A SUPPLEMENT TO

METHODS FOR THE DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

U.S. Geological Survey Techniques of Water-Resources Investigations

Book 5, Laboratory Analysis, Chapter A1

Marvin J. Fishman and Wesley L. Bradford, Editors

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PREFACE

This supplement supersedes those parts of "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments" edited by M. W. Skougstad and others (1979) that are revised herein. It also adds additional methodology to that given in the 1979 chapter.

The individual chapters of Book 5 of Techniques of Water-Resources Investigations of the U.S. Geological Survey that deals with laboratory analysis will be reissued as needed. Between reissuance of a particular chapter, as methods need to be corrected or updated or as additional methods need to be released, supplements will be issued on an interim basis as open-file reports. This report is a supplement to Book 5, Chapter A1, entitled "Methods for the Determination of Inorganic Substances in Water and Fluvial Sediments" (1979).

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

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METHODS FOR THE DETERMINATION OF INORGANIC SUBSTANCES
IN WATER AND FLUVIAL SEDIMENTS--SUPPLEMENT 1, 1982

CONTENTS

FIGURES

TABLES

ABSTRACT

New methods and revisions of selected procedures for the analysis of water and fluvial sediments in use by laboratories of the U.S Geological Survey are contained herein.

Phosphorus and nitrogen, nitrite plus nitrate automated methods were rewritten for dissolved and total values in water to accomodate the use of mercuric chloride as a preservative of nutrient samples:

New methods include:

Atomic absorption spectrometric - Selenium and tin.

Atomic emission spectrometric - Quantitative inductively-coupled argon plasma for barium, beryllium, cadmium, calcium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, silver, sodium, strontium, vanadium, and zinc.

Calculations - Suspended total and suspended recoverable constituents.

Colorimetric - Boron

Electrometric - pH and specific conductance.

TWRI, Book 5, Chapter A1, contains methods used by the Geological Survey to analyze water and suspended sediments for their content of inorganic substances. Each analytical method includes conditions for application of the method, a summary of the method, interferences, required apparatus and reagents, analytical procedures, calculations, reporting of results, and estimation of precision. The same format was followed for this supplement to TWRI, Book 5, Chapter A1.

INTRODUCTION

Purpose

The purpose of this supplement to TWRI Book 5, Chapter A1, is to describe new and revised analytical methods used by the U.S. Geological Survey for the analysis of water and fluvial sediments for inorganic substances. The analytical methods are intended for the chemist who applies his expertise to the analysis of water and fluvial sediments. Generally, each analytical method is described in sufficient detail for an experienced chemist to use with a reasonable assurance of success.

Scope

The supplement includes techniques and procedures suitable for the analysis of samples of water and fluvial sediments. Methods are grouped according to the analytical techniques involved and include:

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

This supplement includes calculation methods and atomic absorption spectrometry, colorimetry and electrometry procedures, in addition to a new group of atomic emission spectrometry techniques using an inductively-coupled argon plasma (ICP).

Most of the groups of techniques are introduced by a brief description of the chemical or instrumental principles of the technique involved, followed, where appropriate, by a discussion of the types of analytical operations that may be required, the sensitivity that may be expected from the technique, interferences, applications and general references.

Each section also includes a detailed description of all methods in which that technique is used, first as they may apply to the determination of constituents in solution (dissolved), then to the determination of total or total recoverable constituents (substances both in solution and adsorbed on or a part of suspended sediment) and finally to the determination of total or recoverable constituents from samples of bottom material.

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

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

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

Definitions

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

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

Suspended, recoverable.--Pertains to the constituents that are retained on a 0.45-um membrane filter and that are brought into solution by digestion (usually using a dilute acid solution). Complete dissolution of all the particulate matter is often not achieved by the digestion treatment, and thus the determination represents something less than the "total" amount (that is, less than 95 percent) of the constituent present in the sample. To achieve comparability of analytical data, equivalent digestion procedures would be required of all laboratories performing such analyses, because different digestion procedures are likely to produce different analytical results.

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

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

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

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

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

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

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

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

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

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

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

Significant figures

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

Chemical milliequivalents per liter are computed by multiplying the reported concentration of the individual constituents, in milligrams per liter, by the reciprocal of their equivalent weights.

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

Selenium, dissolved, atomic absorption spectrometric, hydride, automated (I-2667-81)
Parameter and Code: Selenium, dissolved (ug/L): 01145

1. Application

This method may be used to analyze waters containing at least 1 ug/L of selenium. Samples containing more than 15 ug/L must be diluted before analysis.

2. Summary of method

2.1 Organic selenium-containing compounds are decomposed by hydrochloric acid-potassium persulfate digestion. The selenium so liberated, together with inorganic selenium originally present, is then reduced to the tetravalent state using a stannous chloride-potassium iodide mixture, and is further reduced to selenium hydride with sodium borohydride. The selenium hydride gas is stripped from the solution by a stream of nitrogen gas and conveyed to a tube furnace placed in the optical path of an atomic absorption spectrometer where it is decomposed to atomic selenium. The optical absorbance is measured and related to the selenium concentration in the original sample.

2.2 For additional information on the determination of selenium in water, see Goulden and Brooksbank (1974) and Pierce, and others (1976).

3. Interferences

3.1 No interferences have been observed with the decomposition of selenium hydride in the tube furnace and its subsequent measurement.

3.2 Goulden and Brooksbank (1974) report no significant interferences in the digestion, reduction, and selenium hydride generation processes.

3.3 Pierce and Brown (1976) report interferences from trace elements commonly found in water at trace element concentrations above 300 ug/L only if sodium borohydride is introduced in the sample stream before hydrochloric acid.

3.4 It has been reported that excess nitric acid, above that normally added as a preservative, causes erratic results.

4. Apparatus

4.1 Atomic absorption spectrometer and recorder.

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

Grating.....Ultraviolet
Wavelength counter.....196.0 nm
Source (electrodeless
discharge lamp).....Selenium

4.2 Autotransformer, variable: Superior Powerstat type 3 PN 1010 or equivalent. Two are needed, one for the stripping column and one for the tube furnace.

4.3 Dri-bath, 0°-110°C. Thermolyne Model DB16525 or equivalent.

4.4 Pyrometer, portable, 0°-1200°C. Thermolyne Model PM-20700 or equivalent.

4.5 Stripping-condensing column, Pyrex, packed with 3- to 5-mm pyrex beads (fig. 1). Wrap the stripping column with heating tape and cool the condensing column with water. The nitrogen gas flow rate is adjusted for maximum sensitivity by analyzing a series of identical standards. A flow rate of approximately 200 mL/min has been found satisfactory.

4.6 Tube furnace, quartz, 10-mm ID X 100-mm length with a quartz eyelet at each end of tube to anchor nickel-chrome wire and tube fused at the center with a 2-mm ID quartz tube. Wrap the tube furnace with 5.5 m (18 ft) of 26-gauge nickel-chrome wire and cover with asbestos cloth. Mount lengthwise in the optical path of the atomic absorption spectrometer.

4.7 Technicon AutoAnalyzer II, consisting of sampler, manifold, proportioning pump, and heating bath.

Heating bath temperature.....95°C
Cam.....30(1/2)

4.8 Test Tubes, graduated, 25-mL capacity, Pyrex 9802 or equivalent.

5. Reagents

5.1 Hydrochloric acid, HCl, concentrated (sp gr 1.19).

5.2 Nitrogen gas, N_2.

5.3 Potassium iodide solution, 20 g/L: Dissolve 20 g KI in demineralized water and dilute to 1 liter.

5.4 Potassium persulfate solution, 20 g/L: Dissolve 20 g $K_2S_2O_8$ in demineralized water and dilute to 1 liter.

5.5 Selenium standard solution I, 1.00 mL = 1.00 mg Se: Dissolve 2.3928 g Na_2SeO_4 in demineralized water. Add 1 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.6 Selenium standard solution II, 1.00 mL = 10.0 ug Se: Dilute 5.00 mL selenium standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 500 mL with demineralized water. Discard after 3 months.

5.7 Selenium standard solution III, 1.00 mL = 0.10 ug Se: Dilute 5.00 mL selenium standard solution II and 1 mL concentrated HNO_3 (sp gr 1.41) to 500 mL with demineralized water. Prepare fresh weekly.

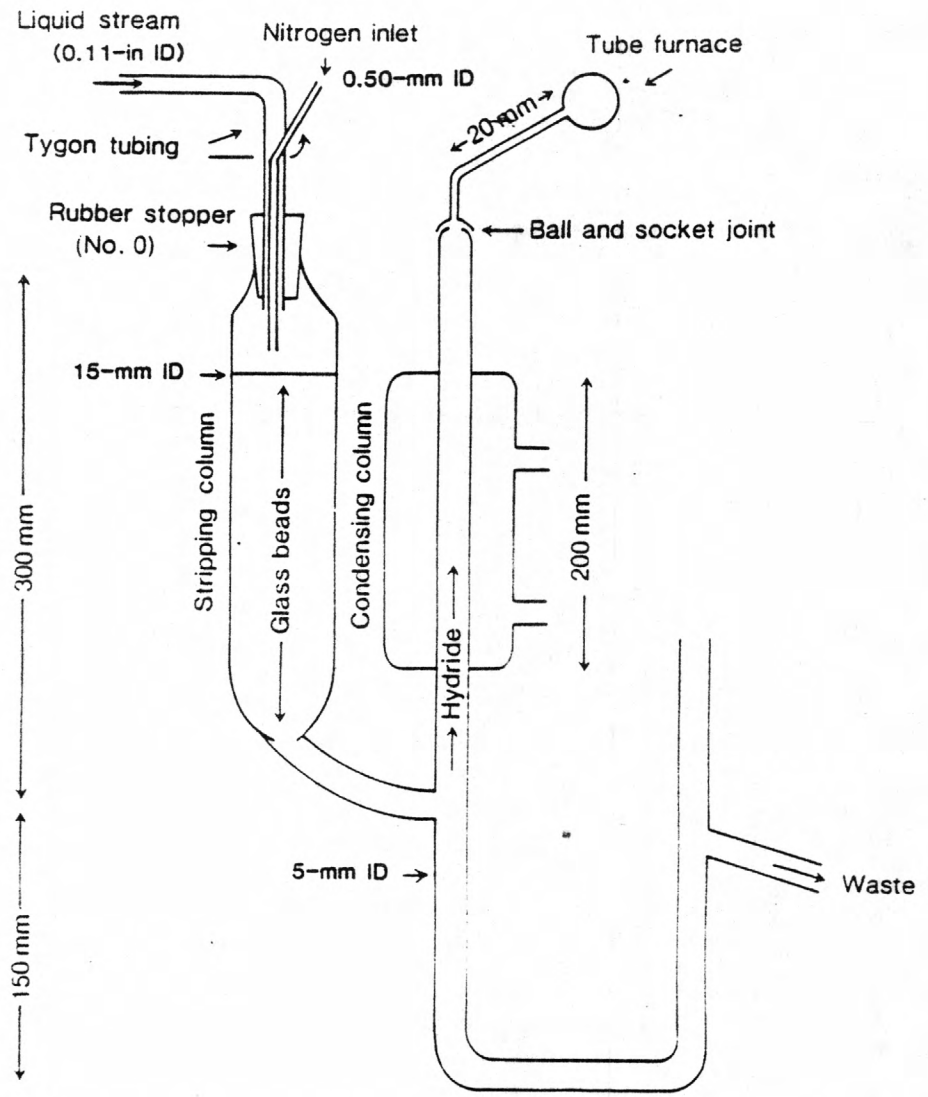

Figure 1.--Stripping-condensing column and quartz-tube furnace.

5.8 Selenium working standards: Prepare, daily, a blank and 100 mL each of a series of selenium working standards containing 0.15 mL concentrated HNO_3 by appropriate quantitative dilution of selenium standard solution III.

Selenium standard solution III (mL)	Selenium concentration (ug/L)
1.0	1
2.0	2
5.0	5
10.0	10
15.0	15

5.9 Sodium borohydride solution, 0.5 g/L: Dissolve 0.5 g $NaBH_4$ and 4 g NaOH in demineralized water and dilute to 1 liter.

5.10 Stannous chloride solution, 1.3 g/L: Dissolve 1.6 g $SnCl_2 \cdot 2H_2O$ in 1 liter concentrated hydrochloric acid.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.225 ug Se (15 mL max) into a 25-mL graduated test tube.

6.2 Pipet 15 mL blank and a complete set of standard solutions (sufficient to satisfy the requirements of 6.8) containing from 1.0 to 15.0 ug/L into 25-mL graduated test tubes.

6.3 To each tube, add 1.5 mL $K_2S_2O_8$ solution, 0.3 mL concentrated HCl, and mix.

6.4 Add a boiling stone and place the test tubes in a dri-bath at a temperature of 110°C and boil each tube for a minimum of 15 min but no longer than 20 min. Cool the solution to room temperature and make up to 17.0 mL with demineralized water and mix (Note 1).

NOTE 1: A different volume may be used as long as the volumes of standards and samples used in a given run are the same.

6.5 Set up manifold (fig. 2). (Note 2)

NOTE 2. It is necessary to change the acid flex tubing weekly.

6.6 Set stripping column and tube furnace temperatures by applying necessary voltage as follows:

Stripping column temperature.....75°C (about 36 V)
Tube furnace temperature.....800°C (about 47 V)

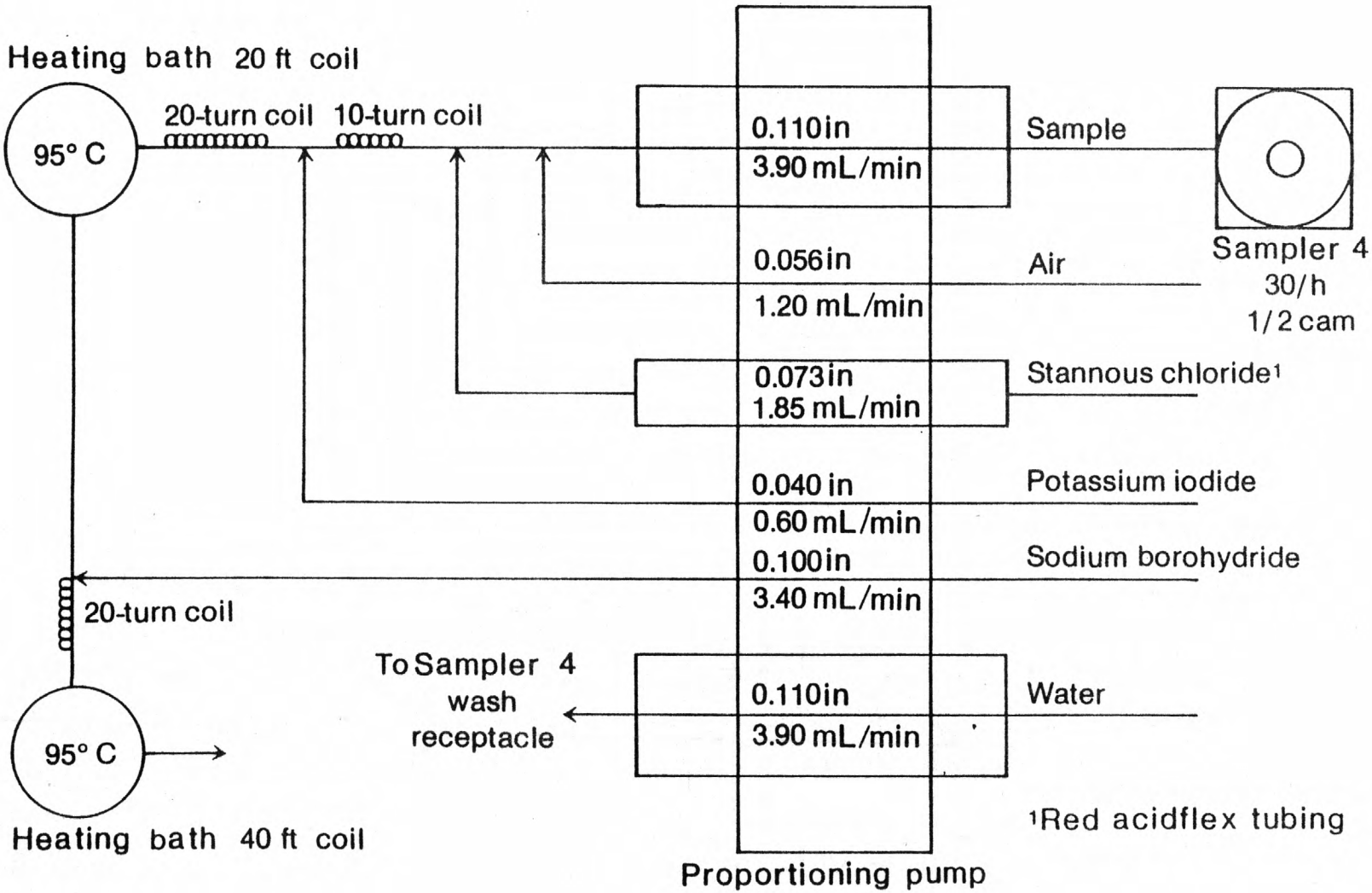

Figure 2.--Selenium manifold

Stripping column temperatures above 75°C cause the peak to split. Monitor the tube furnace temperature using portable pyrometer with the thermocouple placed in the middle of the tube, and the waste-stream temperature using a laboratory thermometer. Adjust voltages on the autotransformers as appropriate to control these temperatures.

6.7 Initially, feed all reagents through the system using demineralized water in the sample line and allow the baseline to stabilize.

6.8 Prepare the sample tray as follows: (1) In the first tray, place three tubes of the most concentrated standard followed by one tube each of the remaining standards and blank in decreasing concentrations; (2) place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent trays; (3) fill remainder of each sample tray with unknown samples.

6.9 When the baseline stabilizes, remove the sample line from the demineralized wash solution and begin analysis.

6.10 With a 5 mV recorder, 10 ug/L of selenium will give a peak approximately 60 percent of full scale. If the sensitivity drops by 30 percent or more, replace or treat the cell by one of the following methods;

A. Soak the tube furnace for 30 minutes in 1:1 water-hydrofluoric acid solution and rinse with demineralized water.

B. Grind the cell with silicon carbide as follows: Mount cell with suitable cushioning in a 3/4- inch chuck on a slowly-revolving shaft. Wet inside of cell and apply grinding compound such as commercial auto valve-grinding compound. Using a standard speed drill and an aluminum oxide grinding wheel suitably reduced in diameter to give adequate clearance, and plenty of water, begin grinding cell with a steady movement from inside to outside of cell. Grind one-half of cell at a time and regrind if necessary to achieve an even frosting.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective selenium concentration; use the value from the third tube for the reading on the most concentrated standard (the first two tubes usually give low readings).

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

8. Report

Report selenium (Se), dissolved (01145), concentrations as follows: Less than 10 ug/L, nearest ug/L; 10 ug/L and above, two significant figures.

9. Precision

9.1 Analysis of four test samples five times each by one operator, resulted in mean values of 3.3, 4.2, 6.4, and 8.5 ug/L and standard deviations of 0.1, 0.4, 0.2, and 0.1, respectively.

9.2 The precision may also be expressed in terms of percent relative standard deviation as follows:

Number of replicates	Mean, ug/L	Relative Standard deviations, percent
5	3.3	3
5	4.2	10
5	6.4	3
5	8.5	1

References

Goulden, P. D., and Brooksbank, Peter, 1974, Automated atomic absorption determination of arsenic, antimony, and selenium in natural waters: Analytical Chemistry, v. 46, p. 1431-1436.

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

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

Selenium, total in bottom material, atomic absorption spectrometric, hydride, automated (I-6667-81)

Parameter and Code: Selenium, total in bottom material (ug/g): 01148

1. Application

1.1 This method may be used to analyze bottom materials containing at least 1 ug/g of selenium. For samples containing more than 5.6 ug/g, use less sediment.

1.2 The amount of sediment that can be used is limited to 40 mg dry weight because, with greater amounts, selenium will not be recovered completely from some organic selenium compounds such as diphenyl selenide.

1.3 Bottom materials may be analyzed by this procedure after they have been prepared as directed in Method I-0520.

2. Summary of method

2.1 Organic selenium-containing compounds are decomposed by hydrochloric acid-potassium persulfate digestion. The selenium so liberated, together with inorganic selenium originally present, is then reduced to the tetravalent state using a stannous chloride-potassium iodide mixture, and is further reduced to selenium hydride with sodium borohydride. The selenium hydride gas is stripped from the solution by a stream of nitrogen gas and conveyed to a tube furnace placed in the optical path of an atomic absorption spectrometer where it is decomposed to atomic selenium. The optical absorbance is measured and related to the selenium concentration in the original sample.

2.2 For additional information on the determination of selenium in water, see Goulden and Brooksbank (1974) and Pierce, and others (1976).

3. Interferences

3.1 No interferences have been observed with the decomposition of selenium hydride in the tube furnace and its subsequent measurement.

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4. Apparatus

4.1 Atomic absorption spectrometer and recorder.

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

Grating.....Ultraviolet
Wavelength counter.....196.0 nm
Source (electrodeless discharge lamp).....Selenium

4.2 Autotransformer, variable: Superior Powerstat type 3 PN 1010 or equivalent. Two are needed, one for the stripping column and one for the tube furnace.

4.3 Dri-bath, 0°-110°C. Thermolyne Model DB16525 or equivalent.

4.4 Pyrometer, portable, 0°-1200°C. Thermolyne Model PM-20700 or equivalent.

4.5 Stripping-condensing column, Pyrex, packed with 3- to 5-mm pyrex beads (fig. 3). Wrap the stripping column with heating tape and cool the condensing column with water. The nitrogen gas flow rate is adjusted for maximum sensitivity by analyzing a series of identical standards. A flow rate of approximately 200 mL/min has been found satisfactory.

4.6 Tube furnace, quartz, 10-mm ID X 100-mm length with a quartz eyelet at each end of tube to anchor nickel-chrome wire and tube fused at the center with a 2-mm ID quartz tube. Wrap the tube furnace with 5.5 m (18 ft) of 26-gauge nickel-chrome wire and cover with asbestos cloth. Mount lengthwise in the optical path of the atomic absorption spectrometer.

4.7 Technicon AutoAnalyzer II, consisting of sampler, manifold, proportioning pump, and heating bath.

Heating bath temperature.....95°C
Cam.....30(1/2)

4.8 Test Tubes, graduated, 25-mL capacity, Pyrex 9802 or equivalent.

5. Reagents

5.1 Hydrochloric acid, HCl, concentrated (sp gr 1.19).

5.2 Nitrogen gas, N_2.

5.3 Potassium iodide solution, 20 g/L: Dissolve 20 g KI in demineralized water and dilute to 1 liter.

5.4 Potassium persulfate solution, 20 g/L: Dissolve 20 g $K_2S_2O_8$ in demineralized water and dilute to 1 liter.

5.5 Selenium standard solution I, 1.00 mL = 1.00 mg Se: Dissolve 2.3928 g Na_2SeO_4 in demineralized water. Add 1 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

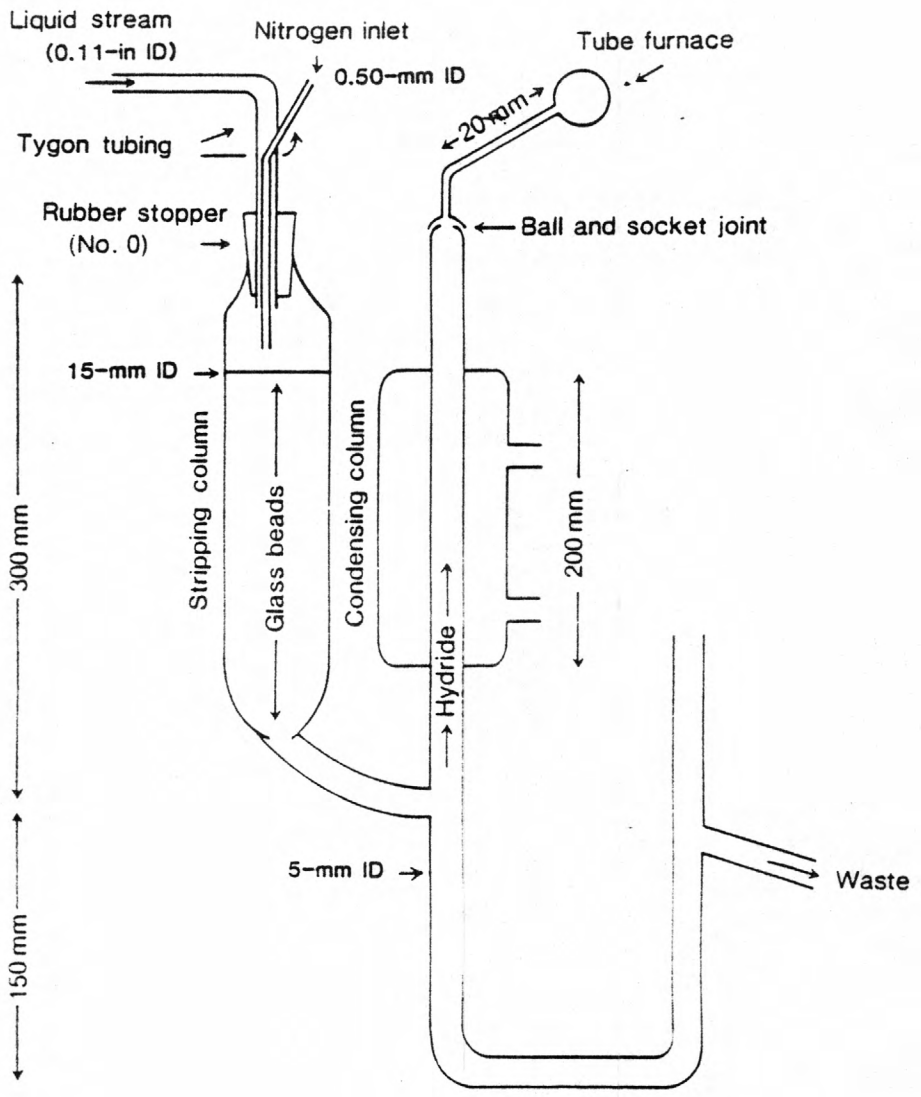

Figure 3.--Stripping-condensing column and quartz tube furnace.

5.6 Selenium standard solution II, 1.00 mL = 10.0 ug Se: Dilute 5.00 mL selenium standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 500 mL with demineralized water. Discard after 3 months.

5.7 Selenium standard solution III, 1.00 mL = 0.10 ug Se: Dilute 5.00 mL selenium standard solution II and 1 mL concentrated HNO_3 (sp gr 1.41) to 500 mL with demineralized water. Prepare fresh weekly.

5.8 Selenium working standards: Prepare daily a blank and 100 mL each of a series of selenium working standards containing 0.15 mL concentrated HNO_3 by appropriate quantitative dilution of selenium standard solution III.

Selenium standard solution III (mL)	Selenium concentration (ug/L)
1.0	1
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5.9 Sodium borohydride solution, 0.5 g/L: Dissolve 0.5 g $NaBH_4$ and 4 g NaOH in demineralized water and dilute to 1 liter.

5.10 Stannous chloride solution, 1.3 g/L: Dissolve 1.6 g $SnCl_2 \cdot 2H_2O$ in 1 liter concentrated hydrochloric acid.

6. Procedure

6.1 Weigh 40 mg or less of bottom material sample (0.225 ug Se max) and transfer into a 25 mL graduated test tube and add 15 mL demineralized water.

6.2 Pipet 15 mL blank and a complete set of standard solutions (sufficient to satisfy the requirements of 6.8) containing from 1.0 to 15.0 ug/L into 25-mL graduated test tubes.

6.3 To each tube, add 1.5 mL $K_2S_2O_8$ solution, 0.3 mL concentrated HCl, and mix.

6.4 Add a boiling stone and place the test tubes in a dri-bath at a temperature of 110°C and boil each tube for a minimum of 15 min but no longer than 20 min. Cool the solution to room temperature and make up to 17.0 mL with demineralized water and mix (Note 1)

NOTE 1: A different volume may be used as long as the volumes of standards and samples used in a given run are the same.

6.5 Set up manifold (fig. 4). (Note 2)

NOTE 2. It is necessary to change the acid flex tubing weekly.

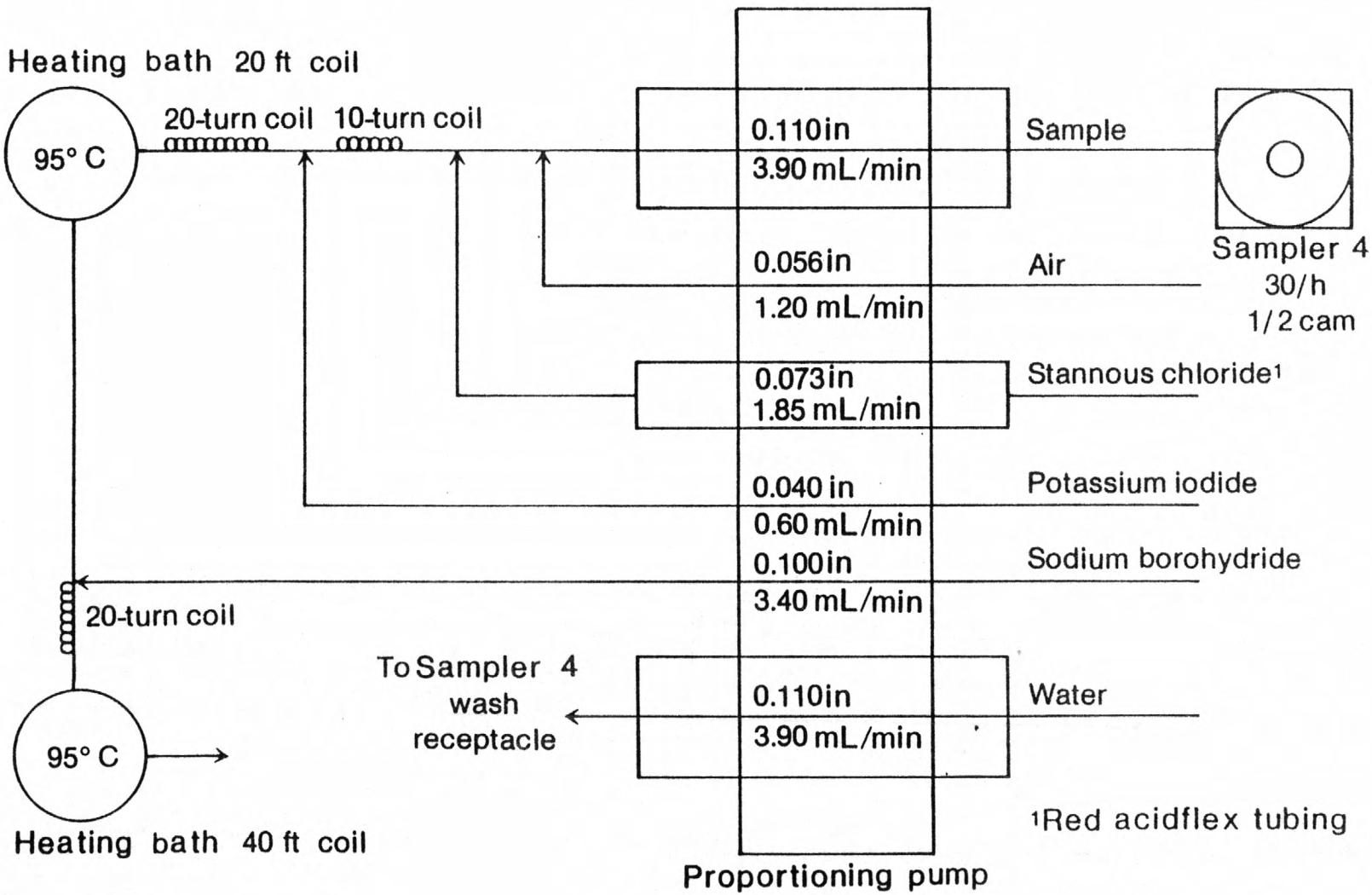


Figure 4.--Selenium manifold.

