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

Chapter A1

METHODS FOR DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

By Marvin J. Fishman and Linda C. Friedman, Editors

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LABORATORY ANALYSIS

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PREFACE

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

This chapter was prepared with the assistance of many chemists and hydrologists of the U.S. Geological Survey as a means of documenting and making available the methods used by the U.S. Geological Survey to analyze water, water-sediment mixtures, and sediment samples.

Any use of trade names, commercial products, manufacturers, or distributors is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

This chapter supersedes "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments" by M. W. Skougstad, M. J. Fishman, L. C. Friedman, D. E. Erdmann, and S. S. Duncan (U.S. Geological Survey Techniques of Water-Resources Investigation, book 5, chapter A1, 1979) and "A Supplement to Methods for the Determination of Inorganic Substances in Water and Fluvial Sediments" by M. J. Fishman and W. L. Bradford (U.S. Geological Survey Open-File Report 82-272, 1982).

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TECHNIQUES OF WATER-RESOURCES INVESTIGATIONS OF THE U.S. GEOLOGICAL SURVEY

The U.S. Geological Survey publishes a series of manuals describing procedures for planning and conducting specialized work in water-resources investigations. The manuals published to date are listed below and may be ordered by mail from the U.S. Geological Survey, Books and Open-File Reports Section, Federal Center, Box 25425, Denver, Colorado 80225 (an authorized agent of the Superintendent of Documents, Government Printing Office).

Prepayment is required. Remittance should be sent by check or money order payable to U.S. Geological Survey. Prices are not included in the listing below as they are subject to change. Current prices can be obtained by writing to the USGS address shown above. Prices include cost of domestic surface transportation. For transmittal outside the U.S.A. (except to Canada and Mexico) a surcharge of 25 percent of the net bill should be included to cover surface transportation. When ordering any of these publications, please give the title, book number, chapter number, and "U.S. Geological Survey Techniques of Water-Resources Investigations."

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TWRI 2-F1.	Application of drilling, coring, and sampling techniques to test holes and wells, by Eugene Shuter and W.E. Teasdale.
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TWRI 3-A6.	General procedure for gaging streams, by R.W. Carter and Jacob Davidian. 1968. 13 pages.
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TWRI 3-A11.	Measurement of discharge by moving-boat method, by G.F. Smoot and C.E. Novak. 1969. 22 pages.
TWRI 3-A12.	Fluorometric procedures for dye tracing, by J.F. Wilson, Jr., E.D. Cobb, and F.A. Kilpatrick. 1986. 41 pages.
TWRI 3-A13.	Computation of continuous records of streamflow, by E.J. Kennedy. 1983. 53 pages.
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TWRI 3-A15.	Computation of water-surface profiles in open channels, by Jacob Davidian. 1984. 48 pages.
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METHODS FOR DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

By Marvin J. Fishman and Linda C. Friedman, editors

Abstract

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

A brief discussion of the principles of the analytical techniques involved and their particular application to water and sediment analysis is presented. The analytical methods of these techniques are arranged alphabetically by constituent. For each method, the general topics covered are the application, the principle of the method, the interferences, the apparatus and reagents required, a detailed description of the analytical procedure, reporting results, units and significant figures, and analytical precision data, when available. More than 125 methods are given for the determination of 70 inorganic constituents and physical properties of water, suspended sediment, and bottom material.

Introduction

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

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

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

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

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

Purpose

Rapid changes in technology are constantly providing new and improved methods for the study of water-quality characteristics. Therefore, methods manuals must be updated frequently in order to gain the advantages of improved technology. The purpose of this chapter is to record and disseminate methods used by the U.S. Geological Survey to analyze samples of water, suspended sediment, and bottom material collected in water-quality investigations. This chapter is an update of Techniques of Water-Resources Investigation (TWRI) of the U.S. Geological Survey, book 5, chapter A1, "Methods for determination of inorganic substances in water and fluvial sediments," by Skougstad and others, published in 1979 and of a supplement published by Fishman and Bradford in 1982.

Although excellent and authoritative manuals on water analysis are available (American Public Health Association and others, 1980; American Society for Testing and Materials, 1978, 1984), most of them emphasize primarily either municipal, industrial, or agricultural water utilization. No single reference or combination meets all requirements as a guide to the broader phases of water-quality investigations conducted by the U.S. Geological Survey. These investigations are intended to define the chemical, physical, and biological characteristics of the Nation's surface- and ground-water resources, as well as to indicate the suitability of these resources for various beneficial uses.

Scope

This manual includes techniques and procedures suitable for the analysis of representative samples of water and fluvial sediments. The methods and techniques include:

- Gravimetry
- Titrimetry
- Atomic absorption spectrometry
- Atomic emission spectrometry
- Colorimetry
- Electrometry
- Ion-exchange chromatography
- Sample preparation and pretreatment
- Calculation methods

For each method, the general topics covered are application, principle of the method, interferences, apparatus and reagents required, a detailed description of the analytical procedure, reporting results, units and significant figures, and analytical precision data, when available. Each method, where applicable, applies to the determination of constituents in solution (dissolved), the determination of total or total recoverable constituents (substances both in solution and adsorbed on or a part of suspended sediment), and finally the determination of total or recoverable constituents from samples of bottom material.

This chapter includes methods for determining the following constituents and physical properties:

Dissolved constituents and physical properties

Acidity
Alkalinity

Aluminum
Antimony
Arsenic

Barium
Beryllium
Boron

Bromide
Cadmium

Calcium
Carbon-dioxide
Chloride
Chromium
Chromium(VI)
Cobalt
Copper
Cyanide
Fluoride

Hardness
Hardness, non-carbonate
Iodide

Dissolved constituents and physical properties—Continued

- Iron
- Lead
- Lithium
- Magnesium
- Manganese
- Mercury
- Molybdenum
- Nickel
- Nitrogen, ammonia
- Nitrogen, ammonia plus organic
- Nitrogen, nitrate
- Nitrogen, nitrite
- Nitrogen, nitrite plus nitrate
- pH
- Phosphorus
- Phosphorus, orthophosphate plus hydrolyzable
- Phosphorus, orthophosphate
- Phosphorus, hydrolyzable plus organic
- Potassium
- Selenium
- Silica
- Silver
- Sodium
- Sodium adsorption ratio
- Sodium, percent
- Solids, sum of constituents
- Solids, nonvolatile-on-ignition
- Solids, volatile-on-ignition
- Solids, residue on evaporation at 105°C
- Solids, residue on evaporation, at 180°C
- Specific conductance
- Strontium
- Sulfate
- Thallium
- Tin
- Vanadium
- Zinc

Suspended constituents

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

Total recoverable constituents and physical property

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

Total constituents and physical properties

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

Constituents recoverable from bottom material

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

Total constituents in suspended or bottom material

- Aluminum
- Antimony
- Arsenic
- Boron
- Cadmium
- Calcium
- Chromium
- Cobalt
- Copper
- Cyanide
- Iron
- Lead
- Lithium
- Magnesium
- Manganese
- Nickel
- Nitrogen
- Nitrogen, ammonia
- Nitrogen, ammonia plus organic

Total constituents in Suspended or bottom material—continued

Nitrogen, nitrite plus nitrate
Oxygen demand, chemical
Phosphorus
Potassium
Selenium
Silica
Sodium
Solids, volatile on ignition
Strontium
Titanium
Zinc

Each method is identified by one or more four-digit numbers 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 the identification of each method and the updating of the chapter as new or revised methods are introduced.

Definitions

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

Dissolved.—Pertains to the constituents in a representative water sample that pass through a 0.45-μm membrane filter. The "dissolved" constituents are determined from subsamples of the filtrate. This convenient operational definition is used by Federal agencies that collect water data.

Suspended, recoverable.—Pertains to the constituents in a representative water sample that are retained on a 0.45-μm membrane filter and that are brought into solution by digestion (usually by using a dilute acid solution). Complete dissolution of all the particulate matter is often not achieved by the digestion treatment, and thus the determination may represent 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.

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

Suspended, total.—Pertains to the constituents in a representative water sample that are retained on a 0.45-μm membrane filter. This term is used only when the analytical procedure assures measurement of at least 95 percent of the constituent determined. A knowledge of the expected form of the constituent in the sample, as well as of 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 calculating the difference between the dissolved and the total concentrations of the constituent.

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

Total.—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 in both the dissolved and the suspended phases of the sample. A knowledge of the expected form of the constituent in the sample, as well as of the analytical methodology used, is required to judge when the results should be reported as "total." (Note that the word "total" indicates 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 may represent 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 the 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 constituents in the sample, as well as of the analytical methodology used, is required to judge when the results should be reported as "total in bottom material."

A description of an analytical method must compare the result obtained by the method with the value that is sought, which is usually the true concentration of the chemical substance in the sample. Definitions of terms that are used for this purpose are given below.

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

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

Limit of detection.—The minimum concentration of a substance that can be identified, measured, reported with 99-percent confidence that the analyte concentration is greater than zero, and determined from analysis of a sample in a given matrix containing analyte.

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 U.S. Geological Survey in reporting the results of analysis in milligrams or micrograms per liter represent a compromise between the desire to achieve both precision of measurement and a degree of uniformity in tabulations of analytical data. A common method used to express the precision of a determination is to include all digits known with certainty and the first (and only the first) doubtful digit. This method has one obvious disadvantage: published data so reported may not be interpreted to mean the same thing by all users of the data.

Table 1.—Factors for converting milligrams per liter to milliequivalents per liter
[1975 atomic weights]

Ion	Sum of atomic weights	Conversion factor	Ion	Sum of atomic weights	Conversion factor
Ag^{+1}	107.868	0.00927	I^{-1}	126.9045	0.00788
Al^{+3}	26.9815	.11119	K^{+1}	39.0983	.02558
As^{+3}	74.9216	.04004	Li^{+1}	6.941	.14407
AsO_4^{-3}	138.9192	.02160	Mg^{+2}	24.305	.08229
Ba^{+2}	137.33	.01456	Mn^{+2}	54.9380	.03640
Be^{+2}	9.01218	.22192	Mn^{+4}	54.9380	.07281
BO_3^{-3}	58.8082	.05101	Mo^{+3}	95.94	.03127
Br^{-1}	79.904	.01252	Na^{+1}	22.9898	.04350
Ca^{+2}	40.08	.04990	NH_4^{+1}	18.0383	.05544
Cd^{+2}	112.41	.01779	Ni^{+2}	58.70	.03407
Cl^{-1}	35.453	.02821	NO_2^{-1}	46.0055	.02174
Co^{+2}	58.9332	.03394	NO_3^{-1}	62.0049	.01613
CO_3^{-2}	60.0092	.03333	OH^{-1}	17.0073	.05880
Cr^{+3}	51.996	.05770	Pb^{+2}	207.2	.00965
CrO_4^{-2}	115.9936	.01724	PO_4^{-3}	94.97136	.03159
CN^{-1}	26.0177	.03844	S^{-2}	32.06	.06238
Cu^{+2}	63.546	.03147	SeO_4^{-2}	142.9576	.01399
F^{-1}	18.9984	.05264	Sn^{+2}	118.69	.01685
Fe^{+2}	55.847	.03581	Sn^{+4}	118.69	.03370
Fe^{+3}	55.847	.05372	SO_4^{-2}	96.0576	.02082
H^{+1}	1.0079	.99216	Sr^{+2}	87.62	.02283
Hg^{+2}	200.59	.00997	V^{+2}	50.9415	.03926
HCO_3^{-1}	61.0171	.01639	VO^{+2}	66.9409	.02988
HPO_4^{-2}	95.97926	.02084	VO_3^{-1}	98.9397	.01011
$H_2PO_4^{-1}$	96.98716	.01031	Zn^{+2}	65.38	.03059

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

The factors for the conversion of milligrams per liter to milliequivalents per liter for the more commonly determined constituents are given in table 1.

Milliequivalents per liter as reported by the Geological Survey are numerical expressions of milligrams per liter and for uniformity are carried to three decimal places regardless of the magnitude of the milligrams-per-liter value; the significant figures shown do not reflect the precision of the measurement; the milligrams-per-liter values do reflect that precision.

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Quality control

Accuracy of analysis

Some errors are practically unavoidable in analytical work. Errors are inherent in the methods or instruments employed, or may arise from impurities in reagents and even in distilled or demineralized water. The analyst's skill and general judgment have a direct bearing on the accuracy of the analytical statement. After the chemical analysis of the water sample has been completed, the validity of the results can be evaluated by several methods. No one method of checking gives conclusive proof of the accuracy of the determinations, but the process of checking may reveal some dubious results or some additional constituents of the sample that were not considered in the analysis.

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

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

Basic laboratory and field requirements

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

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

The analysis of an improperly collected sample is meaningless. To minimize errors and variation in data due to sampling, field personnel must maintain records on sampling, including field measurements. Appropriate field measurements and information peculiar to the sample need to be supplied with the sample to the laboratory. Samples must be preserved, if required, and must be shipped without delay in bottles and containers appropriate to the determinations. Time-critical determinations need to be performed within the allowable time either in the laboratory or in the field.

Analyses performed in the field must be carefully monitored. Reference materials must be used, instruments must be calibrated regularly prior to going to the field, and personnel must be thoroughly trained for field analyses.

Chemical ionic balance

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

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

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

or

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

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

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

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

Multivalent ions present difficulties in the ionic balance unless the ionic states are differentiated by the analysis. Orthophosphates may occur in water as PO_4^{-3}, HPO_4^{-2}, and $H_2PO_4^{-1}$; the proportion of each of these ions is related to the pH of the water. The PO_4^{-3} ion occurs only above about pH 10.5. Because natural waters almost never attain this pH, a general assumption can be made that the PO_4^{-3} ion is not present in natural waters. For the purpose of ionic balance, the proportion of HPO_4^{-2} and $H_2PO_4^{-1}$ present can be calculated from the pH relation as shown in table 3 for waters having pH values of 10.0 or less. If HPO_4^{-2} and $H_2PO_4^{-1}$ are included in the ionic balance, the milliequivalents per liter of alkalinity must be corrected because HPO_4^{-2} and $H_2PO_4^{-1}$ will partially titrate as alkalinity. Normally, this correction is not necessary because the concentration of phosphorus in water is seldom high enough to affect the ionic balance.

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

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

Table 3.—Percent orthophosphate mixtures as related to pH

pH	HPO_4^{-2} (percent)	$H_2PO_4^{-1}$ (percent)	pH	HPO_4^{-2} (percent)	$H_2PO_4^{-1}$ (percent)
4.5	0.2	99.8	7.3	55.3	44.7
4.6	.2	99.8	7.4	60.9	39.1
4.7	.3	99.7	7.5	66.0	34.0
4.8	.4	99.6	7.6	71.2	28.8
4.9	.5	99.5	7.7	75.6	24.4
5.0	.6	99.4	7.8	79.7	20.3
5.1	.8	99.2	7.9	83.1	16.9
5.2	1.0	99.0	8.0	86.1	13.9
5.3	1.2	98.8	8.1	88.7	11.3
5.4	1.5	98.5	8.2	90.7	9.3
5.5	1.9	98.1	8.3	92.5	7.5
5.6	2.4	97.6	8.4	93.7	6.3
5.7	3.0	97.0	8.5	95.1	4.9
5.8	3.8	96.2	8.6	96.1	3.9
5.9	4.7	95.3	8.7	96.9	3.1
6.0	5.8	94.2	8.8	97.5	2.5
6.1	7.2	92.8	8.9	98.0	2.0
6.2	8.9	91.1	9.0	98.4	1.6
6.3	11.0	89.0	9.1	98.7	1.3
6.4	13.5	86.5	9.2	99.0	1.0
6.5	16.2	83.8	9.3	99.2	.8
6.6	19.8	80.2	9.4	99.4	.6
6.7	23.6	76.4	9.5	99.5	.5
6.8	28.2	71.8	9.6	99.6	.4
6.9	33.0	67.0	9.7	99.7	.3
7.0	38.3	61.7	9.8	99.7	.3
7.1	43.9	56.1	9.9	99.8	.2
7.2	49.5	50.5	10.0	99.8	.2

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

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

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

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

where

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

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

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

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

Chemical balance is an indication of only the gross validity of the analysis. If only chemical-balance checks are used, very large errors in the determination of minor constituents can go unnoticed and compensating errors can go undetected. Large deviations indicate either a large error in one or more determinations or the presence of some undetermined constituent, but a good balance is not conclusive evidence that each of the determinations is accurate or that all constituents have been determined. Chemical balance is one tool for evaluating the validity and comprehensiveness of an analysis, but it must not be the only goal of the analyst.

Relation of residue on evaporation to calculated dissolved solids

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

Relation of specific conductance to residue on evaporation

For most natural waters of mixed type the specific conductance, in microsiemens per centimeter at 25°C multiplied by a factor of 0.65, approximates the residue on evaporation in milligrams per liter. This equation is not an exact relation because the conductance of a solution is dependent on the type and total quantity of ions in solution. More precise relations can be developed for specific water types.

The specific conductance in microsiemans per centimeter at 25°C divided by 100 approximates the milliequivalents per liter of anions and cations. This relation is particularly helpful for detecting the location of error (in anions or cations), as well as for estimating the comprehensiveness of an analysis.

Precision of analysis

Each analytical procedure in this chapter includes a statement, if data are available, indicating the precision to be expected for that procedure. In general, these statements have been calculated from data obtained through multi-laboratory analyses of test samples prepared by U.S. Geological Survey laboratories. For most procedures, precision data are within the concentration range specified; however, in some, the data do not cover the entire range, and in a few, the data are all below the lower range (for example, the determination of cobalt by direct atomic absorption spectrometry). Reference materials were not available for the latter element. At the other extreme, precision data for several procedures exceed the upper concentration limit and information is not available to determine if the samples were analyzed with or without dilution.

The precision is expressed in terms of the percent relative standard deviation, the ratio of the standard deviation to the mean times 100 percent. A convenient formula to calculate the standard deviation is

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

where

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

If enough data are available and if the precision appears to vary with the concentration of the constituent, the precision is also expressed in terms of a regression equation over a stated range. If the precision does not appear to vary with concentration, it has been calculated by pooling the individual standard deviations over the stated range, and the pooled standard deviation and its 95-percent confidence interval are stated.

The stated precision of the analytical method needs to be considered when interpreting analytical data. For example, a concentration of 15 mg/L for total-recoverable iron and a concentration of 17 mg/L for dissolved iron cannot be considered to be significantly different if the precision of the analysis is ±20 percent; however, these same two values are interpreted as significantly different if the analytical precision is ±5 percent.

Reference material

Reference materials must be used to monitor the analyses. Two forms of reference materials are used for water analyses: ampouled concentrates and prepared natural waters. Each type has certain advantages for quality control.

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

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

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

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

The Central Laboratories

Use and documentation of standard laboratory procedures

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

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

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

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

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

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

In addition, each section chief promptly receives and evaluates information on all reference samples submitted by the management. The largest proportion of reference materials is submitted daily by the laboratory management directly to the laboratory as unknowns. Field personnel submit to the laboratory, daily or week depending on the frequency of an analysis, samples that are totally "blind."

Analytical review procedures

Control charts for each method must be kept by the analyst and periodically reviewed by the section chief. The amount of scatter and the trends in values can then be easily spotted. Control charts on which reference samples near both the upper and lower range of the method are plotted may be particularly useful. See chapter A6 (Friedman and Erdmann, 1982) for more information on the preparation and use of control charts.

In addition to evaluating control-chart and reference-material data, the Central Laboratories quality-control staff reviews the completed analysis report for each sample prior to releasing the information. This review is aided by more than 100 computerized checks that are made prior to printing the analysis report. The computerized checks include computation of the ionic balance and comparison to an allowable-error curve; comparison of dissolved solids to specific conductance and of the dissolved solids-specific conductance ratio to predetermined expected ranges; a check on whether a total constituent concentration is equal to or greater than the corresponding dissolved concentration; and a check on the constituents known to interfere in current methodology above a certain concentration level.

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

Depending on reference-sample results or on other checks and after considering the precision of the method, the reviewer may decide to have a water-quality sample reanalyzed. The reviewer must take into account possible interferences in a method and should consider recommending to the analyst that a different method be used. The resulting concentration of the reanalysis must be examined carefully, possibly with further analyses made on the sample, before the value is accepted. If an error has been made, an updated value is entered into the data file, and a revised analytical report is generated. This report receives another check by the laboratory's quality control staff and is then released to the requestor.

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Laboratory Equipment and Techniques

Glassware and other containers

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

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

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

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

Chemicals and solutions

Purity

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

Water used to dilute samples or to prepare chemical solutions shall first be demineralized by passage through mixed cation-anion exchange resins or by distillation. Its specific conductance at 25 °C must not exceed 1.0 μS/cm, and it shall be stored in resistant glass or polyethylene bottles. If more pure water is required, this requirement is stated in the individual methods.

Carbon dioxide-free water may be prepared by boiling and cooling demineralized water immediately before use. An equally effective means of removing carbon dioxide is bubbling pure nitrogen in the water. Also, some ion-exchange cartridges will remove dissolved carbon dioxide.

The pH of carbon-dioxide free water should be between 6.2 and 7.2.

Ammonia-free water may be prepared by passing distilled water through a mixed-bed ion-exchange resin.

Standard solutions

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

Nonstandard solutions

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

Accuracy of measurement

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

Required accuracy for measurement of volume in the analysis and preparation of reagents is shown similarly. Standard solutions are always prepared in and measured from volumetric glassware. The significant figures given for such measurements are in practical agreement with the tolerance limits for volumetric glassware used; for example, "Add 5.0 mL of reagent" requires the use of a volumetric pipet for the addition, but "add 5 mL" requires the use of a serological pipet; "dilute to 1,000 mL" requires the use of a volumetric flask, but "dilute to 1 L" permits the use of a graduated cylinder.

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

The concentration of some inorganic constituents in a water sample often will exceed the working ranges as recommended in the application section of each method. For example, sodium in brines will exceed the recommended range several fold. Dilution is normally used to bring the concentration of any of these constituents into the appropriate range. This procedure with proper technique is satisfactory for dilutions of 1 to 1,000. The following techniques must be observed: A volumetric pipet (Class A) smaller than 5.0 mL must never be used and all volumetric flasks used must be Class A.

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Analytical Techniques

Gravimetry

Principles

Gravimetric determinations are based on the accurate measurement of the mass of a chemical compound of known composition and purity. The trend in modern analytical laboratories is away from the long, tedious, time-consuming gravimetric methods and toward faster instrumental techniques, particularly techniques that permit simultaneous determination of several constituents. Nevertheless, some determinations can be performed only gravimetrically. These include the determinations of the various forms of dissolved and suspended solids in a water sample.

Analytical balance

An analytical balance is an essential part of every gravimetric method. For many years, the balance commonly used for this purpose is the single-pan, direct-reading type, capable of measuring the mass of an object to within 0.1 mg. In order to maintain this sensitivity, great care must be observed in the use and maintenance of the balance. The balance must be located apart from the chemical laboratory, in a room free of laboratory fumes and strong drafts. The balance must be placed on a vibration-free stand, table, or shelf. Cleanliness is exceedingly important, and any material spilled in the balance case must be cleaned up immediately. Objects to be weighed must not be handled with the bare hands, but only with ivory-tipped forceps or platinum-tipped tongs.

Cleaning the balance thoroughly periodically and, at each time, checking its calibration is advisable. Weights conforming to Class S tolerances are satisfactory for routine water-analysis applications.

No chemicals are ever placed directly on the balance pan for weighing. At the very least a tared weighing paper or aluminum pan is used. Most commonly the material to be weighed is contained in a porcelain or platinum crucible or dish, or in a glass weighing bottle.

Increasingly, electronic analytical balances are used. Because they immediately read the weight to 0.1 mg (or even to 0.01 mg), they are rapid and extremely accurate. Because most weights are determined by differences, electronic balances are easy to use and accurate for determining solids as well as weighing of primary standards. However, these balances require calibration more frequently than do non-electronic types. The following procedure is recommended:

1. Allow balance to warm at least 10 min.
2. Locate the calibration control on your balance and zero the balance.
3. Place weights on the pan to the total capacity of balance. If the balance does not read the same as the weight on the pan, turn the calibration control until it does.
4. Remove the weights from pan and again zero the balance.
5. Repeat steps 1–4 until the balance gives the proper reading. Dual-range balances need to be calibrated separately and will have separate controls.

Balances are more and more being used in conjunction with computers or their own microprocessors for routine determinations. In these cases, weights are printed out and calculations made so analytical data are transmitted directly to a data base with no manual data handling needed.

Accuracy

Gravimetric determinations can be among the most accurate of all quantitative determinations; they are time consuming, however. In quantitative gravimetric measurements of the solids content of water samples, the uncertainties about the composition of the material being weighed usually exceed the uncertainty involved in determining its mass.

Titrimetry

Principles

Titrimetric analytical determinations are based on the reaction of an accurately measurable volume of a solution of known concentration with an exact equivalent amount of the substance being determined. The process of adding reagent solution to react with the sample is known as titration, and the reactant added during the course of the titration is known as a standard solution. Titrimetric determinations are inherently simpler than gravimetric determinations, and hence are usually preferred where simplicity, ease, and speed of analysis are important. Their sensitivity and accuracy can approach those of careful gravimetric measurements.

To be suitable as a basis for a titrimetric determination, the chemical reaction involved must proceed rapidly to completion with no side reactions. The reaction between a strong acid and a strong base is a good example of an ideal reaction for a titrimetric determination. The titration of the anion of a weak acid with a strong acid does not involve an ideal reaction, but the reaction does proceed to an identifiable point of completion. Such a reaction is used to determine the alkalinity of water samples, wherein the carbonate and bicarbonate anions are titrated with standard acid until poorly dissociated carbonic acid is formed.

In addition to a straightforward chemical reaction, an abrupt change of some property of the solution must occur at the equivalence point of the titration. This may be a change in hydrogen-ion concentration, a sharp increase in the concentration of one of the titrant ions, a change in the electromotive potential, or even a change in the electrical conductivity of the solution. This abrupt change may sometimes be made apparent by adding to the system a color-change indicator solution that changes color abruptly when the reaction is complete at the equivalence point. When the equivalence point is accompanied by a rapid change of pH, an indication of its occurrence may be monitored with a glass electrode. Such titrations are called electrometric titrations.

