95 percent.

Pyrrolidine: (May be obtained from K & K Laboratories, 117–10 93rd Avenue, Jamaica, N. Y. 11433; K & K No. 17221).

Procedure

1. Dissolve 45 ml of pyrrolidine in 100 ml ethanol in a 300-ml round-bottom flask.
2. Attach the reflux condenser and cool the flask for 30 min (minutes) in an ice-water bath.
3. Slowly add through the condenser three 10-ml portions of CS_2. Addition of the CS_2 produces a strong warming effect; therefore, keep the flask cooled with ice at all times.
4. Immediately, add 75 ml 8*N* ammonium hydroxide.
5. Collect the crystals, which form on cooling, on a suction filter and wash with ethanol at least three times. A Buchner funnel fitted with a Whatman No. 41 paper is satisfactory for the filtration.
6. The yield is between 40–45 grams, approximately 50 percent of theoretical.

Standard-addition method.—Another technique widely used in both emission and absorption analysis, where interferences cannot be otherwise 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 avoids matrix effects and interferences, since both sample and standard will be equally affected.

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-absorption 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 9. Although illustrated for flame absorption, the standard-addition technique may be applied equally well to flame-emission analysis.

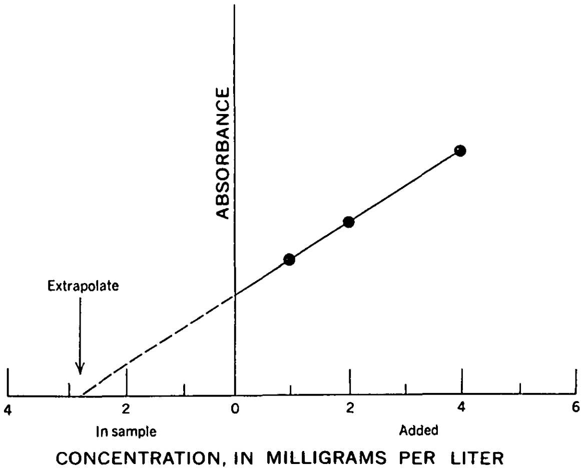

Figure 9.—Example of standard-addition method.

Internal-standard method.—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.

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 is measured by successive scanning of the two emission lines. The ratio of the 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 log intensity ratio versus log concentration produces a straight line from which the concentration of the element sought in the samples 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 increase 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 salts 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 removed from the flame, and the interference is eliminated.

Matrix effects.—Unequal amounts of dissolved solids in samples and standards may cause errors in the analysis due to different handling of such solutions by the atomizer. This may usually be controlled by matching the density of samples and standards, or by adding a salt to the standards.

Spectral line effects.—Some instances have been noted of interference between spectral lines of the elements, but these are rare and not of general concern.

Polarography

Polarography, or voltametry, is an electrochemical method of analyzing aqueous solutions containing oxidizable or 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 negative voltage of from 0 to 2 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 value 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:

$$O_2+2H_2O+2e \rightarrow H_2O_2+2OH^{-1}$$ (neutral or alkaline solution)

$$O_2+2H^{+1}+2e \rightarrow H_2O_2$$ (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 adsorbed 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 platinized electrodes. The null point is detected by an a-c (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 adsorb gases and catalyzes their reunion, thereby minimizing polarization.

The electrode cell may be either the dip 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 cells are preferable for fieldwork.

For many years a bridge fabricated within the Geological Survey has been used sucessfully for the determination of specific conductances ranging from about 25 to 35,000 micromhos/cm. This bridge is used with a pipet cell (cell constant of approximately 0.3 reciprocal cm). Above about 3,000 micromhos 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 reciprocal cm. 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 one such instrument 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, and transistorized, solid-state circuitry makes the instrument durable for field use.

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 pH 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 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 the whole 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:

$$\underbrace{\mathrm{Ag^{\circ}:AgCl}\ \Big\|\ \begin{matrix}\text{Solution of}\\ \text{known pH;}\end{matrix}\ \begin{matrix}\text{Glass}\\ \text{membrane;}\end{matrix}}_{\text{Glass electrode}}\ \begin{matrix}\text{Solution of}\\ \text{unknown pH}\end{matrix}\ \Big\|\ \mathrm{Hg^{\circ}:HgCl.}$$

The voltage 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 voltage an electron-tube voltmeter 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, and the calibration should be checked during extended periods of operation.

Turbidity

Methods for measuring turbidity in water will, in general, fall into one of the three following categories:

1. Procedures which measure the ratio of intensity of light scattered at right angles by the suspended matter to the intensity of the incident light.
2. Procedures which measure the ratio of the light transmitted through the water in a straight line to the intensity of the incident light.
3. Procedures which measure the depth at which an object disappears from view beneath the surface of the water.

Newell (1902) defined a standard for turbidity based on the third category above, as follows:

> * * * a water which contains 100 parts of silica per million in such a state of fineness that a bright platinum wire 1 millimeter in diameter can just be seen when the center of the wire is 100 millimeters below the surface of the water and the eye of the observer is 1.2 meters above the wire, the observation being made in the middle of the day, in the open air, but not in sunlight, and in a vessel so large

that the sides do not shut out the light so as to influence the results. The turbidity of such water shall be 100.

A turbidity rod calibrated for use under these conditions was designed by the Geological Survey and used for many years. However, because of the large number of variables that must be controlled to measure accurately the turbidity of a water body or sample, a simpler method was needed to measure the same characteristic as defined by the standard for turbidity. The Jackson candle turbidimeter made it possible to determine turbidity in the laboratory and simplified the measurement somewhat. Since shortly after the turn of the century, the Jackson turbidimeter has been considered by most water chemists to be the referee instrument for the turbidity determination, although uniform results still require control of several variables, and turbidity values cannot be determined below 25 units. The Jackson turbidimeter was based on the second category above, and is still used today, especially for the measurement of high turbidities.

More recently, other instruments simpler in operation and more sensitive to small differences in turbidity have been marketed. The advertisement for some of these instruments has stated that the results are comparable to the Jackson turbidimeter. Experimentation has shown that the nature of the suspended material has a bearing on the degree of similarity of the results.

The Geological Survey now uses the Hach Model 2100 turbidimeter as a standard turbidity-measuring instrument, primarily because of its sensitivity for measurements of low turbidity and because of the need for results that are reproducible and comparable between the different laboratories. This instrument falls into the first category above, and uses a synthetic polymer suspension, Formazin, as a standard of turbidity. Measurement of turbidity of this material has indicated a high degree of stability and reproducibility, both in concentrated suspensions and prepared dilutions.

Laboratory safety

Every analyst should always be aware of the inherent dangers involved in chemical operations and take every precaution to prevent personal injury and damage to the laboratory and equipment. The injurious nature of concentrated acids and alkalis, the poisonous nature of cyanides, and the explosive potential of perchloric acid is generally recognized, but the precautions necessary for the safe use of these and other dangerous reagents is often too infrequently emphasized. In addition, adequate safety equipment and properly trained personnel are often not available to properly handle an emergency situation. In order to minimize fire, explosions, and accidental injury, each laboratory should have the following items (Manufacturing Chemists' Association, Inc., 1954):

1. A staff composed of safety-minded individuals.
2. A capable safety staff consisting of a safety group or committee, the leader or chairman of which should be the head of the laboratory or another person of substantial responsibility.
3. An education program to promote safety and fire prevention.
4. Proper supervision of all work in various divisions of the laboratory by experienced men.
5. Regular inspection program of all working areas.
6. Corrective discipline for unsafe practices of laboratory personnel.
7. Adequate safeguards against physical exposure to hazardous chemicals and equipment.
8. A policy of encouraging the use of personal protective equipment, such as suitable clothing, eye protection, face shields, and masks.
9. First-aid facilities including competent personnel.
10. Complete records of all accidents.

The multitude of conditions ranging from laboratory design to chemical toxicity, that are implied by the above items, is too vast to be considered in this manual. It is, however, urged that responsible laboratory personnel become familiar with, and make available to their staff, such standard texts as "Dangerous Properties of Industrial Materials" (Sax, 1963); and "Guide for Safety in the Chemical Laboratory," Manufacturing Chemists' Association, Inc. (1954).

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Part III. Analysis of samples

Sample storage

Although preservatives may be added to samples at the time of collection to minimize changes in composition, such precautions cannot be relied upon to prevent entirely alterations in water quality between the time of collection and analysis of a sample. Some general observations on the effect of sample storage on water quality have been presented by the American Public Health Association and others, 1965) as follows:

> In general, the shorter the time that elapses between collection of a sample and its analysis, the more reliable will be the analytical results. For certain constituents and physical values, immediate analysis in the field is required in order to obtain dependable results, because the composition of the sample may change before it arrives at the laboratory.
>
> It is impossible to state unequivocally how much time may be allowed to elapse between collection of a sample and its analysis; this depends upon the character of the sample, the particular analyses to be made, and the conditions of storage. Changes caused by the growth of organisms may be greatly retarded by keeping the sample in the dark and at a low temperature until it can be analyzed * * *

Composited samples

When samples are collected at frequent intervals at a station, analysis of each individual sample would be prohibitive in cost and for many streams would result in needless duplication. Consequently, the compositing of several samples into a single sample for chemical analysis is a common practice, but it should be avoided whenever possible.

Such composites are generally made on the basis of dissolved mineral content as indicated by measurements of conductivity of the daily samples, supplemented by other easily obtained information such as concentration of chloride, river stage, weather conditions, appearance of sample, and previous history of the stream.

Water-quality data obtained by the analysis of composite samples does not satisfy current needs of regulatory agencies and others concerned with water-quality management and control. This practice, therefore, is to an ever-increasing degree being superseded by other procedures, largely statistical in nature, that more closely meet present requirements for water-quality data. Studies have indicated that sufficiently satisfactory correlations may be developed between dissolved-solids concentrations and specific conductance to permit the computation of annual loads from analyses of periodic grab samples. Such correlations often permit the computation of individual ion loads at some stations. Maximum and minimum values may also be obtained by detailed analysis of samples selected on the basis of daily specific conductance measurements.

Where individual program requirements cannot be met by some form of correlation technique, individual daily samples may be composited for analysis on either a time-weighted or discharge-weighted basis. A detailed discussion of both of these compositing procedures is presented by Rainwater and Thatcher (1960).

Order of analysis

The validity of the analytical statement and the time required for analysis are affected by the order in which constituents are determined and by the manner in which the sample is treated. The following discussion concerns mainly that group of constituents and measurements included in the standard chemical analysis normally made by most of the laboratories of the Geological Survey and does not include the determinations of volatile materials or constituents readily changed by aeration or bacterial action. Such determinations will normally be made on separate samples collected specifically for the special determination, and such samples should be analyzed according to the requirements of the individual determination.

Constituents and measurements most susceptible to change are determined first. The pH and relative proportions of the alkalinity and acidity components are related to the gas content of the sample and are the least stable. Filtration may alter the gas content of the sample. Hence, pH and alkalinity or acidity of the unfiltered sample should be determined immediately after the bottle is uncapped. Composite samples should not be prepared far in advance of analysis.

The specific conductance gives an indication of the total ionic concentration of the sample and is, therefore, useful in the selection of the volume of sample to be taken for the individual determinations. The specific conductance is not affected by moderate turbidity and can be determined from either a raw or filtered sample.

If the sample requires clarification, a sufficient volume should be filtered at one time to provide samples for all remaining determinations. This has two advantages: Less time is required for one filtration than for several individual filtrations, and if any solution or exchange of ions is progressing at the sediment-water interface, an early separation is desirable. The single filtrate provides identical water for analysis, whereas there is no assurance that individual filtrations at different times would provide identical samples.

A loss of carbon dioxide from solution converts bicarbonate to carbonate. Calcium carbonate, which is only sparingly soluble, may precipitate soon after a bottle is uncapped. Precipitation of calcium carbonate affects the validity of the pH, alkalinity, specific-conductance, calcium, titrated-hardness, and dissolved-solid values. Consequently, aliquots for the determination of calcium, hardness, and dissolved solids should be withdrawn soon after the bottle is opened. All samples should be inspected visually for evidences of calcium carbonate precipitation when received in the laboratory. If precipitation is evident, the analytical statement will not represent the chemical character of the sample at the time of collection unless special techniques are used. Proper handling of such samples requires special treatments and may involve the omission of some determination from the analysis. Selected constituents and measurements, even calcium and total alkalinity, can be determined with a reasonable degree of accuracy. The selected special treatment will depend on the nature of the precipitate and the constituents that are considered most important in the analysis.

Other constituents and measurements can be determined in any order. Time is important, however, and the analysis should be carried to completion without undue delay. It has been observed that, because of changes in chemical composition of the water, the validity of the analytical statement often decreases as the time consumed in the analysis increases. All required determinations should be made within 1 week after the sample is opened.

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 manual.

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 a chemically balanced system, the sum of the equivalents of cations in solution equals the sum of the anions. If all of the predominant ions have been determined, the milliequivalents per liter (me/l) should be in reasonable 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 pH of the sample,

$$\mathrm{pH}=\log\frac{1}{a_{\mathrm{H}^{+1}}}$$

or

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

where

a=activity, and

where the base of hydrogen is the effective concentration (activity) of hydrogen ions. The calculated pH of standard solutions of sulfuric acid has been compared with determined pH, and the agreement is good up to 2.0 mg/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 possible error is introduced in converting pH to hydrogen-ion concentration because of the effect of other ions on the activity of the hydrogen ion. pH meters determine the activity of the hydrogen ion as distinguished from concentration. The chemist is referred to the works of Kolthoff and Laitinen (1941) and Bates (1964) for a full discussion of the subject.

pH	*me/l* H^{+1}
4.25–3.85	0.1
3.80–3.60	.2
3.55–3.50	.3
3.45–3.40	.4
3.35–3.30	.5
3.25–3.20	.6
3.15	.7
3.10	.8
3.05	.9
3.00	1.0
2.95	1.1
2.90	1.3
2.85	1.4
2.80	1.6
2.75	1.8
2.70	2.0
2.65	2.2
2.60	2.5
2.55	2.8
2.50	3.2

Multivalent ions present difficulties in the ionic balance unless the ionic states are differentiated by the analysis. Fortunately, these ions are present in only minor amounts in many waters and rarely influence the ionic balance appreciably. 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 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 1.

Table 1.—Orthophosphate mixtures as related to pH

pH	HPO_4 (*percent*)	H_2PO_4 (*percent*)
4.5	0.2	99.8
4.6	.2	99.8
4.7	.3	99.7
4.8	.4	99.6
4.9	.5	99.5
5.0	.6	99.4
5.1	.8	99.2
5.2	1.0	99.0
5.3	1.2	98.8
5.4	1.5	98.5
5.5	1.9	98.1
5.6	2.4	97.6
5.7	3.0	97.0
5.8	3.8	96.2
5.9	4.7	95.3
6.0	5.8	94.2
6.1	7.2	92.8
6.2	8.9	91.1
6.3	11.0	89.0
6.4	13.5	86.5
6.5	16.2	83.8
6.6	19.8	80.2
6.7	23.6	76.4
6.8	28.2	71,8
6.9	33.0	67.0
7.0	38.3	61.7
7.1	43.9	56.1
7.2	49.5	50.5
7.3	55.3	44.7
7.4	60.9	39.1
7.5	66.0	34.0
7.6	71.2	28.8
7.7	75.6	24.4
7.8	79.7	20.3
7.9	83.1	16.9
8.0	86.1	13.9
8.1	88.7	11.3
8.2	90.7	9.3
8.3	92.5	7.5
8.4	93.7	6.3
8.5	95.1	4.9
8.6	96.1	3.9
8.7	96.9	3.1
8.8	97.5	2.5
8.9	98.0	2.0
9.0	98.4	1.6
9.1	98.7	1.3
9.2	99.0	1.0
9.3	99.2	.8
9.4	99.4	.6
9.5	99.5	.5
9.6	99.6	.4
9.7	99.7	.3
9.8	99.7	.3
9.9	99.8	.2
10.0	99.8	.2

$$H_2PO_4^{-1}\rightarrow H^{+1}+HPO_4^{-2}$$

$$K_i=\frac{[H^{+1}]\,[HPO_4^{-2}]}{[H_2PO^{-2}]}$$

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

where

$K_i=6.2\times10^{-8}$.

Other forms of phosphorus cannot be differentiated in this manner, nor are suitable methods available for other multivalent ions. 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.

Dissociation also must be considered in balancing analyses. Many of the determinations, particularly those for the heavy metals, do not differentiate between dissociated and undissociated constituents. Constituents that hydrolyze to give undissociated products determined along with the ionized forms in the analysis cannot be included directly in the ionic balance. Published dissociation constants give some indication of the possible ionized concentration, but complete confidence cannot be placed in these values when considering complex solutions such as natural water.

The deviations from 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. With careful work and a comprehensive analysis of the sample, it is customary for the deviation between equivalents per million of cations and anions not to exceed 1 or 2 percent of the total concentration for analyses of waters with more than about 150 mg/l of dissolved solids. A deviation of as much as 3 percent may result from the accumulation of small unavoidable errors in the analysis of water containing about 100 mg/l of dissolved solids and of about 5 percent for waters with as little as 25 or 30 mg/l.

Chemical balance is only an indication of the gross validity of the analysis. Very large errors in the determination of minor constituents can go unnoticed; neither are compensating errors detected. Conclusions that can be drawn from deviations in anion and cation balance are usually negative. 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.

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 of the comprehensiveness of an analysis. Several important factors have a bearing on this comparison. First, the residue on evaporation might contain appreciable amounts of organic and some inorganic materials that are not determined in the analysis. Second, water of hydration may also be contained in the residue. Ignition loss is sometimes determined as a rough estimate of the water of hydration and combustible organic materials. The calculated dissolved solids is usually between the value obtained as residue on evaporation and the residue on evaporation minus the ignition loss. Third, volatile solids which are determined in the course of the analysis may be lost during evaporation. If volatile solids are lost, the residue on evaporation may be less than the calculated value. Fourth, the alkalinity determination is influenced by weak-acids residuals other than carbonate and bicarbonate. Phosphate, borate, and silicate, measured collectively as alkalinity and reported as carbonate and bicarbonate, may be redetermined individually in specific analyses. If so, the solids determined by calculation may be higher than by evaporation. Other factors such as the behavior of acid waters and iron compounds during evaporation also complicate the relation between residue on evaporation and the calculated dissolved solids.

Values reported for dissolved solids less than 1,000 mg/l are determined by evaporation of a filtered sample and weighing the residue which has been dried at 180°C. Values in excess of 1,000 mg/l are calculated from the determined constituents.

Specific conductance relation

For most natural waters of mixed type the specific conductance, in micromhos, multiplied by a factor of 0.65±0.1 approximates the residue on evaporation in milligrams per liter. This does not approach an exact relation because the conductance of a solution is dependent on the type and total quantity of ions in solution. More precise relations can be developed for specific water types. The factor of 0.65 is applicable only with comparatively dilute solutions and usually increases as the dissolved-salt content exceeds 2,000–3,000 mg/l. For waters that contain appreciable concentrations of free acid, caustic alkalinity, or sodium chloride, the factor may be much less than 0.65. The factor for some other specific types of water may be higher. Nonionized silica will also disturb the ratio of residue on evaporation to conductance. With similar limitations, the specific conductance divided by 100 approximates the milliequivalents per liter of anions or 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.

Rossum (1949) proposed a method for checking analyses that is based on a comparison of the specific conductance of dilute solutions with the summation of the added increments of conductance contributed by each determined ion in solution. This procedure is known as the diluted-conductance method. The sample is diluted with redistilled water until the conductance of the solution is between 90 and 120 micromhos. This observed conductance is recorded. The exact dilution ratio, *D*, is then computed as follows:

$$D=\frac{\begin{pmatrix}\text{volume of}\\ \text{sample}\end{pmatrix}+\begin{pmatrix}\text{volume of re-}\\ \text{distilled water}\end{pmatrix}}{\text{volume of sample}}$$

Next, the conductance of the redistilled water, K_w, is determined and the true diluted conductance, K_d, is calculated:

$$K_d = \text{observed diluted conductance} - (D-1)K_w.$$

The diluted conductance is then compared with the summation of the conductances of the determined ions.

Diluted-conductance factor for ions commonly found in water

[After Rossum, 1949]

Ion	Micromhos/ me/l at 25°C.	Micromhos/ mg/ at 25°C.
Bicarbonate	43.6	0.715
Calcium	52.0	2.60
Carbonate	84.6	2.82
Chloride	75.9	2.14
Magnesium	46.6	3.82
Nitrate	71.0	1.15
Potassium	72.0	1.84
Sodium	48.9	2.13
Sulfate	73.9	1.54

The American Public Health Association and others (1965) recommends that a recheck of the chemical analysis is advisable if the diluted conductance is more than 1.5 percent greater or 2 percent lower than the sum of the conductances of the determined ions. This degree of accuracy may be somewhat excessive for routine water analysis, unless the dilutions are made with extreme care.

The diluted-conductance method of checking is not applicable to waters whose initial conductances are less than 90 micromhos, or to samples whose pH values are not between 6 and 9, or to samples that contain appreciable quantities of ions not listed in the above table. The conductance contributed by hydrogen and hydroxyl ions is greater than that by other common ions.

A good check by the diluted-conductance method is conclusive proof that no major ion has been omitted from the determination.

Precision of analysis

The precision of procedures for water analysis cannot be measured in absolute terms of either concentration or percentage, nor is it desirable to do so for practicable purposes. Generally, more precise measurements are required when the concentration of a constituent is low than when the concentration is high. For example, in potable water supplies the difference between 1.0 and 1.5 mg/l of fluoride is very important, but the difference between 10.0 and 10.5 mg/l is not significant, although the absolute error is the same. Neither is percentage of error a good gage of the precision of the analysis. For example, an absolute error of ±1.0 mg/l is an error of 100 percent when the concentration of the constituent is only 1.0 mg/l.

Another factor that complicates the problem of designating precision of analysis is the inherent tendency of most analytical determinations to vary in accuracy throughout the concentration range of the constituent in a manner that is akin neither to absolute nor percentage quantities. The analytical procedure for each determined constituent includes a statement, where data are available, indicating the precision to be expected for that procedure. These statements were calculated from data obtained through "round-robin" analysis of test samples prepared and analyzed by Geological Survey laboratories. This testing program of standard reference samples is conducted on a continuing basis in accordance with procedures specified by the American Society for Testing and Materials (1966). These procedures attempt to provide analytical data for a given method in accordance with principles of statistical design, in order to determine the effect of the different sources of variance. Such sources include: apparatus, laboratory, operator, and level. Analysis of the number of replicate samples required for consideration of these variables produces data from which may be calculated the precision, or standard deviation, of the method. A convenient formula for this calculation is:

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

where

i = first analysis,

m = number of analyses,

X_i = individual values of analyses,

$\overline{X}$ = average value of analyses, and

S_t = standard deviation.

A statement of precision, determined in this manner, has been provided for each method in this manual where data were available.

Reporting of results

Categories of determined constituents

Chemical constituents are reported in three categories: (1) dissolved, (2) suspended, and (3) total (dissolved-plus-suspended).

Dissolved material is that which goes through a 0.45-μm membrane filter. Determinations of dissolved constituents are made on aliquots of a filtrate. Alternatively, determinations may be made on aliquots of an unfiltered sample, if it is known that the presence of suspended material has no effect on the determination.

Suspended material is that which is retained by a 0.45-μm membrane filter. Determinations of suspended constituents are made either by analyzing portions of the material collected on the filter disk or, more commonly, by difference, based on determinations of (1) dissolved and (2) total (dissolved-plus-suspended) concentrations of the constituent.

Total (dissolved-plus-suspended) material is the total amount present in the whole sample, regardless of its physical or chemical form. The specified treatment and analytical procedure define the material reported by the analysis.

To be completely explicit, the method of treatment and analysis should also be reported. However, when a widely recognized and accepted method is used, mention of the procedure may be omitted; for example, see "Nitrogen, Organic."

Significant figures for reporting results

The significant figures used by the Geological Survey in reporting the results of analysis 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 tables of analyses.

One of the commonly used methods, which applies only to the expression of the precision of a determination, is to include all certain digits 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. Possible confusion and misinterpretation is minimized if the tabulated analytical results represent the certainty of the reported results within reasonable limits. In analytical results published by the Survey, the last digit may not be absolutely accurate in all analyses, but it is a figure that can be used with a good degree of confidence in most applications of water-analysis data. Instructions for the number of significant figures to be used in reporting concentration of the determined constituent are given in each analytical procedure.

Chemical milliequivalents per liter are computed by multiplying the reported concentration of the individual constituents, in mg/l, by the reciprocal of their combining weights. The reciprocal factors of the more commonly determined constituents are given in table 2.

Table 2.—Factors for converting mg/l to me/l

[1961 atomic weights]

Ion	Sum of atomic weights	Multiply mg/l by	Ion	Sum of atomic weights	Multiply mg/l by
Al^{+3}	26.9815	0.11119	Li^{+1}	6.939	0.14411
Br^{-1}	79.909	.01251	Mg^{+2}	24.312	.08226
Ca^{+2}	40.08	.04990	Mn^{+2}	54.9380	.03640
Cl^{-1}	35.453	.02821	Mn^{+4}	54.9380	.07281
CO_3^{-3}	60.0094	.03333	Na^{+1}	22.9898	.04350
F^{-1}	18.9984	.05264	NO_3^{-1}	62.0049	.01613
Fe^{+2}	55.847	.03581	OH^{-1}	17.0074	.05880
Fe^{+3}	55.847	.05372	S^{-2}	32.064	.06238
H^{+1}	1.00797	.99209	SO_4^{-2}	96.062	.02082
HCO_3^{-1}	61.0173	.01639	Sr^{+2}	87.62	.02282
I^{-1}	126.9044	.00788	Zn^{+2}	65.37	.03060
K^{+1}	39.102	.02557			

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

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Part IV. Analytical procedures

Acidity

Acidity is a measure of the concentration of solutes (electrolytes) capable of reacting with hydroxyl ion, as in a neutralization titration. It is reported as the equivalent concentration of hydrogen ions in milligrams per liter. Alternatively, acidity may be reported as an equivalent amount of calcium carbonate; that is, the amount of calcium carbonate that would be required to exactly neutralize the sample.

Solutes contributing to acidity as measured by titration with a strong base include both strong and weak acids as well as certain metal ions which form stable hydroxy complexes. The latter substances may also form insoluble hydroxy-salts, hydroxides, or oxides, or be oxidized during the titration. At room temperature the rates of some of these reactions are slow compared to normal neutralization reactions, and their actual contribution to the measured acidity of a given sample may be difficult to determine.

Examples of some of the reactions which occur in the neutralization titration are:

Strong acids

$$H^{+1}+OH^{-1} \leftrightarrows H_2O$$

$$HSO_4^{-1}+OH^{-1} \leftrightarrows SO_4^{-2}+H_2O.$$

Dissolved gases

$$H_2S(aq)+OH^{-1} \leftrightarrows HS^{-1}+H_2O$$

$$CO_2(g)+OH^{-1} \leftrightarrows HCO_3^{-1}.$$

Metal ions

$$Fe^{+2}+OH^{-1} \leftrightarrows Fe(OH)^{+1}$$

$$Fe(OH)^{+1}+OH^{-1} \leftrightarrows Fe(OH)_2 \downarrow$$

$$Fe(OH)_2^{+1}+OH^{-1} \leftrightarrows Fe(OH)_3 \downarrow$$

$$Al^{+3}+OH^{-1} \leftrightarrows Al(OH)^{+2}.$$

Dissolved gases which form weak acids in aqueous solution may be lost from the sample during collection, handling, and storage of the sample prior to analysis, or even during the titration. Their loss, of course, represents an error in the determination.

Because of the differing nature of the several types of acid solutes, attempts are sometimes made to distinguish among them. Thus the contribution of free mineral acids and gases may be estimated by rapid titration at room temperature, under which conditions the contribution of the complex-forming metal ions is minimal. Alternatively, if the sample is boiled and cooled prior to titration, the acid-forming gases which are present will have been driven off, and the titration provides an estimate of the remaining acids. Boiling the sample prior to titration, however, also removes dissolved oxygen, usually an important factor in the oxidation of certain metal ions during the course of the titration—a factor which may be of considerable significance.

Finally, because titrations performed rapidly at room temperature do not allow completion of those reactions involving the formation of metal-hydroxy complexes, an estimate of the contribution of these materials can sometimes be made by first titrating rapidly at room temperature, and then heating the sample to just below boiling for a brief period. Heating increases the rates of the hydrolysis reactions, and a decrease in pH occurs during heating. The titration is then resumed on the cooled sample, and the overall titration becomes an indication of the concentration of all solutes reacting with strong base. The difference between the results of the two titrations, moreover, indicates the probable contribution of hydrolyzable metal ions.

From the foregoing, it is apparent that the acidity determination can encompass a complicated system of reactions involving a variety of solutes. In fact, such is more often the case than not. Only when the acidity is due primarily to strong acids, and the neutralization takes the form of a strong acid–strong base titration, is the determination straightforward. In such samples, there is a change of several pH units in the vicinity of the equivalence point, and the titration can be performed with full confidence.

When weak acids and hydrolyzable metals are present in significant amounts, the determination is neither simple nor readily predictable. The construction of a titration curve, by recording the sample pH after successive small measured additions of titrant, permits both a more reliable understanding of the reactions taking place during the neutralization and a more judicious selection of the proper equivalence point based on the observed inflection point of the curve. Very complicated systems may not produce titration curves with a readily distinguishable inflection point. Measurement of the acidity of such systems is highly uncertain, and attempts to assess the relative importance of the several types of acids may be impossible.

When a titration curve is not constructed, the titration is usually carried out to an endpoint pH of 8.3, corresponding to the pH at which carbonic acid is essentially completely converted to bicarbonate ions:

$$H_2CO_3+OH^{-1}\rightarrow H_2O+HCO_3^{-1}.$$

Titration to pH 8.3 represents complete neutralization of strong mineral acids plus essentially complete neutralization of all titratable weak acids.

The following procedure provides for the determination of acidity by direct titration at room temperature, but with heating at the end point to facilitate certain hydrolysis reactions. It is probably the most useful, simple method for indicating sample acidity.

Electrometric titration method

1. Summary of method

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. 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.

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 tends to expel 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, 2N*: Cover approximately 100 g NaOH with water until the surface coating is dissolved. Discard the supernatant liquid and immediately dissolve the remaining NaOH in approximately 1 liter of carbon-dioxide-free water. Store in a tightly capped polyethylene bottle.

5.2 *Sodium hydroxide* standard solution, 0.0248*N*, 1.00 ml$\approx$0.0250 mg H^{+1}: Dilute in 12 ml 2*N* NaOH with carbon-dioxide-free water to approximately 1 liter. Standardize the solution against primary standard potassium acid phthalate as follows: Lightly crush 3 g of the salt to a fineness of approximately 100 mesh and dry for at least 1 hr 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 to pH 8.6:

$$\text{Normality of NaOH} = \frac{\text{g } KHC_8H_4O_4 \text{ in 50.0 ml} \times 4.8964}{\text{ml NaOH}}$$

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 0.0248N NaOH (1.00 ml $\backsimeq$ 0.0250 mg H^{+1}) 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. Record the final volume of titrant used (ml_b).

7. Calculations

7.1 $$\text{Acidity, me/l} = \frac{\mathrm{ml}_b}{\mathrm{ml}_s} \times N_b \times 10^3.$$

7.2 Acidity, mg/l as H^{+1}

$$= \frac{\mathrm{ml}_b}{\mathrm{ml}^s} \times N_b \times 10^3 \times 1.008.$$

7.3 Acidity, mg/l as $CaCO_3$

$$= \frac{\mathrm{ml}_b}{\mathrm{ml}_s} \times N_b \times 10^3 \times 50.05$$

where

ml_b and ml_s = volumes of standard base and sample, respectively, and

N_b = Normality of standard base.

8. Report

Report acidity values in me/l or mg/l as H^{+1} as follows: Less than 10 me/l (mg/l), one decimal; 10 me/l (mg/l) and above, nearest whole number.

Report acidity values in mg/l as $CaCO_3$ as follows: Less than 1,000 mg/l, whole numbers; 1,000 mg/l and above, three significant figures.

9. Precision

Precision data are not available. However, the precision of the titration is generally much greater than the uncertainties involved in sampling and handling of the sample prior to analysis, and even of determining the appropriate end-point pH in the case of complex mixtures of weak acids.

Alkalinity

Alkalinity is the capacity of a water to react with hydrogen ions to pH 4.5. Alkalinity in water is caused primarily by bicarbonates, carbonates, and hydroxides. Their relative concentrations are a function of the temperature, pH, and concentration of other dissolved solids. The chemist is referred to the works of Barnes (1964), Langelier (1946), and Weber and Stumm (1963) for a discussion of the equilibria involved. Minor acid radicals such as borates, phosphates, and silicates also add to the alkalinity of the water.

Because the alkalinity of many waters is primarily a function of the carbonate, bicarbonate, and (or) hydroxide content, the alkalinity determination is normally taken as an indication of the concentration of these constituents. Such values are maximums and include other titrable weak-acid radicals when present. The effect of phosphate can be corrected for by utilizing the relations given in "Part III, Chemical Balance." No suitable methods for correcting for the other acid radicals are available.

Carbonates and bicarbonates are common to most waters because of the abundance of carbonate minerals in nature and because carbon dioxide, which helps dissolve them and other minerals, is readily available. Direct contribution to alkalinity by hydroxides is rare in nature, and their presence can usually be attributed to water treatment or to contamination.

The alkalinity, in milliequivalents per liter, in excess of the alkaline earths has a bearing on the suitability of a water for irrigation (Eaton, 1954). If this excess alkalinity, termed "residual sodium carbonate," exceeds 2.5 me/l the water is generally not suitable for irrigation; water containing 1.25 to 2.5 me/l is marginal, and that containing less than 1.25 me/l is probably safe (U.S. Salinity Laboratory Staff, 1954).

Electrometric titration method

1. Summary of method

Alkalinity is determined by titrating the water sample with a standard solution of strong acid. The end points of the titration are selected as the inflection points in the titration of Na_2CO_3 with H_2SO_4. The carbonate end point is taken as pH 8.3 and the bicarbonate as pH 4.5. The following reactions occur:

Titration to pH 8.3:

$$CO_3^{-2}+H^{+1}\rightarrow HCO_3^{-1}$$

Titration to pH 4.5:

$$HCO_3^{-1}\ (\text{from } CO_3^{-2})+H^{+1}\rightarrow H_2O+CO_2$$

$$HCO_3^{-1}\ (\text{natural})+H^{+1}\rightarrow H_2O+CO_2$$

The presence of hydroxide is indicated when the carbonate titrant volume exceeds the bicarbonate titrant volume.

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.

Selection of pH 4.5 as the titration end point is arbitrary, and corresponds to the true end-point pH only under ideal conditions. The error is not serious for most ordinary samples, however, since the slope of the titration curve in the vicinity of pH 4.5 is usually quite steep, and a small deviation of the true end-point pH from 4.5 corresponds to only a slight difference in titrant volume. When greater accuracy is needed, the titration end point is determined for each sample by adding the titrant in small increments in the vicinity of pH 4.5 and measuring the pH of the solution after each addition. The end point is then determined from either (a) a plot of pH versus titrant volume, where the end point is the pH corresponding to a change in slope of the curve, or (b) a plot of

$$\frac{\Delta\ \text{pH}}{\Delta\ \text{ml titrant}}$$

versus titrant volume, where the end point is that volume at which occurs the maximum rate of change of pH per volume of titrant added. The several factors involved in an accurate measurement of bicarbonate alkalinity, particularly under field conditions, have been summarized by Barnes (1964).

2. Application

The 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.

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, 1.00 ml $\widehat{=}$ 1.00 mg HCO_3^{-1}: Dry 1.0 g primary standard Na_2CO_3 at 150°–160°C for 2 hr. Cool in a desiccator and dissolve exactly 0.8686 g in carbon-dioxide-free water; dilute to 1,000 ml.

5.2 *Sulfuric acid* standard solution, $0.01639N$, 1.00 ml $\widehat{=}$ 1.00 mg HCO_3^{-1}: 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 (1.00 ml $\widehat{=}$ 1.00 mg HCO_3^{-1}) to pH 4.5. Adjust the concentration of the sulfuric acid standard solution to exactly $0.01639N$ 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.

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^{-1} (50.0 ml maximum) into a suitable beaker.

6.2 Insert beaker in titration assembly and record the pH.

6.3 Titrate immediately with $0.01639N$ H_2SO_4 and record the titrant volume at pH 8.3 and 4.5.

7. Calculations

7.1 Alkalinity as $CaCO_3$ in mg/l

$$= \frac{1{,}000}{\text{ml}_s} \times 0.82 \times \text{ml}_a.$$

7.2

$$\text{OH}^{-1} \text{ in mg/l} = \frac{1{,}000}{\text{ml}_s} \times [(\text{ml}_a \text{ to pH } 8.3) - (\text{ml}_a \text{ pH } 8.3 \text{ to } 4.5)] \times 0.2788.$$

7.3

$$\text{CO}_3^{-2} \text{ in mg/l} = \frac{1{,}000}{\text{ml}_s} \times [(\text{ml}_a \text{ to pH } 8.3) \times 0.9835] - (\text{mg/l OH}^{-1} \times 3.527).$$

7.4

$$\text{HCO}_3^{-1} \text{ in mg/l} = \frac{1{,}000}{\text{ml}_s} \times [(\text{ml}_a \text{ pH } 8.3 \text{ to } 4.5) - (\text{ml}_a \text{ to pH } 8.3)],$$

where

ml_a and ml_s = volumes of standard acid and sample, respectively.

8. Report

Report alkalinity concentrations as follows: Less than 1,000 mg/l, whole numbers; 1,000 mg/l and above, three significant figures.

9. Precision

The determination of the bicarbonate alkalinity of a test sample by 25 laboratories using this method resulted in a mean value of 34.69 mg/l and a standard deviation of 1.17 mg/l. The precision of the determinations of carbonate and hydroxyl ions may be expected to be comparable.

References

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Aluminum

Aluminum forms complex alumino silicates, and combined with other metals these alumino silicates are among the most abundant minerals in the earth's crust. Yet aluminum is usually only a minor constituent in water. It is highly resistant to removal by solution during weathering, and during the process of rock decomposition remains behind persistently in the form of clay minerals in the soil and anhydrous minerals in shale and similar sediments. Aluminum is amphoteric and can exist as either the natural cation or the aluminate anion. However, the normal buffer system in natural water tends to maintain the pH between 5 and 9, in which range neither unassociated aluminum nor aluminate ions can exist at equilibrium in concentrations greater than a few tenths of a milligram per liter. Colloidal aluminum species which are not determined by the usual analytical procedures may be present in some waters in this pH range. The chemical behavior of aluminum in dilute solutions has been described by Hem and Roberson (1967), and some factors controlling its solubility are discussed by Roberson and Hem (1969). Aluminum ions form strong complexes with organic matter, sulfate, and fluoride, a fact which tends to stabilize high concentrations of aluminum in some waters.

No evidence has been found that aluminum is harmful to human beings (California State Water Quality Control Board, 1963). It is of little importance in irrigation waters, although very high concentrations could be toxic to some crops. Aluminum compounds in water in concentrations as low as 0.05 mg/l may cause trouble in certain industries such as laundries. The recommended maximum permissible concentration of Al in water used for rayon manufacturing is 0.25 mg/l.