6.6 Set stripping column and tube furnace temperatures by applying necessary voltage as follows:

Stripping column temperature.....75°C (about 36 V)
Tube furnace temperature.....800°C (about 47 V)

Stripping column temperatures above 75°C cause the peak to split. Monitor the tube furnace temperature using portable pyrometer with the thermocouple placed in the middle of the tube, and the waste-stream temperature using a laboratory thermometer. Adjust voltages on the autotransformers as appropriate to control these temperatures.

6.7 Initially, feed all reagents through the system using demineralized water in the sample line and allow the baseline to stabilize.

6.8 Prepare the sample tray as follows: (1) In the first tray, place three tubes of the most concentrated standard followed by one tube each of the remaining standards and blank in decreasing concentrations; (2) place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent trays; (3) fill remainder of each sample tray with unknown samples.

6.9 When the baseline stabilizes, remove the sample line from the demineralized wash solution and begin analysis.

6.10 With a 5 mV recorder, 10 ug/L of selenium will give a peak approximately 60 percent of full scale. If the sensitivity drops by 30 percent or more, replace or treat the cell by one of the following methods;

A. Soak the tube furnace for 30 minutes in 1:1 water-hydrofluoric acid solution and rinse with demineralized water.

B. Grind the cell with silicon carbide as follows: Mount cell with suitable cushioning in a 3/4-inch chuck on a slowly-revolving shaft. Wet inside of cell and apply grinding compound such as commercial auto valve-grinding compound. Using a standard speed drill and an aluminum oxide grinding wheel suitably reduced in diameter to give adequate clearance, and plenty of water, begin grinding cell with a steady movement from inside to outside of cell. Grind one-half of cell at a time and regrind if necessary to achieve an even frosting.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective selenium concentration; use the value from the third tube for the reading on the most concentrated standard (the first two tubes usually give low readings).

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

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

$$\text{Se in ug/g} = \frac{\text{ug/L Se X 0.015 L}}{\text{wt of sample in grams}}$$

8. Report

Report selenium (Se), total in bottom material (01148), concentrations as follows: Less than 10 ug/g, nearest ug/g; 10 ug/g and above, two significant figures.

9. Precision

9.1 Analysis of four bottom material test samples five times each by one operator resulted in mean values of 1.4, 1.7, 2.4, and 3.4 ug/g and standard deviations of 0.3, 0.1, 0.2, and 0.1, respectively.

9.2 The precision may also be expressed in terms of percent relative standard deviation as follows:

Number of replicates	Mean, ug/g	Relative Standard deviation, percent
5	1.4	21
5	1.7	6
5	2.4	8
5	3.4	3

References

Goulden, P. D., and Brooksbank, Peter, 1974, Automated atomic absorption determination of arsenic, antimony, and selenium in natural waters: Analytical Chemistry, v. 46, p. 1431-1436.

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

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

Selenium, total, atomic absorption spectrometric, hydride, automated (I-4667-81)
Parameter and Code: Selenium, total (ug/L): 01147

1. Application

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

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

1.3 Suspended sediment concentrations must be less than 2.6 g/L. Higher concentrations can cause less than 100 percent recovery of selenium from some organic selenium compounds such as diphenyl selenide.

2. Summary of method

2.1 Organic selenium-containing compounds are decomposed by hydrochloric acid-potassium persulfate digestion. The selenium so liberated, together with inorganic selenium originally present, is then reduced to the tetravalent state using a stannous chloride-potassium iodide mixture, and is further reduced to selenium hydride with sodium borohydride. The selenium hydride gas is stripped from the solution by a stream of nitrogen gas and conveyed to a tube furnace placed in the optical path of an atomic absorption spectrometer where it is decomposed to atomic selenium. The optical absorbance is measured and related to the selenium concentration in the original sample.

2.2 For additional information on the determination of selenium in water, see Goulden and Brooksbank (1974) and Pierce, and others (1976).

3. Interferences

3.1 No interferences have been observed with the decomposition of selenium hydride in the tube furnace and its subsequent measurement.

3.2 Goulden and Brooksbank (1974) report no significant interferences in the digestion, reduction, and selenium hydride generation processes.

3.3 Pierce and Brown (1976) report interferences from trace elements commonly found in water at trace element concentrations above 300 ug/L if sodium borohydride only is introduced in the sample stream before hydrochloric acid.

3.4 It has been reported that excess nitric acid, above that normally added as a perservative, causes erratic results.

4. Apparatus

4.1 Atomic absorption spectrometer and recorder.

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

Grating.....Ultraviolet
Wavelength counter.....196.0 nm
Source (electrodeless discharge lamp).....Selenium

4.2 Autotransformer, variable: Superior Powerstat type 3 PN 1010 or equivalent. Two are needed, one for the stripping column and one for the tube furnace.

4.3 Dri-bath, 0°-110°C. Thermolyne Model DB16525 or equivalent.

4.4 Pyrometer, portable, 0°-1200°C. Thermolyne Model PM-20700 or equivalent.

4.5 Stripping-condensing column, Pyrex, packed with 3- to 5-mm pyrex beads (fig. 5). Wrap the stripping column with heating tape and cool the condensing column with water. The nitrogen gas flow rate is adjusted for maximum sensitivity by analyzing a series of identical standards. A flow rate of approximately 200 mL/min has been found satisfactory.

4.6 Tube furnace, quartz, 10-mm ID X 100-mm length with a quartz eyelet at each end of tube to anchor nickel-chrome wire and tube fused at the center with a 2-mm ID quartz tube. Wrap the tube furnace with 5.5 m (18 ft) of 26-gauge nickel-chrome wire and cover with asbestos cloth. Mount lengthwise in the optical path of the atomic absorption spectrometer.

4.7 Technicon AutoAnalyzer II, consisting of sampler, manifold, proportioning pump, and heating bath.

Heating bath temperature.....95°C
Cam.....30(1/2)

4.8 Test Tubes, graduated, 25-mL capacity, Pyrex 9802 or equivalent.

5. Reagents

5.1 Hydrochloric acid, HCl, concentrated (sp gr 1.19).

5.2 Nitrogen gas, N_2.

5.3 Potassium iodide solution, 20 g/L: Dissolve 20 g KI in demineralized water and dilute to 1 liter.

5.4 Potassium persulfate solution, 20 g/L: Dissolve 20 g $K_2S_2O_8$ in demineralized water and dilute to 1 liter.

5.5 Selenium standard solution I, 1.00 mL = 1.00 mg Se: Dissolve 2.3928 g Na_2SeO_4 in demineralized water. Add 1 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

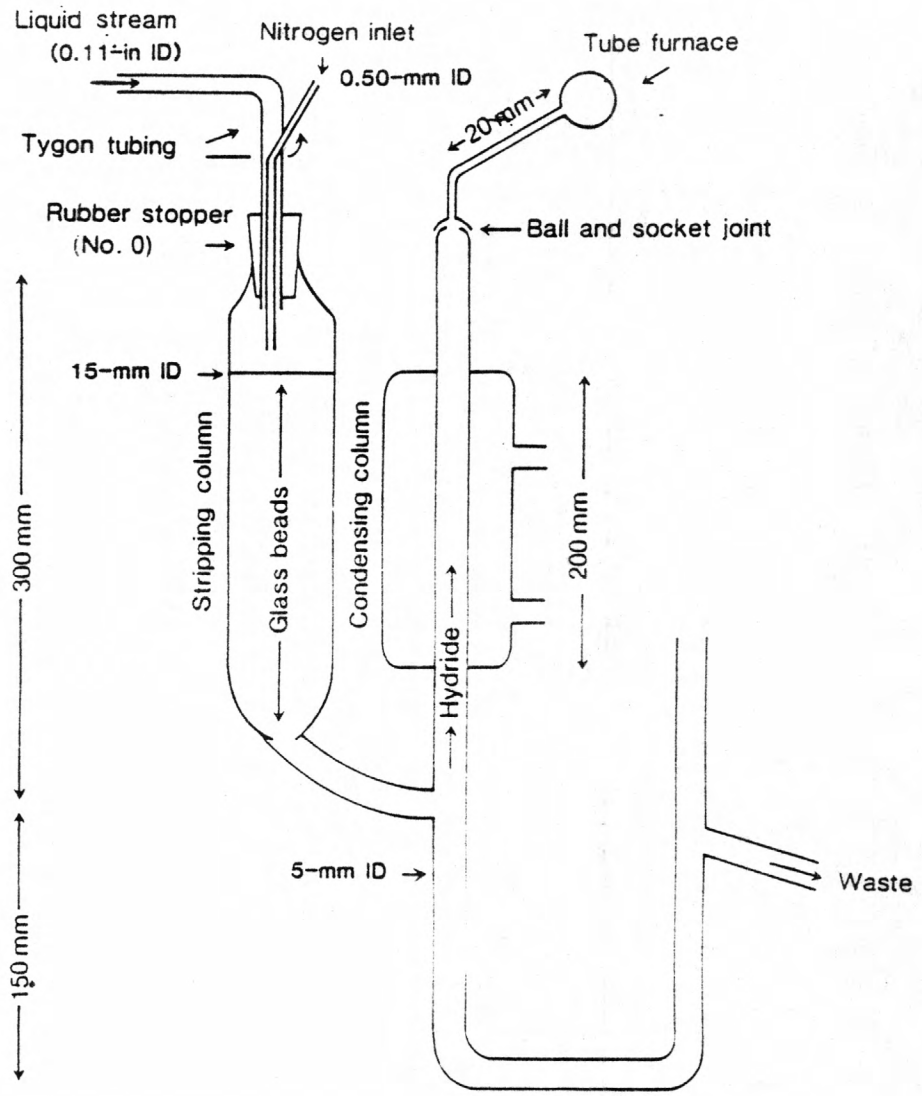


Figure 5.--Stripping-condensing column and quartz tube furnace.

5.6 Selenium standard solution II, 1.00 mL = 10.0 ug Se: Dilute 5.00 mL selenium standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 500 mL with demineralized water. Discard after 3 months.

5.7 Selenium standard solution III, 1.00 mL = 0.10 ug Se: Dilute 5.00 mL selenium standard solution II and 1 mL concentrated HNO_3 (sp gr 1.41) to 500 mL with demineralized water. Prepare fresh weekly.

5.8 Selenium working standards: Prepare daily a blank and 100 mL each of a series of selenium working standards containing 0.15 mL concentrated HNO_3 by appropriate quantitative dilution of selenium standard solution III.

Selenium standard solution III (mL)	Selenium concentration (ug/L)
1.0	1
2.0	2
5.0	5
10.0	10
15.0	15

5.9 Sodium borohydride solution, 0.5 g/L: Dissolve 0.5 g $NaBH_4$ and 4 g NaOH in demineralized water and dilute to 1 liter.

5.10 Stannous chloride solution, 1.3 g/L: Dissolve 1.6 g $SnCl_2 \cdot 2H_2O$ in 1 liter concentrated hydrochloric acid.

6. Procedure

6.1 Pipet a volume of well-mixed sample containing less than 0.225 ug Se (15 mL max) into a 25-mL graduated test tube.

6.2 Pipet 15 mL blank and a complete set of standard solutions (sufficient to satisfy the requirements of 6.8) containing from 1.0 to 15.0 ug/L into 25-mL graduated test tubes.

6.3 To each tube, add 1.5 mL $K_2S_2O_8$ solution, 0.3 mL concentrated HCl, and mix.

6.4 Add a boiling stone and place the test tubes in a dri-bath at a temperature of 110°C and boil each tube for a minimum of 15 min but no longer than 20 min. Cool the solution to room temperature and make up to 17.0 mL with demineralized water and mix (Note 1).

NOTE 1: A different volume may be used as long as the volumes of standards and samples used in a given run are the same.

6.5 Set up manifold (fig. 6). (Note 2)

NOTE 2. It is necessary to change the acid flex tubing weekly.

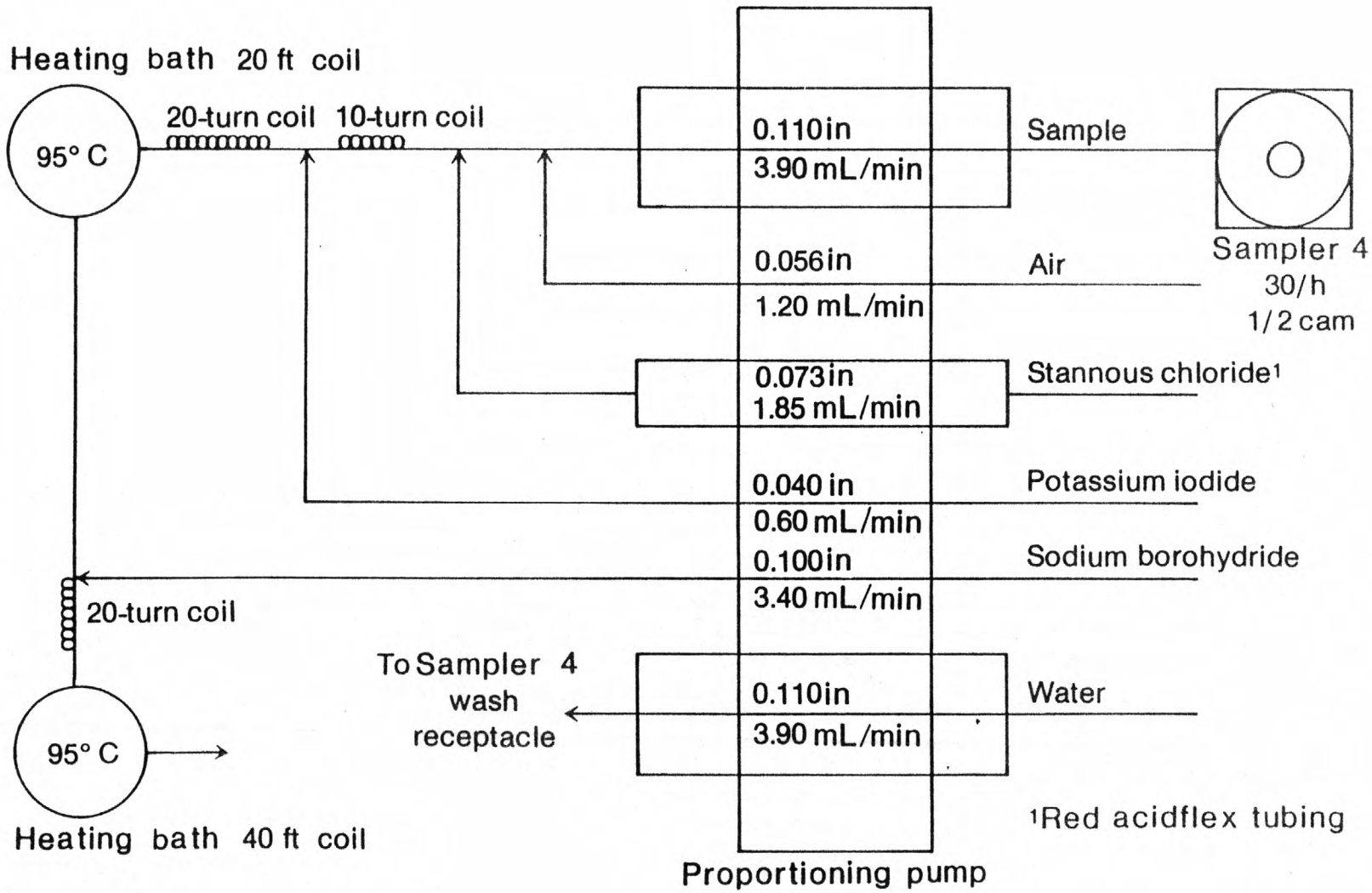


Figure 6.--Selenium manifold.

6.6 Set stripping column and tube furnace temperatures by applying necessary voltage as follows:

Stripping column temperature.....75°C (about 36 V)
Tube furnace temperature.....800°C (about 47 V)

Stripping column temperatures above 75°C cause the peak to split. Monitor the tube furnace temperature using portable pyrometer with the thermocouple placed in the middle of the tube, and the waste-stream temperature using a laboratory thermometer. Adjust voltages on the autotransformers as appropriate to control these temperatures.

6.7 Initially, feed all reagents through the system using demineralized water in the sample line and allow the baseline to stabilize.

6.8 Prepare the sample tray as follows: (1) In the first tray, place 3 tubes of the most concentrated standard followed by one tube each of the remaining standards and blank in decreasing concentrations; (2) place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent trays; (3) fill remainder of each sample tray with unknown samples.

6.9 When the baseline stabilizes, remove the sample line from the demineralized wash solution and begin analysis.

6.10 With a 5 mV recorder, 10 ug/L of selenium will give a peak approximately 60 percent of full scale. If the sensitivity drops by 30 percent or more,replace or treat the cell by one of the following methods;

A. Soak the tube furnace for 30 minutes in 1:1 water-hydrofluoric acid solution and rinse with demineralized water.

B. Grind the cell with silicon carbide as follows: Mount cell with suitable cushioning in a 3/4-inch chuck on a slowly-revolving shaft. Wet inside of cell and apply grinding compound such as commercial auto valve-grinding compound. Using a standard speed drill and an aluminum oxide grinding wheel suitably reduced in diameter to give adequate clearance, and plenty of water, begin grinding cell with a steady movement from inside to outside of cell. Grind one-half of cell at a time and regrind if necessary to achieve an even frosting.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective selenium concentration; use the value from the third tube for the reading on the most concentrated standard (the first two tubes usually give low readings).

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

8. Report

Report selenium (Se), total (01147), concentrations as follows: Less than 10 ug/L, nearest ug/L; 10 ug/L and above, two significant figures.

9. Precision

9.1 Analysis of four test samples five times each by one operator, resulted in mean values of 2.0, 8.6, 10.4, and 20.0 ug/L and standard deviations of 0.5, 0.2, 0.3, and 0.9, respectively.

9.2 The precision may also be expressed in terms of percent relative standard deviation as follows:

Number of replicates	Mean, ug/L	Relative Standard deviation, percent
5	2.0	25
5	8.6	2
5	10.4	3
5	20.0	4

References

Goulden, P. D., and Brooksbank, Peter, 1974, Automated atomic absorption determination of arsenic, antimony, and selenium in natural waters: Analytical Chemistry, v. 46, p. 1431-1436.

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

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

Tin, dissolved, atomic absorption spectrometric, hydride,automated (I-2851-81)
Parameter and Code: Tin, dissolved (ug/L): 01100

1. Application

1.1 This method may be used to analyze waters containing at least 1 ug/L of inorganic tin. Samples containing more than 10 ug/L must be diluted.

2. Summary of method

2.1 Tin is reduced to tin hydride with sodium borohydride. Interferences from most major and trace elements in the hydride-generation step are reduced to insignificance by addition of EDTA. The tin hydride is stripped from the solution by a stream of nitrogen gas and conveyed to a tube furnace placed in the optical path of an atomic absorption spectrometer where it is decomposed to atomic tin. The optical absorbance is measured and related to the tin concentration in the original sample.

2.2 For additional information see Vijan and Chan (1976) and Pyen and Fishman (1979).

3. Interferences

3.1 No interferences in the hydride-generation process have been observed from aluminum, iron, barium, beryllium, cadmium, chromium, cobalt, lead, lithium, manganese, mercury, molybdenum, nickel, selenium, and zinc at concentrations up to 1 mg/L each, nor from calcium, potassium and sodium at concentrations up to 1000 mg/L each.

3.2 Antimony, arsenic, copper, and silver at concentrations greater than 200 ug/L, 100 ug/L, 300 ug/L and 100 ug/L, respectively, depress the tin absorption. At 300 ug/L of antimony, 200 ug/L of arsenic, 400 ug/L of copper, and 200 ug/L of silver, the depression is approximately 16, 15, 8, and 20 percent, respectively.

3.3 Magnesium at concentrations greater than 300 mg/L depresses the tin absorption. At 400 and 1,000 mg/L, the depression is approximately 20 and 24 percent, respectively.

4. Apparatus

4.1 Atomic absorption spectrometer and recorder.

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

Grating.....Ultraviolet
Wavelength counter.....286.3 nm
Source (electrodeless
discharge lamp).....Tin

4.2 Autotransformer, variable: Superior Powerstat Type 3 PN 1010 or equivalent.

4.3 Pyrometer, portable, 0° - 1200°C. Thermolyne Model PM-20700 or equivalent.

4.4 Stripping-condensing column, pyrex, packed with 3- to 5-mm pyrex beads (fig.7). The condensing column need not be cooled. The nitrogen gas flow rate is adjusted for maximum sensitivity by analysing a series of identical standards. A flow rate of approximately 225 mL/min has been found satisfactory.

4.5 Tube furnace, quartz, 10-mm ID X 100-mm length with a quartz eyelet at each end of tube to anchor nickel-chrome wire and tube fused at the center with a 2-mm ID quartz tube. Wrap the tube furnace with 5.5 m (18 ft) of 26-gauge nickel-chrome wire and cover with asbestos cloth. Mount lengthwise in the optical path of the atomic absorption spectrometer.

4.6 Technicon AutoAnalyzer II, consisting of sampler, manifold, and proportioning pump.

Cam.....20(2/1)

5. Reagents (Note 1)

NOTE 1: Since tin is used extensively in metal products, its occurrence in laboratories is ubiquitous. Extreme care is required in the preparation of reagents to avoid contamination. Wash all glassware, including pipets with 1:1 HCl just prior to use in the preparation of reagent and standard solutions.

5.1 (Ethylenedinitrilo) tetraacetic acid, tetrasodium salt solution, 41.6 g/L: Dissolve 41.6 g Na_4 EDTA in demineralized water and dilute to 1 L.

5.2 Hydrochloric acid, 3M: Add 250 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.3 Nitrogen gas, N_2.

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

5.5 Tin standard solution I, 1.00 mL = 1.00 mg Sn: Dissolve 1.0 g tin metal in 15 mL of aqua regia in a beaker. Heat to dissolve the tin metal and evaporate just to dryness. To the residue add 100 mL concentrated HCl (sp gr 1.19). Mix until the residue dissolves. Transfer the solution to a volumetric flask containing demineralized water and dilute to 1,000 mL. Prepare fresh standard every 6 months.

5.6 Tin standard solution II, 1.00 mL = 10.0 ug Sn: Dilute 5.00 mL tin standard I and 50 mL concentrated HCl (sp gr 1.19) to 500 mL with demineralized water. Prepare fresh every 3 months.

5.7 Tin standard solution III, 1.00 mL = 0.10 ug Sn: Dilute 5.00 mL tin standard solution II and 50 mL concentrated HCl (sp gr 1.19) to 500 mL with demineralized water. Prepare fresh weekly.

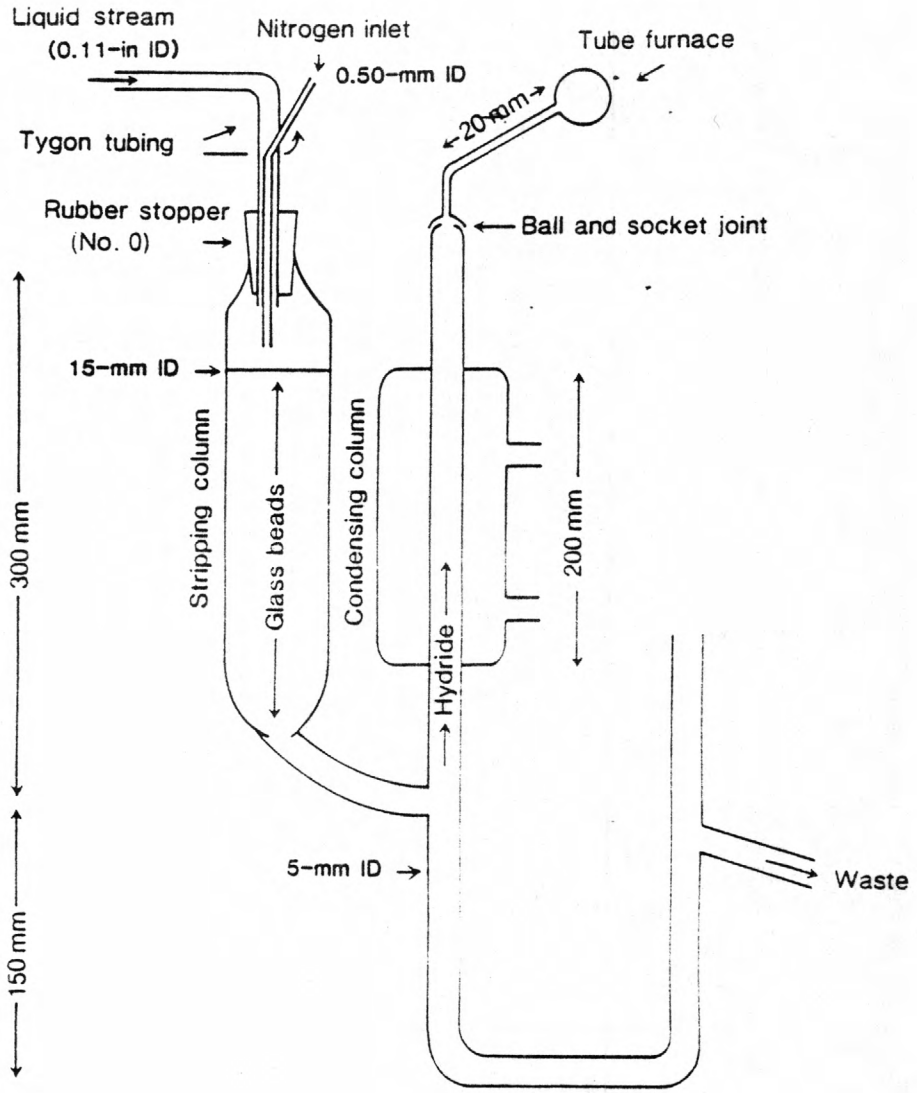


Figure 7.--Stripping and condensing column and quartz tube furnace.

5.8 Tin working standards: Prepare daily a blank and 200 mL each of a series of tin working standards by appropriate quantitative dilution of tin standard solution III and concentrated HCl (sp gr 1.19) as follows:

Tin standard solution III (mL)	Concentrated HCl (mL)	Tin concentration (ug/L)
0.0	2.0	0
2.0	1.8	1
4.0	1.6	2
10.0	1.0	5
20.0	0.0	10

6. Procedure

6.1 Set up manifold (fig. 8).

6.2 Set the tube furnace temperature at 850°C (about 47 V on the autotransformer) and monitor using the portable pyrometer with the thermocouple placed in the center of the tube. Adjust voltage on the autotransformer as appropriate.

6.3 Initially, feed all reagents through the system using demineralized water in the sample line and allow the baseline to stabilize.

6.4 Prepare the sample trays as follows: (1) In the first tray, place three tubes of the most concentrated standard followed by one tube each of the remaining standards and blank in decreasing concentrations; (2) place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent trays; (3) fill remainder of each sample tray with unknown samples.

6.5 When the baseline stabilizes, remove the sample line from the demineralized wash solution and begin analysis.

6.6 With a 5 mV recorder, 10 ug/L of tin will give a peak approximately 60 percent of full scale. If the sensitivity drops by 30 percent or more,replace or treat the cell by one of the following methods;

A. Soak the tube furnace for 30 minutes in 1:1 water-hydrofluoric acid solution and rinse with demineralized water.

B. Grind the cell with silicon carbide as follows: Mount cell with suitable cushioning in a 3/4-inch chuck on a slowly-revolving shaft. Wet inside of cell and apply grinding compound such as commercial auto-valve grinding compound. Using a standard speed drill and an aluminum oxide grinding wheel suitably reduced in diameter to give adequate clearance, and plenty of water, begin grinding cell with a steady movement from inside to outside of cell. Grind one-half of cell at a time and regrind if necessary to achieve an even frosting.

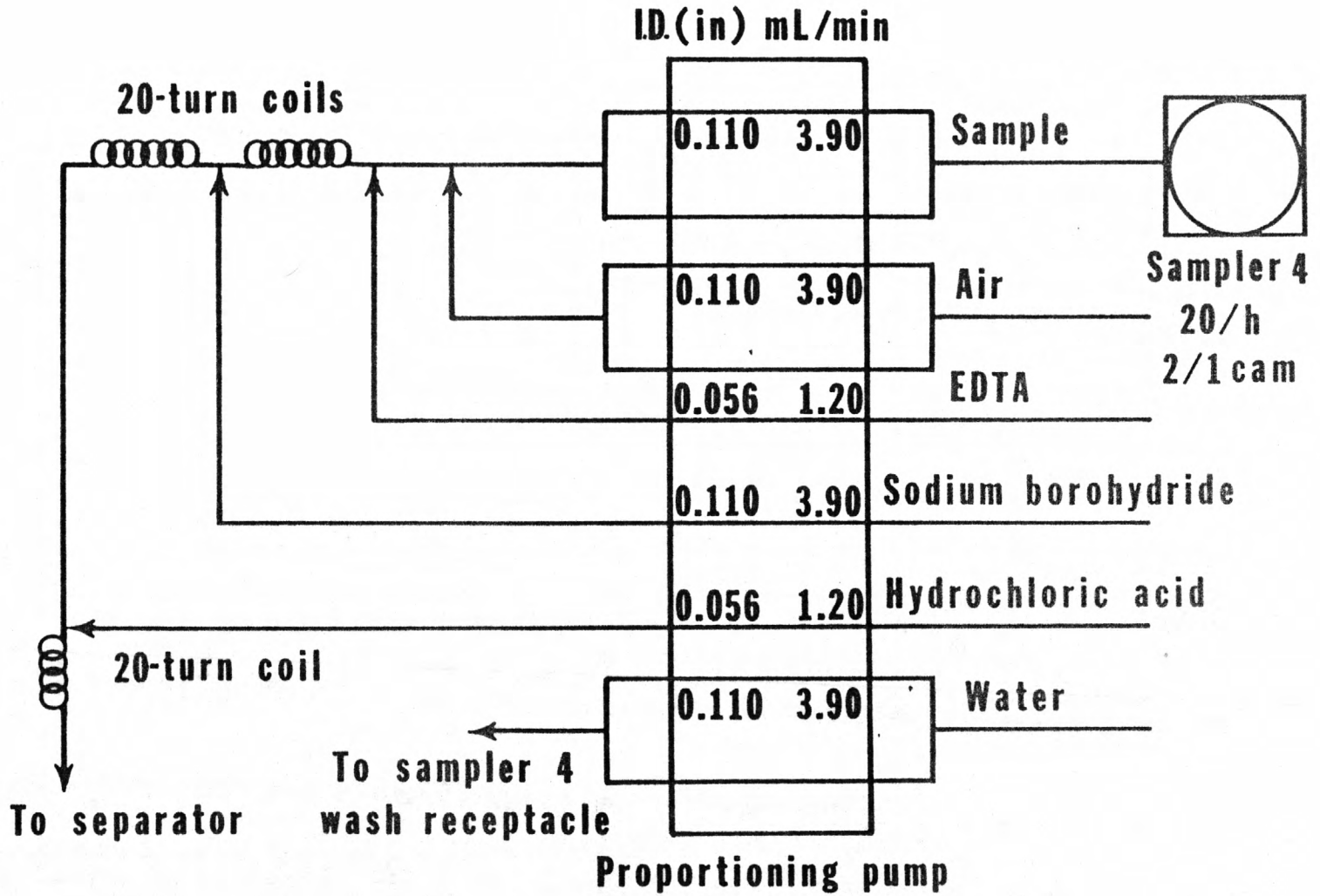


Figure 8.--Tin manifold.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective tin concentration; use the value from the third tube for the reading on the most concentrated standard (the first two tubes usually read low).

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

8. Report

Report tin (Sn), dissolved (01100), concentrations as follows: Less than 10 ug/L, nearest ug/L; 10 ug/L and above, two significant figures.

9. Precision

9.1 Analysis of four test samples 10 times each by one operator, resulted in mean values of 5.1, 9.2, 9.7, and 10.0, ug/L and standard deviations of 0.3, 0.3, 0.4, and 0.1, respectively.