Standard solutions

The standard solution used in titrimetry must be simple to prepare and preferably stable for a comparatively long time to avoid the need for frequent restandardization. Quite commonly, the standard solution is not prepared directly, but is prepared at a concentration very close to that desired and then standardized by titrating an accurately measured amount of a primary standard. The primary standard must be of high purity, or at least of accurately known purity, must be stable, and easily dried and weighed. An example of a good primary standard substance is the sodium carbonate used to standardize the strong acid used in neutralization titrations. Many other primary standards are useful for various purposes; these standards are available, on specification, from chemical supply companies. The National Bureau of Standards supplies certified primary standard substances for the common titrimetric applications.

Factor-weight computations

The concentration of the titrant may be adjusted so that when a sample of given size is taken for analysis, the volume of titrant in milliliters is in simple proportion to the concentration of the sought constituent, for example, in milligrams per liter. Some time is involved in initial adjustment of the titrant concentration, but time is saved in the long run when many analyses are performed. Simplifying computations in this manner also minimizes arithmetic error in handling the data.

Automated titrations

Systems are available that automate the entire process of a titrimetric determination including the initial measurement of a sample aliquot into a titration vessel. Titrations involving colorimetric as well as electrometric detection of the equivalence point may be automated.

The samples are placed in a revolving tray or moving platform and are sequentially moved into position for titration. As each titrant is completed, a printer records the sample number and the exact volume of titrant added. Such automatic titrators speed the analytical process by freeing the analyst for other duties while the titrations are being carried out. They also have the advantage of duplicating equivalence-point conditions for all samples, avoiding individual judgment on the part of the analyst. Such automated equipment is particularly desirable when a great many routine samples are to be analyzed.

The trend in titrimetric titrations is also toward microprocessors, which automatically calculate and transmit the concentration of desired constituents. Understanding the chemistry behind these reactions is increasingly important to properly program these sophisticated data-handling systems—now used in conjunction with both colorimetric and electrometric detection of equivalence point.

Atomic absorption spectrometry

Basic principles

When a beam of radiant energy is passed through a cloud of atomic vapor, certain very specific wavelengths characteristic of the element(s) in the vapor are absorbed. This principle forms the basis of a very sensitive and highly selective method of analysis for most metallic elements (Walsh, 1955).

Each element absorbs energy at a series of wavelengths that constitutes the unique atomic spectrum of that element. Selectivity is achieved by careful choice of the wavelength of radiant energy passed through the sample. Because atomic absorption occurs in extremely narrow (approximately 0.002 nm) intervals of the electromagnetic spectrum (Robinson, 1975), a wavelength can usually be selected that is absorbed by only one constituent of a sample.

Under ideal conditions, the extent of absorption at a specific wavelength is related to the concentration, c, of a given element in the vapor and to the length, b, of the path that the beam traverses through the vapor, according to Beer's Law:

$$A = a\ b\ c \qquad (1)$$

In this equation, a is a constant of proportionality and A, the absorbance, is defined as:

$$A = \log P_o/P \qquad (2)$$

where P_o is the radiant power of the unabsorbed beam (measured in the absence of atomic vapor) and P is the radiant power of the beam after it has passed through the atomic vapor.

Instrumental principles

Instrumentation for atomic absorption spectrometry consists of the following components, listed in the order of their function in the instrument:

(1) Source of radiant energy
(2) Sample chamber
(3) Wavelength selector
(4) Detector of radiant energy
(5) Readout device (information processor)

A brief operational description of each component follows.

Radiant energy source

The source of radiant energy must produce intense radiation at the exact wavelength absorbed by element to be determined. If Beer's law is applied, the width of the emission lines in the spectrum of the source must to be narrower than the absorption lines of the element in the sample. This is achieved by exciting radiation from low-pressure vapor of the element. Two types of lamps are commonly used to produce atomic radiation: the hollow cathode lamp (HCL) and the electrodeless discharge lamp (EDL).

The HCL consists of a glass or quartz tube containing a small metallic cup that is lined with (or made of) the element to be determined. This cup is given a negative electrical charge so that positively-charged ions of a low-pressure fill-gas, such as argon, are accelerated toward it, releasing metal atoms when they strike the cup. These atoms are struck by other fill-gas ions, imparting energy that raises them to excited atomic states. Characteristic atomic spectra are emitted by these excited atoms when they return to the ground (normal) electronic state.

In an EDL, a small amount of the element to be determined is sealed under vacuum in a small quartz bulb, which is surrounded by a coil. When a radio-frequency alternating current is passed through this coil, its energy is imparted to the metal vapor, causing it to emit the characteristic atomic spectrum of the metal.

Either type of lamp is capable of producing the spectrum of only one element (a few mixed-element lamps are made that can produce spectra of 2 to 5 elements, but these are usually less desirable due to lower intensity). HCL's tend to be less intense than EDL's and have relatively limited lifetimes, even if infrequently used. EDL's are generally preferred for those elements for which they are available.

The radiant-energy beam from the source lamp is usually modulated, either by "chopping" the beam with a rotating mechanical shutter or by modulating the power supplied to the lamp. This modulation enables the detector to distinguish the source beam from unmodulated radiation produced in the flame or furnace.

Sample chamber

Atomic vapors may be produced by aspirating metal salt solutions into flames, by vaporizing solutions in electrically-heated graphite tubes, or by chemically producing volatile metal hydrides that are decomposed to atoms in quartz tube-furnaces. Only one commonly determined element, mercury, is volatile enough to produce measurable atomic vapor at room temperature. These methods are designated "flame," "electrothermal," "hydride-generation," and "cold-vapor" atomic absorption spectrometry, respectively. The principal factors to be considered in selecting among these methods are the speed and ease of analysis, the detection limit required, and the quantity of sample available.

For flame atomic absorption, the sample is converted to an aerosol in a nebulizer and mixed with fuel and oxidant gases. This mixture is burned in a long, narrow burner that provides a long path-length for the radiant energy beam. Because the sample is greatly diluted by fuel and oxidant gases, detection limits by flame atomic absorption are generally limited to 10–100 micrograms of metal per liter of solution. Because the sample quickly passes through the flame and is lost, aspiration is continuous during the analysis time. Therefore a relatively large volume (several milliliters) of sample is required. Operational ease and relatively fewer interferences make flame atomic absorption the fastest and simplest of the methods.

In electrothermal atomic absorption, a few microliters of sample are deposited into a small graphite tube at room temperature. The tube is then electrically heated through a pre-programmed cycle of four distinct steps:

1. Evaporation of solvent (approx 120 °C)
2. Charring of volatile (organic) matter (several hundred degrees)
3. Atomization of the metal at high temperature and determination (800–2500 °C)
4. Cleanout at very high temperature (3000 °C)

This process has until recently been subject to so many interferences that the method of standard additions has almost universally been required. Recently, basic studies of the nature and origin of these interferences have lead to some revised techniques, that help to optimize the rate of vaporization and, thus, have reduced interferences significantly. Among these new techniques are vaporization of the sample on a small graphite platform (L'vov platform) mounted inside the furnace and addition of chemical matrix modifiers.

Elements such as arsenic, selenium, antimony, and tin are usually converted to gaseous metal hydrides, that are introduced into small quartz tube furnaces where the hydrides decompose to produce atomic vapor. Mercury is reduced to the elemental state and swept by a stream of inert gas into a cool quartz tube in the sample chamber.

Wavelength selector

After the radiant energy beam has passed through the sample, a monochromator is used to select only one of the characteristic lines of the element being determined. Monochromators use diffraction gratings to spread the beam into a spectrum and from this spectrum an exit slit selects one wavelength for analysis. That wavelength may be in the visible (400–700 nm) or ultraviolet (200–400 nm) region of the spectrum.

For most elements, a principal wavelength and possibly one or more alternate wavelengths are specified in approved methods. The selected principal wavelength is very intense in the source-lamp spectrum, strongly absorbed by the atomic vapor, and free from interferences by other elements commonly found in water samples. Alternate wavelengths chosen for lower sensitivity may be used for more concentrated samples, *if specified in the approved method.*

Instrument performance is affected by slit width. A slit too narrow may degrade a detection limit because too little energy passes to the detector, and a slit too wide may result in noisy signals or in erronous readings due to excessive background radiation or excessive curvature in the calibration.

Detector

The detector is usually a light-sensitive vacuum tube called a photomultiplier. When a bias voltage of several hundred volts is applied to a photomultiplier, it generates an electrical current proportional to the power of radiant energy incident upon it. These devices are very delicate and should never be exposed to strong room lights, especially when the bias voltage is on. Such an exposure will produce "noisy" readings for several days thereafter or may permanently damage the detector.

Information processing

Electronic circuitry, often including microprocessors, is employed to convert the P_o and P values registered by the photomultiplier into human- or machine-readable indications of absorbance, or (by comparison to standard solutions of known concentration) into actual concentration readings. In older instruments, these readings were registered on chart recorders or on panel meters. Modern instruments provide digital readout, either on a display panel or on a printer, and may be able to transmit readings to computers.

Readings for flame atomic absorption are usually steady signals, which are averaged over a period of 0.5 to 5 seconds as appropriate to the noisiness of the signal. In contrast, electrothermal atomic absorption signals are transient, rising to a peak and decaying back to zero in only a few seconds. Such signals are measured by either the height of the peak, or by integrating the area under the peak. The choice will depend on the relative precision and accuracy obtained by the two methods, which are governed by such factors as the sharpness of the peak and the shape, position, and intensity of the background absorption signal.

Analytical procedures

Direct

The sample may be analyzed by direct introduction into the flame or furnace, if the concentration of the element to be determined is great enough, and the interference effects are small enough. Concentration is calculated by comparison of the sample's absorbance to the absorbances of a series of standard solutions. This is performed either manually by constructing an analytical curve, or electronically by "curve fitting" in a microprocessor-controlled instrument. Although Beer's Law predicts a straight-line relation between absorbance and concentration, some curvature is often found, and is tolerable up to a point.

Chelation-extraction

It is possible to react many metal ions with an organic chelating reagent, such as ammonium pyrrolidine dithiocarbamate (APDC) or 8-hydroxyquinoline and then extract the resulting chelate into a water-immiscible solvent such as methyl isobutyl ketone (MIBK), where the concentration of the metal to be determined is too low for direct measurement, or where serious interferences are present. If, as is typically the case, 100 mL of a water sample is extracted with 10 mL of MIBK, the concentration of metal ions in MIBK is approximately 10-fold greater than in the original sample. In addition, detection limits are generally improved in organic solvents, so the actual improvement in detection may be actually much greater than 10-fold.

Chelation-extraction can also be used to eliminate interfering substances which are not extracted under the conditions chosen. On the other hand, some substances in the sample may interfere with the chelation reaction by reacting preferentially with the chelating agent.

APDC is used in several of the chelation-extraction procedures in this chapter. Although it may be obtained commercially, a somewhat superior product may be prepared in the laboratory. The preparation is simple, rapid, and requires little equipment.

CAUTION: The reagents and reactions are potentially hazardous. Safety gloves and safety glasses must be worn, and a well-ventilated hood must be used in all steps of the procedure. Reactions that occur release heat and must be performed in an ice bath with constant stirring.

Apparatus

Condenser, reflux, with ground glass joint 24/40.
Flask, Erlenmeyer, 1000-mL capacity with ground glass joint 24/40.
Funnel, Buchner, 16-cm diameter.
Funnel, separatory, 250 mL.
Magnetic stirrer.

Reagents

Ammonium hydroxide, 8 N: In a well-ventilated hood, dilute 133 mL conc NH_4OH (sp gr 0.90) to 250 mL with demineralized water and mix.
Carbon disulfide, reagent-grade: CAUTION: **Vapor is very toxic and can be sorbed through skin. Flammable.**
Ethanol, 95-percent: Denatured ethanol may be used.
Pyrrolidine, practical: CAUTION: **Vapors are very toxic and liquid causes burns. Highly flammable.**

Procedure

1. Dissolve 135 mL pyrrolidine, with continuous mixing, in 300 mL ethanol in a 1000-mL Erlenmeyer flask.
2. Attach the reflux condenser to the flask and place in an ice bath. Cool for 30 min. Stir solution continuously, with a magnetic stirring device.
3. Place 90 mL CS_2 in a 250-mL separatory funnel and slowly add the CS_2 dropwise (2 to 3 drops per second) through the condenser. Addition of the CS_2 produces a strong warming effect; therefore, cool the flask with ice at all times and stir continuously. After the CS_2 has been added, cool the mixture for an additional 15 min.
4. Add 225 mL 8 N NH_4OH. APDC crystals will form rapidly. Chill the mixture for at least 1 h. For maximum yield, place the flask in a freezer for several hours.
5. Assemble a Buchner funnel, fitted with a Whatman No. 41 paper, and vacuum-filtering flask. Rinse the funnel with several milliliters of chilled ethanol.
6. Dislodge the APDC crystals from the walls of the flask with a glass rod. Decant the solution and APDC crystals into the funnel, and apply vacuum.
7. Rinse the flask with a small portion of chilled ethanol and pour over the APDC in the funnel. Repeat this procedure until the filtrate appears clear. Rinse the APDC twice more with chilled ethanol.
8. Dry the APDC by continuing the vacuum for about 1 h.
9. Remove the APDC from the funnel, place in an amber bottle, and store in a refrigerator. The yield is approx 180 g, about 75 percent of theoretical.

Standard additions

The method of standard additions is a frequently used analytical technique when certain

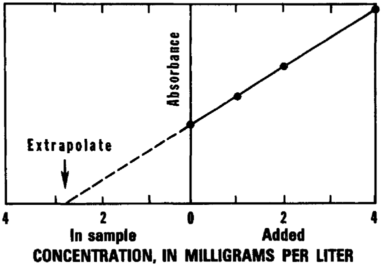

Figure 1.—Example of standard-addition method

types of interferences are present, or are suspected because of unfamiliarity with the nature of the sample or the method of analysis. It is carried out by adding equal volumes of a blank and three different known standard solutions of the metal to be determined to four aliquots of the sample. The absorbance of each of these solutions is plotted on the vertical axis of a graph whose horizontal axis is concentration of metal added (to the right) and concentration of the unknown (to the left). An example is plotted in figure 1. The concentration of the unknown solution is determined by extrapolating the line through the experimental points to the horizontal axis. This is clearly too time-consuming a procedure for high-volume routine analysis, because four measurements are required to produce a single analysis.

Matrix effects, ionization interferences and chemical interferences may be detected and/or overcome by the method of standard additions, but *two very important limitations must be noted carefully*:

(1) The method of standard additions is *not* effective insurance against errors due to background absorption or spectral lines interference;

(2) A linear calibration curve throughout the entire concentration range utilized is *absolutely required.*

Methods for detecting and removing background effects and spectral line interferences are discussed in a later section. Nonlinearity can be checked by analyzing the sample under several successive dilutions from full concentration down to the detection limit of the method.

Interferences

Numerous types of effects can destroy the ideally simple relationship between absorbance and concentration. It is important that the analyst understand the basic nature and cause of each of these effects, so that potential sources of error can be anticipated and avoided.

Ionization effects

A significant fraction of the atoms may be ionized if excessive heat is applied to a vaporized sample. Because ions do not absorb at the same wavelength as neutral atoms, ionization will cause a decrease in the intensity of the absorption signal. No systematic analytical error will result, as long as this decrease occurs equally in the calibration standards and in the sample. If, however, a particular sample contains a large amount of some easily-ionized element, an excess of electrons will be produced. These excess electrons will repress the ionization equilibrium of the analyte metal, leading to an enhancement of the absorption signal in that particular sample. A common example is the enhancement of the potassium signal in samples that contain high concentrations of sodium. Elements on the left side of the periodic table (notably alkali and alkaline earth metals) tend to be the most easily ionized, and are most subject to ionization effects.

Ionization interferences are controlled in one of two ways; first, by keeping flame or furnace temperatures as low as possible when measuring easily-ionized elements, or secondly, by adding a large excess of an easily-ionized substance (such as cesium) to both standards and the samples, so that the ionization equilibrium is entirely driven toward the neutral atom in all samples and standards.

Chemical effects

Some metals tend to form thermally-stable compounds when heated in flames or furnaces. These compounds prevent the formation of atoms in the sample chamber of the spectrometer, and thus lead to erroneously low absorbance readings. The reduction of the absorbance of calcium when phosphate or silica is present at high concentration is a classic example of a chemical interference because calcium phosphate and calcium silicate are dissociated only at very high temperatures. A "releasing agent" (something that reacts with these anions more strongly than does calcium) will liberate calcium by tying up the interfering anions. Strontium and lanthanum are commonly used releasing agents for calcium and magnesium. Alternatively, a hotter flame may be able to thermally dissociate the stable compound.

Another example of chemical interference is the formation of refractory (i.e., heat-stable) oxides and carbides by certain heavy metals. In this case, the use of hotter flames will at least partially dissociate these compounds. Table 4 shows the temperatures attained in commonly used analytical flames. The nitrous oxide-acetylene flame is frequently used to dissociate thermally stable compounds such as calcium phosphate and refractory oxides. Oxide-forming metals may benefit from the use of fuel-rich flames, so as to decrease the availability of oxygen atoms. Carbide-forming elements, on the other hand, may best be determined in nonhydrocarbon flames such as air-hydrogen, or in the presence of excess aluminum as a releasing agent (Price, 1979).

Table 4.—Temperatures of premixed flames

Oxidant	Fuel	Temperature (degrees Celsius)
Air	Natural gas	1700-1900
Air	Hydrogen	2000-2050
Air	Acetylene	2175-2400
Nitrous oxide	Acetylene	2600-2800

Matrix effects

Although both of the interferences previously discussed might be called "matrix effects", this term is usually reserved for the simple physical effect of viscosity and surface tension on the efficiency of the nebulization process in flame atomic absorption. Typical of these effects is the general decrease in absorbance signals which occurs with increasing acidity of the sample. Acid affects the viscosity and surface tension of the sample, and therefore the rate at which the sample is nebulized into the flame. The best way to combat such interferences is to calibrate using standards that have the same acidity as the samples to be analyzed. Unequal amounts of dissolved solids in samples and standards also may cause errors in the analysis due to different nebulization of such solutions by the atomizer. Again, this may usually be controlled by matching the density or viscosity of samples and standards, or by adding a noninterfering salt to the standards. Where matrix effects are severe or the matrix is completely unknown, the method of standard additions is highly recommended.

Spectral-line effects

Spectral-line interference occurs when there is overlap between the spectral line of the element sought and that of another element in the sample. Because wavelengths for analysis are selected to avoid overlapping lines, this problem seldom arises. However, when a nonanalyte element is present at very high concentration, its lines are broadened and may overlap the line of the sought-for element. The analyst needs to be alert to the possibility of errors due to interference of this type in samples of unusual or unknown composition. One means of detecting spectral-line interference is to perform the determination at two different wavelengths. Spectral-line interference is suspected when determinations at two wavelengths yield different concentration values.

Background absorption

Background absorption is a collective term used to describe the combined effects of flame absorption, molecular absorption, and "light scattering" by particles in the light path. Each of these effects results in a broad, flat absorption band which is superimposed on the atomic line absorption, resulting in erroneously high absorbance readings. Background absorption is particularly severe in the graphite furnace. This effect is eliminated by use of a background correction device which automatically subtracts the "off-peak" absorbance, or background, from the "on-peak" absorbance.

The most common type of background corrector is the deuterium-arc (a continuum, or broad-spectrum source). Light from this continuum source is passed through the flame or furnace simultaneously with the hollow cathode or electrodeless discharge lamp (sharp-line source). Because the lines in atomic spectra are so narrow, the absorbance measured by the continuum source is caused almost entirely by background, whereas the sharp-line source measures both atomic and background absorption. The atomic absorption is computed by subtraction of the background from the atomic-source absorbance.

A more recent development in background correction is the Zeeman Effect background corrector. When a body of atomic vapor is subjected to a strong magnetic field, a typical atomic absorption line is split into three components, one at the original wavelength and one on either side of it. These absorption lines are polarized, with the center one having opposite polarization from the two lines to the sides. Thus, under one condition of polarization of the source beam, the atomic vapor does not absorb and only background absorption is measured at the center-line wavelength; whereas, under opposite polarization both the atomic vapor and the background absorption are measured. Some loss of sensitivity is usually experienced, with a corresponding degradation of the detection limit. Also, some atomic lines give atypical splittings which do not lead to useable results. However, in most cases Zeeman spectrometers are capable of handling extremely high backgrounds due to very "dirty" matrices. Although available for flame atomic absorption, the Zeeman Effect is primarily applied to electrothermal atomic absorption.

Automation techniques

Autosamplers for both flame and electrothermal atomic absorption spectrometers are commercially available. These devices are microprocessor controlled and, when used in conjunction with a printer, permit unattended operation for 40 to 60 samples. A few more advanced autosamplers have the capability to perform standard additions and (for furnaces) to introduce matrix modifiers with each sample.

Hydride generation may be automated using continuous-flow systems to add reagents in sequence and to provide the required heating and reaction-time delays. The volatile metal hydrides so generated are separated from the sample solution in a packed separator column, and are then swept into an electrically-heated quartz tube furnace by a stream of inert gas. The cold-vapor method for mercury may be similarly automated.

A significant recent advance in automation of atomic absorption is flow injection analysis (Betteridge, 1978; Wolf and Stewart, 1979). Under microcomputer control, a few microliters of sample are injected by means of a loop sampling valve into a pumped stream of a carrier liquid which flows continuously into the nebulizer of a flame atomic absorption spectrometer. The "plug" of sample disperses in the carrier stream, producing a transient signal reminiscent of that observed in a graphite furnace analysis or chromatography. The area under this peak is integrated and compared to standards for quantitation. Principal advantages of this method are (1) speed (as many as 400 determinations per hour) and (2) increased precision due to the excellent control of the aspiration process afforded by precision pumping of the sample stream.

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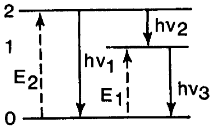
Atomic emission spectrometry

Principles

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:

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



$$E_2 = h\nu_1$$

$$E_2 = h\nu_2 + h\nu_3$$

$$E_1 = h\nu_3$$

Figure 2.—Energy level diagram

The energy of each of the emitted photons, $h\nu$, equals the difference between the energies in the higher and lower energy levels (fig. 2). 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. 2) the population of atoms in the excitation source can be excited to either energy level one or two. Emission can occur by transition 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 occurs in a similar way, but because 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 phenomenon to be used in quantitative chemical analyses, the following are necessary: (1) the sample must be atomized (constituents of interest converted to atoms or ions in the gas phase) and the resulting atoms or ions excited; (2) the resulting characteristic emission lines must be spectrally separated and their relative intensities measured by a suitable dispersion-detection system (spectrometer or spectrograph); and (3) the resulting intensities must be compared with standards of known elemental composition. Solid samples are usually analyzed by arc or spark exitation sources that 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 of the fraction if 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: an increasing concentration of atoms or ions in the exitation source results from increasing temperatures. Although the analytical sensitivity might seem to increase and the detection limit decrease almost without limit by increasing the temperature of the excitation sources at higher temperatures, several other phenomena occur that 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 importantly, 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, multi-elemental analysis. The principal limitation is that atomization-excitation conditions can simultaneously be optimized to a degree satisfactory for quantitative analysis for only a limited number of constituents. This limitation results 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 those in higher temperature sources. With high-temperature sources, the population of excited atoms is large, but high background and complex spectra are produced that can adequately be resolved only by a high-resolution spectrometric system. The other serious limitation is compound formation in the atomization-exitation source, an effect that 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 and inexpensive to operate, and the temperatures developed in the flames are adequate to excite 10 to 20 metals, enabling analyses in water at the milligram-per-liter concentration range or less. The temperatures of the most commonly used flames range from the 2,000 to 3,000 K; this range results in good analytical sensitivity for elements that have relatively low excitation energies and that are atomized to an appreciable extent in the flame, that is, those having no strong tendency toward compound formation.

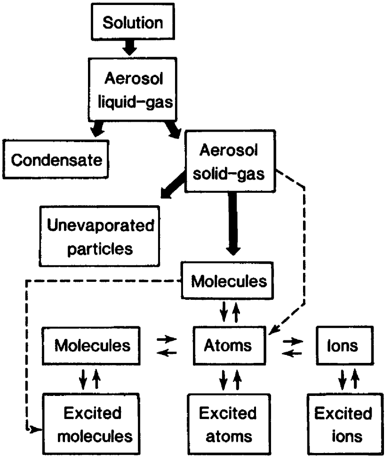


Figure 3.—Schematic of the nebulization, desolvation, atomization, and excitation processes

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 3. Many nebulizer and burner designs have been developed. These are extensively reviewed by Mavrodineanu and Boiteux (1965).

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, but ionization is a limiting factor for only 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. In the general equilibrium:

$$M+O \rightleftarrows MO$$

the forward reaction is exothermic, so an increase in temperature shifts the equilibrium toward the free metal atom if the oxygen concentration remains the same. A decrease in the oxygen concentration also shifts the equilibrium toward the free metal atom. Because one normally has little control over the temperature in chemical flames, the more common approach to shift the equilibrium 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: (1) temperatures much above 3,000 K cannot be obtained with the usual fuel-oxidant combinations; for many elements with high excitation energies this temperature is too low to excite a population of atoms adequate for good analytical sensitivity; (2) the chemical environment of the flame fosters compound formation which effectively removes metal atoms of interest from the atomic emission process; and (3) 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 (d-c) arc discharge (Slavin, 1971) is a widely used spectrochemical 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 in some other gas mixture at atmospheric pressure. Electrodes are most often made from high-purity carbon, or graphite, because of their 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. Although resulting in poorer detection limits than the d-c arc, the alternating-current spark discharge 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 that 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 a 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 two 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. 4). One end of the quartz tube is open and the other end receives the gas supply. 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, simultaneously, thermally stabilizes the plasma. The heat from the plasma is continuously removed by cool argon gas flowing between the outer 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 temperature for the argon plasma is about 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.

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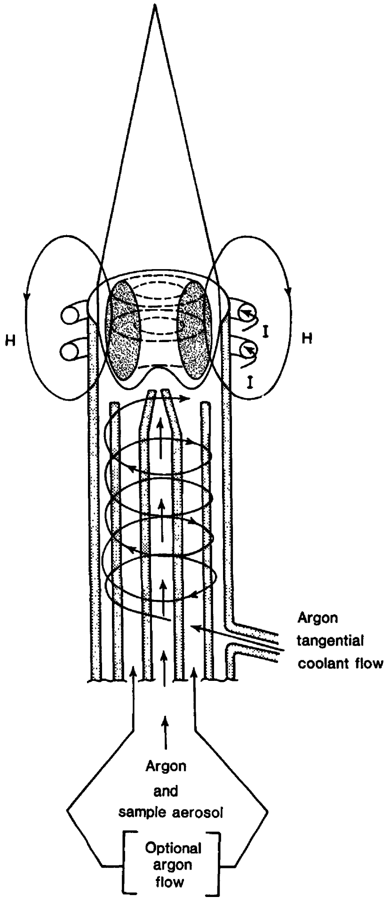

←Figure 4.—Plasma torch configuration

Colorimetry

Basic principles

Colorimetric and spectrophotometric methods in analytical chemistry are founded on the conversion of the constituent of interest into a substance whose solution or suspension is strongly colored and, thus, will absorb radiant energy (Sandell, 1959; Skoog and West, 1982).