Ferron-orthophenanthroline method

1. 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.

2. Application

This method may be applied to any water containing more than 0.05 mg of aluminum per liter. Smaller concentrations are detectable, but are not considered accurately measureable.

3. Interferences

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.

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 1.00 mg of aluminum per liter:

Constituent	*Milligrams per liter*	*Al found (mg/l)*
Mg	40	1.04
Mg	80	1.09

Constituent	*Milligrams per liter*	*Al found (mg/l)*
Zn	5	1.05
Mn	5	1.17
Mn	10	1.28
F	1	.94
F	2	.90
F	5	.80

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 and turbidity interfere in the aluminum determination, and a correction is usually required.

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.

In the analytical sequence, manganese and fluoride should be determined before aluminum so that the necessary corrections can be applied. These corrections are derived from the data in the above table of interferences. They apply with accuracy only at the 1-mg-aluminum level. However, because concentrations of interfering ions are generally not greatly in excess of aluminum in most waters, the indicated correction is 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.

Additional information on the determination is given by Davenport (1949) and by Smith and Richter (1944).

4. Apparatus

Spectrophotometer, for use at 370 and 520 nm (nanometers), Beckman Model B, or equivalent.

With the Beckman instrument the following operating conditions are recommended:

	Al	Fe
Wavelength	370 nm	520 nm.
Cells	40 mm (millimeters)	40 mm.
Phototube	Blue-sensitive	Blue-sensitive.
Filter	Blue	None.
Blank	Demineralized water, plus reagents.	Demineralized water plus reagents.
Initial sensitivity setting	2	2.
Slit width (approximate)	1.0 mm	0.1 mm.

The following absorbances have been observed for iron and aluminum:

(mg) Fe	Absorbance (370 nm)	Absorbance (520 nm)	Al (mg)	Absorbance (370 nm)
0.025	0.07	0.51	0.025	0.64
.050	.125	1.02	.050	1.14
.075	.185	1.53	.075	1.60
.100	.25	1.95		
.125	.305	2.33		

5. Reagents

5.1 *Aluminum* standard solution I, 1.00 ml=0.100 mg Al^{+3}: Dissolve 1.758 g $AlK(SO_4)_2 \cdot 12H_2O$ in demineralized water. Add 0.5 ml $CHCl_3$ and dilute to 1,000 ml with demineralized water.

5.2 *Aluminum* standard solution II, 1.00 ml=0.010 mg Al^{+3}: Dilute 25.0 ml aluminum standard solution I to 250 ml with demineralized water.

5.3. *Ferron-orthophenanthroline* reagent: Add 1.0 g ferron and 1.0 g orthophenanthroline to 1 liter demineralized water. Stir for several hours until the maximum solution is obtained. The ferron will not always dissolve completely. Allow any solids to settle out and decant the clear supernatant 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 liter with demineralized water. (CAUTION: Beryllium compounds are toxic and should be handled with care.)

5.5 *Iron* standard solution I, 1.00 ml= 0.400 mg 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= 0.004 mg Fe: Dilute 10.00 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: Dissolve 350 g anhydrous $NaC_2H_3O_2$ in demineralized water and dilute to 1 liter.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet a volume of sample containing less than 0.075 mg Al^{+3} and 0.10 mg 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 volumes to 25.0 ml.

6.3 Add 2 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 is prolonged until all iron is in solution (overnight standing is a good practice).

6.4 Add 5.00 ml ferron-orthophenanthroline reagent and stir.

6.5 Add 2 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 as directed in "Part II, Instrumental Techniques."

7. Calculations

7.1 Determine the mg Fe in the sample from a plot of absorbances of standards at 520 nm.

7.2 Fe in mg/l$=\frac{1,000}{\text{ml sample}}\times$mg Fe in sample.

7.3 Determine the apparent mg Al^{+3} in the sample from a plot of absorbances of standards at 370 nm.

7.4 Apparent Al^{+3} in mg/l$=\frac{1,000}{\text{ml sample}}$ $\times$apparent mg Al^{+3} in sample.

7.5 Al^{+3} in mg/l=apparent mg/l Al^{+3} $-0.12\times$mg/l Fe$-0.04\times$mg/l Mn$+0.05$ mg/l F^{-1}.

8. Report

Report Al concentrations as follows: Less than 1,000 μg/l, one significant figure; 1,000 μg/l and above, two significant figures.

9. Precision

A test sample containing Al was analyzed by 12 laboratories with a mean of 0.54 mg/l and a standard deviation of 0.06 mg/l.

References

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Arsenic

Arsenic compounds are present naturally in some waters, but the occurrence of quantities detrimental to health is rare. Weed killers, insecticides, and many industrial effluents contain arsenic and are potential sources of water pollution. The U.S. Public Health Service (1962) states that the concentration of arsenic in drinking water on carriers subject to Federal quarantine regulations should not exceed 0.01 mg/l, and concentrations in excess of 0.05 mg/l are grounds for rejection of the supply. The lethal dose for animals is believed to be about 20 mg per animal pound (Miller and

Byers, 1935). Concentrations of 2–4 mg of arsenic per liter are reported not to interfere with the self-purification of streams (Rudolfs and others, 1944), but concentrations in excess of 15 mg/l may be harmful to some fish.

Silver diethyldithiocarbamate method

1. Summary of method

Inorganic arsenic compounds are reduced to arsine by zinc in an acid medium. The resulting mixture of gases is passed through a scrubber containing glass wool impregnated with lead acetate solution and into an absorbing tube containing silver diethyldithiocarbamate dissolved in pyridine. Arsine reacts with silver diethyldithiocarbamate to form a soluble red substance having maximum absorbance at about 535 nm. The absorbance of the solution is measured spectrophotometrically, and arsenic is determined by reference to an analytical curve prepared from standards.

2. Application

The method may be used to analyze samples containing from 0.02 to 1.0 mg of arsenic per liter. Water samples containing more or less arsenic must first be either diluted or concentrated by evaporation.

3. Interferences

Ordinarily, ground- and surface-water samples are relatively free of interferences. Occasional samples might contain hydrogen sulfide; however, commonly encountered quantities are effectively removed by the 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 that passes into the absorber and causes high results.

The blank and standards fade slowly on standing, but not enough to influence results significantly during the first 20 min.

Additional information on the determination is given by Stratton and Whitehead (1962).

4. Apparatus

4.1 *Arsine generator,* scrubber, and absorber (fig. 10), Fisher Scientific Co. No. 1–405, or equivalent.

4.2 *Spectrophotometer,* Beckman Model B, or equivalent.

With this instrument the following oper-

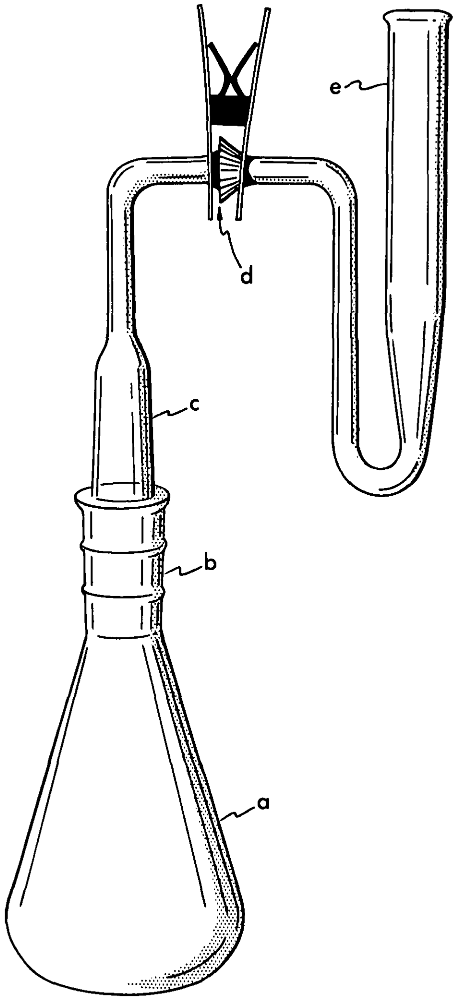

Figure 10.—Arsine generator, scrubber, and absorber (Fisher Scientific Co. No. 1–405, or equivalent). (a) Generator, 125 ml erlenmeyer flask. (b) Standard taper neck. (c) Scrubber, lead acetate on glass wool. (d) Ground glass ball-and-socket joint. (e) Absorber, contains silver diethyldithiocarbamate solution.

ating conditions have been found satisfactory:

Wavelength	535 nm.
Cells	10 mm.
Phototube	Blue-sensitive.
Initial sensitivity setting	2.
Slit width (approximate)	0.02 mm.

Under these conditions the following absorbances have been observed:

As (μg)	*Absorbance*
1.0	0.065
5.0	.340
10	.680

5. Reagents

5.1 *Arsenic* standard solution I, 1.00 ml =1.00 mg As: Dissolve 1.320 g As_2O_3, dried at least 1 hr at 110°C, in 10 ml of 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 ml with demineralized water.

5.3 *Arsenic* standard solution III, 1.00 ml=1.00 μg As: Dilute 10.0 ml arsenic standard solution II to 100 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: Dissolve 10 g $Pb(C_2H_3O_2)_2{\cdot}3H_2O$ in 100 ml demineraized water. Keep tightly stoppered.

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

5.7 *Silver diethyldithiocarbamate* solution: Dissolve 1 g $AgSCSN(C_2H_5)_2$ in 200 ml of pyridine. This solution is stable when stored in an amber bottle.

5.8 *Stannous chloride* solution: Dissolve 40 g of 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.

5.9 *Zinc:* Use granular zinc, about 20 mesh, with arsenic content not greater than 1×10^{-6} percent.

6. Procedure

Clean apparatus with nitric acid before beginning the analysis.

6.1 Pipet a volume of sample containing less than 20 μg As (25.0 ml maximum) into a generating flask and dilute to 25 ml. If concentrating the samples seems desirable, acidify an appropriate volume, usually 100 or 200 ml, with HCl and evaporate to approximately 25 ml.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to approximately 25 ml with demineralized water.

6.3 To each flask add successively, with thorough mixing after each addition, 5 ml concentrated HCl, 2 ml KI solution, and 8 drops $SnCl_2$ solution. Allow about 15 min for reduction of the arsenic to the tervalent state.

6.4 Place in each scrubber a plug of 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 of silver diethyldithiocarbamate–pyridine solution to each absorber. Add glass beads to the absorbers until the liquid just covers them.

6.5 Disconnect each generator, add 3 g zinc, and reconnect immediately.

6.6 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 absorbance of the standards and samples against the blank without unnecessary delay, as the color developed is not permanent.

7. Calculations

7.1 Determine the μg of As in the sample from a plot of absorbances of standards.

7.2 $\text{As in mg/l}=\frac{\mu g\text{ As in sample}}{\text{ml sample}}.$

8. Report

Report As concentrations as follows: Less than 100 μg/l, nearest 10 μg/l; 100 μg/l and above, two significant figures.

9. Precision

A test sample was analyzed by seven laboratories using this method, resulting in a mean value of 0.038 mg/l and a standard deviation of 0.018 mg/l.

References

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Barium

Naturally occurring barium ores contain barium carbonate and barium sulfate, neither of which is appreciably soluble in water (California State Water Quality Control Board, 1963). Since most natural surface and ground waters contain appreciable amounts of carbonate and (or) sulfate ions, barium is not usually found in such waters in readily measurable concentrations. Although barium ions have been detected in some springs and in effluents from areas where barium-containing ores are mined, its presence in water is generally limited to certain types of brines and industrial wastes and to normal waters of extremely low sulfate content.

Although evidence exists for high, acute toxicity from ingested soluble barium salts, no study appears to have been made of the amounts of barium that may be tolerated in drinking water. Because of the seriousness of its toxic effects, however, the U.S. Public Health Service (1962) considers an excess of 1.0 mg/l as grounds for rejection of a water supply.

Gravimetric method

1. Summary of method

Barium is precipitated from an acidified sample as the sulfate, then ignited and weighed (Kolthoff and Sandell, 1952).

2. Application

The gravimetric method is recommended for water whose barium content is greater than 10 mg/l and for brines and industrial wastes when the complexometric method fails. When the barium concentration of the sample is less than 10 mg/l, the quantity of barium sulfate precipitate is so small that results obtained by the gravimetric method may be in appreciable error.

3. Interferences

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.

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*: Mix 50 ml concentrated H_2SO_4 (sp gr 1.84) with water and dilute to 1 liter.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Dilute or concentrate the filtrate from a gravimetric calcium determination to a convenient volume. Pipet an aliquot containing at least 1 mg Ba^{+2} into a porcelain casserole.

6.2 Evaporate the aliquot to dryness and decompose the ammonium salts by gentle heating over an open flame.

6.3 Take up the residue with hot water and add 5–10 drops concentrated HCl.

6.4 Filter off any insoluble material through Whatman No. 42 paper and wash three times with hot 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 1*M* 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 water until a sample of the filtrate develops no turbidity with $AgNO_3$.

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 hr.

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 water and dilute to 100 ml. Digest for 1 hr on the steam bath, filter and wash with a little hot water, ignite, and weigh (Hillebrand and Lundell, 1929).

7. Calculations

$$Ba^{+2} \text{ in mg/l} = \frac{1{,}000}{\text{ml sample}} \times \text{mg } BaSO_4 \times 0.5884.$$

8. Report

Report Ba concentrations as follows: Less than 1,000 μg/l, nearest 100 μg/l; 1,000 μg/l and above, two significant figures.

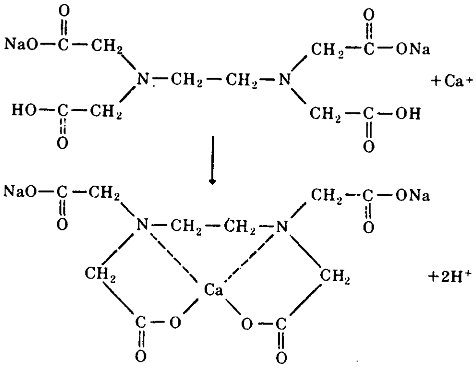
9. Precision

Precision data for this determination are not available. However, with care, it may reasonably be expected that the results can be reproduced to within 0.25 mg.

Complexometric method

1. Summary of method

Barium is determined by the difference between the titrant volume of Na_2EDTA (disodium dihydrogen ethylenediamine tetraacetate) required by an untreated sample and a sample from which barium has been precipitated as barium sulfate. Na_2EDTA forms a slightly ionized colorless stable complex with the alkaline earths. A solution of Eriochrome Black T dye 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_2-EDTA complex. Hence by using Eriochrome Black T as an indicator, the alkaline earths can be titrated with Na_2EDTA. For example, with calcium:



Barium titrates approximately stoichiometrically with calcium. The optimum pH for the reaction is 10.4 or higher.

2. Application

The complexometric method is applicable to most natural and treated waters whose barium content ranges from 0 to 10 mg/l. The method fails conspicuously at times with acid or polluted waters that contain excessive amounts of heavy metals.

3. Interferences

The determination is not strictly quantitative because coprecipitation errors are involved in the precipitation of barium, especially in the presence of strontium. Interferences of heavy metals with the Na_2-EDTA hardness titration are not significant to the barium determination because their net effect may be assumed to be identical in both samples. Interference of heavy metals with detection of the end point, however, may cause an error in the determination of barium unless this interference is removed. Precision is improved if the end point is compared with a color blank of dilution water plus reagents.

4. Apparatus

Visual titration assembly: Some analysts prefer to use conventional lighting and hand stirring. Others have reported better results by using a visual titration assembly consisting of a motor-driven or magnetic 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 $\simeq$1.00 mg $CaCO_3$: Suspend 1.000 g $CaCO_3$, dried at 180°C for 1 hr before weighing, in approximately 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: Dissolve 0.40 g Eriochrome Black T in 100 ml demineralized water and dilute to 1 liter with 95-percent ethanol. This indicator is stable for at least 2 months. The Eastman Kodak Co. reagent product has been found to be satisfactory.

5.4 *Hydroxylamine hydrochloride* solution: Dissolve 30 g $NH_2OH{\cdot}HCl$ in demineralized water and dilute to 1 liter.

5.5 *Sodium cyanide* solution (CAUTION: NaCN is a deadly poison, and the reagent solution must be so marked): Dissolve 2.5 g NaCN in demineralized water and dilute to 100 ml.

5.6 Na_2*EDTA* standard solution, 1.00 ml$\simeq$1.00 mg $CaCO_3$: Dissolve 3.720 g Na_2-EDTA, which has been dried overnight in an H_2SO_4 desiccator, in demineralized water and dilute to 1,000 ml. Check the titer of the reagent by titrating 25.00 ml $CaCl_2$ standard solution as described in the procedure for sample analysis. This Na_2EDTA solution is identical to that used in the hardness determination.

5.7 *Sodium sulfate* solution: Dissolve 10 g Na_2SO_4 in demineralized water and dilute to 100 ml.

5.8 *Sulfuric acid,* 1*M*: Mix 5 ml concentrated H_2SO_4 (sp gr 1.84) with demineralized water and dilute to 100 ml.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet a volume of sample containing less than 0.5 mg Ba^{+2} (50.00 ml maximum) into a 150-ml beaker, and adjust the volume to approximately 50 ml.

6.2 Insert the beaker in the titration assembly and start stirrer.

6.3 Add 1 ml $NH_2OH{\cdot}HCl$ solution.

6.4 Add 1 ml NH_4OH (when not tightly stoppered it tends to lose strength; weak NH_4OH will not buffer the solution to the necessary pH).

6.5 Add 2 ml NaCN solution (CAUTION: Deadly poison). The addition of

NaCN is necessary only when the sample contains heavy metals which decrease the sharpness of the end point.

6.6 Add 2.0 ml Eriochrome Black T indicator solution.

6.7 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 detection of the end point may be facilitated by comparison of the titration solution with a color blank prepared of demineralized water and the reagents.

6.8 Record the titrant volume (ml_t) to the nearest 0.05 ml.

6.9 Measure approximately 75 ml sample into a 150-ml beaker.

6.10 Add 1.5 ml 1*M* H_2SO_4.

6.11 Add 1.5 ml Na_2SO_4 solution.

6.12 Mix and allow the sample to stand several hours for the $BaSO_4$ to settle.

6.13 Pipet a volume of clear supernatant identical with that taken in step 6.1, and adjust the volume to approximately 50 ml.

6.14 Treat the sample as directed in steps 6.2–6.8, with the exception of adding 2 ml NH_4OH rather than 1 ml as in step 6.4. The additional NH_4OH is required to neutralize the acid added in step 6.10.

7. Calculations

$$\text{Ba}^{+2}\text{ in mg/l} = \frac{1{,}000}{\text{ml sample}} \times \left[\text{ml}_t - \left(\frac{\text{ml}_{\text{Ba}}}{0.96}\right)\right] \times 1.37,$$

where

ml_t = titrant volume for the first titration, and

ml_{Ba} = titrant volume after barium is removed.

8. Report

Report Ba 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 for this determination are not available. However, with care, it may reasonably be expected that the results can be reproduced to within 0.1 mg.

Atomic-absorption method—direct

1. Summary of method

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

2. Application

Samples containing at least 0.1 mg of barium per liter may be analyzed by this method. Samples containing more than 5.0 mg/l must be diluted, or less scale expansion used.

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, and to control this effect each standard and sample is adjusted to contain approximately 900 mg/l of sodium ion.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Visible.
Wavelength counter	276.8 (5536A).
Slit	3.
Scale expansion	10×.
Lamp current	25 ma (milliamperes).
Source (shielded hollow-cathode lamp)	Ba.
Response time control	1.
Burner	Nitrous oxide (Aztec part no. AB–50).
Nitrous oxide pressure	See instrument instruction manual.
Acetylene pressure	

With these operating conditions the following readings have been observed:

Barium concentration (mg/l)	*Scale reading*
0.1	1.7
.5	8.0
1.0	16.6
3.0	50.0
5.0	83.5

5. Reagents

5.1 *Barium* standard solution, 1.00 ml =0.100 mg 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 standard working solutions containing from 0 to 10.0 mg of barium per liter by diluting barium standard solution. To each standard working solution, add 1.0 ml sodium chloride solution for each 10 ml of standard.

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

6. Procedure

6.1 Filter the sample (0.45-μm membrane filter) when necessary to avoid clogging the atomizer-burner.

6.2 Add 1.0 ml sodium chloride solution to 10.0 ml sample and mix thoroughly.

6.3 Measure the scale reading of each sample and standard. Repeat, and average the two values.

7. Calculations

Determine the mg/l Ba in the sample from a plot of scale readings of standards. Because a scale expansion of 10× is used, scale readings need not be converted to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Ba concentrations as follows: Less than 100 μg/l, nearest 10 μg/l; 100 μg/l and above, two significant figures.

9. Precision

No precision data are available for this method.

References

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3–A, p. 142.

Hillebrand, W. F., and Lundell, G. E. F., 1929, Applied inorganic analysis: New York, John Wiley & Sons, Inc., 929 p.

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis [3d ed.]: New York, Macmillan Co., 759 p.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 8.

Beryllium

Beryllium is comparatively rare in the earth's crust, being only slightly more abundant than arsenic. It is found mainly in the mineral beryl, or beryllium aluminosilicate, $Be_3Al_2Si_6O_{18}$. Although beryllium chloride and nitrate are very soluble in water, the carbonate and hydroxide are practically insoluble. Therefore, beryllium is not a common constituent of natural waters. Although there is at present considerable disagreement regarding the toxicity of beryllium salts to human life, their toxicity to animals has been demonstrated in the laboratory (California State Water Quality Control Board, 1963). Elemental beryllium has been found responsible for pulmonary ailments of workers exposed to beryllium dusts. No limit for beryllium in interstate water supplies has been established by the U.S. Public Health Service.

Atomic-absorption method—direct

1. Summary of method

Beryllium is determined by atomic-absorption spectrophotometry. Calcium chloride is added to control ionization of beryllium in the flame.

2. Application

Samples containing at least 10 μg of beryllium per liter may be analyzed by this method. Samples containing more than 200 μg/l must be diluted or less scale expansion used.

3. Interferences

Beryllium is slightly ionized in the nitrous oxide–acetylene flame, and to control this effect each standard and sample is adjusted to contain approximately 900 mg/l of calcium ion. Bicarbonate ion interferes; however, its effect is eliminated if the samples are acidified with nitric acid to pH 1.5.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	235.2 (2352A).
Slit	5.
Scale expansion	10×.
Lamp current	30 ma.
Source (shielded hollow-cathode lamp)	Be.
Response time control	2.
Burner	Nitrous oxide (Aztec part no. AB–50).
Nitrous oxide pressure	See instrument instruction manual.
Acetylene pressure	

With these operating conditions the following readings have been observed:

Beryllium concentration (*μg/l*)	*Scale reading*
10	3.1
25	8.1
50	16.5
100	32.6
200	64.0

5. Reagents

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 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 standard solutions containing from 0 to 200 μg of beryllium per liter by diluting beryllium standard solution II. To each standard working solution, add 1.0 ml calcium chloride solution for each 10.0 ml of standard.

5.4 *Calcium chloride* solution: Suspend 25 g $CaCO_3$ in demineralized water and dissolve with a minimum of dilute HCl. Dilute to 1 liter with demineralized water.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Filter the sample (0.45-μm membrane filter) when necessary to avoid clogging the atomizer-burner.

6.2 Add 1.0 ml calcium chloride solution to 10.0 ml sample and mix thoroughly.

6.3 Aspirate each sample, blank, and standard and record the scale readings observed. Repeat, and average the two values.

7. Calculations

Determine the μg/l Be in the sample from a plot of scale readings of standards. Because a scale expansion of 10× is used, scale readings need not be converted to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Be concentrations of less than 1,000 μg/l to the nearest 10 μg/l.

9. Precision

No precision data are available.

Reference

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3–A, p. 145.

Boron

The boron content in most surface waters seldom exceeds 1 mg/l, but some ground waters, particularly those affected by igneous rocks, may contain appreciably more. The form or forms in which boron exists in natural waters is not known with certainty and may not be uniform for all waters; hence, the boron content is reported as elemental boron.

In normal concentrations, boron in drinking water is not regarded as a hazard to humans, but the boron content of irrigation water is highly important. Although boron is an essential plant nutrient, the presence of as little as 1 mg/l has been known to injure citrus trees and walnut and bean crops, while waters containing more than 2 mg/l will in time cause trouble with many common crops (U.S. Salinity Laboratory Staff, 1954).

Dianthrimide method

1. 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 nature of the vessel in which the reaction occurs, the temperature and duration of heating, and the concentration of reagent and of boron. Maximum color development is achieved after the reaction has proceeded for 3 hr at 90°C.

2. Application

The dianthrimide method is suitable for most natural waters except those containing high concentrations of oxidizing or reducing materials and dissolved organic matter. However, it is not affected by buffering solutions or high concentrations of total salts. Water containing between 0.02 and 1.0 mg of boron per liter may be analyzed by this method; higher concentrations require dilution.

3. Interferences

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 1–2 hr, 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. In cleaning glassware avoid the use of chromic-sulfuric acid.

Some boric acid is probably volatilized during the 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 *Stoppers* to fit absorption cells: Teflon or polyethylene are satisfactory, rubber can be used with caution, glass-stoppered cells are preferable.

4.3 *Spectrophotometer,* Beckman Model B, or equivalent.

With this instrument the following operating conditions have been used:

Wavelength	620 nm.
Cells	23 mm or 25 mm.
Phototube	Blue-sensitive.
Blank	Dilution water carried through the procedure with the sample.
Initial sensitivity setting	2.
Slit width (approximate)	0.6 mm.

With these operating conditions the following absorbances have been observed:

Boron (mg)	*Absorbance*
0.001	0.26
.002	.52
.005	1.30

5. Reagents

5.1 *Boron* standard solution I, 1.00 ml=0.100 mg B: Dissolve 10 g $Na_2B_4O_7\cdot 10H_2O$ in 50 ml demineralized water at 50°–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 0.8819 g in demineralized water and dilute to 1,000 ml. Store in plastic bottle.

5.2 *Boron* standard solution II, 1.00 ml =0.001 mg 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* solution I: 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.

5.4 *1,1′-dianthrimide* solution II: 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.

5.5 *Sulfuric acid,* concentrated (sp gr 1.84).

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet a volume of sample containing less than 0.005 mg B (5.00 ml maximum) into the absorption cell, and adjust volume to 5.0 ml.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust volumes to 5.0 ml.

6.3 Add 1.0 ml concentrated H_2SO_4 and mix by swirling the contents of the cell.

6.4 Evaporate overnight 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 by swirling.

6.6 Incubate for 3 hr at 90°C.

6.7 Cool and immediately add 10.0 ml concentrated H_2SO_4. Mix thoroughly but carefully with a stirring rod. The contents must not be spattered on the upper walls of the cell. Stopper the cells, but do not let the stopper come in contact with the acid contents.

6.8 Remove all traces of acid, reagent, and fingerprints from the exterior surface of the cell, and determine the absorbance of the sample and standards against the blank.

7. Calculations

7.1 Determine the mg B in the sample from a plot of absorbances of standards.

7.2 $$\text{B in mg/l} = \frac{1{,}000}{\text{ml sample}} \times \text{mg B in sample.}$$

8. Report

Report B concentrations as follows: Less than 100 μg/l, nearest 10 μg/l; 100 μg/l and above, two significant figures.

9. Precision

Analysis of a test sample by four laboratories using this method resulted in a mean value of 0.530 mg/l and a standard deviation of 0.064 mg/l.

Carmine method

1. Summary of method

In acid solution, boron forms a colored complex with carmine. The color change is from red to blue. Maximum color development requires approximately 1 hr, 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 hr.

Additional information on the principle of the determination is given by Hatcher and Wilcox (1950).

2. Application

The method finds maximum utility for waters whose boron content exceeds 1 mg/l or when the precision required does not exceed 0.1 mg/l. The optimum range for the procedure on undiluted or unconcentrated samples is 0.5–10 mg/l of boron. Samples containing less than 0.5 mg/l must first be concentrated by evaporation in strong alkaline solution to prevent the loss of volatile boric acid.

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 0.5 mg/l of boron the determined value may be about 20 percent high in the presence of

5 or 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 *Spectrophotometer,* Beckman Model B, or equivalent.

With this instrument the following operating conditions have been used:

Wavelength	600 nm.
Phototube	Blue-sensitive.
Cells	25 mm.
Initial sensitivity setting	2.
Slit width	0.1 mm.

With these operating conditions the following values have been observed:

Boron (mg)	*Absorbance*
0.005	0.24
.010	.48
.015	.70
.020	.93

5. Reagents

5.1 *Boron* standard solution I, 1.00 ml=0.100 mg B: Dissolve approximately 10 g $Na_2B_4O_7 \cdot 10H_2O$ in demineralized water at 50°–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 0.8813 g in demineralized water and dilute to 1,000 ml. Store in plastic bottle.

5.2 *Boron* standard solution II, 1.00 ml =0.010 mg B: Dilute 100.0 ml boron standard solution I to 1,000 ml with demineralized water. Store in plastic bottle.

5.3 *Carmine* solution: Suspend 0.50 g carmine in 1 liter concentrated H_2SO_4 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 liter.

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

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet a volume of sample containing between 0.001 and 0.020 mg B (2.00 ml maximum) into a 150-ml flask. If the sample contains less than 0.5 mg/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.

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 volumes to 2.0 ml.

6.3 Add 2 drops concentrated HCl, 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 approximately 1 hr.

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 mg B in the sample from a plot of absorbances of standards.

7.2 $$\text{B in mg/l} = \frac{1{,}000}{\text{ml sample}} \times \text{mg B in sample.}$$

8. Report

Report B concentrations as follows: Less than 100 μg/l, nearest 10 μg/l; 100 μg/l and above, two significant figures.

9. Precision

Analysis of a test sample by five laboratories using this method resulted in a mean value of 0.522 mg/l and a standard deviation of 0.078 mg/l.

References

Ellis, G. H., Zook, E. G., and Baudisch, Oskar, 1949, Colorimetric determination of boron using 1,1′-dianthrimide: Anal. Chemistry, v. 21, p. 1345.

Hatcher, J. T., and Wilcox, L. V., 1950, Colorimetric determination of boron using carmine: Anal. Chemistry, v. 22, p. 567.

Rainwater, F. H., 1959, Determination of boron with 1,1′-dianthrimide: Am. Water Works Assoc. Jour., v. 51, p. 1046.

U.S. Salinity Laboratory Staff, 1954, Diagnosis and improvement of saline and alkali soils: U.S. Dept. Agriculture, Agriculture Handb. 60, p. 81.

Bromide

Bromide is a minor constituent in the earth's crust and is normally present in natural waters in only minute quantities. Measurable amounts may be found in some streams that receive industrial wastes, and some natural brines contain rather high concentrations.

Hypochlorite oxidation method

1. Summary of method

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 Sandell, 1952).

$$3OCl^{-1}+Br^{-1}\rightarrow BrO_3^{-1}+3Cl^{-1}$$
$$3OCl^{-1}+I^{-1}\rightarrow IO_3^{-1}+3Cl^{-1}.$$

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 using starch as the indicator.

$$I_2+2S_2O_3^{-2}\rightarrow S_4O_6^{-2}+2I^{-1}.$$

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.

2. Application

The oxidation method is generally applicable to natural waters containing at least 1.0 mg of bromide per liter. Highly concentrated brines may require dilution.

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.

4.2 *Iodine flasks,* 250-ml.

5. Reagents

5.1 *Acetic acid,* 2.2*M*: Mix 125 ml glacial $HC_2H_3O_2$ (sp gr 1.049) with water and dilute to 1 liter.

5.2 *Bromine water,* saturated: Add to approximately 250 ml of 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 water and dilute to 100 ml.

5.6 *Methyl red indicator* solution: Dissolve 0.01 g water-soluble methyl red in 100 ml water.

5.7 *Potassium fluoride,* crystals, $KF\cdot 2H_2O$.

5.8 *Potassium hypochlorite* solution: Dissolve 6.2 g KOH in 100 ml water, then saturate the solution with bromine-free Cl_2 while continually cooling and stirring. Store in 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 water, acidifying with 1 or 2 drops concentrated H_2SO_4, and adding 2–3 ml starch indicator. Immediate appearance of a blue color indicates the presence of IO_3^{-1}; slow color formation is due to atmospheric oxidation.

5.10 *Sodium acetate* solution: Dissolve 273 g $NaC_2H_3O_2 \cdot 3H_2O$ in water and dilute to 1 liter.

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 water, acidifying with 1 or 2 drops concentrated H_2SO_4 (sp gr 1.84), and adding 2–3 ml starch solution. Immediate appearance of 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: Dissolve 50 g $NaCHO_2$ in hot water and dilute to 100 ml. Prepare fresh daily.

5.13 *Sodium molybdate* solution: Dissolve 1.0 g $Na_2MoO_4 \cdot 2H_2O$ in 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 water, add 1 g Na_2CO_3, and dilute to 1,000 ml.

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 water and standardize against KIO_3 as follows: Dry approximately 0.5 g KIO_3 for 2 hr at 180°C. Dissolve 0.3567 g in water and dilute to 1,000 ml. Pipet 25.00 ml of the KIO_3 into a 250-ml iodine flask, then add successively 75 ml 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 $Na_2S_2O_3$ using 2 ml starch indicator as the end point is approached (light-straw color).

5.16 *Sulfuric acid,* 3.6*M*: Mix 200 ml concentrated H_2SO_4 (sp gr 1.84) with water and dilute to 1 liter.

6. Procedure

6.1 Remove soluble iron, manganese, and organic matter by adding a slight excess of CaO to approximately 400 ml of sample, shake, let stand about 1 hr, and filter through dry 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 maximum) into a 250-ml iodine flask, and adjust the volume to approximately 100 ml.

6.3 Prepare a blank of approximately 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 approximately 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 $NaCHO_2$ solution, taking precautions 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 approximately 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* $Na_2S_2O_3$, adding 2–3 ml starch indicator 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 maximum) into a 250-ml iodine flask, and adjust the volume to approximately 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 $3.6M$ H_2SO_4.

6.15 Add 15.0 ml $NaC_2H_3O_2$ solution, 5.0 ml $2.2M$ $HC_2H_3O_2$, 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 $NaCHO_2$ solution 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 through the mouth of the flask. If any iron precipitates at this point, add 0.5 g $KF{\cdot}2H_2O$.

6.18 Add approximately 1 g KI, 10 ml $3.6M$ H_2SO_4, and let stand 5 min in the dark.

6.19 Titrate the liberated I_2 with $0.010N$ $Na_2S_2O_3$, adding 2–3 ml starch indicator as the end point is approached. Disregard any return of the blue color after the end point has been reached.

7. Calculations

7.1 $$Br^{-1} + I^{-1} \text{ in epl} = \frac{1{,}000}{\text{ml sample}} \times \frac{0.01}{6} \times (\text{ml}_t - \text{ml}_b).$$

7.2 $$I^{-1} \text{ in epl} = \frac{1{,}000}{\text{ml sample}} \times \frac{0.01}{6} \times (\text{ml}_I - \text{ml}_b).$$

7.3 $$Br^{-1} \text{ in mg/l} = 79.92 \times [\text{epl}\,(I^{-1} + Br^{-1}) - \text{epl}\,I^{-1}]$$

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 Br^{-1} concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

Results are reproducible to ±0.05 mg.

Catalytic oxidation method

1. Summary of method

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. Application

The method is applicable to natural waters containing from 0.001 to 0.10 mg of bromide per liter. Higher concentrations must be reduced by dilution.

3. Interferences

Interference from certain other ions occurs if the following concentrations are exceeded: Iodine 10 mg/l, silver 0.5 mg/l, zinc 1 mg/l, manganese 1 mg/l, or ferric iron 0.5 mg/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. These must be thoroughly rinsed with dilute HCl before each use. Those with teflon stopcocks are preferable.

4.2 *Spectrophotometer,* Beckman Model B, or equivalent.

With this instrument the following operating conditions have been used:

Wavelength	515 nm.
Cells	10 mm.
Phototube	Blue-sensitive.

Initial sensitivity setting.... 2.
Slit width (approximate)..0.05 mm.

With these operating conditions the following values have been observed:

Bromide (*mg*)	*Ratio,* $\frac{\text{Absorbance sample}}{\text{Absorbance control}}$
0.0000	1.000
.0002	.593
.0004	.381
.0006	.272
.0008	.190
.0010	.140

5. Reagents

5.1 *Bromide* standard solution I, 1.00 ml=0.100 mg Br^{-1}: Dissolve 0.149 g KBr 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: Dissolve 1.31 g KI, dried overnight over 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: Dissolve 6.32 g $KMnO_4$ in demineralized water and dilute to 1,000 ml. 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 maximum) 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 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 (0.0°–0.2°C). Allow 30–45 min for samples to reach equilibrium.

6.5 At zero time add 1.0 ml 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 10–15 sec (seconds). Withdraw the carbon tetrachloride layer into 10-mm absorption cells.

6.7 Measure the absorbance at 515 nm using carbon tetrachloride as a reference.

7. Calculations

7.1 Construct a calibration curve by plotting the ratio $\frac{A_s}{A_c}$ against mg of Br^{-1} on semilog paper; A_s= absorbance of standard, and A_c=absorbance of control.

7.2 From the curve, determine the mg of Br^{-1} corresponding to the absorbance ratio obtained for a given unknown sample.

7.3 $$\text{Br}^{-1} \text{ in mg/l} = \frac{1{,}000}{\text{ml sample}} \times \text{mg Br}^{-1} \text{ in sample.}$$

Report Br^{-1} concentrations as follows: Less than 0.1 mg/l, three decimals; 0.1 mg/l and above, two decimals.

9. Precision

Replicate determinations made on standard solutions containing no interfering substances and at bromide concentrations of 0.020, 0.050, and 0.100 mg/l gave standard deviations of 0.0008, 0.0012, and 0.0029 mg/l, respectively.

References

Fishman, M. J., and Skougstad, M. W., 1963, Indirect spectrophotometric determination of traces of bromide in water: Anal. Chemistry, v. 35, p. 146.

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis: New York, Macmillan Co., p. 585.

Shiota, M., Tusumi, S., and Iwasaki, I., 1959, Determination of bromide by its catalytic action: Nippon Kagaku Zasshi, v. 80, p. 753–757; Chem. Abs., v. 54, no. 19278d.

Cadmium

This element is found in nature largely in the form of the sulfide, and as an impurity in zinc-lead ores. The carbonate and hydroxide are not very soluble in water and will precipitate at high pH values; the chloride, nitrate, and sulfate are soluble and remain in solution under most pH conditions.

The extensive use of the element and its salts in metallurgy, electroplating, ceramics, and photography make it a frequent component of industrial wastes. Welsch and Lieber (in California State Water Quality Control Board, 1963) reported ground-water contamination from electroplating wastes on Long Island, N. Y., in the amount of 3.2 mg of cadmium per liter.

Cadmium poisoning of humans has resulted from consumption of foods prepared and left in cadmium-plated containers. There are many references in the literature attesting to the toxicity of cadmium and its salts and its general undesirability in water used for domestic, irrigation, and recreational purposes. The U.S. Public Health Service (1962) established as grounds for rejection any water containing more than 0.01 mg of cadmium per liter.