9.2 The precision may also be expressed in terms of the percent relative standard deviation as follows:

Number of replicates	Mean, ug/L	Relative standard deviation, percent
10	5.1	6
10	9.2	3
10	9.7	4
10	10.0	1

References

Pyen, G., and Fishman, M. J., 1978, Automated determination of tin in water: Atomic Absorption Newsletter, v. 18, p. 34-36.

Vijan, P. N., and Chan, C. Y., 1976, Determination of tin by gas phase atomization and atomic absorption spectrometry: Analytical Chemistry, v. 48, p. 1788-1792.

Tin, recoverable in bottom material, atomic absorption spectrometric, hydride automated (I-6851-81)

Parameter and Code: Tin, recoverable in bottom material (ug/g): 01103

1. Application

1.1 This method may be used to analyze bottom materials containing at least 0.1 ug/g of inorganic tin. Prepared sample solutions (Method I-5485) containing more than 10 ug/L must be diluted.

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

2. Summary of method

2.1 Tin is reduced to tin hydride with sodium borohydride. Interferences from most major and trace elements in the hydride generation step are reduced to insignificance by addition of EDTA. The tin hydride is stripped from the solution by a stream of nitrogen gas and conveyed to a tube furnace placed in the optical path of an atomic absorption spectrometer where it is decomposed to atomic tin. The optical absorbance is measured and related to the tin concentration in the original sample.

2.2 For additional information see Vijan and Chan (1976) and Pyen and Fishman (1979).

3. Interferences

3.1 No interferences in the hydride-generation process have been observed from aluminum, iron, barium, beryllium, cadmium, chromium, cobalt, lead, lithium, manganese, mercury, molybdenum, nickel, selenium, and zinc at concentrations up to 1 mg/L each, nor from calcium, potassium and sodium at concentrations up to 1000 mg/L each.

3.2 Antimony, arsenic, copper, and silver at concentrations greater than 200 ug/L, 100 ug/L, 300 ug/L and 100 ug/L in the prepared sample solutions, respectively, depress the tin absorption. At 300 ug/L of antimony, 200 ug/L of arsenic, 400 ug/L of copper, and 200 ug/L of silver, the depression is approximately 16, 15, 8, and 20 percent, respectively.

3.3 Magnesium at concentrations greater than 300 mg/L in the prepared sample solution depresses the tin absorption. At 400 and 1,000 mg/L, the depression is approximately 20 and 24 percent, respectively.

4. Apparatus

4.1 Atomic absorption spectrometer and recorder.

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

Grating.....Ultraviolet
Wavelength counter.....286.3 nm
Source (electrodeless
discharge lamp).....Tin

4.2 Autotransformer, variable: Superior Powerstat Type 3 PN 1010 or equivalent.

4.3 Pyrometer, portable, 0° - 1200°C. Thermolyne Model PM-20700 or equivalent.

4.4 Stripping-condensing column, pyrex, packed with 3- to 5-mm pyrex beads (fig. 9). The condensing column need not be cooled. The nitrogen gas flow rate is adjusted for maximum sensitivity by analysing a series of identical standards. A flow rate of approximately 225 mL/min has been found satisfactory.

4.5 Tube furnace, quartz, 10-mm ID X 100-mm length with a quartz eyelet at each end of tube to anchor nickel-chrome wire and tube fused at the center with a 2-mm ID quartz tube. Wrap the tube furnace with 5.5 m (18 ft) of 26-gauge nickel-chrome wire and cover with asbestos cloth. Mount lengthwise in the optical path of the atomic absorption spectrometer.

4.6 Technicon AutoAnalyzer II, consisting of sampler, manifold, and proportioning pump.

Cam.....20(2/1)

5. Reagents

NOTE 1: Since tin is used extensively in metal products, its occurrence in laboratories is ubiquitous. Extreme care is required in the preparation of reagents to avoid contamination. Wash all glassware, including pipets with 1:1 HCl just prior to use in the preparation of reagent and standard solutions.

5.1 (Ethylenedinitrilo) tetraacetic acid, tetrasodium salt solution 41.6 g/L: Dissolve 41.6 g Na_4 EDTA, tetrasodium salt in demineralized water and dilute to 1 liter.

5.2 Hydrochloric acid, 3M: Add 250 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 liter.

5.3 Nitrogen gas, N_2.

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

5.5 Tin standard solution I, 1.00 mL = 1.00 mg Sn: Dissolve 1.0 g tin metal in 15 mL of aqua regia in a beaker. Heat to dissolve the tin metal and evaporate just to dryness. To the residue add 100 mL concentrated HCl (sp gr 1.19). Mix until the residue dissolves. Transfer the solution to a volumetric flask containing demineralized water and dilute to 1,000 mL. Prepare fresh every 6 months.

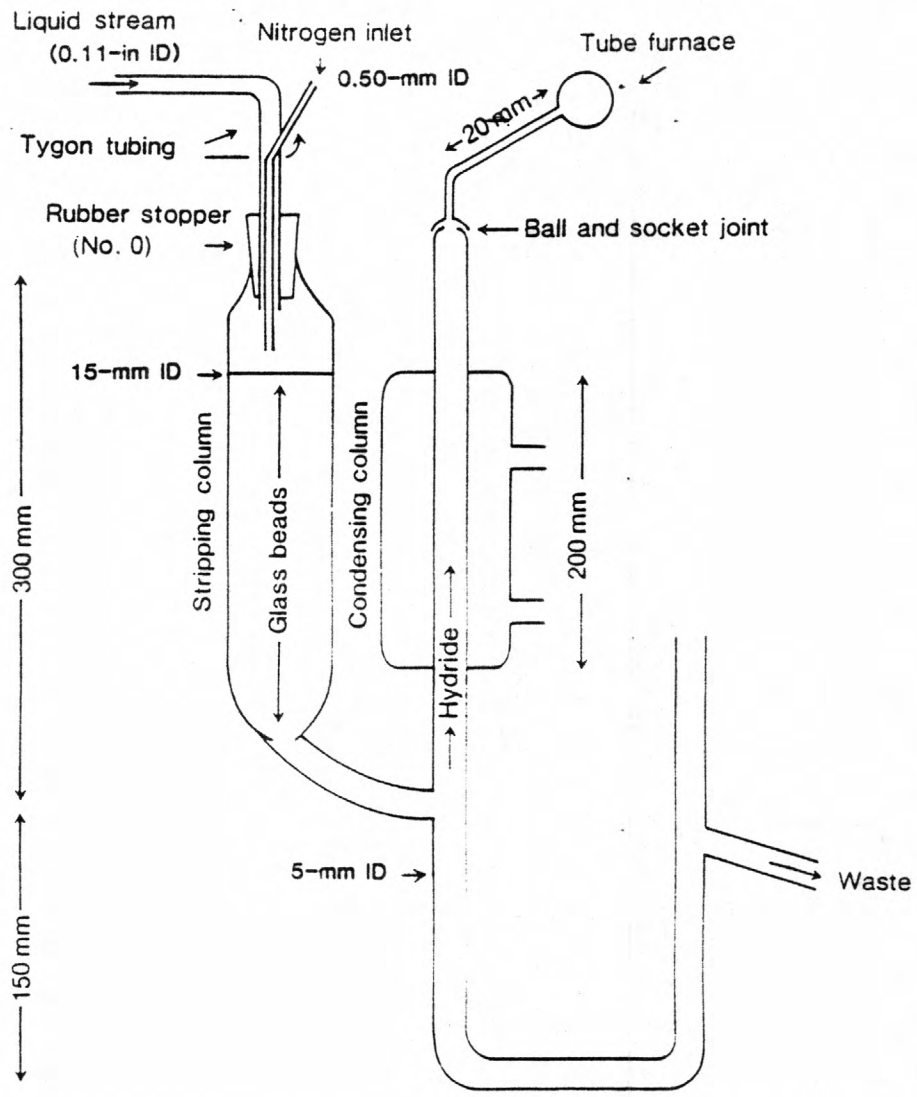


Figure 9.--Stripping and condensing column and quartz tube furnace.

5.6 Tin standard solution II, 1.00 mL = 10.0 ug Sn: Dilute 5.00 mL tin standard solution I and 50 mL concentrated HCl (sp gr 1.19) to 500 mL with demineralized water. Prepare fresh every 3 months.

5.7 Tin standard solution III, 1.00 mL = 0.10 ug Sn: Dilute 5.00 mL tin standard solution II and 50 mL concentrated HCl (sp gr 1.19) to 500 mL with demineralized water. Prepare fresh weekly.

5.8 Tin working standards: Prepare daily a blank and 200 mL each of a series of tin working standards by appropriate quantitative dilution of tin standard solution III and concentrated HCl (sp gr 1.19).

Tin standard solution III (mL)	Concentrated HCl (mL)	Tin concentration (ug/L)
0.0	2.0	0
2.0	1.8	1
4.0	1.6	2
10.0	1.0	5
20.0	0.0	10

6. Procedure

6.1 Set up manifold (fig. 10).

6.2 Set the tube furnace temperature at 850°C (about 47 V on the autotransformer) and monitor using the portable pyrometer with the thermocouple placed in the center of the tube. Adjust voltage on the autotransformer as appropriate.

6.3 Initially, feed all reagents through the system using demineralized water in the sample line and allow the baseline to stabilize.

6.4 Prepare the sample tray as follows: (1) In the first tray, place three tubes of the most concentrated standard followed by one tube each of the remaining standards and blank in decreasing concentrations; (2) place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent trays; (3) fill remainder of each sample tray with unknown samples.

6.5 When the baseline stabilizes, remove the sample line from the demineralized wash solution and begin analysis.

6.6 With a 5 mV recorder, 10 ug/L of tin will give a peak approximately 60 percent of full scale. If the sensitivity drops by 30 percent or more,replace or treat the cell by one of the following methods;

A. Soak the tube furnace for 30 minutes in 1:1 water-hydrofluoric acid solution and rinse with demineralized water.

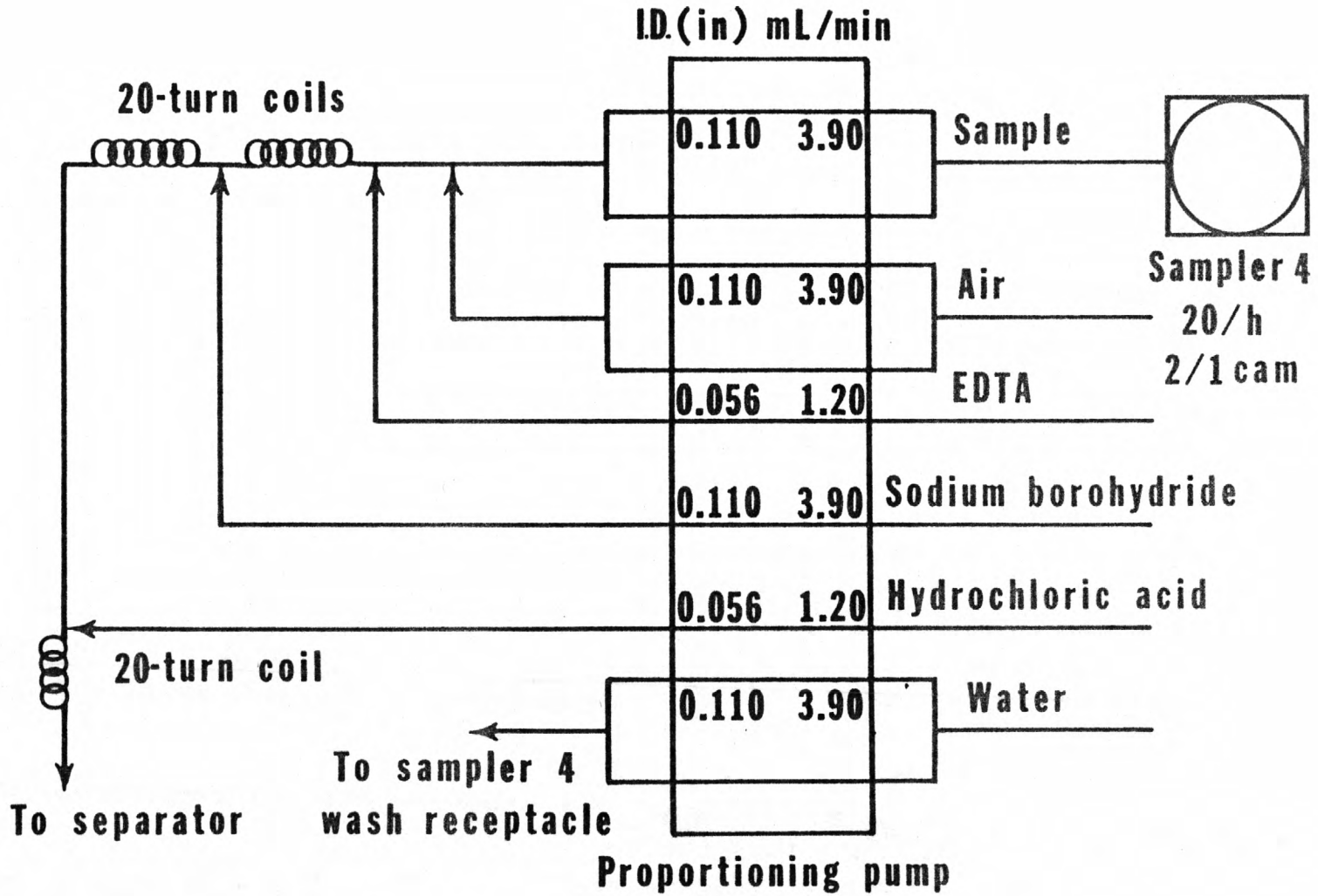


Figure 10.--Tin manifold.

B. Grind the cell with silicon carbide as follows: Mount cell with suitable cushioning in a 3/4-inch chuck on a slowly-revolving shaft. Wet inside of cell and apply grinding compound such as commercial auto-valve grinding compound. Using a standard speed drill and an aluminum oxide grinding wheel suitably reduced in diameter to give adequate clearance, and plenty of water, begin grinding cell with a steady movement from inside to outside of cell. Grind one-half of cell at a time and regrind if necessary to achieve an even frosting.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective tin concentration; use the value from the third tube for the reading on the most concentrated standard (the first two tubes usually read low).

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

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

$$\text{Sn in ug/g} = \frac{\text{ug/L Sn X mL of digest/1000}}{\text{wt of sample in grams}}$$

8. Report

Report tin (Sn), recoverable in bottom material (01103), concentrations as follows: Less than 1.0 ug/g, nearest 0.1 ug/g; 1.0 ug/g and above, two significant figures.

9. Precision

9.1 Analysis of four test samples 10 times each by one operator, resulted in mean values of 0.36, 0.56, 0.68, and 0.94 ug/g and standard deviations of 0.04, 0.03, .03, and .02 respectively.

9.2 The precision may also be expressed in terms of percent relative standard deviation as follows:

Number of replicates	Mean, ug/g	Relative standard deviation, percent
10	0.36	11
10	0.56	5
10	0.68	4
10	0.94	2

References

Pyen, G., and Fishman, M. J., 1978, Automated determination of tin in water: Atomic Absorption Newsletter, v. 18, p. 34-36.

Vijan, P. N., and Chan, C. Y., 1976, Determination of tin by gas phase atomization atomic absorption spectrometry: Analytical Chemistry, v. 48, p. 1788-1792.

Tin, total recoverable, atomic absorption spectrometric, hydride, automated (I-4851-81)
Parameter and Code: Tin, total (ug/L): 01102

1. Application

1.1 This method may be used to analyze waters containing at least 1 ug/L of inorganic tin. Prepared sample solutions (Method I-3485) containing more than 10 ug/L must be diluted.

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

2. Summary of method

2.1 Tin is reduced to tin hydride with sodium borohydride. Interferences from most major and trace elements in the hydride-generation step are reduced to insignificance by addition of EDTA. The tin hydride is stripped from the solution by a stream of nitrogen gas and conveyed to a tube furnace placed in the optical path of an atomic absorption spectrometer where it is decomposed to atomic tin. The optical absorbance is measured and related to the tin concentration in the original sample.

2.2 For additional information see Vijan and Chan (1976) and Pyen and Fishman (1979).

3. Interferences

3.1 No interferences in the hydride-generation process have been observed from aluminum, iron, barium, beryllium, cadmium, chromium, cobalt, lead, lithium, manganese, mercury, molybdenum, nickel, selenium, and zinc at concentrations up to 1 mg/L each, nor from calcium, potassium and sodium at concentrations up to 1000 mg/L each.

3.2 Antimony, arsenic, copper, and silver at concentrations greater than 200 ug/L, 100 ug/L, 300 ug/L and 100 ug/L, respectively, depress the tin absorption. At 300 ug/L of antimony, 200 ug/L of arsenic, 400 ug/L of copper, and 200 ug/L of silver, the depression is approximately 16, 15, 8, and 20 percent, respectively.

3.3 Magnesium at concentrations greater than 300 mg/L in the prepared sample solution depresses the tin absorption. At 400 and 1,000 mg/L, the depression is approximately 20 and 24 percent, respectively.

4. Apparatus

4.1 Atomic absorption spectrometer and recorder.

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

Grating.....Ultraviolet
Wavelength counter.....286.3 nm
Source (electrodeless discharge lamp).....Tin

4.2 Autotransformer, variable: Superior Powerstat Type 3 PN 1010 or equivalent.

4.3 Pyrometer, portable, 0^{o} - 1200^{o}C. Thermolyne Model PM-20700 or equivalent.

4.4 Stripping-condensing column, pyrex, packed with 3- to 5-mm pyrex beads (fig.11). The condensing column need not be cooled. The nitrogen gas flow rate is adjusted for maximum sensitivity by analysing a series of identical standards. A flow rate of approximately 225 mL/min has been found satisfactory.

4.5 Tube furnace, quartz, 10-mm ID X 100-mm length with a quartz eyelet at each end of tube to anchor nickel-chrome wire and tube fused at the center with a 2-mm ID quartz tube. Wrap the tube furnace with 5.5 m (18 ft) of 26-gauge nickel-chrome wire and cover with asbestos cloth. Mount lengthwise in the optical path of the atomic absorption spectrometer.

4.6 Technicon AutoAnalyzer II, consisting of sampler, manifold, and proportioning pump.

Cam.....20(2/1)

5. Reagents

NOTE 1: Since tin is used extensively in metal products, its occurrence in laboratories is ubiquitous. Extreme care is required in the preparation of reagents to avoid contamination. Wash all glassware, including pipets with 1:1 HCl just prior to use in the preparation of reagent and standard solutions.

5.1 (Ethylenedinitrilo) tetraacetic acid, tetrasodium salt solution, 41.6 g/L: Dissolve 41.6 g Na_4 EDTA, tetrasodium salt in demineralized water and dilute to 1 liter.

5.2 Hydrochloric acid, 3M: Add 250 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 liter.

5.3 Nitrogen gas, N_2

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

5.5 Tin standard solution I, 1.00 mL = 1.00 mg Sn: Dissolve 1.0 g tin metal in 15 mL of aqua regia in a beaker. Heat to dissolve the tin metal and evaporate just to dryness. To the residue add 100 mL concentrated HCl (sp gr 1.19). Mix until the residue dissolves. Transfer the solution to a volumetric flask containing demineralized water and dilute to 1,000 mL. Prepare fresh every 6 months.

5.6 Tin standard solution II, 1.00 mL = 10.0 ug Sn: diulute 5.00 mL tin standard I and 50 mL concentrated HCl (sp gr 1.19) to 500 mL with demineralized water. Prepare fresh every 3 months.

5.7 Tin standard solution III, 1.00 mL = 0.10 ug Sn: Dilute 5.00 mL tin standard solution II and 50 mL concentrated HCl (sp gr 1.19) to 500 mL with demineralized water. Prepare fresh weekly.

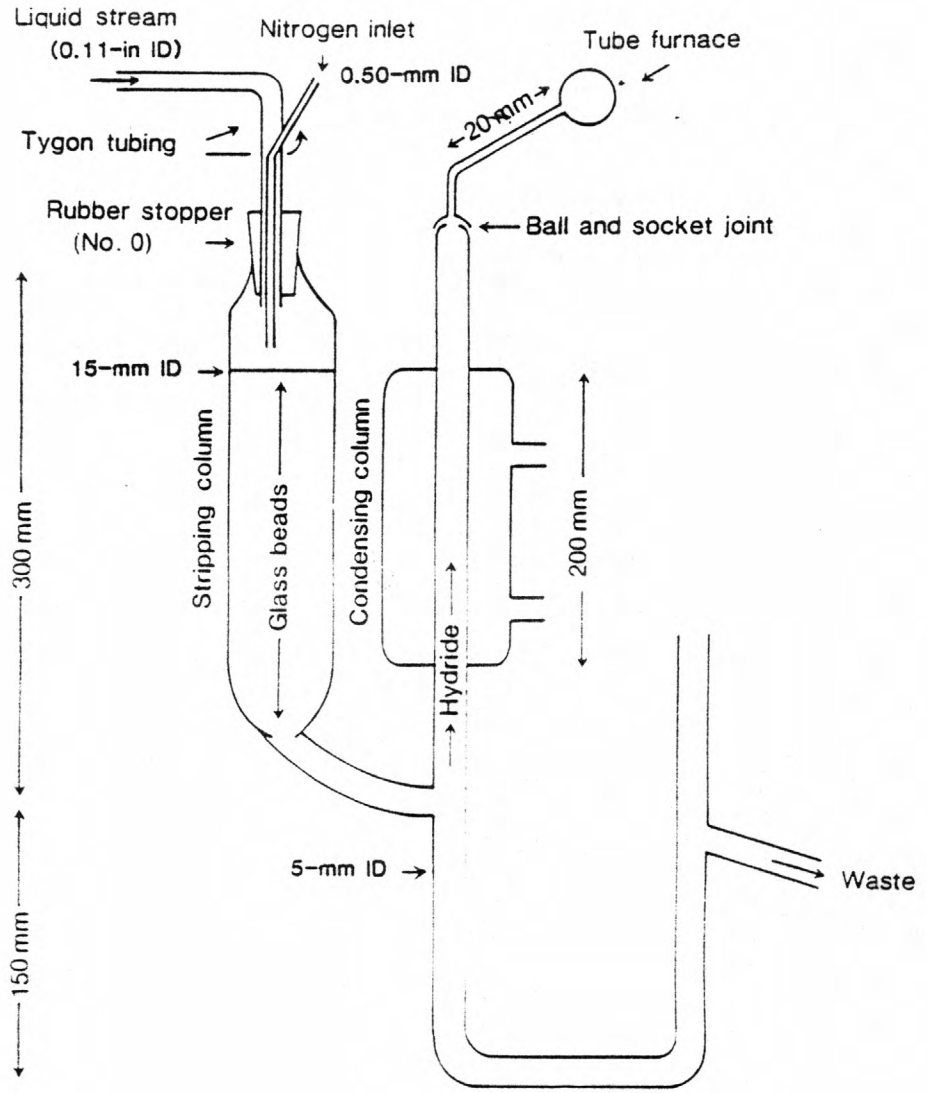


Figure 11.--Stripping and condensing column and quartz tube furnace.

5.8 Tin working standards: Prepare daily a blank and 200 mL each of a series of tin working standards by appropriate quantitative dilution of tin standard solution III and concentrated HCl (sp gr 1.19).

Tin standard solution III (mL)	Concentrated HCl (mL)	Tin concentration (ug/L)
0.0	2.0	0
2.0	1.8	1
4.0	1.6	2
10.0	1.0	5
20.0	0.0	10

6. Procedure

6.1 Set up manifold (fig. 12).

6.2 Set the tube furnace temperature at 850°C (about 47 V on the autotransformer) and monitor using the portable pyrometer with the thermocouple placed in the center of the tube. Adjust voltage on the autotransformer as appropriate.

6.3 Initially, feed all reagents through the system using demineralized water in the sample line and allow the baseline to stabilize.

6.4 Prepare the sample tray as follows: (1) In the first tray, place 3 tubes of the most concentrated standard followed by one tube each of the remaining standards and blank in decreasing concentrations; (2) place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent trays; (3) fill remainder of each sample tray with unknown samples.

6.5 When the baseline stabilizes, remove the sample line from the demineralized wash solution and begin analysis.

6.6 With a 5 mV recorder, 10 ug/L of tin will give a peak approximately 60 percent of full scale. If the sensitivity drops by 30 percent or more,replace or treat the cell by one of the following methods;

A. Soak the tube furnace for 30 minutes in 1:1 water-hydrofluoric acid solution and rinse with demineralized water.

B. Grind the cell with silicon carbide as follows: Mount cell with suitable cushioning in a 3/4-inch chuck on a slowly-revolving shaft. Wet inside of cell and apply grinding compound such as commercial auto-valve grinding compound. Using a standard speed drill and an aluminum oxide grinding wheel suitably reduced in diameter to give adequate clearance, and plenty of water, begin grinding cell with a steady movement from inside to outside of cell. Grind one-half of cell at a time and regrind if necessary to achieve an even frosting.

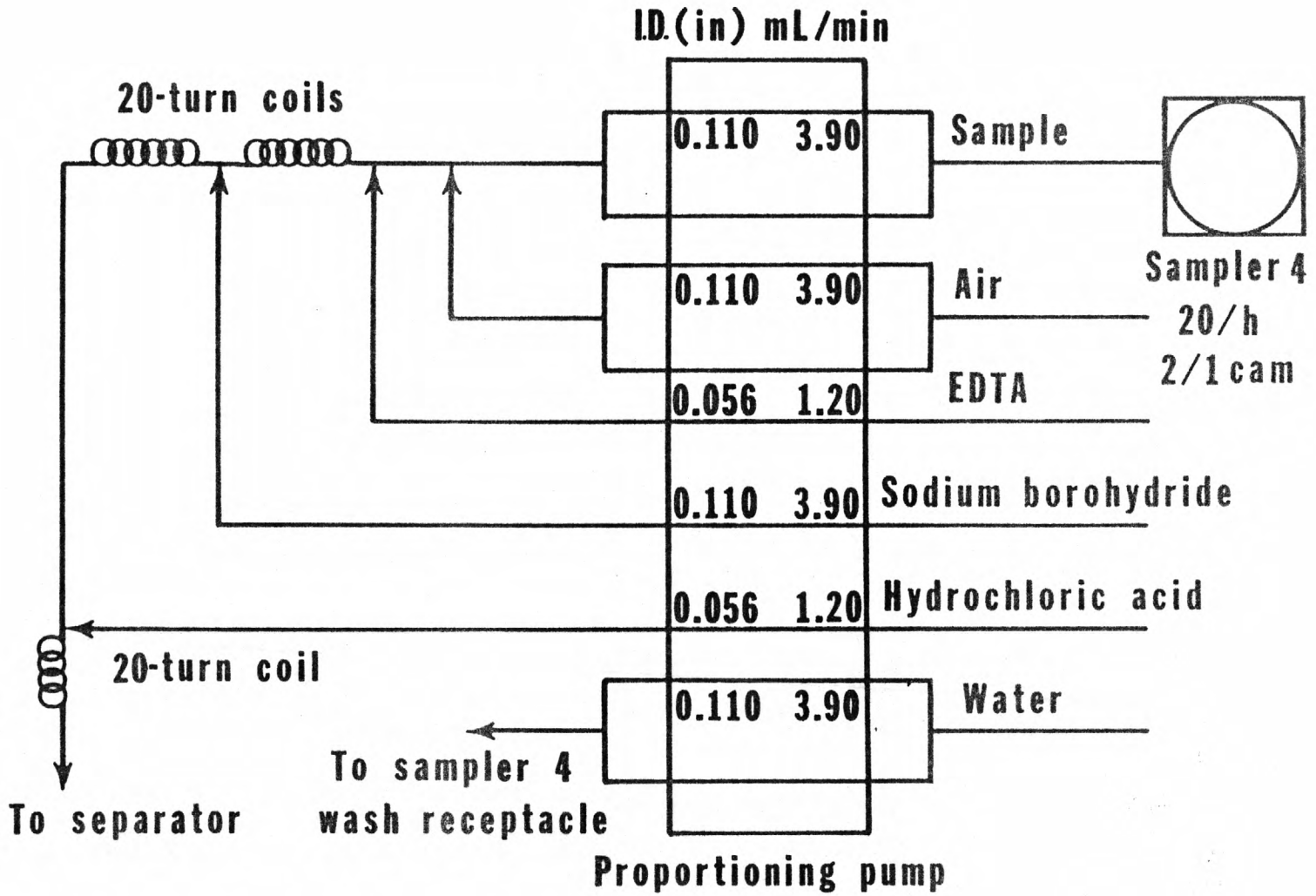


Figure 12.--Tin manifold.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective tin concentration; use the value from the third tube for the reading on the most concentrated standard (the first two tubes usually read low).

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

8. Report

Report tin, total (01102), concentrations as follows: Less than 10 ug/L, nearest ug/L; 10 ug/L and above, two significant figures.

9. Precision

9.1 Analysis of five test samples 10 times each by one operator, resulted in mean values of 5.3, 9.8, 10.1, 10.5, and 11.7 ug/L and standard deviations of 0.2, 0.4, 0.2, 0.3, and 0.5, respectively.

9.2 The precision may also be expressed in terms of the percent relative standard deviation as follows:

Number of replicates	Mean, ug/L	Relative standard deviation, percent
10	5.3	4
10	9.8	4
10	10.1	2
10	10.5	3
10	11.7	4

References

Vijan, P. N., and Chan, C. Y., 1976, Determination of tin by gas phase atomization and atomic absorption spectrometry: Analytical Chemistry, v. 48, p. 1788-1792.

Pyen, G., and Fishman, M. J., 1978, Automated determination of tin in water: Atomic Absorption Newsletter, v. 18, p. 34-36.

ATOMIC EMISSION SPECTROMETRY

Introduction

Emission Phenomenon

When a metal atom in the gas phase ground state (M) is heated in an exitation source, energy is supplied to the atom via collision with high-temperature atoms and molecules resulting in transitions of electrons within the metal atom to higher energy states. The excited atom M* can then lose energy by emission of a photon. The process can be represented thus:

$$M + \text{energy} \rightarrow M^* \rightarrow M + h\nu$$

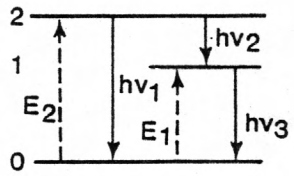
The energy of each of the emitted photons, $h\nu$, equals the difference between the energies in the higher and lower energy levels (fig. 13). Each transition emits a photon at a wavelength given by $\lambda = c/\nu$, and each element has a characteristic pattern of emission wavelengths. In the simplified example, (fig. 13) the population of atoms in the excitation source can be excited to either energy level one or two. Emission can occur by transitions from energy levels one or two to the ground state, or by an intermediate transition from level two to one. Usually, one or more transitions ending in the ground state is the most probable, resulting in one of the characteristic emission wavelengths (lines) of greatest intensity.

Emission from ions can be described in a similar way but since the energy levels are different from those of the atoms, the characteristic emission wavelengths are normally different as well.

Quantitative Analysis by Emission

In order for the emission phenomena to be used in quantitative chemical analyses, the following are necessary: (a) the sample must be atomized (constituents of interest converted to atoms or ions in the gas phase) and the resulting atoms or ions excited; (b) the resulting characteristic emission lines must be spectrally separated and their relative intensities measured employing a suitable dispersion-detection system (spectrometer or spectrograph); and (c) the resulting intensities must be compared with standards of known elemental composition. Solid samples are usually analysed by arc or spark exitation sources which atomize and excite elements directly from the sample. Solutions are generally analyzed with flame or plasma exitation sources into which the sample is aspirated. In both cases, one or more elements can be quantified simultaneously from the emission lines.

The fraction of sample atoms excited varies exponentially with the excitation source temperature, the Boltzmann distribution (Mavrodineanu and Boiteux, 1965) being a good approximation where the source attains or approaches thermodynamic equilibrium. Thus the higher the temperature of the excitation source, the greater the emission intensity for a given atomic concentration in the source. Moreover, the atomization (formation of atoms in the source) of many sample media is more complete at higher temperatures resulting in an increasing concentration of atoms or ions in the exitation source with increasing temperatures.