The basic principle dealing with the absorption of all types of electromagnetic radiation is commonly called Beer's law, but has also been called Lambert-Beer or Bouguer-Beer. Stated mathematically:

$$A = -\log_{10} T = \log P_o/P = abc$$

where

A = absorbance,
T = transmittance (0–100 percent),
P_o = radiant power incident upon the sample,
P = radiant power leaving the sample,
a = absorptivity,
b = light-path length in centimeters, and
c = concentration of the absorbing species.

As this equation shows, the relation between absorbance and concentration or pathlength is linear, and for a fixed concentration of an absorbing substance, the absorbance will vary with path length. No exceptions have ever been found to this relationship. On the other hand, Beer's law also states that absorbance and concentration are directly proportional; many exceptions to this have been found, and these must be considered in the evaluation of the utility of Beer's law in chemical analysis. Such exceptions are usually caused by either chemical effects or instrumental limitations or both. Chemical effects may result because Beer's law only holds for dilute solutions and instrumental limitations result from the use of light of insufficient monochromaticity or from a lack of proportionality between photocell (or equivalent) response and light intensity. For more detailed discussions of Beer's law, the reader is directed to any basic analytical chemistry text (e.g. Kolthoff and others, 1969; Skoog and West, 1980, 1982; Willard and others, 1981).

Instrumental principles

Colorimetry (visible-light range) and spectrophotometry (ultraviolet- and visible-light range, measuring absorption at a single wavelength) can be viewed as the instrumental measurement of the absorption of radiant energy by a solution at a fixed wavelength. Instruments designed and used for this purpose all contain five basic components, not necessarily housed within a single unit. These are (1) a stable source of radiant energy, (2) a device that can be used to control wavelength, (3) transparent containers for the sample and the solvent, (4) a detector that measures radiant energy and converts it to some measurable signal, and (5) a readout device (Skoog and West, 1980; Willard and others, 1981).

1. Radiant energy source–usually a tungsten-filament incandescent lamp for the visible region; hydrogen or deuterium discharge lamps for the ultraviolet region.
2. Wavelength control–a number of devices are available including filters (absorption and interference) and monochromators utilizing either diffraction gratings or prisms.
3. Sample and solvent containers–these must be manufactured from material that permits passage of the radiation of the wavelengths of interest; commonly used materials include quartz, fused silica, silicate glasses, and plastic.
4. Detector–commonly some type of photoelectric device that converts radiant energy into an electrical current, usually a photovoltaic cell, a phototube, a photoconductive cell, or a photomultiplier tube.
5. Readout–typically some kind of meter, a digital readout, or a chart recorder.

Detailed descriptions of the various components can be found in several texts such as Skoog and West (1980) and Willard and others (1981) or in manufacturers' brochures.

Analytical procedures

Quantitative analysis by colorimetry is an extremely useful tool because it has wide applicability, high sensitivity, moderate- to-high selectivity, good accuracy, and is easy and convenient to use (Skoog and West, 1980). Additionally, many colorimetric procedures are readily automatable, which leads to significant increases in throughput rates.

Before analysis is conducted, a set of working conditions and (or) instrumental settings must be selected. The selection of a wavelength at which absorbance measurements are made is of primary importance. The wavelength selected is commonly an absorbance peak, because changes in absorbance per unit of concentration are at a maximum. In this way, maximum sensitivity is obtained. This wavelength selection, in turn, provides several advantages in addition to extending the determination to the lower concentration ranges: the interferences from other ions are minimized, the effect of natural color and (or) turbidity is reduced and may become insignificant, small sample volumes can be used, measurements are made less sensitive to problems associated with a lack of monochromaticity, and Beer's law is adhered to in the analysis.

Once working conditions have been selected, analysis of samples can begin. In its simplest form, colorimetry or spectrophotometry entails the duplication of a color formed by the constituent of interest by some type of reagent or reagents. Thus, the color of some unknown sample solution becomes exactly the same as that of a solution containing a known concentration of the constituent being measured when both solutions have the same amount of colored substance in a fixed volume (when Beer's law is followed). In actual practice, such a procedure requires a great deal of time and effort and is generally impractical. Commonly, an analytical curve for the constituent being determined is constructed by plotting absorbance versus concentration for known solutions. The standards used to construct such a curve are selected such that they approximate the concentration range of the unknown samples that are being analyzed and generally cover a range in which Beer's law is obeyed. The standards are treated in exactly the same fashion as an unknown sample solution for the development of color and for the measurement of absorbance. Plots of absorbance versus concentration are made; then, by measurement of the absorbance of an unknown solution, constituent concentration can be determined by reference to the existing analytical curves. Such standard curves may be used repeatedly if identical analytical conditions are maintained; but, experience has shown that these curves must be checked frequently because identical conditions are rarely achieved even over short periods of time (for example daily).

Interferences

Several factors influence the absorbance of a material. These include the type of solvent, the temperature, the solution pH, high electrolyte levels, and the presence of interfering substances. The effects of these variables must be known and accounted for in establishing analytical conditions. Through proper selection and maintenance of constant conditions, many of these variables can be dealt with effectively so that precise and accurate results are produced simply by following the analytical procedure; however, some cases do require additional measures to produce good analyses. Typically, additional measures are needed because of the presence of interfering substances that can have either a positive effect (providing increased color leading to higher absorbance readings and hence, spuriously high results) or a negative effect (reducing the color causing lower absorbances and, hence, spuriously low results).

Interferences tend to be of two types, either physical or chemical. Physical effects encompass such things as natural color and turbidity, and almost always cause positive interferences. Chemical effects can cause either positive or negative interferences. An example of a positive chemical interference is the presence of a substance that reacts with a color reagent in the same way as does the constituent of interest. Thus, the resulting color represents not only the constituent, but also the foreign substance. An example of a negative interference is the presence of a substance that inhibits the formation of color by complexing the constituent of interest so that it cannot react with the color reagent.

The simplest way of dealing with interfering substances is to dilute them to the point of insignificance. This strategy works only if the sensitivity of the method is sufficient to determine the constituent of interest at low concentrations. Where dilution is not feasible, other means must be used either to remove the interfering substance, to increase the selectivity of the method, or to compensate for the effect of the interfering substance. Removal may be accomplished in a number of possible ways. However, because the selection of an appropriate procedure is dependent upon the sample matrix and the constituent of interest, care must be exercised before adopting any procedure. If turbidity is the problem, sample filtration through a 0.45 μm membrane filter may eliminate it. Centrifugation is sometimes another satisfactory alternative. If color interferes, oxidation (using HNO_3, or H_2O_2) or bleaching may possibly eliminate it. Chemical interferences can sometimes be removed by using ion-exchange resins, solvent extraction, or precipitation.

There are several ways to improve method selectivity. Among such means are (1) adjusting the pH such that the constituent of interest complexes with the color reagent much more favorably than with interfering ions or (2) using masking compounds such as EDTA that form stable, unreactive complexes with interfering ions and, thus prevent their reaction with the color reagent. Compensation can be accomplished in several ways. Direct compensation can be made by adding all reagents except the color reagent to the sample, placing the sample in the spectrophotometer, setting the absorbance to zero, and then adding the color reagent and measuring the absorbance. This procedure eliminates the natural absorbance of the water, but it has limited utility (it can be used only when the absorbance curve has a shallow slope in the operating region). Another procedure entails subtraction of natural color absorbance. To do this, determine the absorbance of the test sample versus the blank sample specified for the method. Then determine the absorbance of the natural-color sample versus distilled water under the same spectrometric conditions used for the test sample. The difference between the two readings is the corrected absorbance and this value is used to obtain concentration. The natural-color sample is prepared by adding all reagents but the indicator (color) reagent to the same volume of sample water as used for the test sample. Instead of the color reagent, add an equal volume of indicator solvent (usually distilled water).

Automated analyses

The popularity of automated analyzers has increased greatly over the years because of their ability to analyze samples at a much faster rate than is possible using manual procedures. Additionally, for many substances automated analyzers can produce results that are more precise and accurate than those of manual procedures. Finally, most automated analyzers can be networked to mini-computers or mainframe computers, which facilitates sample handling, increases the speed and accuracy of data transfers, and often provides real-time quality control. Today, automated analyzers for colorimetry or spectrophotometry tend to fall into one of three categories: continuous segmented flow, discrete, or flow injection.

Continuous segmented flow systems, such as the Technicon Autoanalyzer, consist of a sampler, a proportioning pump, a cartridge (chemistry) manifold, a filter photometer, a recorder, and a printer. Solutions are introduced into the analytical system by the sampler. The sample solutions are poured into small cups or test tubes that are placed in a rotating turntable, which advances at preset times, and the samples are aspirated from each cup. A wash solution is aspirated for a timed interval between samples. The proportioning pump works on a peristaltic principle and meters samples, reagents, and air bubbles into the flow system through various sizes of flow-calibrated pump tubing. The cartridge manifold comprises the arrangement of reagent additions, mixing coils, delay coils, and a heating bath (if needed to make the reaction proceed at an acceptable rate). These components vary in complexity and detail for each determination. The colorimeter is usually a two-photocell filter photometer. The output from the colorimeter is measured on a recorder and, possibly, on a printer. An analytical curve can be constructed after a sufficient number of standards have been analyzed. Sample concentrations are then obtained from the curve. Alternatively, a printer can be used, that reads directly in concentration, but these values must also be adjusted by reference to an analytical curve.

Flow injection analyzers are continuous flow systems that utilize an unsegmented analytical stream; thus, they differ from continuous segmented flow systems because no air bubbles are involved. In construction, flow injection systems are similar to segmented flow analyzers in that they require a sampler, a pump, a reaction manifold, a detector, and readout device. The differences involve the use of an injection valve and a microprocessor. The latter is necessary to control the timing of the system and to reduce the data. A sample is introduced into the system as a plug (or slug) through the use of an injection valve. This plug is then placed into a continuously flowing system that consists of a carrier (usually distilled water, but reagents may also be included). Mixing of samples and reagents occurs through diffusion processes. As a result, the reactions that produce color or turbidity rarely go to completion (do not achieve a steady state). Therefore, three critical factors must remain constant: (1) sample injection volumes, (2) pumping rates for the carrier and reagents, and (3) residence time in the analytical manifold and detector.

As samples are drawn into the system by an automatic sampler, a pump simultaneously moves the carrier into the sample stream. A sample fills the injection valve until it is loaded; the valve is then opened and the analytical stream is flushed out the valve, thus creating the requisite plug. This stream then moves into a reaction manifold where analytical processing (addition of reagents, heating, dialysis, ion exchange, etc.) takes place. The resulting solution is then passed through the flowthrough cell of an appropriate detector, as in a segmented system. As with segmented flow, an analytical curve must be established so that sample concentrations can be obtained. The absence of air segmentation leads to higher sample throughput and there is little or no carryover between samples.

Discrete analyzers, such as the American Monitor IQAS or the Coulter IKL, differ from both continuous segmented flow and flow injection systems in that they operate exposed to the atmosphere, rather than sealed in tubing and glass. Each reaction, which produces a colored or turbid product, takes place in a discrete (hence the name) container, which is usually disposable. In essence, these systems are "robot chemists," capable of performing a large variety of tests (as many as 32), using the same instrumentation. Requisite chemicals and diluents, for each test, are stored in the unit and dispensed as needed. These types of analyzers are operated by programmable mini-computers that control sampling, reagent type and volume, mixing, heating (if needed), incubation time, wavelength selection, color measurement, calculation of analytical curves, and determination of sample concentrations. These concentrations do not require additional correction because they are automatically calculated from an analytical curve. Data are provided in print and are also stored in the mini-computer for direct transfer to a mainframe system. Because discrete analyzers use open-reaction containers, certain types of analytical procedures either cannot be employed or require that samples undergo some type of pretreatment prior to insertion in the system. For example, the cadmium-reduction method for the determination of nitrate plus nitrite cannot be adapted to a discrete analyzer. Likewise, the methylthymol blue method for the determination of sulfate, which calls for the removal of divalent cations through the use of an ion-excange column, cannot be run directly as with a continuous flow system. However, if the samples undergo pretreatment to remove divalent cations, a discrete analyzer can be used to quantitate sulfate using this method.

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Electrometry

Voltammetry

Voltammetry, polarography, is based on current-voltage measurements at an electrode. When a potential is applied across an electrode pair, the working electrode becomes polarized by assuming the applied potential. The working electrode remains polarized, with no flow of current, until the potential difference between the electrodes is sufficient to exceed the decomposition potential of a particular electroactive analyte in solution. At potentials greater than the decomposition potential, the electroactive analyte is deposited on the working electrode and the current begins to flow. As the applied potential is increased further, the change in current levels, and becomes diffusion-limited.

The potential at which the current produced by the electrochemical reaction reaches one half its diffusion-controlled value is the half-wave potential, $E_{1/2}$. The half-wave potential is characteristic of the particular electroactive analyte undergoing reaction and may be used for identification purposes; however $E_{1/2}$ is a function of solution conditions such as the supporting electrolyte, the pH, and the solvent system, to name a few.

The current measured is the sum of the Faradiac, capacitative, and residual contributions. Faradiac current is a result of electron transfer across the electrode-solution interface as the result of the oxidation or reduction of the electroactive analyte at the working electrode. Faradiac current is proportional to the concentration of the analyte.

Capacitative current is the current needed to charge the double-layer capacitance at the surface of the working electrode. The separation of charge at the solution-electrode interface acts much like a large capacitor with respect to the external circuitry and requires current for charging. Capacitative current represents an inherent offset or noise and can be the principal limitation to sensitivity of a polarographic measurement. However, capacitative current can be minimized by modulating the applied potential and by maintaining a constant working electrode area.

The residual-current contribution to the total diffusion current can be evaluated by measuring the current resulting from the supporting electrolyte alone. The residual current at any particular potential can then be subtracted from the total current at that potential.

Polarography uses two basic forms for the working electrode—liquid or solid. The majority of polarographic techniques use various configurations of elemental mercury electrodes. Mercury electrodes generally take form either as a suspended mercury drop, known as the hanging mercury drop (HMD) electrode or as a dispersed thin-film electrode deposited on a conducting substrate, commonly referred to as the mercury thin-film (MTF) electrode. In general, greater sensitivity may be obtained on MTF electrodes, but HMD electrodes are simpler to use and more versatile. Solid electrodes include platinum, gold, and various forms of graphite. Major limitations of solid working electrodes are their variability in the activity of the deposited analyte and their inability to accommodate more than one simultaneously reduced analyte. Both limitations of solid electrodes prevent useful current-potential response when applied to stripping polarographic techniques.

Modern polarographic instrumentation employs a three-electrode system composed of a working electrode, an auxiliary electrode, and a reference electrode. The electrochemical reaction takes place at the working electrode, and the auxiliary electrode completes the circuit between the working electrode and the solution. The reference electrode serves as a contact to measure potentials applied to the working electrode. Platinum wires and foils are commonly used as auxiliary electrodes. Reference electrodes are usually either the familiar calomel reference electrode or the silver-silver chloride reference electrode.

A technique based on polarographic principles is anodic stripping voltammetry (ASV). ASV consists of two sequential steps. First the electroactive analytes are preconcentrated, or deposited, in the working electrode by reduction. After sufficiently long deposition times, the concentration of the analyte will be greater in the electrode than in the sample solution. Secondly each analyte is subsequently stripped, or oxidized, from the working electrode. In ASV the deposition step occurs at a sufficiently negative potential as to deposit all the desired analyte species into the working electrode. During the stripping step the applied potential is stepped anodically under carefully controlled conditions, and the preconcentrated analytes are subsequently stripped completely into the bulk solution. Carefully controlled conditions are necessary to obtain precise current-potential responses for quantification and identification, respectively.

The total current generated by the electrochemical reaction during ASV is, again, the sum of the Faradiac, capacitative, and residual contributions. Differential pulse anodic stripping voltammetry (DPASV) minimizes the capacitative contribution by using a working electrode having a fixed electrode area and by superimposing a modulated pulse on the applied potential step. Two current measurements are made during each potential step. The first occurs just prior to the occurrence of the modulation pulse and the second, immediately following it. The change in current between the pair of measurements minimizes the capacitative current and therefore enhances the signal-to-noise ratio. The contribution due to the residual current can be eliminated by subtracting the reagent-blank voltammogram from the sample voltammogram.

Ion-selective electrodes

Ion-selective electrodes are electrochemical sensors that relate concentration to electrical potential. They operate in the same way, irrespective of type, as does the classical glass electrode for the measurement of pH. Each sensor consists of an internal electrode and a membrane that establish a potential. This potential is linearly dependent on the logarithm of the activity of a given ion in solution. Effective concentration ranges usually cover several orders of magnitude. This electrode response is called "Nernstian" and can be expressed mathematically as follows:

$$E = E_x + 2.3\, RT/nF \log A$$

E is the total potential, in millivolts (mv), developed between the selective ion and the reference electrodes; E_x, in mv, varies with the choice of reference electrode; 2.3 RT/nF is the Nernst factor, where R is the gas constant, F is the Faraday constant, n is the charge on the ion, including the sign, T is the temperature in degrees Kelvin; and A is the activity of the ion to which the electrode is responding. The term 2.3 RT/nF is equal (at T=25 °C) to 59.16 mv when n=1, 29.58 mv when n=2, etc.

As noted in the above equation, the electrochemical potential determined under real conditions is a measure of the activity of the ion in question. This relates concentration to the interaction of the specific ion with all other ions in solution. The activity-concentration relationship A can be described by the following equation:

$$A = cf$$

where c is the concentration of the ion determined and f is the activity coefficient. The magnitude of the interaction depends on the total ionic strength of the solution. This can be maintained at a constant level by the addition of a high concentration of an inert electrolyte to the system. Properly chosen, this addition would not affect the equilibrium of the ion being measured and would stabilize the activity coefficient. Therefore, to determine concentration, one needs only to provide the means for measuring with a readout device of some type this electrochemical potential with respect to a constant reference potential. By relating the potential measured by such a system to a series of known standard solutions, one can calibrate, and, subsequently, determine the concentration of the ion in an "unknown" sample. Additional information on the theory of ion-selective electrodes and instrumentation may be found in the manufacturers' literature; in Marenthal and Taylor, 1973; in Andelman, 1971; in Moody and Thomas, 1971; and in Durst, 1969.

For the purpose of discussion, ion-selective electrodes can conveniently be grouped into three general types: solid state, liquid membrane, and gas sensing. Each one finds use in water-quality applications.

Solid-state, ion-selective electrodes are normally constructed by sealing a crystal membrane in an epoxy tube or other appropriate holder. Two types are available, either homogeneous or heterogeneous crystalline electrodes. The homogeneous membrane electrode consists of an appropriate crystalline material prepared from either a single compound or from a homogeneous mixture of compounds having satisfactory electrical resistance. The principal advantages of homogeneous electrodes are their low cost, fast response, long operative life, resistance to corrosive acid and alkaline media, and Nernstian behavior throughout many decades of use. Electrodes of this type have been developed with high selectivity for bromide, chloride, fluoride, iodide, silver, and sulfide.

The fluoride ion-selective electrode consists of a single crystal of lanthanum fluoride (LaF_3) membrane bonded into an epoxy body. A solution containing fluoride ions and a silver wire, which provides electrical contact to the back of the crystal, are sealed inside. The crystal is an ionic conductor in which only fluoride ions are mobile. When the electrode is placed in an external solution containing fluoride, fluoride ions migrate across the membrane in an attempt to reach a state of equilibrium. A stable potential is developed that is measured.

The heterogeneous electrode consists of an active substance or a mixture of active substances mixed with an inert matrix, such as silicone rubber or polyvinyl chloride, or placed on hydrophobized graphite, to form a sensing membrane that is heterogeneous in nature. An example of this type of solid-state electrode is silver iodide embedded into silicone rubber to provide iodide ion-selective response.

The second type of electrodes, liquid-membrane sensors, is similar to the solid-state electrodes. Instead of a crystal-type membrane, these electrodes use a liquid ion exchanger tailored as a specific carrier for the ion of interest. The ion exchanger is held in place by a thin, porous, inert membrane. There is no shortage of prospective liquid cation- and anion-exchanger materials for possible use in ion-selective electrodes; however, the successful fabrication of these electrodes presents problems, many of which are mechanical. The liquid ion exchanger must be in electrolytic contact with the sample, but any mixing of phases must be minimal; must not be too soluble in the sample solution, which will effect the limit of detection; must have a viscosity high enough to prevent its rapid loss by flow across the membrane; must possess good stability; and must be available in a state of high purity with high-exchanger capacity. The liquid ion exchangers are usually high-molecular-weight organic compounds dissolved in an organic solvent. The organic molecule has charged sites where the ion of interest can bind to it. Both the exchanger and the ion of interest move through the membrane. An internal filling solution and a silver wire coated with silver chloride provide the electrical contact. As with the solid-state electrode, a stable potential is developed and measured. A calcium selective-ion electrode as described by Willard and others, 1974, is a good example. An organic derivative of phosphoric acid is used as the liquid ion exchanger that selectively forms a strong salt with calcium. Liquid-membrane electrodes selective for potassium, nitrate, and fluoroborate, to name a few, are also available.

The most recent type of membrane introduced, which is useful in water analysis, is the gas-sensing electrode. In addition to being used for measuring dissolved gases in solution, they can be used for measuring the ionic form of a constituent after appropriate sample treatment to convert the ion to a gas. The sensor, composed of an indicating and a reference electrode, uses a gas-permeable membrane to separate the sample solution from a thin film of an intermediate solution, which is either held between the gas membrane and the ion-sensing membrane of the electrode or is placed on the surface of the electrode using a wetting agent (for example, in air-gap electrodes). This intermediate solution interacts with the gaseous species in such a way as to produce a change in a measured value (e.g., pH) of the intermediate solution. This change is then sensed by the ion-selective electrode and is proportional to the partial pressure of the gaseous species in the sample. An example is the ammonia-sensing electrode, which uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode-internal solution. Dissolved ammonia in the sample diffuses through the membrane in proportion to its concentration, and, in turn, reacts in the internal solution to produce hydroxide ions. This changes the pH of the internal solution. This change is measured by a pH electrode located behind the membrane. Because the pH varies directly with the ammonia concentration, the electrode responds directly to ammonia.

Similar schemes can be devised for other gases, including nitrogen oxides (NO_x), carbon dioxide (CO_2), hydrogen sulfide (H_2S), and hydrogen cyanide (HCN). The ion-selective electrode does not have to be a pH electrode as in the case for ammonia; the choice is dependent upon the reaction of the gas in the internal solution.

A reference electrode is required to complete the measuring circuit by providing a conductive path from the sensing electrode, through the solution, to the readout device. The reference electrode is the half of the electrode pair that provides a constant potential regardless of solution composition. The potential developed by the sensing electrode is measured with respect to this reference potential to give an overall system potential, which can be converted to the level of the species sensed. Numerous types of reference electrodes are available. The analyst should consult the manufacturer's manual for the reference electrode that should be used for a specific selective-ion electrode. Differences in performance among the various forms of reference electrodes can be a major factor in optimizing a method of potentiometric analysis.

Instrumentation required for potentiometric analysis with ion-selective electrodes is relatively simple and inexpensive. Measurements can be made with conventional pH meters that provide scale expansion. This type of instrument displays voltages, pH units, or other concentration units by means of a needle pointer and scale. Modern, direct-reading, solid-state potentiometers are ideally suited for the requirements of water analysis. This type of meter provides digital display in millivolt or pH units. Operator error is reduced with digital instruments, because there is no need for interpolation and no risk of confusing scales. Instruments are available under the designation of "Selective Ion-Meter," which measure the potential of pH- and ion-selective electrodes and display it directly in concentration or activity units on a logarithmic scale. Millivolt scales are also provided for titrations and to verify proper electrode operation.

An electrode interference is any species, other than the ion being measured, in a sample solution that can alter the potential measured by a sensing electrode. Two types of interferences exist: "electrode" and "method." Electrode interferences are those substances that give a response similar to that of the ion being measured and whose presence generally results in an apparent increase in activity or concentration of the ion being determined—those substances that interact with the membrane so as to change its chemical composition; and electrolytes present at a high concentration that produce appreciable liquid-junction potentials. Method interferences are substances that interact with the ion being measured so as to decrease its activity or apparent concentration, although the electrode continues to report the true activity.

Generally, interferences for solid-state electrodes (except for fluoride) are species that form more insoluble salts or metal sulfides than does the ion of interest. Liquid-membrane electrodes react to the interfering ion as though it were the ion of interest. Gas-sensing electrodes are affected by any species that has a finite vapor pressure under the measuring conditions of the gas of interest. For a discussion of interferences for a particular species, see the individual constituent of interest in this chapter.

Specific conductance

Specific conductance is determined by using a Wheatstone bridge, in which a variable resistance is adjusted so that it is equal to the resistance of an unknown solution between two electrodes either of platinized platinum or of other suitable material such as graphite. The null point is detected by an alternating current galvanometer, cathode-ray tube or digital readout. Alternating current is necessary to prevent polarization of the electrodes. Direct current produces gas bubbles on the electrodes that greatly increase the resistance and change the concentration of the electrolyte in the vicinity of the electrodes. The electrodes are coated with a thin layer of amorphous platinum, which tends to absorb gases and catalyzes their reunion, thereby minimizing polarization.

The electrode cell may be the dip, cup, or pipet type. The pipet cells are generally preferred for routine laboratory use: because they require a smaller volume of water for the determination, the water can be drawn directly from a narrow-mouth sample bottle without transferring it to another container, the total time for the determination is less, and the water sample undergoes less mechanical agitation. Dip- or cup-type cells are preferable for field work.

Temperature is an important factor in determining the specific conductance of a solution. When the temperature of a solution increases, the conductance almost always increases. By convention, 25 °C is the standard reference temperature in most water-resources applications. Thus, all specific-conductance determinations are adjusted to and specified at 25 °C. The adjustment to 25 °C is achieved either automatically with a thermistor within the sensor or manually at the conductivity bridge. Automatic or manual temperature compensation is proportional to the inverse of the resistance of a standard potassium chloride solution.