Atomic-absorption method—direct

1. Summary of method

Cadmium is determined by atomic-absorption spectrophotometry. The sample is aspirated directly with no pretreatment other than dilution or filtration as may be required.

2. Application

Water containing between 0.025 and 0.25 mg of cadmium per liter may be aspirated directly into the flame for analysis; higher concentrations must either be reduced by dilution or less scale expansion used.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	228.8 (2288A).
Slit	4.
Lamp current	6–8 ma.
Scale expansion	10×.
Source (hollow-cathode lamp)	Cd.
Response time control	1.
Burner	Boling.
Air pressure	28 psi (pounds per square inch); 7.5 on flowmeter.
Acetylene pressure	8 psi; 9.0 on flowmeter.

With these operating conditions the following readings have been observed:

Cadmium concentration (mg/l)	*Scale reading*
0.05	12.5
.10	25.5
.15	38.2
.20	51.2
.25	64.0

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 and dilute to 1,000 ml with demineralized water.

5.2 *Cadmium* standard solution II, 1.00 ml=1.00 μg Cd: Dilute 20.0 ml of cadmium standard solution I and 1 ml concentrated HNO_3 to 1,000 ml with demineralized water. This standard is used to prepare working curves at time of analysis.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Filter the sample (0.45-μm membrane filter) when necessary to avoid clogging the atomizer-burner.

6.2 Atomize each sample, blank, and standard, and record scale readings observed. Repeat, and average the two values.

7. Calculations

Determine the mg/l Cd in each sample from a plot of scale readings of standards. Because a scale expansion of 10× is used, scale readings need not be converted to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Cd concentrations as follows: Less than 100 μg/l, nearest 10μg/l; 100 μg/l and above, two significant figures.

9. Precision

Although no determinations of standard deviation are available for this method, results should be reproducible within 0.02 mg/l.

Atomic-absorption method—chelation-extraction

1. Summary of method

Cadmium is determined by atomic-absorption spectrophotometry. The element is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of the spectrophotometer.

2. Application

The extraction procedure given may be used to analyze water containing from 0 to 25 μg of cadmium per liter, although dilution prior to extraction is required for samples containing more than 5 μg of cadmium per liter.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	228.8 (2288A).
Slit	4.
Lamp current	6 ma.
Scale expansion	5×.
Source (hollow-cathode lamp)	Cd.
Response time control	1.
Burner	Boling.
Air pressure	28 psi; 6.0 on flowmeter.
Acetylene pressure	8 psi; 4.0 on flowmeter.

With these operating conditions the following readings have been observed:

Cadmium concentration (μg/l)	*Scale reading*
1.25	14.0
2.50	28.5
3.75	41.2
5.00	56.4

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution: Dissolve 1.0 g APDC in 100 ml demineralized water. Prepare fresh daily.

5.2 *Bromphenol blue indicator* solution: Dissolve 0.1 g bromphenol blue in 100 ml 50-percent ethanol.

5.3 *Cadmium* standard solution I, 1.00 ml=50 μg Cd: Dissolve 0.0571 g CdO in a minimum quantity of concentrated HNO_3 and dilute to 1,000 ml with demineralized water.

5.4 *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 to 1,000 ml with demineralized water.

5.5 *Cadmium* standard solution III, 1.00 ml=0.05 μg Cd: Immediately before use, dilute 10.0 ml cadmium standard solution II to 100 ml with demineralized water. This standard is used to prepare working curves at time of analysis.

5.6 *Hydrochloric acid,* 0.3*M*: Mix 25.0 ml concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 liter.

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

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet a volume of sample containing less than 0.5 μg Cd (100 ml maximum) into a 200-ml volumetric flask, and adjust volume to approximately 100 ml.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to approximately 100 ml with demineralized water.

6.3 Add 2 drops bromphenol blue indicator solution.

6.4 Adjust the pH of the sample by addition of 2.5*M* NaOH by drops until a blue color persists. Add 0.3*M* HCl by drops until the blue just disappears in both the standards and sample. Then add 2.0 ml 0.3*M* HCl in excess. The pH should then be 2.4.

6.5 Add 2.5 ml APDC solution and mix. The pH at this point will be approximately 2.8.

6.6 Add 10.0 ml MIBK and shake vigorously for 1 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 Aspirate the ketone layer and record the scale reading for each standard and sample. Repeat, and average the duplicate results.

7. Calculations

Determine the μg/l Cd in the sample from a plot of scale readings of standards. Since a scale expansion of 5× is used, it is not necessary to convert scale readings to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Cd concentrations as follows: Less than 10 μg/l, nearest μg/l; 10 μg/l and above, two significant figures.

9. Precision

Single-operator precision of this method based on eight determinations at the 2.5-μg/l level was found to be 0.07 μg/l.

References

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 149.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 8.

Calcium

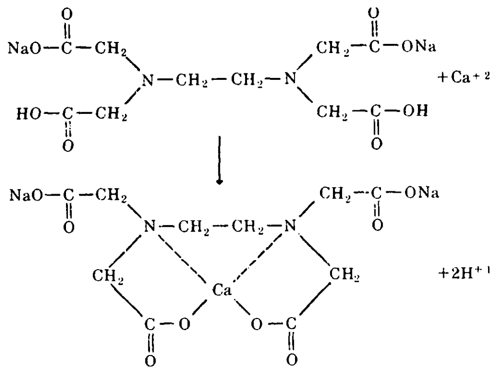
Calcium is dissolved from practically all rocks but is usually found in greater quantities in waters leaching deposits of limestone, dolomite, gypsum, or gypsiferous shale. Waters associated with granite or siliceous sand may contain less than 10 mg of calcium per liter. Many waters from limestone areas contain 30 to 100 mg/l, and waters that traverse gypsiferous shale may contain several hundred milligrams per liter.

Calcium imparts the property of hardness to water, and when present with alkalinity or sulfate it may cause boiler scale. A little calcium carbonate is desirable in water used domestically because of the protective coating that it may form in the pipes. A high ratio of calcium to sodium is desirable in water used for irrigation because calcium flocculates the soil colloids and tends to maintain good soil structure and permeability.

Complexometric method

1. Summary of method

Disodium dihydrogen ethylenediamine tetraacetate (Na_2EDTA) forms a slightly ionized colorless stable complex with calcium ions. Murexide is dark purple in the absence of calcium, but with calcium forms a light-salmon-colored complex which has an ionization constant higher than the Na_2EDTA complex. Hence, by using murexide as an indicator, a solution containing calcium ions may be titrated with Na_2EDTA. The optimum pH of the titration is 10.4 or above.



Additional information on the principle of the determination is given by Banks (1952).

2. Application

The method is applicable to most natural waters, but may fail in the analysis of brines or some acid or polluted waters that contain excessive amounts of heavy metals.

3. Interferences

The salt, Na_2EDTA, reacts with iron, manganese, copper, zinc, lead, cobalt, nickel, barium, strontium, calcium, magnesium, and several other metals. Murexide reacts with strontium but not with magnesium or barium; however, the end point in the presence of strontium is sluggish, and the titration is not strictly stoichiometric. Barium does not titrate as calcium, but affects the indicator in some unknown way so that no end point, or at best a poor end point, is obtained. Barium can be removed by prior precipitation with sulfuric acid. The interference of heavy metals is minimized by the addition of hydroxylamine and cyanide, which reduce and (or) complex the metals. Concentrations of 5 mg of iron and 10 mg of manganese per liter can be tolerated.

The interference of heavy metals is relatively easy to detect because of the typical end point. Conventional methods of hydroxide and sulfide treatment can be used, if necessary, to remove these metals from solution before titration. Magnesium in high concentrations may precipitate as magnesium hydroxide, but the precipitation is not significant.

4. Apparatus

Visual titration assembly: Consists 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 the side and at about 90° from the line of vision.

5. Reagents

5.1 *Calcium* standard solution, 1.00 ml $=0.400$ mg Ca^{+2}: Suspend 1.000 g $CaCO_3$, dried at 180°C for 1 hr before weighing, in approximately 600 ml demineralized water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 ml.

5.2 *Hydroxylamine hydrochloride* solution: Dissolve 30 g $NH_2OH{\cdot}HCl$ in demineralized water and dilute to 1 liter.

5.3 *Murexide,* dry mixture: Mix thoroughly 1.0 g ammonium purpurate with 200 g sucrose. Eastman Kodak Co. reagent-grade product has been found to be satisfactory. Provide the bottle with a dispensing spoon of 0.2-g capacity.

5.4 *Sodium cyanide* solution (CAUTION: NaCN is a deadly poison, and the reagent must be so marked): Dissolve 25 g NaCN in water and dilute to 1 liter.

5.5 *Sodium hydroxide, 2M*: Dissolve 80 g NaOH in 800 ml water. Cool and dilute to 1 liter.

5.6 Na_2*EDTA* solution, 1.00 ml $\bumpeq$ 0.500 mg Ca^{+2}: Dissolve 4.65 g Na_2EDTA, which has been dried overnight in an H_2SO_4 desiccator, in demineralized water and dilute to 1,000 ml. (The titrant is stable for several months and is usually prepared in larger quantities.) Standardize the titrant by titrating 25.00 ml $CaCl_2$ solution (1.00 ml$=$ 0.40 mg Ca^{+2}) as described in the procedure for sample analysis.

NOTE—Alternatively, the same titrant solution may be used here as is used for the hardness titration (1.00 ml$\bumpeq$0.400 mg Ca^{+2}; see "Hardness"). If the more dilute titrant is used, the calculation factor (sec. 7) must be corrected.

6. Procedure

6.1 Pipet a volume of sample containing less than 10 mg Ca^{+2} (50.0 ml maximum) into a 150-ml beaker, and adjust the volume to approximately 50 ml.

6.2 Insert beaker in titration assembly and start stirrer.

6.3 Add 1 ml $NH_2OH{\cdot}HCl$ and 1 ml 2*M* NaOH.

6.4 Add 1 ml NaCN (CAUTION: Deadly poison). The addition of NaCN may be omitted if it is known that the sample being analyzed contains no heavy metals which would interfere with the detection of the end point.

6.5 Add 0.2 g murexide indicator and proceed immediately with the titration.

6.6 Titrate with Na_2EDTA standard solution until purple swirls begin to show. The end point is reached when the sample color changes from salmon to orchid purple. At the end point, the addition of a small increment of titrant will not cause a deepening of the purple color.

6.7 Determine a blank correction by similarly treating 50 ml demineralized water. The normal blank correction is 0.05 or 0.10 ml.

7. Calculations

$$\text{Ca}^{+2} \text{ in mg/l} = \frac{1{,}000}{\text{ml sample}} \times (\text{ml titrant} - \text{ml blank}) \times 0.500.$$

8. Report

Report Ca concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

A test sample was analyzed by this method by nine laboratories with a mean of 12.78 mg/l and a standard deviation of 0.63 mg/l.

Atomic-absorption method—direct

1. Summary of method

Calcium is determined by atomic-absorption spectrophotometry. Lanthanum chloride is added to mask interferences (Fishman and Downs, 1966).

2. Application

Most natural waters containing as much as 100 mg of calcium per liter may be analyzed by this method. Samples containing from 0 to 20 mg/l may be analyzed without dilution, whereas those containing more than 20 mg/l must be diluted or analyzed using the alternate operating conditions described.

Two analytical ranges are provided: From 0.0 to 20 mg of Ca per liter, and from 10 to 100 mg/l.

3. Interferences

Phosphate, sulfate, and aluminum interfere but are masked by the addition of lanthanum. Since low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute hydrochloric acid solution. Concentrations of magnesium greater than 1,000 mg/l also cause low calcium values. Concentrations of up to 500 mg/l each of sodium, potassium, and nitrate cause no interference.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Calcium concentration range: 0.0–20 mg/l

Grating	Visible.
Wavelength counter	211.4 (4227A).
Slit	5.
Lamp current	10 ma.
Scale expansion	1×.
Source (hollow-cathode lamp)	Ca.
Response time control	1.
Burner	Standard "303."
Air pressure	28 psi; 8.0 on flowmeter.
Acetylene pressure	8 psi; 9.0 on flowmeter.

With these operating conditions the following readings have been observed:

Calcium concentration (mg/l)	*Scale reading*
1.0	6.2
5	26.4
10	43.6
15	54.4
20	61.8

NOTE.—A Boling burner may be used instead of the standard "303" burner; however, the maximum concentration of Ca which can then be determined will be about 10 mg/l.

Calcium concentration range: 10–100 mg/l

Scale expansion	2×.
Burner	"290" rotated 90°
Air pressure	28 psi; 6.0 on flowmeter.
Acetylene pressure	8 psi; 6.5 on flowmeter.

All other operating conditions are the same as used for concentration range 0.0 to 20 mg of calcium per liter.

With these operating conditions the following readings have been observed:

Calcium concentration (mg/l)	*Scale reading*
5.0	6.2
10	11.4
50	46.2
100	79.2

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 hr before weighing, in distilled 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 standard solutions containing from 0 to 100 mg of calcium per liter 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: Dissolve 29 g of La_2O_3, slowly and in small portions, in 250 ml concentrated HCI (CAUTION: Reaction is violent) and dilute to 500 ml with demineralized water.

6. Procedure

6.1 Filter the sample (0.45-μm membrane filter) when necessary to avoid clogging the atomizer-burner.

6.2 Add 1.0 ml of lanthanum chloride solution to 10.0 ml of sample.

6.3 Measure the percent absorption or scale reading of the sample and standards against the demineralized-water blank. Repeat, and average the two values. If the calcium concentration is greater than 100 mg per liter, the sample must be diluted.

7. Calculations

7.1 Concentration range 0.0 to 20 mg of calcium per liter: Since scale expansion of 1× is used, scale readings observed are equivalent to percent absorption. Convert percent absorption to absorbance, and determine the calcium concentration (mg/l) 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.

7.2 Concentration range 10 to 100 mg of calcium per liter: Divide the scale readings observed by 2 to obtain percent absorption. Convert to absorbance, and determine the calcium concentration (mg/l) in each sample from a plot of absorbances of standards. For samples containing more than 100 mg of calcium per liter, multiply by the proper dilution factor. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Ca concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

Analysis of a test sample by 15 laboratories using this method resulted in a mean value of 12.67 mg/l with a standard deviation of 0.44 mg/l.

References

Banks, J., 1952, The volumetric determination of calcium and magnesium by the ethylenediamine tetraacetate method: Analyst, v. 77, p. 484.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geol. Survey Water-Supply Paper 1540-C, p. C26-C28.

Carbon dioxide

Air contains about 0.03 percent carbon dioxide by volume, and the concentration in distilled water in equilibrium with air will approach 0.5 mg/l at 25°C. Streams are normally rather low in carbon dioxide, but some ground waters contain large quantities in their natural environment. Carbon dioxide is a respiration product of aquatic plants and animals and is a byproduct of the decomposition of organic matter. Acids from natural sources or pollution liberate carbon dioxide from bicarbonate. Most of the carbon dioxide in water is from these sources.

Carbon dioxide in drinking water is not physiologically important to man and livestock, but it has a marked effect on fish. Tolerances differ widely with the species, dissolved oxygen, and other chemical properties of the water. Of waters of the United States that support good fish fauna, 50 percent have less than 1.5 mg/l, and 95 percent have less than 5 mg/l (California State Water Quality Control Board, 1963). Free carbon dioxide contributes to the corrosiveness of the water and is likely to damage calcareous building material such as cement.

It has been recommended that concrete be coated if it is in contact with water containing 20 mg/l carbon dioxide (Terzaghi, 1949).

Calculation method

1. Summary of method

Carbon dioxide concentration is calculated from measured values of pH and bicarbonate ion. The pH is determined instrumentally, and the bicarbonate ion by the electrometric titration method (see "Alkalinity").

Gaseous carbon dioxide hydrolyzes slightly

$$CO_2(aq)+H_2O\rightleftharpoons H_2CO_3, \qquad (1)$$

for which the hydrolysis constant expression is

$$K_{hydr}=\frac{[H_2CO_3]}{[CO_2]}=2.6\times10^{-3}. \qquad (2)$$

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 concentration can, therefore, be calculated within experimental accuracy from equations (1) and (3) and their corresponding equilibrium-constant expressions as follows:

$$K_{hydr}=\frac{[H_2CO_3]}{[CO_2]}=2.6\times10^{-3} \qquad (5)$$

$$K_{al}=\frac{[H^{+1}][HCO_3^{-2}]}{[H_2CO_3]}=1.7\times10^{-4}. \qquad (6)$$

Multiplying equations (5) and (6)

$$K_{hydr}K_{al}=\frac{[H^{+1}][HCO_3^{-1}]}{[CO_2]}$$

$$=4.4\times10^{-7} \qquad (7)$$

and solving for $[CO_2]$

$$[CO_2]=\frac{[H^{+1}][HCO_3^{-1}]}{4.4\times10^{-7}}. \qquad (8)$$

This equation can then be used to determine the CO_2 concentration when $[HCO_3^{-1}]$, or alkalinity, 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 alkalinity (HCO_3^{-1}) concentrations are usually expressed in units of mg/l rather than moles per liter, and hydrogen-ion concentrations normally as pH units:

$$\text{mg } CO_2/l=1.60\times10^{(6.0-pH)}\times\text{mg } HCO_3^{-1}/l. \qquad (9)$$

For convenience in making the calculations, the values of $1.60\times10^{(6.0-pH)}$ may be tabulated for a range of pH values (table 3).

For additional information on the theory of this method see De Martini (1938), Langelier (1936), Larson and Buswell (1942), and Moore (1939).

2. Application

This method may be applied to any sample for which measured values of pH and bicarbonate ion are available.

3. Interferences

The values of the constants K_{hydr} and K_{al} 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 the values of K_{hydr} and K_{al} for a particular sample. For practical purposes and for most samples containing less than 800 mg of solutes per liter, a value for $(K_{hydr}\times K_{al})$ of 4.54×10^{-7} has been recommended, and was used in calculating the constant factor of equation (9).

Carbon dioxide is easily lost from solution, and precautions must be taken to prevent or minimize such losses when collecting the sample. Preferably, the pH and alkalinity should be determined in the field at the time of collection. If this is impossible, and a reliable measure of pH, bicarbonate, and CO_2 concentrations is required, a separate small sample should be collected, avoiding any aeration of the sample during collection. The sample bottle should be filled, with no air space remaining in the bottle, and the sample should be stored at a temperature below that at which it was collected.

Although it is usual for samples to lose CO_2 between sampling and analysis, it is not impossible for some samples to show an increase in CO_2 concentration indicating solution of finely divided calcium carbonate (hydrolysis):

$$CaCO_3+H_2O\rightarrow 2Ca(HCO_3)_2+CO_2.$$

4. Apparatus

None.

5. Reagents

None.

6. Procedure

None.

7. Calculations

Calculate mg/l CO_2 as follows:

$$CO_2 \text{ in mg/l}=1.60\times 10^{(6.0-pH)}\times \text{mg } HCO_3{}^{-1}/\text{l}.$$

Table 3.—Values of $1.60\times 10^{(6.0-pH)}$

pH	$1.60\times 10^{(6.0-pH)}$	pH	$1.60\times 10^{(6.0-pH)}$
6.0	1.60	7.6	.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	0.160	8.6	.004
7.2	.100	8.8	.003
7.4	.063	9.0	.002

8. Report

Report CO_2 concentrations as follows: Less than 10 mg/l, one decimal; from 10 to 999 mg/l, whole numbers; 1,000 mg/l and above, three significant figures.

9. Precision

No precision data are available for this method.

References

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3–A, p. 156.

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Chloride

Most naturally occurring chlorides are very soluble. Chloride concentration in natural waters ranges widely from less than 1 mg/l in some waters to many thousand mg/l in brines. Chloride is the major anion in most brines of the United States. The discharge of some industrial wastes into streams or ground-water reservoirs may considerably increase their chloride content. Human and animal excreta are high in chloride and nitrogenous material. The presence of abnormal concentrations of the two together in water supplies indicates possible pollution by human or animal wastes.

A high concentration of chloride imparts a salty taste to the water, but the threshold of detection varies with individuals. Although water with a chloride content of 1,000 mg/l may be physiologically safe for drinking purposes, the U.S. Public Health Service (1962) recommends that the concentration not exceed 250 mg/l in water on carriers subject to Federal quarantine regulations.

Chlorides may accelerate corrosion in pipes, boilers, and other fixtures (Taylor, 1958). Many crops may be injured by waters containing excessive quantities of chloride. Chloride is generally about twice as toxic to crops as sulfate (Eaton, 1954).

Mohr method

1. Summary of method

In the well-known Mohr method for determination of chloride, use is made of the fact that, in the titration of sodium chloride with silver nitrate, 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:

$$Ag^{+1}+Cl^{-1}\rightarrow AgCl$$
$$2Ag^{+1}+CrO_4^{-2}\rightarrow Ag_2CrO_4\downarrow.$$

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

$$CrO_4^{-2}+H^{+1}\leftrightharpoons HCrO_4^{-1}.$$

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 acid 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.

Additional information on the principle of the determination is given by Kolthoff and Sandell (1952).

2. Application

The procedure is recommended for samples whose chloride concentration is less than 2,000 mg/l and more than 10 mg/l. It can be used satisfactorily for measuring chloride concentrations up to 5,000 mg/l.

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 masks 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.

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 in demineralized water and dilute to 1,000 ml.

5.2 *Potassium chromate indicator* solution: 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 $\approx$5.00 mg Cl^{-1}: Pulverize approximately 30 g $AgNO_3$ crystals in a clean mortar and dry at 105°–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 $\approx$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 10.00 ml chloride standard solution. Store in a lightproof bottle.

6. Procedure

6.1 Pipet a volume of sample containing less than 50 mg Cl^{-1} (50.00 ml maximum) into a porcelain evaporating dish, and adjust the volume to approximately 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 10–15 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

$$\text{Cl}^{-1} \text{ in mg/l} = \frac{1{,}000}{\text{ml sample}} \times (\text{ml titrant} - \text{ml blank}) \times (\text{mg Cl}^{-1} \text{ per ml titrant}).$$

8. Report

Report Cl^{-1} concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

Analysis of a test sample by 19 laboratories resulted in a mean value of 27.4 mg/l and a standard deviation of 1.2 mg/l.

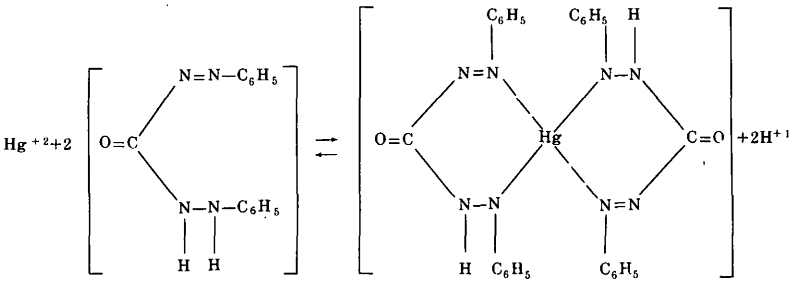
Mercurimetric method

1. Summary of method

Mercuric and chloride ions form a highly stable, soluble complex

$$Hg^{+2} + 2Cl^{-1} \leftrightarrows HgCl_2.$$

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).



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 bromphenol blue indicator and carefully adding dilute nitric acid or sodium hydroxide to adjust the sample to the desired pH.

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.

2. Application

This method may be used to determine chloride in all samples containing at least 0.1 mg of chloride per liter. Smaller concentrations must be increased by evaporation.

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, calcium, or aluminum do not interfere. One mg/l 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 100 mg/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 mg/l. Chromate and ferric ions, if present at concentrations exceeding 10 mg/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, fluoride, 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,* mechanical or magnetic.

5. Reagents

5.1 *Chloride* standard solution, 1.00 ml ≎1.00 mg Cl^{-1}: Dissolve 1.648 g of primary standard NaCl crystals in demineralized water and dilute to 1,000 ml.

5.2 *Hydrogen peroxide,* 30 percent.

5.3 *Hydroquinone* solution: 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 1.42) and dilute to 1,000 ml. Filter, if necessary, and standardize by titrating 25.00 ml chloride standard solution diluted to 50 ml.

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 1.42) and dilute to 1,000 ml. Filter, if necessary, and standardize by titrating 10.00 ml chloride standard solution diluted to 50 ml.

5.6 *Mixed indicator* solution: Dissolve 0.5 g crystalline s-diphenylcarbazone (Eastman Kodak No. 4459) and 0.05 g bromphenol 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 1.42) to 1 liter with demineralized water.

5.8 *Sodium hydroxide* solution, 0.05*M*: Dissolve 2.0 g NaOH in demineralized water and dilute to 1 liter.

6. Procedure

6.1 Pipet a volume of sample containing not more than 20 mg chloride (50.0 ml maximum) into a 125-ml erlenmeyer flask, and adjust the volume to approximately 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 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.
Sensitivity setting	2.
Slit width (approximate)	0.09 mm.
End point	At 0.29 absorbance.
Cells	100-ml beakers.

All other necessary apparatus and reagents are identical to those specified for the visual determination using the mercurimetric method.

7. Calculations

$$Cl^{-1} \text{ in mg/l} = \frac{1000}{\text{ml sample}} \times (\text{ml titrant} - \text{ml blank}) \times (\text{mg } Cl^{-1} \text{ per ml titrant}).$$

8. Report

Report Cl^{-1} concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

Analysis of a test sample by eight laboratories resulted in a mean value of 26.2 mg/l and a standard deviation of 0.9 mg/l.

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Thomas, J. F., 1954, Mercurimetric determination of chlorides: Am. Water Works Assoc. Jour., v. 46, p. 257.

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Chlorine, residual

Residual chlorine includes "free available chlorine" and "combined chlorine." Chlorine hydrolyzes imediately in water

$$Cl_2+H_2O\rightarrow HOCl+H^{+1}+Cl^{-1}$$
$$HOCl\rightleftharpoons H^{+1}+OCl^{-1}.$$

Through common usage the term "free available chlorine" is recognized to include HOCl and OCl^{-1}, and "combined available chlorine" to include chloramines and other chloro derivatives. Both free and combined chlorine may be present together. Results are reported in terms of chlorine (Cl_2).

Chlorination is used in the treatment of public water supplies and sewage effluents. Industrial processes, particularly those that use bleaching operations, may discharge free or combined chlorine to watercourses. Chlorine is unstable in solution; strong light accelerates its dissipation.

It is generally agreed that the small amounts of residual chlorine that are present in palatable drinking water are harmless; low concentrations of chlorine are reported to be toxic to fish, but the degree to which chlorine is harmful is dependent on pH, temperature, dissolved oxygen, and synergism and antagonism of other pollutants (California State Water Quality Control Board, 1963).

Industrial water supplies are often chlorinated to control bacteria and other slime-producing organisms. Concentrations not exceeding 2.0 mg/l are recommended for the manufacture of fine paper. In concentrations normally found, chlorine is not reported to be injurious to land crops.

Orthotolidine-arsenite method

1. Summary of method

In dilute solution, hydrolyzed chlorine oxidizes orthotolidine to give a yellowish-brown complex. The color developed is compared with that of standards or standardized colored-glass disks. Other free halogens react quantitatively. The reaction is practically instantaneous with free available chlorine but proceeds more slowly with the combined forms. This difference in reaction rates is utilized in differentiating between the two. Arsenite inhibits the reaction but does not reverse it.

The pH must be below 1.3 for proper color development, and the ratio of orthotolidine to chlorine should be at least 1 to 3. The reaction is temperature sensitive, the precision of the test increasing with decreasing temperature. A reaction temperature of less than 20°C is recommended.

Reproducibility of results is dependent on close adherence to the prescribed procedure, on temperature, and on the relative concentrations of free and combined available chlorine.

2. Application

This method may be used to determine residual chlorine in most unpolluted natural waters, industrial and process waters, and domestic water supplies.

3. Interferences

Iron, manganese, nitrite, algae, and lignocellulose interfere and increase the color. The effect of these interferences is evaluated by development of color in presence of arsenite and compensated for in the calculations.

4. Apparatus

Color comparator, with standard color disks covering ranges of 0.00–0.10, 0.10–1.0, and 1.0–2.0 mg/l.

5. Reagents

5.1 *Orthotolidine* reagent: Dissolve 1.35 g orthotolidine hydrochloride in 450 ml water. Add this solution with constant stirring to a solution of 375 ml concentrated HCl (sp gr 1.19) and 125 ml water. Dilute to 1 liter. Store in amber or actinic bottle and protect from light. The reagent is stable for 6 months.

5.2 *Sodium arsenite* solution: Dissolve 5.0 g $NaAsO_2$ in water and dilute to 100 ml.

6. Procedure

Because of its instability, residual chlorine should be determined immediately after collection of the sample.

6.1 Pipet equal volumes of sample containing less than 0.01 mg residual chlorine as Cl_2 (50.0 ml maximum) into three flasks, and adjust the volumes to 50 ml.

6.2 To the first flask add 0.5 ml $NaAsO_2$ solution and mix. Add 5.0 ml orthotolidine reagent, mix rapidly, and immediately compare the color with standard color disks in the comparator. The value observed is the blank correction (B_1) for the free available chlorine.

6.3 Make a second observation on the contents of the first flask 5.0 min after addition of the orthotolidine. This value is the blank correction (B_2) for the total available chlorine.

6.4 To the second flask add 5.0 ml orthotolidine reagent. Mix quickly, and immediately add 0.5 ml $NaAsO_2$ solution. Immediately compare the color. The observed value (A) is the free available chlorine plus the effect of interfering substances that react rapidly.

6.5 To the third flask add 5.0 ml orthotolidine reagent, mix, and compare the color after 5.0 min. The observed value (OT) is the total residual chlorine plus the effect of interfering substances that react in 5.0 min.

7. Calculations

7.1 Total residual chlorine in

$$\text{mg/l} = \frac{50}{\text{ml sample}}(OT - B_2).$$

7.2 Free available chlorine in

$$\text{mg/l} = \frac{50}{\text{ml sample}}(A - B_1).$$

7.3 Combined available chlorine in

$$\text{mg/l} = \frac{50}{\text{ml sample}}[(OT - B_2) - (A - B_1)].$$

8. Report

Report Cl_2 concentrations as follows: Less than 1.0 mg/l, two decimals; 1.0 mg/l and above, two significant figures.

9. Precision

No precision data are available, but it appears that a precision of at least ±0.1 mg/l can be expected.

Reference

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 162.

Chromium, hexavalent

Few if any waters contain chromium from natural sources. Hexavalent chromium salts are used in metal pickling and plating, anodizing aluminum, and in the manufacture of paints, dyes, explosives, ceramics, paper, and many other substances. Tervalent chromium salts are used as mordants in textile dyeing, in the ceramic and glass industries, and in photography. Chromium is a corrosion inhibitor and may be present in treated cooling waters. Waste products from many of these activities may contain chromium.

The U.S. Public Health Service (1962) states that the concentration of hexavalent chromium shall not exceed 0.05 mg/l in drinking and culinary water on carriers subject to Federal quarantine regulations; no limit is given for the tervalent form. The toxicity of chromium salts to aquatic life differs widely with the species, temperature, pH, valence of chromium, and other factors (California State Water Quality Control Board, 1963).

The procedures given determine hexavalent chromium only. All ionic forms of chromium are determined if the sample is first oxidized with $KMnO_4$; tervalent chromium may then be calculated by difference.

Diphenylcarbazide method

1. Summary of method

This method determines only the hexavalent chromium in solution.

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 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. Application

Most natural water containing between 0.05 and 4 mg of hexavalent chromium per liter may be analyzed by this method. Higher concentrations must be reduced by dilution.

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 mg/l show only a small effect. Vanadium should not be present in concentrations exceeding 4 mg/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 mg/l, no vanadium color persists after 10 min.

Additional information on the principle of the determination is given by Sandell (1950).

4. Apparatus

Spectrophotometer, Beckman Model B, or equivalent.

With this instrument the following operating conditions have been used:

Wavelength	540 nm.
Cells	10 mm.
Phototube	Blue-sensitive.
Blank	Demineralized water plus reagents.
Initial sensitivity setting	1.
Slit width (approximate)	0.1 mm.

With these operating conditions the following absorbances have been observed:

Chromium (mg)	*Absorbance*
0.01	0.70
.02	1.2
.03	1.7
.045	2.5

5. Reagents

5.1 *Chromium* standard solution, 1.00 ml=0.10 mg Cr^{+6}: Dissolve 0.3734 g K_2CrO_4 dried overnight in H_2SO_4 desiccator 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

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet a volume of sample containing less than 0.03 mg Cr^{+6} (10.00 ml maximum) 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 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 correction for water color as directed in "Part II, Instrumental Techniques."

7. Calculations

7.1 Determine the mg Cr^{+6} in the sample from a plot of absorbances of standards.

7.2 Cr^{+6} in

$$\text{mg/l} = \frac{1{,}000}{\text{ml sample}} \times \text{mg } Cr^{+6} \text{ in sample.}$$

8. Report

Report Cr^{+6} concentrations as follows: Less than 100 μg/l, nearest 10 μg/l; 100 μg/l and above, two significant figures.

9. Precision

Analysis of a test sample by five laboratories resulted in a mean value of 0.81 mg/l and a standard deviation of 0.04 mg/l.

Atomic-absorption method—chelation-extraction

1. Summary of method

Chromium is determined by atomic-absorption spectrophotometry. The element is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of the spectrophotometer (Midgett and Fishman, 1967).

2. Application

The method may be used to analyze samples containing from 1.0 to 25 μg of chromium per liter. Samples containing more than 25 μg/l may be either diluted or aspirated directly into the spectrophotometer without chelation and extraction.

3. Interferences

The method is free from interference from elements commonly found in fresh water.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	357.9 (3579A).
Slit	3.
Lamp current	20 ma.
Scale expansion	10×.
Source (hollow-cathode lamp)	Cr.
Response time control	1.
Burner	Boling.
Air pressure	28 psi; 7.0 on flowmeter.
Acetylene pressure	8 psi; 5.0 on flowmeter.

With these operating conditions the following readings have been observed:

Chromium concentration (μg/l)	*Scale reading*
5.0	18.8
10	36.8
15	54.2
20	73.8
25	86.5

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution: Dissolve 1.0 g APDC in demineralized water and dilute to 100 ml. Prepare fresh daily.

5.2 *Bromphenol blue indicator* solution: Dissolve 0.1 g bromphenol blue *in 100 ml* 50-percent ethanol.

5.3 *Chromium* standard solution I, 1.00 ml=100 μg Cr: Dissolve 0.2829 g pure dried $K_2Cr_2O_7$ in demineralized water and dilute to 1,000 ml.

5.4 *Chromium* standard solution II, 1.00 ml=10.0 μg Cr: 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: 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 liter.

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 liter.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

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 approximately 100 ml.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to approximately 100 ml.

6.3 Add 2 drops bromphenol blue indicator solution.

6.4 Adjust the pH by addition of $1M$ NaOH solution by drops until a blue color persists. Add $0.12M$ H_2SO_4 by drops until the blue color just disappears in both the standards and sample. Then add 2.0 ml $0.12M$ H_2SO_4 in excess. The pH at this point should be 2.4.

6.5 Add 5.0 ml APDC solution and mix. The pH should then be approximately 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-APDC complex is stable for at least 36 hr.

6.8 Aspirate the ketone layer and record the scale reading for each sample and standard against the blank. Repeat, and average the duplicate results.

7. Calculations

Determine the $\mu g/l$ Cr^{+6} in each sample from a plot of scale readings of standards. Since a scale expansion of 10× is used, it is not necessary to convert scale readings to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Cr^{+6} concentrations as follows: Less than 10 $\mu g/l$, nearest $\mu g/l$; 10 $\mu g/l$ and above, two significant figures.

9. Precision

Precision obtainable with this method should be equal to that for "Chromium, Hexavalent and Tervalent, Atomic-Absorption Method—Chelation-Extraction."

References

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 165.

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.

Sandell, E. B., 1950, Colorimetric determination of traces of metals [2d ed.]: New York, Interscience Publishers, Inc., p. 260.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 8.

Chromium, hexavalent and tervalent

Permanganate-azide method

1. Summary of method

All ionic forms of chromium are determined by oxidizing tervalent chromium to the hexavalent state with potassium permanganate prior to diphenylcarbazide color development. (See "Chromium, Hexavalent, Diphenylcarbazide Method.") The excess oxidant is destroyed with sodium azide.

Attention should be given to the glassware used, because scratched glassware may adsorb chromium. Any glassware cleaned with chromic acid cleaning solution should be recleansed with hydrochloric acid to remove the last traces of chromium.

Additional information on the principle of the determination is given by Saltzman (1952) and Lieber (1956).

2. Application

See "Chromium, Hexavalent, Diphenylcarbazide Method."

3. Interferences

See "Chromium, Hexavalent, Diphenylcarbazide Method."

4. Apparatus

See "Chromium, Hexavalent, Diphenylcarbazide Method."

5. Reagents

5.1 *Ammonium hydroxide*, $7.5M$: Mix 50 ml concentrated NH_4OH (sp gr 0.900) with demineralized water and dilute to 100 ml.

5.2 *Chromium* standard solution, 1.00 ml=0.002 mg Cr^{+3}: Dissolve 0.2263 g pure dried $K_2Cr_2O_7$ in demineralized water and dilute to 1,000 ml. Pipet 5.00 ml into an erlenmeyer flask. Add approximately 15 mg Na_2SO_3 and 0.5 ml concentrated HNO_3 (sp gr 1.42). Evaporate to dryness gently; strong heating reoxidizes the Cr. Add 0.5 ml concentrated HNO_3 and again evaporate to dryness to destroy any excess sulfite. Take up in 1 ml concentrated HNO_3 with warming, and dilute to 200.0 ml with demineralized water.

5.3 *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.

5.4 *Potassium permangate* solution: Dissolve 0.32 g $KMnO_4$ in 100 ml demineralized water. Allow to stand several days and decant if necessary.

5.5 *Sodium azide* solution: Dissolve 5 g NaN_3 in 100 ml demineralized water.

5.6 *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.

5.7 *Sulfuric acid,* 0.25*M*: Slowly add 14 ml concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 liter.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet a volume of sample containing less than 0.30 mg Cr (50.0 ml maximum) into a 250-ml erlenmeyer flask, and adjust the volume to approximately 50 ml.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approximately 50 ml with demineralized water.

6.3 Add 10 ml 0.25*M* H_2SO_4 and mix.

6.4 Add approximately 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 Remove from steam bath, and while warm add NaN_3 solution by drops until $KMnO_4$ color disappears. Allow about 10 sec between each drop of NaN_3; 3–5 drops are usually sufficient.

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 10.00-ml aliquot into a 50-ml beaker and proceed as directed in "Chromium, Hexavalent, Diphenylcarbazide Method," beginning with step 6.3. No color correction is necessary.

7. Calculations

7.1 Determine the mg Cr in the aliquot from a plot of absorbances of standards.

7.2 $$\text{Cr in mg/l} = \frac{1{,}000}{\text{ml sample}} \times \frac{100}{\text{ml aliquot}} \times \text{mg Cr in aliquot.}$$

8. Report

Report Cr concentrations as follows: Less than 100 μg/l, nearest 10 μg/l; 100 μg/l and above, two significant figures.