$E_2 = h\nu_1$

$E_2 = h\nu_2 + h\nu_3$

$E_1 = h\nu_3$

Figure 13.--Energy level diagram

One might at first expect that the analytical sensitivity could be increased and the detection limit decreased almost without limit by increasing the temperature of the excitation sources. But at higher temperatures, several other phenomina occur which limit the benefit of higher source temperatures. Ionization of the sample atoms which removes atoms from one emitting population to another becomes increasingly important; the spectrum becomes more complex as more upper-level lines are excited; and, perhaps most important, the source background emission also increases rapidly.

The principal advantages of atomic emission are low analytical detection limits for many elements, simple instrumentation, good specificity and speed of analysis, and adaptation to simultaneous, multielemental analysis. The principle limitation is that atomization-excitation conditions can be optimized to a degree satisfactory for quantitative analysis for only a limited number of constituents simultaneously. This limitation comes about from the interdependence of the atomization and excitation processes. Conditions to optimize one process may cause interferences in another. For example, with relatively low-temperature sources, which minimize ionization and background, the population of excited atoms is low and the analytical sensitivity and detection level are poor relative to that in higher temperature sources. With high-temperature sources, the population of excited atoms is large but high background and complex spectra are produced which can be adequately resolved only by a high resolution spectrometric system. The other serious limitation is compound formation in the atomization-exitation source, an effect which reduces the atomic population in the source and places an upper limit on sensitivity for many elements.

Types of excitation sources

Flames

The chemical flame is the oldest emission source dating from the 1860's and it is still in wide use today. Various types of chemical flames and burner designs have been developed for analytical work. As emission sources, flames have much to offer. They are simple, inexpensive to operate, and the temperatures developed in the flames are adequate to exite 10 to 20 metals, enabling analyses in water at the milligram per liter concentration range or below. The temperatures of the most commonly used flames are in the 2,000 to 3,000 K region, which results in good analytical sensitivity for elements which have relatively low excitation energies and are atomized to an appreciable extent in the flame, that is, those having no strong tendency toward compound formation.

Flames are used most for analysis of liquid samples, either aqueous solutions or organic solvents. Samples are introduced into the flame through a nebulizer which converts the sample solution into a fine mist. Once in the flame, several processes occur in rapid succession: desolvation, atomization and excitation as illustrated in figure 14. Many nebulizer and burner designs have been developed. These are extensively reviewed by Mavrodineanu and Boiteux (1965).

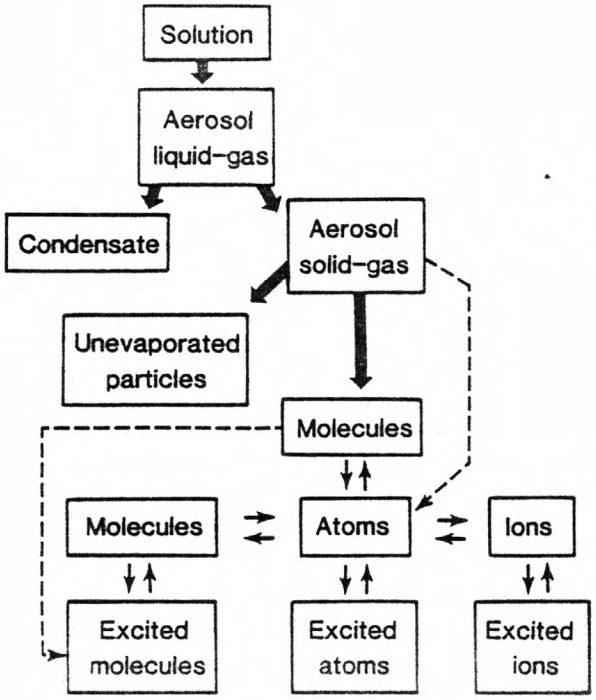


Figure 14.--Schematic of the nebulization, desolvation, atomization, and excitation processes

The production of gas phase metal atoms from the sample depends initially on the thermodynamics and kinetics of the desolvation-atomization processes. Commonly only a small fraction of the sample reaches the flame. Additional atoms can be lost from the population of emitting atoms by compound formation with flame gas products and by ionization. Ionization is important only for a few elements that are easily ionized in relatively hot flames. By far the most important loss mechanism is compound formation of analyte atoms with flame gas radicals. Many elements form stable compounds in the flame, notably metal monoxides. Considering the general equilibrium:

$$M + O \leftrightharpoons MO$$

the foreward reaction is exothermic so that an increase in temperature shifts the equilibrium toward the free metal atom, assuming the oxygen concentration remains the same. A decrease in the oxygen concentration also shifts the equilibrium toward the free metal atom. Since one normally has little control over the temperature in chemical flames, the more common approach is to lower the free oxygen content of the gases. One means of doing this, especially in hydrocarbon flames, is to make the flame fuel rich. The slight drop in flame temperature under fuel-rich conditions does not reduce the exitation efficiency substantially so a net gain in free metal atom is achieved. Extracting the constituents of interest from aqueous solution into organic solvents reduces compound formation by reducing source cooling from the aqueous solvent and by improving the nebulization and desolvation efficiencies.

Flames also have some important limitations for use as emission sources: (a) temperatures much above 3,000 K cannot be obtained with the usual fuel-oxidant combinations; for many elements with high excitaion energies this temperature is too low to excite a population of atoms adequate for good analytical sensitivity; (b) the chemical environment of the flame fosters compound formation which effectively removes metal atoms of interest from the atomic emission process; and (c) considerable background emission may be present in certain spectral regions (for example, the OH emission between 300 and 350 nm and the C_2, CN, and CH emissions from hydrocarbon-fueled flames). Despite these limitations, flame atomic emission remains one of the simplest and most sensitive analytical methods for easily excited elements that do not form highly stable compounds at high temperatures, such as alkali, alkaline earth, and several transition elements.

Direct-current arc

The direct-current arc (d-c) discharge (Slavin, 1971) is a widely used specrochemical excitation source and is almost always employed with a spectrograph or multichannel spectrometer. A high-current, low-voltage discharge is maintained between two electrodes (usually graphite), one containing the sample (usually the anode), and operating in air (free-burning) or some other gas mixture at atmospheric pressure. Electrodes are most often made from high-purity carbon or graphite because of its high-temperature stability, ease of fabrication, and ease of purification.

With a high arc temperature, the analytical sensitivity is high, and low detection limits for most elements result. Due primarily to wandering of the arc on the electrode surfaces during the discharge, the reproducibility of the emission from sample to sample is poor. Consequently, reproducibilities in analyses are seldom better than about ±20 percent. This makes the d-c arc source better suited to qualitative or semiquantitative analyses, rather than quantitative work. The tremendous sensitivity of this high-temperature source combined with the capability for simultaneous multielement analysis make the d-c arc a very powerful and useful analytical tool despite poor reproducibility.

The d-c arc is used mostly for analysis of solid samples, usually in powder form. Liquid samples can be analyzed by first evaporating the sample to dryness in a cup electrode or by rotating a disc electrode into the liquid sample and then into the arc.

Alternating-current spark

The alternating-current or radiofrequency spark discharge is another widely used emission source (Slavin, 1971). It too is almost always employed with a spectrograph or direct-reading, multichannel spectrometer. While resulting in poorer detection limits than the d-c arc, it provides a higher degree of reproducibility and can be used for quantitative analysis.

The spark occurs repeatedly over a small area of the sample, and each spark is followed by an "off" period. As a result of this alternating heating-cooling cycle, the bulk of the sample is not heated to emission so that homogeneity and limited-area studies can be made on solid samples and solutions can be analyzed directly. However, the small amount of sample consumed leads to poorer analytical sensitivity and detection limits compared to other methods.

Conducting samples (for example, metals) are usually ground flat and used as one electrode with a pointed graphite counterelectrode (point-to-plane technique). Powdered samples (conducting and nonconducting) are usually mixed with graphite powder and pressed into a pellet which is used as the plane electrode. Solutions are usually analyzed using a porous cup (graphite) electrode or a rotating disc electrode. The former consists of a porous-bottom graphite cup containing the sample solution and the counterelectrode beneath the cup, discharging to the wet bottom of the porous cup. The rotating disc electrode consists of a rotating graphite disc, the lower edge of which dips into the sample solution and carries it to the spark discharge region at the top of the disc. Numerous other electrode arrangements have been used, but these are the most popular.

Direct-current argon plasma (plasma jet)

The d-c plasma jet developed by Margoshes and Scribner (1959) is produced by forcing argon gas through an orifice housing a d-c arc discharge. Liquid samples are drawn into the plasma by an apparatus described by Keirs and Vickers (1977) in which liquid samples are aspirated into a chamber, mixed with argon and swept through the orifice.

The temperature of the plasma approaches 10,000 K and in addition to the usual nonionized spectral lines, spectra of ionized atoms are produced and in some situations predominate. The actual temperature of the plasma depends on the arc current, electrode geometry, and gas flow rates. When gas flow is increased, electrical conductivity rises. This, in turn, results in a higher current and as a consequence, higher temperatures at the core of the discharge. Often, this effect varies as the composition of samples changes. To overcome problems in analysis caused by these effects, an excess of an easily-ionized cation is usually added to the samples to buffer the ionization, and an internal standard is used for calibration.

Only a small fraction of the sample aerosol particles actually enters the plasma. Because of this and the intense plasma background emission, a high-resolution optical system is needed to achieve high analytical sensitivity. Reednick (1979) has described a commercially available d-c arc plasma jet used with a high resolving power echelle spectrometer.

Inductively-coupled argon radiofrequency plasma torch

In recent years, inductively coupled radiofrequency plasma (ICP) torches have been applied for spectrochemical analysis in both emission spectroscopy (Greenfield and others, 1964; Wendt and Fassel, 1965) and absorption spectroscopy. This type of torch was first described by Reed (1961) as a new method of generating a stable plasma at atmospheric pressure.

The equipment for producing an inductively-coupled radiofrequency plasma torch consists of a quartz tube surrounded by a few turns of water-cooled tubular copper coil connected to an induction-heating power generator (fig. 15). One end of the quartz tube is open and the gas is supplied at the other end. The gas is heated by the currents induced in the plasma.

The coupling between field and plasma improves as the plasma approaches the coil causing the plasma to expand. The outer tube prevents the plasma from reaching the coil and causing a short circuit and at the same time thermally stabilizes the plasma. The heat from the plasma is continuously removed by cool argon gas flowing between the outside and middle tubes. A laminar stream of cold argon flowing through the space between the outer and the middle tubes surrounds the plasma, stabilizes the torch, and prevents wall contamination. The inner nozzle permits the injection of an aerosol.

In general, inductively coupled plasmas have many properties in common with d-c argon plasmas. The core temperatures for the argon plasma is around 10,000 K. The combination of high excitation temperature and inert atmosphere provides a highly stable sensitive and relatively interference free excitation source for solution samples.

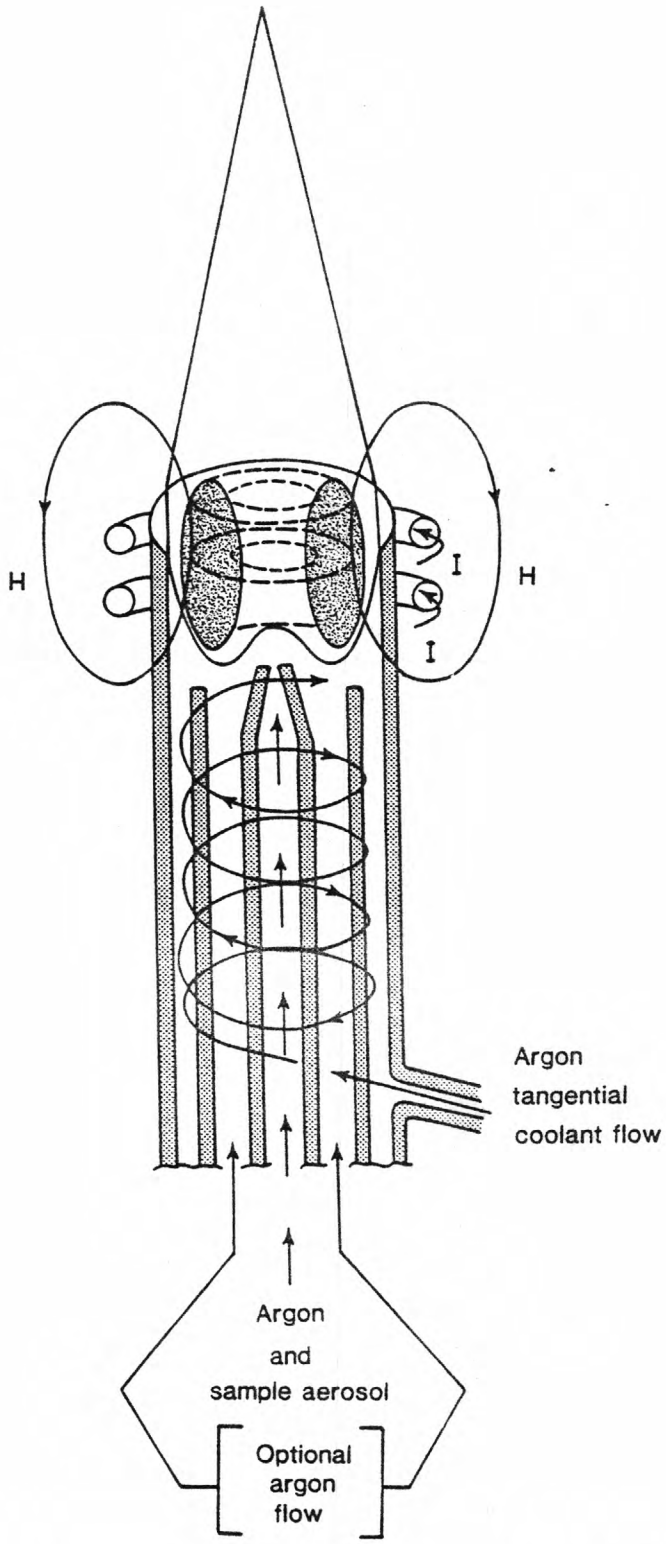


Figure 15.--Plasma torch configuration.

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Greenfield, S., Jones, I. L., and Berry, C. T., 1964, High-pressure plasmas as spectroscopic emission sources: Analyst, v. 89, p. 713.

Keirs, C. D., and Vickers, T. J., 1977, DC plasma arcs for elemental analysis: Applied Spectroscopy, v. 31, p. 273.

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ATOMIC EMISSION SPECTROMETRIC METHODS

Multiple element metal analysis, dissolved, atomic emission spectrometric, ICP direct (I-1472-81)
Parameter and Code:

Parameter	Code	Parameter	Code
Barium	01005	Magnesium	00925
Beryllium	01010	Manganese	01056
Cadmium	01025	Molybdenum	01060
Calcium	00915	Silica (SiO_2)	00955
Cobalt	01035	Sodium	00930
Copper	01040	Strontium	01080
Iron	01046	Vanadium	01085
Lead	01049	Zinc	01090
Lithium	01130		

1. Application

1.1 This method may be used only for the determination of dissolved constituents in waters which have a measured specific conductance of less than 2,000 umho/cm at 25°C. Table 1 specifies the upper and lower concentration limits. Samples containing analyte concentrations greater than the upper concentration limit may be analyzed for calcium, magnesium, silica, and sodium if the sample is diluted and if, after dilution, the specific conductance is below 2,000 umho/cm. Trace metals can also be determined in samples which have a measured specific conductance greater than 2,000 umho/cm by dilution; however detection levels and sensitivity will change proportionally.

1.2 Analyses must be performed on filtered and acidified samples. Water-suspended sediment mixtures, or bottom materials cannot be analyzed.

1.3 The ICP technology is so new that instruments and associated data processing equipment and software available on the commercial market are not standardized and operating conditions vary enormously. Until such time as operating conditions of various manufacturer's instruments become more comparable and the equivalency of methods using those instruments established by extensive testing, the ICP methods approved for Geological Survey use will be linked to a specific instrument and associated software. This does not imply endorsement of one product over another but rather acknowledges that the state-of-the-art in ICP technology is rapidly changing and developing.

2. Summary of method

All parameters are determined simultaneously on a single sample by a direct reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. Samples are pumped into a pneumatic nebulizer and atomized. Each analysis is determined on the basis of the average of two replicate exposures, each of which is background corrected by a spectrum shifting technique. Calibration is performed by standardizing with a series of four mixed-element standards and a blank.

Table 1.--Working ranges of constituents

Constituent	Lower limit (ug/L) (except where noted)	Upper limit (ug/L) (except where noted)	Wavelength (nm)
Barium	2	10,000	455.5
Beryllium	.5	10,000	313.0
Cadmium	1	10,000	214.4
Calcium (1)	.02 mg/L	100 mg/L	396.8
Calcium (2)	100	1,000 mg/L	315.8
Cobalt	3	10,000	238.8
Copper	10	10,000	324.7
Iron	3	10,000	259.9
Lead	10	10,000	220.3
Lithium	4	100,000	670.7
Magnesium	.004 mg/L	100,000	279.5
Manganese	1	10,000	257.6
Molybdenum	10	10,000	203.8
Silica (SiO_2)	.009 mg/L	100 mg/L	288.1
Sodium (1)	.2 mg/L	100 mg/L	589.0
Sodium (2)	100	1,000 mg/L	330.2
Strontium	.5	10,000	421.5
Vanadium	6	10,000	292.4
Zinc	3	10,000	206.0*

*Second order.

3. Interferences

3.1 Several interelement interference effects have been evaluated. Interelement correction factors have been programmed into the proprietary data system software and corrections are automatically applied, internally, to the data before it is printed on the output. An example of corrections are shown in table 2.

3.2 Samples containing high dissolved solids exhibit a variety of unidentified interference effects. Therefore, analyses must be limited to samples with a specific conductance of 2,000 umho/cm or less.

4. Apparatus (do not substitute)

4.1 Emission Spectrometry System (see fig. 16) consisting of:

4.1.1 Spectrometer, Jarrel-Ash Plasma Atom Comp, 0.75-meter focal curve with spectrum shifter background correction and crossflow pneumatic nebulizer or Babington-type nebulizer as described by Garbarino, and Taylor, 1980. (See table 1 for element wavelengths).

4.1.2 Computer, Digital Equipment Co., PDP8e.

4.1.3 Quartz Torch, (see fig. 17)

4.1.4 Radio Frequency Generator, Plasma-Therm Inc., Model HFS-2000D, 27.1 MHz.

4.1.5 Peristaltic Pump, Gilson, Model HP4. (see fig. 18).

4.2 Refer to the Jarrell-Ash Instruction Manual, Atom Comp 750 for operating techniques.

4.3.1 Operating conditions:

Incident RF power.....1.25 kW
Reflected RF power ..... 10 W
Vertical observation position .....16 mm (above load coil)
Horizontal observation position .....Center
Argon head pressure .....40 lb/in^2
Sample argon pressure for crossflow nebulizer .....17 lb/in^2
Sample argon pressure for Babington nebulizer .....30 lb/in^2
Sample argon flow rate for crossflow nebulizer .....0.9 L/min
Sample argon flow rate for Babington nebulizer approximately .....0.6 L/min
Plasma argon flow rate (for both nebulizers) .....0 L/min
Coolant argon flow rate .....18 L/min
Sample pumping rate for crossflow nebulizer .....10 percent above aspiration
Sample pumping rate for Babington nebulizer .....3-5 mL/min.
Refractor plate position .....Optimized for Hg profile
Spectrum shifter .....Full shift

Table 2.--Example of Jarrell - Ash software matrix. See instruction manual, Atom Comp Model 750 for details.

```
#PR
MX NAME:ICAP
MX NAME:IC
# OF LCN'S:19   # OF SM'S: 1
MODE:CN
FORMAT: 1 10  9
IS# 1    PCN:26 PRTY: 1 PREBRN: 0 EXPOSR:  4
IS# 2
IS# 3
IS# 4
STD# 1   BLNK
STD# 2   MIX1
STD# 3   MIX2
STD# 4   MIX3
STD# 5   MIX4
```

									Background constants	Mixed standard concentrations			
1	BA	25	1	0	4	1	4	1	AAAA	1.000	10.00	0	1.000	0
2	BE	11	1	0	3	1	4	1	AAAA	1.000	10.00	0	1.000	0
3	CA	20	1	0	5	1	4	1	AAAA	1.000	10.00	0	1.000	0
4	C2	7	1	0	5	1	4	1	AAAA	1.000	10.00	0	1.000	0
5	CD	4	1	0	2	1	4	1	AAAA	1.000	10.00	0	1.000	0
6	CO	48	1	0	3	1	4	1	AAAA	1.000	10.00	0	1.000	0
7	CU	12	1	0	3	1	4	1	AAAA	1.000	10.00	0	1.000	0
8	FE	45	1	0	2	1	4	1	AAAA	1.000	10.00	0	1.000	0
9	LI	24	1	0	4	1	4	1	AAAA	0	10.00	0	1.000	0
10	MG	18	1	0	5	1	4	1	AAAA	1.000	10.00	0	1.000	0
11	MN	47	1	0	2	1	4	1	AAAA	1.000	10.00	0	1.000	0
12	MO	49	1	0	4	1	4	1	AAAA	1.000	10.00	0	1.000	0
13	NA	23	1	0	5	1	4	1	AAAA	0	50.00	0	1.000	0
14	N2	40	1	0	5	1	4	1	AAAA	1.000	50.00	0	1.000	0
15	PB	5	1	0	2	1	4	1	AAAA	1.000	10.00	0	1.000	0
16	SI	9	1	0	4	1	4	1	AAAA	1.000	10.00	0	1.000	0
17	SR	22	1	0	3	1	4	1	AAAA	1.000	10.00	0	1.000	0
18	V	43	1	0	3	1	4	1	AAAA	1.000	10.00	0	1.000	0
19	ZN	21	1	0	2	1	4	1	AAAA	1.000	10.00	0	1.000	0

Interelement correction factors
47 45 .0024
12 25 .0017
5 11 .0027
5 48 .0015
48 45 .0103
12 45 .0011
45 24 .0009
11 43 .0036

```
CURVE NAME :AAAA
1000.00 1000.00
      0       0
```

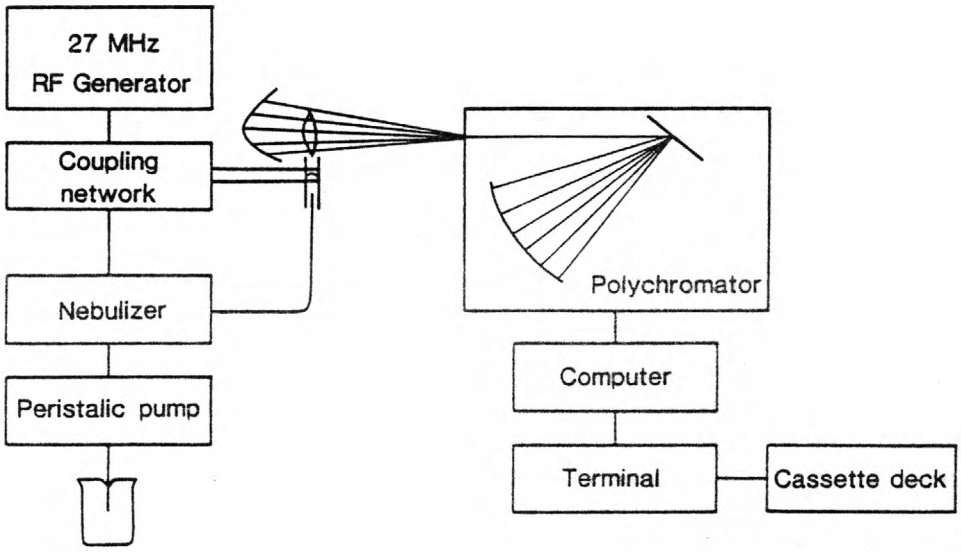


Figure 16.--Block diagram of spectrometer system.

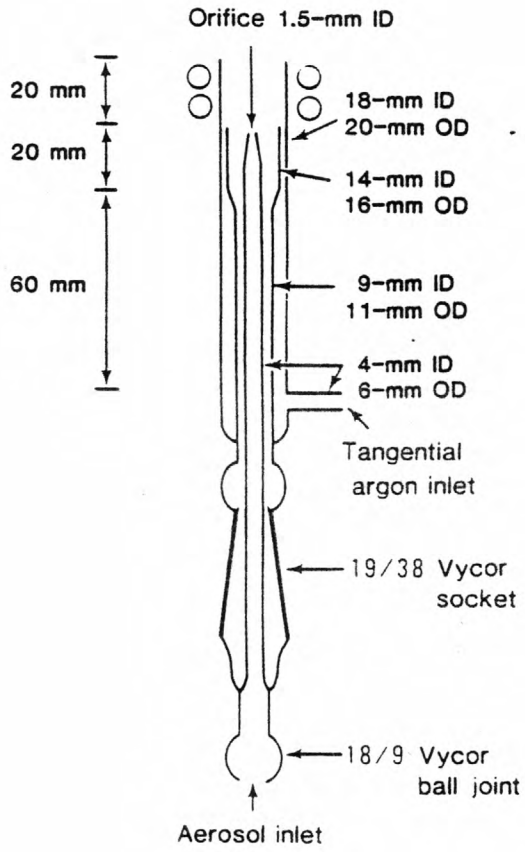
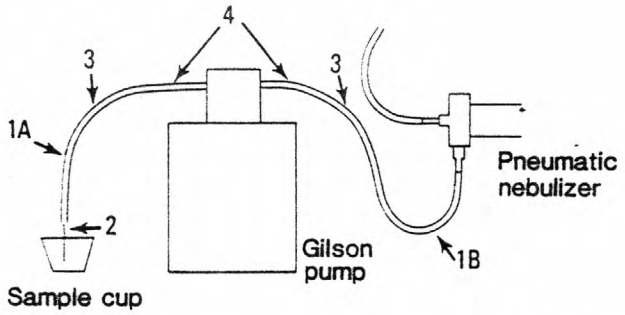


Figure 17.--Quartz torch.



1 Technicon tubing SMA$_{TM}$, flow rate 0.42 mL/min
part 116-0549PO8, collar color-orange
(1A-4 inches, 1B-6 inches)
2 Teflon tubing 26TW NAT: 4 inches
3 Tube connector part 116-0003-0
4 Technicon tubing SMA$_{TM}$, flow rate 0.80 mL/min
part 116-0549P10 collar color-red-standard

Figure 18.--Pump system.

4.3.2 The software matrix containing all the required parameters for data acquisition is shown in table 2. Only three of these parameters ever require an update. The background constants should be updated wherever the plasma torch position has been changed. Background constants are obtained by first setting them equal to 1.000, except for Li channel 24 and Na channel 23, aspirating the blank solution, and making several measurements in intensities. From these intensity measurements new background constants are calculated using the formula:

$$B = \frac{I_N + I_B}{I_B}$$

where B = new background constant, I_N = net intensity and I_B = background intensity. The new background constants are then entered into the matrix.

When background constants are updated the interelement correction factors must be updated. Interelement correction factors are obtained by first setting them equal to zero, standardizing the instrument, analyzing each interfering element standard stock solution, and printing out the results in concentration units. These results are used to calculate the interelement correction factors for each element using the formula:

$$I_e = A_e/C_i$$

where I_e = interelement correction factor for element e, A_e = the apparent concentration of element e, and C_i = concentration of the interfering element i. The units of I_e are milligrams per liter of element e per milligrams per liter of interfering element i. New interelement correction factors are then entered into the matrix.

Finally, in some cases it is impractical to make standard stock solutions at concentrations of exactly 100.0 mg/L. Therefore, the concentration for each element should be entered into the matrix.

5. Reagents

5.1 Acids used in the preparation of standards must be Ultrex grade or equivalent.

5.1.1 Aqua regia: Cautiously mix 3 parts concentrated HCl (sp gr 1.19) and 1 part concentrated HNO_3 (sp gr 1.41) just before use.

5.1.2 Hydrochloric acid, 6M: Add 500 mL concentrated HCl (sp gr 1.19) to 400 mL demineralized water and dilute to 1 L.

5.2 Prepare standard stock solutions from Spex HiPure grade chemicals or equivalent. Dry all salts for 1 h at 105°C unless otherwise specified. Do not dry hydrated salts. Clean all metals thoroughly with the appropriate acid and dry prior to weighing.

5.2.1 Barium standard solution I, 1 mL = 100 ug Ba: Dissolve 0.1516 g $BaCl_2$ dried at 180°C for 1 h in 10 mL demineralized water with 1 mL 6M HCl. Add 10.0 mL 6M HCl and dilute to 1,000 mL with demineralized water.

5.2.2 Beryllium standards solution I, 1 mL = 100 ug Be: Dissolve 0.1000 g beryllium flakes in a minimum of aqua regia. Heat to increase rate of dissolution. Add 10.0 mL of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water. (Caution, Note 1).

NOTE 1. Beryllium is extremely toxic. May be fatal if swallowed or inhaled.

5.2.3 Calcium standard solution I, 1 mL = 100 ug Ca: Suspend 0.2498 g $CaCO_3$ dried at 180°C for 1 h before weighing in demineralized water and dissolve cautiously with a minimum amount of dilute HNO_3. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.4 Cadmium standard solution I, 1 mL = 100 ug Cd: Dissolve 0.1000 g cadmium splatters in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.5 Cobalt standard solution I, 1 mL = 100 ug Co: Dissolve 0.4939 g cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$, in demineralized water. Add 10.0 mL of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.6 Copper standard solution I, 1 mL = 100 ug Cu: Dissolve 0.1000 g copper shot in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.7 Iron standard solution I, 1 mL = 100 ug Fe: Dissolve 0.1000 iron wire in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL if concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.8 Lead standard solution I, 1 mL = 100 ug Pb: Dissolve 0.1000 lead shot in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.9 Lithium standard solution I, 1 mL = 100 ug Li: Dissolve 0.5323 g Li_2CO_3, slowly in a minimum amount of dilute HNO_3. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.10 Magnesium standard solution I, 1 mL = 100 ug Mg: Dissolve 0.1000 magnesium rod in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.11 Manganese standard solution I, 1 mL = 100 ug Mn: Dissolve 0.1000 manganese flakes in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.12 Molybdenum standard solution I, 1 mL = 100 ug Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in demineralized water. Dilute to 1,000 mL with demineralized water.

5.2.13 Silica standard solution I, 1 mL = 100 ug SiO_2: Dissolve 0.3531 g $Na_2SiO_3.5H_2O$ in demineralized water. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.14 Sodium standard solution I, 1 mL = 100 ug Na: Dissolve 0.2542 g NaCl in demineralized water. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.15 Strontium standard solution I, 1 mL = 100 ug Sr: Dissolve 0.2416 g $Sr(NO_3)_2$ in demineralized water. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.16 Vanadium standard solution I, 1 mL = 100 ug V: Dissolve 0.2297 g NH_4VO_3 in a minimum amount of concentrated HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 with demineralized water.

5.2.17 Zinc standard solution I, 1 mL = 100 ug Zn: Dissolve 0.1000 zinc powder in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.3 Mixed working-standard solutions

5.3.1 Prepare four mixed standard solutions as follows: Pipet 50.0 mL of each appropriate standard stock solution into a 500-mL volumetric flask. Dilute with demineralized water. Transfer to acid-rinsed PTFE bottle for storage. Fresh mixed standards should be prepared weekly. Final concentration will be 1.0 mL = 10.0 ug for all parameters. Composition for mixed standards should be as follows:

5.3.2 Mixed standard solution I - Iron, manganese, cadmium, lead, and zinc.

5.3.3 Mixed standard solution II - Beryllium, copper, strontium, vanadium, and cobalt.

5.3.4 Mixed standard solution III - Molybdenum, silica, lithium, and barium.

5.3.5 Mixed standard solution IV - Calcium, magnesium, and sodium.

5.3.6 Reagent blank is prepared by diluting 1 mL concentration HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.4 Check Standard Solution: Pipet 5.00 mL of each standard stock solution into a 100-mL volumetric flask. Dilute with demineralized water. Transfer to PTFE bottle for storage. Fresh check standard solution should be prepared weekly. Final concentration will be 1.0 mL = 5.00 ug for all parameters, with the exception of Na which will be 1.0 mL = 8.83 ug (due to the Na in the SiO_2 standard).