Many direct-reading conductivity bridges are commercially available that are well suited for both laboratory and field work. Manufacturers, such as Beckman, Lab-line, YSI, etc., produce lines of durable, lightweight equipment. These direct-reading conductivity instruments have either a dial for manual temperature compensation or automatic temperature compensation built into the conductivity cell and bridge circuit. As with all instruments, the manufacturers' instructions and supplemental instructions should be followed exactly for good precision and accuracy.

pH

pH meters measure the electrical potential between two electrodes immersed in the solution to be tested. The reference electrode maintains a constant potential, and the indicating electrode maintains a potential dependent on the hydrogen-ion activity of the solution. The calomel electrode, which is a widely used reference electrode in water analysis, consists of a mercury-calomel rod immersed in a saturated solution of potassium chloride. This electrode has a half-cell potential of +0.246 volt. Electrical connection with the sample is provided through porous fibers sealed into the immersion end. A hydrogen-ion-selective glass electrode is normally used as an indicating electrode. The glass electrode has several features that recommend it for pH measurements. Among the most important are that it is not affected by oxidizing or reducing substances in the sample and that it can be used to measure the pH of turbid samples or colloidal suspensions or both. The basic design is a silver-silver chloride or mercury-mercurous chloride electrode immersed in a solution of known pH and completely sealed in glass.

The mechanism by which the glass membrane responds to hydrogen-ion activity involves absorption of hydrogen ions on both sides of the membrane proportional to the activity of the hydrogen ions in solution. The cell for measuring the pH of a solution is of the following type:

$$\underbrace{\mathrm{Ag^{0} : AgCl} \;\Big\|\; \begin{array}{c}\text{Solution of}\\ \text{known pH;}\end{array} \quad \begin{array}{c}\text{Glass}\\ \text{membrane;}\end{array}}_{\text{Glass electrode}} \quad \begin{array}{c}\text{Solution of}\\ \text{unknown pH}\end{array} \;\Big\|\; \mathrm{Hg^{0} : HgCl.}$$

The half-cell potential of the glass electrode is a logarithmic function of the difference in hydrogen-ion activity of the solutions on either side of the glass membrane. To measure this potential a high-impedance electrometer circuit is used, because the resistance of the glass membrane is so great.

Desired features in a line-operated pH meter are a built-in voltage regulator; an accuracy of at least 0.02 pH; stability of calibration; a built-in temperature-compensating mechanism; durable electrodes; and a design that permits insertion of the electrodes, a stirrer, and a buret into a suitable vessel for titrations. For pH determinations in the field, the instrument should also be rugged, compact, and battery operated. pH meters should be carefully calibrated with two buffer solutions that bracket the pH range of the test samples, and the calibration should be checked during extended periods of operation. A third standard buffer should be used—the data of this third buffer will automatically indicate stressed or faulty electrodes if the theoretical versus actual curve is non-linear.

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Ion chromatography

Principles

Ion chromatography (IC) has been used since the early 1940's for separation of both organic and inorganic species. Analysis was relatively easy when the ion being eluted from an ion-exchange column had a directly measurable property, such as absorption in the ultraviolet or visible region of the spectrum, that could be distinguished from the background. Specific-conductance measurements were also used, but high-background conductance of the electrolyte (eluent) usually overwhelmed the conductance of eluting ions. Small and others (1975) solved this detection problem by adding a suppressor column downstream from the separator column that suppressed or neutralized ions of the background electrolyte. Recent advances in cells and electronic suppression have revived the original technique. However, methodology in this manual uses the technique of Small and others (1975), and discussion is limited to the two-column technique.

A sample is injected into a liquid mobile phase being pumped through two ion-exchange columns placed in series. In the first column, called the separator, ions are separated on the basis of their affinity for exchange sites on the resin. The second column, called the suppressor, decreases the background conductivity of the mobile phase, called the eluent, to a minimal level and pairs the ions in the sample to some highly conductive species. Separated ions are quantitated with a specific-conductance cell. The basic procedure for anions, such as fluoride, is shown in figure 5. A typical chromatogram for seven of the common anions found in water is shown in figure 6.

IC is most useful for the determination of the major ionic constituents of aqueous samples in which no single ion is in great excess of the other ions. The ions are determined sequentially using only a small aliquot of sample, and detection limits for many of the ions are lower when IC is used instead of other techniques. Chromatographic separation of the ions eliminates many of the interferences associated with other techniques, permits the use of universal detectors, and is capable of determining different species of the same ion in some cases.

Apparatus

The IC technique and equipment are rapidly changing and improving. Better pumps, sample

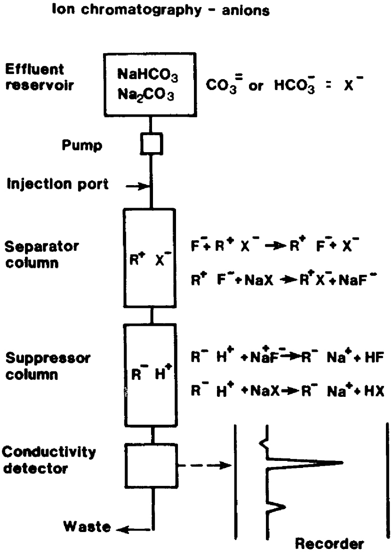


Figure 5.—Ion chromatography system for anions

injection systems, separator resins, suppression techniques, and a proliferation of detectors promise greater accuracy, precision, and versatility.

Pumps

Liquid chromatography requires a highly reproducible eluent flow rate for reproducible results. For this reason, intermittent-displacement-type pumps are used in IC instruments. Recent advances in pump technology have resulted in a new generation of intermittent-displacement-type pumps for IC use. They have pump heads made entirely of nonmetallic parts and can operate at pressures as high as 2,000 pounds per square inch. These pumps also incorporate a precision pressure transducer in dual-pressure and flow-rate feedback loops to provide a constant-pressure, essentially pulseless, eluent flow.

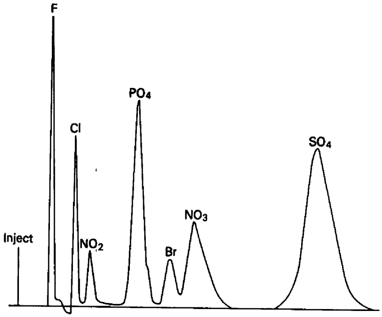


Figure 6.—A typical chromatogram for seven anions

Determining low concentrations of ions in precipitation samples requires that the conductivity meter on the ion chromatograph be set to more sensitive scales. Hence the "water and carbonate dip" interference with fluoride and chloride determinations at low concentrations is more pronounced. To eliminate the "water and carbonate dip," a stronger eluent is added to each sample to increase the conductivity to the same level as that of the eluent that flows through the system. This modification of the ion chromatograph can be made by installing two pulseless pumps, which permit the automatic addition of stronger eluent to each sample. The ion chromatographic schematic in figure 7 includes this automatic addition.

Sample-injection systems

Reproducible sample injection can be very difficult to achieve in IC. One problem is that the ions amenable to determination are ubiquitous in the laboratory environment, presenting substantial opportunities for sample contamination. Especially problematic is the determination of ions at low levels in samples such as precipitation or boiler feed water.

The most common sample-injection technique for IC is to manually rinse and fill a sample loop from a plastic syringe, and then place the loop into the chromatographic system, causing the

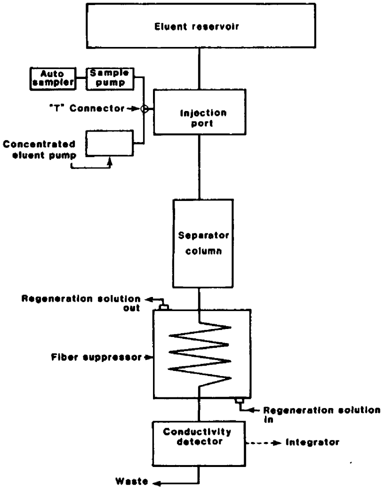


Figure 7.—Ion chromatographic schematic diagram

sample to be swept onto the separator column by the eluent flow.

Automated instruments may use a pump to fill the sample loop. This pump should always be on the waste side of the sample loop to prevent contamination from the pump mechanism. Another approach is to use an automatically actuated valve to open a vacuum line and draw the sample through the sample loop. In any case, some means must be incorporated in the injection- system design to divert eluent flow while the sample loop is being filled or moved in and out of the chromatographic system. Otherwise, a pressure spike will upset the system upon sample injection.

Separator resins

The most commonly used separator resins are S-DVB (styrenedivinylbenzene) based. These are pellicular resins, which have exchange sites only at or very near the surface of the S-DVB support. This leads to high efficiency by minimizing the diffusional pathways of the sample ions and results in good mass-transfer characteristics for the resin.

The stability of these resins throughout the entire pH range is their most important feature. S-DVB packings do not undergo degradation even under drastic conditions. Swelling in organic solvents is minimal. Ion selectivities on these resins are similar to those for conventional S-DVB packings. They are resistant to overloading and poisoning.

Depending on the analyte, two types of S-DVB-separator packings are used. Cation separators use surface-sulfonated S-DVB resin and have typical capacities in the range of 0.005 to 0.1 me/g. Anion-separator resins have an inert, hydrophobic, S-DVB-polymer core. Surrounding this core is a layer of solvated sulfonic acid groups similar to that used in cation separators. This layer is coated with a uniform monolayer of laminated latex. The latex is attached to the sulfonated surface by a combination of electrostatic and Van der Waals forces. The capacity of these anion-exchange resins is similar to the capacity of the cation exchangers.

Pellicular silica-based packings, which have functional ion-exchange groups attached by the usual silane reactions, are of some use in IC, as well as resins such as silica-coated polyamide crown resins (Igawa and others, 1981), dynamically coated reverse phases (Cassidy and Elchuk, 1982), and specially treated polymeric adsorbents of high-surface pourous polymers (Gjerde and Fritz, 1981). These techniques are in their infancy, having the pH limitations of silica, the liability of the silyl-carbon bond, or mechanical instability under the conditions necessary for good ion separations.

Suppressor resins

The original suppressors, still widely used, are columns packed with Dowex 1X8, 200–400 mesh in the hydroxide form for cation analysis and Dowex 50W X8, 200–400 mesh in the hydrogen form for anion analysis. These columns convert eluent ions to a low-conductivity species and paired analyte ions to highly conductive hydronium or hydroxide ions. These two processes, collectively called suppression, enable for very sensitive conductivity detection of ionic analytes.

This type of suppression system has two major drawbacks. The suppressor resin is slowly exchanged during a series of analyses and must be regenerated to the hydrogen or hydroxide form periodically. Regenerating the suppressor resin is time consuming and requires an entire IC-instrument subsystem consisting of a regenerant reservoir, a regenerant liquid pump, valving, and plumbing. The other major drawback is the increase in system volume that results from the suppressor column. Although having as large a suppressor as possible is desirable to avoid frequent regeneration, the larger the suppressor bed, the greater the peak broadening and general loss of chromatographic resolution.

Recently, Stevens and others (1981) introduced a hollow-fiber ion-exchange suppressor as shown in figure 8. It shows the reactions that occur across the membrane wall. Sodium bicarbonate/sodium carbonate eluent flows through the interior of the fiber and sulfuric acid regeneration solution flows countercurrently. The fiber is a cation exchanger containing sulfonate (R-SO_3^{-1}) exchange sites. When an eluent is flowing through the fiber, the cationic Na^{+1} ions are attracted to the SO_3^{-1} groups in the membrane wall, as are the protons present in the regenerant solution. The fiber-suppressor reactions are as follows:

Inside a tubular cation-exchange membrane:

$$2\,Na^{+1} + CO_3^{-2} + 2(\text{resin } H^{+1}) \rightarrow H_2CO_3 + 2(\text{resin } Na^{+1})$$

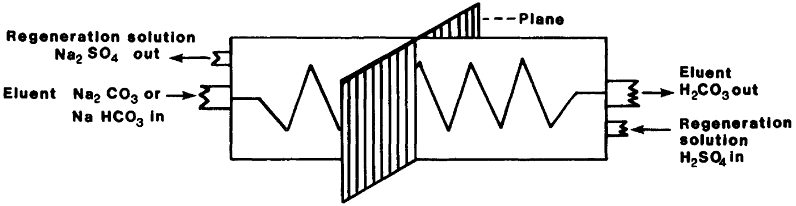
$$Na^{+1} + HCO_3^{-1} + \text{resin } H^{+1} \rightarrow \text{resin } Na^{+1} + H_2CO_3$$

$$\text{Resin } H^{+1} + NaF \rightarrow \text{resin } Na^{+1} + H^{+1}F^{-1}$$

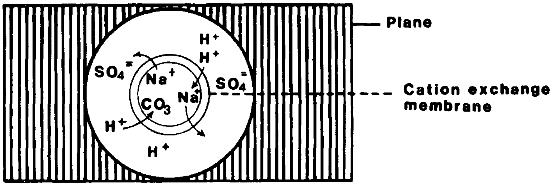
Outside a tubular cation-exchange membrane:

$$H_2SO_4 \rightarrow 2H^{+1} + SO_4^{-2}$$

$$2Na^{+1} + SO_4^{-2} \rightarrow Na_2SO_4 \text{ (to waste)}$$



Side view of fiber suppressor



Top view of fiber suppressor

Figure 8.—Fiber suppressor

This device enables the near steady-state exchange of ions across the wall of a sulfonated polyethylene hollow fiber, resulting in the suppression of eluent and analyte ions.

The hollow-fiber suppressor eliminates the need for periodic suppressor regeneration, but results in greater band spreading and subsequent loss of resolution than is obtained using a small bed-volume, resin-filled suppressor column. Stevens and others (1982) reported that band spreading is reduced and resolution improved when the hollow fiber is surrounded with inert beads. Although some problems still need resolution, the steady-state suppressor device should improve greatly the utility of IC for accurate and precise quantitation. Upon entering a fiber suppressor, the eluting base, for example, NaOH, is removed by the acid resin:

$$\text{Resin } H^{+1} + Na^{+1}OH^{-1} \rightarrow \text{resin } Na^{+1} + H_2O$$

and the analyte anions (A^-) are converted to their acids:

$$\text{Resin } H^{+1} + M^{+1}A^{-1} \rightarrow \text{resin } M^{+1} + H^{+1}A^{-1}$$

which pass through the fiber suppressor and into a flow-through conductivity cell where they are detected.

Detectors

Small and others (1975) stated that it would be desirable to employ some form of conductimetric detection as a means of monitoring ionic species in a column effluent, because conductivity is a universal property of ionic species in solution and because conductance shows a simple dependence on species concentration. However, with older types of conductivity detectors the species of interest was generally "swamped out" by the more abundant eluting electrolyte. With the addition of the suppressor column, this problem was solved as discussed previously. Again, note that modern conductivity detectors have been refined to electronically suppress the eluting electrolyte. This will not be discussed further since the methods in this chapter utilize chemical suppression.

One problem with using conductivity for detection is its dependence on temperature. For each 1 °C change in temperature, there is a corresponding change of about 2 percent in the equivalent conductance. This temperature dependence severely limits analytical reproducibility if precautions are not taken to ensure temperature stability during IC analyses. Instruments, which are presently produced, incorporate a microprocessor-controlled conductivity detector that allows precise, accurate compensation for environmental-temperature fluctuations. This imparts both long- and short-term baseline stability and improved signal-to-noise ratios.

Conductivity is not the only means of detection compatable with IC. Electrochemical detectors are also commercially available. This type of detector works best in a high-conductivity background environment so no eluent suppression is required. The detector consists of a flow cell with three electrodes: a silver-silver chloride reference electrode, a platinum or steel counter electrode, and a silver or platinum working electrode.

The silver working electrode can be used to determine species such as cyanide, sulfide, and bromide. Setting the operating potential properly enables the detection of small amounts of bromide, for instance, in the presence of chloride concentrations high enough to swamp the bromide signal from a conductivity detector (Pyen and Erdmann, 1983). Unfortunately, reactions at the silver working electrode involve the catalytic oxidation of the silver electrode itself. For this reason variations in detector response within relatively short periods of time must be expected and frequent cleaning of the electrode surface is required. Suppression is unncecessary and toxic analytes, such as cyanide, remain in basic solution throughout the analysis (Bond and others, 1982).

Recently, post-column-reaction technology has been developed to produce complexes with the analyte ions that absorb in the near ultraviolet and visible portions of the spectrum. Detection is achieved using a photometer equipped with a flow-through cell. Some transition metals and different species of the same metal ion have been determined by this technique. One of the interesting applications involves the use of eluents such as tartaric acid. This weakly acidic eluent permits the use of high-efficiency, silica-based separator resins. The resulting metal-tartrate complexes are monitored photometrically as they elute off the separator column.

An endless variety of detector types and configurations seem to be available. This instrumentation is perhaps where real progress in IC methodology will come in the near future.

Automation

Either peak height or peak area can be used to quantitate IC analyses with conductimetric detection. Measuring the peak heights or peak areas of both samples and standards can be tedious and time consuming because large amounts of data are generated in analyzing a sample. The use of an electronic integrator capable of reporting and storing both peak heights and areas facilitates the process. Hedley and Fishman (1981) described an automated system that was used for the determination of six anions in precipitation samples. The ion chromatograph was interconnected to an autosampler and a computing integrator. Slaina and others (1979) also described a data-acquisition and reduction system using a minicomputer. Presently, commercially automated instrumentation is available.

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Sample Preparation and Pretreatment

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

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

Sample preparation, bottom-material

(P-0520-85)

1. Application

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

2. Summary of method

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

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

3. Interferences

None.

4. Apparatus

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

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

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

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

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

5. Reagents

None required.

6. Procedure

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

6.2 Air-dry the sample. Spread a representative portion of the sample in a thin layer on a flat enamelware tray or glass watchglass, and allow it to stand exposed for 24 h, or until dry.

The drying must be conducted in a place free of potential contamination.

6.3 Portions of the resulting air-dried and well-mixed sample are taken for subsequent analyses.

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

7. Calculations

7.1 Compute the loss in weight of the sample, in grams, on heating at 105 °C.

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

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

8. Report

Report percentage of moisture to two significant figures.

9. Precision

Precision data are not available for this method.

Subsampling, bottom-material, coring

(P-0810-85)

1. Application

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

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

2. Summary of method

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

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

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

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

3. Interferences

None.

4. Apparatus

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

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

5. Reagents

None.

6. Procedure

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

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

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

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

6.4 Weigh the subsample to determine its wet weight.

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

7. Calculations

Compute the dry weight of a subsample as follows:

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

where

W= wet weight of the sample, grams,

and

M= percent of moisture as determined by method P-0590.

8. Report

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

9. Precision

Precision data are not available for this method.

Subsampling, bottom-material, splitting

(P-0811-85)

1. Application

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

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

2. Summary of method

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

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

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

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

3. Interferences

Certain samples, especially those with a large proportion of sand-size material, may clog the Jones-type splitter, which results in an uneven split.

4. Apparatus

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

4.2 *Splitter*, Teflon, Jones-type.

5. Reagents

None.

6. Procedure

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

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

6.2 Accurately weigh the rest of the sample.

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

6.4 Accurately weigh the split subsample.

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

7. Calculations

Compute the dry weight of a split subsample as follows:

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

where

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

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

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

and,

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

8. Report

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

9. Precision

Precision data are not available for this method.

Percent moisture, total in-bottom-material, gravimetric

(P-0590-85)

1. Application

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

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

2. Summary of method

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

3. Interferences

None.

4. Apparatus

4.1 *Crucible*, platinum or porcelain.

4.2 *Desiccator.*

4.3 *Oven*, 105 °C.

5. Reagents

None.

6. Procedure

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

6.2 Weigh sample and crucible to the nearest 0.1 mg.

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

7. Calculations

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

where

W= total wet weight of sample, grams,

and

D= dry weight of sample, grams.

8. Report

Report percentage of moisture to two significant figures.

9. Precision

Precision data are not available for this method.

Extraction procedure, bottom-material

(I-5485-85)

1. Application

This method must be used as preliminary treatment of bottom-material samples to destroy organic matter and to desorb and solubilize metals. If it has been determined that greater than 95 percent of the substance is solubilized, the results should be reported as "total." If less than 95 percent is solubilized, the results should be reported as "total recoverable." Only that portion of bottom material that passes a 2-mm sieve is taken for analysis.

2. Summary of method

2.1 The determination of acid-soluble metals occurring in or associated with sediment and bottom material involves (1) destruction and removal of all organic matter, followed by (2) treatment to dissolve acid-soluble substances, and (3) measurement of the concentration of constituents in the resulting solution.

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

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

3. Interferences

There are no interferences in the acid digestion.

4. Apparatus

Filter paper, Whatman No. 41 or equivalent.

5. Reagents

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

5.2 *Hydrochloric acid*, double-distilled, 1*M*: Add 17 mL of 6*M* HCl (double-distilled) to demineralized water and dilute to 100 mL with demineralized water.

5.3 *Hydrochloric acid*, double-distilled, 0.3*M*: Add 50 mL of 6*M* HCl (double-distilled) to 950 mL demineralized water.

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

5.5 *Nitric acid*, dilute (1+4): Add 1 volume of concentrated HNO_3 (sp gr 1.42) to 4 volumes of demineralized water.

6. Procedure

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

6.2 Weigh, to the nearest milligram, between 4 and 10 g of thoroughly homogenized, undried sample that has passed a 2-mm nonmetallic sieve (method P-0810 or P-0811). Compute the dry weight of the sample by determining the percent moisture on a *separate* subsample (method P-0590).

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

6.4 Check the acidity of the solution with litmus paper. Make acidic by the dropwise addition of 1*M* HCl, if necessary.

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

NOTE 1. A demineralized water blank must be carried through the procedure. Add equivalent amounts of 30-percent H_2O_2 and acid to the blank.

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

6.7 Dilute the mixture to 200 mL with demineralized water.

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

6.9 Filter the hot mixture (Whatman No. 41 filter paper, or equivalent) and collect the filtrate in a 250-mL volumetric flask. Wash the residue on the filter paper at least three times with hot 0.3*M* HCl.

6.10 Cool the filtrate to room temperature, and dilute to volume with demineralized water, and mix thoroughly.

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

7. Calculations

See individual method for each metal.

8. Report

See individual method for significant figures to be reported.

9. Precision

See individual method for each metal.

Extraction procedure, water-suspended sediment

(I-3485-85)

1. Application

This method must be used as preliminary treatment of samples of water-suspended sediment to desorb and solubilize metals associated with the suspended sediment phase of the sample. If it has been determined that greater than 95 percent of the substance to be determined is solubilized, the results should be reported as "total." If less than 95 percent is solubilized, the results should be reported as "total recoverable."

2. Summary of method

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

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

3. Interferences

There are no interferences in the acid digestion.

4. Apparatus

Filter paper, Whatman No. 41 or equivalent.

5. Reagents

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

5.2 *Hydrochloric acid*, double-distilled, 0.3*M*: Add 50 mL of 6*M* HCl (double-distilled) to 950 mL demineralized water.

5.3 *Nitric acid*, dilute (1+4): Add 1 volume of concentrated HNO_3 (sp gr 1.42) to 4 volumes of demineralized water.

6. Procedure

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

6.2 Mark the level of the sample on the bottle and determine the volume by weight.

6.3 Transfer the entire contents of the sample bottle to a beaker or fleaker.

6.4 Add 5 mL double-distilled 6*M* HCl to the sample bottle for each 100 mL of original sample. Shake vigorously and add this solution to the beaker. Heat solution in beaker to just below boiling and continue heating until the volume is reduced approximately 20 percent (NOTE 1).

NOTE 1. A demineralized water blank must be carried through the procedure. Add an equivalent amount of acid to the blank.

6.5 Filter the hot mixture (Whatman No. 41 filter paper or equivalent) into the original sample bottle. Wash the residue on the filter paper three times with 5-mL portions of hot 0.3*M* HCl.

6.6 Cool to room temperature, and dilute to the original volume with demineralized water. Mix thoroughly.

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

7. Calculations

See individual method for each metal.

8. Report

See individual method for significant figures to be reported.

9. Precision

See individual method for each metal.

Total decomposition, sediment

(I-5473-85)
(I-5474-85)
(I-5475-85)

1. Application

1.1 These methods may be used to analyze suspended and bottom sediment for the determination of total concentration of constituents present.

1.2 Analyses must be performed on dried and ground samples that either have been fused with a lithium metaborate-lithium tetraborate flux with the resulting bead dissolved in acidified deionized water or have been solubilized with a combination of nitric, hydrofluoric, and perchloric acids heated in open teflon beakers.

2. Summary of method

2.1 See method I-5473, metals, major, total in sediment; method I-5474, metals, major and minor, total in sediment; and method I-5475, metals, minor, total in sediment, for complete solubilization procedures.

2.1 After solubilization the solutions are analyzed by atomic absorption spectrometry.

Analytical methods

Acidity, electrometric titration

Parameters and Codes:
Acidity, I-1020-85 (mg/L as H^{+1}): 71825 (mg/L as $CaCO_3$): 00435

1. Application

This method is applicable to many acidic samples. When the sample is suspected or known to contain mostly weak acids, however, the construction of a neutralization curve is imperative, and the acidity value is reported and interpreted in terms of the character of the curve obtained.

2. Summary of method

2.1 Acidity is determined by titrating the sample with a standard solution of a strong base to an electrometrically observed end point pH of 8.3. The titration is carried out at room temperature, except that the sample is heated briefly near the end of the titration to increase the rate of hydrolysis of metal ions present.

2.2 For additional information concerning the determination of acidity and for instructions for constructing an electrometric titration curve, see ASTM Method D 1067-82, "Standard Methods of Test for Acidity or Alkalinity of Water," (American Society for Testing and Materials, 1984).

3. Interferences

Dissolved gases that are acidic, such as CO_2 and H_2S, may easily be lost from the sample. If any substantial part of the acidity is due to gaseous solutes, special care must be taken to prevent their escape prior to and during the titration. Gases are less soluble in warm water than in cold; hence, the sample must be kept chilled until analyzed, and even then the analysis must be performed as soon as possible. Stirring and agitation of the sample cause expulsion of dissolved gases; care must be taken to avoid unnecessary agitation of the sample. A tightly capped bottle is essential for storing and transporting samples. The determination should be performed at the time of sampling for greatest accuracy.

4. Apparatus

4.1 *Buret*, 50-mL capacity.

4.2 *Hotplate.*

4.3 *pH meter.*

4.4 *Stirrer*, magnetic.