9. Precision

Single-operator analysis of a test sample indicated a mean of 0.72 mg/l and a standard deviation of 0.04 mg/l.

Atomic-absorption method—chelation-extraction

1. Summary of method

The procedure used for determination of chromium is the same as that used for hexavalent chromium, 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 chromium 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.

2. Application

Water containing from 0 to 25 μg of chromium per liter may be analyzed by this method, whereas concentrations greater than 25 μg/l must be determined either by dilution or directly on the aqueous sample.

3. Interferences

The optimum pH for the extraction of the Cr-APDC complex by 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. The method is otherwise free from interference from elements commonly found in fresh water.

4. Apparatus

See "Chromium, Hexavalent, Atomic-Absorption Method—Chelation-Extraction."

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution: Dissolve 1.0 g APDC in demineralized water and dilute to 100 ml. Prepare fresh daily.

5.2 *Bromphenol blue indicator* solution: Dissolve 0.1 g bromphenol blue in 100 ml 50-percent ethanol.

5.3 *Chromium* standard solution I, 1.00 ml=80 μg Cr^{+6}: Dissolve 0.2263 g pure dried $K_2Cr_2O_7$ 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 1.42). 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 and dilute to 200 ml 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: 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: 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 liter.

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 liter.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

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 approximately 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. Prepare a blank and sufficient standards, and adjust volumes to approximately 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 $KMnO_4$ 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 which has a brownish precipitate or coloration which may interfere with the pH adjustment.

6.8 Add 2.0 ml 1*M* NaOH and 2 drops bromphenol blue indicator solution. Continue the addition of $1M$ NaOH by drops to all samples and standards in which the indicator change from yellow to blue has not occurred. Add $0.12M$ H_2SO_4 by drops until the blue color just disappears, then add 2.0 ml in excess. The pH at this point will be 2.4.

6.9 Add 5.0 ml APDC solution and mix. The pH at this point will be 2.8.

6.10 Add 10.0 ml MIBK and shake vigorously for 3 min.

6.11 Allow the layers to separate and 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-APDC complex is stable for at least 36 hrs.

6.13 Aspirate the ketone layer and record the scale reading for each standard and sample against the blank. Repeat, and average the duplicate results.

7. Calculations

Determine the μg/l Cr in each sample from a plot of scale readings of standards. Since a scale expansion of 10× is used, it is not necessary to convert scale readings to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Cr concentrations as follows: Less than 10 μg/l, nearest μg/l; 10 μg/l and above, two significant figures.

9. Precision

Single-operator precision of this method based on 10 determinations at the 5.0-μg/l level was found to be 0.57 μg/l.

References

Lieber, Maxim, 1956, Permanganate-azide test for total chromium in water: Am. Water Works Assoc. Jour., v. 48, p. 295.

Saltzman, B., 1952, Microdetermination of chromium with diphenylcarbazide by permanganate oxidation: Anal. Chemistry, v. 24, p. 1016.

Cobalt

Cobalt occurs in nature in the minerals smaltite, $CoAs_2$, and cobaltite, CoAsS. Alluvial deposits and soils derived from shales often contain cobalt in the form of phosphate or sulfate, but other soil types may be markedly deficient in cobalt in any form (Bear, 1955). Ruminant animals may be adversely affected by grazing on land deficient in cobalt.

Solutions containing cobaltous ions (Co^{+2}) are relatively stable, whereas cobaltic ions (Co^{+3}) are strong oxidizing agents and therefore unstable in natural waters.

Although trace amounts of cobalt seem to be essential to the nutrition of some animals, large amounts have pronounced toxic effects on both plant and animal life. For domestic water supplies, no maximum safe concentration has been established on the basis of present knowledge (California State Water Quality Control Board, 1963). Most waters rarely contain more than trace concentrations of cobalt from natural sources.

Atomic-absorption method—chelation-extraction

1. Summary of method

Cobalt is determined by atomic-absorption spectrophotometry. The element is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of the spectrophotometer (Fishman and Midgett, 1968).

2. Application

The extraction procedure given may be used to analyze water containing from 0 to 20 μg of cobalt per liter. Higher concentrations must either be reduced by dilution or less scale expansion used.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	240.9 (2409A).
Slit	3.
Lamp current	30 ma.

Scale expansion	10×.
Source (hollow-cathode lamp)	Co.
Response time control	2.
Burner	Boling.
Air pressure	28 psi; 6.0 on flowmeter.
Acetylene pressure	8 psi; 4.0 on flowmeter.

With these operating conditions the following readings have been observed:

Cobalt concentration ($\mu g/l$)	*Scale reading*
2.50	12.1
5.00	22.2
10.0	41.9
20.0	84.0

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution: Dissolve 1.00 g APDC in 100 ml demineralized water. Prepare fresh before use.

5.2 *Bromphenol blue indicator* solution: Dissolve 0.1 g bromphenol blue in 100 ml 50-percent ethanol.

5.3 *Colbalt* 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, and dilute to 1,000 ml.

5.4 *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 to 1,000 ml with demineralized water.

5.5 *Cobalt* standard solution III, 1.00 ml=0.2 μg Co: Immediately before use, dilute 10.0 ml cobalt standard solution II to 100 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 liter.

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

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet a volume of sample containing less than 2.0 μg Co (100 ml maximum) into a 200-ml volumetric flask, and adjust the volume to approximately 100 ml.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to approximately 100 ml with demineralized water.

6.3 Add 2 drops of bromphenol blue indicator solution.

6.4 Adjust the pH of the sample 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 in both standards and sample. Then add 2.0 ml in excess. The pH should then be 2.4.

6.5 Add 2.5 ml APDC solution and mix. The pH should then be approximately 2.8.

6.6 Add 10.0 ml MIBK and shake vigorously for 1 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 Aspirate the ketone layer and record the scale reading for each standard and sample against the prepared blank. Repeat, and average the duplicate results.

7. Calculations

Determine the μg/l Co in the sample from a plot of scale readings of standards. Since a scale expansion of 10× is used, it is not necessary to convert scale readings to absorbances. Exact reproducibility is not obtained, and a working curve must be prepared for each set of samples.

8. Report

Report Co concentrations as follows: Less than 100 μg/l, nearest μg/l; 100 μg/l and above, two significant figures.

9. Precision

No precision data are available.

References

Bear, F. E., 1955, Chemistry of the soil: New York, Reinhold Co., 373 p.

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 166.

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: Am.

Chem. Soc., Advances in Chemistry Ser., no. 73, p. 230.

Color

The color of water as considered herein is that due only to substances in solution. Color in water may be of natural mineral, animal, or vegetable origin. It may be caused by metallic substances, humus material, peat, algae, weeds, or protozoa. Industrial wastes may also color water. Color may range from zero to several hundred units.

In domestic water, any noticeable color is undesirable. Color-imparting solutes may dull clothes or stain food and fixtures. The U.S. Public Health Service (1962) states that the color shall not exceed 15 units in drinking and culinary water on carriers subject to Federal quarantine regulations. Color is undesirable in water for many industries, particularly food processing, laundering, ice manufacturing, bottled beverage, photographic, and textile (California State Water Quality Control Board, 1963).

Comparison method

1. 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 of platinum per liter. 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.

2. Application

This method may be used to measure the color of samples whose colors reasonably match the Hazen scale and which contain no excessive amount of sediment.

3. Interferences

Turbidity generally causes the observed color to be higher 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 adsorption on suspended material. Filtration of samples to remove turbidity frequently removes some of the color-imparting solutes by adsorption 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 0–500 color units.

5. Reagents

None.

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 distilled or demineralized water in the second tube as a blank.

6.3 The color comparison is made by revolving the disk until the colors of the two tubes match. Waters that have colors greater than 70 should be diluted.

7. Calculations

The color is read directly from the matching color standard, and the proper dilution factor is appplied.

8. Report

Report color as follows:

Color unit	*Record units to nearest*
1–50	1
51–100	5
101–250	10
251–500	20

9. Precision

Because of the many complicating factors involved, the measurement of color is not a precise determination. No statements on the reproducibility of the tests can be made.

References

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3–A, p. 168.

Hazen, Allen, 1892, A new color standard for natural waters: Am. Chem. Soc. Jour., v. 12, p. 427.

Lamar, W. L., 1949, Determination of color of turbid waters: Anal. Chemistry, v. 21, p. 726.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 6.

Copper

Most copper minerals are relatively insoluble, and only very low concentrations can be expected from natural sources. The presence of copper in more than trace amounts can usually be attributed to corrosive action of water on copper pipes, to industrial wastes, or to the use of copper salts for the control of algae and other aquatic growths.

Copper imparts a disagreeable metallic taste to water. As little as 1.5 mg/l can usually be detected, and 5 mg/l can render the water unpalatable. Copper is not considered to be a cumulative systemic poison like lead and mercury; most copper ingested is excreted by the body. The pathological effects of copper are controversial, but it is generally believed very unlikely that humans could unknowingly ingest toxic quantities from palatable drinking water. The U.S. Public Health Service (1962) recommends that copper concentrations should not exceed 1.0 mg/l in drinking and culinary water on carriers subject to Federal quarantine regulations. The toxicity to aquatic organisms differs significantly not only with the species but also with the chemical and physical characteristics of the water, such as temperature, hardness, turbidity, and carbon dioxide content (California State Water Quality Control Board, 1963).

Copper is undesirable in water used for canning foods and for metal-plating baths. Although copper is an essential or beneficial plant nutrient, crops differ widely in their tolerances. Low concentrations have been found to be injurious to orange seedlings, flax, sugar beets, tomatoes, and barley, but high concentrations have no effect on oats or kale. On the basis of literature examined, the following maximum concentrations of copper are indicated for specific beneficial uses (California State Water Quality Control Board, 1963):

Domestic supply	1 mg/l.
Irrigation	0.1 mg/l.
Fish and aquatic life:	
Fresh water	0.02 mg/l.
Sea water	0.05 mg/l.

Atomic-absorption method—direct

1. Summary of method

Copper is determined by atomic-absorption spectrophotometry. The sample is aspirated directly with no pretreatment other than filtration or dilution as required (Fishman and Downs, 1966).

2. Application

Water containing between 0.05 and 0.50 mg of copper per liter may be aspirated directly into the flame for analysis, but higher concentrations must either be reduced by dilution or less scale expansion used.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	324.7 (3247A).
Slit	4.
Lamp current	15 ma.
Scale expansion	10×.
Source (hollow-cathode lamp)	Cu.
Response time control	1.
Burner	Boling.

Air pressure	28 psi; 7.5 on flowmeter.
Acetylene pressure	8 psi; 9.0 on flowmeter.

With these operating conditions the following readings have been observed:

Copper concentration (mg/l)	*Scale reading*
0.10	10.5
.20	21.5
.50	55.0

5. Reagents

5.1 *Copper* standard solution I, 1.00 ml=1.00 mg 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=0.005 mg Cu: Dilute 5.0 ml copper standard solution I and two drops concentrated HNO_3 to 1,000 ml with demineralized water. This standard is used to prepare working standards at time of analysis.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Filter the sample (0.45-μm membrane filter) when necessary to avoid clogging the atomizer-burner.

6.2 Aspirate and record the scale reading of each sample and standard against the demineralized-water blank. Repeat, and average the duplicate results.

7. Calculations

Determine the mg/l Cu in each sample from a plot of scale readings of standards. Since a scale expansion of 10× is used, scale readings need not be converted to absorbances. Exact reproducibility is not obtained, and a working curve must be prepared for each set of samples.

8. Report

Report Cu concentrations as follows: Less than 100 μg/l, nearest 10 μ/gl; 100 μg/l and above, two significant figures.

9. Precision

Analysis of a test sample by 19 laboratories using this method resulted in a mean value of 0.119 mg/l and a standard deviation of 0.030 mg/l.

Atomic-absorption method—chelation-extraction

1. Summary of method

Copper is determined by atomic-absorption spectrophotometry. The element is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of the spectrophotometer.

2. Application

The extraction procedure given may be used to analyze water containing from 0 to 10 μg of copper per liter. Higher concentrations must be either reduced by dilution or less scale expansion used.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	324.7 (3247A).
Slit	4.
Lamp current	15 ma.
Scale expansion	10×.
Source (hollow-cathode lamp)	Cu.
Response time control	1.
Burner	Boling.
Air pressure	28 psi; 6.0 on flowmeter.
Acetylene pressure	8 psi; 4.0 on flowmeter.

With these operating conditions the following readings have been observed:

Copper concentration (μg/l)	*Scale reading*
2.5	23.0
5.0	40.5
7.5	61.7
10.0	82.5

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution: Dissolve 1 g APDC in 100 ml demineralized water. Prepare fresh before use.

5.2 *Bromphenol blue indicator* solution:

Dissolve 0.1 g bromphenol blue in 100 ml 50-percent ethanol.

5.3 *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.

5.4 *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 to 1,000 ml with demineralized water. This standard is used to prepare working standards at time of analysis.

5.5 *Hydrochloric acid,* 0.3*M*: Mix 25 ml concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 liter.

5.6 *Methyl isobutyl ketone* (MIBK).

5.7 *Sodium hydroxide,* 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 ml.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet a volume of sample containing less than 1.0 μg Cu (100 ml maximum) into a 200-ml volumetric flask, and adjust the volume to approximately 100 ml.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to approximately 100 ml with demineralized water.

6.3 Add 2 drops bromphenol blue indicator solution.

6.4 Adjust the pH of the sample 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 in both standards and sample. Then add 2.0 ml in excess. The pH should then be approximately 2.4.

6.5 Add 2.5 ml APDC solution and mix. The pH should then be approximately 2.8.

6.6 Add 10.0 ml MIBK and shake vigorously for 1 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 Aspirate the ketone layer and record the scale reading for each standard and sample against the prepared blank. Repeat, and average the duplicate results.

7. Calculations

Determine the μg/l Cu in the sample from a plot of scale readings of standards. Since a scale expansion of 10× is used, it is not necessary to convert scale readings to absorbances. Exact reproducibility is not obtained, and a working curve must be prepared for each set of samples.

8. Report

Report Cu concentrations as follows: Less than 10 μg/l, nearest μg/l; 10 μg/l and above, two significant figures.

9. Precision

Although no precision data are available, recovery tests indicate that results may be reproduced to within 0.36 μg/l.

References

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3–A, p. 171.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geol. Survey Water-Supply Paper 1540–C, p. 28.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 7.

Cyanide

Cyanides are not found free in nature, but may become contaminants of water supplies by means of effluents from gasworks, coke ovens, steelmills, electroplating processes, and chemical industries. In natural streams and organic soils, simple cyanides are decomposed by bacterial action, whereas the metal-cyanide complexes are often quite stable and more resistant to degradation. The U.S. Public Health Service (1962) set a recommended limit of 0.01 mg cyanide per liter and a mandatory limit of 0.2 mg/l for waters subject to interstate regulations.

Pyridine-pyrazolone method

1. Summary of method

This spectrophotometric 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 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 Public Health Association and others (1965).

2. Application

The method may be used to determine cyanide in waters containing at least 10 μg cyanide per liter.

3. Interferences

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.

These interferences may be removed or their effect minimized as follows:

Sulfide:

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. The sample should be filtered immediately, the precipitate washed with demineralized water, and the washings added to the filtrate.

Fatty acids:

Fatty acids are removed by acidifying a 400-ml sample aliquot with acetic acid to pH 6–7 and extracting with 80 ml of either isooctane or hexane. A single extraction is usually sufficient.

Oxidizing agents:

Oxidizing agents are removed by adding sodium sulfite solution to 400 ml of sample until a negative test with starch-iodide paper is obtained.

Other interferences:

Most remaining interferences are removed by the distillation.

4. Apparatus

4.1 *Distillation train,* figure 11. An efficient gas washer is very 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 *Spectrophotometer,* Beckman Model B, or equivalent.

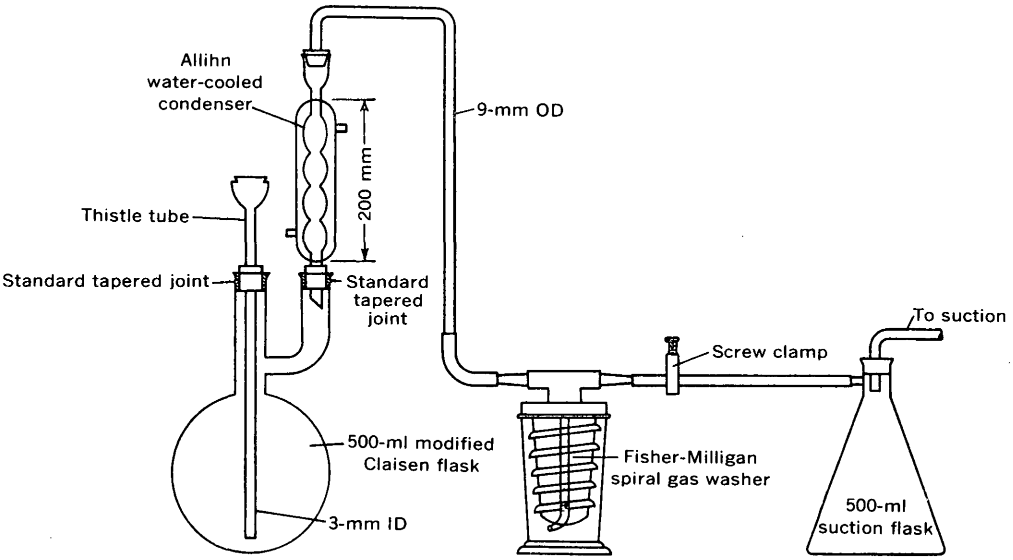

Figure 11.—Cyanide distillation apparatus.

With this instrument the following operating conditions have been used:

Wavelength	620 nm.
Cells	23 mm.
Phototube	Red-sensitive.
Initial sensitivity setting	1.
Blank	Demineralized water plus reagents.

With this instrument the following readings have been observed:

Cyanide (*μg*)	*Absorbance*
0.50	0.2
1.0	.4

5. Reagents

5.1 *Acetic acid, 3M*: Mix 172 ml glacial $HC_2H_3O_2$ with demineralized water and dilute to 1 liter.

5.2 *Chloramine-T* solution: 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=1.00 mg CN: Dissolve 2.51g KCN in 1 liter demineralized water. Standardize with silver nitrate standard solution, 0.0192*N*, 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 0.5–1.0 ml paradimethylaminobenzalrhodanine 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.

5.4 *Cyanide* standard solution II, 1.00 ml=0.010 mg CN: Mix 10.0 ml cyanide standard solution I with 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: Mix 10.0 ml cyanide standard solution II with demineralized water and dilute to 100 ml. This solution must be prepared fresh before use.

5.6 *Magnesium chloride* solution: Dissolve 51 g $MgCl_2 \cdot 6H_2O$ in 100 ml demineralized water.

5.7 *Paradimethylaminobenzalrhodanine indicator* solution: Dissolve 0.02 g paradimethylaminobenzalrhodanine 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, and 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 with cyanide within 25 hrs.

5.11 *Pyridine.*

5.12 *Silver nitrate* standard solution, 0.0192*N*, 1.00 ml=1.00 mg Ag: Dissolve 3.27 g $AgNO_3$ in 950 ml demineralized water and standardize as follows: (1) Pipet 25 ml standard sodium chloride solution (1 ml= 1.00 mg Cl^{-1}) into a porcelain evaporating dish. (2) Add 5 drops K_2CrO_4 indicator solution. (3) With constant stirring, titrate with $AgNO_3$ until the pink-red Ag_2CrO_4 persists for 10–15 sec. (4) Determine blank correction by titration of 50 ml demineralized water. (5) Adjust volume of silver nitrate standard, and store in a lightproof bottle.

5.13 *Sodium chloride* standard solution, 1 ml=1.00 mg Cl^{-1}: Dissolve 1.6484 g NaCl in demineralized water and dilute to 1,000 ml.

5.14 *Sodium hydroxide, 1M*: Dissolve 4 g NaOH in 100 ml demineralized water.

5.15 *Sulfuric acid,* concentrated (sp gr 1.84).

6. Procedure

6.A *Distillation*

6.A.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 250–500 ml) to the boiling flask. Add *exactly* 50 ml 1*M* NaOH and 100 ml de-ionized water to the gas washer. Connect train and adjust suction so that 1–2 bubbles per second enter the boiling flask through the air inlet. Do not increase airflow beyond 2 bubbles per second.

6.A.2 Add 10 ml $MgCl_2$ solution through the thistle tube, and allow the airflow to mix for 3 min. Rinse air tube with de-ionized water, then slowly add 20 ml concentrated H_2SO_4. Rinse the tube again.

NOTE.—Some procedures provide for the addition of mercuric chloride or cuprous chloride to the digestion mixture to facilitate decomposition of complex cyanides. The precise effects of these additives have not been verified.

6.A.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 hr. Turn off heat, but permit airflow to continue for 15 min.

6.A.4 Transfer gas washer contents to 200-ml volumetric flask. Wash tube from condenser to gas washer, and the gas washer, with small amounts of de-ionized water and add to contents of flask. Dilute contents of volumetric flask to 200 ml.

6.A.5 Refill the gas washer with NaOH and water, as in 6.A.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.B *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.B.1 Prepare a blank by pipetting 15 ml of 0.25*M* NaOH into a 23-mm tube 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.B.2 Take 15-ml aliquots (or smaller volumes diluted to 15 ml with 0.25*M* NaOH) of the distillate from the purification procedure and place in 23-mm stoppered cells.

6.B.3 Neutralize samples, blank, and standards to pH 6.5–7.0 with 3*M* acetic acid, using phenolphthalein indicator solution.

6.B.4 To samples, blank, and standard add 4 drops chloramine-T solution, stopper, and shake. Allow 2 min for the reaction.

6.B.5 Add 5.0 ml mixed pyridine-pyrazolone solution and mix well. Allow 20 min for color development.

6.B.6 Read absorbances at 620 nm using the red photocell. 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 hr, and can probably be read during this period with some decrease in accuracy.

7. Calculations

7.1 $$F=[(1{,}000/\text{original sample volume}) \times (\text{ml distillate/aliquot volume}) \times (\text{mg standard})] \times [1/A_{\text{standard}}].$$

7.2 CN in mg/l $= F \times A$ sample,

where

F=factor

A=absorbance.

8. Report

Report CN 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

No precision data are available.

References

American Public Health Association and others, 1965, Standard methods for the examination of water and wastewater [12th ed.]: New York, Am. Public Health Assoc., Inc., p. 448.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 6.

Density

Density is the mass of any substance per unit volume at a designated standard temperature. Density should not be confused with specific gravity, which is a mass-to-mass relation.

The density value has some use in industries that utilize brines and whose basic unit of concentration of dissolved material is density. Density is used primarily by the chemist in the computation of parts per million for highly mineralized waters. In the analysis, weight per sample volume is determined, and these values must be converted to parts per million. Parts per million by definition is the weight of dissolved material per 1 million equal weights of solution (milligrams per kilogram). Concentrations in milligrams per liter may be converted to equivalent concentrations in parts per million by multiplying by the inverse of the density of the sample.

The Geological Survey no longer reports results of analyses in terms of parts per million, so the determination of density is not essential. Previously reported results in parts per million may be converted to milligrams per liter by multiplying the value in ppm by the reported density of the sample. In computing concentrations in ppm, no correction is necessary unless the dissolved-solids concentration exceeds 7,000 mg/l and (or) the specific conductance exceeds 10,000 micromhos/cm. When the solute concentration exceeds this value, the solution density is sufficiently different from 1.000, so that ppm and mg/l units are no longer equivalent within experimental error.

Gravimetric method

1. 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.

2. Application

This method may be used to determine density of any water from which the suspended sediment may be satisfactorily removed.

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, a 50-ml pycnometer can be used; it must be calibrated also.

4.2 *Water bath,* constant temperature, 20°C±0.5.

4.3 *Weighing bottle,* 50-ml capacity.

5. Reagents

None.

6. Procedure

6.1 Adjust the temperature of the sample to 20.0°C.

6.2 Transfer exactly 50.0 ml 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

$$\text{Density}=\frac{\text{g sample}}{\text{ml sample}}.$$

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:

$$\frac{\text{Relative density (20°C)}}{\text{Relative density (test temperature in °C)}}.$$

8. Report

Report density to three decimal places in terms of grams per milliliter at 20°C.

9. Precision

No precision data are available for this method, but results are believed reproducible to ±0.005 g/ml.

Fluoride

Unlike chlorides, most fluorides are sparingly soluble and are present in most natural waters in only small amounts. Cacium fluoride (fluorite) is the principal source of fluoride. The element is often characteristic of waters from deep strata and is frequently found in saline water from oil wells and in water from areas that have been subjected to recent vulcanism. Fluorides are used as insecticides, disinfectants, and preservatives. They are seldom found in large quantities in industrial wastes, except as the result of spillage.

Pathological changes in man attributable to fluoride absorption are related to ostosis. Daily intakes of about 15–20 mg of fluoride over a period of several years are required to induce chronic fluorosis in an adult man (California State Water Quality Control Board, 1963). Excessive quantities in drinking water during calcification may cause discoloration in the teeth of children; adults are not affected. Available evidence indicates that water containing less than 1.0 mg/l of fluoride seldom causes mottling of children's teeth, and the literature describing the beneficial effect of 1.0–1.5 mg/l in drinking water as an aid in the reduction of tooth decay in children is abundant. The U.S. Public Health Service (1962) states:

> When fluoride is naturally present in drinking water, the concentration should not average more than the appropriate upper limit in Table I. Presence of fluoride in average concentrations greater than two times the optimum values in Table I shall constitute grounds for rejection of the supply.
>
> Where fluoridation (supplementation of fluoride in drinking water) is practiced, the average fluoride concentration shall be kept within the upper and lower control limits in Table I.

[From U.S. Public Health Service, 1962, table 1, p. 8]

Annual average of maximum daily air temperatures[1] [°F]	Recommended control limits—Fluoride concentrations in mg/l		
	Lower	Optimum	Upper
50.0–53.7	0.9	1.2	1.7
50.8–58.3	.8	1.1	1.5
58.4–63.8	.8	1.0	1.3
63.9–70.6	.7	.9	1.2
70.7–79.2	.7	.8	1.0
79.3–90.5	.6	.7	.8

[1] Based on temperature data obtained for a minimum of 5 years.

Manufacturers of products for internal consumption generally limit the fluoride content of water to about 1.0 mg/l. In normal concentrations it is not significant in irrigation; it is generally concluded that the fluoride content of irrigation water has no consistent influence on the fluoride content of plants. The effect of fluoride on livestock is similar to that on humans (California State Water Quality Control Board, 1963).

Zirconium-Eriochrome Cyanine R method

1. Summary of method

The Zirconium-Eriochrome Cyanine R method is a modified version of the procedure of Megregian (1954).

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.

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.

The method includes a distillation step for the elimination of 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.

2. Application

Samples containing from 0.0 to 3.0 mg of fluoride per liter may be analyzed by this method. Higher concentrations must be reduced by dilution.

3. Interferences

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 gives a positive interference which is eliminated by allowing the solution to stand for at least 2 hr before making color comparison. Up to 10 mg/l of aluminum can be tolerated.

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.

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 iron, zinc, lead, cyanide, and phosphate cause no appreciable interference if the sample is allowed to stand overnight.

The determination shows "salt effect"; the sensitivity is depressed by 5–10 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 Hellige scale is equivalent to an absorbancy 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.

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. 12).

4.2 *Spectrophotometer*, Beckman Model B, or equivalent.

With this instrument the following operating conditions have been used:

Wavelength	540 nm.
Cells	40 mm.
Phototube	Blue-sensitive.
Blank	Demineralized water plus reagents.
Initial sensitivity setting	3.
Slit width (approximate)	0.3 mm.

With these operating conditions the following absorbances have been observed:

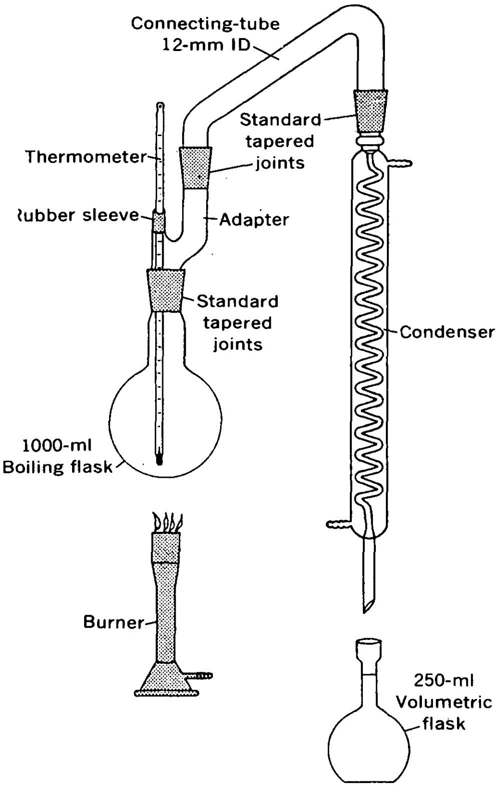

Figure 12.—Distillation apparatus.

F^{-1} (*mg*)	*Absorbance*
0.00	1.50
.01	1.15
.02	.82
.03	.56

5. Reagents

5.1 *Eriochrome Cyanine R* solution: 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. With other products, a precipitate sometimes forms when the indicator solution is prepared.

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 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. The solution is consumed rapidly, and a larger volume is normally prepared.

5.6 *Silver sulfate,* powder.

5.7 *Stannous chloride* solution: Dissolve 1 g $SnCl_2{\cdot}2H_2O$ in 10 ml concentrated HCl (sp gr 1.19) and dilute to 50 ml.

5.8 *Sulfuric acid,* concentrated (sp gr 1.84).

5.9 *Zirconyl nitrate* solution: Dissolve 0.49 g $ZrO(NO_3)_2{\cdot}2H_2O$ in 200 ml 6*M* HCl.

6. Procedure

6.A *Distillation*

In the absence of color or other interfering substances the distillation may be omitted.

6.A.1 Place 400 ml distilled water in a 1-liter 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.A.2 Cool to room temperature.

6.A.3 *Cautiously,* and with constant swirling, add 250 ml sample to the acid mixture in the distillation flask.

6.A.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 the proportion of 5 μg/mg of choride.

6.B *Colorimetric procedure*

6.B.1 Pipet a volume of sample or a volume of the cooled distillate (step 6.A.4) containing less than 0.03 mg F^{-1} (10.0 ml maximum) into a 50-ml centrifuge tube or test tube.

6.B.2 Prepare a blank and sufficient standards, and adjust the volumes to 10.0 ml.

6.B.3 If chromate, residual chlorine, or other strong oxidizing agents are present in the sample, add 0.1 ml 2-percent $SnCl_2$ and let the solution stand for 10 min.

6.B.4 Add 25.0 ml mixed indicator solution.

6.B.5 Allow the solution to stand overnight for barium sulfate to settle.

6.B.6 Decant approximately 25 ml clear supernatant solution, taking care not to disturb the precipitate.

6.B.7 Determine the absorbance of the test sample and standards against the blank, and when necessary make correction for water color.

7. Calculations

7.1 Determine mg F^{-1} in sample from a plot of absorbances of standards.

7.2 F^{-1} in mg/l

$$=\frac{1,000}{\text{ml sample}}\times \text{mg } F^{-1} \text{ in sample.}$$

8. Report

Report F^{-1} concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

Analysis of a test sample by 15 laboratories resulted in a mean value of 1.05 mg/l and a standard deviation of 0.080 mg/l.

Ion-selective electrode method

1. Summary of method

Fluoride is determined potentiometrically in a buffered sample using 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).

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), F^{-1} (0.001M)/LaF_3/test solution/SCE.

2. Application

This method is applicable to the measurement of fluoride in finished waters, natural waters, brines, and industrial waste waters. Concentrations of at least 0.1 mg/l can be determined with confidence.

3. Interferences

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.

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.

Several polyvalent cations capable of complexing fluoride ion interfere. These include Fe^{+3} and Al^{+3}, and possibly 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 citrate in the buffer solution complexes up to at least 5.0 mg of Fe^{+3} per liter, displacing any bound fluoride. The citrate is not effective in displacing the fluoride complexed with Al^{+3}, however, and Al^{+3} concentrations of as little as 0.2 mg/l will cause a significant error in the determination (Harwood, 1969).

Phosphate, at concentrations as high as 10.0 mg/l, and sulfate and chloride, as high as 3,000 mg/l, do not interfere (Harwood, 1969).

4. Apparatus

4.1 *Fluoride-ion 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 5.0–5.5: To approximately 500 ml demineralized water in a 1-liter beaker add 57 ml glacial $HC_2H_3O_2$, 58 g sodium chloride, and 0.30 g sodium citrate. Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5*M* sodium hydroxide (about 150 ml will be required). Dilute to 1 liter 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 mg/l F^{-1} in each sample.

8. Report

Report F^{-1} concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

No precision data are available.

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Hardness

Hardness of water is the property attributable to the presence of alkaline earths. Calcium and magnesium are the principal alkaline earths in natural waters, whereas strontium and barium are usually present only in small quantities.

Water hardness results from the solution of alkaline-earth minerals from the soil and rocks and from direct pollution by wastes. Calcium and magnesium carbonates (limestone and dolomite) are prevalent in the earth's crust but are only sparingly soluble in pure water. Water that contains carbon dioxide or other acidic constituents readily dissolves carbonate minerals; in the presence of carbon dioxide, the carbonates are converted to the more soluble bicarbonates

$$CaCO_3+CO_2+H_2O \rightarrow Ca(HCO_3)_2.$$

Many waters with a hardness of less than 200–300 mg/l may derive practically all of their alkaline earths from carbonate rocks.

Gypsiferous shale and evaporites often contain large quantities of more soluble sulfates and chlorides of calcium and magnesium, and waters that traverse these deposits may have a hardness of several hundred mg/l or more.

Water is classified with respect to hardness according to the following table, in terms of the amount of calcium carbonate or its equivalent:

Hardness (*mg/l* $CaCO_3$)	*Classification*
0–60	Soft.
61–120	Moderately hard.
121–180	Hard.
More than 180	Very hard.

Hard water is not generally believed to have harmful effects on man, although the relation to urinary concretions is controversial. Hard water decreases the sensitivity of fish to toxic metals (California State Water Quality Control Board, 1963), but experiments with calves and chicks have indicated that those supplied with hard water develop somewhat better than those supplied with distilled water.

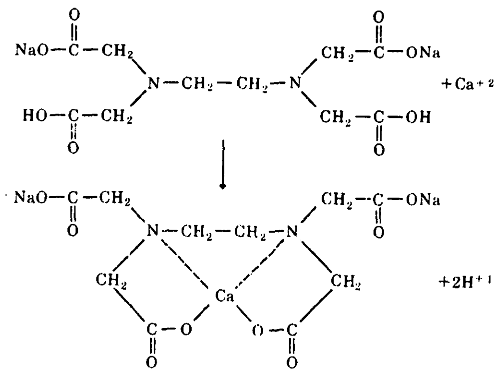
Hardness in conjunction with other chemical properties, such as acidity and other polyvalent cations, is an indication of the soap-consuming power of the water. Soap will not cleanse or lather until these constituents have either been neutralized or precipitated as insoluble salts of the fatty acids. Hard water is recognized by the curd formed with soap. Carbonates and some sulfates of the alkaline earths are sparingly soluble and tend to precipitate on evaporation; heating converts bicarbonate to carbonate, which precipitates calcium and magnesium carbonate in boilers, pipes, and cooking vessels. Calcium sulfate and silica may compose a portion of many incrustations found in home and industrial plumbing installations.

Hardness limitations for water used in steam generation are very exacting and only 2 mg/l or less is generally considered permissible in feed water for boilers operating at 400 psi or more. The tolerances of process water differ from one industry to another and range from less than 10 to several hundred mg/l (California State Water Quality Control Board, 1963). Hard water is usually superior to soft water for irrigation.

Complexometric method

1. Summary of method

Disodium dihydrogen ethylenediamine tetraacetate (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:



All alkaline earths titrate approximately stoichiometrically. The titration should proceed immediately upon addition of the indicator, as the color of the solution will fade upon standing. The optimum pH of the titration is 10.4 or above. Because all alkaline-earth elements are titrated, the value obtained is reported as total hardness.

Additional information on the principle of the determination is given by Goetz, Loomis, and Diehl (1950) and Botha and Webb (1952).

2. Application

The 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.

3. Interferences

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 metal concentrations as high as 10 mg/l of iron, copper, zinc, or lead.

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.

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 hr before weighing, in approximately 600 ml demineralized water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 ml.

5.3 *Eriochrome Black T indicator* solution: Dissolve 0.40 g Eriochrome Black T in 100 ml demineralized water and dilute to 1 liter 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: Dissolve 30 g $NH_2OH{\cdot}HCl$ in demineralized water and dilute to 1 liter.

5.5 *Potassium ferrocyanide,* crystals.

5.6 *Sodium cyanide* solution (CAUTION: NaCN is a deadly poison, and the reagent solution must be so marked): Dissolve 2.5 g NaCN in demineralized water and dilute to 100 ml.

5.7 Na_2*EDTA* standard solution, 1.00 ml ≈ 1.00 mg $CaCO_3$: Dissolve 3.72 g Na_2EDTA, which has been 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 25.00 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 (50.00 ml maximum) into a 150-ml beaker, and adjust the volume to approximately 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 $K_4Fe(CN)_6{\cdot}3H_2O$. 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

Hardness, as $CaCO_3$, in mg/l

$$=\frac{1{,}000}{\text{ml sample}}\times \text{ml titrant.}$$

8. Report

Report hardness as follows: Less than 10 mg/l, whole numbers; 10 mg/l and above, two significant figures.

9. Precision

Analysis of a test sample by eight laboratories resulted in a mean value of 42.2 mg/l and a standard deviation of 1.2 mg/l.

Calculation method

1. 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.

2. Application

This method may be used to calculate hardness for any sample for which determined values for barium, calcium, strontium, and magnesium are available.

3. Interferences

None.

4. Apparatus

None.

5. Reagents

None.

6. Procedure

None.

7. Calculations

Hardness, as $CaCO_3$, in mg/l $=(\Sigma$ me/l $Ca+Mg+Ba+Sr)\times 50.05$.

8. Report

Report hardness, as $CaCO_3$, as follows: Less than 10 mg/l, whole numbers; 10 mg/l and above, two significant figures.

9. Precision

No precision data are available, but results are believed as reproducible as those of the individual determinations.

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: Inst. Water Engineers Jour., v. 6.

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 197.

Goetz, C. A., Loomis, T. C., and Diehl, Harvey, 1950, Total hardness in water—the stability of standard disodium dihydrogen ethylenediamine tetraacetate solutions: Anal. Chemistry, v. 22, p. 798.

Hardness, carbonate and noncarbonate

That fraction of hardness which is equivalent to the alkalinity is called carbonate hardness, and any excess is called noncarbonate hardness. The presence of noncarbonate hardness indicates that a portion of the hardness is due to alkaline-earth salts other than carbonates and bicarbonates. When the alkalinity equals or exceeds the hardness, all of the hardness is caused by alkaline-earth carbonate and bicarbonate salts. These terms approximate the terms "temporary" and "permanent" hardness, which are based on the fact that upon boiling hard water the bicarbonate is decomposed, and most of the calcium corresponding to the bicarbonate is precipitated as calcium carbonate. The consumption of soap is normally the same whether the hardness is carbonate or noncarbonate.