6. Procedure

6.1 Set up instrument with proper operating parameters (paragraph 4.3) and ignite plasma. Instrument must warm for 30 min prior to standardization.

6.2 Retrieve the appropriate proprietary software matrix for memory. Set the Time and Date. Set number of cycles for spectrum shifter to 5. Enter the following "coded string" for Standardization (QEGGAIN).

6.3 Position the mercury pen lamp in front of the entrance slit. Initiate the "profile" computer command and profile the instrument by averaging the micrometer settings obtained at identical intensity positions on each side of the mercury spectral line. Position the micrometer to the average setting.

6.4 Standardize the data system by running a blank and the series for four mixed standard solutions using an "O" command to initiate each run. Identify the standard at the end of each run when demanded by the computer. Pump blank solution for 30 s between standards. Allow 30 s for equilibration each time a new solution is introduced.

6.5 Change the "coded string" to the following (QEGGAC). Analyze the check standard described in 5.4. Concentration values obtained should not deviate from the actual values by more than 2 percent. If values do deviate more than 2 percent, inspect nebulizer for malfunction.

6.6 Check standardization by running secondary reference samples or equivalent certified reference samples in natural matrix materials. The determined concentration must be within one standard deviation unit of the elemental mean given for the reference material.

6.7 Analyze samples allowing 30 s for equilibration. Pump blank solution for 30 s between samples. Check calibration after analyzing 10 samples, by rerunning a reference sample and the check standard. The results for the reference sample and check standard must be within one standard deviation unit of the elemental mean given for the reference material and less than $\pm$ 2 percent for each element respectively. If not, data system must be restandardized as described starting at paragraph 6.3.

6.8 Reprofile instrument (paragraph 6.3) at least once every hour. If profile position changes by more than 4 micrometer units, instrument must be restandardized (starting with paragraph 6.2).

7. Calculations

7.1 All calculations are performed internally by the computer data system. SiO_2 will be labeled Si if headings are used to identify the results.

7.2 If dilutions were performed, multiply the results by the appropriate dilution factor.

8. Report

8.1 All results are printed out directly in milligrams per liter (NOTE 2).

NOTE 2. If either the reported calcium or sodium concentration is greater than 100 mg/L, report the second value given, otherwise only the first value should be reported. Trace metal results must be converted to micrograms per liter.

8.2 Report the dissolved constituent concentrations as follows:

8.2.1 Calcium (00915), magnesium (00925), silica (00955), and sodium (00930): less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

8.2.2 Beryllium (01010), cadmium (01025), manganese (01056), and strontium (01080): less than 10 ug/L, nearest ug/L; 10 ug/L and above two significant figures.

8.2.3 Barium (01005), cobalt (01035), iron (01046), lithium (01130), and zinc (01090): less than 10 ug/L, nearest ug/L to the lower limit of detection as specified in Table 1; below limit of detection, "less than" value; 10 ug/L and above, two significant figures.

8.2.4 Copper (01040), lead (01049), molybdenum (01060), and vanadium (01085); less than 100 ug/L, nearest 10 ug/L; 100 ug/L and above, two significant figures.

9. Precision

9.1 Within its designated range (Table I) single operator-precision of the method for each metal may be expressed as described in table 3. A minimum of 10 replicate analyses were preformed to obtain each regression equation shown.

9.2 Interlaboratory precision data obtained on Standard Reference Water Samples are shown in table 4. The specific instrument described in this method may not have been used. Laboratories were not asked to provide this information.

References

Garbarino, J. R., and Taylor, H. E., 1980, A Babington-type nebulizer for use in the analysis of natural water samples by inductively coupled plasma spectrometry: Applied Spectroscopy, v. 34, p. 584-590.

Table 3.--Precision for quantitative ICP metal

Constituent	Slope	Intercept	Units
Barium	0.0061	0.83	ug/L
Beryllium	.0061	.06	Do.
Cadmium	.0203	.30	Do.
Cobalt	.0650	.40	Do.
Copper	.0039	1.32	Do.
Iron	.0071	.059	Do.
Lead	.1210	5.0	Do.
Lithium	.0240	.076	Do.
Manganese	.0042	.30	Do.
Molybdenum	.1220	.18	Do.
Strontium	.0089	.076	Do.
Zinc	.0059	1.24	Do.
Calcium	.0044	.30	mg/L
Magnesium	.0060	.018	Do.
Silica	.0040	.019	Do.
Sodium	.0077	.26	Do.

[Standard deviation, S_o, is calculated by $S_o = mx + b$, where m is slope of line, x is concentration of constituent in units specified, and b is intercept.]

Table 4.--Interlaboratory precision data

Constituent	Number of laboratories	Mean (ug/L) (except where noted)	Standard deviation (ug/L) (except where noted)	Relative standard deviation, percent
Barium	9	17.8	1.6	9
Do.	6	73.3	5.1	7
Do.	7	163	3.7	5
Beryllium	6	5.0	1.6	31
Do.	5	20.4	3.1	15
Cadmium	7	8.3	.8	10
Calcium	9	7.3 mg/L	.5 mg/L	7
Do.	10	62.8 mg/L	2.5 mg/L	4
Cobalt	4	5.2	4.6	88
Do.	4	14.2	2.8	20
Copper	7	64.0	9.0	14
Iron	4	102	10.2	10
Do.	11	376	22.6	6
Lead	5	20.2	10.7	53
Lithium	5	88.0	8.8	10
Do.	5	254	10.2	4
Magnesium	10	2.0 mg/L	.1 mg/L	7
Do.	10	13.6 mg/L	.5 mg/L	4
Maganese	5	38.0	4.2	11
Do.	10	528	10.6	2
Molybdenum	5	12.2	3.2	26
Sodium	10	2.7 mg/L	.5 mg/L	17
Do.	9	58.4 mg/L	3.5 mg/L	6
Strontium	6	102	10.2	10
Do.	7	586	70.3	12
Vanadium	5	7.4	2.3	31
Zinc	9	237	9.5	4

Suspended total constituents, calculation, total minus dissolved (I-7001-81)

Parameter	Code	Parameter	Code
Antimony, suspended total (ug/L)	01096	Nitrogen, ammonia plus organic, suspended total (mg/L)	00624
Arsenic, suspended total (ug/L)	01001	Selenium, suspended total (ug/L)	01146
Fluoride, suspended total (ug/L)	82299		

1. Application

This method may be used to calculate suspended total constituents on any sample on which the total constituents and dissolved constituents have been determined.

2. Summary of method

Suspended total constituents are determined by subtracting each dissolved constituent from the total constituents.

7. Calculations

suspended total constituent, mg/L or ug/L = T - D
where
T = total constituent, mg/L or ug/L, and
D = dissolved constituent, mg/L or ug/L.

8. Report

Report as directed in the individual total constituent method.

9. Precision

See the individual total constituent method. Precision will depend on that obtained for both the dissolved and total constituent.

Suspended recoverable constituents, calculation, total recoverable minus dissolved (I-7000-81)

Parameter	Code
Aluminum, suspended recoverable (ug/L)	01107
Barium, suspended recoverable (ug/L)	01006
Beryllium, suspended recoverable (ug/L)	01011
Boron, suspended recoverable (ug/L)	01021
Cadmium, suspended recoverable (ug/L)	01026
Calcium, suspended recoverable (mg/L)	81357
Chromium, suspended recoverable (ug/L)	01031
Cobalt, suspended recoverable (ug/L)	01036
Copper, suspended recoverable (ug/L)	01041
Iron, suspended recoverable (ug/L)	01044
Lead, suspended recoverable (ug/L)	01050
Lithium, suspended recoverable (mg/L)	01131
Magnesium, suspended recoverable (mg/L)	00926
Manganese, suspended recoverable (ug/L)	01054
Mercury, suspended recoverable (ug/L)	71895
Molybdenum, suspended recoverable (ug/L)	01061
Nickel, suspended recoverable (ug/L)	01066
Silver, suspended recoverable (ug/L)	01076
Strontium, suspended recoverable (ug/L)	01081
Tin, suspended recoverable (ug/L)	01101
Zinc, suspended recoverable (ug/L)	01091

1. Application

This method may be used to calculate suspended recoverable constituents on any sample on which the total recoverable constituents and dissolved constituents have been determined.

2. Summary of method

Suspended recoverable constituents are determined by subtracting the dissolved constituents from the total recoverable constituents.

7. Calculations

Suspended recoverable constituent, mg/L or ug/L = TR - D
where
TR = total recoverable constituent, mg/L or ug/L, and
D = dissolved constituent, mg/L or ug/L.

8. Report

Report as directed in the individual total recoverable constituent method.

9. Precision

See the individual dissolved and total recoverable constituent method. Precision will depend on that obtained for both the dissolved and total constituent.

Phosphorus species, calculation, hydrolyzable, dissolved; hydrolyzable, total; organic, dissolved; organic, total.

Parameters and codes: Phosphorus, dissolved, hydrolyzable (mg/L as P): 00672
Phosphorus, total, hydrolyzable (mg/L as P): 00669
Phosphorus, dissolved, organic (mg/L as P): 00673
Phosphorus, total, organic (mg/L as P): 00670

1. Application

This method may be used to calculate both dissolved and total hydrolyzable phosphorus, and both dissolved and total organic phosphorus on which the following parameters have been determined:

Parameters	Method No.
Phosphorus, dissolved, orthophosphate	I-1601-79 or I-2601-81
Phosphorus, total, orthophosphate	I-4601-81
Phosphorus, dissolved orthophosphate plus hydrolyzable	I-1602-79 or I-2602-81
Phosphorus, total, or orthophosphate plus hydrolyzable	I-4602-81
Phosphorus, dissolved	I-1600-79 or I-2600-81
Phosphorus, total	I-4600-81

2. Summary of method

Dissolved or total hydrolyzable phosphorus is determined by subtracting dissolved or total orthophosphate plus hydrolyzable phosphorus from dissolved or total orthophoshpate-phosphorus, respectively. Dissolved or total organic phosphorus is determined by subtracting dissolved or total orthophoshpate plus hydrolyzable phosphorus from dissolved or total phosphorus, respectively.

7. Calculations

7.1 Phosphorus, dissolved, hydrolyzable (mg/L) = phosphorus, dissolved, orthophosphate plus hydrolyzable (mg/L) - phosphorus, dissolved, orthophosphate (mg/L).

7.2 Phosphorus, total, hydrolyzable (mg/L) = phosphorus, total, orthophosphate plus hydrolyzable (mg/L) - phosphorus, total, orthophosphate (mg/L).

7.3 Phosphorus, total, organic (mg/L) = phosphorus, dissolved, (mg/L) - phosphorus, dissolved, orthophosphate plus hydrolyzable (mg/L).

7.4 Phosphorus, total, organic (mg/L) = phosphorus, total, dissolved (mg/L) - phosphorus, total, orthophosphate plus hydrolyzable (mg/L).

8. Report

Report phosphorus, dissolved hydrolyzable (00672), phosphorus, total hydrolyzable (00669), phosphorus, dissolved organic (00673), and phosphorus, total organic (00670) as follows: Less than 1 mg/L, two decimals; 1 mg/L and above two significant figures.

9. Precision

See the individual phosphorus, dissolved or total orthophosphate, phosphorus, dissolved or total orthophosphate plus hydrolyzable, and phosphorus, dissolved or total methods. Precision will depend on that obtained for the above.

Boron, dissolved, colorimetric, azomethine H, automated (I-2115-81)

Parameter and Code: Boron, dissolved (ug/L): 01020

1. Application

This method may be used to determine concentrations of boron in unacidified water samples in the range of 10 to 400 ug/L. Sample solutions containing more than 400 ug/L boron must be diluted.

2. Summary of method

The condensation product of H-acid (8-amino-1-napthol-3,6-disulphonic acid) and salicylaldehyde is azomethine H which forms a yellow complex with boron. The absorbance of this complex is then measured colorimetrically at 410 nm (Basson, Bohmer, and Stanton, 1969; Basson, Pille, and DuPreez, 1974; Spencer and Erdmann, 1979). Interferences from iron and zinc are minimized by addition of diethylenetriamine pentaacetic acid (DTPA). Interferences from bicarbonate are eliminated by careful acidification to pH 3-5.

3. Interferences

Iron, zinc and bicarbonate interfere at concentrations above 400, 2000 and 150 mg/L respectively in the absence of pretreatment with DPTA and acidification.

4. Apparatus

4.1 Technicon AutoAnalyzer consisting of a sampler, proportioning pump, manifold, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range 10 to 400 ug/L:

Absorption cell.....50 mm
Wavelength.....410 nm
Cam.....30/h(2/1)

5. Reagents

5.1 Ammonium acetate buffer: Dissolve 300 g $NH_4C_2H_3O_2$ in 1,000 mL of demineralized waterer. Adjust the pH to 6.35 with 20 percent sulfuric acid and filter.

5.2 Azomethine H syntheseis: Dissolve 18 g of H-acid (8-amino-1-naphthol-3,-6-disulphonic acid) in 1,000 mL of demineralized water with gentle heating. Filter, with suction, through Whatman No. 40 filter paper. Neutralize the solution to pH 7 with 10 percent KOH. While continuously stirring, add concentrated HCl (sp gr 1.19) until the pH is about 1.5. To the resulting mixture add 20 mL of salicylaldehyde and stir vigorously overnight (approx. 12 h). Centrifuge (2,000 r/min, 20 min) to separate the azomethine H (orange product) and wash 2-3 times with ethanol. Dry to constant weight at 100°C for 3 h and store in a dessicator.

5.3 Azomethine H reagent: Dissolve 4.5 g of azomethine H and 10 g of ascorbic acid (analytical grade) in 500 mL of demineralized water with gentle heating. Filter, with suction, through Whatman No. 40 filter paper. Store in a plastic bottle wrapped with aluminum foil to prevent the entrance of light. Hydrolysis of this compound, and consequently baseline drift, is minimized by placing this reagent bottle in a beaker containing a mixture of ice and water during analysis. This reagent should be prepared daily for optimal results.

5.4 Boron standard solution I, 1.00 mL = 0.100 mg B:

5.4.1 Purify reagent by dissolving 10 g $Na_2B_4O_7 \cdot 10H_2O$ in 50 mL demineralized water at 50° to 60°C. Recrystallize by placing in a refrigerator for several hours. Filter, with suction, through Whatman No. 40 paper and dry by washing with alcohol followed by ether. Do not dry in oven.

5.4.2 Dissolve 0.8819 g of purified reagent in demineralized water and dilute to 1,000 mL. Store in plastic bottle.

5.5 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.

5.6 Boron standard solution III, 1.00 mL = 0.001 mg B: Dilute 100.0 mL boron standard solution II to 1,000 mL with demineralized water. Store in plastic bottle.

5.7 Boron working standards: Prepare a blank and 500 mL each of a series of boron working standards by appropriate quantitative dilution of the boron standard solutions (II and III), as follows:

Boron standard solutions (mL)	Boron concentration (ug/L)
0.0	0.0
5.0 of III	10.0
15.0 Do.	30.0
25.0 Do.	50.0
50.0 Do.	100.0
100.0 Do.	200.0
15.0 of II	300.0
20.0 Do.	400.0

5.8 Brij-35 solution, 30-percent aqueous solution (Baker No. C706, or equivalent).

5.9 DTPA reagent, 0.05M: Suspend 19.7 g of DTPA in approx 900 mL of demineralized water. Add 5M NaOH to a pH of 5-6 and continue stirring until all the DTPA dissolves. Add 6 mL of 30 percent Brij-35 solution and dilute to 1 liter and filter.

6. Procedure

6.1 Set up manifold (fig. 19).

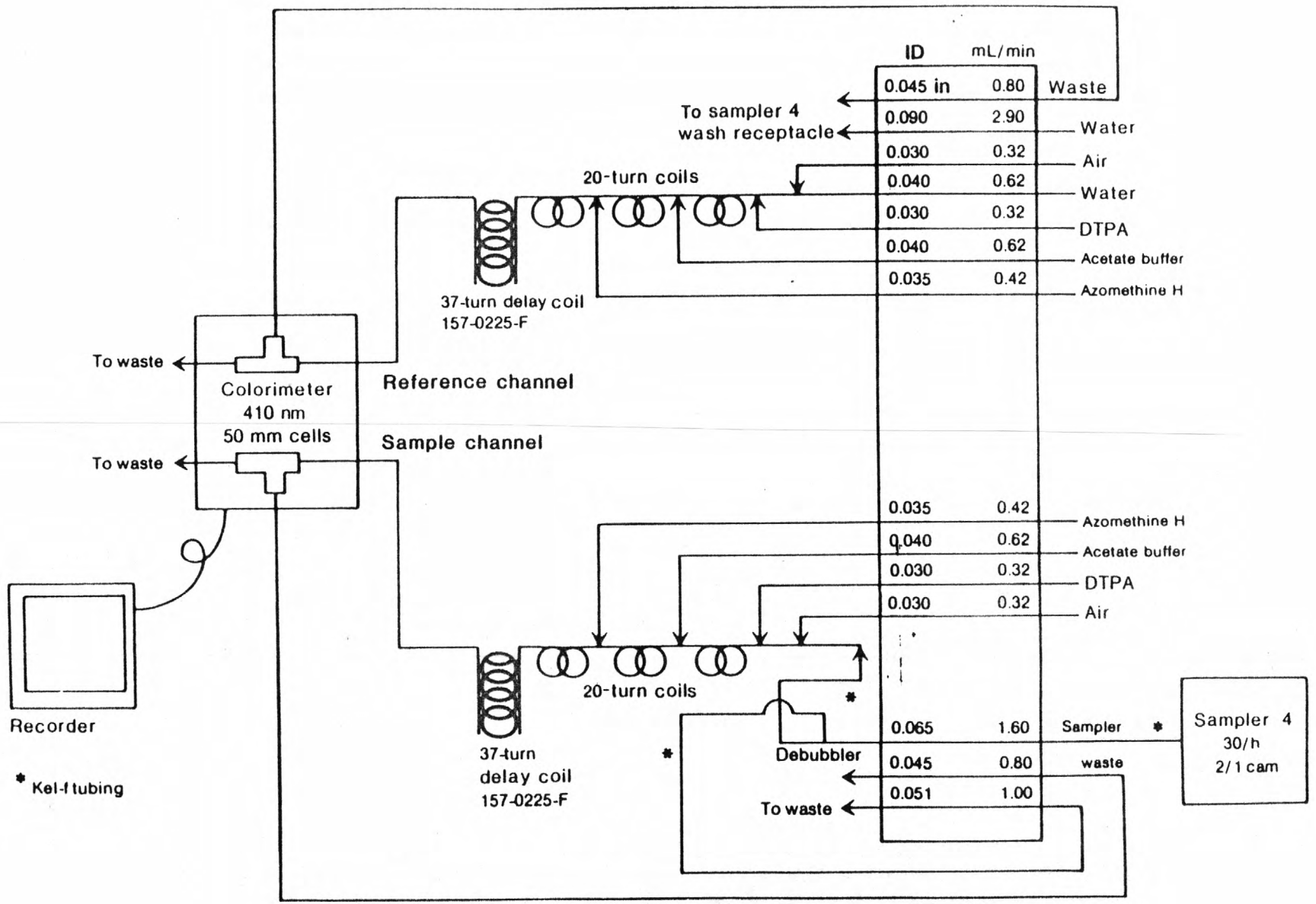


Figure 19.--Boron manifold.

6.2 Initially feed reagents with demineralized water in the sample line through the system and allow approximately 30 min for stabilization of the baseline and instrument warmup. Adjust baseline to read 5 chart divisions on the recorder (25 ug/L on printer). It is necessary to include the reference channel in the manifold to compensate for base-line drift due to hydrolysis of the azomethine H.

6.3 Place a complete set of standards and a blank in the first positions of the first sample tray beginning with the most concentrated standard. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples. Use plastic sample cups to avoid possible boron contamination from glass containers.

6.4 Begin analysis. When the peak from the highest standard appears on the recorder, adjust the STD CAL control until the printer reads 425 ug/L on the 0-500 range.

7. Calculations

7.1 Obtain concentration of sample directly from the printer and correct for the baseline reading.

7.2 Alternatively, prepare an analytical curve by plotting the height of each standard peak, subtracting the baseline drift, versus the respective boron concentration. Obtain the boron concentration of each sample by comparing its corrected reading to the analytical curve.

8. Report

8.1 Report boron (B), dissolved (01020), concentrations as follows:

Less than 100 ug/L, nearest 10 ug/L; 100 ug/L and above, two significant figures.

9. Precision

9.1 Analysis of 12 replicates on two test samples by a single laboratory resulted in mean values of 16 and 329 ug/L and standard deviations of 3 and 5 ug/L, respectively.

9.2 The precision may also be expressed in terms of the percent relative standard deviation as follows:

Number of replicates	Mean, ug/L	Relative standard deviation, percen
12	16	19
12	329	2

References

Basson, W. D., Bohmer, R. G., and Stanton, D. A., 1969, Automated procedure for the determination of boron in plant tissue: Analyst, v. 94, p. 1135-1141.

Basson, W. D., Pille, P. P., and DuPreez, A. L., 1974, Automated in situ preparation of azomethine H and the subsequent determination of boron in aqueous solution: Analyst, v. 99, p. 168-170.

Spencer, R. R, and Erdmann, D. E., 1979, Azomethine H colorimetric method for determining dissolved boron in water: Environmental Science and Technology, v. 13, p. 954-56.

Nitrogen, nitrite plus nitrate, dissolved, colorimetric, cadmium reduction-diazotization, automated (I-2545-81)

Parameter and Code: Nitrogen, nitrite plus nitrate, dissolved (mg/L as N): 00631

1. Application

This method may be used to determine the sum of nitrite plus nitrate nitrogen concentrations in surface, domestic, and industrial waters and brines in the range from 0.1 to 5.0 mg/L. Samples containing higher concentrations must first be diluted.

2. Summary of method

2.1 Nitrate is reduced to nitrite by a copper-cadmium column. The sample stream is then treated with sulfanilamide under acidic conditions to yield a diazo compound which couples with N-1-naphthylethylenediamine dihydrochloride to form a red compound, the absorbance of which is measured colorimetrically. The final result is the sum of the nitrite originally present plus that formed by the reduction of the nitrate (Brewer and Riley, 1965; Kamphake and others, 1967; Morris and Riley, 1963; Strickland and Parsons, 1972; U.S. Environmental Protection Agency, 1979, p. 207-214 and G. G. Ehrlich and D. K. MacDonald, written communs., 1969).

2.2 Interferences from Hg^{2+} added to the samples as a preservative are overcome by adjusting the pH of the ammonium chloride buffer to 6.3.

3. Interferences

3.1 The concentrations of potentially interfering substances are seldom high enough to introduce error. High concentrations of oxidizing agents, reducing agents, and some metals, such as Cu^{+2} interfere. See American Society for Testing and Materials, Part 31 (1981) for details on potential interferences.

3.2 Acids destroy the cadmium column; therefore, acid treated samples cannot be analyzed by this method.

3.3 Repeated analysis of waters containing concentrations of sulfide over 2 mg/L S^{2-} will rapidly deactivate the cadmium column by formation of cadmium sulfide (Strickland and Parsons, 1972).

4. Apparatus

4.1 Technicon AutoAnalyzer II, consisting of sampler, cartridge manifold (including copper-cadmium reduction column), proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.1 to 5.0 mg/L $NO_2 + NO_3$ (as N):

Absorption cell.....15 mm
Wavelength.....520 nm
Cam.....40/h(4/1)

5. Reagents

5.1 Ammonium chloride solution, 10 g/L: Dissolve 10 g NH_4Cl in demineralized water and dilute to approx 950 mL. Adjust pH to 6.3 ± 0.2 with dilute NH_4OH solution and dilute to 1 L. Add 0.5 mL Brij-35 solution.

5.2 Brij-35 solution, 30-percent aqueous solution (Baker No. C706, or equivalent).

5.3 Cadmium powder, coarse, (99 percent pure) (Technicon No. T11-5063, or equivalent): Wash cadmium powder with diethyl ether or 1M HCl followed by demineralized water. Allow to air dry. Shake the dry powder with copper sulfate solution (20 g/L). The weight of the solution should be approx 10 times that of the cadmium. Wash thoroughly with demineralized water to remove colloidal copper which is visible as a blue color in the wash solution. A minimum of 10 washings is usually required to eliminate the perceptible blue color.

5.4 Color reagent: Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to approx 1,500 mL demineralized water. Dissolve completely (warm if necessary). Add 1.0 g N-1-naphthylethylenediamine dihydrochloride and dissolve completely. Dilute to 2 L with demineralized water. Add 1.0 mL Brij-35 solution. Store in a refrigerator. This reagent is stable for approximately 1 month.

5.5 Copper sulfate solution, 20 g/L: Dissolve 20 g $CuSO_4$ (anhydrous) in demineralized water and dilute to 1 L.

5.6 Hydrochloric acid, 1.0M: Add 83.3 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.7 Nitrate-nitrogen standard solution I, 1.00 mL = 0.50 mg NO_3-N: Dissolve 3.609 g KNO_3, dried overnight over concentrated H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.8 Nitrate-nitrogen standard solution II, 1.00 mL = 0.025 mg NO_3-N: Quantitatively dilute 50.0 mL nitrate-nitrogen standard solution I to 1,000 mL with demineralized water.

5.9 Nitrate-nitrogen working standards: Prepare a blank and 500 mL each of a series of nitrate-nitrogen working standards by appropriate quantitative dilution of nitrate standard solution II as follows:

Nitrate-nitrogen standard solution II (mL)	Nitrate-nitrogen concentration (mg/L)
0.0	0.00
2.0	.10
5.0	.25
10.0	.5
20.0	1.0
30.0	1.5
40.0	2.0
60.0	3.0
80.0	4.0
100.0	5.0

6. Procedure

6.1 Set up manifold (fig. 20).

6.2 Allow the color reagent to come to room temperature.

6.3 Allow colorimeter and recorder to warm for at least 30 min.

6.4 Fill the reduction column, which is a U-shaped, 36-cm length of 2.0-mm ID glass tubing (Technicon No. 189-0000, or equivalent), with water. This prevents entrapment of air bubbles when filling the tube with cadmium. Transfer the prepared cadmium granules to the reduction column. After the filling is completed, insert borosilicate glass wool in the exit end of the tube. This column should be good for several hundred samples before it needs to be refilled (Note 1).

NOTE 1. The reduction efficiency of the column should be checked regularly by comparing the peak heights of nitrite and nitrate standards. Equal concentration standards should give equal peak heights. Replace the column if the efficiency falls below 90 percent.

6.5 Begin pumping reagents but do not connect the reduction column to the manifold system until air has been pumped from the reagent and sample tubes (Note 2).

NOTE 2. It is important to avoid introduction of air bubbles into the reduction column because they adversely affect sample contact with the cadmium powder and decrease the reduction efficiency. Column must be replaced if air bubbles are introduced.

6.6 Activate and stabilize the reduction column by pumping a 3.0 mg/L NO_3-N standard through the system until a steady state is attained.

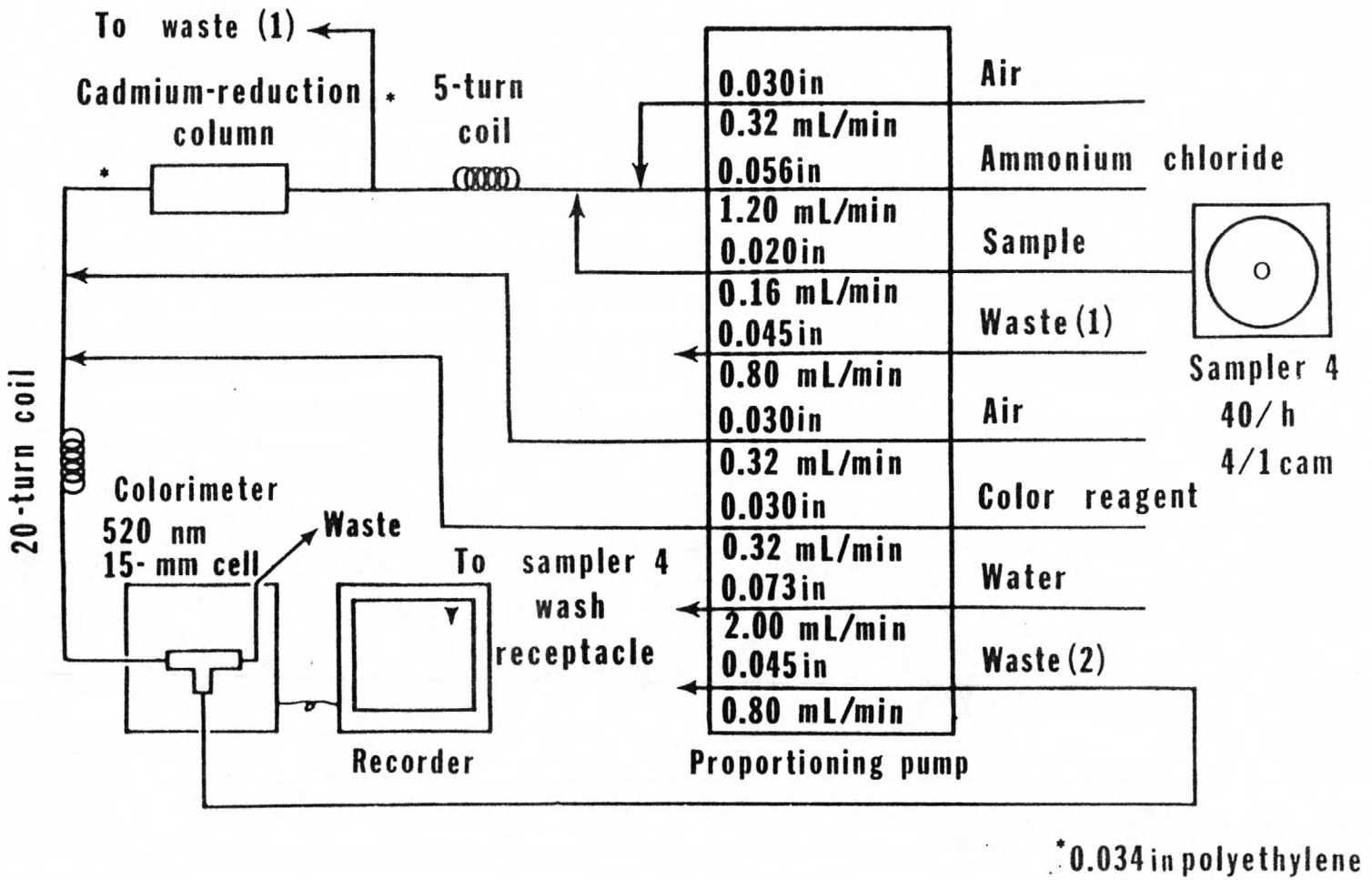


Figure 20.--Nitrogen, nitrite plus nitrate, manifold.

6.7 Switch to demineralized water in the sample line and adjust the baseline to read zero scale divisions on the recorder.

6.8 Place a complete set of standards and two blanks in the first positions of the first sample tray beginning with the most concentrated standard. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.9 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

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

7.2 Compute the concentration of nitrogen, nitrite plus nitrate, as N, in milligrams per liter in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report nitrogen, nitrite plus nitrate ($NO_2 + NO_3$), dissolved, as N (00631), concentrations as follows: 0.1 to 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

The precision of this method within the range of 0.1 to 5.0 mg/L may be expressed as follows:

$$S_T = 0.080X + 0.011$$

where

S_T = overall precision, milligrams per liter and
X = concentration of nitrogen, milligrams per liter.