5. Reagents

5.1 *Sodium hydroxide stock solution*, approx. 2*N*: Dissolve 80 g NaOH in carbon dioxide-free water and dilute to 1 L with carbon dioxide-free water. Store in a tightly capped polyethylene bottle.

5.2 *Sodium hydroxide standard solution*, approx. 0.025*N*: Dilute 12.5 mL 2*N* NaOH with carbon dioxide-free water to approx 1 L. Standardize the solution against primary standard potassium hydrogen phthalate ($KHC_8H_4O_4$) as follows: Lightly crush 3 g of the salt to a fineness of approx 100 mesh and dry for at least 1 h at 110°C. Dissolve about 2 g, accurately weighed to the nearest milligram, in carbon dioxide-free water and dilute to 500.0 mL. Titrate 50.0 mL of the solution with the NaOH standard solution to pH 8.6:

$$\text{Normality of NaOH} = \frac{\text{g } KHC_8H_4O_4 \text{ in 50.0 mL} \times 4.896}{\text{mL NaOH}}$$

6. Procedure

6.1 Samples should be collected in tightly capped polyethylene bottles, with as little agitation as possible, particularly if it is suspected or known that any significant part of the acidity is due to dissolved gases. Chill or otherwise keep the sample cool during transportation to the laboratory and perform the determination as soon as possible. Do not open the sample bottle until ready to determine the acidity, and then perform the determination without delay once the bottle has been opened.

6.2 Carefully pipet an aliquot of sample containing less than 1.0 mg H^{+1} (50.0 mL max) into a 150-mL beaker. Avoid disturbing any sediment in the sample bottle. Do not filter.

6.3 Insert the beaker in the titration assembly and record the pH.

6.4 Titrate the sample with standard NaOH solution to pH 8.3.

6.5 Heat the solution to about 90 °C (do not boil), and maintain this temperature for 2 min.

6.6 Cool to room temperature and resume the titration, titrating again to a final pH of 8.3. Record the total volume of titrant used (mL_b).

7. Calculations

7.1 Determine acidity as me/L as follows:

$$\text{Acidity, me/L} = \frac{mL_b}{mL_s} \times N_b \times 10^3$$

7.2 Determine acidity as hydrogen ion in mg/L as follows:

$$\text{Acidity, mg/L as } H^{+1} = \frac{mL_b}{mL_s} \times N_b \times 1.008 \times 10^3$$

7.3 Determine acidity as $CaCO_3$ in mg/L as follows:

$$\text{Acidity, mg/L as } CaCO_3 = \frac{mL_b}{mL_s} \times N_b \times 10^3 \times 50.05$$

where

mL_b and mL_s=volumes of standard NaOH solution and sample, respectively,

and

N_b=normality of standard NaOH solution.

8. Report

8.1 Report acidity values in milliequivalents per liter or milligrams per liter as hydrogen ion as follows: less than 10 me/L (mg/L), one decimal; 10 me/L (mg/L) and above, two significant figures.

8.2 Report acidity, hydrogen ion (71825), concentrations as milligrams per liter.

8.3 Report acidity, calcium carbonate (00435), concentrations in milligrams per liter as follows: less than 100 mg/L, whole numbers; 100 mg/L and above, two significant figures.

9. Precision

The precision for one sample expressed in both standard deviation and percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L as H^{+1})	Standard deviation (mg/L as H^{+1})	Relative standard deviation (percent)
21	26.0	0.9	3.5

Reference

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 125–133.

Alkalinity, electrometric titration

Parameter and Code:

Alkalinity, I-1030-85 (mg/L as $CaCO_3$): 00410

1. Application

This method is suitable for analyzing water with any amount of alkalinity, but aliquots for analysis should be taken to avoid a titration volume of standard acid in excess of 50 mL.

2. Summary of method

2.1 Alkalinity is determined by titrating the water sample with a standard solution of strong acid. The end point of the titration is selected as pH 4.5.

2.2 For waters that contain only small quantities of dissolved mineral matter, the alkalinity determination is likely the largest single source of error in the analysis. Alkalinity is very susceptible to change between time of collection and analysis, with changes occurring more rapidly after the sample bottle is opened. The overall alkalinity value is probably somewhat more stable than the relative values of the common alkalinity components. Unless a gross error is made in the initial determination of alkalinity, it is seldom advisable to try to check the results if several days have elapsed since the bottle was first opened. The alkalinity of some samples may change appreciably in a few hours. The determination should be performed at the time of sampling for highest accuracy.

2.3 Selection of pH 4.5 as the titration end point for determining total alkalinity is arbitrary and corresponds to the true equivalence point only under ideal conditions. The equivalence point of the bicarbonate-carbonic acid titration varies with the concentration of bicarbonate present; the deviation from pH 4.5 is particularly serious at low bicarbonate-ion concentrations. When greater accuracy in the determination is needed, the titration equivalence point may be determined for each sample by adding the titrant in small increments in the vicinity of pH 4.5 and by recording the pH of the solution after each measured addition. The true end point is then determined from either (1) a plot of pH versus total titrant volume, where the end point is the pH corresponding to a change in slope of the curve, or (2) a plot of

$$\frac{\delta \mathrm{pH}}{\Delta \mathrm{mL\ titrant}} \text{ versus titrant volume}$$

where the end point is that volume at which there occurs a maximum rate of change of pH per volume of titrant added.

2.4 There are other methods for arriving at a more reliable determination of total alkalinity. Barnes (1964) discusses the several factors involved in the accurate measurement of alkalinity, particularly under field conditions. A routine laboratory method for determining total alkalinity with improved accuracy for widely differing types of water has been described by Larson and Henley (1955) and further evaluated by Thomas and Lynch (1960). A rather complete consideration of carbonate equilibria and their analytic considerations may be found in a publication by Stumm and Morgan (1970).

3. Interferences

3.1 Any ionized substance that reacts with a strong acid can contribute to alkalinity if the reaction occurs at a pH above that of the specified end point; examples are salts of weak organic and inorganic acids.

3.2 Oils and greases, if present, may tend to foul the pH-meter electrode and prevent its proper operation.

4. Apparatus

4.1 *Buret*, 50-mL capacity.

4.2 *pH meter*.

4.3 *Stirrer*, magnetic.

5. Reagents

5.1 Sodium carbonate standard solution, 1.0 mL ≎ 1.00 mg HCO_3^{-1}: Dry 1.0 g primary standard Na_2CO_3 at 150 to 160°C for 2 h. Cool in a desiccator and dissolve 0.8685 g in carbon dioxide-free water; dilute to 1,000 mL.

5.2 *Sulfuric acid standard solution*, 0.01639*N*, 1.00 mL ≎ 1.00 mg HCO_3^{-1}: *Cautiously* add 0.5 mL concentrated H_2SO_4 (sp gr 1.84) to 950 mL water. (The titrant is stable for several months if protected from ammonia fumes and is usually prepared in larger quantities.) After the solution has been thoroughly mixed, standardize by titrating 25.00 mL Na_2CO_3 standard solution (1.00 mL ≎ 1.00 mg HCO_3^{-1}) to pH 4.5. Adjust the concentration of the sulfuric acid standard solution to exactly 0.01639*N* by dilution with water or by addition of dilute acid as indicated by the first titration. Confirm the exact normality by restandardization. Although the sulfuric acid standard solution is reasonably stable, its normality should be verified at least monthly (NOTE 1).

NOTE 1. Preparing standard sulfuric acid that is not exactly 0.01639*N* may be more convenient. Standard sulfuric acid that is approximately 0.01639*N* (but the exact normality of which is known) can be used if the appropriate factor is applied in the calculations.

6. Procedure

6.1 Water samples for the determination of alkalinity should not be filtered, diluted, concentrated, or altered in any way. The determination should be performed without delay after the sample bottle has been opened.

6.2 From a settled, unfiltered sample, pipet a volume containing less than 40 mg alkalinity as HCO_3^{-1} (50.0 mL max) into a suitable beaker.

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

7. Calculations

Total alkalinity as $CaCO_3$ in mg/L=

$$\frac{1{,}000}{\mathrm{mL}_s} \times 0.8202 \times (\mathrm{mL}_a \text{ to pH } 4.5)$$

where

mL_a and mL_s=volumes of standard acid and sample, respectively.

8. Report

Report alkalinity, total (00410), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

9.1 Precision for alkalinity for 36 samples within the range of 3.6 to 316 mg/L calcium carbonate may be expressed as follows:

$$S_T = 0.034X + 1.93$$

where

S_T= overall precision, milligrams per liter, and

X= concentration of alkalinity as $CaCO_3$, milligrams per liter.

The correlation coefficient is 0.5308.

9.2 Precision for alkalinity for six of the 36 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L as $CaCO_3$)	Relative standard deviation (percent)
25	3.6	25
14	56.7	11
27	107	13
31	119	3
30	183	6
26	316	2

References

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535-H, 17 p.

Larson, T. E., and Henley, Laurel, 1955, Determination of low alkalinity or acidity in water: Analytical Chemistry, v. 27, p. 851-2.

Stumm, Werner, and Morgan, J. J., 1970, Aquatic Chemistry: New York, John Wiley and Sons, 583 p.

Thomas, J. F. J., and Lynch, J. J., 1960, Determination of carbonate alkalinity in natural waters: American Water Works Association Journal, v. 52, p. 259-68.

Alkalinity, electrometric titration, automated

Parameter and Code:

Alkalinity, I-2030-85 (mg/L as $CaCO_3$): 00410

1. Application

This method is suitable for analyzing water with any amount of alkalinity. Sample aliquots for analysis and maximum titration volume of standard acid will depend on specifications in the manufacturer's instruction manual.

2. Summary of method

2.1 Alkalinity is determined by titrating the water sample with a standard solution of a strong acid. The end point of the titration is selected as pH 4.5.

2.2 For additional information on the principles of the method see alkalinity (I-1030).

3. Interferences

See alkalinity (I-1030).

4. Apparatus

4.1 *Automatic titrator*, with potentiometric assembly.

4.2 *Combination electrode* (glass and reference). Separate glass and reference electrodes are also satisfactory.

5. Reagents

5.1 *Sodium carbonate standard solution*, 1.00 mL ≎ 1.00 mg HCO_3^{-1}: Dry 1 g primary standard Na_2CO_3 at 150 to 160 °C for 2 h. Cool in a desiccator and dissolve 0.8685 g in carbon dioxide-free water; dilute to 1,000 mL.

5.2 *Sulfuric acid standard solution*, 0.01639*N*, 1.00 mL ≎ 1.00 mg HCO_3^{-1}: *Cautiously* add 0.5 mL concentrated H_2SO_4 (sp gr 1.84) to 950 mL water. (The titrant is stable for several months if protected from ammonia fumes, and it is usually prepared in larger quantities.) After the solution has been thoroughly mixed, standardize by titrating 25.00 mL Na_2CO_3 standard solution (1.00 mL ≎ 1.00 mg HCO_3^{-1}) to pH 4.5. Adjust the concentration of the sulfuric acid standard solution to exactly 0.01639*N* by dilution with water or by addition of dilute acid as indicated by the first titration. Confirm the exact normality by restandardization. Although the sulfuric acid standard solution is reasonably stable, its normality should be verified at least monthly (NOTE 1).

NOTE 1. Preparing standard sulfuric acid that is not exactly 0.01639*N* may be more convenient. Standard sulfuric acid that is approximately 0.01639*N* (but the exact normality of which is known) can be used if the appropriate factor is applied in the calculations.

6. Procedure

6.1 Water samples for the determination of alkalinity should not be filtered, diluted, concentrated, or altered in any way. The determination should be performed without delay after the sample bottle has been opened.

6.2 Set up the automatic titrator according to the directions given in the instruction manual.

6.3 From a settled, unfiltered sample, transfer or pipet a volume of sample to the vessel specified by the manufacturer.

6.4 Set the end point to pH 4.5 following the instructions provided with the instrument.

6.5 Place the samples in position in the titration assembly and activate the automatic potentiometric titration, using 0.01639*N* H_2SO_4 as titrant. Continue titrations until all samples have been titrated.

7. Calculations

Total alkalinity as $CaCO_3$ (mg/L)=

$$\frac{1{,}000}{mL_s} \times 0.8202 \times (mL_a \text{ to pH } 4.5)$$

where

mL_a and mL_s= volumes of standard acid and sample, respectively.

8. Report

Report alkalinity, total (00410), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

9.1 The standard deviation for alkalinity within the range of 18.4 to 303 mg/L for 17 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 6.7 mg/L ranged from 5.8 to 7.9 mg/L.

9.2 Precision for alkalinity for five of the 17 samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L as $CaCO_3$)	Relative std. deviation (percent)
7	18.4	13
3	101	17
3	101	2
5	151	12
10	303	2

Aluminum, atomic emission spectrometric, d-c plasma

Parameters and Codes:

Aluminum, dissolved, I-1054-85 (μg/L as Al): 01106
Aluminum, total recoverable, I-3054-85 (μg/L as Al): 01105
Aluminum, suspended recoverable, I-7054-85 (μg/L as Al): 01107

1. Application

1.1 This method may be used to analyze finished water, natural water, industrial water, and water-suspended sediment containing from 10 to 1000 μg/L of aluminum. Samples containing more than 1000 μg/L aluminum and (or) with specific conductances greater than 10,000 μS/cm need to be diluted.

1.2 Suspended recoverable aluminum is calculated by subtracting dissolved aluminum from total recoverable aluminum.

1.3 Total recoverable aluminum in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

2. Summary of method

Aluminum is determined by a direct-reading emission spectrometer which utilizes a d-c argon plasma as an excitation source (Johnson and others, 1979 a,b, 1980). A mixture of lithium chloride, sulfuric acid, and glycerin is added to samples and standards to provide a common background matrix and to compensate for viscosity changes. The liquid mixture is then converted by a ceramic nebulizer into a fine aerosol and introduced into the plasma via a plastic spray chamber and Pyrex injection tube. Aluminum is determined on the basis of the average of two replicate exposures, each of which is performed on a 10-second integrated intensity. Calibration is performed by standardization with a high-standard solution and a blank.

3. Interferences

Stray-light effects in a high-resolution, single-element d-c argon plasma emission spectrometer are negligible.

4. Apparatus

4.1 Spectrometer, Spectrometrics, Spectrospan IV with d-c argon plasma or equivalent, with Echelle optics, printer, autosampler, and periastaltic pump.

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

Plasma viewing position	+1 (fig. 9)
Gas ----------------	Argon
Sleeve pressure ------	50 psi
Nebulizer pressure ---	25 psi
Entrance slit --------	25×300 μm
Exit slit ------------	50×300 μm
Voltage -------------	1000 V
Wavelength ---------	308.215 nm
Signal amplification --	40- to 60-percent full-scale (1000 μg/L)

5. Reagents

5.1 *Aluminum standard solution I*, 1 mL= 100 μg Al: Dissolve 0.100 g aluminum powder in a minimun of 6*M* HCl using a Teflon beaker. Heat to increase rate of dissolution. Add 10.0 mL 6*M* HCl and dilute to 1,000 mL with demineralized water. Store in plastic bottle.

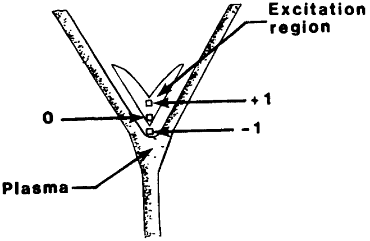

Figure 9.—Plasma position on entrance slit for aluminum

5.2 *Aluminum standard solution II,* 1.00 mL=10.0 μg Al: Dilute 100.0 mL aluminum standard solution I to 1000 mL with demineralized water. Store in plastic bottle.

5.3 *Aluminum working standard,* 1.00 mL= 1.00 μg Al: Dilute 100.0 mL aluminum standard solution II to 1000 mL with demineralized water. Store in plastic bottle.

5.4 *Glycerin,* USP.

5.5 *Hydrochloric acid,* concentrated (sp gr 1.19), Ultrex or equivalent.

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

5.7 *Lithium chloride,* LiCl, reagent-grade.

5.8 *Matrix modifier:* Dissolve 367 g LiCl in 1,000 mL demineralized water. Allow the solution to cool. Transfer to a 4-L polyethylene container, and add with stirring 2,000 mL of glycerin. In a Teflon beaker slowly add with stirring 400 mL concentrated H_2SO_4 to 400 mL demineralized water. When the dilute acid has reached room temperature, add the acid slowly, with stirring, to the glycerin-LiCl mixture. Dilute to 4,000 mL with demineralized water.

5.9 *Sulfuric acid,* concentrated (sp gr 1.84), Ultrex or equivalent.

6. Procedure

6.1 Pipet 10.0 mL sample into a disposable plastic test tube.

6.2 Pipet 100 mL demineralized-water blank and working standard into plastic bottles.

6.3 Add 2.0 mL matrix modifier to the sample and 20.0 mL to the blank and working standard.

6.4 Place plastic caps on the tube and bottles and mix well.

6.5 Refer to manufacturer's manual for computer-operating and wavelength-optimization procedures. Use the prepared blank and aluminum working standard for instrument calibration and all subsequent recalibrations.

6.6 Refer to manufacturer's manual for autosampler-operating procedures. Pour samples in autosampler tray, positioning a blank and working standard after every 3 samples for recalibration. Begin analysis (NOTE 1).

NOTE 1. Because of thermal instability inherent with the high-resolution spectrometer, repeak the analytical line if the aluminum standard drifts more than 3 percent.

7. Calculations

The computer system is designed so that the blank and the 1,000 μg/L of aluminum standard are used to establish a two-point calibration curve. The system will convert instrument intensity readings to analytical concentrations. The printer display includes the blank and working-standard instrument intensity readings, blank and standard concentrations, sample instrument intensity readings, sample concentrations, average of sample concentrations, and standard deviation.

8. Report

Report aluminum, dissolved (01106), total-recoverable (01105), and suspended-recoverable (01107), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

9.1 Precision, based on 14 to 18 determinations by a single operator during a 47-day period, expressed in terms of standard deviation and percent relative standard deviation, is as follows:

Number of determinations	Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
17	12.9	1.9	14.7
14	30.5	3.0	9.8
14	73.1	8.9	12.2
15	132	11	8.3
18	221	6.0	2.7
18	437	18	4.1
18	763	32	4.2

9.2 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable aluminum will be greater than that reported for dissolved aluminum.

References

Johnson, G. W., Taylor, H. E., and Skogerboe, R. K., 1979a, Determination of trace elements in natural waters by the D.C. argon-plasma, multielement atomic emission spectrometer (DCP-MAES) technique: Spectrochimica Acta, v. 34B, p. 197–212.

______1979b, Evaluation of spectral interferences associated with a direct current plasma-multielement atomic emission spectrometer (DCP-MAES) system: Applied Spectroscopy, v. 33, p. 451–456.

______1980, Characterization of an interelement enhancement effect in a dc plasma atomic emission spectrometry system: Applied Spectroscopy, v. 34, p. 19–24.

Aluminum, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:
Aluminum, dissolved, I-1052-85 (μg/L as Al): 01106
Aluminum, total recoverable, I-3052-85 (μg/L as Al): 01105
Aluminum, suspended recoverable, I-7052-85 (μg/L as Al): 01107

1. Application

1.1 This method may be used to analyze water, brines, and water-suspended sediment containing from 10 to 1,000 μg/L of aluminum. Samples containing more than 1,000 μg/L should either be diluted prior to chelation-extraction or be analyzed by the atomic absorption spectrometric direct method.

1.2 Suspended recoverable aluminum is calculated by subtracting dissolved aluminum from total recoverable aluminum.

1.3 Total recoverable aluminum in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485 before being determined.

1.4 If the iron concentration of the sample exceeds 10,000 μg/L, determine aluminum by the atomic absorption spectrometric direct method.

2. Summary of method

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

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

3. Interferences

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

3.2 Manganese concentrations as great as 80,000 μg/L do not interfere if the turbidity in the MIBK extract is allowed to settle (preferably overnight).

3.3 Magnesium, as little as 25 mg/L, forms an insoluble chelate with 8-hydroxyquinoline at pH 8.0 and tends to coprecipitate aluminum 8-hydroxyquinolate. However, the magnesium 8-hydroxyquinolate forms rather slowly (approx 4 to 6 min); its interference can be avoided if the aluminum 8-hydroxyquinolate is extracted with MIBK immediately after the sample is buffered to pH 8.

4. Apparatus

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

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

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

5. Reagents

5.1 *Aluminum standard solution I*, 1.00 mL=100 μg Al: Dissolve 0.100 g Al powder in a minimun of 6*M* HCl. Heat to increase rate of dissolution. Add 10.0 mL 6*M* HCl and dilute to 1000 mL with demineralized water.

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

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

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

5.5 *Methyl isobutyl ketone* (MIBK).

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+9) and rinse with demineralized water immediately before use.

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

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

6.4 Add 2 mL 8-hydroxyquinoline solution and mix (NOTE 1).

NOTE 1. Proceed to paragraph 6.5 if only dissolved aluminum is to be determined. If total recoverable aluminum is to be determined, add 2.2 mL concentrated NH_4OH (sp gr 0.90) to the sample solutions that undergo digestion-solubilization (paragraph 1.3), and then proceed to paragraph 6.5.

6.5 Add 10 mL NH_4OH-$NH_4C_2H_3O_2$ buffer solution to *one* sample and *immediately* add 10.0 mL MIBK. Shake vigorously for 15 sec. Each sample must be treated individually to avoid interference from magnesium. Each remaining sample, blank, and standard is treated in a like manner.

6.6 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask (NOTE 2).

NOTE 2. If the layers do not separate, allow to stand overnight.

6.7 Aspirate the ketone layer of the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

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

7.2 To determine micrograms per liter of suspended recoverable aluminum, subtract dissolved-aluminum concentration from total-recoverable-aluminum concentration.

8. Report

Report aluminum, dissolved (01106), total-recoverable (01105), and suspended-recoverable (01107), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved aluminum within the range of 74 to 793 μg/L for 10 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 58.5 μg/L ranged from 47.8 to 77.0 μg/L.

9.2 Precision for dissolved aluminum for six of the 10 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
6	74	15
4	82	37
4	195	9
4	252	29
5	650	23
3	793	3

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable aluminum will be greater than that reported for dissolved aluminum.

References

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

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

Aluminum, atomic absorption spectrometric, direct

Parameters and Codes:

Aluminum, dissolved, I-1051-85, (µg/L as Al): 01106
Aluminum, total recoverable, I-3051-85 (µg/L as Al): 01105
Aluminum, suspended recoverable I-7051-85 (µg/L as Al): 01107
Aluminum, recoverable-from-bottom-material, dry wt, I-5051-85 (µg/g as Al): 01108

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 100 µg/L of aluminum. Sample solutions containing more than 5,000 µg/L need either to be diluted or to be read on a less expanded scale. Sample solutions containing less than 100 µg/L and brines need to be analyzed by the atomic absorption spectrometric chelation-extraction method, provided that the interference limits discussed in that method are not exceeded.

1.2 Suspended recoverable aluminum is calculated by subtracting dissolved aluminum from total recoverable aluminum.

1.3 This method may be used to analyze bottom material containing at least 5 µg/g of aluminum.

1.4 Total recoverable aluminum in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable aluminum in bottom materials needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

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

3. Interferences

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

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

4. Apparatus

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

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

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

5. Reagents

5.1 *Aluminum standard solution*, 1.00 mL = 100 µg Al: Dissolve 0.100 g Al powder in a minimum of 6*M* HCl. Heat to increase rate of dissolution. Add 10.0 mL 6*M* HCL and dilute to 1,000 mL with demineralized water.

5.2 *Aluminum working standards*, Prepare at least six working standards containing from 100 to 5,000 µg/L of Al by appropriate dilution of aluminum standard solution. Add 1.0 mL NaCl solution and 1.0 mL bis(2-ethoxyethyl)-ether for each 10 mL of working standard. Prepare fresh daily.

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

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

6. Procedure

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

6.2 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

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

7.2 To determine micrograms per liter of suspended recoverable aluminum, subtract dissolved-aluminum concentration from total-recoverable-aluminum concentration.

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

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

8. Report

8.1 Report aluminum, dissolved (01106), total-recoverable (01105), and suspended-recoverable (01107), concentrations as follows: less than 10,000 µg/L, nearest 100 µg/L; 10,000 µg/L and above, two significant figures.

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

9. Precision

9.1 Precision for dissolved aluminum for 17 samples within the range of 40 to 811 µg/L, may be expressed as follows:

$$S_T = 0.253X + 9.84$$

where

S_T= overall precision, micrograms per liter, and

X= concentration of aluminum, micrograms per liter.

The correlation coefficient is 0.7779.

9.2 Precision for dissolved aluminum for six of the 17 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
7	40	135
7	40	85
5	138	79
8	144	31
15	513	19
7	811	9

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable aluminum and for recoverable aluminum in bottom material will be greater than that reported for dissolved aluminum.

9.4 Precision for total recoverable aluminum expressed in terms of percent relative standard deviation for two water-suspended sediments is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
12	4450	13
7	5530	33

References

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

Aluminum, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:

Aluminum, total, I-5473-85 (mg/kg as Al): none assigned
Aluminum, total, I-5474-85 (mg/kg as Al): none assigned

2. Summary of method

2.1 A sediment is dried, ground, and homogenized. The sample is then treated and analyzed by one of the following techniques.

2.1.1 The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1000°C. The resulting bead is dissolved in acidified, boiling, demineralized water, and aluminum is determined by atomic absorption spectrometry. See method I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

2.1.2 The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker, heated on a hotplate at 200°C. Aluminum is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Antimony, atomic absorption spectrometric, hydride

Parameters and Codes:

Antimony, dissolved, I-1055-85 (μg/L as Sb): 01095
Antimony, total, I-3055-85 (μg/L as Sb): 01097
Antimony, suspended total, I-7055-85 (μg/L as Sb): 01096
Antimony, total-in-bottom material, dry wt, I-5055-85 (μg/g as Sb): 01098

1. Application

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

1.2 Suspended total antimony is calculated by subtracting dissolved antimony from total antimony.

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

1.4 Total antimony in water-suspended sediment may be determined after each sample has been thoroughly mixed by vigorous shaking and a suitable sample portion has been rapidly withdrawn from the mixture.

2. Summary of method

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

3. Interferences

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

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

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

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

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

4.3 *Stibine vapor analyzer* (fig. 10) consisting of ______

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

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

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

5. Reagents

5.1 *Antimony standard solution I*, 1.00 mL= 100 μg Sb: Dissolve 0.100 g Sb metal in a minimum amount of aqua regia. Add demineralized water to increase rate of dissolution and dilute to 1000 mL with demineralized water.