Calculation method

1. Summary of method

Carbonate and noncarbonate hardness are computed from the hardness and alkalinity determinations. 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, carbonate and noncarbonate hardness of the mixture must be computed from the average hardness and average alkalinity and not by averaging the noncarbonate hardnesses of the individual samples.

2. Application

This method may be used to compute carbonate and noncarbonate hardness for any water for which determined values are available for hardness and alkalinity.

3. Interferences

None.

4. Apparatus

None.

5. Reagents

None.

6. Procedure

None.

7. Calculations

7.1 Carbonate hardness, as $CaCO_3$, in mg/l=alkalinity, as $CaCO_3$, in mg/l.

7.2 Noncarbonate hardness, as $CaCO_3$, in mg/l=50.05(me/l hardness−me/l alkalinity).

8. Report

Report carbonate and noncarbonate hardness, as $CaCO_3$, as follows: Less than 10 mg/l, whole numbers; 10 mg/l and above, two significant figures.

9. Precision

No precision data are available, but reproducibility should be comparable to that of the individual determinations.

Iodide

Iodide, like bromide, is a minor constituent in the earth's crust and is normally present in natural waters in only minute quantities. Measurable amounts may be found in streams that receive industrial wastes, and some natural brines contain rather high concentrations.

Bromine oxidation method

1. Summary of method

Iodide in a buffered solution is oxidized with bromine to iodate, and the excess bromine is subsequently removed with sodium formate (Kolthoff and Sandell, 1952)

$$I^{-1}+3Br_2+3H_2O \rightarrow IO_3^{-1}+6HBr.$$

Iodine equivalent to the iodate is then liberated by addition of potassium iodide to an acid solution

$$IO_3^{-1}+5I^{-1}+6H^{+1} \rightarrow 3I_2+3H_2O.$$

The liberated iodine is then titrated with standard thiosulfate, using starch as the indicator.

$$I_2+2S_2O_3^{-2} \rightarrow S_4O_6^{-2}+2I^{-1}.$$

2. Application

This method may be applied to any natural or treated water from which interfering substances have been removed.

3. Interferences

Iron, manganese, and organic material interfere with the basic reactions of the method, but their interference can be prevented by preliminary treatment with calcium oxide.

4. Apparatus

4.1 *Buret,* 10-ml.

4.2 *Iodine flasks.*

5. Reagents

5.1 *Acetic acid,* 2.25*M*: Mix 125 ml glacial $HC_2H_3O_2$ (sp gr 1.049) with water and dilute to 1 liter.

5.2 *Bromine water,* saturated: Add to approximately 250 ml water slightly more liquid Br_2 than will dissolve when shaken.

Store in a glass-stoppered actinic-glass bottle.

5.3 *Calcium oxide,* anhydrous powder.

5.4 *Methyl red indicator* solution: Dissolve 0.01 g water-soluble methyl red in 100 ml water.

5.5 *Potassium fluoride,* $KF \cdot 2H_2O$, 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 2–3 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.

5.7 *Sodium acetate* solution: Dissolve 273.5 g $NaC_2H_3O_2 \cdot 3H_2O$ in water and dilute to 1 liter.

5.8 *Sodium formate*: Dissolve 50 g $NaCHO_2$ in hot water and dilute to 100 ml. Prepare fresh daily.

5.9 *Sodium thiosulfate* standard solution I, 0.1*N*: Dissolve 25 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.

5.10 *Sodium thiosulfate* standard solution II, 0.010*N*: Dilute 100.0 ml sodium thiosulfate standard solution I to 950 ml with carbon-dioxide-free water and standardize against KIO_3 as follows: Dry approximately 0.5 g KIO_3 for 2 hr at 180°C. Dissolve 0.3567 g in water and dilute to 1,000 ml. Pipet 25.00 ml of the KIO_3 into a 250-ml iodine flask, then add successively 75 ml 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 $Na_2S_2O_3$ using 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,* stable.

5.12 *Sulfuric acid,* 3.6*M*: Mix 200 ml concentrated H_2SO_4 (sp gr 1.84) with demineralized water and dilute to 1 liter.

6. Procedure

6.1 Remove soluble iron, manganese, and organic matter by adding a slight excess of CaO to approximately 400 ml of sample, shake, let stand about 1 hr, and filter through dry 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 maximum) into a 250-ml iodine 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 barely acidify with 3.6*M* H_2SO_4.

6.5 Add 15.0 ml $NaC_2H_3O_2$ solution and 5.0 ml 2.25*M* $HC_2H_3O_2$.

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 $NaCHO_2$ 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, in order, 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 $Na_2S_2O_3$ standard solution II, adding 2-3 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

$$I^{-1} \text{ in mg/l} = \frac{1{,}000}{\text{ml sample}} \times 21.15$$

$$\times [(\text{ml titrant} - \text{ml blank}) \times N],$$

where

N=normality of thiosulfate.

8. Report

Report I^{-1} concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

No precision data are available.

Ceric-arsenious oxidation method

1. 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 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).

2. Application

This method may be used to determine iodide in fresh waters and brines containing from 0.0 to 0.06 mg of iodide per liter. Higher concentrations must be reduced by dilution.

3. Interferences

Most substances normally present in natural water do not interfere.

Low values for I^{-1} may result if the reaction test tubes are not thoroughly clean. Rinsing each sample tube with HCl removes possible contaminants.

Bromide ion does not interfere, and any substance which oxidizes iodide to iodine has no effect on the reaction.

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 *Spectrophotometer,* Beckman Model B, or equivalent.

With this instrument the following operating conditions have been used:

Wavelength	450 nm.
Cells	23 mm.
Phototube	Blue-sensitive.
Initial sensitivity setting	1.
Slit width	0.3 mm.
Blank	Demineralized water.

With these operating conditions the following ratios have been observed:

I^{-1} *(mg)*	*Ratio* $\frac{A_s}{A_o}$
0.0000	1.00
.0002	.57
.0004	.32
.0006	.18
.0008	.11
.0010	.059
.0012	.030

where

A_s=absorbance of standard, and

A_o=absorbance of standard containing no iodide.

5. Reagents

5.1 *Arsenious acid* standard solution, $0.3N$ H_3AsO_3: Add 14.84 g As_2O_3 to 500 ml demineralized wather in a 1,000-ml beaker. Next, add slowly 28 ml concentrated H_2SO_4 (sp gr 1.84), and warm the mixture until the As_2O_3 is dissolved. Cool, transfer to a 1-liter volumetric flask, and dilute to 1,000 ml with demineralized water. Add a small piece of metallic arsenic to stabilize the solution.

5.2 *Ceric sulfate* standard solution, $0.1N$ $Ce(HSO_4)_4$: Dissolve 52.80 g anhydrous $Ce(HSO_4)_4$ in 600 ml $5N$ H_2SO_4 contained in a 1-liter beaker. Warm the mixture and stir occasionally, until a clear solution is obtained (1 hr). When cool, transfer to a 1.0-liter volumetric flask and dilute to volume with $5N$ H_2SO_4.

5.3 *Iodide* standard solution I, 1.00 ml=0.01 mg I^{-1}: Dissolve 0.0131 g KI, 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: Dissolve 0.10 g $AgNO_3$ in 1 liter demineralized water. Store in a dark bottle.

6. Procedure

6.1 Pipet samples containing less than 0.0012 mg I^{-1} (20.0 ml maximum) into 23-mm absorption cells.

6.2 Prepare a series of standards containing from 0.0000 to 0.0012 mg I^{-1} in 23-mm absorption cells.

6.3 Dilute samples and standards to 20.0 ml, and add 0.50 ml concentrated H_2SO_4 to each tube and mix.

6.4 Add 1.0 ml H_3AsO_3 standard solution to each tube and mix.

6.5 Place all tubes in a constant temperature bath at 30°C. Allow 30–45 min for tubes to reach 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.

6.8 Measure the absorbance of standards and samples against a demineralized-water blank.

7. Calculations

7.1 Construct an analytical curve by plotting the ratio A_s/A_o against mg I^{-1} on semilog paper (A_s=absorbance of standard and A_o=absorbance of standard containing no iodide).

7.2 From the curve, determine mg I^{-1} corresponding to the absorbance ratio obtained for each sample.

8. Report

Report I^{-1} concentrations as follows: Less than 0.1 mg/l, three decimals; 0.1 mg/l and above, two significant figures.

9. Precision

No precision data are available.

References

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis [3d ed.]: New York, Macmillan Co., p. 585.

Mitchell, C. G., 1966, Semimicroanalytical method for the determination of iodide in water: U.S. Geol. Survey Water-Supply Paper 1822, p. 77.

Iron

Iron is one of the most abundant metals in the earth's crust. It occurs in the dark-colored silicate minerals of igneous rocks and as sulfides and oxides. In sandstone, iron oxide and iron hydroxide are often present as cementing materials. Iron is also present as oxides and sulfides in shale. Some of the common humic complexes causing color in water may also be iron bearing.

Because iron is readily precipitated as the hydroxide, it is seldom one of the major constituents in water. The metal occurs in water in both the ferrous and ferric states. Ferrous iron in solution is unstable in the presence of oxygen

$$2Fe^{+2}+4HCO_3^{-1}+H_2O+\tfrac{1}{2}O_2 \rightarrow 2Fe(OH)_3+4CO_2.$$

If the sample is subjected to a strong reducing environment the reaction is reversed, and the solution may contain large quantities of ferrous iron. The solubility of iron in natural water is governed by pH, redox potential (Eh), and concentrations of bicarbonate and sulfide (Hem and Cropper, 1959; Hem, 1960a, 1960b). Colloidal particles of ferric hydroxide may be present in some waters.

Concentrations greater than 1 mg of iron per liter are rare in alkaline surface water. However, higher concentrations are common in ground water and acid surface water.

Iron in concentrations much greater than 0.20 mg/l is objectionable in waters for public supply. The U.S. Public Health Service (1962) recommends that the concentration of iron in drinking and culinary water on carriers subject to Federal quarantine regulations not exceed 0.3 mg/l. This limit is based not on toxicity, but on esthetic and taste considerations. Iron tends to stain laundry and porcelain, and it can be tasted in concentrations higher than about 0.5–1.0 mg/l. Livestock is sensitive to the taste of iron and may not drink water with a high iron content. Ninety-five percent of the waters that support good fish fauna in the United States have 0.7 mg/l or less of iron (Ellis, 1937).

Industries' tolerance for iron varies, but concentrations exceeding 0.1 mg/l are generally not satisfactory (California State Water Quality Control Board, 1963). It has been established that iron in irrigation water is of no practical significance to plant growth or soil texture.

The category "iron" includes ferric and ferrous iron in the ionized form and in suspension as the colloidal hydroxide; they are discussed in "Iron, Ferrous and Ferric." In all probability the iron bound in the common humic complexes is also determined. In the procedures given, iron is determined by the atomic-absorption procedure or by the bipyridine-reduction procedure. Ferrous iron is determined by the bipyridine procedure without reduction, and ferric iron by difference.

Atomic-absorption method—direct

1. Summary of method

Iron is determined by atomic-absorption spectrophotometry. The sample is aspirated directly with no pretreatment other than filtration or dilution as required.

2. Application

Samples containing between 0.10 and 1.0 mg of iron per liter may be analyzed by this method. Higher concentrations must either be reduced by dilution or less scale expansion used.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	248.3 (2483A).
Slit	3.
Lamp current	30 ma.
Scale expansion	10×.
Source (shielded hollow-cathode lamp)	Fe.
Response time control	1.
Burner	Boling.
Air pressure	28 psi; 7.5 on flowmeter.
Acetylene pressure	8 psi; 9 on flowmeter.

With these operating conditions the following readings have been observed:

Iron concentration (mg/l)	*Scale reading*
0.10	7.0
.25	17.4
.50	35.0
1.00	69.8

5. Reagents

5.1 *Iron* standard solution I, 1.00 ml=0.100 mg Fe: Weigh out 0.100 g 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.

5.2 *Iron* standard solution II, 1.00 ml=0.001 mg Fe: Dilute 10.00 ml iron standard solution I and 1 ml concentrated HCl to 1,000 ml with demineralized water. Dilutions of this standard are used to prepare working curves at time of analysis.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Filter the sample (0.45-μm membrane filter) when necessary to avoid clogging the atomizer-burner.

6.2 Aspirate and record the scale readings of the sample and standards against a demineralized-water blank. Repeat, and average the two values.

7. Calculations

Determine the mg/l Fe in each sample from a plot of scale readings of standards. Because a scale expansion of 10× is used, scale readings need not be converted to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Fe concentrations as follows: Less than 100 µg/l, nearest 10 µg/l; 100 µg/l and above, two significant figures.

9. Precision

Analysis of a test sample by three laboratories using this method resulted in a mean value of 0.390 mg/l and a standard deviation of 0.026 mg/l.

Bipyridine method

1. 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. The color develops immediately and is stable for several hours. The color intensity is independent of pH in the range 3 to 10.

2. Application

The method is applicable to most natural waters containing between 0.05 and 4.0 mg of iron per liter.

3. Interferences

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 and bismuth must be absent. The procedure can be used with undiluted samples for analysis of water having metal concentrations as high as:

	mg/l		*mg/l*
Sb	20	Hg	1
Cd	50	Ni	2
Cr	20	Sn	20
Co	10	W	10
Cu	10	Zn	10

Interfering anions must be limited to the following concentrations:

	mg/l		*mg/l*
CN	10	PO_4	20
CrO_4	20	P_2O_7	20

At 520 nm, the wavelength used in the determination, the natural color of the water contributes a measurable absorbance and must be corrected for if the color exceeds about 50 units. This applies only to the "normal" type of yellow color found in water.

4. Apparatus

Spectrophotometer, Beckman Model B, or equivalent.

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.
Blank	Demineralized water plus reagents.

With these operating conditions the following readings have been observed:

Fe (*mg*)	*Absorbance*
0.0125	0.265
.0250	.540
.0500	1.070
.1000	2.140

5. Reagents

5.1 *Bipyridine* solution: 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). Add 1 g $BeSO_4{\cdot}2H_2O$. Dilute to 1 liter with demineralized water. (CAUTION: Beryllium compounds are toxic and must be handled with care.)

5.3 *Iron* standard solution I, 1.00 ml= 0.400 mg 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.

5.4 *Iron* standard solution II, 1.00 ml= 0.004 mg 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).

5.5 *Sodium acetate* solution: Dissolve 350 g $NaC_2H_3O_2$ in demineralized water and dilute to 1 liter.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet a volume of sample containing less than 0.10 mg Fe (25.00 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 volumes 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 $NaC_2H_3O_2$ solution and mix.

6.6 Determine the absorbances of the sample and standards against the blank and, when necessary, correct for water color as directed in "Part II, Instrumental Techniques," to obtain true sample absorbance.

7. Calculations

7.1 Determine mg Fe in the sample from a plot of absorbances of standards.

7.2 Fe in mg/l

$$=\frac{1,000}{\text{ml sample}}\times\text{mg Fe in sample.}$$

8. Report

Report Fe concentrations as follows: Less than 100 μg/l, nearest 10 μg/l; 100 μg/l and above, two significant figures.

9. Precision

Analysis of a test sample by 17 laboratories using this method indicated a mean of 0.397 mg/l and a standard deviation of 0.0186 mg/l.

References

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3–A, p. 204.

Ellis, M. M., 1937, Detection and measurement of stream pollution: U.S. Dept. Commerce, Bur. Fisheries Bull. 22.

Hem, J. D., 1960a, Restraints on dissolved ferrous iron imposed by bicarbonate, redox potential, and pH: U.S. Geol. Survey Water-Supply Paper 1459–B, p. 33–55.

———1960b, Some chemical relationships among sulfur species and dissolved ferrous iron: U.S. Geol. Survey Water-Supply Paper 1459–C, p. 57–73.

Hem, J. D., and Cropper, W. H., 1959, Survey of ferrous-ferric chemical equilibria and redox potentials: U.S. Geol. Survey Water-Supply Paper 1459–A, p. 1–31.

Moss, M. L., and Mellon, M. G., 1942, Colorimetric determination of iron with 2,2′-bipyridyl and with 2,2′,2″-terpyridyl: Indus. Eng. Chemistry, Anal. Ed., v. 14, p. 862.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 7.

Iron, ferrous and ferric

Bipyridine method

1. Summary of method

This method is identical to that given under "Iron, Bipyridine Method," except that no reductant is added to reduce ferric iron in solution to ferrous.

2. Application

See "Iron, Bipyridine Method."

3. Interferences

See "Iron, Bipyridine Method."

4. Apparatus

See "Iron, Bipyridine Method."

5. Reagents

See "Iron, Bipyridine Method."

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet a volume of sample containing less than 0.1 mg Fe^{+2} (25.00 ml maximum) into a 50-ml beaker, and adjust the volume to 29.0 ml with demineralized water.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volumes to 25.0 ml.

6.3 Add 1.0 ml bipyridine solution to samples, standards, and blank.

6.4 Treat the blank and standards *only* as follows:

(a) Add 2.0 ml hydroxylamine–hydrochloric acid reagent, mix, and allow the solution to stand 30 min.

(b) Add 2.0 ml $NaC_2H_3O_2$ solution and mix.

6.5 Determine the absorbances of the sample and standards against the blank, and when necessary make correction for water color, as directed in "Part II, Instrumental Techniques," to obtain true sample absorbance.

7. Calculations

7.1 Determine mg Fe^{+2} in sample from a plot of absorbances of standards.

7.2 Fe^{+2} in mg/l

$$=\frac{1,000}{\text{ml sample}}\times \text{mg } Fe^{+2} \text{ in sample.}$$

7.3 Fe^{+3} in mg/l=mg/l Fe—mg/l Fe^{+2}.

8. Report

Report Fe^{+2} and Fe^{+3} concentrations as follows: Less than 100μg/l, nearest 10 μg/l; 100 μg/l and above, two significant figures.

9. Precision

Analysis of a test sample by 17 laboratories using this method indicated a mean of 0.3967 mg/l and a standard deviation of 0.0186 mg/l.

Lead

Lead is only a minor element in most natural waters, but industrial or mine and smelter effluents may contain relatively large amounts of lead. Many of the commonly used lead salts are water soluble. Lead acetate is used in printing and dyeing operations; lead chloride and sulfate are used in the manufacture of some paints; lead nitrate is used in photography, dyeing, engraving, and in the manufacture of certain explosives.

Lead is a cumulative poison to humans and animals, but the individual sensitivity differs. Lead does not have to be in solution to be toxic. Reports on human tolerance for lead vary widely, but the U.S. Public Health Service (1962) states that lead shall not exceed 0.05 mg/l in drinking and culinary water on carriers subject to Federal quarantine regulations. The maximum safe concentration for animal watering has been reported to be 0.5 mg/l (Pierse, 1938). Lead toxicity to fish results from a film of coagulated mucus which forms over the gills and causes suffocation. The toxicity to fish is decreased by water hardness; 50 mg/l of calcium has destroyed the toxic effect of 1.0 mg/l lead (Ohio River Valley Water Sanitation Commission, 1950).

Atomic-absorption method—chelation-extraction

1. Summary of method

Lead is determined by atomic-absorption spectrophotometry. The element is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of the spectrophotometer (Fishman and Midgett, 1968).

2. Application

Water containing between 1.0 and 20.0 μg of lead per liter may be analyzed by this procedure; higher concentrations must either be reduced by dilution or less scale expansion used.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	217.0 (2170A).
Slit	4.
Lamp current	30 ma.
Scale expansion	10×.
Source (shielded hollow-cathode lamp)	Pb.
Response time control	1.
Burner	Boling.
Air pressure	28 psi; 6 on flowmeter.
Acetylene pressure	8 psi; 4 on flowmeter.

With these operating conditions the following readings have been observed:

Lead concentration (μg)	*Scale reading*
2.5	6.4
5.0	12.5
10.0	25.4
20.0	48.6

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution: Dissolve 1.0 g

APDC in 100 ml demineralized water. Prepare fresh daily.

5.2 *Bromphenol blue indicator* solution: Dissolve 0.1 g bromphenol blue in 100 ml 50-percent ethanol.

5.3 *Hydrochloric acid,* 0.3*M*: Mix 25.0 ml concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 liter.

5.4 *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 and dilute to 1,000 ml.

5.5 *Lead* standard solution II, 1 ml= 2.00 µg Pb: Dilute 10.0 ml lead standard solution I and 1 ml concentrated HNO_3 to 1,000 ml with demineralized water. This standard is used to prepare working curves at time of analysis.

5.6 *Methyl isobutyl ketone* (MIBK).

5.7 *Sodium hydroxide,* 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 ml.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

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

6.1 Pipet a volume of sample containing less than 2.0 µg Pb (100 ml maximum) into a 200-ml volumetric flask, and adjust volume to approximately 100 ml.

6.2 Prepare a demineralized-water blank and sufficient standards, and adjust the volume of each to approximately 100 ml with demineralized water.

6.3 Add 2 drops bromphenol blue indicator solution.

6.4 Adjust the pH 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 in both the standards and sample. Then add 2.0 ml 0.3*M* HCl in excess. The pH at this point should be 2.4.

6.5 Add 2.5 ml APDC solution and mix. The pH should be approximately 2.8.

6.6 Add 10.0 ml MIBK and shake vigorously for 1 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 Aspirate the ketone layer and record the scale reading for each standard and sample against the blank. Repeat, and average the duplicate results.

7. Calculations

Determine the µg/l Pb in each sample from a plot of scale readings of standards. Since a scale expansion of 10× is used, scale readings need not be converted to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Pb concentrations as follows: Less than 10 µg/l, nearest µg/l; 10 µg/l and above, two significant figures.

9. Precision

No precision data are available.

References

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: Am. Chem. Soc., Advances in Chemistry Ser., no. 73, p. 230.

Ohio River Valley Water Sanitation Commission, 1950, Metal Finishing Industries Action Comm., Subcomm. on Toxicities, Rept. 3.

Pierse, R. R., 1938, Some cases of interest met with in practice—Chronic lead poisoning [in cows]: Veterinary Rec., v. 50, p. 145.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 8.

Lithium

Lithium is present in some minerals but is not abundant in nature. From available information, most fresh waters rarely contain lithium of concentrations exceeding 10 mg/l, but larger quantities may be present in brines and thermal waters. Lithium is used in metallurgy, medicinal water, and some types of glass and storage batteries. Waste from such industries may contain lithium.

Atomic-absorption method—direct

1. Summary of method

Lithium is determined by atomic-absorption spectrophotometry. The sample is aspirated directly with no pretreatment other than filtration or dilution as required (Fishman and Downs, 1966).

2. Application

Fresh waters and brines containing at least 0.005 mg of lithium per liter may be analyzed by this method. Brines must first be diluted to concentrations of 15,000 mg/l or less total dissolved solids.

Three analytical ranges are included: From 1.0 to 10 mg Li per liter, from 0.1 to 1.0 mg/l, and from 0.00 to 0.25 mg/l.

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 mg/l.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Lithium concentration range: 1.0–10 mg/l

Grating	Visible.
Wavelength	335.4 (6708A).
Slit	5.
Lamp current	20 ma.
Scale expansion	1×.
Source (hollow-cathode lamp)	Li.
Response time control	1.
Burner	Standard "303."
Air pressure	28 psi; 9.0 on flowmeter.
Acetylene pressure	8 psi; 9.0 on flowmeter.

With these operating conditions the following readings have been observed:

Lithium concentration (mg/l)	*Absorption (percent)*
2.0	28.0
4.0	47.8
6.0	59.6
8.0	67.4
10.0	73.5

Lithium concentration range: 0.1–1.0 mg/l

Scale expansion	5×.

All other operating conditions the same as used for concentration range of 1.0 to 10 mg lithium per liter.

With these operating conditions the following readings have been observed:

Lithium concentration (mg/l)	*Scale reading*
0.25	18.5
.50	37.2
.75	54.0
1.0	74.2

Lithium concentration range: 0.00–0.25 mg/l

Scale expansion	10×.
Burner	Boling.
Air pressure	28 psi; 7.5 on flowmeter.
Acetylene pressure	8 psi; 9.0 on flowmeter.

All other operating conditions the same as used for concentration range of 1.0 to 10 mg lithium per liter.

With these operating conditions the following readings have been observed:

Lithium concentration (mg/l)	*Scale reading*
0.01	2.5
.10	26.0
.25	62.5

5. Reagents

5.1 *Lithium* standard solution I, 1.00 ml =1.00 mg Li: Dissolve 9.9357 g $LiNO_3$ in demineralized water and dilute to 1,000 ml.

5.2 *Lithium* standard solution II, 1.00 ml=0.010 mg 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.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Filter the sample (0.45-µm membrane filter) when necessary to prevent clogging the atomizer-burner.

6.2 Aspirate and record the scale reading of the sample and standards against a demineralized-water blank. Repeat, and average the two values. If the lithium concentration is greater than 10 mg/l, the sample must be diluted.

7. Calculations

7.1 Concentration range 1.0–10 mg

lithium per liter: Convert percent absorption to absorbance, and determine the mg/l lithium in the sample from a plot of absorbances of standards. For samples containing more than 10 mg lithium per liter, multiply by proper dilution factor.

7.2 Concentration ranges 0.10–1.0 mg lithium per liter and 0.00–0.25 mg lithium per liter: Determine the mg/l lithium in the sample from a plot of scale readings of standards. Because scale expansions of 5× and 10× are used, scale readings need not be converted to absorbances.

8. Report

Report Li concentrations as follows: Less than 100 μg/l, nearest 10 μg/l; 100 μg/l and above, two significant figures.

9. Precision

Analysis of a test sample by 18 laboratories using this method resulted in a mean value of 0.484 mg/l and a standard deviation of 0.025 mg/l.

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geol. Survey Water-Supply Paper 1540–C, p. 30–32.

Loss on ignition

The loss of weight on ignition of residue on evaporation is frequently taken as a measure of the organic matter in the water. By subtracting loss on ignition from the residue on evaporation a value for the so-called fixed residue is obtained. For some waters, the loss on ignition may be chiefly water that was not removed by drying at 180°C. In the majority of samples, the only value of the determination is to afford a check on the residue on evaporation and provide another reference point for comparison of the calculated dissolved solids. This latter value should lie somewhere between residue on evaporation and residue after ignition (Collins, 1928).

Gravimetric method

1. Summary of method

A measured volume of sample is evaporated to dryness at 180°C to determine the residue on evaporation. This residue is then strongly heated and reweighed, the difference in weight being termed loss on ignition.

2. Application

This method may be applied to all natural and treated waters.

3. Interferences

None of the substances commonly occurring in natural waters interferes with this method.

4. Apparatus

4.1 *Desiccator,* charged with indicating silica gel or other efficient desiccant.

4.2 *Muffle furnace,* 600°C.

4.3 *Platinum dish,* 100-ml capacity.

5. Reagents

None.

6. Procedure

6.1 Determine the dissolved solids.

6.2 Place the weighed platinum dish containing the evaporated (180°) residue in a muffle furnace at 600°C and heat for 1 hr.

6.3 Remove, and cool in a desiccator. Weigh and record the weight to the nearest 0.1 mg.

7. Calculations

Loss on ignition in mg/l

$$=\frac{1{,}000}{\text{ml sample}}\times[\text{mg}(ER)-\text{mg}(IR)],$$

where

ER=weight of evaporated residue, grams and

IR=weight of ignited residue, grams.

8. Report

Report loss on ignition as follows: Less than 1,000 mg/l, whole numbers; 1,000 mg/l and above, three significant figures.

9. Precision

No precision data are available.

Reference

Collins, W. D., 1928, Notes on practical water analysis: U.S. Geol. Survey Water-Supply Paper 596–H, p. 247.

Magnesium

Magnesium is relatively abundant in the earth's crust. Ferromagnesian minerals in igneous rocks and magnesium carbonate in carbonate rocks are generally considered to be the principal sources of magnesium in natural waters. Carbon dioxide plays an important role in the solution of magnesium from both silicate and carbonate minerals. Water associated with granite and siliceous sand may contain less than 5 mg/l of magnesium, but water from dolomite or limestone rich in magnesium may contain 10–50 mg/l. Sulfates and chlorides of magnesium are very soluble, and water in contact with such deposits may contain several hundred mg per liter. Magnesium is widely used in industry, and some industrial wastes add appreciable quantities to streams and ground water.

It is believed that water cannot contain toxic quantities of magnesium and remain potable. Magnesium salts act as cathartics and diuretics. High concentrations of magnesium may cause scouring diseases among livestock, but less than 5,000 mg/l is reported to be harmless to cattle that have become accustomed to it (Frens, 1948).

Magnesium imparts the property of hardness to water and is therefore of concern to industrial users of water. Magnesium acts similarly to calcium in that it flocculates soil colloids and tends to maintain good soil structure and permeability, hence it complements calcium in consideration of sodium ratios in irrigation water.

Calculation method

1. Summary of method

The milliequivalents per liter of hardness (Ca + Mg) is first determined by complexometric titration ("Hardness, Complexometric Method"). The milliequivalents per liter of calcium is then determined by a similar titration ("Calcium, Complexometric Method") and subtracted to determine the magnesium concentration.

2. Application

The calculation method is applicable to all waters on which satisfactory complexometric calcium and hardness determinations can be made.

3. Interferences

Strontium does not interfere, because it will normally be included in both the hardness and the calcium titrations. Barium will interfere, and when it is present in significant amounts, the magnesium should be determined by atomic-absorption spectrophotometry or by a suitable gravimetric method.

4. Apparatus

See "Calcium and Hardness, Complexometric Methods."

5. Reagents

See "Calcium and Hardness, Complexometric Methods."

6. Procedure

See "Calcium and Hardness, Complexometric Methods."

7. Calculations

7.1 Hardness in me/l

$$=\frac{1{,}000}{\text{ml hardness sample}}\times \text{ml titrant}\times 0.01998.$$

7.2 Ca in me/l

$$=\frac{1{,}000}{\text{ml Ca sample}}\times(\text{ml titrant}-\text{ml blank})\times 0.5\times 0.0499.$$

7.3 Mg in mg/l

$$=12.16\times(\text{me/l hardness}-\text{me/l Ca}).$$

8. Report

Report Mg concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

Analysis of a test sample by 12 laboratries using this method resulted in a mean value of 2.20 mg/l and a standard deviation of 0.19 mg/l.

Atomic-absorption method—direct

1. Summary of method

Magnesium is determined by atomic-absorption spectrophotometry. Lanthanum chloride is added to mask interferences (Fishman and Downs, 1966).

2. Application

Most natural waters containing at least 0.05 mg of magnesium per liter may be analyzed by this method.

Two analytical ranges are included: from 0.0 to 2.0 mg Mg per liter, and from 1.0 to 50 mg/l.

3. Interferences

The interference caused by aluminum at concentrations greater than 2 mg/l is masked by addition of lanthanum. Since low magnesium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute hydrochloric acid. Sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/l.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Magnesium concentration range: 0.0–2.0 mg/l

Grating	Ultraviolet.
Wavelength counter	285.2 (2852A).
Slit	5.
Lamp current	10 ma.
Scale expansion	1×.
Source (hollow-cathode lamp)	Mg.
Response time control	1.
Burner	Standard "303."
Air pressure	28 psi; 8.0 on flowmeter.
Acetylene pressure	8 psi; 9.0 on flowmeter.

With these operating conditions the following readings have been observed:

Magnesium concentration (mg/l)	*Absorption (percent)*
0.5	20.2
1.0	35.6
1.5	48.3
2.0	58.8

Magnesium concentration range: 1.0–50 mg/l

Burner	"290," rotated 90°.
Air pressure	28 psi; 6.0 on flowmeter.
Acetylene pressure	8 psi; 6.5 on flowmeter.

All other operating conditions are the same as used for concentration range 0.0–2.0 mg/l.

With these operating conditions the following readings have been observed:

Magnesium concentration (mg/l)	*Absorption (percent)*
1.0	5.7
5.0	24.1
10	41.5
25	71.9
50	89.4

5. Reagents

5.1 *Lanthanum chloride* solution: Dissolve 29 g La_2O_3, slowly and in small portions, in 250 ml concentrated HCl (CAUTION: Reaction is violent), and 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 solution: Prepare a series of standard solutions containing from 0 to 50 mg magnesium per liter by diluting magnesium standard soluation I. To each standard working solution, add 1.0 ml and $LaCl_3$ solution for each 10 ml of standard.

6. Procedure

6.1 Filter the sample (0.45-μm membrane filter) when necessary to avoid clogging the atomizer-burner.

6.2 Add 1.0 ml lanthanum chloride solution to 10.0 ml of sample and demineralized-water blank.

6.3 Aspirate and record the percent absorption of the sample and standards against the blank. Repeat, and average the two values. If the magnesium concentration is greater than 50 mg/l, the sample must be diluted.

7. Calculations

Convert percent absorption to absorbance, and determine the mg/l magnesium 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 Mg concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

Analysis of a test sample by 18 laboratories using this method resulted in a mean value of 2.1 mg/l and a standard deviation of 0.32 mg/l.

References

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geol. Survey Water-Supply Paper 1540-C, p. 32-34.

Frens, A. M., 1948, Salt drinking water for cows: Water Pollution Abs. 21.

Manganese

Manganese dissolved in natural water is in the divalent state. Divalent, tervalent, and tetravalent manganese species occur widely in rocks and soils. The solubility of manganese in natural water is largely a function of pH and redox potential (Eh). Reduced manganese species are relatively soluble in aerated water at near neutral pH, but may be oxidized and precipitated by relatively small changes in Eh and pH (Hem, 1963). Thus, manganese oxides may be precipitated in bottom muds of lakes and reservoirs when the water is relatively oxidizing, and be released to solution later if the water near the bottom becomes depleted in oxygen.

Waters containing less than 0.1 mg/l seldom prove troublesome as public supplies, but those containing more than 0.5 mg/l may form objectionable deposits on cooked food, laundry, and plumbing fixtures. In concentrations that do not cause unpleasant taste, manganese is not regarded to be toxicologically significant. The U.S. Public Health Service (1962) recommends that the concentration of manganese not exceed 0.05 mg/l in drinking and culinary water on carriers subject to Federal quarantine regulations.

Tolerances for manganese in industrial water supplies are generally very low (less than 0.2 mg/l), particularly for textile dyeing, food processing, distilling and brewing, paper, plastics, and photography. Manganese stimulates the growth of *Crenothrix* and similar organisms that are troublesome in wells and water-supply systems. Crop tolerances to manganese differ widely; concentrations ranging from 0.5 to 500 mg/l have been reported to be harmful (California State Water Quality Control Board, 1963).

Atomic-absorption method—direct

1. Summary of method

Manganese is determined by atomic-absorption spectrophotometry. The sample is aspirated directly with no pretreatment other than filtration or dilution as required (Fishman and Downs, 1966).

2. Application

Water containing at least 0.05 mg of manganese per liter may be analyzed by this method. Samples containing more than 0.50 mg/l must first be diluted or less scale expansion used.

3. Interferences

Iron in excess of 25 mg/l or magnesium in excess of 100 mg/l may present some interference, especially when the manganese concentration exceeds 0.50 mg/l. Other cations and anions found in water do not interfere.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	279.5 (2795A).
Slit	4.
Lamp current	10-15 ma.
Scale expansion	10×.
Source (hollow-cathode lamp)	Mn.
Response time control	1.
Burner	Boling.
Air pressure	28 psi; 7.5 on flowmeter.
Acetylene pressure	8 psi; 9.0 on flowmeter.

With these operating conditions the following readings have been observed:

Magnesium concentration (mg/l)	*Scale reading*
0.05	6.7
.25	33.2
.50	67.5

5. Reagents

5.1 *Manganese* standard solution I, 1.00 ml=0.100 mg Mn: Heat 0.5 g $MnSO_4 \cdot H_2O$ for 1 hr at 180°C. Dissolve 0.2749 g in demineralized water containing 1 ml concentrated H_2SO_4 (sp gr 1.84). Add 2.0 ml formalin to inhibit mold growth, and dilute to 1,000 ml with demineralized water.

5.2 *Manganese* standard solution II, 1.00 ml = 0.010 mg 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 solutions containing from 0.00 to 0.50 mg manganese per liter by diluting manganese standard solution II.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Filter the sample (0.45-μm membrane filter) when necessary to avoid clogging the atomizer-burner.

6.2 Aspirate and record the percent absorption or scale reading of the sample and standards against a demineralized-water blank. Repeat and average the two values.

7. Calculations

Determine the mg/l Mn in each sample from a plot of scale readings of standards. Because a scale expansion of 10× is used, scale readings need not be converted to absorbance. Exact reproductibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Mn concentrations as follows: Less than 100 μg/l, nearest 10 μg/l; 100 μg/l and above, two significant figures.

9. Precision

Analysis of a test sample by 18 laboratories using this method resulted in a mean value of 0.30 mg/l and a standard deviation of 0.045 mg/l.

Atomic-absorption method—chelation-extraction

1. Summary of method

Manganese is determined by atomic-absorption spectrophotometry. The element is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of the spectrophotometer. Because the chelate is unstable in MIBK, the analysis must be completed without delay.

2. Application

The chelation-extraction procedure may be used to analyze fresh waters and brines containing less than 50 μg of manganese per liter. Higher concentrations in brines must be reduced by dilution or less scale expansion used. Concentrations greater than 50 μg/l in fresh waters must be reduced by dilution, or the manganese determined directly on the aqueous sample without extraction.

3. Interferences

Concentrations of iron in excess of 25 mg/l or magnesium in excess of 100 mg/l may present some interference, especially when the manganese concentration exceeds 0.50 mg/l. Other elements normally found in water do not interfere.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	279.5 (2795A).
Slit	4.
Lamp current	10–15 ma.
Scale expansion	10×.
Source (hollow-cathode lamp)	Mn.
Response time control	1.
Burner	Boling.
Air pressure	28 psi; 3.0 on flowmeter.
Acetylene pressure	8 psi; 4.0 on flowmeter.

With these operating conditions the following readings have been observed:

Magnesium concentration (*μg*)	*Scale reading*
10.0	16.4
20.0	33.0
30.0	49.2
40.0	63.7
50.0	82.0

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution: Dissolve 4 g APDC in demineralized water and dilute to 100 ml. Prepare fresh daily.

5.2 *Bromcresol green indicator* solution: Dissolve 0.1 g bromcresol green in 100 ml 20-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 liter.

5.4 *Manganese* standard solution I, 1.00 ml = 100 μg Mn: Heat 0.5 g $MnSO_4 \cdot H_2O$ for 1 hr at 180°C. Dissolve 0.2749 g in demineralized water containing 1 ml concentrated H_2SO_4 (sp gr 1.84). Add 2 ml formalin to inhibit mold growth, and dilute to 1,000 ml with demineralized water.

5.5 *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.

5.6 *Methyl isobutyl ketone* (MIBK).

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet a volume of sample containing less than 50.0 μg of Mn (25.0 ml maximum) into a 50-ml volumetric flask.

6.2 Prepare a demineralized-water blank and sufficient standards, and adjust the volume of each to approximately 25 ml with demineralized water.

6.3 Add 2 drops bromcresol green indicator solution and adjust pH of sample to 4.0 (light-olive-green color) with addition of 0.3*M* HCl by drops.