9.2 The precision may also be expressed in terms of the percent relative standard deviation as follows:

Number of labs	Mean, mg/L	Relative standard deviation, percent
15	0.46	14
10	2.85	8
19	4.88	11

References

American Society for Testing and Materials, 1981, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 508.

Brewer, P. G., and Riley, J. P., 1965, The automatic determination of nitrate in sea water: Deep Sea Research, v. 12, p. 765-772.

Kamphake, L. Hannah, S., and Cohen, J., 1967, Automated analysis for nitrate by hydrazine reduction: Water Research, v. 1, p. 205-216.

Morris, A. W., and Riley, J. P., 1963, The determination of nitrate in sea water: Analytica Chimica Acta, v. 29, p. 272-279.

Strickland, J. D. H., and Parsons, T. R., 1972, A practical handbook of sea water analysis: Canada Fisheries Research Board Bull. 167, pp. 310.

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Washington, U.S. Government Printing Office, p. 353.2-1.

Nitrogen, nitrite plus nitrate, total in bottom material, colorimetric, cadmium reduction-diazotization, automated (I-6545-81)

Parameter and Code: Nitrogen, nitrite plus nitrate, total in bottom material, dry wt (mg/kg as N): 00633

1. Application

This method may be used to determine the sum of nitrite-plus-nitrate nitrogen concentrations in bottom material containing at least 2 mg/kg. Prepared sample solutions (sec. 6.1) containing more than 5.0 mg/L must first be diluted.

2. Summary of method

2.1 An acidified sodium chloride extraction procedure is used to extract nitrate and nitrite from bottom material for this determination (Jackson, 1958).

2.2 Nitrate is reduced to nitrite by a copper-cadmium column. The sample stream is then treated with sulfanilamide under acidic conditions to yield a diazo compound which couples with N-1-naphthylethylenediamine dihydrochloride to form a red compound, the absorbance of which is measured colorimetrically. The final result is the sum of the nitrite originally present plus that formed by the reduction of the nitrate (Brewer and Riley, 1965; Kamphake and others, 1967; Morris and Riley, 1963; Strickland and Parsons, 1972; U.S. Environmental Protection Agency, 1979, p. 207-214; and G. G. Ehrlich and D. K. MacDonald, written communs., 1969).

3. Interferences

3.1 The concentrations of potentially interfering substances are seldom high enough to introduce error. High concentrations of oxidizing agents, reducing agents, and some metals, such as Cu^{+2} interfere. See American Society for Testing and Materials, Part 31, (1981) for details on potential interferences. Interferences from Hg^{+2} is eliminated by adjusting the pH of the ammonium chloride buffer to 6.3.

3.2 Acids destroy the cadmium column: therefore, acid treated samples cannot be analyzed by this method.

3.3 Repeated analysis of waters containing concentrations of sulfide over 2 mg/L S^{2-} will rapidly deactivate the cadmium column by formation of cadmium sulfide (Strickland and Parsons, 1972).

4. Apparatus

4.1 Centrifuge.

4.2 Shaker, wrist-action.

4.3 Technicon AutoAnalyzer II, consisting of sampler, cartridge manifold (including copper-cadmium reduction column), proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.4 With this equipment the following operating conditions have been found satisfactory for the range from 0.1 to 5.0 mg/L (NO_2 + NO_3) as N:

Absorption cell.....15 mm
Wavelength.....520 nm
Cam.....40/h(4/1)

5. Reagents

5.1 Ammonium chloride solution, 10 g/L: Dissolve 10 g NH_4Cl in demineralized water and dilute to approx 950 mL. Adjust pH to 6.3 ± 0.2 with dilute NH_4OH solution and dilute to 1 L. Add 0.5 mL Brij-35 solution.

5.2 Brij-35 solution, 30-percent aqueous solution (Baker No. C706, or equivalent).

5.3 Cadmium powder, coarse, (99 percent pure) (Technicon No. T11-5063, or equivalent): Wash cadmium powder with diethyl ether or 1M HCl followed by demineralized water. Allow to air dry. Shake the dry powder with copper sulfate solution (20 g/L). The weight of the solution should be approx 10 times that of the cadmium. Wash thoroughly with demineralized water to remove colloidal copper which is visible as a blue color in the wash solution. A minimum of 10 washings is usually required to eliminate perceptible blue color.

5.4 Color reagent: Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to approx 1,500 mL demineralized water. Dissolve completely (warm if necessary). Add 1.0 g N-1-naphthylethylenediamine dihydrochloride and dissolve completely. Dilute to 2 L with demineralized water. Add 1.0 mL Brij-35 solution. Store in a refrigerator. This reagent is stable for approx 1 month.

5.5 Copper sulfate solution, 20 g/L: Dissolve 20 g $CuSO_4$ (anhydrous) in demineralized water and dilute to 1 L.

5.6 Hydrochloric acid, 1.0M: Add 83.3 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.7 Nitrate-nitrogen standard solution I, 1.00 mL = 0.50 mg NO_3-N: Dissolve 3.609 g KNO_3, dried overnight over concentrated H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.8 Nitrate-nitrogen standard solution II, 1.00 mL = 0.025 mg NO_3-N: Quantitatively dilute 50.0 mL nitrate-nitrogen standard solution I to 1,000 mL with demineralized water.

5.9 Nitrate-nitrogen working standards: Prepare a blank and 500 mL each of a series of nitrate-nitrogen working standards by appropriate quantitative dilution of nitrate standard solution II with sodium chloride solution (paragraph 5.10) as follows:

Nitrate-nitrogen standard solution II (mL)	Nitrate-nitrogen concentration (mg/L)
0.0	0.00
2.0	.10
5.0	.25
10.0	.5
20.0	1.0
30.0	1.5
40.0	2.0
60.0	3.0
80.0	4.0
100.0	5.0

5.10 Sodium chloride solution, 100 g/L, acidified: Dissolve 100 g NaCl in 950 mL ammonia-free water. Acidify with concentrated HCl (sp gr 1.19) to a pH of 2.5. Dilute to 1 L.

6. Procedure

6.1 Extraction Procedure

6.1.1 Weigh approx. 5 g of sample, prepared as directed in Method I-0520, and transfer to a 250-mL erlenmeyer flask.

6.1.2 Add 50 mL NaCl solution (5.10) and shake on the wrist-action shaker for 30 min.

6.1.3 Carefully transfer the entire sample, including all sediment particles, to a centrifuge tube. Centrifuge for 5 min; if the sample does not flocculate, add a drop of concentrated HCl (sp gr 1.19) and recentrifuge.

6.1.4 Transfer the supernatant solution to a 100-mL volumetric flask, taking care not to disturb the residue in the bottom of the centrifuge tube.

6.1.5 Wash the sediment in the centrifuge tube with 20 mL sodium chloride solution, recentrifuge and transfer the clear wash solution to the volumetric flask. Adjust to volume with sodium chloride solution (paragraph 5.10).

6.2 Colorimetric Procedure

6.2.1 Set up manifold (fig. 21).

6.2.2 Allow the color reagent to come to room temperature.

6.2.3 Allow colorimeter and recorder to warm for at least 30 min.

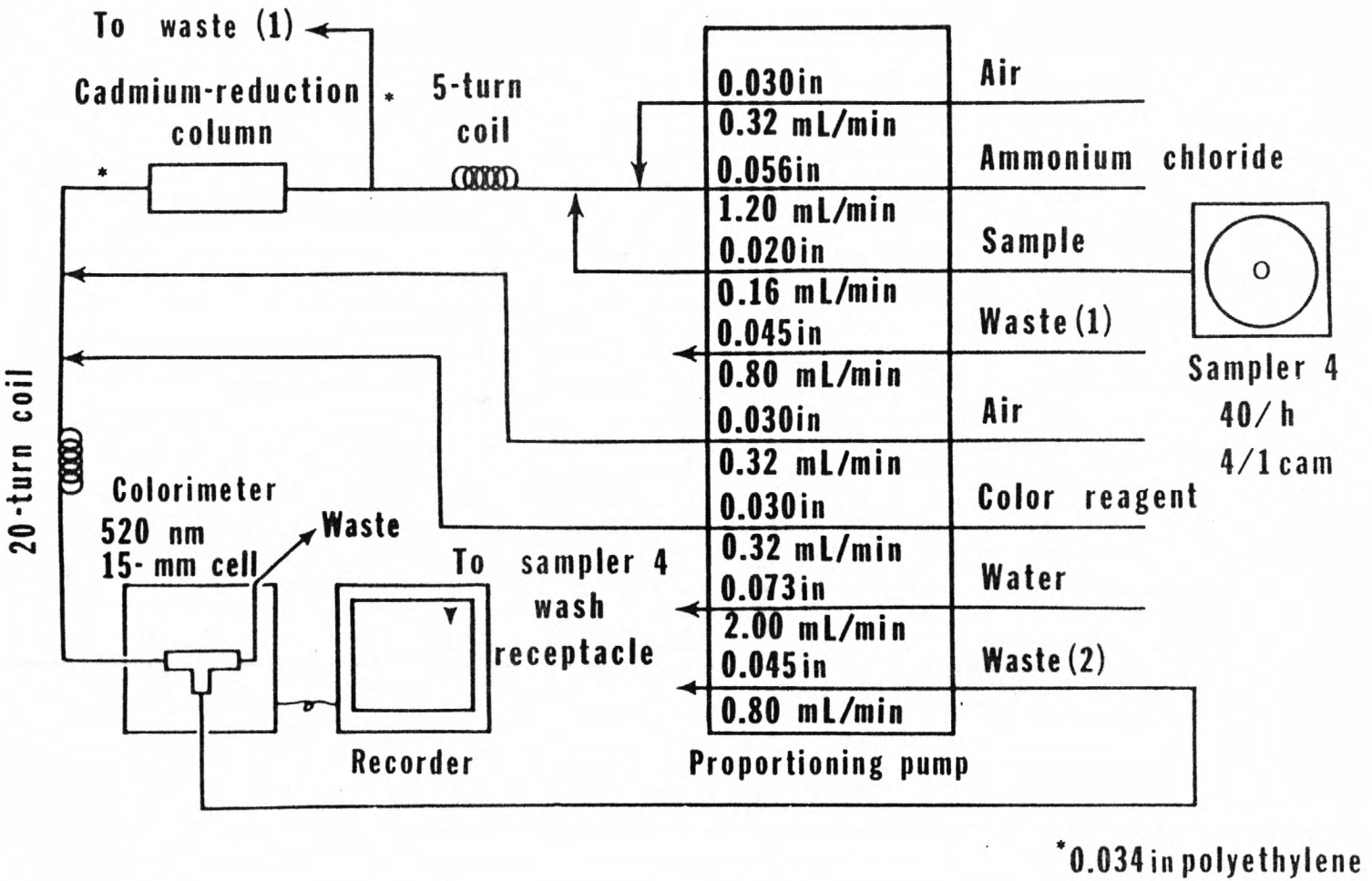


Figure 21.--Nitrogen, nitrite plus nitrate, manifold.

6.2.4 Fill the reduction column, which is a U-shaped, 36-cm length of 2.0-mm ID glass tubing (Technicon No. 189-0000, or equivalent), with water. This prevents entrapment of air bubbles when filling the tube with cadmium. Transfer the prepared cadmium granules to the reduction column. After the filling is completed, insert borosilicate glass wool in the exit end of the tube. This column should be good for several hundred samples before it needs to be refilled. (Note 1).

NOTE 1. The reduction efficiency of the column should be checked regularly by comparing the peak heights of nitrite and nitrate standards. Equal concentration standards should give equal peak heights. Replace the column if the efficiency falls below 90 percent.

6.2.5 Begin pumping reagents but do not connect the reduction column to the manifold system until air has been pumped from the reagent and sample tubes. (Note 2).

NOTE 2. It is important to avoid introduction of air bubbles into the reduction column because they adversely affect sample contact with the cadmium powder and decrease the reduction efficiency. Column must be replaced if air bubbles are introduced.

6.2.6 Activate and stabilize the reduction column by pumping a 3.0 mg/L NO_3-N standard through the system until a steady state is attained.

6.2.7 Switch to demineralized water in the sample line and adjust the baseline to read zero scale divisions on the recorder.

6.2.8 Place a complete set of standards and two blanks in the first positions of the first sample tray beginning with the most concentrated standard. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.2.9 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

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

7.2 Compute the concentration of nitrogen, nitrite plus nitrate, as N, in milligrams per liter in each sample by comparing its peak-height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

$$NO_3\text{-}N + NO_2\text{-}N\ (mg/kg) = \frac{C_N \times 100}{\text{wt of sample in grams}}$$

where

C_N = NO_3-N + NO_2-N concentration, milligrams per liter.

8. Report

Report nitrite plus nitrate (NO_2 + NO_3), total in bottom material as N (00633), concentrations as follows: Less than 10 mg/kg, one decimal: 10 mg/kg and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation of this method is greater than 14 percent in the lower portion of the analytical range.

References

American Society for Testing and Materials, Annual book of ASTM standards, part 31, water: Philadelphia, American Society for Testing and Materials, p. 508.

Brewer, P. G., and Riley, J. P., 1965, The automatic determination of nitrate in sea water: Deep Sea Research, v. 12, p. 765-772.

Kamphake, L., Hannah, S., and Cohen, J., 1967, Automated analysis for nitrate by hydrazine reduction: Water Research, v. 1, p. 205-216.

Morris, A. W., and Riley, J. P., 1963, The determination of nitrate in sea water: Analytica Chimica Acta, v. 29, p. 272-279.

Strickland, J. D. H., and Parsons, T. R., 1972, A manual of sea water analysis: Canada Fisheries Research Board Bull. 167, pp 310.

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Washington, U.S. Government Printing Office, p. 353.2-1.

Nitrogen, nitrite plus nitrate, total colorimetric, cadmium reduction-diazotization, automated (I-4545-81)

Parameter and Code: Nitrogen, nitrite plus nitrate,total (mg/L as N): 00630

1. Application

1.1 This method may be used to determine the sum of nitrite-plus-nitrate-nitrogen concentrations in surface, domestic, and industrial waters and brines in the range from 0.1 to 5.0 mg/L. Samples containing higher concentrations must first be diluted.

1.2 Water-suspended sediment mixtures may be analyzed by this procedure by decanting a suitable portion from a well-settled sample.

2. Summary of method

2.1 Nitrate is reduced to nitrite by a copper-cadmium column. The sample stream is then treated with sulfanilamide under acidic conditions to yield a diazo compound which couples with N-1-naphthylethylenediamine dihydrochloride to form a red compound, the absorbance of which is measured colorimetrically. The final result is the sum of the nitrite originally present plus that formed by the reduction of the nitrate (Brewer and Riley, 1965; Kamphake and others, 1967; Morris and Riley, 1963; Strickland and Parsons, 1965; U.S. Environmental Protection Agency, 1979, p. 207-214; and G. G. Ehrlich and D. K. MacDonald, written communs., 1969).

2.2 Interferences from Hg^{2+} added to the samples as a preservative are overcome by adjusting the pH of the ammonium chloride buffer to 6.3.

3. Interferences

3.1 The concentrations of potentially interfering substances are seldom high enough to introduce error. High concentrations of oxidizing agents, reducing agents, and some metals, such as Cu^{+2} interfere. See American Society for Testing and Materials, Part 31 (1981) for details on potential interferences.

3.2 Acids destroy the cadmium column; therefore, acid treated samples cannot be analyzed by this method.

3.3 Repeated analysis of waters containing concentrations of sulfide over 2 mg/L S^{2-} will rapidly deactivate the cadmium column by formation of cadmium sulfide (Strickland and Parsons, 1972).

4. Apparatus

4.1 Technicon AutoAnalyzer II, consisting of sampler, cartridge manifold (including copper-cadmium reduction column), proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.1 to 5.0 mg/L (NO_2 + NO_3) as N:

Absorption cell.....15 mm
Wavelength.....520 nm
Cam.....40/h(4/1)

5. Reagents

5.1 Ammonium chloride solution, 10 g/L: Dissolve 10 g NH_4Cl in demineralized water and dilute to approx 950 mL. Adjust pH to 6.3 ± 0.2 with dilute NH_4OH solution and dilute to 1 L. Add 0.5 mL Brij-35 solution.

5.2 Brij-35 solution, 30-percent aqueous solution (Baker No. C706, or equivalent).

5.3 Cadmium powder, coarse, (99 percent pure) (Technicon No. T11-5063, or equivalent): Wash cadmium powder with diethyl ether or 1M HCl followed by demineralized water. Allow to air dry. Shake the dry powder with copper sulfate solution (20 g/L). The weight of the solution should be approx 10 times that of the cadmium. Wash thoroughly with demineralized water to remove colloidal copper which is visible as a blue color in the wash water. A minimum of 10 washings is usually required to eliminate the perceptible blue color.

5.4 Color reagent: Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to approx 1,500 mL demineralized water. Dissolve completely (warm if necessary). Add 1.0 g N-1-naphthylethylenediamine dihydrochloride and dissolve completely. Dilute to 2 L with demineralized water. Add 1.0 mL Brij-35 solution. Store in a refrigerator. This reagent is stable for approximately 1 month.

5.5 Copper sulfate solution, 20 g/L: Dissolve 20 g $CuSO_4$ (anhydrous) in demineralized water and dilute to 1 L.

5.6 Hydrochloric acid, 1.0M: Add 83.3 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.7 Nitrate-nitrogen standard solution I, 1.00 mL = 0.50 mg NO_3-N: Dissolve 3.609 g KNO_3, dried overnight over concentrated H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.8 Nitrate-nitrogen standard solution II, 1.00 mL = 0.025 mg NO_3-N: Quantitatively dilute 50.0 mL nitrate-nitrogen standard solution I to 1,000 mL with demineralized water.

5.9 Nitrate-nitrogen working standards: Prepare a blank and 500 mL each of a series of nitrate-nitrogen working standards by appropriate quantitative dilution of nitrate standard solution II as follows:

Nitrate-nitrogen standard solution II (mL)	Nitrate-nitrogen concentration (mg/L)
0.0	0.00
2.0	.10
5.0	.25
10.0	.5
20.0	1.0
30.0	1.5
40.0	2.0
60.0	3.0
80.0	4.0
100.0	5.0

6. Procedure

6.1 Set up manifold (fig. 22).

6.2 Allow the color reagent to come to room temperature.

6.3 Allow colorimeter and recorder to warm for at least 30 min.

6.4 Fill the reduction column, which is a U-shaped, 36-cm length of 2.0-mm ID glass tubing (Technicon No. 189-0000, or equivalent), with water. This prevents entrapment of air bubbles when filling the tube with cadmium. Transfer the prepared cadmium granules to the reduction column. After the filling is completed, insert borosilicate glass wool in the exit end of the tube. This column should be good for several hundred samples before it needs to be refilled. (Note 1).

NOTE 1. The reduction efficiency of the column should be checked regularly by comparing the peak heights of nitrite and nitrate standards. Equal concentration standards should give equal peak heights. Replace the column if the efficiency falls below 90 percent.

6.5 Begin pumping reagents but do not connect the reduction column to the manifold system until air has been pumped from the reagent and sample tubes. (Note 2).

NOTE 2. It is important to avoid introduction of air bubbles into the reduction column because they adversely affect sample contact with the cadmium powder and decrease the reduction efficiency. Column must be replaced if air bubbles are introduced.

6.6 Activate and stabilize the reduction column by pumping a 3.0 mg/L NO_3-N standard through the system until a steady state is attained.

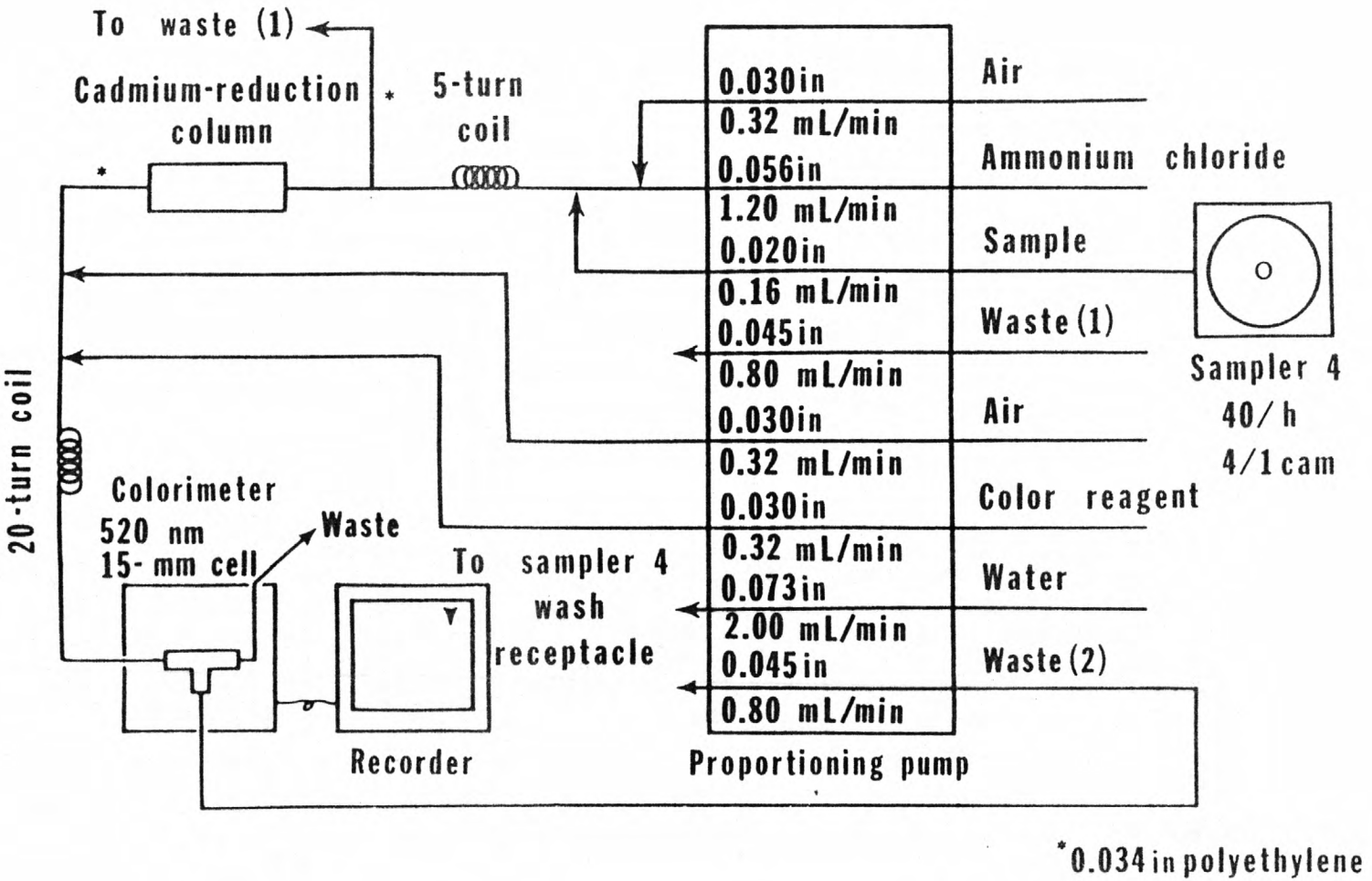


Figure 22.--Nitrogen, nitrite plus nitrate, manifold.

6.7 Switch to demineralized water in the sample line and adjust the baseline to read zero scale divisions on the recorder.

6.8 Place a complete set of standards and two blanks in the first positions of the first sample tray beginning with the most concentrated standard. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.9 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

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

7.2 Compute the concentration of nitrogen, nitrite plus nitrate, (NO_2 + NO_3), as N, in milligrams per liter in each sample by comparing its peak-height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report nitrite plus nitrate (NO_2 + NO_3), total as N (00630), concentrations as follows: Less than 0.1 to 1.0 mg/L, two decimals, 1.0 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation of this method is greater than 14 percent at 0.46 mg/L and greater than 11 percent at 4.88 mg/L.

References

American Society for Testing and Materials, Annual book of ASTM standards, part 31, water 1981 ASTM, Philadelphia, American Society for Testing and Materials p. 508.

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Phosphorus, dissolved, colorimetric, phosphomolybdate, automated (I-2600-81)

Parameter and Code: Phosphorus, dissolved (mg/L as P): 00666

1. Application

This method may be used to determine concentrations of dissolved phosphorus in most waters, waste waters, and brines in the range from 0.01 to 2.0 mg/L P. Samples containing higher concentrations must first be diluted.

2. Summary of method

2.1 All forms of phosphorus, including organic phosphorus, are converted to orthophosphate by an acid-persulfate digestion.

2.2 Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid which, upon reduction with ascorbic acid, produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales, Julian, and Kroner, 1966).

2.3 Mercuric chloride-preserved samples are fortified with 50 mg/L NaCl to overcome the interference from mercury in the analysis.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a phosphate precipitate but the effect is normally negligible in natural waters. The interference from silica, which forms a pale-blue complex, is small and can be considered negligible . Nitrite interferes, but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L.

3.3 Arsenic as arsenate (AsO_4^{3-}) produces a similar color as phosphate (Murphy and Riley, 1962) and may cause a positive interference in the analysis of high-arsenic waters.

4. Apparatus

4.1 Autoclave.

4.2 Technicon AutoAnalyzer II, consisting of sampler, cartridge manifold, proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L P:

Absorption cell.....15 mm
Wavelength.....880 nm or 660 nm
Cam.....40/h(5/1).
Heating bath temperature.....37.5°C

4.4 Glass tubes with plastic caps, disposable: 18 mm x 150 mm.

5. Reagents

5.1 Ammonium molybdate solution, 35.6 g/L: Dissolve 40 g ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.2 Ascorbic acid solution, 18 g/L: Dissolve 18 g of ascorbic acid ($C_6H_8O_6$) in 800 mL demineralized water and dilute to 1 L. Keep in a dark bottle and refrigerate. The solution is stable for one week.

5.3 Antimony potassium tartrate solution, 3 g/L: Dissolve 3.0 g antimony potassium tartrate $K(SbO)C_4H_4O_6.\frac{1}{2}H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.4 Combined working reagent: Combine reagents together in order listed below (this reagent is stable for about 8 h):

Sulfuric acid, 2.45M.....50 mL
Ammonium molybdate solution.....15 mL
Ascorbic acid solution.....30 mL
Antimony potassium tartrate solution...5 mL

5.5 Levor IV solution or equivalent.

5.6 Phosphate standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4(sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.7 Phosphate standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.8 Phosphate working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution with demineralized water of phosphate standard solution II. Dissolve in each working standard 8 mg mercuric chloride ($HgCl_2$) and 200 mg sodium chloride (NaCl). For example:

Phosphate standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
5.0	.25
10	.50
20	1.00
30	1.50
40	2.00

5.9 Potassium persulfate solution, 4 g/L: Dissolve 4.0 g $K_2S_2O_8$ in demineralized water and dilute to 1 L.

5.10 Sulfuric acid, 2.45M: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool and dilute to 1 L with demineralized water.

5.11 Sulfuric acid, 0.45M: Slowly, and with constant stirring and cooling, add 25.2 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool and dilute to 1 L with demineralized water.

5.12 Sulfuric acid-persulfate reagent, (1+1): Mix equal volumes of 0.45M sulfuric acid and potassium persulfate solution.

5.13 Water diluent: Dissolve 20g NaCl in 800 mL demineralized water. Add 2.0 mL Levor IV and dilute to 1L with demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.02 mg P (10.0 mL maximum) into a disposable glass tube and adjust the volume to 10.0 mL.

6.2 Prepare sufficient standards and a blank with demineralized water and adjust the volume of each to 10.0 mL.

6.3 Add 4.0 mL sulfuric acid-persulfate reagent.

6.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 lbs pressure. After the samples have cooled, the caps may be pushed down.

6.5 Set up manifold (fig. 23).

6.6 Allow colorimeter, recorder and heating bath to warm for at least 30 minutes or until the temperature of the heating bath reads 37.5°C.

6.7 Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

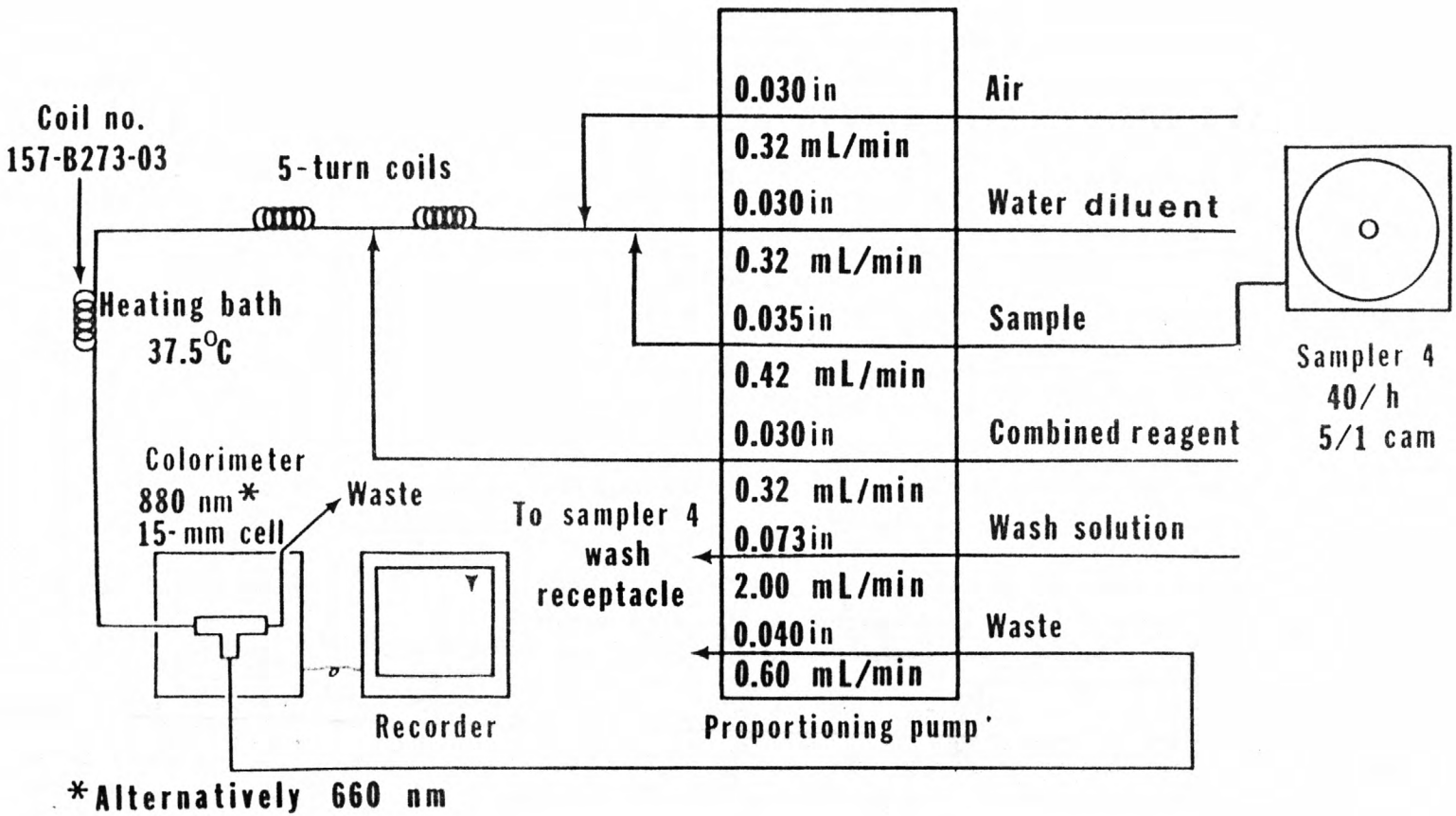

Figure 23.--Phosphorus manifold.

6.8 Place a complete set of standards and a blank in the first positions of the first sample tray beginning with the most concentrated standard. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.9 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

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

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

8. Report

8.1 Report phosphorus, dissolved (00666), concentrations as follows: Less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision.