5.2 *Antimony standard solution II*, 1.00 mL=10.0 μg Sb: Dilute 50.0 mL antimony standard solution I to 500.0 mL with demineralized water.

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

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

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

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

5.7 *Sodium borohydride solution*, 4 g/100 mL: Dissolve 4 g $NaBH_4$ and 2 g NaOH in 100 mL demineralized water. Prepare fresh before each use.

5.8 *Stannous chloride solution*, 4.2 g/100 mL concentrated HCl: Dissolve 5 g $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl (sp gr 1.19). This solution is unstable. Prepare fresh daily.

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

6. Procedure

6.1 Follow instructions in paragraph 6.1.1 for water or water-suspended sediment and in paragraph 6.1.2 for bottom material.

6.1.1 Pipet a volume of well-mixed sample containing less than 1.5 μg Sb (100 mL max) into a 200-mL Berzelius beaker and dilute to 100 mL with demineralized water.

6.1.2 Weigh a portion of the prepared bottom-material sample containing less than 1.5 μg Sb (100 mg max); transfer to a 200-mL Berzelius beaker and add 100 mL demineralized water (NOTE 1).

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

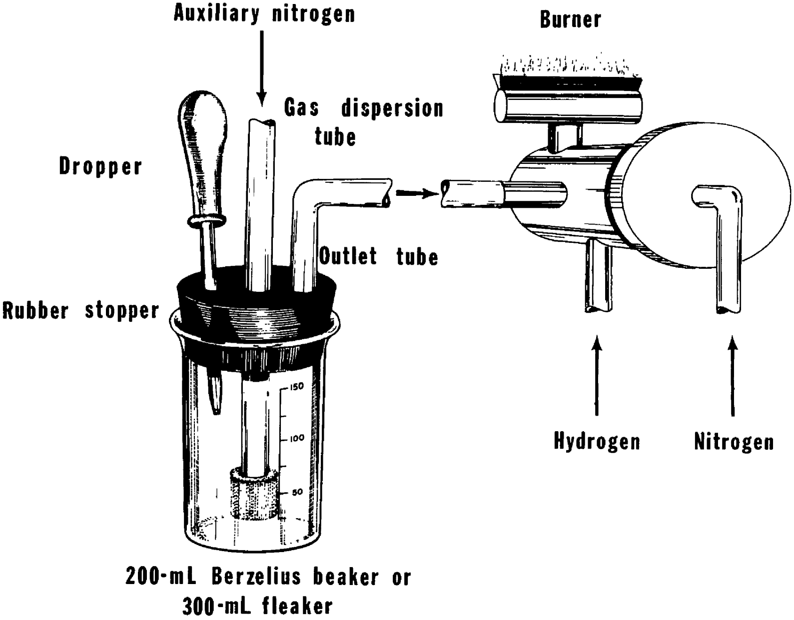

Figure 10.—Stibine vapor analyzer

6.2 Prepare, in 200-mL Berzelius beakers, a blank and sufficient standards containing from 0.1 to 1.5 μg Sb by diluting 1.0 to 15.0 mL portions of antimony standard solution III to 100 mL with demineralized water.

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

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

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

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

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

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

7. Calculations

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

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

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

7.3 To determine the concentration of suspended total antimony, subtract dissolved-antimony concentration from total-antimony concentration.

7.4 Determine the concentration of antimony in air-dried bottom material as follows:

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

8. Report

8.1 Report antimony, dissolved (01095), total (01097), and suspended-total (01096), concentrations as follows: less than 100 $\mu g/L$, nearest microgram per liter; 100 $\mu g/L$ and above, two significant figures.

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

9. Precision

9.1 Precision for dissolved antimony for seven samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean ($\mu g/L$)	Relative standard deviation (percent)
3	2.0	0
3	2.0	50
3	2.3	26
3	4.3	28
3	4.3	35
3	4.7	13
3	8.0	0

9.2 It is estimated that the percent relative standard deviation for total and suspended total antimony and for total antimony in bottom material will be greater than that reported for dissolved antimony.

Antimony, total-in-sediment, atomic absorption spectrometric, hydride

Parameter and Code:
Antimony, total, I-5475-85 (mg/kg as Sb): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Antimony is determined on the resulting solution by atomic absorption spectrometry. See method I-5475, metals, minor, total-in-sediment, atomic absorption spectrometric, hydride.

Arsenic, atomic absorption spectrometric, hydride

Parameters and Codes:3

Arsenic, dissolved, I-1062-85 (μg/L as As): 01000
Arsenic, total, I-3062-85 (μg/L as As): 01002
Arsenic, suspended total, I-7062-85 (μg/L as As): 01001
Arsenic, total-in-bottom-material, dry wt, I-5062-85 (μg/g as As): 01003

1. Application

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

1.2 Suspended total arsenic is calculated by subtracting dissolved arsenic from total arsenic.

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

1.4 Total arsenic in water-suspended sediment may be determined after each sample has been thoroughly mixed by vigorous shaking and a suitable sample portion has been rapidly withdrawn from the mixture.

1.5 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the strong-acid digestion, paragraphs 6.4 and 6.5 of the procedure.

2. Summary of method

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

3. Interferences

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

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

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

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

4.3 *Arsine vapor analyzer* (fig. 11) consisting of ——

4.3.1 *Beaker, Berzelius*, 200-mL capacity, or fleaker, 300-mL capacity.

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

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

5. Reagents

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

5.2 *Arsenic standard solution II*, 1.00 mL= 10.0 μg As: Dilute 5.00 mL arsenic standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 500.0 mL with demineralized water. Discard after 3 months.

5.3 *Arsenic standard solution III*, 1.00 mL= 0.10 μg As: Dilute 5.00 mL arsenic standard solution II and 1 mL concentrated HNO_3 (sp gr 1.41) to 500.0 mL with demineralized water. Prepare fresh weekly.

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

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

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

5.7 *Sodium borohydride solution*, 4 g/100 mL: Dissolve 4 g $NaBH_4$ and 2 g NaOH in 100 mL demineralized water. Prepare fresh before each use.

5.8 *Stannous chloride solution*, 33.6 g/100mL concentrated HCl: Dissolve 40g $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl. This solution is unstable. Prepare fresh daily.

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

6. Procedure

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

6.2 Follow instructions in paragraph 6.2.1 for water or water-suspended sediment and paragraph 6.2.2 for bottom material.

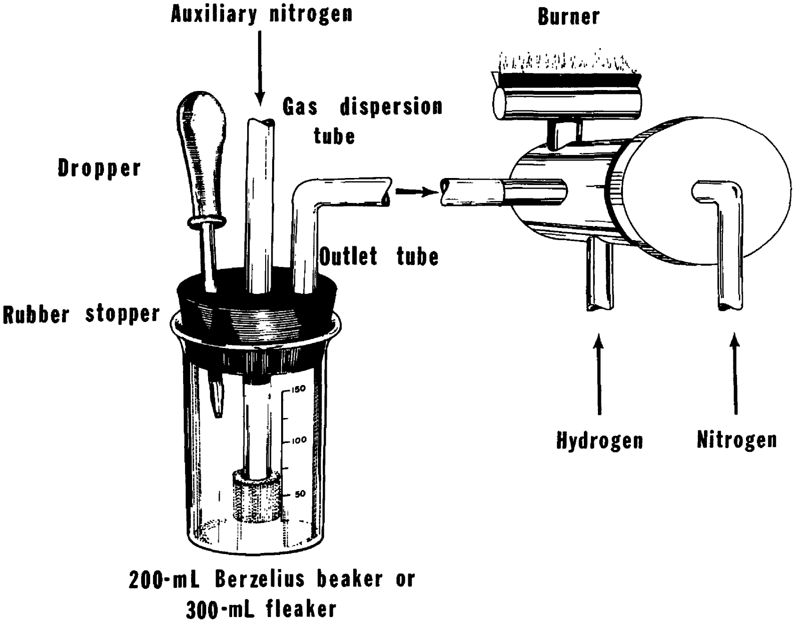

Figure 11.—Arsine vapor analyzer

6.2.1 Pipet a volume of well-mixed sample containing less than 1.0 μg As (50 mL max) into a 200-mL Berzelius beaker or 300-mL fleaker and dilute to 50 mL (NOTE 1).

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

6.2.2 Weigh a portion of prepared bottom-material sample containing less than 1 μg of As (100 mg max) (NOTE 2); transfer to a 200-mL Berzelius beaker or 300-mL fleaker and add 50 mL demineralized water (NOTE 1).

NOTE 2. Do not use more than 100 mg of bottom material to avoid severe bumping and loss of arsenic.

6.3 Prepare, in 200-mL Berzelius beakers or 300-mL fleakers, a blank, and sufficient standards containing from 0.1 to 1.0 μg As by diluting 1.0 to 10.0-mL portions of arsenic standard solution III. Dilute each to approx 50 mL.

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

NOTE 3. If only inorganic arsenic is to be determined, omit steps 6.4 and 6.5.

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

6.6 To each beaker, add successively, with thorough mixing after each addition, 8 mL concentrated HCl, 4 mL KI solution, and 1 mL $SnCl_2$ solution. Allow about 15 min for reduction of the arsenic to the tervalent state.

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

6.8 Fill the medicine dropper with 2 mL $NaBH_4$ solution and insert into the hole in the rubber stopper. Alternatively, the $NaBH_4$ solution may be delivered from an automatic pipettor.

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

7. Calculations

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

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

$$\text{As } (\mu g/L) = \mu g \text{ As in sample} \times \frac{1000}{\text{mL sample}}$$

7.3 To determine the concentration of suspended total arsenic, subtract dissolved-arsenic concentration from total-arsenic concentration.

7.4 Determine the concentration of arsenic in air-dried bottom-material samples as follows:

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

8. Report

8.1 Report arsenic, dissolved (01000), total (01002), and suspended-total (01001), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

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

9. Precision

9.1 Precision for dissolved arsenic for 14 samples within the range of 1.8 to 43.7 μg/L may be expressed as follows:

$$S_T = 0.262X + 0.346$$

where

S_T= overall precision, micrograms per liter, and

X= concentration of arsenic, micrograms per liter.

The correlation coefficient is 0.8801.

9.2 Precision for dissolved arsenic for five of the 14 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
5	1.8	61
7	10.9	30
8	19.5	32
6	41.7	18
6	43.7	35

9.3 It is estimated that the percent relative standard deviation for total and suspended arsenic and for total arsenic in bottom material will be greater than that reported for dissolved arsenic.

9.4 Precision for total arsenic for two water-suspended sediments expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
6	16	22
9	6.1	38

Arsenic, atomic absorption spectrometric, hydride, automated

Parameters and Codes:
Arsenic, dissolved, I-2062-85 (μg/L as As): 01000
Arsenic, total, I-4062-85 (μg/L as As): 01002
Arsenic, suspended total, I-7062-85 (μg/L as As): 01001
Arsenic, total-in-bottom-material, dry wt, I-6062-85 (μg/g as As): 01003

1. Application

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

1.2 Suspended total arsenic is calculated by subtracting dissolved arsenic from total arsenic.

1.3 This method may be used to analyze bottom material containing at least 1 μg/g of arsenic (NOTE 1). For samples containing more than 20 μg/g, use less sediment.

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

1.4 Bottom material may be analyzed by this procedure after it has been prepared as directed in method P-0520.

1.5 Total arsenic in water-suspended sediment may be determined after each sample has been thoroughly mixed by vigorous shaking and a suitable portion has been rapidly withdrawn from the mixture (NOTE 2).

NOTE 2. Do not use a sample containing more than 1 g/L sediment. Concentrations greater than 1 g/L cause erratic results.

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

2. Summary of method

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

2.2 For additional information on the determination of arsenic in water, see Pierce and others (1976), and Fishman and Spencer (1977).

3. Interferences

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

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

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

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

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

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

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

4.5 *Stripping-condensing column*, Pyrex, packed with 3- to 5-mm Pyrex beads (fig. 12). Cooling of the condensing column is not required. 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.

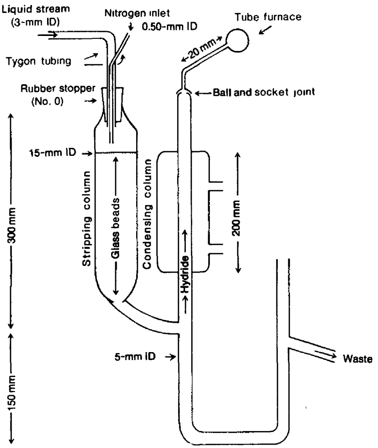

Figure 12.—Stripping-condensing column and quartz-tube furnace

4.6 *Tube furnace*, quartz, 10-mm ID×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 with stirrer, manifold, ultraviolet digestor (optional, NOTE 3), proportioning pump, and heating bath (optional, NOTE 4).

Heating-bath temperature --- 95°C.

NOTE 3. The ultraviolet digestor can be used only when determining dissolved arsenic; it cannot be used when analyzing water-suspended sediment or bottom material.

NOTE 4. The heating bath is used only in the acid-persulfate digestion procedure.

5. Reagents

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

5.2 *Arsenic standard solution II*, 1.00 mL=10.0 μg As: Dilute 5.00 mL arsenic standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 500.0 mL with demineralized water. Discard after 3 months.

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

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

Arsenic standard solution III (mL)	Arsenic concentration (μg/L)
1.0	1
2.0	2
5.0	5
10.0	10
15.0	15
20.0	20

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

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

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

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

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

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

6. Procedure

6.1 Set up manifold-acid persulfate (fig. 13) or ultraviolet radiation (fig. 14). See NOTE 2.

6.2 Apply a voltage of 47 volts or more (variable autotransformer) as necessary to the tube furnace to maintain a constant temperature of 800°C. Monitor the tube-furnace temperature

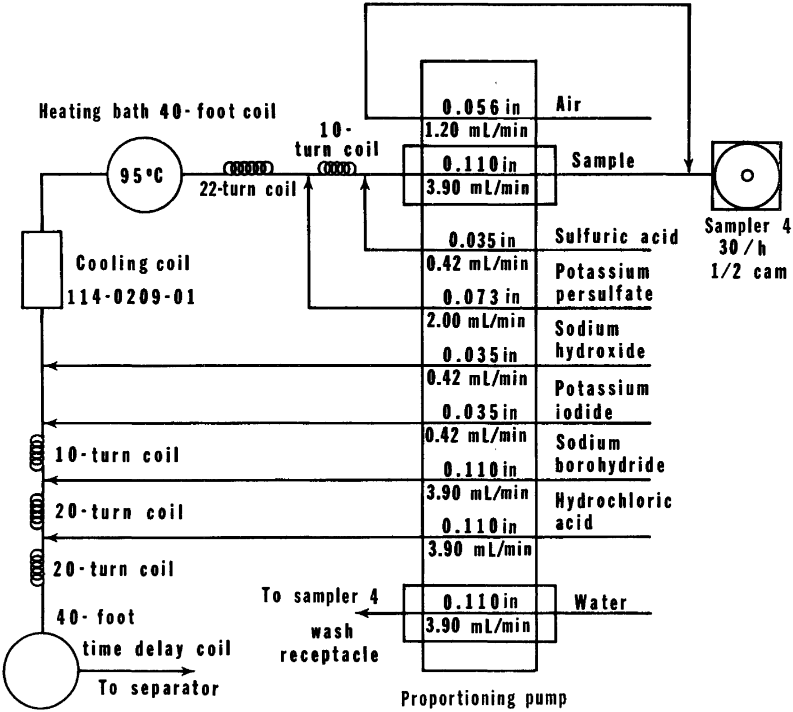

Figure 13.—Arsenic, acid-persulfate manifold

using portable pyrometer with the thermocouple placed in the middle of the tube.

6.3 If bottom-material samples are being analyzed, weigh 100 mg or less of bottom-material sample (2.0 μg As max), transfer to a 100-mL volumetric flask, and dilute to volume with demineralized water. Sample as directed for water and water-suspended sediment samples in paragraph 6.5 (NOTE 5).

NOTE 5. Bottom material may be manually digested using method I-5062 (arsenic, atomic absorption spectrometric) if standards and blank are treated identically. Adjust pH of digested solutions to between 2 and 3 before proceeding to paragraph 6.5.

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

6.5 Beginning with the most concentrated standard (NOTE 6), place a complete set of standards in the first positions of the first sample tray. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent trays. Fill remainder of each sample tray with unknown samples (well mixed).

NOTE 6. It is best to place two or three samples of the most concentrated standard at the beginning, since the first peak is usually low.

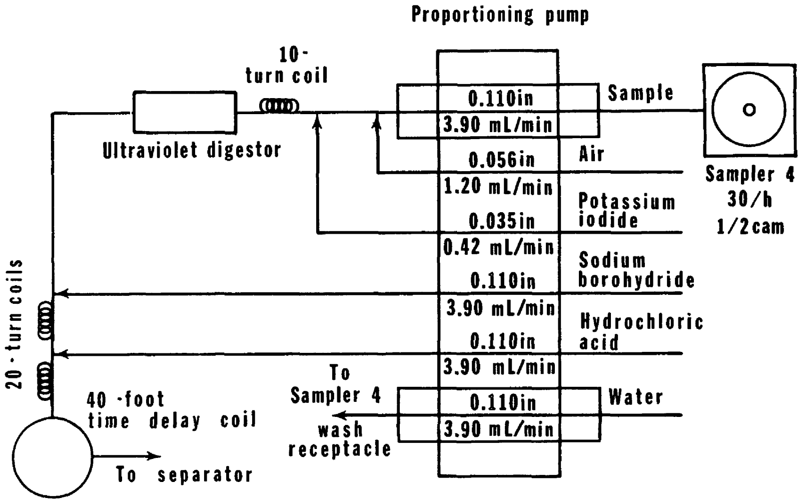

Figure 14.—Arsenic, ultraviolet radiation manifold

The first standard should not be used in any of the calculations.

6.6 Remove the sample line from the demineralized-water wash solution when the baseline stabilizes and begin the analyses (NOTE 7).

NOTE 7. When the analyses are complete, the tubes in the manifold and the separator-condensor column should be cleaned if any sediment is present.

6.7 With 10 mV recorder, 20 μg/L of arsenic 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:

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

6.7.2 Grind the cell with silicon carbide as follows: Mount cell with suitable cushioning in a ¾-in. 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 arsenic concentration.

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

7.3 To determine the concentration of suspended total arsenic, subtract dissolved-arsenic concentration from total-arsenic concentration.

7.4 To determine the concentration of arsenic in bottom-material samples, first determine the micrograms per liter of arsenic in each sample as in paragraph 7.2, then

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

8. Report

8.1 Report arsenic, dissolved (01000), total (01002), and suspended-total (01001), concentrations as follows: less than 10 µg/L, nearest microgram per liter; 10 µg/L and above, two significant figures.

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

9. Precision

9.1 Acid-persulfate digestion: Precision, for dissolved arsenic for replicate analysis by one operator expressed in terms of percent relative standard deviation, is as follows:

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

9.2 Ultraviolet radiation: Precision for dissolved arsenic for replicate analysis by one operator expressed in terms of percent relative standard deviation is as follows:

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

9.3 It is estimated that the percent relative standard deviation for total and suspended arsenic and for arsenic in bottom material will be greater than that reported for dissolved arsenic.

References

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

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

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

Arsenic, colorimetric, silver diethyldithiocarbamate

Parameters and Codes:

Arsenic, dissolved, I-1060-85 (μg/L as As): 01000
Arsenic, total, I-3060-85 (μg/L as As): 01002
Arsenic, suspended total, I-7060-85 (μg/L as As): 01001
Arsenic, total-in-bottom-material, dry wt, I-5060-85 (μg/g as As): 01003

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 5 to 200 μg/L of arsenic. Samples containing more than 200 μg/L need to be diluted.

1.2 Suspended total arsenic is calculated by subtracting dissolved arsenic from total arsenic.

1.3 This method may be used to analyze bottom material containing from 5 to 200 μg/g of arsenic. Usually, a 100-mg sample of prepared bottom material (method P-0520) is taken for analysis. If the sample contains more than 200 μg/g of arsenic, a smaller sample needs to be used.

1.4 Total arsenic in water-suspended sediment may be determined after each sample has been thoroughly mixed by vigorous shaking and a suitable sample portion has been rapidly withdrawn from the mixture.

1.5 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the strong-acid digestion, paragraphs 6.4 and 6.5 of the procedure.

2. Summary of method

2.1 Organic compounds are decomposed by adding sulfuric and nitric acids, and by repeatedly evaporating the samples to fumes of sulfur trioxide. The arsenic (V) so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsenic (III) by potassium iodide and stannous chloride, and finally to gaseous arsine by zinc in hydrochloric acid solution. The resultant mixture of gases is passed through a scrubber consisting of borosilicate glass wool impregnated with lead acetate solution, and into a gas absorber containing silver diethyldithiocarbamate (AgDDC) dissolved in pyridine. Arsine reacts with AgDDC to form a soluble red complex having maximum absorbance at about 535 nm. The absorbance of the solution is measured spectrophotometrically, and arsenic determined by reference to an analytical curve prepared from standards.

2.2 Additional information on the determination is given by Liederman and others (1959); by Ballinger and others (1962); by Stratton and Whitehead (1962); and by Fresenius and Schneider (1964).

3. Interferences

3.1 Some samples may contain sulfides; however, small quantities are effectively removed by a lead acetate scrubber. Several metals—cobalt, nickel, mercury, silver, platinum, copper, chromium, and molybdenum—interfere with the evolution of arsine. Antimony salts, under the reducing conditions in the generator, form stibine, which passes into the absorber and causes high results.

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

4. Apparatus

4.1 *Arsine generator, scrubber, and absorber* (fig. 15).

4.2 *Spectrophotometer*, for use at 535 nm.

4.3 Refer to the manufacturer's manual to optimize instrument.

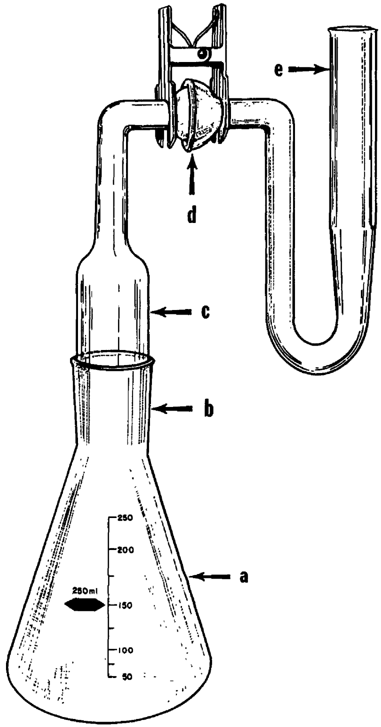

Figure 15.—Arsine generator, scrubber, and absorber

5. Reagents

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

5.2 *Arsenic standard solution II*, 1.00 mL= 10.0 μg As: Dilute 5.00 mL arsenic standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 500.0 mL with demineralized water. Discard after 3 months.

5.3 *Arsenic standard solution III*, 1.00 mL= 1.00 μg As: Dilute 10.0 mL arsenic standard solution II and 1 mL concentrated HNO_3 (sp gr 1.41) to 100.0 mL with demineralized water. Prepare fresh weekly.

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

5.5 *Lead acetate solution*, 8.6 g/100 mL: Dissolve 10 g $(CH_3COO)_2Pb\cdot3H_2O$ in 100 mL demineralized water. Keep tightly stoppered.

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

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

5.8 *Silver diethyldithiocarbamate (AgDDC) solution*, 0.5 g/100 mL: Dissolve 1 g $(C_2H_5)_2NCSSAg$ in 200 mL pyridine. This solution is stable when stored in an amber bottle.

5.9 *Stannous chloride solution*, 33.6 g/100 mL concentrated HCl: Dissolve 40 g arsenic-free $SnCl_2\cdot2H_2O$ in 100 mL concentrated HCl. This solution is unstable. Prepare fresh daily.

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

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

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+4) and rinse with demineralized water immediately before each use. The absorbers must also be rinsed with acetone and air-dried or briefly oven-dried.

6.2 Follow instructions in paragraph 6.2.1 for water or water-suspended sediment and in paragraph 6.2.2 for bottom material.

6.2.1 Pipet a volume of well-mixed sample containing less than 20 μg As (100 mL max) into the flask of an arsine generator. Rinse the pipet with demineralized water to remove adhering particles and combine with the sample. Dilute the sample to approx 100 mL if less than 100 mL is used.

6.2.2 Weigh a portion (NOTE 1) of prepared bottom-material sample (method P-0520) containing less than 20 μg As and transfer to the flask of an arsine generator. Add approx 100 mL demineralized water.

NOTE 1. The sample weight must not exceed 100 mg; otherwise severe bumping and loss of arsenic may occur.

6.3 Prepare a blank and sufficient standards (20 μg As max), and adjust the volume of each to approx 100 mL with demineralized water.

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

6.5 Cool, and adjust the volume to approx 100 mL. (NOTE 2).

NOTE 2. If only inorganic arsenic is to be determined, omit steps 6.4 and 6.5.

6.6 To each flask add successively, with thorough mixing after each addition, 10 mL concentrated HCl, 4 mL KI solution, and 1 mL $SnCl_2$ solution. Allow about 15 min for reduction of the arsenic to the tervalent state.

6.7 Place in each scrubber a plug of borosilicate glass wool that has been impregnated with lead acetate solution. Assemble the generator, scrubber, and absorber, making certain that all parts fit and are correctly adjusted. Add 3.00 mL silver diethyldithiocarbamate-pyridine solution to each absorber. Add glass beads to the absorbers until the liquid just covers them.

6.8 Disconnect each generator, add 6 g granular zinc, and reconnect immediately.

6.9 Allow 30 min for complete evolution of the arsine. Warm the generator flasks for a few minutes to make sure that all the arsine is released, and then pour the solutions from the absorbers directly into the spectrophotometer's cells. Determine the absorbances of the standards and samples against the blank without unnecessary delay, as the color developed is not permanent.

7. Calculations

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

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

$$\text{As } (\mu\text{g/L}) = \frac{1000}{\text{mL sample}} \times \mu\text{g As in sample}$$

7.3 To determine the concentration of suspended total arsenic, subtract dissolved-arsenic concentration from total-arsenic concentration.