6.4 Add 5.0 ml APDC solution and mix. The pH should then be 6.0.

6.5 Add 5.0 ml MIBK and shake for 2 min.

6.6 Allow the layers to separate and add demineralized water until the ketone layer is entirely in the neck of the flask.

6.7 Aspirate the ketone layer and record the scale reading for each standard and sample against the blank. Repeat, and average the duplicate results.

7. Calculations

Determine the μg/l Mn in each sample from a plot of scale readings of standards. Since a scale expansion of 10× is used, it is not necessary to convert scale readings to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Mn concentrations as follows: Less than 10 μg/l, nearest μg/l; 10 μg/l and above, two significant figures.

9. Precision

No precision data are available.

References

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 215.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geol. Survey Water-Supply Paper 1540-C, p. 35.

Hem, J. D., 1963, Chemical equilibria and rates of manganese oxidation: U.S. Geol. Survey Water-Supply Paper 1667-A, 64 p.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 7.

Molybdenum

Molybdenum occurs naturally in the form of the sulfide ore, molybdenite, MoS_2. It is a minor element in many soils, where its concentration ranges from 0.1 to about 5 mg/kg. The element is used in electronics and is an important constituent of alloy steels.

The maximum concentration of molybdenum found in the water supplies of the nation's 100 largest cities was 68 μg/l, and the median concentration was 1.4 μg/l (Durfor and Becker, 1964). More recently, however, considerably higher concentrations were identified in one public supply (Barnett and others, 1969). No limiting concentration has been established by the U.S. Public Health Service for potable water supplies.

Dithiol method

1. Summary of method

This method is based on the formation of a green dithiol-molybdenum complex which is extracted into an organic solvent and determined spectrophotometrically at 680 nm (Snell and Snell, 1959; Delaughter, 1965). A comparison of this and other methods for molybdenum was reported by Fishman and Mallory (1968).

2. Application

Samples containing from 1.0 to 50 μg of molybdenum per liter can be analyzed by this method. Higher concentrations must first be reduced by dilution.

3. Interferences

Iron interference is eliminated by reducing ferric iron to the ferrous state with potassium iodide, and decolorizing the liberated iodine with sodium thiosulfate. Tartaric acid is added to eliminate tungsten interference, and tin does not interfere if absorbance is measured at 680 nm.

4. Apparatus

Spectrophotometer, Beckman Model DB, or equivalent.

With this instrument the following operating conditions have been used:

Wavelength	680 nm.
Cells	1 cm.
Slit width	Narrow.

With these operating conditions the following absorbances have been observed:

Molybdenum (μg)	*Absorbance*
1.0	0.008
5.0	.040
10.0	.085
25.0	.205
50.0	.410

5. Reagents

5.1 *Dithiol* reagent: (a) Dissolve 5 g dithiol in 2,500 ml 0.25*M* NaOH solution and mix for 30 min; (b) add thioglycolic acid by drops until a permanent opalescence appears. Store in refrigerator and mix thoroughly before use. (CAUTION: Avoid contact with the skin. Wear plastic gloves when handling this reagent.)

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

5.3 *Methyl isobutyl ketone* (MIBK).

5.4 *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. Make just acid with 0.1*M* HCl and dilute to 1,000 ml with demineralized water.

5.5 *Molybdenum* standard solution II, 1.0 ml = 1.0 μg Mo: Dilute 10.0 ml molybdenum standard solution I to 1,000 ml with demineralized water.

5.6 *Potassium iodide* solution: Dissolve 50 g KI in 10 ml demineralized water.

5.7 *Sodium chloride,* crystals.

5.8 *Sodium sulfate,* anhydrous powder.

5.9 *Sodium thiosulfate* solution: Dissolve 10 g $Na_2S_2O_3$ in 100 ml demineralized water.

5.10 *Tartaric acid* solution: Dissolve 50 g $H_2C_4H_4O_6$ in 100 ml demineralized water.

6. Procedure

6.1 Transfer a volume of sample containing less than 50.0 μg molybdenum (500 ml maximum) into a 1,000-ml volumetric flask, and dilute to 500 ml with demineralized water.

6.2 Similarly, prepare a series of standards containing from 0.0 to 50.0 μg molybdenum.

6.3 Add and dissolve 160 g sodium chloride in each sample, standard, and blank.

6.4 Add, successively, 30 ml concentrated hydrochloric acid and 2 ml potassium iodide solution. If a yellowish-brown color appears, add sodium thiosulfate solution by drops until the color just disappears.

6.5 Add, successively, 1 ml tartaric acid solution and 50 ml dithiol reagent and let stand for 2 min.

6.6 Add 10 ml methyl isobutyl ketone (MIBK), shake for 2 min, and let stand 15 min for the phases to separate.

6.7 Add demineralized water until the ketone layer is entirely in the neck of the flask. With a pipet, carefully transfer the ketone layer to a test tube containing a small amount of anhydrous sodium sulfate.

6.8 Measure the absorbance of each sample and standard against the blank at a wavelength of 680 nm, using 1-cm cells.

7. Calculations

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

7.2 Mo in μg/l

$$=\frac{1{,}000}{\text{ml sample}}\times\mu\text{g Mo in sample.}$$

8. Report

Report Mo concentrations as follows: Less than 10 μg/l, nearest μg/l; 10 μg/l and above, two significant figures.

9. Precision

No precision data are available.

References

Barnett, P. R., Skougstad, M. W., and Miller, K. J., 1969, Chemical characterization of a public water supply: Am. Water Works Assoc. Jour., v. 61, p. 60–67.

Delaughter, B., 1965, The determination of sub-ppm concentrations of chromium and molybdenum in brines: Atomic Absorption Newsletter, v. 4, p. 273.

Durfor, E. N., and Becker, E., 1964, Public water supplies of the 100 largest cities in the United States, 1962: U.S. Geol. Survey Water-Supply Paper 1812, p. 78.

Fishman, M. J., and Mallory, E. C., Jr., 1968, Determination of molybdenum in fresh waters—A comparison of methods: Water Pollution Control Federation Jour., v. 40, pt. 2, p. R67.

Snell, F. D., and Snell, C. T., 1959, Colorimetric methods of analysis: New York, D. Van Nostrand Co., v. II–A, 793 p.

Nickel

Elemental nickel seldom occurs in nature, but its compounds are found in many ores and minerals. Many nickel salts are quite soluble and may contribute to water pollution, especially when discharged from metal-plating industries.

The U.S. Public Health Service (1962) has not placed a limit on nickel concentration in public water supplies.

Atomic-absorption method—chelation-extraction

1. Summary of method

Nickel is determined by atomic-absorption spectrophotometry. The element is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of the spectrophotometer (Fishman and Midgett, 1968).

2. Application

The extraction procedure given may be used to analyze water containing from 1.0 to 20.0 μg of nickel per liter. Higher concentrations must be reduced by dilution or less scale expansion used. Concentrations greater than 10 μg/l may be determined by direct aspiration.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	232.2 (2322A).
Slit	3.
Lamp current	25 ma.
Scale expansion	10×.
Source (shielded hollow-cathode lamp)	Ni.
Response time control	2.
Burner	Boling.
Air pressure	28 psi; 6.0 on flowmeter.
Acetylene pressure	8 psi; 4.0 on flowmeter.

With these operating conditions the following readings have been observed:

Nickel concentration (μg)	*Scale reading*
2.5	10.2
5.0	20.6
10.0	37.6
20.0	65.0

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution: Dissolve 1.0 g APDC in 100 ml demineralized water. Prepare fresh daily.

5.2 *Bromphenol blue indicator* solution: Dissolve 0.10 g bromphenol 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 liter.

5.4 *Methyl isobutyl ketone* (MIBK).

5.5 *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 and dilute to 1,000 ml with demineralized water.

5.6 *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.

5.7 *Sodium hydroxide,* 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 ml.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet a volume of sample containing less than 2.0 μg of nickel (100 ml maximum) into a 200-ml volumetric flask, and adjust volume to approximately 100 ml.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approximately 100 ml with demineralized water.

6.3 Add 2 drops bromphenol blue indicator solution.

6.4 Adjust the pH 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 in both the standards and sample. Then add 2.0 ml 0.3*M* HCl in excess. The pH at this point should be approximately 2.4.

6.5 Add 2.5 ml APDC solution and mix. The pH should be approximately 2.8.

6.6 Add 10.0 ml MIBK and shake vigorously for 1 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 Aspirate the ketone layer and record the scale reading for each sample and standard against the blank. Repeat, and average the duplicate results.

7. Calculations

Determine the μg/l Ni in each sample from a plot of scale readings of standards. Since a scale expansion of 10× is used, it is not necessary to convert scale readings to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Ni concentrations as follows: Less than 10 μg/l, nearest μg/l; 10 μg/l and above, two significant figures.

9. Precision

No precision data are available.

References

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: Am. Chem. Soc., Advances in Chemistry Ser., no. 73, p. 230.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, 61 p.

Nitrogen, ammonia

Ammonia nitrogen includes nitrogen in the forms of NH_3 and NH_4^{+1}. As a component of the nitrogen cycle, it is often present in water, but usually in only small amounts. Ammonia is used in some water-treatment processes. More than 0.1 mg/l usually indicates organic pollution (Rudolph, 1931).

There is no evidence that ammonia nitrogen in water is physiologically significant to man or livestock. Fish, however, cannot tolerate large quantities. The toxicity to fish is directly related to the amount of undissociated ammonia in solution; hence, the toxicity is dependent on the pH of the water. Ammonia decreases the ability of hemoglobin to combine with oxygen, and the fish suffocate. Although the tolerances of fish differ, 2.5 mg/l of ammonia nitrogen is considered harmful in the 7.4–8.5 pH range (Ellis and others, 1948).

The low concentrations of ammonia in natural waters are of little industrial significance, except that ammonium salts are destructive to concrete.

Distillation method

1. Summary of method

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 is then Nesslerized. Essentially, Nesslerization is the reaction between potassium mercuric iodide and ammonia which forms a red-brown complex of mercuric ammonobasic iodide:

$$HgI_2 \cdot 2KI + NH_3 \rightarrow Hg(NH_2)I + 2KI + HI.$$

Concentrations of ammonia are then determined by standard spectrophotometric measurements. Alternatively, the distillate may be titrated with standard sulfuric acid solution.

Additional information on the principle of the determination is given by Kolthoff and Sandell (1952, p. 633) and by Blaedel and Meloche (1963).

2. Application

This method is recommended for analysis of samples containing less than 2 mg of ammonia and ammonium ion per liter. Higher concentrations may be determined by the alternate titration procedure provided.

3. Interferences

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 a little lead carbonate.

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 distilled into H_3BO_3 and titrated with standard H_2SO_4.

4. Apparatus

4.1 *Kjeldahl distillation apparatus*, 1,000-ml flasks.

4.2 *Spectrophotometer*, 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	0.3 mm.
Blank	Ammonia-free water plus reagents.

With these operating conditions the following absorbances have been observed:

Nitrogen (mg)	*Absorbance*
0.02	0.24
.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 ammonium chloride standard solution I to 1,000 ml with ammonia-free water. Prepare fresh.

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 liter with ammonia-free water.

5.4 *Boric acid* solution: Dissolve 20 g H_3BO_3 in ammonia-free water and dilute to 1 liter.

5.5 *Methyl red indicator* solution: Dissolve 0.1 g methyl red indicator in 100 ml ethanol.

5.6 *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 liter. Allow the reagent to stand at least overnight and filter through a fritted-glass crucible.

5.7 *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.

5.8 *Sodium hydroxide* solution, 1*M*: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

5.9 *Sulfuric acid* standard solution, 0.0357*N*, 1.00 ml = 0.5 mg N: Mix 1.3 ml concentrated H_2SO_4 (sp gr 1.84) with demineralized water and dilute to 950 ml before standardization. Standardize by titrating 25.0 ml 0.0357*N* Na_2CO_3 to pH 4.5.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment." If acid has been added to the sample as a preservative at the time of collection, this must be neutralized with NaOH solution before proceeding with the analysis.

All glassware should be rinsed with ammonia-free water, prepared as directed in "Part II, Chemicals and Solutions."

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 (500 ml maximum) into a 600-ml beaker, and adjust the volume to approximately 500 ml with ammonia-free water.

6.3 Add 25 ml borate buffer solution, and adjust the pH to 9.5 with 1*M* NaOH, if necessary.

6.4 Immediately transfer the solution into the distillation flask and distill at a rate of not more than 10 ml nor less than 6 ml per minute; catch the distillate in a 500-ml volumetric flask containing 50 ml boric acid solution. The tip of the delivery tube must be below the surface of the boric acid.

6.5 Collect approximately 250 ml of distillate, dilute to 500 ml with ammonia-free water, and mix.

6.6.A *Nesslerization procedure*

6.6.A.1 Pipet an aliquot of distillate containing less than 0.1 mg ammonia nitrogen (50.00 ml maximum) into a graduate, and adjust the volume to 50.0 ml with ammonia-free water.

6.6.A.2 Prepare a blank of ammonia-free water and sufficient standards. Add 5 ml boric acid solution to each, and adjust the volumes to 50.0 ml.

6.6.A.3 Add 1.0 ml Nessler reagent (CAUTION: Deadly poison), and mix.

6.6.A.4 Allow the solutions to stand at least 10 min, but not over 30 min.

6.6.A.5 Determine absorbance of test sample and standards against the blank.

6.6.B *Titration procedure*

6.6.B.1 To the distillate, and an ammonia-free water blank containing the same volume of H_3BO_3, add 3 drops methyl red indicator solution, and titrate with sulfuric acid standard solution.

7. Calculations

7.A *Nesslerization procedure*

7.A.1 Determine mg N in aliquot from a plot of absorbances of standards.

7.A.2 Ammonia nitrogen as N, in mg/l

$$= \frac{1,000}{\text{ml sample}} \times \frac{500}{\text{ml aliquot}} \times \text{mg N in aliquot.}$$

7.B *Titration procedure*

7.B.1 Ammonia nitrogen as N, in mg/l

$$= \frac{V_a \times N_a \times 14,000}{V_s},$$

where

V_a = ml standard H_2SO_4 used in titration of sample minus ml used to titrate blank,

N_a = normality of standard H_2SO_4, and

V_s = ml of original sample used for distillation.

7.C Ammonia nitrogen as NH_4^{+1}, in mg/l = mg/l as N × 1.288. Ammonia nitrogen as free NH_3, in mg/l = mg/l as N × 1.216.

8. Report

Report ammonia nitrogen concentrations as follows: Less that 1.0 mg/l, two decimals; 1 mg/l and above, two significant figures.

9. Precision

No precision data are available.

References

Blaedel, W. J., and Meloche, V. W., 1963, Elementary quantitative analysis: Theory and practice [2d ed.]: New York, Harper & Row, 826 p.

Ellis, M. M., Westfall, B. A., and Ellis, M. D., 1948, Determination of water quality: U.S. Fish Wildlife Service Research Rept. 9, 122 p.

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis [3d ed.]: New York, Macmillan Co.

Rudolph, Z., 1931, Principles of the determination of the physical and chemical standards of water for drinking, industrial, and domestic purposes: Water Pollution Abs. 4 [March].

Nitrogen, nitrate

Nitrate is usually the most prevalent form of nitrogen in water, because it is the end product of the aerobic decomposition of organic nitrogen. Nitrate from natural sources is attributed to the oxidation of nitrogen of the air by bacteria and to the decomposition of organic material in the soil. Fertilizers may add nitrate directly to water resources. Nitrate concentrations range from a few tenths to several hundred milligrams per liter, but in unpolluted water seldom exceed 10 mg/l. Nitrate and chloride are major components of human and animal wastes, and abnormally high concentrations of both suggest pollution.

Cyanosis due to methemoglobinemia may occur in infants whose drinking or formula water contains a high concentration of nitrates. The nitrates, when ingested, are converted to nitrites in the digestive system of some infants. The nitrite ion oxidizes hemoglobin to methemoglobin, and thereby causes cyanosis. It is widely recommended that water containing more than 10–20 mg/l of nitrate nitrogen should not be used in infant feeding (Comly, 1945).

Nitrates in large amounts are injurious to the dyeing of wool and silk and are undesirable in fermentation processes (California State Water Quality Control Board, 1963). At least 2 mg/l of nitrate prevents intercrystalline cracking of steel in steam boilers.

Brucine method

1. Summary of method

The reaction between the alkaloid, brucine, and nitrate in acid medium produces a yellow color that may be measured by standard spectrophotometric procedures. Close attention must be given to procedural technique if accuracy and precision are to be obtained. The procedure is similar to that of Jenkins and Medsker (1964).

2. Application

This method may be applied to essentially colorless water containing up to 5.0 mg of nitrate per liter. Any significant amount of color should be removed. Samples containing higher concentrations must be diluted.

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 *Spectrophotometer,* Beckman Model B, or equivalent.

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 (approximate)	0.10 mm.

With these operating conditions the following absorbances have been observed:

NO_3 *(mg)*	*Absorbance*
0.005	0.115
.010	.220
.020	.440
.030	.640
.040	.800
.050	.950

5. Reagents

5.1 *Brucine–sulfanilic acid* reagent: Dissolve 1 g brucine sulfate (CAUTION: Very poisonous) and 0.1 g 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* standard solution I, 1.00 ml=1.00 mg NO_3: Dissolve 1.631 g KNO_3, dried overnight over concentrated H_2SO_4, in demineralized water and dilute to 1,000 ml.

5.3 *Nitrate* standard solution II, 1.00 ml = 0.010 mg NO_3: Dilute 10.0 ml nitrate standard solution I to 1,000 ml with demineralized water.

5.4 *Sodium chloride* solution: Dissolve 300 g NaCl in 1 liter demineralized water.

5.5 *Sulfuric acid, 29N*: Add 500 ml concentrated H_2SO_4 (sp gr 1.84) to 125 ml demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.05 mg NO_3 (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 tubes into a cold-water bath (15°–20°C) and add 10.0 ml 29*N* 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.—If a deep pink color forms immediately upon addition of the brucine–sulfanilic acid reagent, it is an indication of a 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 rack of tubes 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 tubes are placed in it. This step is critical. All tubes must be heated uniformly.

6.7 Remove the tubes 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 tubes uniformly. Circulation of water in the bath is desirable.

6.8 Determine the absorbance of the sample and standards against the blank without unnecessary delay.

7. Calculations

7.1 Determine the mg of NO_3 in the sample from a plot of absorbances of standards.

7.2 NO_3 in mg/l$=\frac{1{,}000}{\text{ml sample}}\times$ mg NO_3 in sample.

7.3 To convert NO_3 to N, multiply by 0.2259.

8. Report

Report NO_3 concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

Single-laboratory analysis of two test samples resulted in mean values of 0.9 and

2.9 mg/l, and standard deviations of 0.09 and 0.11 mg/l, respectivcely.

Reduction method

Samples containing more than 30 mg/l of NO_3^{-1} 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) and by Kolthoff and Sandell (1952). For high concentrations of nitrate, the method yields results which are comparable in accuracy to those obtained by the brucine method.

References

Blaedel, W. J., and Meloche, V. W., 1963, Elementary quantitative analysis: Theory and practice [2d ed.]: New York, Harper & Row, 826 p.

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 226.

Comly, H. H., 1945, Cyanosis in infants caused by nitrates in well water: Am. Med. Assoc. Jour., v. 129.

Jenkins, D., and Medsker, L. L., 1964, Brucine method for determination of nitrate in ocean, estuarine, and fresh waters: Anal. Chemistry, v. 36, p. 610.

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis [3d ed.]: New York, Macmillan Co., 759 p.

Nitrogen, nitrite

Nitrite is unstable in the presence of oxygen and is, therefore, absent or present in only minute quantities in most natural waters under aerobic conditions. The presence of nitrite in water is sometimes an indication of organic pollution.

Recommended tolerances of nitrite in domestic water supplies differ widely. A generally accepted limit is 2 mg/l, but as little as 0.1 mg/l has been proposed (California State Water Quality Control Board, 1963). Nitrite is undesirable in water used in dyeing wool and silk and in brewing.

Diazotization method

1. Summary of method

Nitrite is diazotized with sulfanilamide, and the resulting diazo compound is coupled with 1-naphthylethylenediamine dihydrochloride to form an intensely colored red dye (Rider and Mellon, 1945). The absorbance of the dye is proportional to the amount of nitrite present (Fishman and others, 1964).

2. Application

This method may be applied to samples containing less than 4 mg nitrite per liter. Samples containing higher concentrations must first be diluted.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

Spectrophotometer, Beckman Model B, or equivalent.

With this instrument the following operating conditions have been used:

Wavelength	535 nm.
Cells	10 mm.
Phototube	Blue-sensitive.
Initial sensitivity setting	2.
Slit width	0.08 mm.

With these operating conditions the following absorbances have been observed:

NO_2 (*mg*)	*Absorbance*
0.05	0.53
.10	1.06
.15	1.59
.20	2.04

5. Reagents

5.1 *Formic acid,* 87–90 percent.

5.2 *1-naphthylethylenediamine dihydrochloride* solution: Dissolve 0.5 g 1-naphthylethylenediamine dihydrochloride in 100 ml demineralized water. Store in refrigerator.

5.3 *Nitrite* standard solution I, 1.00 ml =1.00 mg NO_2: Dissolve 1.850 KNO_2 in demineralized water and dilute to 1,000 ml.

5.4 *Nitrite* standard solution II, 1.00 ml =0.010 mg NO_2: Dilute 10.0 ml nitrite standard solution I to 1,000 ml with demineralized water.

5.5 *Sulfanilamide* solution: Dissolve 0.5 g sulfanilamide in 100 ml demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.20 mg NO_2 (50.0 ml maximum) into a 100-ml volumetric flask, and adjust the volume to 50 ml with demineralized water.

6.2 In a similar manner, prepare a blank and sufficient standards containing 0.00–0.20 mg NO_2, and adjust the volume of each to 50 ml with demineralized water. Place in ice bath and allow to cool for about 2 min.

6.3 Add successively, while in the ice bath, and mixing thoroughly after each addition: 1.0 ml sulfanilamide solution, 4.0 ml formic acid, and 1.0 ml 1-naphthylethylenediamine dihydrochloride solution.

6.4 Remove the flasks from the ice bath and allow at least 15 min for maximum color development. Adjust each to exact volume with demineralized water. Mix thoroughly and measure the absorbance of samples and standards against the blank.

7. Calculations

7.1 Determine the mg NO_2 in the test samples from a plot of absorbances of standards.

7.2 NO_2 in mg/l

$$= \frac{1{,}000}{\text{ml aliquot}} \times \text{mg } NO_2 \text{ in sample.}$$

7.3 To convert NO_2 to N, multiply by 0.3043.

8. Report

Report NO_2 concentrations as follows: Less than 1.0 mg/l, two decimals; 1.0 mg/l and above, two significant figures.

9. Precision

No precision data are available.

References

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3–A, p. 226.

Fishman, M. J., Skougstad, M. W., and Scarbro, G. F., 1964, Diazotization method for nitrate and nitrite: Am. Water Works Assoc. Jour., v. 56, p. 633.

Rider, B. F., and Mellon, M. G., 1945, Colorimetric determination of nitrites: Indus. Eng. Chemistry, Anal. Ed., v. 18, p. 76.

Nitrogen, organic

Organic nitrogen includes all nitrogenous organic compounds, such as amino acid, polypeptides, and proteins. It is present naturally in all surface waters as the result of inflow of nitrogenous products from the watershed and the normal biological life of the stream. Effluents of sewage and waste from slaughterhouses and chemical plants often contain nitrogen in varying combinations. Organic nitrogen in unpolluted ground water is usually very low.

Organic nitrogen is not pathologically significant but is sometimes an indication of pollution. Organic nitrogen is important to considerations involving aquatic biology.

Kjeldahl method

1. Summary of method

Organic nitrogen is degraded to the ammonium ion by digestion with sulfuric acid in the presence of copper sulfate, which acts as a catalyst. The solution is made alkaline with sodium hydroxide, and the free ammonia is distilled off and Nesslerized. The color developed is proportional to the organic nitrogen content.

Additional information on the principle of the determination is given by Kolthoff and Sandell (1952, p. 537).

2. Application

This method may be applied to most natural water containing less than 2 mg of nitrogen per liter. Higher concentrations must be reduced by dilution.

3. Interferences

Nitrate and nitrite do not interfere. The effect of ammonium ions and ammonia is strictly additive. Therefore, the organic nitrogen is normally determined on the residue of the ammonia nitrogen determination.

Calcium, magnesium, iron, and sulfide interfere with the Nesslerization, but the interference of the metals is eliminated by the distillation. Sulfides interfere and must be precipitated in the distillation flask with a little lead carbonate before addition of sodium hydroxide.

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 distilled into H_3BO_3 and titrated with standard H_2SO_4.

4. Apparatus

4.1 *Kjeldahl distillation apparatus,* 1,000-ml flasks.

4.2 *Spectrophotometer,* Beckman Model B, or equivalent.

With this instrument the following operating conditions have been used:

Wavelength	425 nm.
Cells	40 mm.
Phototube	Blue-sensitive.
Blank	Ammonia-free water plus reagents.
Initial sensitivity setting	1.
Slit width (approximate)	0.3 mm.

With these operating conditions the following absorbances have been observed:

N (*mg*)	*Absorbance*
0.02	0.24
.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 to 1,000 ml with ammonia-free water. Prepare fresh.

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 liter with ammonia-free water.

5.4 *Boric acid* solution: Dissolve 20 g H_3BO_3 in ammonia-free water and dilute to 1 liter.

5.5 *Copper sulfate* solution: Dissolve 10 g $CuSO_4 \cdot 5H_2O$ in ammonia-free water and dilute to 100 ml.

5.6 *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 liter. Allow the reagent to stand at least overnight and filter through a fritted-glass crucible.

5.7 *Sodium hydroxide* solution, 10*N*: Dissolve 400 g NaOH in ammonia-free water and dilute to 1 liter.

5.8 *Sulfuric acid,* concentrated (sp gr 1.84).

6. Procedure

All glassware should 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 The residue from the ammonia nitrogen determination may be used for this determination. Alternatively, buffer a volume of sample containing less than 1.0 mg organic nitrogen (500.0 ml maximum) to pH 9.5 with borate buffer solution, and evaporate to approximately 20 percent of original volume to drive off ammonia.

6.3 Cool; add 10 ml concentrated H_2SO_4 and 1 ml $CuSO_4$ solution.

6.4 Digest under a hood until copious fumes are given off, and the liquid becomes colorless or pale yellow.

6.5 Cool and dilute to approximately 300 ml with ammonia-free water.

6.6 Add 50 ml 10*N* NaOH cautiously down the side of the flask.

6.7 Immediately connect the flask to the distillation apparatus, and cautiously mix the contents by swirling gently.

6.8 Distill at a rate of no more than 10 ml nor less than 6 ml per minute; catch the distillate in a 500-ml volumetric flask containing 50 ml boric acid solution. The tip of the delivery tube must be below the surface of the boric acid.

6.9 Collect approximately 250 ml distillate, dilute to 500 ml with ammonia-free water, and mix.

6.9.A *Nesslerization procedure*

Proceed as directed in "Nitrogen, Ammonia," steps 6.6.A.1–6.6.A.5.

6.9.B *Titration procedure*

Proceed as directed in "Nitrogen, Ammonia," step 6.6.B.1.

7. Calculations

7.A *Nesslerization procedure*

7.A.1 Determine a reagent blank for each new batch of H_2SO_4 by taking 300 ml ammonia-free water through the entire procedure:

$$\text{mg reagent blank} = \text{mg N per 10 ml } H_2SO_4 \times \frac{\text{ml aliquot}}{\text{ml distillate}}.$$

7.A.2 Determine the mg N in the aliquot from a plot of absorbances of standards.

7.A.3

Organic nitrogen as N, in mg/l

$$= \frac{1{,}000}{\text{ml sample}} \times \frac{500}{\text{ml aliquot}} \times [(\text{mg N in aliquot}) - (\text{mg reagent blank})].$$

7.B *Titration procedure*

Ammonia nitrogen as N, in mg/l

$$= \frac{V_a \times N_a \times 14{,}000}{V_s}$$

where

V_a=ml standard H_2SO_4 used in titration of sample minus ml used to titrate blank,

N_a=normality of standard H_2SO_4, and

V_s=ml of original sample used for distillation.

7.C Ammonia nitrogen as NH_4^{+1}, in mg/l =mg/l as N$\times$1.288.

Ammonia nitrogen as free NH_3, in mg/l =mg/l as N$\times$1.216.

8. Report

Report organic nitrogen concentrations as follows: Less than 1.0 mg/l, two decimals; 1 mg/l and above, two significant figures.

9. Precision

No precision data are available.

Reference

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis [3d ed.]: New York, Macmillan Co., 759 p.

Oxygen demand (COD)

The oxygen-demand determination is a measure of the readily oxidizable material in the water, and furnishes an approximation of the minimum amount of organic and reducing material present. In reality, the term "chemical oxygen demand" is defined by the method used for its determination. In the method given below it is defined as the amount of oxygen used by the sample when refluxed 2 hr with an excess of acid–potassium dichromate solution. The determined value may correlate with natural-water color or with carbonaceous organic pollution from sewage or industrial wastes.

Tolerances for oxygen-demand values in feed water for low- and high-pressure boilers are 15 and 3 mg/l, respectively. Wash water containing more than 8 mg/l has been reported to impart a bad odor to textiles; concentrations for water used in beverages and brewing range from 0.5 to 5.0 mg/l (California State Water Quality Control Board, 1963).

Dichromate oxidation method

1. 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 (American Society for Testing and Materials, 1968).

2. Application

This method can be used for analysis of natural waters and industrial wastes containing less than 2,000 mg/l chloride ion and more than 50 mg/l chemical oxygen demand (COD). Samples containing less than this amount of COD should be analyzed as directed in step 6.9. COD values for waters containing more than 2,000 mg/l of chloride ion should be corrected as indicated in step 6.10.

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 Cl^{-1} 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 mg 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 *Hotplate* or heating mantle.

5. Reagents

5.1 *Ferrous ammonium sulfate* standard solution, 0.2500*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, cool, and dilute to 1 liter. To standardize: Dilute 25.0 ml standard 0.25*N* $K_2Cr_2O_7$ solution to 250 ml. Add 20 ml concentrated H_2SO_4 and cool. Titrate with the ferrous ammonium sulfate solution, using 8–10 drops Ferroin indicator. The solution must be standardized daily, or before use.

5.2 *Mercuric sulfate,* powdered $HgSO_4$.

5.3 *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 of water. The prepared indicator is available commercially.

5.4 *Potassium dichromate* standard solution, 0.2500*N*: Dissolve 12.259 g $K_2Cr_2O_7$ primary standard, dried for 2 hr at 110°C, in demineralized water and dilute to 1,000 ml.

5.5 *Silver sulfate,* powder.

5.6 *Sulfamic acid,* crystals.

5.7 *Sulfuric acid,* concentrated (sp gr 1.84).

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Pipet 50.0 ml of sample or a smaller aliquot diluted to 50.0 ml into the reflux flask and add slowly, over a period of 2–3 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 hr.

6.3 Cool in ice water and add 75 ml concentrated H_2SO_4, 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.

6.5 Attach flask to condenser, start water flow, and reflux for 2 hr.

NOTE.—If contents are not well mixed, superheating may result, and the contents of the flask may be blown out of the open end of the condenser.

6.6 Allow flask to cool and wash down condenser with 25 ml water.

6.7 Dilute to 300 ml with demineralized water, cool to room temperature, and titrate the excess dichromate with 0.2500*N* ferrous ammonium sulfate solution, using 8–10 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 Samples containing less than 50.0 mg/l COD should be reanalyzed, using 0.025*N* solutions of potassium dichromate and ferrous ammonium sulfate. A sample size should be selected so that no more than half the dichromate is reduced. A further increase in sensitivity may be obtained by evaporating a larger sample to 150 ml in the presence of all reagents. A blank should be treated in a similar manner.

6.10 To obtain more accurate COD values for samples containing more than 2,000 mg/l of chloride ion, the following procedure may be used (Burns and Marshall, 1965). A series of chloride solutions are analyzed by the procedure indicated above, except that 10 mg of $HgSO_4$ is added to each solution for each mg of chloride ion present instead of a constant 1-g quantity. The chloride concentrations should range from 2,000 mg/l to 20,000 mg/l, with the concentration interval not exceeding 4,000 mg/l. Plot the COD values obtained versus mg/l 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

Calculate the COD in each sample as follows:

7.1 For samples not requiring chloride correction:

$$\text{COD in mg/l}=\frac{(a-b)c\times 8{,}000}{\text{ml sample}};$$

7.2 For samples requiring chloride correction:

$$\text{COD in mg/l}=\left[\frac{(a-b)c\times 8{,}000}{\text{ml sample}}\right]-d\times 1.20,$$

where

COD = chemical oxygen demand from dichromate,
a = ml ferrous ammonium sulfate for blank,
b = ml ferrous ammonium sulfate for sample,
c = normality ferrous ammonium sulfate,
d = chloride correction value from graph of chloride concentration versus COD, and
1.20 = empirical compensation factor.

8. Report

Report COD as follows: Less than 10 mg/l, whole numbers; 10 mg/l and above, two significant figures.

9. Precision

No precision data are available. The general precision of COD determinations has been reviewed by the Analytical Reference Service of the U.S. Public Health Service (1965).

References

American Society for Testing and Materials, 1968, Water; atmospheric analysis, pt. 23 *of* 1968 Book of standards: Philadelphia, Am. Soc. Testing Materials, p. 244.

Burns, E. R., and Marshall, C., 1965, Correction for chloride interference in the chemical oxygen demand test: Water Pollution Control Federation Jour., v. 37, p. 1716.

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 233.

U.S. Public Health Service, 1965, Water oxygen demand No. 2: Public Health Service Study no. 21, Pub. 999-WP-26.

Oxygen, dissolved (DO)

Oxygen dissolved in water is derived from the air and from the oxygen given off in the process of photosynthesis by aquatic plants. The solubility of oxygen in water is dependent upon the partial pressure of oxygen in air, the temperature of the water, and the mineral content of the water.

Dissolved oxygen in water has no adverse physiological effect and actually increases the palatability of the water (California State Water Quality Control Board, 1963). In general, no minimum concentration of dissolved oxygen required to support fish life has been listed because the oxygen requirements of fish vary with the species and age, with temperature, and with concentration of other substances in the water. Ellis (1937) believes that under average stream conditions, 3.0 mg/l of dissolved oxygen, or less, should be regarded as hazardous or lethal, and that to maintain a varied fish fauna in good condition the dissolved-oxygen concentration should be at least 5.0 mg/l.

Dissolved oxygen is responsible for many of the corrosion problems in industry. For many industrial uses of water, zero dissolved oxygen would be desirable as a means of inhibiting corrosion.

Alsterberg azide method

1. Summary of method

This method is a modification of the Winkler process for the determination of dissolved oxygen, and the principle is the same. The method depends on the formation of a precipitate of manganous hydroxide. The oxygen dissolved in the water is rapidly absorbed by manganous hydroxide, forming a higher oxide, which may be in the following form:

$$MnSO_4+2KOH \rightarrow Mn(OH)_2+K_2SO_4$$

$$2Mn(OH)_2+O_2 \rightarrow 2MnO(OH)_2.$$

$Mn(OH)_2$ floc acts as a "gathering" agent for oxygen.

Upon acidification in the presence of iodide, iodine is released in a quantity equivalent to the dissolved oxygen present

$$MnO(OH)_2+2KI+H_2O \xrightarrow{H^{+1}} Mn(OH)_2 + I_2+2KOH$$

The liberated iodine is then titrated with standard sodium thiosulfate solution using starch indicator

$$I_2+2S_2O_3^{-2} \rightarrow S_4O_6^{-2}+2I^{-1}.$$

Additional information on the principle of the determination is given by Adams, Barnett, and Keller (1943).

2. Application

This method is applicable to samples which are not heavily polluted. It is not recommended for samples that contain more than 1 mg per liter of ferrous iron or appreciable quantities of sulfite, thiosulfate, polythionate, hypochlorite, or free chlorine.

3. Interferences

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.

In the listed 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 mg/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: Dissolve 10 g $AlK(SO_4)_2 \cdot 12H_2O$ in water and dilute to 100 ml.

5.4 *Manganous sulfate* solution: 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: Dissolve 40 g $KF \cdot 2H_2O$ in water and dilute to 100 ml.

5.6 *Sodium thiosulfate* solution, 0.025*N*: 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 thiosulfate 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 approximately 1 g KIO_3 for 2 hr at 180°C. Dissolve 0.8918 g in water and dilute to 1,000 ml. Pipet 25.00 ml of the KIO_3 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. Allow the stoppered flask to stand 5 min in the dark. Titrate with $Na_2S_2O_3$ using 2 ml starch indicator as end point is approached.

Normality of

$$Na_2S_2O_3=\frac{\text{ml } KIO_3}{\text{ml } Na_2S_2O_3}\times 0.025.$$

5.7 *Starch indicator* solution, stable, or "thyodene," powdered.

5.8 *Sulfuric acid, 3.6M*: Carefully add 200 ml concentrated H_2SO_4 (sp gr 1.84) to 750 ml water and dilute to 1 liter.

6. Procedure

Samples for the determination of dissolved oxygen must be collected and treated as directed in "Part I, Sample Collection and Treatment."

6.1 Pipet an aliquot of treated sample containing less than 2.0 mg O_2 (200.0 ml maximum).

6.2 Titrate the liberated I_2 with 0.025N $Na_2S_2O_3$ to a pale-straw color.

6.3 Add 1–2 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 has been treated with alum as in "Part I, Sample Collection and Treatment," correct the sample volume reacted with $MnSO_4$ as follows:

$$\text{ml sample}=(300\times\text{ml taken for flocculation})\times 1/(\text{ml taken for flocculation}+\text{ml } AlK(SO_4)_2+NH_4OH).$$

7.2 O_2 (DO) in mg/l =

$$\frac{1{,}000}{\text{ml sample}}\times\frac{(\text{ml treated aliquot}+5)}{\text{ml treated aliquot}}\times \text{ml } Na_2S_2O_3\times 0.2.$$

7.3 O_2 (DO) in mg/l at 0°C and 760 mm

$$=O_2 \text{ in mg/l}\times 0.700$$

7.4 O_2 (DO) as percent saturation at 760 mm, the solubility values in the following table may be used. Equations for correcting the listed solubilities to barometric pressures other than 760 mm are given beneath the table (American Public Health Association and others, 1965, table 25, p. 409).