Precision obtained by a single laboratory during a 12 month period on two synthetic (deionized water matrix samples) can be expressed as follows:

Number of replicates	Mean, mg/L	Standard deviation, mg/L	Relative standard deviation, percent
110	0.197	0.023	12
115	.670	.020	3

References

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chimica Acta, v. 27, p. 31.

Phosphorus, orthophosphate plus hydrolyzable, dissolved, colorimetric, phosphomolybdate, automated (I-2602-81)

Parameter and Code: Phosphorus, orthophosphate plus hydrolyzable, dissolved (mg/L as P): 00677

1. Application

This method may be used to determine concentrations of dissolved orthophosphate plus hydrolyzable phosphorus in most waters, and brines in the range from 0.01 to 2.0 mg/L combined acid hydrolyzable and orthophosphate-phosphorus. Samples containing higher concentrations must first be diluted.

2. Summary of method

2.1 Polyphosphates $(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc. and a few organic phosphorus compounds are converted to orthophosphate by an acid hydrolysis.

2.2 Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales, Julian, and Kroner, 1966).

2.3 Mercuric chloride-preserved samples are fortified with 50 mg/L NaCl to overcome the interference from mercury in the analysis.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a phosphate precipitate but the effect is normally negligible in natural waters. The interference from silica, which forms a pale-blue complex, is small and can be considered negligible. Nitrite interferes, but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L.

3.3 Arsenic as arsenate (AsO_4^{3-}) produces a similar color as phosphate (Murphy and Riley, 1962) and may cause a positive interference in the analysis of high-arsenic waters.

4. Apparatus

4.1 Autoclave.

4.2 Technicon AutoAnalyzer II, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L combined hydrolyzable and orthophosphate-phosphorus:

Absorption cell.....15 mm
Wavelength.....880 nm or 660 nm
Cam.....40/h(5/1)
Heating bath temperature.....37.5°C

4.4 Glass tubes with plastic caps, disposable: 18 mm x 150 mm.

5. Reagents

5.1 Ammonium molybdate solution, 35.6 g/L: Dissolve 40 g ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.2 Ascorbic acid solution, 18 g/L: Dissolve 18 g ascorbic acid ($C_6H_8O_6$) in 800 mL demineralized water and dilute to 1 L.

5.3 Antimony potassium tartrate solution, 3 g/L: Dissolve 3.0 g antimony potassium tartrate $K(SbO)C_4H_4O_6.1/2H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.4 Combined working reagent: Combine reagents in order listed below (this reagent is stable for about 8 h):

Sulfuric acid, 2.45M.....50 mL
Ammonium molybdate solution.....15 mL
Ascorbic acid solution.....30 mL
Antimony potassium tartrate solution.....5 mL

5.5 Levor IV solution or equivalent.

5.6 Phosphate standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.7 Phosphate standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.8 Phosphate working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II. Dissolve in each working standard 8 mg mercuric chloride ($HgCl_2$) and 200 mg sodium chloride (NaCl). For example:

Phosphate standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
5.0	.25
10	.50
20	1.00
30	1.50
40	2.00

5.9 Sulfuric acid, 2.45M: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool and dilute to 1 L with demineralized water.

5.10 Sulfuric acid, 0.45M: Slowly, and with constant stirring and cooling, add 25.2 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water.

5.11 Water diluent: Dissolve 20g NaCl in 800 mL demineralized water. Add 2.0 mL Levor IV and dilute to 1L with demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.02 mg combined hydrolzable and orthophosphate-phosphorus (10.0 mL maximum) into a disposable glass tube and adjust the volume to 10.0 mL.

6.2 Prepare sufficient standards and a blank with demineralized water and adjust the volume of each to 10.0 mL.

6.3 Add 2.0 mL 0.45M sulfuric acid.

6.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 lbs pressure. After the samples have cooled, the caps may be pushed down.

6.5 Set up manifold (fig. 27).

6.6 Allow colorimeter, recorder and heating bath to warm for at least 30 minutes or until the temperature of the heating bath reads 37.5°C.

6.7 Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.8 Place a complete set of standards and a blank in the first positions of the first sample tray beginning with the most concentrated standard. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

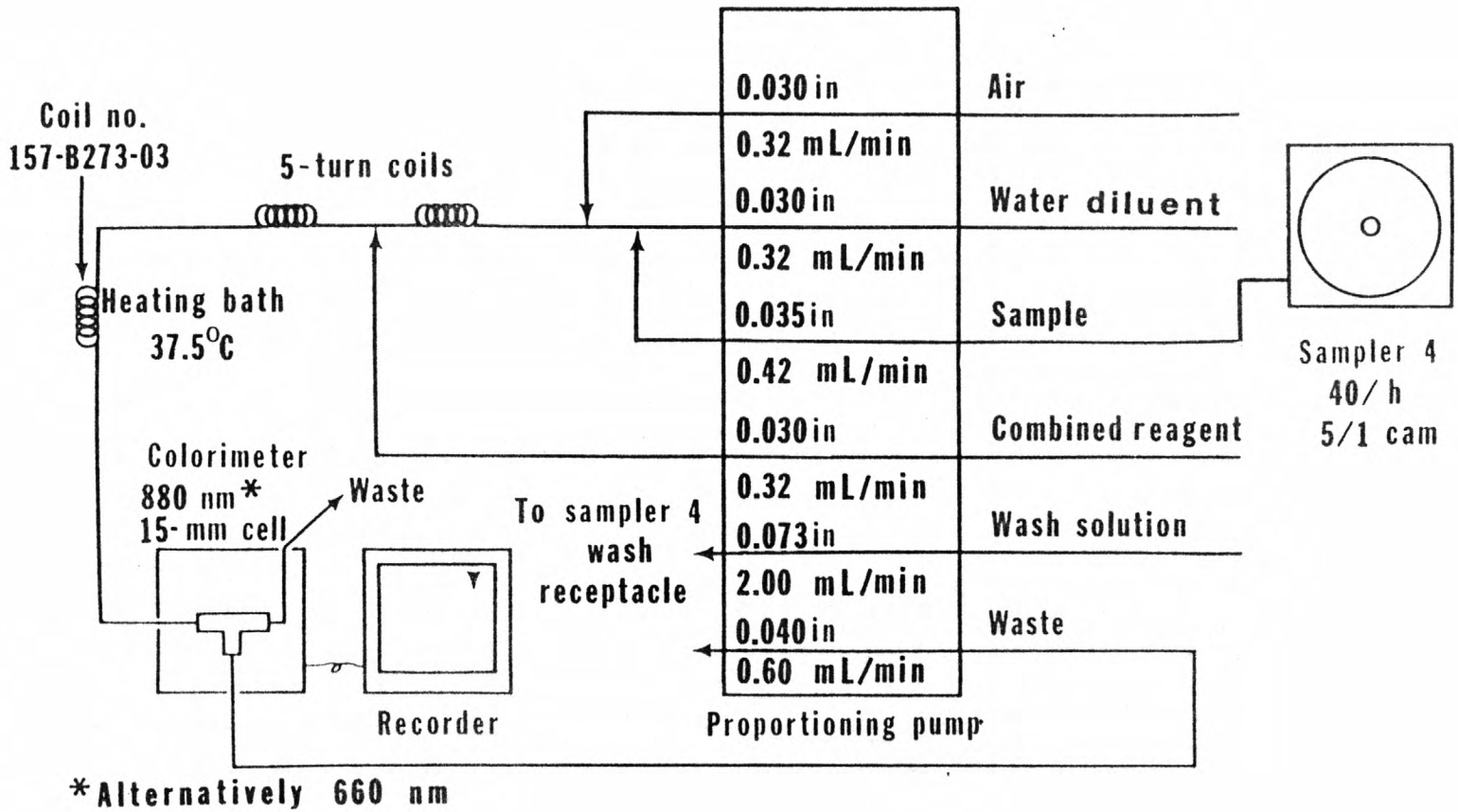

Figure 24.--Phosphorus manifold.

6.9 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

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

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

8. Report

Report phosphorus, orthophosphate plus hydrolyzable (00677), concentrations as follows: Less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation of this method is greater than 12 percent at 0.20 mg/L.

References

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chimica Acta, v. 27, p. 31.

Phosphorus, orthophosphate plus hydrolyzable, total, colorimetric, phosphomolybdate, automated (I-4602-81)

Parameter and Code: Phosphorus, orthophosphate plus hydrolyzable, total (mg/L as P): 00678

1. Application

This method may be used to determine concentrations of orthophosphate plus hydrolyzable phosphorus in water-suspended sediment mixtures in the range from 0.01 to 2.0 mg/L combined acid hydrolyzable and orthophosphate-phosphorus. Samples containing higher concentrations must first be diluted.

2. Summary of method

2.1 Polyphosphates $(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc. and a few organic phosphorus compounds are converted to orthophosphate by an acid hydrolysis.

2.2 Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales, Julian, and Kroner, 1966).

2.3 Mercuric chloride-preserved samples are fortified with 50 mg/L NaCl to overcome the interference from mercury in the analysis.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a phosphate precipitate but the effect is normally negligible in natural waters. The interference from silica, which forms a pale-blue complex, is small and can be considered negligible. Nitrite interferes, but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L.

3.3 Arsenic as arsenate (AsO_4^{3-}) produces a similar color as phosphate (Murphy and Riley, 1962) and may cause a positive interference in the analysis of high-arsenic waters.

4. Apparatus

4.1 Autoclave.

4.2 Technicon AutoAnalyzer II, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L combined hydrolyzable and orthophosphate-phosphorus:

Absorption cell.....15 mm
Wavelength.....880 nm or 660 nm
Cam.....40/h(5/1)
Heating bath temperature.....37.5°C

4.4 Glass tubes with plastic caps, disposable: 18 mm x 150 mm.

5. Reagents

5.1 Ammonium molybdate solution, 35.6 g/L: Dissolve 40 g ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.2 Ascorbic acid solution, 18 g/L: Dissolve 18 g ascorbic acid ($C_6H_8O_6$) in 800 mL demineralized water and dilute to 1 L.

5.3 Antimony potassium tartrate solution, 3 g/L: Dissolve 3.0 g antimony potassium tartrate $K(SbO)C_4H_4O_6\cdot 1/2H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.4 Combined working reagent: Combine reagents in order listed below (this reagent is stable for about 8 h):

Sulfuric acid, 2.45M.....50 mL
Ammonium molybdate solution.....15 mL
Ascorbic acid solution.....30 mL
Antimony potassium tartrate solution.....5 mL

5.5 Levor IV solution or equivalent.

5.6 Phosphate standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.7 Phosphate standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.8 Phosphate working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II. Dissolve in each working standard 8 mg mercuric chloride ($HgCl_2$) and 200 mg sodium chloride (NaCl). For example:

Phosphate standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
5.0	.25
10	.50
20	1.00
30	1.50
40	2.00

5.9 Sulfuric acid, 2.45M: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool and dilute to 1 L with demineralized water.

5.10 Sulfuric acid, 0.45M: Slowly, and with constant stirring and cooling, add 25.2 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool and dilute to 1 L with demineralized water.

5.11 Water diluent: Dissolve 20g NaCl in 800 mL demineralized water. Add 2.0 mL Levor IV and dilute to 1L with demineralized water.

6. Procedure

6.1 Mix each sample and immediately pipet a volume containing less than 0.02 mg combined total hydrolyzable and orthophosphate phosphorus (10.0 mL maximum) into a disposable glass tube, and adjust the volume to 10.0 mL.

6.2 Prepare sufficient standards and a blank with demineralized water and adjust the volume of each to 10.0 mL.

6.3 Add 2.0 mL 0.45M sulfuric acid.

6.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 lbs pressure. Cool and filter the samples through a 0.45 um membrane filter.

6.5 Set up manifold (fig. 25).

6.6 Allow colorimeter, recorder and heating bath to warm for at least 30 minutes or until the temperature of the heating bath reads 37.5°C.

6.7 Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

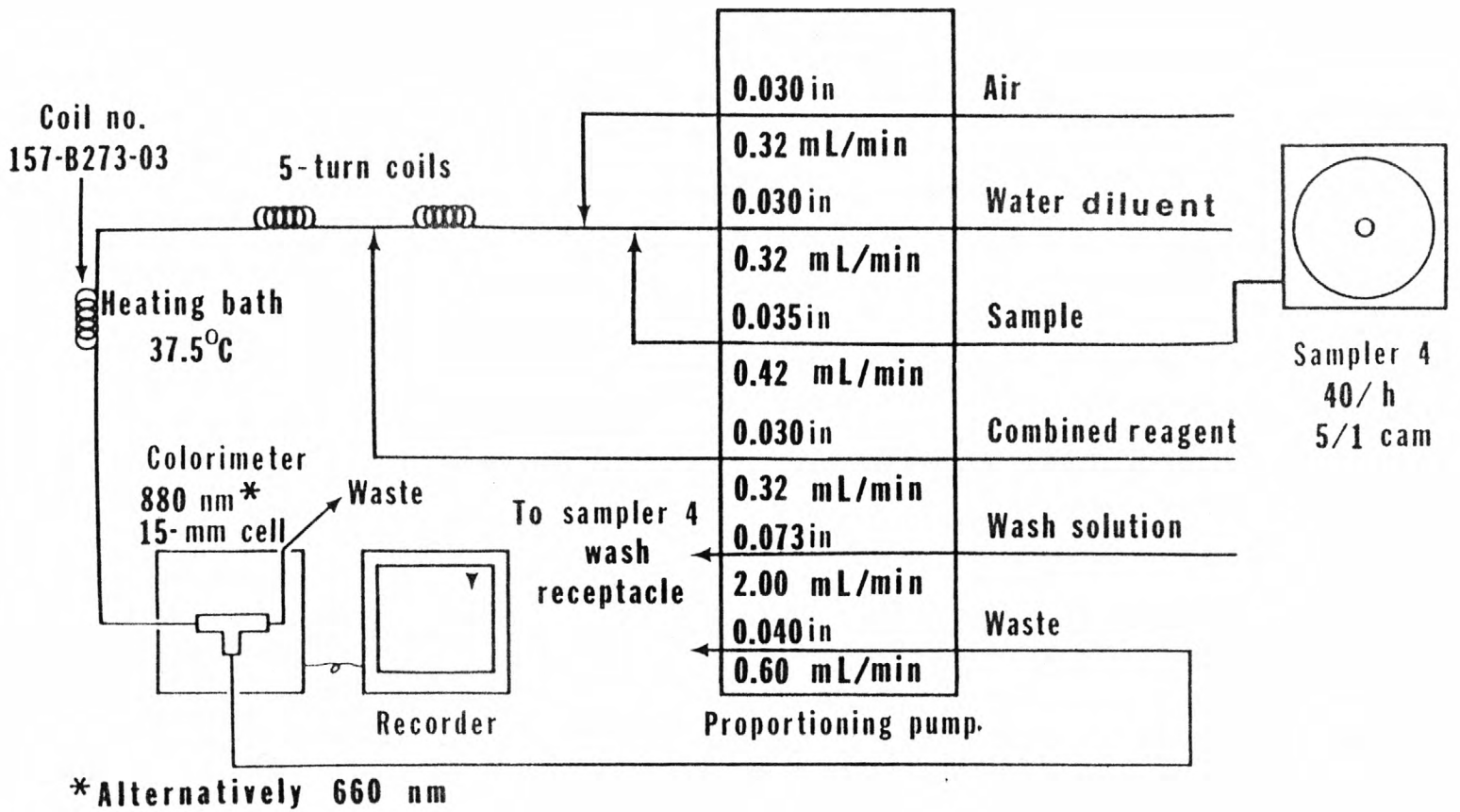

Figure 25.--Phosphorus manifold.

6.8 Place a complete set of standards and a blank in the first positions of the first sample tray beginning with the most concentrated standard. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.9 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

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

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

8. Report

Report phosphorus, orthophosphate plus hydrolyzable (00678), concentrations as follows: Less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation of this method is greater than 12 percent at 0.20 mg/L.

References

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chimica Acta, v. 27, p. 31.

Phosphorus, orthophosphate, dissolved, colorimetric, phosphomolybdate, automated (I-2601-81)

Parameter and Code: Phosphorus, orthophosphate, dissolved (mg/L as P): 00671

1. Application

This method may be used to determine concentrations of orthophosphate-phosphorus in most waters, wastewaters, and brines in the range from 0.01 to 2.0 mg/L P. Samples containing higher concentrations must first be diluted.

2. Summary of method

2.1 Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales, Julian, and Kroner, 1966).

2.2 Mercuric chloride-preserved samples are fortified with 50 mg/L NaCl to overcome the interference from mercury in the analysis.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a phosphate precipitate but the effect is normally negligible in natural waters. The interference from silica, which forms a pale-blue complex, is small and can be considered negligible. Nitrite interferes, but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L.

3.3 Arsenic as arsenate (AsO_4^{3-}) produces a similar color as phosphate (Murphy and Riley, 1962) and may cause a positive interference in the analysis of high-arsenic waters.

4. Apparatus

4.1 Technicon AutoAnalyzer II, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L P.

Absorption cell.....15 mm
Wavelength.....880 nm or 660 nm
Cam.....40/h(5/1)
Heating bath.....37.5°C

5. Reagents

5.1 Ammonium molybdate solution, 35.6 g/L: Dissolve 40 g ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.2 Ascorbic acid solution, 18 g/L: Dissolve 18 g ascorbic acid ($C_6H_8O_6$) in 800 mL demineralized water and dilute to 1 L.

5.3 Antimony potassium tartrate solution, 2.9 g/L: Dissolve 3.0 g antimony potassium tartrate $K(SbO)C_4H_4O_6\cdot 1/2H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.4 Combined working reagent: Combine reagents together in order listed below: This reagent is stable for about 8 h.

Sulfuric acid, 2.45 M.....50 mL
Ammonium molybdate solution.....15 mL
Ascorbic acid solution.....30 mL
Antimony potassium tartrate solution.....5 mL

5.5 Levor IV solution or equivalent.

5.6 Phosphate standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.7 Phosphate standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.8 Phosphate working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II as follows: Dissolve in each working standard 8 mg mercuric chloride ($HgCl_2$) and 200 mg sodium chloride (NaCL).

Phosphate standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
5.0	.25
10	.50
20	1.50
30	1.00
40	2.00

5.9 Sulfuric acid, 2.45M: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool and dilute to 1 L with demineralized water.

5.10 Water diluent: Dissolve 20g NaCl in 800 mL demineralized water. Add 2.0 mL Levor IV and dilute to 1L with demineralized water.

6. Procedure

6.1 Set up manifold (fig. 26).

6.2 Allow colorimeter, recorder and heating bath to warm for at least 30 minutes or until the temperature of the heating bath reads 37.5°C.

6.3 Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.4 Place a complete set of standards and a blank in the first positions of the first sample tray beginning with the most concentrated standard. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.5 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

7. Calculations

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

7.2 Compute the concentration of dissolved orthophosphate-phosphorus (PO_4-P) in each sample by comparing its peak-height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

8. Report

Report orthophosphate-phosphorus (PO_4-P), dissolved (00671), concentrations as follows: Less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

Precision obtained by two laboratories on two synthetic (deionized water matrix) samples can be expressed as follows:

Number of replicates	Mean, mg/L	Standard deviation, mg/L	Relative standard deviation, percent
44	0.050	0.010	20
50	.168	.027	16

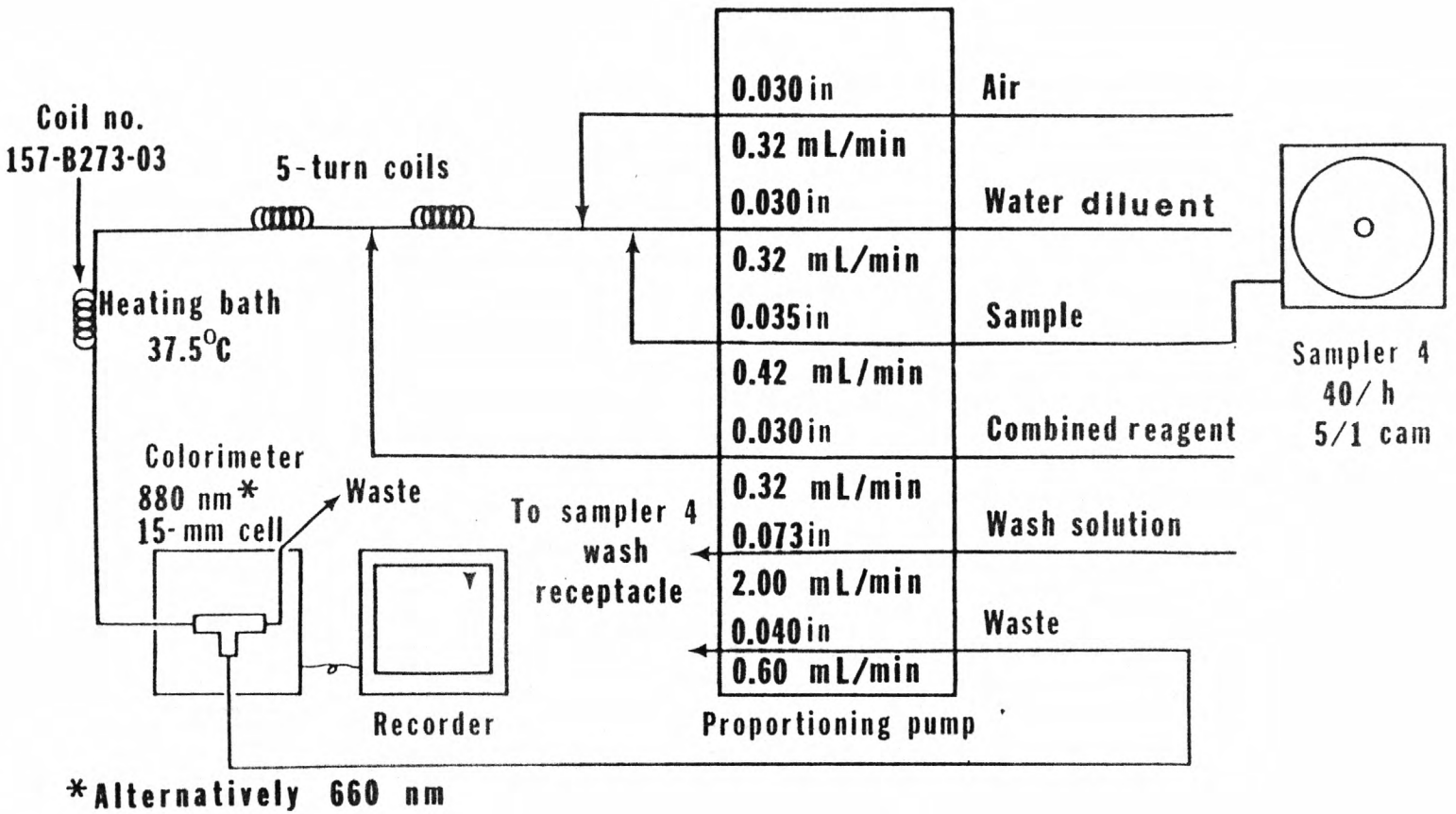

Figure 26.--Phosphorus manifold.

References

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chimica Acta, v. 27, p. 31.

Phosphorus, orthophosphate, total, colorimetric, phosphomolybdate, automated (I-4601-81)

Parameter and Code: Phosphorus, orthophosphate, total (mg/L as P): 70507

1. Application

1.1 This method may be used to determine concentrations of total orthophosphate-phosphorus in water-suspended sediment mixtures in the range of 0.01 to 2.0 mg/L P. Samples containing higher concentrations must first be diluted.

1.2 The suspended sediment in an unfiltered, unacidified sample is allowed to settle in the sample bottle and a portion of the clear supernatant solution is decanted for analysis.

2. Summary of method

2.1 Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales, Julian, and Kroner, 1966).

2.2 Mercuric chloride-preserved samples are fortified with 50 mg/L NaCl to overcome the interference from mercury in the analysis.

3. Interferences

3.1 Inasmuch as phosphorus is easily adsorbed on sediment, the orthophosphate recovered from the supernatant solution above a water-suspended sediment mixture after some time has elapsed may be less than that which would have been determined in the filtrate from a sample that was filtered at the time of collection. The amount recovered may also depend on the type of sediment (clay, sand, and so forth).

3.2 Barium, lead, and silver interfere by forming a phosphate precipitate but the effect is normally negligible in natural waters. The interference from silica, which forms a pale-blue complex, is small and can be considered negligible. Nitrite interferes, but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.3 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L.

3.4 Arsenic as arsenate (AsO_4^{3-}) produces a similar color as phosphate (Murphy and Riley, 1962) and may cause a positive interference in the analysis of high-arsenic waters.

4. Apparatus

4.1 Technicon AutoAnalyzer II, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L P:

Absorption cell.....15 mm
Wavelength.....880 nm or 660 nm
Cam.....40/h (5/1)
Heating bath.....37.5°C

5. Reagents

5.1 Ammonium molybdate solution, 35.6 g/L: Dissolve 40 g ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.2 Ascorbic acid solution, 18 g/L: Dissolve 18 g ascorbic acid ($C_6H_8O_6$) in 800 mL demineralized water and dilute to 1 L.

5.3 Antimony potassium tartrate solution, 3 g/L: Dissolve 3.0 g antimony potassium tartrate $K(SbO)C_4H_4O_6\cdot 1/2H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.4 Combined working reagent: Combine reagents together in order listed below (this reagent is stable for about 8 hr):

Sulfuric acid, 2.45M.....50 mL
Ammonium molybdate solution.....15 mL
Ascorbic acid solution.....30 mL
Antimony potassium tartrate solution.....5 mL

5.5 Levor IV solution or equivalent.

5.6 Phosphate standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.7 Phosphate standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.8 Phosphate working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution with demineralized water of phosphate standard solution II. Dissolve in each working standard 8 mg mercuric chloride ($HgCl_2$) and 200 mg sodium chloride (NaCl). For example:

Phosphate standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
5.0	.25
10	.50
20	1.00
30	1.50
40	2.00

5.9 Sulfuric acid, 2.45M: Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool, and dilute to 1 L with demineralized water.

5.10 Water diluent: Dissolve 20 g NaCl in 800 mL demineralized water. Add 2.0 mL Levor IV and dilute to 1L with demineralized water.

6. Procedure

6.1 Set up manifold (Fig. 27).

6.2 Allow colorimeter, recorder and heating bath to warm for at least 30 minutes or until the temperature of the heating bath reads 37.5°C.

6.3 Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.4 Place a complete set of standards and a blank in the first positions of the first sample tray beginning with the most concentrated standard. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

NOTE 1. Decant a portion of the clear supernatant solution from a settled sample for analysis. Avoid transfer of any particulate matter to the sample cups.

6.5 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

7. Calculations

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

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

8. Report

Report phosphorus, total orthophosphate (70507), concentrations as follows: Less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation of this method is greater than 20 percent at 0.050 mg/L and greater than 16 percent at 0.168 mg/L.

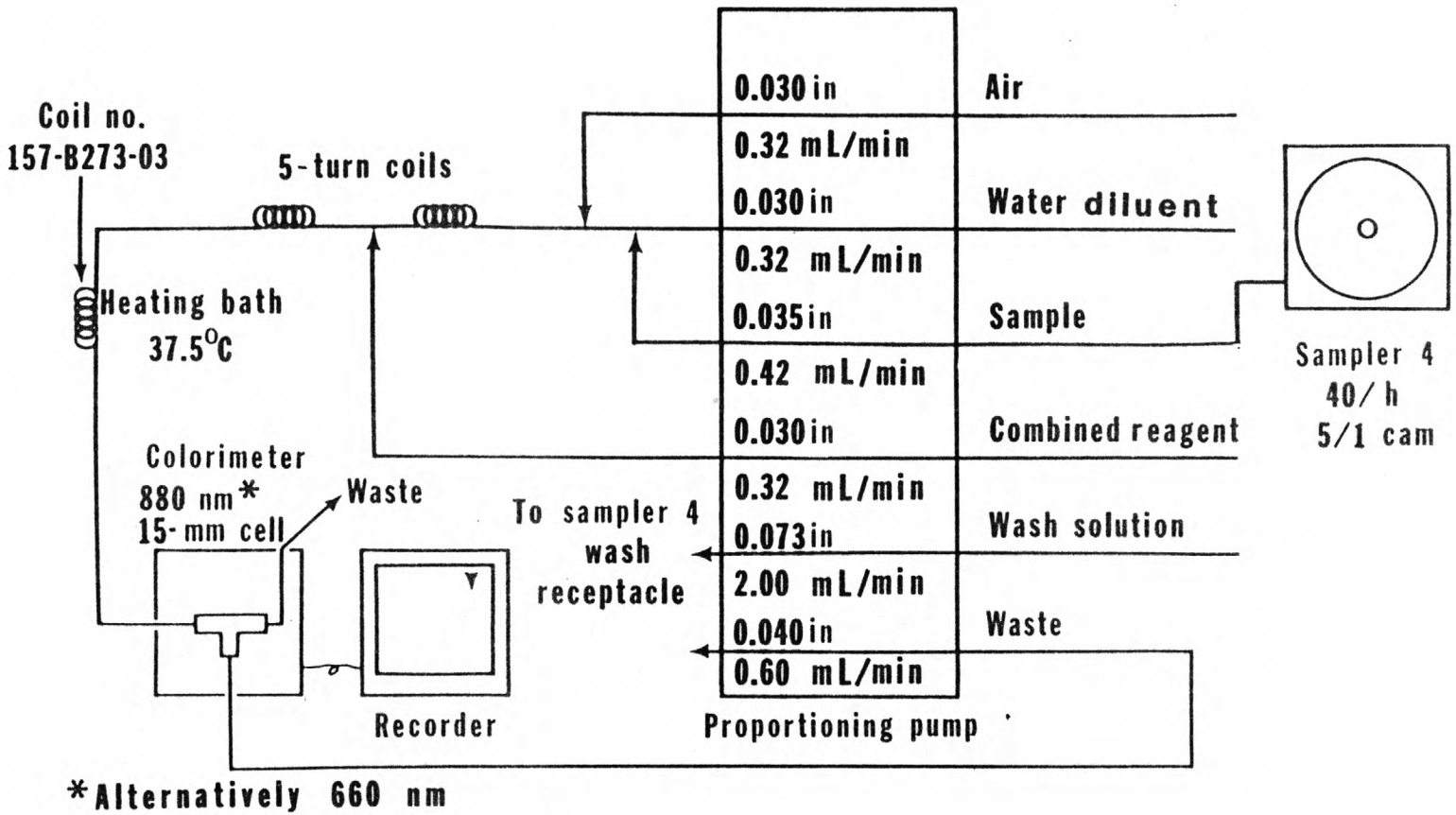

Figure 27.--Phosphorus manifold.

References

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chimica Acta, v. 27, p. 31.

Phosphorus, total, colorimetric, phosphomolybdate, automated (I-4600-81)

Parameter and Code: Phosphorus, total (mg/L as P): 00665

1. Application

This method may be used to determine concentrations of total phosphorus in water-suspended sediment mixtures in the range from 0.01 to 2.0 mg/L P. Samples containing higher concentrations must first be diluted.

2. Summary of method

2.1 All forms of phosphorus, including organic phosphorus, are converted to orthophosphate by an acid-persulfate digestion.

2.2 Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales, Julian, and Kroner, 1966).

2.3 Mercuric chloride-preserved samples are fortified with 50 mg/L NaCl to overcome the interference from mercury in the analysis.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a phosphate precipitate but the effect is normally negligible in natural waters. The interference from silica, which forms a pale-blue complex, is small and can be considered negligible. Nitrite interferes, but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L.

3.3 Arsenic as arsenate (AsO_4^{3-}) produces a similar color as phosphate (Murphy and Riley, 1962) and may cause a positive interference in the analysis of high-arsenic waters.