7.4 Determine the concentration of arsenic in bottom-material samples as follows:

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

8. Report

8.1 Report arsenic, dissolved (01000), total (01002), and suspended-total (01001), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

8.2 Report arsenic, total-in-bottom-material (01003), concentrations as follows: less than 100 μg/g, to the nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved arsenic for 22 samples within the range of 2.7 to 109 μg/L may be expressed as follows:

$$S_T = 0.225X + 2.426$$

where

S_T= overall precision, micrograms per liter, and

X= concentration of arsenic, micrograms per liter.

The correlation coefficient is 0.9430.

9.2 Precision for dissolved arsenic for five of the 22 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
3	2.7	85
12	9.8	42
7	21.0	26
10	40.0	40
16	109	24

9.3 It is estimated that the percent relative standard deviation for total and suspended arsenic and for total arsenic in bottom material will be greater than that reported for dissolved arsenic.

References

Ballinger, D. G., Lishka, R. J., and Gales, M. E., 1962, Application of the silver diethyldithiocarbamate method to the determination of arsenic: American Water Works Association Journal, v. 54, p. 1424-1428.

Fresenius, W., and Schneider, W., 1964, Determination of slight amounts of arsenic with silver diethyldithiocarbamate in water analysis: Journal of Analytical Chemistry, v. 203, p. 417-422.

Liederman, D., Bowen, J. E., and Milner, O. I., 1959, Determination of arsenic in petroleum stocks and catalysts by evolution of arsine: Analytical Chemistry, v. 31, p. 2052-5.

Stratton, G., and Whitehead, H. E., 1962, Colorimetric determination of arsenic in water with silver diethyldithiocarbamate: American Water Works Association Journal, v. 54, p. 861-4.

Arsenic, total-in-sediment, atomic absorption spectrometric, hydride

Parameter and Code:

Arsenic, total, I-5475-85 (mg/kg as As): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Arsenic is determined on the resulting solution by atomic absorption spectrometry. See method I-5475, metals, minor, total-in-sediment, atomic absorption spectrometric, hydride.

Barium, atomic absorption spectrometric, direct

Parameters and Codes:

Barium, dissolved, I-1084-85 (μg/L as Ba): 01005 Barium, total recoverable, I-3084-85 (μg/L as Ba): 01007
Barium, suspended recoverable, I-7084-85 (μg/L as Ba): 01006
Barium, recoverable-from-bottom-material, dry wt, I-5084-85 (μg/g as Ba): 01008

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 100 μg/L of barium. Sample solutions containing more than 5000 μg/L need to be diluted.

1.2 Suspended recoverable barium is calculated by subtracting dissolved barium from total-recoverable barium.

1.3 This method may be used to analyze bottom material containing at least 5 μg/g of barium.

1.4 Total recoverable barium in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable barium in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

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

3. Interferences

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

4. Apparatus

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

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

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

5. Reagents

5.1 *Barium standard solution*, 1.00 mL= 100 μg Ba: Dissolve 0.1516 g $BaCl_2 \cdot 2H_2O$, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Barium working standards*: Prepare a series of at least six working standards containing from 100 to 5,000 μg/L of barium by appropriate dilution of barium standard solution. Add 1.00 mL NaCl solution for each 10 mL of working standard. Similarly prepare a demineralized water blank. Prepare fresh daily.

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

6. Procedure

6.1 Add 1.0 mL NaCl solution to 10.0 mL sample solution and mix thoroughly.

6.2 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

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

7.2 To determine micrograms per liter of suspended recoverable barium, subtract dissolved-barium concentration from total-recoverable-barium concentration.

7.3 To determine micrograms per gram of barium in bottom-material samples, first determine the micrograms per liter of barium in each sample as in paragraph 7.1, then:

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

8. Report

8.1 Report barium, dissolved (01005), total-recoverable (01007), and suspended-recoverable (01006), concentrations as follows: less than 1,000 μg/L, nearest 100 μg/L; 1,000 μg/L and above, two significant figures.

8.2 Report barium, recoverable-from-bottom-material (01008), concentration as follows: less than 100 μg/g, nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved barium within the range of 43 to 800 μg/L for 17 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 93.5 μg/L ranged from 85.3 to 103.2 μg/L.

9.2 Precision for dissolved barium for five of the 17 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
13	43	70
17	112	53
18	294	32
9	756	7
6	800	0

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable barium and for recoverable barium in bottom material will be greater than that reported for dissolved barium.

9.4 Precision expressed in terms of percent relative standard deviation for total recoverable barium for two water-suspended sediments is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
12	91.7	86
10	172	40

Barium, atomic emission spectrometric, ICP

Parameter and Code:

Barium, dissolved, I-1472-85 (μg/L as Ba): 01005

2. Summary of method

Barium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Beryllium, atomic absorption spectrometric, direct

Parameters and Codes:

Beryllium, dissolved, I-1095-85 (μg/L as Be): 01010
Beryllium, total recoverable, I-3095-85 (μg/L as Be): 01012
Beryllium, suspended recoverable, I-7095-85 (μg/L as Be): 01011
Beryllium, recoverable-from-bottom-material, dry wt, I-5095-85 (μg/g as Be): 01013

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 10 μg/L of beryllium. Sample solutions containing more than 200 μg/L need to be diluted.

1.2 Suspended recoverable beryllium is calculated by subtracting dissolved beryllium from total recoverable beryllium.

1.3 This method may be used to analyze bottom material containing at least 0.5 μg/g of beryllium.

1.4 Total recoverable beryllium in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable beryllium in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

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

3. Interferences

3.1 Beryllium is slightly ionized in the nitrous oxide-acetylene flame; to control this effect, calcium chloride solution must be added to each standard and sample.

3.2 Bicarbonate ion interferes; however, this interference is of no consequence if samples preserved by the addition of acid are used for the analysis.

3.3 Aluminum at concentrations greater than 500 μg/L has been reported to depress the beryllium absorbance.

3.4 Sodium and silicon at concentrations in excess of 1000 mg/L have been reported to severely depress the beryllium absorbance (Environmental Protection Agency, 1979).

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	234.9 nm
Source (hollow-cathode lamp)	Beryllium
Burner	Nitrous oxide
Oxidant	Nitrous oxide
Fuel	Acetylene
Type of flame	Fuel-rich

5. Reagents

CAUTION: Beryllium compounds and samples with high concentrations of beryllium should be handled with care; they may be carcinogenic.

5.1 *Beryllium standard solution I*, 1.00 mL=100 μg Be: Dissolve 0.1000 g Be 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 1000 mL with demineralized water.

5.2 *Beryllium standard solution II*, 1.00 mL=10.0 μg Be: Dilute 100.0 mL beryllium standard solution I to 1,000 mL with demineralized water.

5.3 *Beryllium working standards*: Prepare a series of at least six working standards containing from 10 to 200 µg/L beryllium by appropriate dilution of beryllium standard solution II. Add 1.0 mL $CaCl_2$ solution for each 10.0 mL of working standard. Similarly prepare a demineralized water blank. Prepare fresh daily.

5.4 *Calcium chloride solution,* 27.8 g/L: Suspend 25 g $CaCO_3$ in demineralized water and dissolve with a minimun of dilute HCl. Dilute to 1 L with demineralized water.

6. Procedure

6.1 Add 1.0 mL $CaCl_2$ solution to 10.0 mL sample solution and mix thoroughly.

6.2 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable beryllium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing concentrations of beryllium that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per liter of suspended recoverable beryllium, subtract dissolved-beryllium concentration from total-recoverable-beryllium concentration.

7.3 To determine micrograms per gram of beryllium in bottom-material samples, first determine the micrograms per liter of beryllium in each sample as in paragraph 7.1, then:

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

8. Report

8.1 Report beryllium, dissolved (01010), total-recoverable (01012), and suspended-recoverable (01011), concentrations as follows: less than 1,000 µg/L to the nearest 10 µg/L.

8.2 Report beryllium, recoverable-from-bottom-material (01013), as follows: less than 10 µg/g, nearest microgram per gram; 10 µg/g and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved beryllium within the range of 5.4 to 70 µg/L for 17 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 4.11 µg/L ranged from 3.6 to 4.9 µg/L.

9.2 Precision for dissolved beryllium for four of the 17 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
8	5.4	54
8	20.8	19
11	47.7	9
3	70.0	0

9.3 It is estimated that the percent relative standard deviation for total-recoverable and suspended recoverable beryllium and for recoverable beryllium in bottom material will be greater than that reported for dissolved beryllium.

9.4 Precision for total recoverable beryllium expressed in terms of percent relative standard deviation for two water-suspended sediments is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
4	22.5	27
5	64.2	7

Reference

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes, Cincinnati, p. 210.1-1.

Beryllium, atomic emission spectrometric, ICP

Parameter and Code:

Beryllium, dissolved, I-1472-85 (μg/L as Be): 01010

2. Summary of method

Beryllium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Boron, atomic emission spectrometric, d-c plasma

Parameter and Code:

Boron, dissolved, I-1114-85 (µg/L as B): 01020

1. Application

This method may be used to analyze finished water, natural water, and industrial water containing from 10 to 1000 µg/L of boron. Samples containing more than 1000 µg/L boron and/or with specific conductances greater than 10,000 µS/cm need to be diluted.

2. Summary of method

Boron is determined by a direct-reading emission spectrometer that utilizes a d-c argon plasma as an excitation source (Johnson and others, 1979a, b, 1980). A mixture of lithium chloride, sulfuric acid, and glycerin is added to samples and standards to provide a common background matrix and to compensate for viscosity changes. The liquid mixture is then converted by a ceramic nebulizer into a fine aerosol and introduced into the plasma via a plastic spray chamber and Pyrex injection tube. Boron is determined on the basis of the average of two replicate exposures, each of which is performed on a 10 second integrated intensity. Calibration is performed by standardization with a high- standard solution and a blank.

3. Interferences

Stray-light effects in a high-resolution, single-element, d-c argon plasma emission spectrometer are found to be negligible.

4. Apparatus

4.1 *Spectrometer*, Spectrometrics, Spectrospan IV with d-c argon plasma or equivalent, with Echelle optics, printer, autosampler, and peristaltic pump.

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

Plasma viewing position	-1 (fig. 16)
Gas	Argon
Sleeve pressure	50 psi
Nebulizer pressure	25 psi
Entrance slit	25×300 µm
Exit slit	50×300 µm
Voltage	1000 V
Wavelength	249.773 nm
Signal amplification	40- to 60-percent full-scale (1000 µg/L)

5. Reagents

5.1 *Boron standard solution I*, 1.00 mL=100 µg B: Dissolve 0.5720 g high-purity H_3BO_3, dried over desiccant for 24 h, in demineralized water and dilute to 1000 mL. Store in plastic bottle.

5.2 *Boron standard solution II*, 1.00 mL=10.0 µg B: Dilute 100.0 mL boron standard solution I to 1000 mL with demineralized water. Store in plastic bottle.

5.3 *Boron working standard*, 1.00 mL=1.00 µg B: Dilute 100.0 mL boron standard solution II to 1000 mL with demineralized water. Store in plastic bottle.

5.4 *Glycerin*, USP.

5.5 *Lithium chloride*, LiCl, reagent-grade.

5.6 *Matrix modifier*: Dissolve 367 g LiCl in 1000 mL demineralized water. Transfer to a Teflon beaker and add, with stirring, 10.0 mL concentrated H_2SO_4. Heat the solution to 75 to 80 °C on a hotplate (asbestos padded) and slowly add 25 mL methyl alcohol. Stir rapidly for one hour to volatilize of excess methyl alcohol and any trimethyl borate that forms. Repeat the

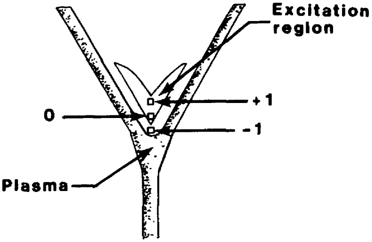

Figure 16.—Plasma position on entrance slit for boron

process two more times. Allow the solution to cool, transfer to a 4-L polyethylene container, and add with stirring 2000 mL glycerin. In a Teflon beaker slowly add, with stirring, 400 mL concentrated H_2SO_4 to 400 mL demineralized water. With stirring and cooling, add 50 mL methyl alcohol. The heat generated should be sufficient to volatilize excess methyl alcohol and any trimethyl borate. When the acid has reached room temperature, add the acid slowly, with stirring (in a hood), to the glycerin-LiCl mixture. Dilute to 4,000 mL with demineralized water.

5.7 *Methyl alcohol*, reagent-grade.

5.8 *Sulfuric acid*, concentrated (sp gr 1.84), Ultrex or equivalent.

6. Procedure

6.1 Pipet 10.0 mL sample into a disposable plastic test tube.

6.2 Pipet 100 mL demineralized-water blank and working standard into plastic bottles.

6.3 Add 2.0 mL matrix modifier to the sample and 20.0 mL to the blank and working standard.

6.4 Place plastic caps on the tube and bottles and mix well.

6.5 Refer to manufacturer's manual for computer-operating procedure. Use the prepared blank and working standard for instrument calibration and all subsequent recalibrations.

6.6 Refer to manufacturer's manual for autosampler-operating procedures. Pour samples in autosampler tray, positioning a blank and working standard after every five samples for recalibration. Begin analysis (NOTE 1).

NOTE 1. Because of thermal instability inherent with the high-resolution spectrometer, repeak the analytical line if the boron standard drifts more than 3 percent.

7. Calculations

The computer system is designed so that the blank and the 1000 μg/L of boron working standard are used to establish a two-point calibration curve. The system will convert instrument-intensity readings to analytical concentrations. The printer display includes the blank and working-standard instrument intensity readings, blank and standard concentrations, sample instrument intensity readings, sample concentrations, average of sample concentrations, and standard deviation.

8. Report

Report boron, dissolved (01020), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

Precision based on 12 determinations by a single operator expressed in terms of standard deviation and percent relative standard deviation is as follows:

Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
30.8	1.8	5.8
40.8	1.8	4.4
215	5.0	2.3
425	1.3	0.3

References

Johnson, G. W., Taylor, H. E., and Skogerboe, R. K., 1979a, Determination of trace elements in natural waters by the D.C. Argon-plasma, multielement atomic emission spectrometer (DCP-MAES) technique: Spectrochimica Acta, v. 34B, p. 197–212.

______1979b, Evaluation of spectral interferences associated with a direct current plasma-multielement atomic emission spectrometer (DCP-MAES) system: Applied Spectroscopy, v. 33, p. 451–456.

______1980, Characterization of an interelement enhancement effect in a dc plasma atomic emission spectrometry system: Applied Spectroscopy, v. 34, p. 19–24.

Boron, colorimetric, azomethine H, automated-segmented flow

Parameter and Code:

Boron, dissolved I-2115-85 (µg/L as B): 01020

1. Application

This method may be used to determine concentrations of boron in unacidified water in the range of 10 to 400 µg/L. Sample solutions containing more than 400 µg/L boron need to 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 measured colorimetrically at 410 nm (Basson and others, 1969; Basson and others, 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 to 5.

3. Interferences

Iron, zinc, and bicarbonate interfere at concentrations above 400 µg/L, 2000 µg/L, and 150 mg/L, respectively in the absence of pretreatment with DTPA 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 µg/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 water. Adjust the pH to 6.35 with 6*N* sulfuric acid and filter.

5.2 *Azomethine H synthesis*: Dissolve 18 g 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 2*M* KOH. While stirring continuously, add concentrated HCl (sp gr 1.19) until the pH is about 1.5. To the resulting mixture, add 20 mL salicylaldehyde and stir vigorously overnight (12 h). Centrifuge (2,000 rpm, 20 min) to separate the azomethine H (orange product) and wash 2 to 3 times with ethanol. Dry to constant weight at 100° C for 3 h and store in a desiccator.

5.3 *Azomethine H reagent*: Dissolve 4.5 g azomethine H and 10 g 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 dark plastic bottle. Hydrolysis of this compound, and, consequently, of 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: Dissolve 0.5720 g high-purity H_3BO_3, dried over desiccant for 24 h, in demineralized water and dilute to 1000 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 (µg/L)
0.0	0.0
5.0 of III	10.0
15.0 of III	30.0
25.0 of III	50.0
50.0 of III	100.0
100.0 of III	200.0
15.0 of II	300.0
20.0 of II	400.0

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

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

6. Procedure

6.1 Set up manifold (fig. 17).

6.2 Initially feed reagents with demineralized water in the sample line through the system and allow approx 30 min for stabilization of the baseline and instrument warmup. Adjust baseline to read 5 chart divisions on the recorder (25 µg/L on printer). It is necessary to include the reference channel in the manifold to compensate for baseline 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 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,

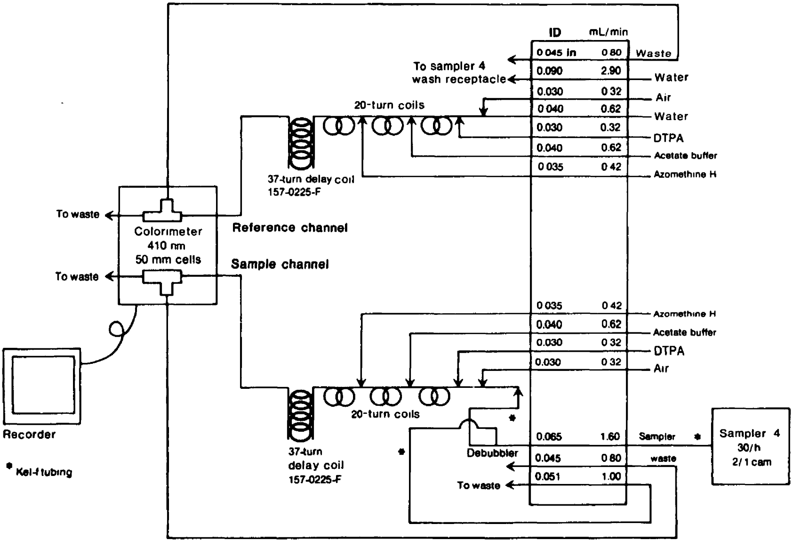

Figure 17.—Boron, azomethine H manifold

adjust the STD CAL control until the printer reads 425 μg/L on the 0- to 500-μg/L 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, minus 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, dissolved (01020), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

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

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

Number of replicates	Mean (μg/L)	Relative standard deviation (percent)
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.

Boron, colorimetric, curcumin

Parameters and Codes:

Boron, dissolved, I-1112-85 (μg/L as B): 01020
Boron, total recoverable, I-3112-85 (μg/L as B): 01022
Boron, suspended recoverable, I-7112-85 (μg/L as B): 01021

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 100 μg/L of boron. The optimum range for the method on undiluted or unconcentrated samples is from 100 to 1,000 μg/L.

1.2 Suspended recoverable boron is calculated by subtracting dissolved boron from total recoverable boron.

1.3 Total recoverable boron in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

2. Summary of method

2.1 When a sample of water containing boron is acidified and evaporated in the presence of curcumin, a red-colored product, called rosocyanine, is formed. The rosocyanine is extracted into a suitable solvent and the red color, which has a maximum absorbance at 540 nm, is measured spectrometrically.

2.2 The method is identical to that found in "Standard Methods for the Examination of Water and Wastewater" (American Public Health Association and others, 1980).

3. Interferences

3.1 Nitrate-nitrogen concentrations greater than 20 mg/L interfere.

3.2 Significantly high results are possible when the total of calcium and magnesium hardness exceeds 100 mg/L as calcium carbonate. Moderate hardness levels also can cause a considerable percentage error in the low boron range. The interference arises from the insolubility of the hardness salts in 95-percent ethanol and consequent turbidity in the final solution. Filter the final solution or pass the original sample through a column of strongly acidic cation-exchange resin in the hydrogen form to remove the interfering cations. The latter procedure enables application of the method to waters and effluents of high hardness or solids content.

4. Apparatus

4.1 *Evaporating dish*, 100- to 150-mL capacity, of Vycor glass, platinum, or other suitable material.

4.2 *Ion-exchange column*, 50-cm long by 1.3-cm diameter.

4.3 *Spectrometer*, for use at 540 nm, and cells with a minimun light-path length of 1 cm.

4.4 Refer to manufacturer's manual to optimize instrument.

4.5 *Water bath*, 55±2°C.

5. Reagents

5.1 *Boron standard solution I*, 1.00 mL=100 μg B: Dissolve 0.5720 g high-purity H_3BO_3, dried over desiccant for 24 h, in demineralized water and dilute to 1000 mL. Store in plastic bottle.

5.2 *Boron standard solution II*, 1.00 L=1.00 μg B: Dilute 10.0 mL boron standard solution I to 1,000 mL with demineralized water. Store in plastic bottle.

5.3 *Cation-exchange resin*: Load the column with a strongly acidic cation-exchange resin. Backwash the column with demineralized water to remove entrained air bubbles. Henceforth, make certain the resin remains covered with liquid at all times. Pass 50 mL 2*M* HCl through the column at a rate of 0.2 mL/min of acid per milliliter of resin in column and then wash it free of acid with demineralized water. The frequency of regeneration depends on the mineral content of the samples.

5.4 *Curcumin reagent*: Dissolve 40 mg finely ground curcumin (Eastman No. 1179 or equivalent) and 5.0 g oxalic acid in 80 mL 95-percent ethanol. Add 4.2 mL concentrated HCl (sp gr 1.19) and dilute to 100 mL with ethanol. The reagent is stable for several days if stored in a refrigerator.

5.5 *Ethanol*, 95-percent.

5.6 *Hydrochloric acid*, *2M*: Mix 166 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

6. Procedure

6.1 *Precautions*: Exercise close control of variables, such as volumes and concentrations of samples, standards, and, reagents, as well as time and temperature of drying. Use evaporating dishes identical in shape, size, and composition to insure equal evaporation time. Increasing the time of evaporation results in intensification of the resulting color.

6.2 For samples having high hardness (100 mg/L $CaCO_3$ or more), proceed as follows (NOTE 1): Pipet 25 mL of sample solution or of a smaller sample of known high boron content diluted to 25 mL onto the resin column. Adjust the rate of flow through the column to about 2 drops per second and collect the effluent in a 50-mL volumetric flask. Wash the column with small portions of demineralized water until the flask is full to the mark and mix.

NOTE 1. For samples containing less than 100 mg/L hardness as $CaCO_3$, start with paragraph 6.3.

6.3 Pipet 1.00 mL of sample solution containing less than 1.0 μg B into an evaporating dish (NOTE 2).

NOTE 2. If the sample contains more than 1,000 μg/L B, make an appropriate dilution with demineralized water, so that a 1.00-mL portion contains approx 0.50 μg B.

6.4 Prepare in evaporating dishes a blank and sufficient standards (1.0 μg B max) and adjust the volume of each to exactly 1.0 mL with demineralized water.

6.5 Add 4.0 mL curcumin reagent to each and swirl each dish gently to mix contents.

6.6 Float the dishes on a water bath set at 55±2°C and let them remain for 80 min, a time usually sufficient for complete drying and removal of HCl. Keep drying time constant for standards and samples.

6.7 After the dishes cool to room temperature, add 10.0 mL 95-percent ethanol to each dish, stirring gently with a polyethylene rod to ensure complete dissolution of the red-colored product.

6.8 Wash the contents of each dish into a 25-mL volumetric flask using 95-percent ethanol and adjust to volume with ethanol. Mix by repeated inversion (NOTE 3).

NOTE 3. If the final sample solution is turbid, filter through No. 30 Whatman filter paper or equivalent.

6.9 Determine the absorbance of samples and standards against the blank. Complete all absorbance readings within 1 h of drying the samples.

7. Calculations

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

7.2 Determine the dissolved or total-recoverable boron concentration in micrograms per liter as follows:

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

7.3 To determine micrograms per liter of suspended recoverable boron, subtract dissolved-boron concentration from total-recoverable-boron concentration.

8. Report

Report boron, dissolved (01020), total-recoverable (01022), and suspended-recoverable (01021), concentrations as follows: less than 1,000 μg/L, nearest 100 μg/L; 1,000 μg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved boron within the range of 65 to 643 μg/L for 16 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 63.4 μg/L ranged from 54.2 to 76.3 μg/L.

9.2 Precision for dissolved boron for four of the 16 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
4	65	37
5	98	60
4	320	20
6	643	10

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable boron will be greater than that reported for dissolved boron.

Reference

American Public Health Association and others, 1980, Standard methods for the examination of water and wastewater (15th ed.): Washington, D.C., p. 257.

Boron, colorimetric, dianthrimide

Parameters and Codes:

Boron, dissolved, I-1110-85 (μg/L as B): 01020
Boron, total recoverable, I-3110-85 (μg/L as B): 01022
Boron, suspended recoverable, I-7110-85 (μg/L as B): 01021
Boron, recoverable-from-bottom-material, dry wt, I-5110-85 (μg/g as B): 01023

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing between 20 and 1,000 μg/L of boron. Sample solutions containing more than 1,000 μg/L need to be diluted.

1.2 Suspended recoverable boron is calculated by subtracting dissolved boron from total recoverable boron.

1.3 This method may be used to analyze bottom material containing at least 10 μg/g of boron. If the sample solution prepared for analysis contains more than 250 μg boron, a portion of it needs to be diluted before analysis.

1.4 Total recoverable boron in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable boron in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

1.5 This method is not suitable for samples containing high concentrations of oxidizing or reducing materials or dissolved organic matter. However, it is not affected by buffering materials or high concentrations of total salts.

2. Summary of method

Boron, when heated with 1,1'-dianthrimide in concentrated sulfuric acid, gives a colored complex (Ellis and others, 1949; Rainwater, 1959). The color change ranges from greenish yellow to blue. The reaction producing the blue color depends on the temperature and duration of heating and on the concentrations of reagent and of boron. Maximum color development is achieved after the reaction has proceeded for 3 h at 90°C.

3. Interferences

3.1 Traces of moisture will precipitate the reagent and interfere in the determination; therefore, precautionary measures given in the procedure must be followed precisely. Nitrate and bicarbonate interfere with color development and must be removed by volatilization as nitric acid and carbon dioxide in the presence of sulfuric acid. Organic matter in high concentrations chars and causes a discoloration of the complex, but this interference is easily recognized; small quantities of organic material cause no trouble. Some success in removal of the organic-material interference has been obtained by heating the sample in the presence of hydrogen peroxide for 1 to 2 h, but all nascent oxygen *must* be volatilized before the dianthrimide is added to the sample. When peroxide digestion is used, the final color complex should be compared with standard boron solutions similarly treated. Oxidizing and reducing constituents also interfere. Do not use glassware cleaned with chromic-sulfuric acid.