Solubility of oxygen in water exposed to water-saturated air *

Temp. °C	Chloride Concentration in Water—*mg/l*: 0	5,000	10,000	15,000	20,000	Difference per 100 mg Chloride
	Dissolved Oxygen—*mg/l*					
0	14.6	13.8	13.0	12.1	11.3	0.017
1	14.2	13.4	12.6	11.8	11.0	.016
2	13.8	13.1	12.3	11.5	10.8	.015
3	13.5	12.7	12.0	11.2	10.5	.015
4	13.1	12.4	11.7	11.0	10.3	.014
5	12.8	12.1	11.4	10.7	10.0	.014
6	12.5	11.8	11.1	10.5	9.8	.014
7	12.2	11.5	10.9	10.2	9.6	.013
8	11.9	11.2	10.6	10.0	9.4	.013
9	11.6	11.0	10.4	9.8	9.2	.012
10	11.3	10.7	10.1	9.6	9.0	.012
11	11.1	10.5	9.9	9.4	8.8	.011
12	10.8	10.3	9.7	9.2	8.6	.011
13	10.6	10.1	9.5	9.0	8.5	.011
14	10.4	9.9	9.3	8.8	8.3	.010
15	10.2	9.7	9.1	8.6	8.1	.010
16	10.0	9.5	9.0	8.5	8.0	.010
17	9.7	9.3	8.8	8.3	7.8	.010
18	9.5	9.1	8.6	8.2	7.7	.009
19	9.4	8.9	8.5	8.0	7.6	.009
20	9.2	8.7	8.3	7.9	7.4	.009
21	9.0	8.6	8.1	7.7	7.3	.009
22	8.8	8.4	8.0	7.6	7.1	.008
23	8.7	8.3	7.9	7.4	7.0	.008
24	8.5	8.1	7.7	7.3	6.9	.008
25	8.4	8.0	7.6	7.2	6.7	.008
26	8.2	7.8	7.4	7.0	6.6	.008
27	8.1	7.7	7.3	6.9	6.5	.008
28	7.9	7.5	7.1	6.8	6.4	.008
29	7.8	7.4	7.0	6.6	6.3	.008
30	7.6	7.3	6.9	6.5	6.1	.008
31	7.5	......	......	......	......	......
32	7.4	......	......	......	......	......
33	7.3	......	......	......	......	......
34	7.2	......	......	......	......	......
35	7.1	......	......	......	......	......
36	7.0	......	......	......	......	......
37	6.9	......	......	......	......	......
38	6.8	......	......	......	......	......
39	6.7	......	......	......	......	......
40	6.6	......	......	......	......	......
41	6.5	......	......	......	......	......
42	6.4	......	......	......	......	......
43	6.3	......	......	......	......	......
44	6.2	......	......	......	......	......
45	6.1	......	......	......	......	......
46	6.0	......	......	......	......	......
47	5.9	......	......	......	......	......
48	5.8	......	......	......	......	......
49	5.7	......	......	......	......	......
50	5.6	......	......	......	......	......

* At a total pressure of 760 mm Hg. Under any other barometric pressure, P (mm; or P', in.), the solubility, S' (mg/l), can be obtained from the corresponding value in the table by the equation:

$$S'=S\frac{P-p}{760-p}$$

in which S is the solubility at 760 mm (29.92 in.) and p is the pressure (mm) of saturated water vapor at the temperature of the water. For elevation less than 3,000 ft and temperatures below 25°C, p can be ignored. The equation then becomes:

$$S'=S\frac{P}{760}=S\frac{P'}{29.92}$$

Dry air is assumed to contain 20.90 percent oxygen.

8. Report

Report dissolved-oxygen concentrations to one decimal.

9. Precision

No precision data are available.

Instrument method

Oxygen dissolved in waters too heavily contaminated to permit analysis by the Alsterberg azide method may be determined by any one of several commercially available instruments. Such instruments usually employ either a polarographic probe covered with a permeable membrane or a dropping-mercury electrode. Studies by the Geological Survey have indicated an acceptable degree of accuracy and precision from both types of instrumentation, if operated with care and according to the manufacturer's instructions.

The instrument selected should meet the following general requirements:

Range of dissolved oxygen: 0–20 mg/l

Accuracy: ±1 percent of maximum range

Operating temperature range: $-5°$ to $+45°C$

Minimum scale readability: 0.05 mg/l O_2

Temperature-compensated, portable, and rugged for field and laboratory use.

References

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American Public Health Association and others, 1965, Standard methods for the examination of water and wastewater [12th ed.]: New York, Am. Public Health Assoc., Inc., p. 409.

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pH

The pH of a solution is a measure of the effective hydrogen-ion concentration, or more specifically, the hydrogen-ion activity ($a_{H^{+1}}$):

$$pH = \log \frac{1}{a_{H+1}} \cdot$$

In water solution, deviations in pH from 7 are primarily the result of the hydrolysis of salts of strong bases and weak acids, or vice versa. Dissolved gases such as carbon dioxide, hydrogen sulfide, and ammonia also affect the pH appreciably. The effect of dissolved salts of strong acids and strong bases is slight.

Because carbonates are prevalent in nature, many natural waters are slightly basic. The overall normal pH range is between 6.0 and 8.0. Industrial wastes, on the other hand, may be strongly acidic or basic, and their effect on the pH of receiving waters is largely dependent on the buffering capacity of the water.

The pH of potable water is not pathologically significant. Water with a pH of less than 4 usually has a sour taste. Optimum pH for fish is between 7.8 and 8.5, while a water whose pH is less than 4.4 or greater than 8.8 generally causes gill irritation and death (Ellis, 1944). pH in conjunction with other factors affects the corrosion potential of water on metals. For detailed discussion the chemist is referred to the work of Bates (1964). Extremes in pH cannot usually be tolerated by industry. The optimum pH for irrigation water depends on the type of crops to be grown and on the physical and chemical properties of the soil. For additional information on some aspects of pH measurement see Barnes (1964) and also, Willard, Merritt, and Dean (1965).

Instrument method

1. Summary of method

See "Part II, Instrumental Techniques," for the principle of pH-meter operation.

2. Application

This method may be applied to any natural or treated water.

3. Interferences

The pH obtained in the laboratory may not be the same as that of the water at the time it was collected owing to reactions with sediment, hydrolysis, and oxidation taking place within the sample bottle. Also, the pH may change appreciably through loss of dissolved gases, absorption of laboratory fumes, and deposition of calcium carbonate or other salts. A value more nearly representative of the pH at the time of collection is obtained if the determination is made as soon as the sample bottle is opened.

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 the method.

The pH measurement is temperature dependent, and a significant error results if the temperature 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

pH meter, with glass and reference electrodes.

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.

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, particularly if the same meter and electrode system is subsequently used for alkalinity or acidity titration.

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. Readymade 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 will differ with the electrodes, hence the analyst is referred to manufacturer's instructions for the computations necessary.

8. Report

Report pH values to the nearest 0.1 pH unit.

9. Precision

Analysis of a test sample by 34 laboratories resulted in a mean of 8.26 pH units, and a standard deviation of 0.12.

References

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geol. Survey Water-Supply Paper 1535-H, 17 p.

Bates, R. G., 1964, Determination of pH—Theory and practice: New York, John Wiley & Sons, 435 p.

Ellis, W. M., 1944, Water purity standards for fresh water fishes: U.S. Fish Wildlife Service Spec. Rept. 2.

Willard, H. H., Merritt, L. L., Jr., and Dean, J. A., 1965, Instrumental methods of analysis [4th ed.]: New York, D. Van Nostrand Co.

Phosphorous

Phosphorus is prevalent in nature both in the organic and inorganic form. Because of its role in animal and vegetable metabolism, phosphorus is a cyclic element, similar to nitrogen, in that the combined form is continually changing by decomposition and synthesis. As phosphate, it is present in several common minerals, but the concentration in water is limited by the relative insolubility of phosphates of the alkaline earths. Both organic and inorganic phosphorus in water may result from leaching of soil and rocks, and from fertilizer, normal decomposition of plants and animals, sewage, and industrial effluents. Waters that have undergone phosphate treatment for removal of hardness can also add phosphorus to water resources.

In concentrations found in water, phosphorus is not reported to be toxic to man, animals, or fish. However, the element does stimulate the growth of algae, which may cause serious problems in public water supplies.

When a filtered sample is analyzed, the procedures described determine the following groups of phosphorus compounds in solution: (1) Dissolved orthophosphate; the filtered, untreated sample is analyzed, determining only phosphate ions in solution. (2) Dissolved orthophosphate and acid-hydrolyzable phosphorus compounds; the filtered sample is treated with acid, thereby hydrolyzing polyphosphates and some organics to orthophosphate. These are then determined as orthophosphate. (3) Dissolved orthophosphate and acid-persulfate hydrolyzable phosphorus compounds; the filtered sample is treated with acid and ammonium persulfate to convert all forms of phosphorus present to orthophosphate (Gales and others, 1966). These are then determined as orthophosphate.

From these separate determinations the individual forms of phosphorous in solution may be calculated.

Orthophosphate is the most common ionized form of phosphorus in water and the only one derived from natural sources. Orthophosphates include the three ionization products of phosphoric acid, $H_2PO_4^{-1}$, HPO_4^{-2}, and PO_4^{-3}, whose relative concentrations in water are a function of the pH. PO_4^{-3} does not exist in solutions below a pH of about 9.4; at a pH of approximately 7.2, HPO_4^{-2} and $H_2PO_4^{-1}$ are present in equal quantities; while at a pH of about 4.4, most of the orthophosphate is present as $H_2PO_4^{-1}$ (Kolthoff and Sandell, 1952; Blaedel and Meloche, 1963). For ionization of orthophosphate at different pH values, see "Part III, Chemical Balance."

The various ionization products are not differentiated by the method of analysis, nor are they chemically or physiologically significant to water uses. Hence, the combined orthophosphates are reported in terms of mg per liter PO_4. The computation of milliequivalents per liter (me/l), however, necessitates consideration of the ionization products; instructions for estimating milliequivalents per liter are given in "Part III, Chemical Balance."

Phosphomolybdate method

1. Summary of method

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.

Orthophosphate is converted to phosphomolybdate by acidified ammonium molybdate reagent:

$$H_3PO_4+12(NH_4)_2MoO_4+21H^{+1} \rightarrow (NH_4)_3PO_4\cdot 12MoO_3+21NH_4^{+1}+12H_2O.$$

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 6–10 min and fades gradually thereafter.

In order to avoid the instability of the single-solution reagent, an appropriate amount of a mixture of the dry reagents—ammonium molybdate, ascorbic acid, and potassium antimonyl tartrate—is dissolved in the required volume of sulfuric acid just before use (Fishman and Skougstad, 1965).

2. Application

The method may be used to analyze most natural, industrial, and sewage-type water samples.

3. Interferences

Barium, lead, mercury, 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.

4. Apparatus

Spectrophotometer, Beckman Model B, or equivalent.

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.
Blank	Demineralized water plus reagents.

With these operating conditions the following values have been observed:

PO_4	*Absorbance*	
(μg)	*(882 nm)*	*(700 nm)*
12.5	0.24	0.18
25.0	.47	.35
37.5	.70	.52
50.0	.94	.70

5. Reagents

5.1 *Ammonium persulfate* $(NH_4)_2S_2O_8$.

5.2 *Phenolphthalein indicator* solution: Dissolve 0.5 g phenolphthalein in 100 ml 50-percent ethanol.

5.3 *Phosphate reagent,* powder: Mix thoroughly the following dry reagents: 6.0 g ammonium molybdate, 5.3 g ascorbic acid, and 0.14 g antimonyl potassium tartrate. The mixture is stable for at least 6 months.

5.4 *Phosphate reagent,* solution: Add 1±0.2 g phosphate reagent powder to 100 ml 1.25*M* H_2SO_4. A pale-yellow-green color develops after 15 min standing. Prepare fresh daily.

5.5 *Phosphate* standard solution I, 1.00 ml=50 μg PO_4: Dissolve 71.6 mg KH_2PO_4, dried overnight over H_2SO_4, in demineralized water. Add 2–3 drops chloroform as preservative and dilute to 1,000 ml.

5.6 *Phosphate* standard solution II, 1.00 ml=1.00 μg PO_4: Dilute 20.0 ml phosphate standard solution I to 1,000 ml with demineralized water containing 2–3 drops chloroform as preservative.

5.7 *Sodium hydroxide,* 3*M*: Dissolve 120 g NaOH in demineralized water and dilute to 1 liter.

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 liter.

5.9 *Sulfuric acid,* 1.25*M*: Add slowly, with constant stirring, 70 ml concentrated H_2SO_4 (sp gr 1.84) to 800 ml demineralized water and dilute to 1 liter.

5.10 *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 liter.

6. Procedure

Samples should be collected as directed in "Part I, Sample Collection and Treatment."

6.A *Dissolved orthophosphate*

6.A.1 Pipet a volume of sample containing less than 50.0 μg PO_4 (50.0 ml maximum) into a 100-ml beaker, and adjust the volume to 50.0 ml.

6.A.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 ml.

6.A.3 Add 10 ml phosphate reagent solution to each sample, blank, and standard and mix.

6.A.4 After 10 min measure absorbance of samples and standards against the blank at either 882 nm or 700 nm.

6.B *Dissolved orthophosphate and acid-hydrolyzable phosphorus compounds*

6.B.1 Pipet a volume of sample containing less than 50.0 μg PO_4 (50.0 ml maximum) into a 125-ml erlenmeyer flask, and adjust the volume to 50.0 ml.

6.B.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 ml.

6.B.3 Add 1.0 ml 6*M* H_2SO_4, and boil gently on hotplate until the volume is reduced to about 10 ml.

6.B.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. Dilute the solution to 50.0 ml with demineralized water.

NOTE.—If an unfiltered, well-mixed sample was taken for analysis, the sample aliquot should be filtered through a 0.45-μm membrane filter after cooling and *before* neutralizing with 3*M* NaOH. This step is necessary to prevent readsorption and loss of phosphate on the suspended particulate matter during the neutralization adjustment.

6.B.5 Proceed as directed in steps 6.A.3 and 6.A.4.

6.C *Dissolved orthophosphate and acid-persulfate hydrolyzable phosphorus compounds*

6.C.1 Pipet a volume of sample containing less than 50.0 μg PO_4 (50.0 ml maximum) into a 125-ml erlenmeyer flask, and adjust the volume to 50.0 ml.

6.C.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 ml.

6.C.3 Add 1.0 ml 6*M* H_2SO_4 and 0.4 g $(NH_4)_2S_2O_8$. Boil gently on hotplate until the volume is reduced to about 10 ml.

6.C.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. Dilute the solution to 50.0 ml with demineralized water.

NOTE.—If an unfiltered, well-mixed sample was taken for analysis, the sample aliquot should be filtered through a 0.45-μm membrane filter after cooling and *before* neutralizing with 3*M* NaOH. This step is necessary to prevent readsorption and loss of phosphate on the suspended particulate matter during the neutralization adjustment.

6.C.5 Proceed as directed in steps 6.A.3 and 6.A.4.

7. Calculations

7.1 Determine the μg PO_4 in each sample from a plot of absorbances of standards.

7.2 $PO_4 \text{ in mg/l} = \dfrac{\mu g\ PO_4 \text{ in sample}}{\text{ml sample}}$

7.3 P in mg/l = mg/l $PO_4 \times 0.3261$.

8. Report

Report concentrations of PO_4 as follows: Less than 1.0 mg/l, two decimals; 1.0 mg/l and above, two significant figures.

9. Precision

Single-laboratory determinations on replicate samples were found to be reproducible to within ±0.01 mg/l.

References

Blaedel, W. J., and Meloche, V. W., 1963, Elementary quantitative analysis [2d ed.]: Theory and practice: New York, Harper & Row, 826 p.

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Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: Am. Water Works Assoc. Jour., v. 58, p. 1363.

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis [3d ed.]: New York, Macmillan Co., p. 440.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Anal. Chim. Acta, v. 27, p. 31.

Potassium

Although potassium is relatively abundant in the earth's crust, the potassium content of natural waters is usually small. Potassium occurs in rocks in a form that is not easily brought into solution. Also, several geochemical processes tend to remove potassium selectively and return it to the solid phase. Most waters contain less than 20 mg/l potassium, although waters containing several hundred mg per liter are occasionally found.

Potassium is essential to animal nutrition, but a concentration of 1,000–2,000 mg/l in stock water is regarded as the extreme limit permissible (Moore, 1950). Potassium in water causes foaming, as does sodium, but apparently it is not otherwise significant in industrial water supplies. Potassium stimulates plankton growth (Lackey and Sawyer, 1946), and is reported to be somewhat more toxic to fish and shellfish than is calcium, magnesium, or sodium (Brandt, 1948).

Atomic-absorption method—direct

1. Summary of method

Potassium is determined by atomic-absorption spectrophotometry. The sample is aspirated directly with no pretreatment other than filtration or dilution as required (Fishman and Downs, 1966).

2. Application

Samples containing up to several thousand mg of potassium per liter may be analyzed by this method. Concentrations above 10 mg/l must be reduced by dilution.

3. Interferences

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

Alternatively, or additionally, 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

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Visible.
Wavelength counter	383.2 (7665A).
Slit	5.
Lamp current	350 ma.
Scale expansion	1×.
Source	Osram potassium vapor-discharge lamp.
Response time control	1.
Burner	Standard "303," positioned 0.05 cm below optical light path.
Air pressure	28 psi; 7.5 on flowmeter.
Acetylene pressure	8 psi; 9.0 on flowmeter.

With these operating conditions the following readings have been observed:

Potassium concentration (*mg/l*)	*Absorption* (*percent*)
2.0	21.5
4.0	37.2
6.0	48.7
8.0	57.3
10	63.3

5. Reagents

5.1 *Potassium* standard solution I, 1.00 ml=0.10 mg K: Dissolve 0.1907 g KCl in demineralized water and dilute to 1,000 ml.

5.2 *Potassium* standard working solutions: Prepare a series of standard working solutions containing from 0.00 to 10.0 mg K per liter by appropriate dilution of the potassium standard solution I.

6. Procedure

6.1 Adjust burner head to 0.05 cm below optical light path.

6.2 Filter the sample (0.45-μm membrane filter) when necessary to avoid clogging the atomizer-burner.

6.3 Measure the scale readings of the samples and standards against a demineralized-water blank. Repeat, and average the two values.

7. Calculations

Convert percent absorption to absorbance, and determine the mg/l K in each sample from a plot of absorbances of standards. For samples containing more than 10 mg K per liter, multiply by the proper dilution factor. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report K concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

Analysis of two test samples by 15 laboratories using this method resulted in mean values of 0.8 and 4.8 mg/l, and standard deviations of 0.011 and 0.726 mg/l, respectively.

References

Brandt, H. J., 1948, Intensified injurious effects on fish, especially the increased toxic effect produced by a combination of sewage poisons: Chem. Abs. 42, p. 9015.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geol. Survey Water-Supply Paper 1540-C, p. 36.

Lackey, J. B., and Sawyer, C. N., 1946, Plankton productivity of certain southeastern Wisconsin lakes as related to fertilization: Sewage Works Jour., v. 17, p. 573.

Moore, E. W., 1950, The desalting of saline waters, a review of the present status: Natl. Research Council Comm. on Sanitary Eng. and Environment, Rept. to Subcomm. on Water Supply.

Selenium

Selenium exists in many forms and is found in many localities. The element is generally more prevalent in the Great Plains and Great Basin than in other parts of the United States. Selenium is normally nonexistent or present only in insignificant quantities in natural waters, but does occur occasionally under certain geologic environments. Scott and Voegeli (1961) found from less than 1 μg to 120 μg of selenium per liter in 11 samples of ground water from Colorado. Highly significant is the fact that selenium from plants, sedimentary rocks, soils, and animals may find its way into water resources. Selenium concentrations in water in excess of 0.5 mg/l are extremely rare, and are limited primarily to seepage from seleniferous soils.

Selenium is a cumulative poison to man and animals; it enters all of the body tissues and is present in all secretions and excretions. Because of its chemical similarity to sulfur, it is taken up nonpreferentially in tissue assimilations and is substituted for sulfur in the proteins. Seleniferous plants can produce either acute or chronic poisoning in livestock. Chronic selenium poisoning is associated with blind staggers and alkali disease. The toxic effect depends on the type of selenium compounds, the animal, and the conditions of ingestion (Maag and Glenn, 1967). Water with 0.4–0.5 mg/l is not believed to be toxic to livestock; such water may contribute to poisoning, but the selenium content of the feed is a more critical factor (California State Water Quality Control Board, 1963). When the selenium content of the air-dried diet exceeds about 5 mg/kg, symptoms of alkali disease occur.

High concentrations of selenium are toxic to some plants, but most plants can absorb relatively large amounts of selenium from irrigation water or the soil without apparent injury to themselves.

The U.S. Public Health Service (1962) states that the selenium concentration shall not exceed 0.01 mg/l in water on carriers subject to Federal quarantine regulations.

Additional information on the occurrence and significance of selenium is given by Trelease and Beath (1949) and Muth and others (1967).

Diaminobenzidine method

1. Summary of method

Oxidation by acid permanganate converts all selenium compounds to selenate. Many carbon compounds are not completely oxidized by acid permanganate, but it is improbable that the selenium-carbon bond will remain intact through this treatment. Experiments demonstrate that inorganic forms of selenium are oxidized by acid permanganate in the presence of much greater concentrations of organic matter than would be anticipated in water supplies.

There is substantial loss of selenium when solutions of sodium selenate are evaporated to complete dryness, but in the presence of calcium all the selenium is recovered. An excess of calcium over the sulfate is not necessary.

Selenate is reduced to selenite in warm 4*M* HCl. Temperature, time, and acid concentrations are specified to obtain quantitative reduction without loss of selenium.

The optimum pH for the formation of piazselenol is found to be approximately 1.5. Above pH 2, the rate of formation of the colored compound is critically dependent upon the pH. When indicators are used to adjust the pH, the results are frequently erratic.

Extraction of piazselenol is not quantitative, but equilibrium is attained rapidly. Above pH 6, the partition ratio of piazselenol between water and toluene is almost independent of the hydrogen-ion concentration. This method is identical to that reported by Rossum and Villarruz (1962).

2. Application

This method may be applied to natural, industrial, and waste waters that do not contain large amounts of iodide or bromide.

3. Interferences

No inorganic compounds give a positive interference.

Negative interference results from compounds that lower the concentration of diaminobenzidine by oxidizing this reagent. The addition of EDTA eliminates negative interference from at least 2.5 mg of ferric iron. Manganese has no effect in any reasonable concentration, probably because it is reduced along with the selenate. Iodide and, to a lesser extent, bromide cause low results.

4. Apparatus

4.1 *pH meter.*

4.2 *Separatory funnels,* 250-ml.

4.3 *Spectrophotometer,* Beckman Model B, or equivalent.

With this instrument the following operating conditions have been used:

Wavelength	420 nm.
Sensitivity setting	3.
Slit width	0.1 mm.
Cells	10 mm.

With these operating conditions the following readings have been observed:

Se (μg)	*Absorbance*
10	0.093
25	.230
50	.440
100	.890

5. Reagents

5.1 *Ammonium chloride* solution: Dissolve 250 g NH_4Cl in 1 liter demineralized water.

5.2 *Ammonium hydroxide, 5M*: Dilute 330 ml concentrated NH_4OH to 1 liter with demineralized water.

5.3 *Calcium chloride* solution: Dissolve 30 g $CaCl_2 \cdot 2H_2O$ in demineralized water and dilute to 1 liter.

5.4 *Diaminobenzidine* solution: Dissolve 100 mg 3,3′-diaminobenzidine hydrochloride in 10 ml demineralized water. This solution is unstable and must be prepared daily.

5.5 *EDTA-sulfate* reagent: Dissolve 100 g of the disodium salt of EDTA and 200 g sodium sulfate in 1 liter demineralized water. Add concentrated ammonium hydroxide by drops while stirring until the solution is complete.

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

5.7 *Hydrochloric acid,* 0.1*M*: Dilute 8 ml concentrated HCl to 1 liter with demineralized water.

5.8 *Methyl orange indicator* solution: Dissolve 0.5 g methyl orange in 1 liter demineralized water.

5.9 *Potassium permanganate* solution: Dissolve 3.2 g $KMnO_4$ in 1 liter demineralized water.

5.10 *Selenium* standard solution I: Place an accurately weighed pellet of ACS-grade metallic selenium into a small beaker. Add 5 ml concentrated HNO_3. 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 Se per liter.)

5.11 *Selenium* standard solution II, 1.00 ml $\approx$ 1.00 μg Se: From a buret, measure an appropriate amount of selenium standard solution I and dilute to exact volume with demineralized water.

5.12 *Sodium hydroxide* solution, 0.1*M*: Dissolve 4 g NaOH in demineralized water and dilute to 1 liter.

6. Procedure

6.1 Prepare a blank and a series of standards containing up to 100 μg Se in 500-ml erlenmeyer flasks. Dilute to approximately 250 ml and add the following: 10

drops methyl orange indicator, 2 ml 0.1*M* HCl, 5 ml $CaCl_2$ solution, 3 drops $KMnO_4$, and sufficient glass beads to prevent bumping.

6.2 Boil vigorously for approximately 5 min.

6.3 To a 1,000-ml sample in a 2-liter beaker, add 10 drops methyl orange indicator.

6.4 Titrate to the methyl orange end point with 0.1*M* HCl and add 2 ml excess.

6.5 Add 3 drops $KMnO_4$, 5 ml $CaCl_2$ solution, and a few glass beads to prevent bumping.

6.6 Heat to boiling, adding $KMnO_4$ as required to maintain a purple tint. A precipitate of MnO_2 will have no adverse effect.

6.7 After the volume has been reduced to approximately 250 ml, quantitatively transfer the solution to a 500-ml erlenmeyer flask.

6.8 Add 5 ml NaOH to the blank, standards, and samples; evaporate to dryness and allow flasks to cool. Avoid prolonged heating of the residue.

6.9 Add 5 ml concentrated HCl and 10 ml NH_4Cl solution. Heat in a boiling-water bath or steam bath for 10±0.5 min.

6.10 Transfer the warm solution, together with any precipitate, to a beaker, washing the flask with 5 ml EDTA-sulfate reagent and 5 ml 5*M* NH_4OH.

6.11 Adjust the pH to 1.5±0.3 with NH_4OH using a pH meter. The precipitate of EDTA will not interfere.

6.12 Add 1 ml diaminobenzidine solution and heat in a boiling-water bath or steam bath for approximately 5 min.

6.13 Cool and add NH_4OH to adjust the pH to 8±1. The precipitate of EDTA will dissolve.

6.14 Pour the sample into a 50-ml graduate, and adjust the volume to 50±1 ml with washings from the beaker.

6.15 Pour the contents of the graduate into a 250-ml separatory funnel and add 10 ml toluene; shake for 30±5 sec.

6.16 Discard the aqueous layer, and transfer the organic phase to a beaker containing a small amount of anhydrous Na_2SO_4.

6.17 Read the absorbance at 420 nm of each standard and sample against the blank. The piazselenol color is stable, but evaporation of toluene concentrates the color to marked degree in a few hours.

7. Calculations

Determine μg Se in each sample from a plot of absorbances of standards:

$$\text{Se in } \mu g/l = \frac{\mu g \text{ Se}}{\text{liters of sample}}.$$

8. Report

Report Se concentrations as follows: Less than 100 μg/l, nearest μg/l; 100 μg/l and above, two significant figures.

9. Precision

Analysis of three test samples by seven laboratories resulted in means of 49, 84, and 10 μg/l, with standard deviations of 6, 8 and 5 μg/l.

Distillation-diaminobenzidine method

1. Summary of method

Selenium is quantitatively separated from most other elements by distillation of the volatile tetrabromide from an acid solution containing bromine. The bromine is generated by the reaction of bromide with hydrogen peroxide in order to avoid the inconvenience of handling the element. Selenium tetrabromide, along with a minimum of excess bromine, is absorbed in water. The excess bromine is removed by precipitation as tribromphenol, and the tetravalent selenium determined with diaminobenzidine as in "Diaminobenzidine Method."

This method is identical to that reported by Rossum and Villarruz (1962).

2. Application

This method may be applied to those samples which cannot be analyzed with "Diaminobenzidine Method" because of bromide or iodide interference.

3. Interferences

No substances are known to interfere.

4. Apparatus

All apparatus listed in "Diaminobenzidine Method," 4.1 through 4.3, plus: *Distillation* *assembly,* all glass, for 500-ml erlenmeyer flasks.

5. Reagents

All reagents listed in "Diaminobenzidine Method," except 5.1, 5.2, and 5.5. In addition, the following are required:

5.1 *Ammonium hydroxide,* concentrated.

5.2 *Hydrochloric acid, 6M*: Dilute 500 ml concentrated HCl to 1 liter with demineralized water.

5.3 *Hydrogen peroxide,* 30-percent.

5.4 *Phenol* solution: Dissolve 5 g phenol in 100 ml demineralized water.

5.5 *Potassium bromide–acid* reagent: Dissolve 10 g KBr in 20 ml demineralized water. Cautiously add 25 ml concentrated H_2SO_4, mixing and cooling under tap water as each increment of acid is added. Prepare immediately before use because $KHSO_4$ will precipitate on cooling, and reheating to dissolve this salt will drive off some of the HBr.

6. Procedure

6.1 Follow procedure given in "Diaminobenzidine Method," steps 6.1 through 6.8, except that glass-stoppered erlenmeyer flasks are used.

6.2 To each of the cool flasks, add 500 ml potassium bromide–acid reagent.

6.3 Add 1 ml 30-percent H_2O_2 and fit the flask to the condenser without delay. Distill under the fume hood until the color of bromine is gone from the flask. The receiver consists of a beaker suitable for the pH adjustment, containing just enough water to immerse the tip of the condenser. Wash the small amount of distillate remaining in the condenser into the beaker with 5 ml demineralized water.

6.4 To the receiver, add phenol solution, by drops, until the color of bromine is discharged. A white precipitate of tribromphenol will form, but a small proportion of the yellow tetrabromphenol causes no trouble.

6.5 Adjust the pH to 1.5±0.3 using concentrated NH_4OH and 6*M* HCl.

6.6 Add 1 ml diaminobenzidine solution and heat in a boiling-water bath or steam bath for approximately 5 min.

6.7 Cool and then add concentrated NH_4OH to adjust the pH to 8±1.

6.8 Pour the sample into a 50-ml graduate, and adjust the volume to 50±1 ml with washings from the beaker.

6.9 Pour contents of each graduate into 250-ml separatory funnels, add 10 ml toluene, and shake for 30±5 sec.

6.10 Discard the aqueous layer, and transfer the toluene layer to a beaker containing a small amount of anhydrous Na_2SO_4.

6.11 Read absorbance of each standard and sample at 420 nm against the blank. The phenol used in step 6.4 causes the yellow piazselenol color slowly to acquire a greenish tint, so that the absorbance readings should be made within 2 hr after extraction.

7. Calculations

Determine the μg Se in each sample from a plot of absorbances of standards:

$$\text{Se in } \mu\text{g/l} = \frac{\mu\text{g Se}}{\text{liters of sample}}.$$

8. Report

Report Se concentrations as follows: Less than 100 μg/l, nearest μg/l; 100 μg/l and above, two significant figures.

9. Precision

No precision data are available, but results should be comparable to that for the diaminobenzidine method.

References

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U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 8.

Silica

Silicon is the most abundant element in igneous rocks and some other types of deposits. Most silica in water is probably derived from the decomposition or metamorphism of silicate minerals rather than from solution of quartz, since quartz is resistant to attack by water. Many waters contain less than 10 mg/l of silica; those that drain deposits high in silicate minerals, particularly feldspars, often contain up to 60 mg/l; concentrations exceeding 100 mg/l are not commonly found. The chemistry of silica in solution is not completely understood. It is believed that most silica is present in an un-ionized form, but the silicate ion is undoubtedly present in some waters.

Silica is not physiologically significant to humans, livestock, or fish, nor is it of importance in irrigation water.

Most industrial processes tolerate silica in the range normally found, but it is particularly undesirable in boiler feed water. A recommended upper limit for boilers operating at 400 psi or above is 1 mg/l. Silica forms a hard coating on steam-turbine blades, and a limiting concentration of 0.1 mg/l in the steam has been recommended (Minhoff, 1948).

Molybdate blue method

1. Summary of method

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).

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-hr 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.

2. Application

This method may be applied to samples containing less than 100 mg of silica per liter. Samples containing more than 100 mg/l of silica should be analyzed by standard gravimetric procedures (American Society for Testing and Materials, 1966; Kolthoff and Sandell, 1952).

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

Spectrophotometer, Beckman Model B, or equivalent.

With this instrument the following operating conditions have been used:

Wavelength	700 nm.
Filter	Red.
Cells	10 mm or 40 mm.
Phototube	Red-sensitive.
Blank	Demineralized water plus reagents.
Initial sensitivity setting	1.
Slit width	0.35 mm.

With these operating conditions the following absorbances have been observed:

SiO_2 (*mg*)	*Cell depth* (*mm*)	*Absorbance*
0.05	40	0.337
.10	40	.675
.10	10	.165
.20	10	.330
.30	10	.495
.50	10	.816

5. Reagents

5.1 *Ammonium molybdate* solution: Dissolve 52 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in water, adjust pH to 7–8 with 10*M* NaOH, and dilute to 1 liter 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 liter.

5.3 *Silica* standard solution I, 1.00 ml= 0.50 mg SiO_2: Stabilize 3 g of the pentahydrate, $Na_2SiO_3\cdot 5H_2O$, by drying over $CaCl_2$ for 2–3 hr. Dissolve 1.765 g 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.

5.4 *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: Dissolve 10 g Na_2EDTA in demineralized water and dilute to 1 liter.

5.6 *Sodium hydroxide* solution, 10*M*: Dissolve 400 g NaOH in demineralized water and dilute to 1 liter.

5.7 *Sodium sulfite* solution: Dissolve 170 g Na_2SO_3 in demineralized water and dilute to 1 liter.

5.8 *Tartaric acid* solution: Dissolve 100 g $H_2C_4H_4O_6$ in demineralized water and dilute to 1 liter.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.5 mg SiO_2 (10.00 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 ml Na_2SO_3 solution and mix.

6.6 Allow to stand approximately 30 min. The color is stable for several hours after this time.

6.7 Determine the absorbance of the test sample and standards against the blank.

7. Calculations

7.1 Determine mg SiO_2 in samples from a plot of absorbances of standards.

7.2 SiO_2 in mg/l

$$=\frac{1{,}000}{\text{ml sample}}\times \text{mg } SiO_2 \text{ in sample.}$$

8. Report

Report SiO_2 as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

No precision data are available.

Atomic-absorption method—direct

1. Summary of method

Silica is determined by atomic-absorption spectrophotometry. The sample is aspirated directly with no pretreatment other than filtration or dilution as required.

2. Application

Samples containing at least 0.5 mg silica per liter may be analyzed by this method. Samples containing more than 35 mg/l must be diluted or less scale expansion used. The sensitivity of the determination of silica by this method 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/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/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.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	251.6 (2516A).
Slit	3.
Scale expansion	10×.
Lamp current	40 ma.
Source (shielded hollow-cathode lamp)	SiO_2.
Response time control	1.
Burner	Nitrous-oxide (Aztec part no. AB–50).
Nitrous-oxide pressure	See instrument instruction manual.
Acetylene pressure	

With these operating conditions the following readings have been observed:

SiO_2 *concentration* (*μg*)	*Scale reading*
1.0	2.4
5.0	12.9
10	25.6
20	50.5
30	73.5

5. Reagents

5.1 *Silica* standard solution, 1.00 ml= 0.500 mg SiO_2: Stabilize 3 g $Na_2SiO_3 \cdot 5H_2O$ by drying over $CaCl_2$ for 2–3 hr. Dissolve 1.765 g 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 standard solutions containing from 0 to 40 mg silica per liter by diluting appropriate aliquots of silica standard solution. Store in plastic bottles.

6. Procedure

6.1 Filter the sample (0.45-μm membrane filter) when necessary to avoid clogging the atomizer-burner.

6.2 Measure the scale reading of each sample and standard. Repeat, and average the two values.

7. Calculations

Determine the mg/l SiO_2 in the sample from a plot of scale readings of standards. Because a scale expansion of 10× is used, scale readings need not be converted to absorbances. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report SiO_2 concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

Single-operator precision of this method, based on 10 determinations at the 2.24, 6.97, and 23.6 mg/l levels, was determined to be ±0.16, 0.32, and 0.48 mg/l, respectively.

References

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Silver

Silver occurs naturally in the elemental state, and in ores combined with chlorine, sulfur, and antimony. From such ores silver ions may be leached into ground and surface waters, but the insolubility of most silver salts precludes significant concentrations. The growing industrial use of all forms of silver may, in the future, be a source of objectionable concentrations in waters receiving wastes from such industries.

The U.S. Public Health Service (1962) places a mandatory limit of 0.05 mg of silver per liter in water subject to these standards.

Atomic-absorption method—chelation-extraction

1. Summary of method

Silver is determined by atomic-absorption spectrophotometry. The element is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of the spectrophotometer.

2. Application

Water containing between 1.0 and 10.0 μg of silver per liter may be analyzed by this procedure. Higher concentrations must be reduced by dilution or less scale expansion used.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	328.1 (3281A).
Slit	4.
Lamp current	12 ma.
Scale expansion	10×.
Source (hollow-cathode lamp)	Ag.
Response time control	1.
Burner	Boling.
Air pressure	28 psi; 6.0 on flowmeter.
Acetylene pressure	8 psi; 4.0 on flowmeter.

With these operating conditions the following readings have been observed:

Silver concentration (μg)	*Scale reading*
2.5	18.4
5.0	37.1
7.5	55.4
10.0	74.1

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate* (APDC) solution: Dissolve 1.0 g APDC in 100 ml demineralized water. Prepare fresh daily.

5.2 *Bromphenol blue indicator* solution: Dissolve 0.1 g bromphenol blue in 100 ml 50-percent ethanol.

5.3 *Hydrochloric acid,* 0.3*M*: Mix 25.0 ml concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 liter.

5.4 *Methyl isobutyl ketone* (MIBK).

5.5 *Silver* standard solution I, 1.00 ml = 100 μg Ag: Dissolve 0.1575 g $AgNO_3$ in demineralized water and dilute to 1,000 ml.

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 to 1,000 ml with demineralized water. This solution is used to prepare working standards at the time of analysis.

5.7 *Sodium hydroxide,* 2.5*M*: Dissolve 10 g NaOH in demineralized water and dilute to 100 ml.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

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 volume to approximately 100 ml.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approximately 100 ml with demineralized water.

6.3 Add 2 drops bromphenol blue indicator solution.

6.4 Adjust the pH 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 in both the standards and sample. Then add 2.0 ml 0.3*M* HCl in excess. The pH should be approximately 2.4.

6.5 Add 2.5 ml APDC solution and mix. The pH should be approximately 2.8.

6.6 Add 10.0 ml MIBK and shake vigorously for 1 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 Aspirate the ketone layer and record the scale reading for each standard and sample against the blank. Repeat, and average the duplicate results.

7. Calculations

Determine the µg/l Ag in each sample from a plot of scale readings of standards. Since a scale expansion of 10× is used, scale readings need not be converted to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Ag concentrations as follows: Less than 10 µg/l, nearest µg/l; 10 µg/l and above, two significant figures.

9. Precision

No precision data are available for this procedure, but results are believed reproducible within ±0.5 µg/l.

Reference

U.S. Public Health Service, 1952, Drinking water standards: Public Health Service Pub. 956, p. 8.

Sodium

Sodium salts are very soluble, and most sodium leached from the soil or rocks tends to remain in solution. The use of sodium salts is common in industry, and industrial wastes may contain large quantities of the element.