4. Apparatus

4.1 Autoclave.

4.2 Technicon AutoAnalyzer II, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.3 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 2.0 mg/L P:

Absorption cell.....15 mm
Wavelength.....880 nm or 660 nm
Cam.....40/h (5/1)
Heating bath temperature.....37.5°C

4.4 Glass tubes with plastic caps, disposable: 18 mm x 150 mm.

5. Reagents

5.1 Ammonium molybdate solution, 35.6 g/L: Dissolve 40 g ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.2 Ascorbic acid solution, 18 g/L: Dissolve 18 g ascorbic acid ($C_6H_8O_6$) in 800 mL demineralized water and dilute to 1 L.

5.3 Antimony potassium tartrate solution, 3 g/L: Dissolve 3.0 g antimony potassium tartrate $K(SbO)C_4H_4O_6.\frac{1}{2}H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.4 Combined working reagent: Combine reagents together in order listed below (this reagent is stable for about 8 h):

Sulfuric acid, 2.45 M .....50 mL
Ammonium molybdate solution.....15 mL
Ascorbic acid solution.....30 mL
Antimony potassium tartrate solution.....5 mL

5.5 Levor IV solution or equivalent.

5.6 Phosphate standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4390 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.7 Phosphate standard solution II, 1.00 mL = 0.010 mg P: Quantitatively dilute 100.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.8 Phosphate working standards: Prepare a blank and 200 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II as follows. Dissolve in each work standard 8 mg mercuric chloride ($HgCl_2$) and 200 mg sodium chloride (NaCl).

Phosphate standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
5.0	.25
10	.50
20	1.00
30	1.50
40	2.00

5.9 Potassium persulfate solution, 4 g/L: Dissolve 4.0 g $K_2S_2O_8$ in demineralized water and dilute to 1 L.

5.10 Sulfuric acid, 2.45M: Slowly, and with constant stirring and cooling, add 136 ml concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool, and dilute to 1 L with demineralized water.

5.11 Sulfuric acid, 0.45M: Slowly, and with constant stirring and cooling, add 25.2 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool, and dilute to 1 L with demineralized water.

5.11 Sulfuric acid-persulfate reagent, (1+1): Mix equal volumes of 0.45M sulfuric acid and potassium persulfate solution.

5.12 Water diluent: Dissolve 20 g NaCl in 800 mL demineralized water. Add 2.0 mL Levor IV and dilute to 1L with demineralized water.

6. Procedure

6.1 Mix each sample and pipet a volume containing less than 0.02 mg total P (10.0 mL maximum) into a disposable glass tube, and adjust the volume to 10.0 mL.

6.2 Prepare sufficient standards and a blank with demineralized water and adjust the volume of each to 10.0 mL.

6.3 Add 4.0 mL acid-persulfate reagent.

6.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 lbs pressure. Cool and filter the sample through a 0.45 um membrane filter.

6.5 Set up manifold (fig. 28).

6.6 Allow colorimeter, recorder and heating bath to warm for at least 30 minutes or until the temperature of the heating bath reads 37.5°C.

6.7 Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

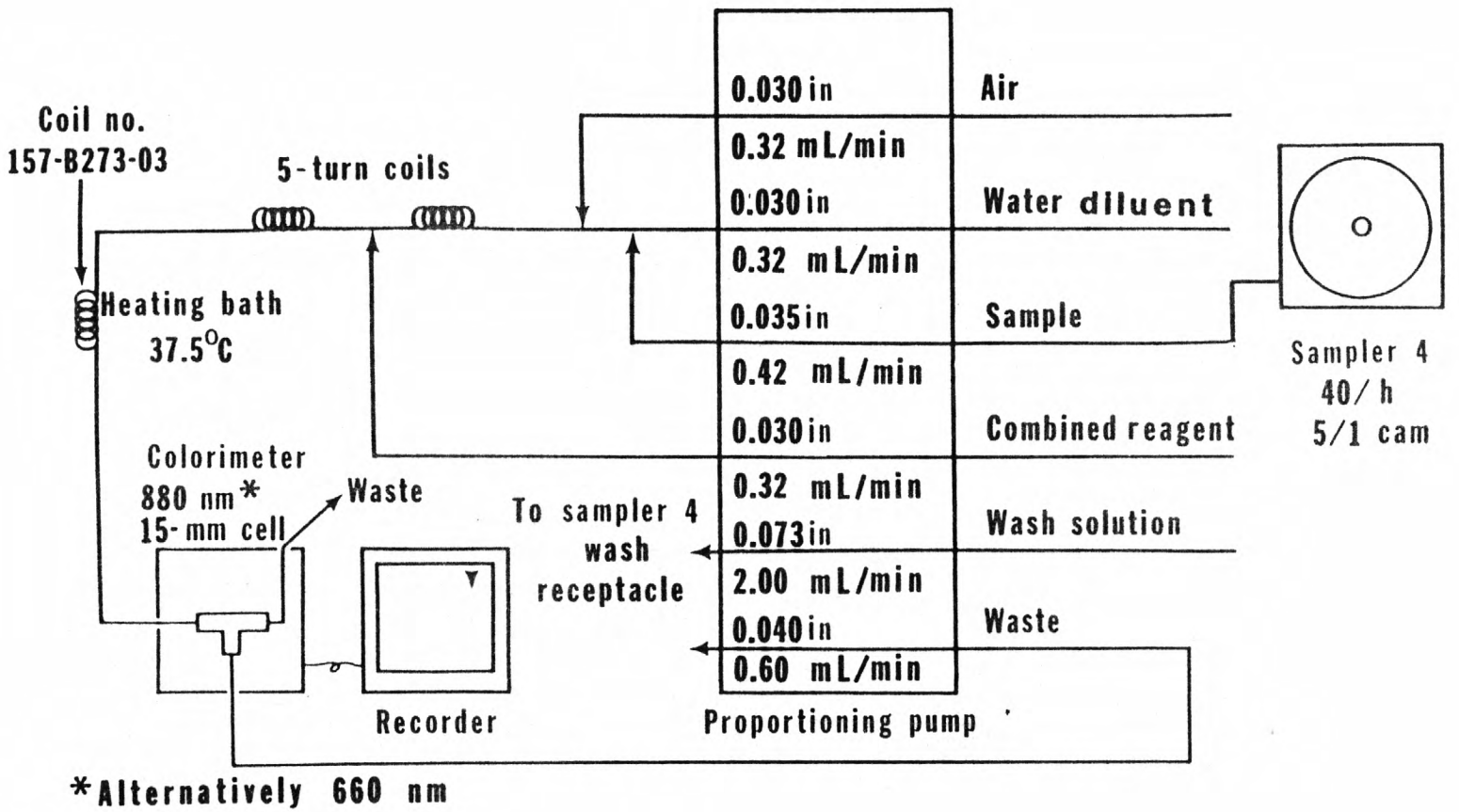

Figure 28.--Phosphorus manifold.

6.8 Place a complete set of standards and a blank in the first positions of the first sample tray beginning with the most concentrated standard. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.9 Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

7. Calculations

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

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

8. Report

Report phosphorus, total (00665), concentrations as follows: Less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation of this method is greater than 12 percent at 0.197 mg/L and greater than 3 percent at 0.67 mg/L.

References

Gales, M. E., Jr., Julian, E. C., and Kroner, R. C., 1966, Method for quantitative determination of total phosphorus in water: American Water Works Association Journal, v. 58, p. 1363.

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chimica Acta, v. 27, p. 31.

pH, electrometric, glass electrode, automated (I-2587-81)

Parameter and Code: pH lab (units): 00403

1. Application

1.1 This method may be used to determine the pH of natural, treated, and wastewaters in the range of 4 to 9, and with specific conductances exceeding 70 umhos/cm.

1.2 This method may be used in conjunction with Method I-2781 to determine pH and specific conductance simultaneously.

2. Summary of method

2.1 For a discussion of the principles of pH-meter operation, see Skougstad and others (1979).

2.2 For additional information on the automated system, see Erdmann and Taylor (1978).

3. Interferences

3.1 The determination is not affected by the presence of color or turbidity or by organic or colloidal material. Oxidizing and reducing substances do not impair the accuracy of the method.

3.2 The pH measurement is temperature dependent, and a significant error results if the temperature of the buffers and samples differs appreciably. However, the use of a thermostatically controlled heating bath and electrode chamber alleviates this problem.

3.3 For samples having abnormally high sodium levels, corrections may be necessary. This correction will differ with electrodes, hence the analyst is referred to the manufacturer's instructions for the necessary computations.

4. Apparatus

4.1 Technicon AutoAnalyzer consisting of a sampler, proportioning pump, potentiometer (ion-selective electrode module, fig. 29), recorder, and printer.

4.2 Flow-through combination pH electrode.

4.3 Sample cups, 16 mm X 75 mm, glass. Glass minimizes pH change caused by the interaction between the sample solution and the sample cup.

4.4 With this equipment a 30/h (6/1) cam and DAMP 1 recorder setting have been found to be satisfactory in the pH range of 4 to 9.

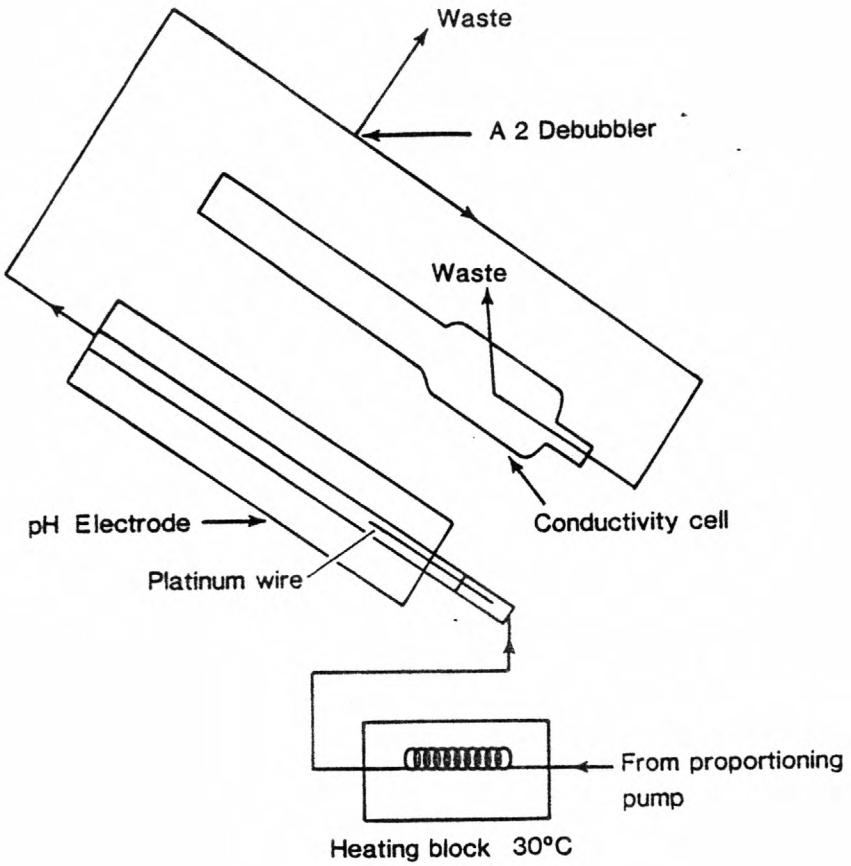

Figure 29.--Compartment arrangement (If specific conductance or pH is not determined, the cell and debubbler or electrode, respectively, may be removed from the system).

5. Reagents

Standard buffer solutions, pH 4.00, 7.00, and 9.00. These buffers should cover the range of pH of the samples to be measured. If samples of pH less than 4.00 or greater than 9.00 are to be analyzed, additional buffers will be required. Ready-made buffer reagents are satisfactory.

6. Procedure

6.1 Set up manifold (fig. 30).

6.2 Allow potentiometer, recorder, and heating bath to warm for at least 30 min or until the temperature of the heating bath stabilizes at 30°C. Demineralized water should be flowing through the sample tube during this warm-up period.

6.3 Electronically calibrate the potentiometer according to the manufacturer's directions.

6.4 Place a series of pH 4 and pH 7 buffer solutions alternatively in the sample tray. Begin the calibration procedure. Use the baseline control to obtain zero scale divisions on the recorder for the pH 4 buffer solution and use the STD CAL control to obtain 60 scale divisions with the pH 7 buffer. Repeat the procedure of alternating the two buffer solutions and adjusting the instrument until the pH for both solutions reads correctly. Record the STD CAL setting. Include a buffer solution of pH 9 after the completion of the above procedure to check on the linearity of the pH response. The reading on this buffer must be within 0.1 units of the buffer value. If not, effect appropriate repairs, check buffers and recalibrate.

6.5 Place standard buffers every twentieth position. Fill the remainder of each sample tray with unknown samples. An unknown sample immediately following a buffer solution should be run in duplicate and the second value read in order to minimize possible electrode memory effects. A distilled water blank may be used in place of a duplicate unknown sample.

6.6 Begin analysis. The recorder tracings will occasionally indicate that the pH value for a poorly buffered sample has not reached equilibrium. This sample must be rerun.

7. Calculations

The pH values may be read directly from the recorder tracing. Any baseline drift that may occur must be taken into account when computing the height of a sample peak.

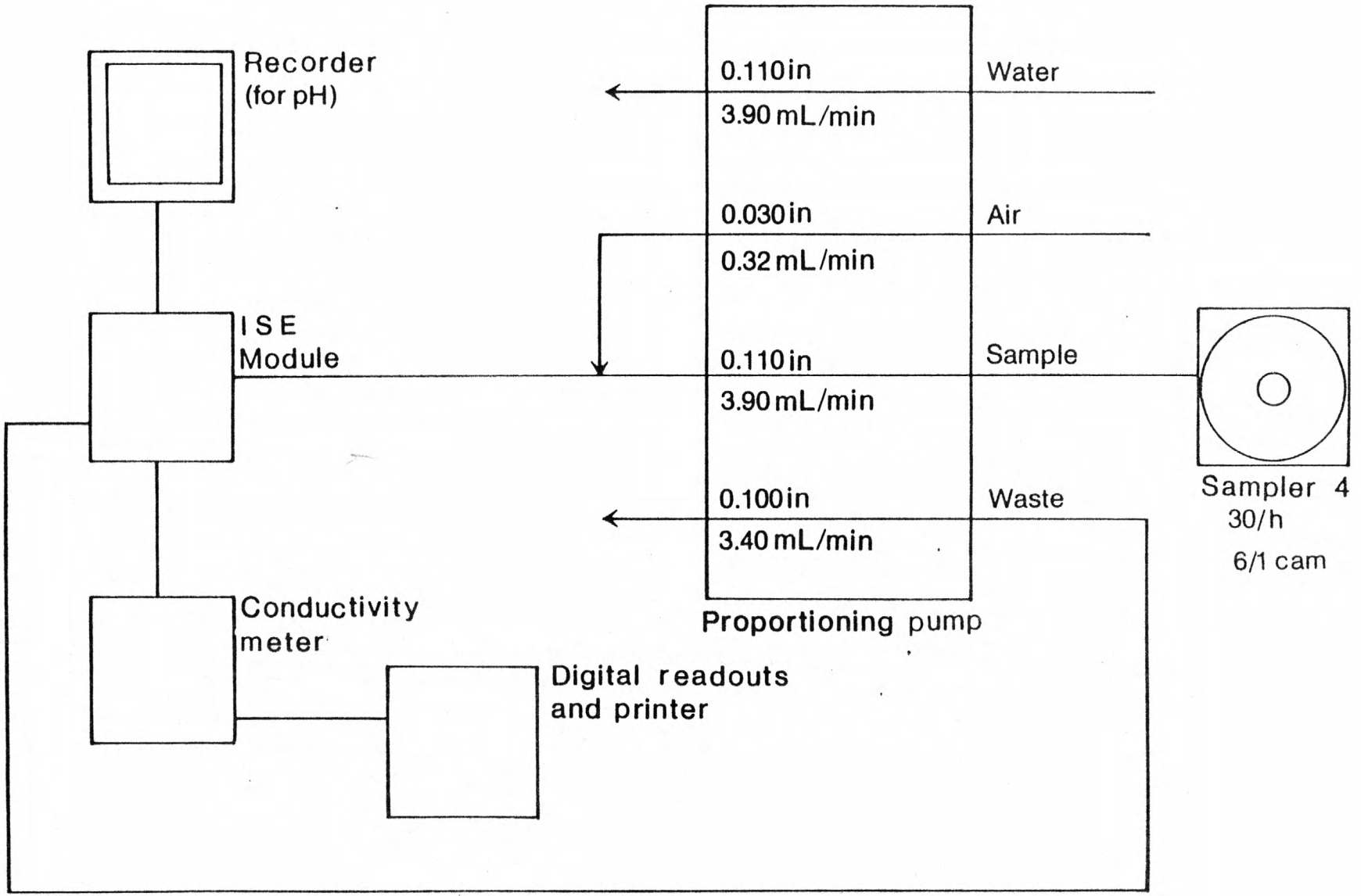

Figure 30.--pH manifold.

8. Report

Report pH values (00400) to the nearest 0.1 pH unit.

9. Precision

Analysis of two test samples by a single laboratory for 25 replicates of each resulted in mean values of 7.58 and 8.07 pH units and standard deviations of 0.05 and 0.03 pH units, respectively.

9.2 The precision may also be expressed in terms of percent relative standard deviation as follows:

Number of replicates	Mean, pH units	Relative standard Deviation, percent
25	7.58	<1
25	8.07	<1

References

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological 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.

Erdmann, D. E., and Taylor, H. E., 1978, An automated procedure for the simultaneous determination of specific conductance and pH in natural water samples: Analytica Chimica Acta, v. 99, p. 269-274.

U. S. Geological Survey, Water Resources Division. 1980. Quality of Water Branch Technical Memorandum 80.19.

Willard, H. H., Merritt, L. L., Jr., and Dean, J. A., 1965, Instrumental methods of analysis 4th ed.: New York, D. Van Nostrand Company.

Specific conductance, electrometric, automated (I-2781-81)

Parameter and Code: Specific Conductance, lab (umho/cm @ 25°C):

1. Application

1.1 This method may be used to determine the specific conductance of natural, treated, and wastwaters in the range of 0 to 17,000 umho/cm. (NOTE 1).

NOTE 1. The range on the conductivity meter lists an upper limit of 15,000 umho/cm: however, this can be extended to 17,000 umho/cm without loss of accuracy.

1.2 This method may be used in conjunction with Method I-2587to determine pH and specific conductance simultaneously.

2. Summary of method

2.1 Specific conductance is a measure of the ability of a solution to carry an electric current which is a function of the concentration and charge of ions in solution and also depends on the mobility of the ions in an electric potential field. Because of its dependence on ion concentrations, specific conductance is an excellent measure of the total ion or dissolved solids concentration.

2.2 The conductivity is measured using a flow-through cell with platinized platinum electrodes and a resistance-measuring instrument patterned after the Wheatstone Bridge.

2.3 Since the conductivity increases about 2 percent per degree Celsius increase in temperature, the temperature of the sample and cell is thermostatically controlled to 30°C. The conductivity value is electronically compensated to specific conductance at 25°C.

2.4 For additional information, see Erdmann and Taylor (1978) and Taylor and Erdmann (1979).

3. Interferences
None

4. Apparatus

4.1 Conductivity cell-flow through cell, platinum electrodes, Radiometer No. CDC314, or equivalent (NOTE 2).

NOTE 2. It is of utmost importance that the conductivity cell remain scrupulously clean. The presence of foreign matter or tiny air bubbles which tend to collect on dirty electrodes will cause erroneous readings. It is recommended that a sample cup containing approx 5% Brij-35 be introduced at the end of each day's run. If further cleaning is needed, chromic acid solution is recommended.

4.2 Conductivity meter - Radiometer No. CDM3 with Manual Temperature Compensator No. CDA100, or equivalent. This meter is electronically modified to automatically switch from the 0 to 1,500 umho/cm range to the 0 to 15,000 umho/cm range if the specific conductance exceeds 1,500 umho/cm.

4.3 Digital readout and printer modules - Digitec or equivalent.

4.3.1 Two Model 2789N Digital Panel Meters and Model 685 Comparator, or equivalent, designed to accommodate the conductivity meter range of 0 to 1,500 and 0 to 15,000 umho/cm with the comparator switching ranges when appropriate.

4.3.2 Model 8130ML Factoring Timer and Model 685 Comparator, or equivalent, designed to activate the printer in conjunction with the sampling rate.

4.3.3 Model 6150 Printer.

4.3.4 Sample cups, 16 mm X 75 mm, glass. Glass is favored when this method is being used in conjunction with method I-2587-81. Plastic may be used when the method is being used alone. In either case, the cups must be scrupulously clean to avoid contamination of the conductivity cell.

4.4 Technicon AutoAnalyzer consisting of a sampler, proportioning pump, and potentiometer (ion-selective electrode module, fig. 31) (NOTE 3).

NOTE 3. The potentiometer is listed because its thermostatically controlled heating bath can be used for both the pH and specific conductance determinations. If pH is not determined, a heating bath and cell chamber which can maintain a sample temperature of $30^{\circ} \pm 0.2^{\circ}C$ can be substituted for the potentiometer.

4.5 With this equipment, a 30/h (6/1) cam has been found to be satisfactory in the 0 to 17,000 umho/cm range.

5. Reagents

5.1 Potassium chloride solution I, 0.00702N: Dissolve 0.5234 g KCl, dried at $180^{\circ}C$ for 1 h, in demineralized water and dilute to 1,000 mL. Specific conductance = 1,000 umho/cm at $25^{\circ}C$.

5.2 Potassium chloride solution II, 0.0200N: Dissolve 1.4911 g KCl, dried at $180^{\circ}C$ for 1 h, in demineralized water and dilute to 1,000 mL. Specific conductance = 2,767 umho/cm at $25^{\circ}C$.

5.3 Potassium chloride solution III, 0.100N: Dissolve 7.4555 g KCl, dried at $180^{\circ}C$ for 1 h, in demineralized water and dilute to 1,000 mL. Specific conductance = 12,900 umhos/cm at $25^{\circ}C$.

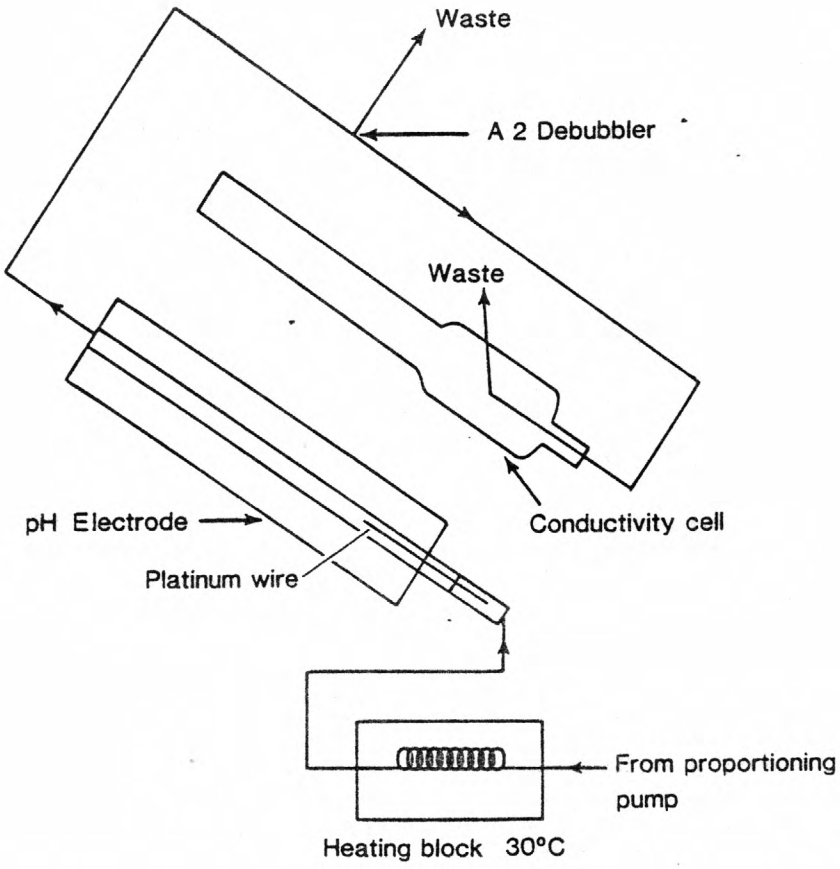

Figure 31.--I.S.E. compartment arrangement (If specific conductance or pH is not determined, the cell and debubbler or electrode, respectively, may be removed from the system).

6. Procedure

6.1 Set up manifold (fig. 32).

6.2 Allow the heating bath, conductivity meter, printer, and digital readouts to warm up for at least 30 min or until the temperature of the heating bath equilibrates at 30 °C. Demineralized water should be flowing through the sample tube during this warm-up period.

6.3 Set the temperature coefficient control on the conductivity meter to 2.0%/°C and the cell constant correction to the value specified on the cell.

6.4 Place two 0.00702N KCl standards in the first two positions of a sample tray. Place a series of 0.1N and 0.02N standards alternatively in the sample tray: 0.1N KCl, demineralized water, 0.02N KCl, 0.1N KCl, and so forth.

6.5 Begin the calibration procedure. Adjust the temperature control on the conductivity meter to give a reading of 1,000 ± 5 on the low-range panel meter when the reading from the 0.00702N KCl standard has peaked (NOTE 4). Adjust the slope control to give a reading of approx 12,900 on the high-range panel meter for the peak from the 0.1N KCl solution. Adjust the offset control to give a reading on the same panel meter of 2,767 ± 5 for the peak from the 0.01N KCl standard.

> NOTE 4. Because of electronic modifications to the conductivity meter, its conductance readings and temperature control setting will not be correct. The temperature control setting, however, should be within ± 5°C of the actual temperature of the heating bath and electrode chamber.

6.6 Repeat the procedure of alternating the 0.1N and 0.01N KCl in the previously specified order and adjusting the slope and offset controls, respectively, until both standards give correct readings (NOTE 5). Record the slope and offset readings.

> NOTE 5. The low range meter must first be calibrated with the 0.00702N KCl solution because adjusting the controls changes the readings on both panel meters whereas the slope and offset controls affect only the high-range.

6.7 Place individual KCl standards in every twentieth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.8 Begin analysis. Certain samples must be rerun if they follow a concentrated sample. The rerun policy is listed below and must be rigorously followed if carryover problems are to be minimized.

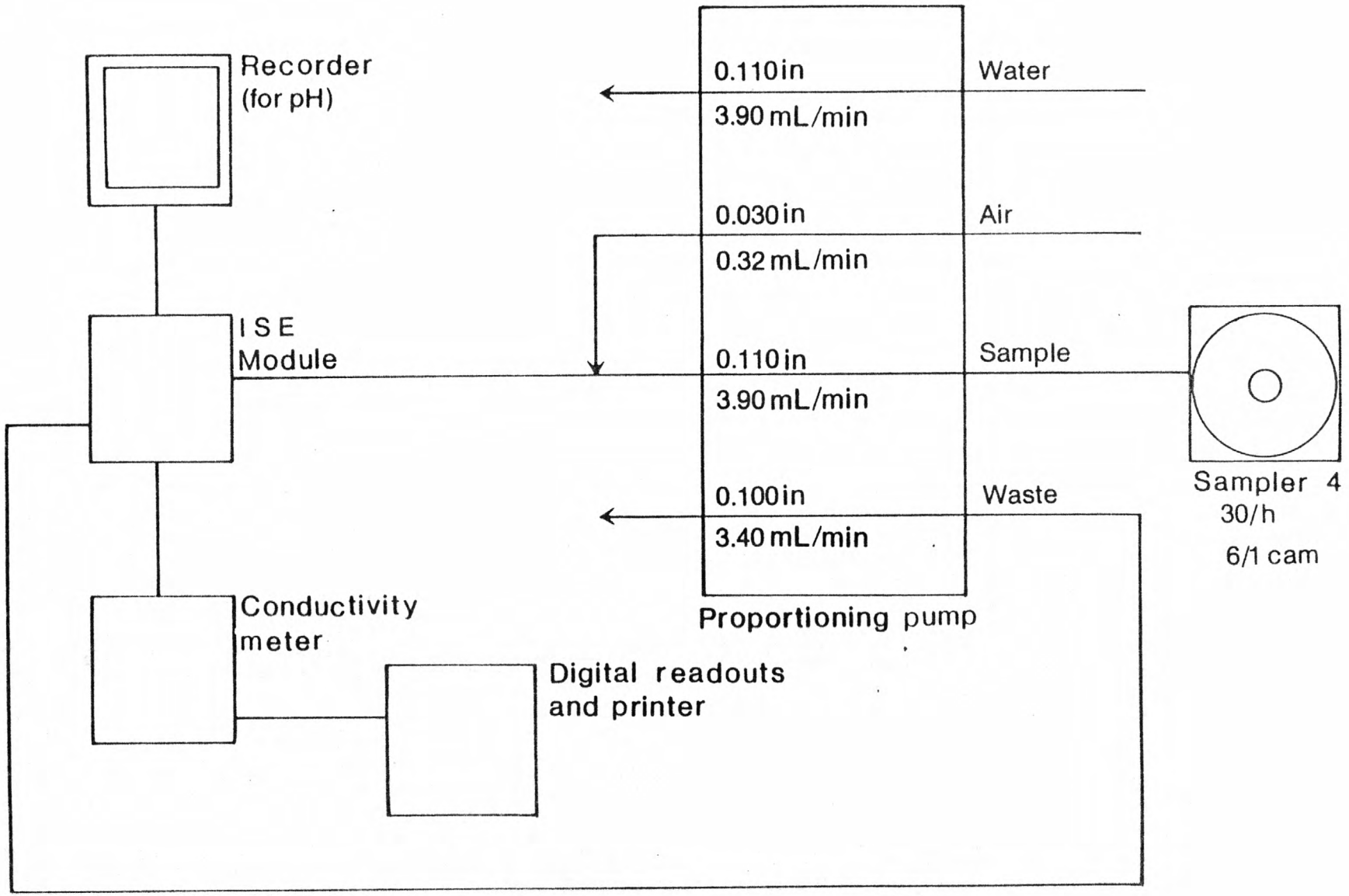

Figure 32.--Specific conductance manifold.

Specific conductance of sample (umho/cm)	Rerun policy on following sample
1. $\leq$7,500	1. No reruns necessary.
2. 7,501 - 10,000	2. Must be rerun if its apparent specific conductance is less than 400.
3. 10,001 - 17,000	3. Must be rerun if its specific conductance is less than 1,500.
4. 17,001 - 50,000 - This sample must be ran manually.	4. Must be rerun.
5. $>$50,000 - This sample must be run manually.	5. Next two samples must be rerun.

7. Calculations

Results are taken directly from printer and no further calculations are necessary.

8. Report

Report specific conductance (micromhos at 25°C) as follows: Less than 1,000 micromhos to whole numbers; greater than 1,000 to three significant figures. The International (SI) unit of conductance is the siemen (symbol S), which is exactly equivalent to the mho. Thus, specific conductance may also be reported as microsiemen per centameter at 25°C.

9. Precision

9.1 Analysis of two test samples by a single laboratory for 25 replicates of each resulted in mean values of 96.9 and 1,664 umho/cm and standard deviations of 0.8 and 11 umho/cm, respectively.

9.2 The precision may also be expressed in terms of percent relative standard deviation as follows:

Number of replicates	Mean, umho/cm	Relative standard deviation percent
25	96.9	$<$1
25	1664	$<$1

References

American Public Health Association and others, 1975, Standard methods for the examination of water and wastewater 14th ed. : New York, American Public Health Association, p. 73.

Daniels, Farrington, and Alberty, R. A., 1966, Physical chemistry 3d ed.: New York, John Wiley & Sons, 671 p.

Erdmann, D. E., and Taylor, H. E., 1978, An automated procedure for the simultaneous determination of specific conductance and pH in natural water samples: Analytica Chimica Acta, v. 99, p. 269-274.

Taylor, H. E., and Erdmann, D. E., 1979, An automated range-switching modification for direct reading specific conductance measurements: Chemical, Biomedical and Environmental Instrumentation, v. 9, p. 49-60.