Sodium is not particularly significant in drinking and culinary water except for those persons having an abnormal sodium metabolism; the water supply in some areas contains sufficient sodium to be a factor in the planning of sodium-free diets (National Research Council, 1954). It has been established that more than 50 mg/l of sodium plus potassium in boiler water causes foaming. For high-pressure boiler feed water a limiting concentration of 2–3 mg/l has been recommended. Water with a high ratio of sodium to calcium plus magnesium is deleterious to soil structure. Sodium tends to disperse the soil colloids with the resultant loss of good tilth and permeability (U.S. Salinity Laboratory Staff, 1954). The sodium-adsorption-ratio (SAR) is a useful index of the sodium hazard of irrigation water.

$$\mathrm{SAR} = \frac{\mathrm{me/l\ Na}}{\sqrt{\dfrac{\mathrm{me/l\ Ca + Mg}}{2}}}$$

Atomic-absorption method—direct

1. Summary of method

Sodium is determined by atomic-absorption spectrophotometry. The sample is aspirated directly with no pretreatment other than filtration or dilution as required (Fishman and Downs, 1966).

2. Application

Samples containing at least 0.1 mg sodium per liter may be analyzed by this method. If the sodium concentration exceeds 60 mg/l, the sample must first be diluted. The method is very sensitive and can be extended to much lower sodium concentrations if necessary.

Two analytical ranges are provided: From 0.0 to 6.0 mg/l, and from 5 to 60 mg/l.

3. Interferences

None of the substances commonly occurring in natural water interferes with this method.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Sodium concentration range: 0.0–6.0 mg/l

Grating	Visible.
Wavelength counter	294.4 (5888A).
Slit	3.
Lamp current	700 ma.
Scale expansion	1×.
Source	Osram sodium vapor-discharge lamp.
Response time control	1.
Burner	Standard "303."
Air pressure	28 psi; 9.0 on flowmeter.
Acetylene pressure	8 psi; 9.0 on flowmeter.

With these operating conditions the following readings have been observed:

Sodium concentration (mg/l)	*Absorption (percent)*
2.0	57.1
4.0	79.5
6.0	89.2

Sodium concentration range: 5.0–60 mg/l

Burner	"290" rotated 90°.
Air pressure	28 psi; 6.0 on flowmeter.
Acetylene pressure	8 psi; 6.5 on flowmeter.

All other operating conditions the same as for concentration range 0.0–6.0 mg/l.

With these operating conditions the following readings have been observed:

Sodium concentration (mg/l)	*Absorption (percent)*
10	29.0
20	49.0
40	72.6
60	84.0

5. Reagents

5.1 *Sodium* standard solution, 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 standard solutions containing from 0 to 60 mg sodium per liter by diluting the Na standard solution. The preparation of an intermediate standard solution is desirable when preparing working solutions of extreme dilution.

6. Procedure

6.1 Filter the sample (0.45-μm membrane filter) when necessary to avoid clogging the atomizer-burner.

6.2 Measure the percent absorption or scale reading of the sample and standards against the demineralized-water blank. Repeat, and average the two values. If the sodium concentration is greater than 60 mg/l, the sample must be diluted.

7. Calculations

Convert percent absorption to absorbance, and determine the mg/l Na in the sample from a plot of absorbances of standards. For samples containing more than 60 mg sodium per liter, multiply by the proper dilution factor. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Na concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

Analysis of a test sample by 15 laboratories using this method resulted in a mean value of 25.53 mg/l and a standard deviation of 0.516 mg/l.

References

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geol. Survey Water-Supply Paper 1540–C, p. 38–41.

National Research Council, 1954, Sodium restricted diets: Pub. 325.

U.S. Salinity Laboratory Staff, 1954, Diagnosis and improvement of saline and alkali soils: U.S. Dept. Agriculture, Agriculture Handb. 60, p. 69–82.

Solids, dissolved

Theoretically, dissolved solids are anhydrous residues of the dissolved substances in water. In reality, the term "dissolved solids" is defined by the method used in the determination, and is not an accurate measure of the weight of substances in solution. The methods used by the Geological Survey reflect experience with thousands of water samples of different total concentrations and chemical compositions, and the results obtained are believed to approach more closely the theoretical definition than results by other methods.

All solutes affect the chemical and physical properties of the water and result in an osmotic pressure. Water with several thousand mg/l of dissolved solids is generally not palatable, although those accustomed to highly mineralized water may complain that less concentrated water tastes flat. A change in the concentration of dissolved solids in drinking water may more often cause gastric disturbances than the actual concentration of dissolved solids in the water itself. The U.S. Public Health Service (1962) recommends that the maximum concentration of dissolved solids not exceed 500 mg/l in drinking and culinary water on carriers subject to Federal quarantine regulations, but permits 1,000 mg/l if no better water is available. Reported livestock tolerances range from 3,000 mg/l (Colorado Agricultural Experiment Station, 1943) to 15,000 mg/l (Heller, 1933). The blood of fresh-water fish has an osmotic pressure equal to approximately 6 atmospheres, or about 7,000 mg/l of sodium chloride. Although some fresh-water fish are adapted to live in more saline waters, for practical purposes any water that has an osmotic pressure greater than 6 atmospheres can be expected to be lethal.

Industrial tolerances for dissolved solids differ widely, but few industrial processes will permit more than 1,000 mg/l. Much natural water contains dissolved solids in concentrations exceeding 1,000 mg/l. Such water is classed as saline. The Geological Survey classifies the degree of salinity of these more mineralized bodies of water as follows (Swenson and Baldwin, 1965):

Dissolved solids (mg/l)	*Degree of salinity*
Less than 1,000	Nonsaline.
1,000 to 3,000	Slightly saline.
3,000 to 10,000	Moderately saline.
10,000 to 35,000	Very saline.
More than 35,000	Brine.

Salinity hazard is an important consideration for irrigation water. The water-uptake relations of plants are controlled by the osmotic-pressure differential between soil solution and the plant solution. A plant cannot draw as much water from a concentrated soil solution as from a dilute soil solution. For most waters that could be considered for irrigation, the following general relation is applicable:

Specific conductance × 0.65 ± 0.1 = dissolved solids.

The U.S. Salinity Laboratory Staff (1954) classifies the salinity hazard of irrigation waters, in terms of specific conductance, as follows: less than 250 micromhos, low; 250–750 micromhos, medium; 750–2,250 micromhos, high; and greater than 2,250 micromhos, very high. However, the satisfactory use of a particular water for irrigation depends on many factors other than water quality, such as soil characteristics, drainage, irrigation practices, and crops grown.

Two methods of determination are given below, but the results obtained are not strictly comparable. The method of determination should be included on the analytical statement.

Residue-on-evaporation method

1. Summary of method

A volume of sample that will yield less than 200 mg residue is evaporated just to dryness on a steam bath. The residue is dried at 180°C for 2.0 hr, cooled in a desiccator, and immediately weighed.

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 percentage of error incurred for any given chemical type of water is independent of the total concentration if the residue film is kept thin.

Bicarbonate is converted to carbonate in the evaporation and drying process. The following other general observations have been reported by Howard (1933). The residues of carbonate-type water that contains considerable magnesium may often be less than would be expected. Residues of calcium and 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.

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.

2. Application

The residue-on-evaporation method is recommended for all waters that contain less than 1,000 mg dissolved solids per liter, and is applicable to all waters regardless of concentration, provided that the residue layer in the evaporating dish is kept sufficiently thin.

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.

6. Procedure

6.1 Pipet a volume of sample containing 10–200 mg total 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 the oven at 180°C for 2.0 hr.

6.4 Cool in desiccator and immediately weigh. Record the weight to the nearest 0.0001 g.

7. Calculations

Dissolved solids in mg/l

$$= \frac{1,000}{\text{ml sample}} \times \text{mg residue.}$$

8. Report

Report dissolved-solids concentrations (ROE at 180°C) as follows: ess than 1,000 mg/l, whole numbers; 1,000 mg/l and above, three significant figures.

9. Precision

Precision data for this method have no meaning because of the variability of the composition of residues obtained from different samples.

Calculation method

1. Summary of method

The concentrations of all determined solid constituents are converted mathematically into the forms in which they would normally exist in an anhydrous residue. These quantities are then summarized. If the water is grossly polluted it is usually necessary to determine the nitrogen components, and perhaps estimate the carbonaceous material, before assuming a relatively complete analysis. 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.

The conversion of the analytical statement to the forms in which the constituents would normally exist in an anhydrous residue involves many variables that are not known. 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 divided by 2.03 to give its equivalent weight as carbonate in the residue. If the bicarbonate alkalinity includes other ions (see "Alkalinity"), the calculated dissolved solids will include these constituents twice. However, occurrence of such errors of significant magnitude is relatively rare. For some constituents, such as boron, arsenic, phosphate, and selenium, the ionic states in solution are not known, much less the forms that the elements will take in the anhydrous residue. Heavy metals may be present in solution either as cations or as colloidal hydroxides, and their forms in the anhydrous residues cannot be predicted either. 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. Dissolved solids calculated by the Geological Survey include all determined material usually existing in solid form at normal temperature and pressure.

The accuracy of the results is dependent on the completeness of the analysis and on the validity of each reported constituent concentration.

2. Application

The calculation method is applicable only to those analyses that are 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, iron, 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.

3. Interferences

None.

4. Apparatus

None.

5. Reagents

None.

6. Procedure

None.

7. Calculations

7.1 Convert reported bicarbonate to carbonate

$$\text{mg/l } CO_3^{-2} = \frac{\text{mg/l } HCO_3^{-1}}{2.03}.$$

7.2 Add all determined dissolved-solid material reported in the analytical statement.

8. Report

Report calculated dissolved-solids concentrations as follows: Less than 1,000 mg/l, whole numbers; 1,000 mg/l and above, three significant figures.

9. Precision

Precision data are of no consequence for this determination.

References

Colorado Agricultural Experiment Station, 1943, Mineral tolerances in livestock drinking water: 56th Ann. Rept.

Heller, V. G., 1933, The effect of saline and alkaline waters on domestic animals: Oklahoma Agr. Mech. Coll. Expt. Sta. Bull. 217.

Howard, C. S., 1933, Determination of total dissolved solids in water analysis: Indus. Eng. Chemistry, Anal. Ed., v. 5, p. 4.

Swenson, H. A., and Baldwin, H. L., 1965, A primer on water quality: Washington, U.S. Govt. Printing Office, 27 p.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 7.

U.S. Salinity Laboratory Staff, 1954, Diagnosis and improvement of saline and alkali soils: U.S. Dept. Agriculture, Agriculture Handb. 60.

Solids, suspended

Filtration method

1. Summary of method

Suspended solids are those that are retained on a 0.45-μm membrane filter. The determined value is fairly representative of the sample but does not accurately represent the suspended-sediment concentration of the stream; suspended-solids values should not be confused with sediment concentration, which is the more accurate measure of material in suspension.

The precision and accuracy of the determination and the significance of the values obtained usually do not warrant the collection of a separate sample. If the suspended material is sufficiently settled to leave a clear supernatant solution for analysis, the suspended-solids determination can be postponed until test samples have been withdrawn for other determinations. The sample bottle is marked at the original waterline, and the volume of water removed for any chemical analysis is replaced by demineralized water. This treatment is not recommended if a significant quantity of material is removed with the test samples.

The sample is mixed well and a suitable volume quickly poured off into a graduated cylinder. Withdrawal must be rapid to get a representative sample, and no attempt should be made to take an exact volume. The suspended solids are collected on a 0.45-μm membrane filter, and the insoluble material dried and weighed.

2. Application

This method may be applied to any natural or treated water or industrial waste.

3. Interferences

None.

4. Apparatus

4.1 *Desiccator.*

4.2 *Filtration apparatus,* consisting of suction flask, 0.45-μm membrane filter disk, and suitable holder. Alternatively, a fine glass-fiber filter disk and holder may be used.

4.3 *Oven,* 110°C.

5. Reagents

None.

6. Procedure

6.1 Mix the suspension well, and rapidly pour off a suitable volume into a graduated cylinder.

6.2 Record the volume.

6.3 Quantitatively collect the insoluble materials on a tared 0.45-μm membrane filter disk, or glass-fiber filter.

6.4 Wash the insoluble material sparingly with demineralized water.

6.5 Dry the residue and filter disk overnight at 110°C.

6.6 Cool in a desiccator and weigh.

7. Calculations

Suspended solids in mg/l

$$= \frac{1{,}000}{\text{ml mixture}} \times \text{mg residue.}$$

8. Report

Report suspended solids as follows: Less than 1,000 mg/l, whole numbers; 1,000 mg/l and above, three significant figures.

9. Precision

No precision data are available.

Specific conductance

The specific conductance of an electrolyte is the reciprocal of specific resistance and is expressed in mhos. Specific resistance is the resistance, in ohms, of a column of solution 1 cm long and 1 cm^2 in cross section. In most waters, the conductance is so low that micromho is used as the unit of expression. The specific conductance is a measure of the ability of the water to carry an electric current and is therefore an indication, within rather wide limits, of the ionic strength of the solution.

Many natural waters in contact only with granite, siliceous sand, well-leached soil, or other difficultly soluble material have a conductance of less than 50 micromhos. Specific conductance of most waters in the Eastern United States is less than 1,000 micromhos, but in the arid western part of the country higher values are common. The specific conductances of some saline lakes and brines may even reach several hundred thousand micromhos.

Wheatstone bridge method

1. Summary of method

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 micromhos per cm, the regression line curves, and beyond 50,000 micromhos, the specific conductance may be an unsatisfactory index of solute ion concentration.

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. The reported units of specific conductance are micromhos/cm at 25°C.

In determining the specific conductance, it would be troublesome to prepare a cell having electrodes exactly 1 cm^2 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 mhos 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,

$$\frac{0.35}{865}=0.00405 \text{ mhos at } 25°\text{C}.$$

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:

$$\text{Micromhos}=(R \text{ of } 0.00702N \text{ KCl at } T \text{ of sample measurement}\times 1{,}000)\times(1/R \text{ of the sample}).$$

New conductivity cells should be cleaned and the electrodes platinized 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 2 dry cells ($1\frac{1}{2}$ volts 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.

The accuracy and reproducibility of results obtainable are dependent to a large extent on the type of bridge used, but may approach ±2–3 percent with this equipment. Close attention to temperature is essential for reliable work.

Additional information on the principle of the determination is given by Daniels and Alberty (1966) and Scofield (1932).

2. Application

This method may be applied to all natural, treated, and industrial waters.

3. Interferences

None.

4. Apparatus

4.1 *Conductivity cell,* pipet-type. 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 (micromhos/cm 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°–50°C, graduated in 0.1°C. Some direct-reading 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 0.5232 g KCl, dried at 180°C for 1 hr, in demineralized water and dilute to 1,000 ml.

6. Procedure

The manufacturer's instruction for operation of the bridge should be followed explicitly. A constant-temperature room or bath at 25°C 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 Prepare a graph of resistance of 0.00702*N* KCl throughout the operating temperature range.

6.2 Rinse the cell with sample.

6.3 Measure the resistance of the sample and record the temperature at the time of measurement. Record temperature to the nearest 0.1°C.

6.4 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.

7. Calculations

$$\text{Specific conductance (micromhos/cm at } 25°\text{C}) = \frac{R \text{ of } 0.00702N \text{ KCl}}{R \text{ of sample}} \times 1{,}000$$

where

R=resistance in ohms.

8. Report

Report conductivities as follows: Less than 1,000 micromhos to whole numbers; greater than 1,000 to three significant figures.

9. Precision

Analysis of two test samples by 22 laboratories resulted in mean specific conductances of 1,253 and 111 micromhos (25°C), and standard deviations of 18.5 and 1.83 micromhos (25°C), respectively.

References

Daniels, Farrington, and Alberty, R. A., 1966, Physical chemistry [3d ed.]: New York, John Wiley & Sons, Inc., 671 p.

Hughes, L. S., 1966, Use of thermistor-thermometer in determination of specific conductance: U.S. Geol. 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. Dept. Agriculture Circ. 232.

Strontium

Strontium occurs in nature chiefly as the sulfate and carbonate salts. These salts are only sparingly soluble and hence contribute little strontium to natural waters. Although elemental strontium has few practical uses, the nitrate and chlorate salts are widely used as color agents in flares and fireworks.

Atomic-absorption method—direct

1. Summary of method

Strontium is determined by atomic-absorption spectrophotometry. Lanthanum chloride and excess potassium chloride are added to mask interferences and control ionization of strontium in the flame (Fishman and Downs, 1966).

2. Application

This method may be used to analyze samples containing more than 0.01 mg of strontium per liter. Concentrations greater than 20 mg/l must be reduced by dilution.

Samples containing more than 2,500 mg total solutes per liter 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 ("Part II, Instrumental Techniques").

Two analytical ranges are included: From 1.0 to 20 mg Sr per liter and from 0.00 to 1.0 mg/l.

3. Interferences

Sodium and potassium decrease the strontium ionization in the flame. To control the ionization, 1,000 mg/l of potassium is added to both standards and samples. Aluminum, phosphate, and silica interfere but are masked by the addition of lanthanum. No interferences occur for concentrations of up to 50 mg/l nitrate and 2,000 mg/l each of sulfate, magnesium, and calcium. Above 2,500 mg/l, dissolved solids and, depending upon the ratio of strontium to dissolved solids present, low strontium values result even in the presence of potassium and lanthanum. For this reason brines and highly mineralized waters must either be diluted or analyzed by the standard-addition method ("Part II, Instrumental Techniques").

4. Apparatus

Atomic - absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Strontium concentration range: 1.0–20 mg/l

Grating	Visible.
Wavelength counter	230.4 (4607A).
Slit	4.
Lamp current	15 ma.
Scale expansion	1×.
Source (hollow-cathode lamp)	Sr.
Response time control	1.
Burner	Boling.
Air pressure	28 psi; 7.5 on flowmeter.
Acetylene pressure	8 psi; 9.0 on flowmeter.

With these operating conditions the following readings have been observed:

Strontium concentration (mg/l)	*Absorption (percent)*
1.0	8.1
5.0	32.2
10	51.9
15	64.4
20	72.9

Strontium concentration range: 0.00–1.0 mg/l

Scale expansion	10×.

All other operating conditions are the same as used for the concentration range 1.0–20 mg/l.

With these operating conditions the following readings have been observed:

Strontium concentration (mg/l)	*Scale reading*
0.10	8.3
.50	42.5
1.0	84.3

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 distilled water.

5.2 *Strontium* standard solution, 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 solutions containing from 0 to 20 mg Sr per liter by diluting strontium standard solution. Add 1.0 ml of $LaCl_3$-KCl solution to each 1.0 ml of the working standards prepared. For example, to 500 ml of a working standard, add 50 ml $LaCl_3$-KCl solution.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Filter the sample (0.45-μm membrane filter) when necessary to avoid clogging the atomizer-burner.

6.2 Add 1.0 ml $LaCl_3$-KCl solution to 10.0 ml of sample.

6.3 Measure the percent absorption or scale reading of the sample and standards against the demineralized-water blank. Repeat, and average the two values. If the strontium concentration is greater than 20 mg/l, the sample must be diluted. Be sure that the diluted sample contains the proper amount of $LaCl_3$-KCl solution.

7. Calculations

7.1 Concentration range 1.0–20 mg Sr per liter: Convert percent absorption to absorbance, and determine the mg/l Sr in the sample from a plot of absorbances of standards. For samples containing more than 20 mg/l, multiply by proper dilution factor. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

7.2 Concentration range 0.00–1.0 mg Sr per liter: Determine the mg/l Sr in the sample from a plot of scale readings of standards. Because a scale expansion of 10× is used, scale readings need not be converted to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Sr concentrations as follows: Less than 100 μg/l, nearest 10 μg/l; 100 μg/l and above, two significant figures.

9. Precision

Analysis of a test sample by 18 laboratories using this method resulted in a mean value of 0.279 mg/l and a standard deviation of 0.028 mg/l.

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geol. Survey Water-Supply Paper 1540–C, p. 41.

Sulfate

Sulfate is dissolved from most sedimentary rocks. Large quantities may be derived from beds of gypsum, sodium sulfate deposits, and some types of shale. Water from mines may be high in sulfate as a result of oxidation of pyrite. Organic material containing sulfur adds sulfate to the water as a phase of the sulfur cycle. Sulfate is discharged in many industrial waste products. In natural waters, concentrations range from a few mg per liter to several thousand mg/l.

Salts of sulfate are saline cathartics, and a quantity equal to that in 1 liter of water containing 1,000–2,000 mg/l sulfate constitutes an average dose. The U.S. Public Health Service (1962) recommends that the sulfate concentration not exceed 250 mg/l in drinking and culinary water on carriers subject to Federal quarantine regulations.

The sulfate content of water is not critical in many industrial processes. The significance is somewhat dependent on the character of the cations (California State Water Quality Control Board, 1963). Sulfates are less toxic to crops than chlorides.

Thorin method

1. Summary of method

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 spectrophotometrically, the preferred titration medium is 80-percent alcohol maintained at a pH of 5 with a sodium acetate buffer.

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 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.

2. Application

This method may be applied to most samples whose sulfate content does not exceed 200 mg/l. Samples with higher concentrations must be either diluted or analyzed by the classical gravimetric method.

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 spectrophotometric reading and require correction as indicated in "Part II, Instrumental Techniques."

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 10–15 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. 13). The column should be filled to within 2–3 inches of the 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 *Spectrophotometric-titration assembly* (fig. 14).

4.5 *Spectrophotometer,* Beckman Model B, or equivalent.

With this instrument, the following operating conditions have been used:

Wavelength	520 nm.
Phototube	Blue-sensitive.
Initial sensitivity	1.
End point	At 0.20 absorbance.

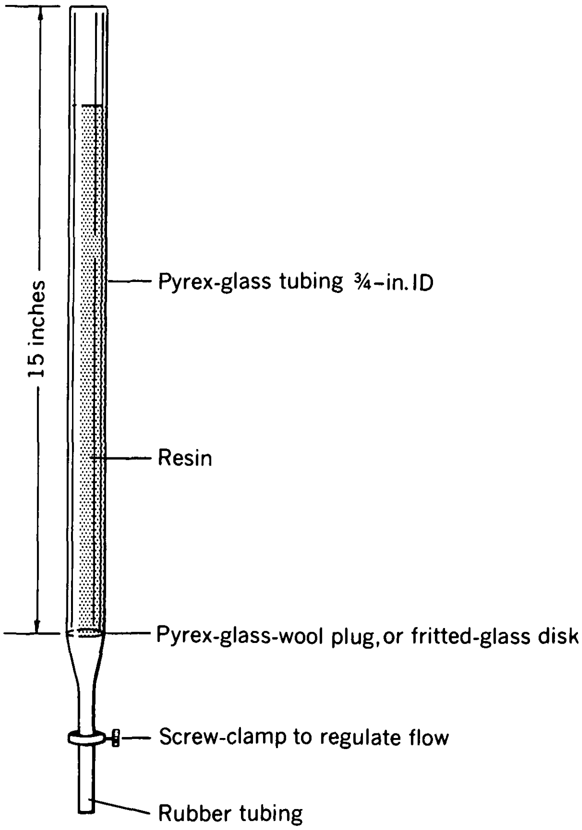

Figure 13.—Cation-exchange column.

5. Reagents

5.1 *Barium* standard solution, 1.00 ml ≎ 0.20 mg SO_4^{-2}: Dissolve 0.434 g anhydrous $BaCl_2$, dried for 1 hr at 180°C, in water, and dilute to 1,000 ml.

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 liter 95-percent ethanol and discard filter paper without washing or rinsing. Add 12 ml glacial $HC_2H_3O_2$ (sp gr 1.049) 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 = mg SO_4^{-2}: Dissolve 1.4787 g Na_2SO_4, dried for 2 hr at 180°C, in water, and dilute to 1,000 ml.

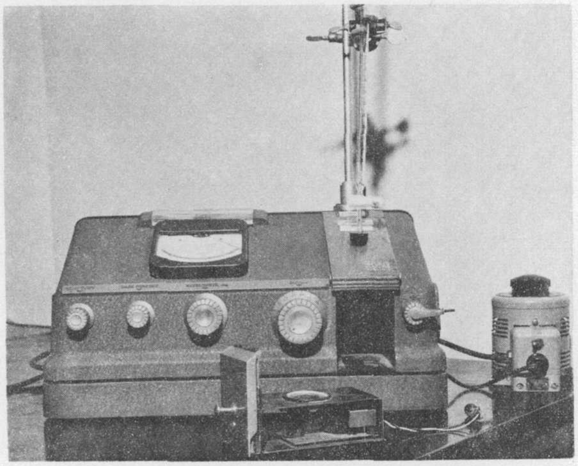

Figure 14.—Spectrophotometric-titration assembly.

6. Procedure

6.1 Rinse the cation-exchange columns with 20–30 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 a 10-ml effluent for the determination.

6.3 Pipet a volume of sample containing less than 2 mg SO_4^{-2} and 10 mg dissolved solids (10.00 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 to 0.100.

6.6 Titrate with $BaCl_2$ (1.00 ml $\Bumpeq$ 0.20 mg SO_4^{-2}) to an absorbance of 0.20, which is stable 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 used. Correct for water color when necessary.

7. Calculations

$$SO_4^{-2} \text{ in mg/l} = \frac{1{,}000}{\text{ml sample}} \times 0.2 \times (\text{ml titrant} - \text{ml blank}).$$

8. Report

Report sulfate concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

Analysis of two test samples by 17 laboratories resulted in mean values of 394 and 21 mg/l with standard deviations of 10 and 1.1 mg/l, respectively.

References

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3–A, p. 275.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 7.

Sulfide

Sulfide occurs in water as a result of bacterial and chemical processes. It usually is present as hydrogen sulfide. Variable amounts may be found in waters receiving sewage and (or) industrial wastes, such as from tanneries, papermills, chemical plants, and gas manufacturing work (California State Water Quality Control Board, 1963).

Waters containing sulfides, especially hydrogen sulfide, may be considered undesirable because of their odor. The U.S. Public Health Service (1962) states that water on carriers subject to Federal quarantine regulations shall have no objectionable taste or odor. The toxicity to aquatic organisms differs significantly with the species.

Iodometric method

1. Summary of method

This iodometric method does not differentiate the forms in which the sulfide exists in solution.

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 Sandell, 1952).

$$S^{-2} + I_2 \xrightarrow{H^{+1}} S + 2I^{-1}$$

$$I_2 + 2S_2O_3^{-2} \xrightarrow{H^{+1}} S_4O_6^{-2} + 2I^{-1}.$$

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. Application

This method may be applied to samples containing more than 0.5 mg of sulfide per liter.

3. Interferences

Reducing substances such as sulfides and heavy-metal ions will use up 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.

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 approximately 25 ml water. Add 1.2691 g resublimed I_2. When solution is complete, dilute to 1,000 ml. Standardize with 0.010*N* $Na_2S_2O_3$ using starch as indicator:

$$\text{Normality of } I_2 = \frac{0.010 \times \text{ml } Na_2S_2O_3}{\text{ml } I_2}.$$

5.3 *Potassium iodide,* 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 2–3 ml starch indicator. Immediate appearance of a blue color indicates the presence of IO_3^{-1}; slow color formation is due to atmospheric oxidation.

5.4 *Sodium thiosulfate* standard solution, 0.01*N*: Dissolve 2.482 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon-dioxide-free water and dilute to 1,000 ml with carbon-dioxide-free water. Standardize against KIO_3 as follows: Dry approximately 0.5 g KIO_3 for 2 hr at 180°C. Dissolve 0.3567 g in water and dilute to 1,000 ml. Pipet 25.00 ml KIO_3 solution into 250-ml erlenmeyer flask, then add successively 75 ml water and 0.5 g iodate-free KI. After solution is complete, add 10 ml concentrated HCl (sp gr 1.19). Allow the stoppered flask to stand 5 min in the dark and titrate with $Na_2S_2O_3$ using starch indicator as end point is approached (light-straw color):

$$\text{Normality of } Na_2S_2O_3 = \frac{0.25}{\text{ml } Na_2S_2O_3}.$$

6. Procedure

Samples for the determination of sulfide should be collected with a minimum of aeration and agitation and treated in accordance with directions given in "Part I, Sample Collection and Treatment."

6.1 Vigorously shake the sample to mix the contents 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 approximately 100 ml.

6.2 Prepare a blank of approximately 100 ml demineralized water, and carry it through the procedure along with the sample.

6.3 Add 10.00 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 2–3 ml starch indicator as the end point is approached.

7. Calculations

$$S^{-2} \text{ in mg/l} = \frac{1{,}000}{\text{ml sample}} \times 0.1603 \times (\text{ml blank titrant} - \text{ml sample titrant}).$$

8. Report

Report S^{-2} concentrations as follows: Less than 10 mg/l, one decimal; 10 mg/l and above, two significant figures.

9. Precision

No precision data are available.

References

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 277.

Kolthoff, I. M., and Sandell, E. G., 1952, Textbook of quantitative inorganic analysis [3d ed.]: New York, Macmillan Co., p. 585.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 6.

Turbidity

The turbidity of a sample is the reduction of transparency due to the presence of suspended particulate matter. Such material may consist of clay or silt, finely divided organic matter, plankton, or other microscopic organisms which cause light to be scattered and absorbed rather than transmitted in straight lines through the sample.

The U.S. Public Health Service (1962) limits the turbidity of water used in interstate carriers to 5 (Jackson candle) units. Some species of fish require clear water, but others thrive in somewhat turbid water. In general, turbidity adversely affects fish production by excluding light and thereby interfering with the growth of plants important in the fish-food cycle (California State Water Quality Control Board, 1963). Turbid water is abrasive to pipes, pumps, and turbine blades.

Attempts to correlate turbidity with the weight concentration of suspended matter are impratical, as the size, shape, and refractive index of the particulate materials are of great importance optically, but bear little direct relationship to the concentration and specific gravity of the suspended matter.

The standard method for the determination of turbidity has been based on the Jackson candle turbidimeter. However, the lowest turbidity value which can be measured directly on this instrument is 25 units. With turbidities of treated water generally falling within the range 0–5 units, indirect, secondary methods have been required to obtain turbidities on such samples. Unfortunately, no instrument has been devised which will duplicate the results obtained on the Jackson candle turbidimeter for all samples. Owing to fundamental differences in optical systems, the results obtained with different types of secondary instruments frequently will not check closely with one another, even though the instruments are all precalibrated against the Jackson candle turbidimeter (American Public Health Association and others, 1965).

A further cause of discrepancies in turbidity analysis is the use of suspensions of different types of particulate matter for preparation of instrumental calibration curves. As with the water samples, prepared suspensions have different optical properties depending upon the particle-size distributions, shapes, and refractive indices. Most commercial turbidimeters available for measuring low turbidities give comparatively good indications of the intensity of light scattered in one particular direction, predominantly at right angles to the incident light.

Nephelometric method

1. Summary of method

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 higher the intensity of scattered light, the higher 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 Jackson turbidity units. 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. Application

The method is generally applicable to any sample that does not contain coarse material that settles rapidly.

3. Interferences

The presence of colored solutes causes measured turbidity values to be low.

4. Apparatus

Hach turbidimeter, Model 2100, or equivalent.

5. Reagents

5.1 *Hexamethylenetetramine* solution: Dissolve 10.0 g hexamethylenetetramine in demineralized water and dilute to 100.0 ml.

5.2 *Hydrazine sulfate* solution: 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-hr standing at 25° ± 3°C, dilute to 100.0 ml with demineralized water and mix well. Prepare fresh monthly.

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 Jackson turbidity units (JTU). 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 interest. 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 run in 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 calibration graphs should be prepared for each range of the instrument.

6.2 *Turbidity less than 1,000 units*: Shake the sample to thoroughly disperse the solids. 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 1,000 units*: Dilute the sample with one or more volumes of nonturbid water until the turbidity falls below 1,000 units.

7. Calculations

$$\text{Jackson turbidity units (JTU)} = \text{observed turbidity} \times \frac{\text{final dilution volume}}{\text{original sample volume}}.$$

8. Report

Report turbidity as follows:

Turbidity range (JTU)	*Report to nearest*
1–10	1
10–100	5
100–500	10
500–1000	50
>1000	100

9. Precision

Precision data are not available.

References

American Public Health Association and others, 1965, Standard methods for the examination of water and wastewater [12th ed.]: New York, Am. Public Health Assoc., Inc., p. 312.

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 290.

U.S. Public Health Service, 1962, Drinking water standards: Public Health Service Pub. 956, p. 6.

Vanadium

Vanadium occurs naturally in the form of two ores; vanadinite, $Pb_5(VO_4)_3Cl$, and carnotite, $K(UO_2)VO_4 \cdot 3/2H_2O$. Vanadium is a common minor element in many soils, where its concentration ranges from around 15 to 500 mg/kg. It is used in the manufacture of specialty steels. Vanadium salts are also used in the manufacture of glass, in photography, and as a dye mordant. Although vanadium has not been shown to be essential in human nutrition, there is evidence that it has some beneficial biological functions (California State Water Quality Control Board, 1963).

Catalytic oxidation method

1. Summary of method

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 spectrophotometrically 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. Application

Concentrations in the range of from 0.1 to 8.0 μg vanadium per liter may be determined. By reducing the reaction time, concentrations in the range of 1–100 μg may be determined.

3. Interferences

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 mg/l; cobalt, 1 mg/l; nickel, 3 mg/l; copper, 0.05 mg/l; chromium, 1 mg/l; and ferrous iron, 0.3 mg/l.

4. Apparatus

4.1 *Water bath,* regulated to 25° ± 0.5°C.

4.2 *Spectrophotometer,* Beckman Model B, or equivalent.

With this instrument the following operating conditions have been used:

Wavelength	415 nm.
Cells	23 mm.
Phototube	Blue-sensitive.
Initial sensitivity setting	2.
Slit width	0.25 mm.

With these operating conditions the following absorbances have been observed:

Vanadium (*μg*)	*Absorbance*
0.000	0.200
.020	.320
.040	.440
.060	.560
.080	6.80

5. Reagents

5.1 *Ammonium persulfate* solution: Dissolve 100 g ammonium persulfate in demineralized water and dilute to 1 liter.

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 phosphoric acid. Let stand for approximately 24 hr before using. Discard after 2 days.

5.3 *Gallic acid* solution: 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: Dissolve 350 mg mercuric nitrate in demineralized water and dilute to 1 liter.

5.5 *Vanadium* standard solution I, 1.0 ml = 100 μg V: Dissolve 0.230 g ammonium metavanadate in demineralized water and dilute to 1,000 ml.

5.6 *Vanadium* standard solution II, 1.0 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: Dilute 10.0 ml vanadium standard solution II to 1,000 ml with demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.08 μg V (10.0 ml maximum) into a 23-mm absorbance cell, and adjust the volume to 10.0 ml.

6.2 Prepare sufficient standards containing from 0.00 to 0.08 μg V, and adjust the volumes to 10.0 ml with demineralized water (standards must be run with each set of samples).

6.3 Add 1.0 ml mercuric nitrate solution 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).

6.6 After about 58 min, remove from the water bath; and, at exactly 60 min, measure the absorbance at 415 nm, using distilled water as a reference (note 2).

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.

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 the V in the sample from a plot of absorbances of standards.

7.2 V in μg/l

$$= \frac{1{,}000}{\text{ml sample}} \times \mu\text{g V in sample.}$$

8. Report

Report V concentrations as follows: Less than 10μg/l, one decimal; 10 μg/l and above, two significant figures.

9. Precision

No precision data are available, but results are believed reproducible to within ±0.2 μg/l at concentration levels below 8 μg/l.

References

California State Water Quality Control Board, 1963, Water quality criteria: Pub. 3-A, p. 292.

Fishman, M. J., and Skougstad, M. W., 1964, Catalytic determination of vanadium in water: Anal. 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 Univ. Debrecen, v. 7, p. 131–135; Chem. Abs., v. 57, 9192e, 1962.

Zinc

Zinc is abundant in rocks and ores but is only a minor constituent in natural water, because the free metal and its oxides are only sparingly soluble. In most alkaline surface and ground waters it is present only in trace quantities, but more may be present in acid water. Chlorides and sulfates of zinc are highly soluble. Zinc is used in many commercial products, and industrial wastes may contain large amounts.

Zinc in moderate concentrations is not known to have adverse physiological effects on man or livestock. The U.S. Public Health Service (1962) recommends that the concentration of zinc not exceed 5 mg/l in drinking and culinary water on carriers subject to Federal quarantine regulations. Small quantities of zinc are toxic to various aquatic animals and plants. The element may also have such a toxic action on the purifying bacterial flora of streams as to present serious sewage pollution problems. A concentration of 0.3 mg/l is toxic to some fresh-water fish (Ellis and others, 1948). High concentrations of zinc are reported to be detrimental to some crops (Kelly and Brown, 1938).

Atomic-absorption method—direct

1. Summary of method

Zinc is determined by atomic-absorption spectrophotometry. The sample is aspirated directly with no pretreatment other than filtration or dilution as required (Fishman and Downs, 1966).

2. Application

Water containing at least 0.01 mg of zinc per liter may be analyzed by this method. Samples containing more than 0.20 mg/l must be diluted or less scale expansion used.

The detection limit may be lowered appreciably if a shielded hollow-cathode lamp is used.

3. Interferences

Magnesium concentrations greater than 100 mg/l interfere unless other cations, such as sodium, are present in the sample. Other cations and anions normally found in water do not interfere.

4. Apparatus

Atomic-absorption spectrophotometer, Perkin-Elmer Model 303, or equivalent.

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	213.8 (2138A).
Slit	5.
Lamp current	12 ma.
Scale expansion	10×.
Source (hollow-cathode lamp)	Zn.
Response time control	1 or 2.
Burner	Boling.
Air pressure	30 psi; 7.5 on flowmeter.
Acetylene pressure	8 psi; 9.0 on flowmeter.

With these operating conditions the following readings have been observed:

Zinc concentration (mg/l)	*Scale reading*
0.05	19.7
.10	39.5
.20	79.0

5. Reagents

5.1 *Zinc* standard solution I, 1.00 ml = 0.10 mg 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 = 0.001 mg Zn: Dilute 10 ml 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 standard solutions containing from 0.00 to 0.20 mg zinc per liter by diluting the zinc standard solution II.

6. Procedure

Samples should be collected according to instructions given in "Part I, Sample Collection and Treatment."

6.1 Filter the sample (0.45-μm membrane filter) when necessary to avoid clogging the atomizer-burner.

6.2 Measure the percent absorption or scale reading of the sample and standards against the demineralized-water blank. Repeat, and average the two values.

7. Calculations

Determine the mg/l Zn in the sample from a plot of scale readings of standards. Because a scale expansion of 10× is used, scale readings need not be converted to absorbance. Exact reproducibility is not obtained, and a working curve must be prepared with each set of samples.

8. Report

Report Zn concentrations as follows: Less than 100 μg/l, nearest 10 μg/l; 100 μg/l and above, two significant figures.

9. Precision

Analysis of a test sample by 19 laboratories using this method resulted in a mean value of 0.112 mg/l and a standard deviation of 0.028 mg/l.

References

Ellis, M. M., Westfall, B. A., and Ellis, M. D., 1948, Determination of water quality: U.S. Fish Wildlife Service Research Rept. 9, 122 p.

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geol. Survey Water-Supply Paper 1540–C, p. 43.

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☆ U.S. GOVERNMENT PRINTING OFFICE: 1970 O—389-621