3.2 Some boric acid is probably volatilized during evaporation of the sample in the presence of sulfuric acid. Prolonged heating or temperatures higher than that recommended volatilize an excessive amount of boron and decrease the sensitivity of the test. The loss of boron is proportional to the boron content of the sample or standard; hence, such loss in no way affects the linearity of the color development if the heating is uniform. Nonlinearity of the concentration-versus-absorbance curve can result from weak reagents. The standards in step 6.2 of the procedure act as a check on linearity of the reaction and on the suitability of the working reagent.

4. Apparatus

4.1 *Oven,* 90°C: Uniformity of temperature throughout the oven is imperative.

4.2 *Spectrometer,* for use at 620 nm.

4.3 Refer to the manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Boron standard solution I,* 1.00 mL=100 μg B: Dissolve 0.5720 g high-purity H_3BO_3, dried over desiccant for 24 h, in demineralized water and dilute to 1000 mL. Store in plastic bottle.

5.2 *Boron standard solution II,* 1.00 mL= 1.0 μg B: Dilute 10.0 mL boron standard solution I to 1,000 mL with demineralized water. Store in plastic bottle.

5.3 *1,1'-Dianthrimide (or 1,1'-iminodianthraquinone) solution I,* 200 mg per 50 mL concentrated H_2SO_4: Dissolve 200 mg 1,1'-dianthrimide in 50 mL concentrated H_2SO_4 (sp gr 1.84). The reagent is stable for a long period if the container is sealed and refrigerated. Store in Teflon bottle.

5.4 *1,1'-Dianthrimide solution II,* (1 + 19): Dilute 1 volume of 1,1'-dianthrimide solution I with 19 volumes of concentrated H_2SO_4 (sp gr 1.84). The reagent is stable for a long period if the container is sealed and refrigerated. Store in Teflon bottle.

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

6. Procedure

6.1 Pipet a volume of sample solution containing less than 5.0 μg B (5.0 mL max) into a Pyrex test tube, and adjust volume to 5.0 mL.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to 5.0 mL.

6.3 *Cautiously* add 1.0 mL concentrated H_2SO_4 and mix by swirling the contents of the tube. Use of a test-tube-vibrating mixer is helpful.

6.4 Evaporate for at least 40 h in an oven at 90°C. At the end of the evaporation, the solution volume should be between 1.0 and 0.5 mL.

6.5 Add 5.0 mL 1,1'-dianthrimide solution II and mix by swirling.

6.6 Heat in oven for 3 h at 90°C.

6.7 Immediately after cooling, *with caution* add 10.0 mL concentrated H_2SO_4. Mix carefully with a stirring rod or test-tube mixer.

6.8 Determine the absorbance of each sample and standard against the blank.

7. Calculations

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

7.2 Determine the dissolved or total-recoverable-boron concentration in micrograms per liter as follows:

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

7.3 To determine micrograms per liter of suspended recoverable boron, subtract dissolved-boron concentration from total-recoverable-boron concentration.

7.4 Determine the boron concentration in micrograms per gram in bottom material as follows:

$$B(\mu g/g) = \frac{\mu g\ B\ \text{in sample} \times \text{mL of original digest}}{\text{wt of sample (g)} \times \text{mL sample}}$$

8. Report

8.1 Report boron, dissolved (01020), total-recoverable (01022), and suspended-recoverable (01021), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

8.2 Report boron, recoverable-from-bottom-material (01023), concentrations as follows: less than 100 μg/g, nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved boron within the range of 20 to 530 μg/L for 16 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 37.2 μg/L ranged from 31.2 to 46.1 μg/L.

9.2 Precision for dissolved boron for five of the 16 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
5	20	105
6	101	17
5	222	24
3	423	3
4	530	12

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable boron and for total recoverable boron in bottom material will be greater than that reported for dissolved boron.

References

Ellis, G. H., Zook, E. G., and Baudisch, Oskar, 1949, Colorimetric determination of boron using 1,1'-dianthrimide: Analytical Chemistry, v. 21, p. 1345-8.

Rainwater, F. H., 1959, Determination of boron with 1,1'-dianthrimide: American Water Works Association Journal, v. 51, p. 1046-50.

Bromide, titrimetric, hypochlorite oxidation

Parameter and Code:

Bromide, dissolved, I-1125-85 (mg/L as Br): 71870

1. Application

This method may be used to analyze any natural or treated water or brine containing at least 1.0 mg/L of bromide. Highly concentrated brines may require dilution.

2. Summary of method

2.1 The determination of bromide involves the determination of bromide and iodide collectively, and then the determination of iodide alone; bromide is calculated by difference. Bromide and iodide are oxidized to bromate and iodate, respectively, by hypochlorite, and the excess hypochlorite is subsequently decomposed with sodium formate (Kolthoff and others, 1969).

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

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

Iodine equivalent to the combined iodate and bromate is then liberated by addition of potassium iodide to an acid solution.

$$BrO_3^{-1} + 6I^{-1} + 6H^{+1} \rightarrow 3I_2 + 3H_2O + Br^{-1}$$

$$IO_3^{-1} + 5I^{-1} + 6H^{+1} \rightarrow 3I_2 + 3H_2O$$

The liberated iodine is titrated with standard thiosulfate with use of starch as the indicator.

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

2.2 Iodide alone is determined by oxidation to iodate with bromine in a buffered solution. Iodine equivalent to the iodate is then liberated from added potassium iodide and titrated with thiosulfate as in the combined determination.

3. Interferences

Iron, manganese, and organic material interfere with the basic reactions of the method, but their interferences are removed by preliminary treatment with calcium oxide.

4. Apparatus

4.1 *Buret*, 10-mL capacity.

4.2 *Iodine flasks*, 250-mL capacity.

5. Reagents

5.1 *Acetic acid*, 2.2*M*: Mix 125 mL glacial $HC_2H_3O_2$ (sp gr 1.069) with demineralized water and dilute to 1 L.

5.2 *Bromine water*, saturated: Add to approx 250 mL demineralized water slightly more liquid Br_2 than will dissolve when mixed. Store in a glass-stoppered, actinic-glass bottle.

5.3 *Calcium carbonate*, powder, $CaCO_3$.

5.4 *Calcium oxide*, anhydrous powder, CaO.

5.5 *Hydrochloric acid*, 6*M*: Mix 50 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 100 mL.

5.6 *Methyl red indicator solution*, 0.01 g/100 mL: Dissolve 0.01 g water-soluble methyl red in 100 mL demineralized water.

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

5.8 *Potassium hypochlorite solution*, 4.4 g/L: Dissolve 6.2 g KOH in 100 mL demineralized water; then saturate the solution with bromine-free Cl_2 while continually cooling and stirring. Store in a glass-stoppered, actinic-glass bottle. Prepare fresh daily.

5.9 *Potassium iodide*, crystals, IO_3^{-1}-free: The KI can be tested for IO_3^{-1} by dissolving about 0.1 g in 5 mL demineralized water, acidifying with 1 or 2 drops concentrated H_2SO_4 (sp gr 1.84), and adding 2 to 3 mL starch indicator solution. Immediate appearance of a blue color indicates the presence of IO_3^{-1}; slow color formation is due to atmospheric oxidation.

5.10 *Sodium acetate solution*, 165 g/L: Dissolve 273 g $NaC_2H_3O_2 \cdot 3H_2O$ in demineralized water and dilute to 1 L.

5.11 *Sodium chloride*, crystals: Free from I^{-1}, IO_3^{-1}, Br^{-1}, and BrO_3^{-1}. The NaCl can be tested for IO_3^{-1} and BrO_3^{-1} by dissolving about 0.1 g in 5 mL demineralized water, acidifying with 1 or 2 drops concentrated H_2SO_4 (sp gr 1.84), and adding 2 to 3 mL starch indicator solution. Immediate appearance of a blue color indicates presence of IO_3^{-1} or BrO_3^{-1}; slow color formation is caused by atmospheric oxidation.

5.12 *Sodium formate solution*, 50 g/100 mL: Dissolve 50 g $NaHCO_2$ in hot demineralized water and dilute to 100 mL. Prepare fresh daily.

5.13 *Sodium molybdate solution*, 1.0 g/100 mL: Dissolve 1.2 g $Na_2MoO_4 \cdot 2H_2O$ in demineralized water and dilute to 100 mL.

5.14 *Sodium thiosulfate solution*, 0.10*N*: Dissolve 25.0 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free, demineralized water; add 1 g Na_2CO_3 and dilute to 1 L.

5.15 *Sodium thiosulfate standard solution*, 0.010*N*: Dilute 100.0 mL 0.10*N* $Na_2S_2O_3$ solution to 950 mL with carbon dioxide-free, demineralized water and standardize against KIO_3 as follows: Dry approx 0.5 g KIO_3 for 2 h at 180°C. Cool and dissolve 0.3567 g in demineralized water, and dilute to 1,000 mL. Pipet 25.00 mL of the KIO_3 solution into a 250-mL iodine flask; then add successively 75 mL demineralized water and 0.5 g KI crystals. After solution is complete, add 10 mL 3.6*M* H_2SO_4. Allow the stoppered flask to stand 5 min in the dark, and then titrate with standard $Na_2S_2O_3$ solution, adding 2 mL starch indicator solution as the end point is approached (light straw color).

$$\text{Normality of } Na_2S_2O_3 = \frac{0.25}{\text{mL } Na_2S_2O_3}$$

5.16 *Starch indicator solution*, stable or "thyodene," powdered (Fisher No. T138 or equivalent).

5.17 *Sulfuric acid*, 3.6*M*: CAUTIOUSLY add 200 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water, cool, and dilute to 1 L.

6. Procedure

6.1 Remove soluble iron, manganese, and organic matter by adding a slight excess of CaO to approx 400 mL sample; mix, let stand about 1 h, and filter through a dry, moderately retentive filter paper. Discard the first 75 mL of filtrate.

6.2 For the combined Br^{-1} and I^{-1} determination, pipet a volume of the filtrate containing less than 5.0 mg Br^{-1} and I^{-1} (100.0 mL max) into a 250-mL iodine flask, and adjust the volume to approx 100 mL.

6.3 Prepare a blank of approx 100 mL demineralized water, and carry it through the procedure along with the sample.

6.4 Add sufficient NaCl to produce a 3.0 g Cl^{-1} content.

6.5 Add a drop of methyl red indicator solution, and make the solution just acidic with 6*M* HCl.

6.6 Add 10 mL KClO solution, 0.5 mL 6*M* HCl, and sufficient $CaCO_3$ to produce an excess of approx 0.1 g.

6.7 Heat the solution to boiling and maintain this temperature for about 8 min.

6.8 Reduce the excess KClO by adding 2 mL $NaHCO_2$ solution, taking precaution to wash down the sides of the flask with a small amount of hot water. Keep the solution hot for an additional 8 min.

6.9 Cool and add several drops of Na_2MoO_4 solution. If any iron precipitates at this point, add 0.5 g $KF \cdot 2H_2O$.

6.10 Add approx 1 g KI and 10 mL 3.6*M* H_2SO_4, and let stand 5 min in the dark.

6.11 Titrate the liberated I_2 with 0.01*N* $Na_2S_2O_3$ standard solution, adding 2 to 3 mL starch indicator solution as the end point is approached. Disregard a return of the blue color after the end point has been reached.

6.12 For the I^{-1} determination, pipet a volume of filtrate (step 6.1) containing less than 5.0 mg I^{-1} (100.0 mL max) into a 250-mL iodine flask, and adjust the volume to approx 100 mL.

6.13 Prepare a blank of 100.0 mL demineralized water and carry through the procedure along with the sample.

6.14 Add a drop of methyl red indicator solution, and make the solution just acidic with 3.6*M* H_2SO_4.

6.15 Add 15.0 mL $NaC_2H_3O_2$ solution, 5.0 mL 2.2*M* $HC_2H_3O_2$, and sufficient bromine water to produce a light-yellow color; mix and allow to stand 5 min.

6.16 Reduce the excess Br_2 by adding $NaHCO_2$ solution drop by drop until the yellow tinge in the sample disappears; then add an excess of 1 mL.

6.17 Wash the sides of the flask with a small amount of water, and blow out Br_2 vapors with a syringe and a glass tube inserted into the mouth of the flask. If any iron precipitates at this point, add 0.5 g $KI{\cdot}2H_2O$.

6.18 Add approx 1 g KI and 10 mL 3.6*M* H_2SO_4, and let stand 5 min in the dark.

6.19 Titrate the liberated I_2 with 0.010*N* $Na_2S_2O_3$ standard solution, adding 2 to 3 mL starch indicator solution as the end point is approached (light-straw color). Disregard a return of the blue color after the end point has been reached.

7. Calculations

7.1 Determine $Br^{-1}+I^{-1}$ in epL as follows:

$$Br^{-1}+I^{-1}(\text{epL})= \frac{1{,}000}{\text{mL sample}} \times \frac{0.01}{6} \times (\text{mL}_t-\text{mL}_b)$$

where

epL= equivalents per liter,

mL_b= titrant volume for blank determination,

mL_t= titrant volume for combined determination,

and

mL_i= titrant volume for I^{-1} determination.

7.2 Determine I^{-1} in epL as follows:

$$I^{-1}(\text{epL})=\frac{1{,}000}{\text{mL sample}} \times \frac{0.01}{6} \times(\text{mL}_i-\text{mL}_b).$$

7.3 Determine Br^{-1} in mg/L as follows:

$$Br^{-1}(\text{mg/L})=79.91\times[\text{epL }(I^{-1}+Br^{-1})-\text{epL } I^{-1}]$$

8. Report

Report bromide, dissolved (71870), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

Single-operator precision of this method (American Society for Testing and Materials, 1984) may be expressed as follows:

$$S_o = 0.0044X$$

where

S_o= single-operator precision, milligrams per liter,

and

X= concentration of bromide, milligrams per liter.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 482-90.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative chemical analysis (4th ed.): New York, Macmillan, 1199 p.

Bromide, ion-exchange chromatographic, automated

Parameters and Codes:

Bromide, dissolved, I-2057-85 (mg/L as Br): 71870
Bromide, dissolved, I-2058-85 (mg/L as Br): 71870

2. Summary of method

Bromide is determined sequentially with six other anions by ion-exchange chromatography. Ions are separated based on their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical-conductivity cell. See method I-2057, anions, ion-exchange chromatographic, automated, and method I-2058, anions, ion-exchange chromatographic, low ionic-strength water, automated.

Bromide, ion-exchange chromatographic-electrochemical, automated

Parameter and Code:

Bromide, dissolved, I-2128-85 (mg/L as Br): 71870

1. Application

1.1 This method may be used to analyze atmospheric precipitation and natural water containing at least 0.01 mg/L of bromide. Samples containing more than 1 mg/L need to be diluted.

1.2 Analyses need to be performed on filtered and unacidified samples.

2. Summary of method

Bromide is determined with an ion chromatograph using an ion-exchange resin in combination with a specific eluent to separate the anions. After the solution has passed through the separator column, the sample stream flows through an electrochemical cell, where a fixed potential is applied. Any electroactive species such as bromide having an oxidation-reduction potential near the applied potential will generate a current, which is directly proportional to the concentration of the electroactive species.

3. Interferences

3.1 Chloride is an interference. When chloride ion passes through the detector, a current generates because of the formation of silver chloride on the surface of the silver-working electrode. The eluent stream, which removes silver chloride, generates a negative peak. The higher the chloride concentration, the longer it takes for the peak to return to baseline conditions. The effects of chloride at various levels of bromide are shown in tables 5 and 6. Chloride interferes with bromide if the chloride-to-bromide ratio is greater than 1,000:1 for the analytical range of 0.01 to 0.1 mg/L of bromide. A similar interference is present when the chloride-to-bromide ratio exceeds 5,000:1 for the 0.1 to 1.0 mg/L analytical range. Samples containing greater than 2,000 mg/L of chloride must first be diluted.

3.2 Sulfite elutes at almost the same time as bromide, however, this interference will not affect bromide since any sulfite in the sample will have had time to oxidize to sulfate before analysis. For example, 10 mg/L of sulfite usually oxidizes to sulfate within 120 h.

4. Apparatus

4.1 *Ion Chromatograph*, Dionex Model 12 or equivalent, using the following operating conditions:

Sample loop --------	200 μL
Eluent flow rate ----	138 mL/h (30 percent of full capacity)
Sample pump flow rate	50 percent of full capacity

4.1.1 *Precolumn*, 4×50 mm, fast-run, anion-resin column (Dionex P/N 030831 or equivalent) placed before the separator column to protect the separator column from being fouled by particulates or species strongly retained by the ion-exchange resin.

4.1.2 *Separator column*, 4×250 mm, fast-run, anion separator column packed with low-capacity, pellicular, anion-exchange resin (Dionex P/N 030830 or equivalent) that is styrene divinylbenzene based. This has been found to be suitable for resolving fluoride, chloride, nitrite, orthophosphate, bromide, nitrate, and sulfate.

4.2 *Pulse damper*, installed just before the injection valve to reduce flow pulsation.

4.3 *Electrochemical detector*, Dionex or equivalent, consisting of cell and potentiostat.

4.3.1 The electrochemical cell is installed after the separator ion-exchange column. The cell is composed of a silver-working electrode, a

Table 5.—Recovery of bromide in the presence of chloride for 0.01 to 0.09 mg/L bromide

	Chloride (mg/L)					
	10	20	30	50	70	90
Bromide (mg/L)	Recovery of bromide (percent)					
0.01	100	90	50	40	10	0
.02	100	100	65	50	50	35
.03	100	100	100	80	67	40
.05	100	100	100	100	80	80
.07	100	100	100	100	100	86
.09	100	100	100	100	100	100

Table 6.—Recovery of bromide in the presence of chloride for 0.01 to 0.09 mg/L bromide

	Chloride (mg/L)					
	500	700	1000	1500	2000	2500
Bromide (mg/L)	Recovery of bromide (percent)					
0.1	100	80	70	10	0	0
.2	100	100	100	75	50	10
.3	100	100	100	100	70	17
.4	100	100	100	100	100	28
.5	100	100	100	100	100	50
.6	100	100	100	100	100	53
.7	100	100	100	100	100	57
.8	100	100	100	100	100	60
.9	100	100	100	100	100	61

stainless steel counter electrode and a Ag/AgCl reference electrode (NOTE 1). CAUTION: Samples containing oil and grease damage the membrane.

NOTE 1. It is necessary to refill the reference electrode with NaCl solution saturated with AgCl and to replace the ion-exchange membrane and membrane gasket when the potentiostat cannot be zeroed (high detector output). This happens when the AgCl in the reference electrode cell is depleted and (or) the membrane is damaged. It is important not to introduce any air bubbles while refilling the reference electrode and replacing the membrane; this causes a loss of sensitivity. The silver-working electrode needs to be cleaned once a month. Polish the surface with a small amount of toothpaste on a Kimwipe to remove the gray tarnish, and then rinse with deionized water. It is desirable to have a spare reference electrode to avoid downtime. If there is difficulty in refilling the reference electrode, contact the manufacturer.

4.3.2 The potentiostat operating conditions are as follows:

Applied potential --- 0.10 V (NOTE 2)
Select mode MEAS - ON
Select mode +/- -- +
Off set multiplier --- X1 uA
Meter select ------- Out Put
Output range ------ 100 nA/V

NOTE 2. The applied potiential setting of the potentiostat that gives the optimum sensitivity for bromide will vary with age and condition of the reference electrode, and needs to be determined.

4.4 *Autosampler*, Technicon IV or equivalent, using a proportioning pump to deliver water to the wash receptacle.

4.5 *Integrator*, Spectra Physics SP–4100 or equivalent, using the following operating conditions:

	Bromide 0.01 to 0.1 mg/L	Bromide 0.1 to 1.0 mg/L
Input range	1V	10 V
Chart speed	1 cm/min	1 cm/min
Calibration	0 (linear)	2 (quadratic fit)
PT (Peak threshold)	60,000	1,500
AT (Attenuation)	512	128
PH (Peak height)	1	1
PW (No. of data samples per bunch)	60	60

4.6 For additional information refer to the manufacturer's instruction manual.

5. Reagents

5.1 *Bromide standard solution I*, 1.00 mL= 1.00 mg Br^{-1}: Dissolve 1.2877 g NaBr in demineralized water and dilute to 1,000 mL.

5.2 *Bromide standard solution II*, 1.00 mL= 0.01 mg Br^{-1}: Dilute 10.0 mL bromide standard solution I to 1,000 mL with demineralized water.

5.3 *Bromide standard solution III*, 1.00 mL= 0.001 mg Br^{-1}: Dilute 100 mL bromide standard solution II to 1,000 mL with demineralized water.

5.4 *Bromide working standards*: Prepare 1,000 mL each of a series of bromide working standards by appropriate quantitative dilution of bromide standard solutions II and III.

Bromide standard solutions (mL)	Bromide concentration (mg/L)
10 of III	0.01
50 of III	.05
10 of II	.1
50 of II	.5
100 of II	1.0

5.5 *Eluent*, 0.003*M* sodium bicarbonate-0.0024*M* sodium carbonate (NOTE 3): Dissolve 0.2520 g $NaHCO_3$ and 0.2544 g Na_2CO_3 in demineralized water and dilute to 1 L.

NOTE 3. Eluent concentration may be varied slightly to obtain the same retention times for each anion when a new separator column is used. The $NaHCO_3$ is subject to thermal decomposition and must be weighed without prior drying.

6. Procedure

6.1 Set up ion chromatographic system according to manufacturer's instructions. Equilibrate the column with eluent until a stable baseline is obtained. Allow approx 30 min for equilibration.

6.2 Enter appropriate program into the main program controller of the ion chromatograph according to the manufacturer's instruction. The system is configured so that the ion chromatograph, controls the autosampler and starts the integrator at the beginning of each sample injection.

6.3 Press the LEVEL key of the integrator, which causes the display of the input voltage. Level the integrator at 10 mV or display 1000 by adjusting coarse dial of potentiostat.

6.4 Press the PT EVAL (peak threshold evaluation) key for integrator to evaluate the detector signal for noise and drift.

6.5 Create an information file in the integrator by pressing the DIALOG key. Create File 1 for bromide concentrations between 0.1 to 1.0 mg/L using a quadratic fit. Create File 2 for bromide concentrations less than 0.1 mg/L using a single-point calibration with intercept of zero.

6.6 Place a complete set of standards in the first positions of the tray, beginning with the least concentrated standard, followed by samples. Place individual standards of differing concentrations in every tenth position of the remainder of the tray.

7. Calculations

The integrator automatically computes the concentration of bromide in each sample by comparing its peak height or peak area to the analytical curve. Retention time for bromide is approximately 5.4 min.

8. Report

Report bromide, dissolved (71870), concentrations as follows: less than 1.0 mg/L, nearest 0.01 mg/L; 1.0 mg/L and above, two significant figures.

9. Precision and accuracy

9.1 Analysis of six test samples 10 times each by a single operator over a period of one month resulted in the following:

Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
0.32	0.005	1.6
.22	.005	2.2
.24	.005	2.2
.30	.008	2.6
.50	.008	1.6
.049	.002	4.7

9.2 Recovery of bromide added to ten water samples resulted in the following:

Chloride present (mg/L)	Bromide present (mg/L)	Bromide added (mg/L)	Bromide found (mg/L)	Recovery (percent)
31	0.59	0.5	1.13	108
263	.49	.5	1.03	108
63	.33	.3	.65	107
56	.30	.3	.61	103
2.28	.22	.3	.51	97
5.95	.040	.05	.089	98
4.59	.037	.05	.086	98
4.78	.031	.03	.062	103
4.89	.029	.01	.039	100
5.05	.031	.03	.064	110

References

Fishman, M. J., and Pyen, G. S., 1979, Determination of selected anions in water by ion chromatography: U.S. Geological Survey Water-Resources Investigations, 79-101, 30 p.

Johnson, E. L., and Cathers, E., 1981, Applications of simultaneous detection in IC: 23rd Rocky Mountain Conference, Denver, Colorado.

Small, H., Stevens, T. S., and Bauman, W. C., 1975, Novel ion exchange chromatographic method using conductimetric detection: Analytical Chemistry, v. 47, p. 1801-09.

Bromide, colorimetric, fluorescein, automated-segmented flow

Parameter and Code:

Bromide, dissolved, I-2129-85 (mg/L as Br): 71870

1. Application

This method may be used to analyze natural water containing from 0.010 to 0.40 mg/L of bromide. Samples containing greater concentrations need to be diluted.

2. Summary of method

The sample is buffered to pH 5.6 with an acetic acid buffer solution and then reacted with chloramine T to oxidize the bromide to hypobromous acid. The hypobromous acid formed then reacts with fluorescein to form the pink eosin (tetrabromo fluorescein), which is proportional to the bromide concentration.

$$Br^{-1} + HOCl \rightarrow BrOH + Cl^{-1}$$

$$BrOH + \text{Fluorescein} \rightarrow \text{Tetrabromo Fluorescein (pink)}$$

3. Interferences

Iodide interferes quantitatively, but in most waters the iodide concentration is negligible. It is recommended that a determination for iodide be performed and that the concentration that is found be subtracted from the apparent bromide concentration. Cyanide, as much as 0.50 mg/L, and chloride, as much as 500 mg/L, do not interfere. Thiocyanate interferes linearly, but in most waters its concentration is negligible.

4. Apparatus

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

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.010 to 0.40 mg/L bromide.

Absorption cell -----	50 mm
Wavelength --------	520 nm
Cam ---------------	30/h (2/1)

5. Reagents

5.1 *Bromide standard solution I*, 1.00 mL= 0.100 mg Br^{-1}: Dissolve 0.149 g KBr, dried overnight over concentrated H_2SO_4, in demineralized water and dilute to 1,000 mL with demineralized water.

5.2 *Bromide standard solution II*, 1.00 mL= 0.010 mg Br^{-1}: Dilute 100.0 mL bromide standard solution I to 1,000 mL with demineralized water.

5.3 *Bromide working standards*: Prepare a blank and 1000 mL each of a series of bromide working standards by appropriate quantitative dilution of bromide standard solution II as follows:

Bromide standard solution II (mL)	Bromide concentration (mg/L)
1.0	0.010
5.0	.050
10.0	.100
25.0	.250
40.0	.400

5.4 *Buffer solution*: Dissolve 9.426 g NH_4Cl in 500 mL demineralized water and add 57 mL glacial acetic acid (sp. gr. 1.06). Add dropwise, 5*N* KOH solution until the pH of the solution is 5.6. Dilute to 1,000 mL with demineralized water.

5.5 *Chloramine-T solution*, 0.5 g/100 mL: Dissolve 0.500 g chloramine-T in 100 mL of demineralized water. Prepare fresh daily.

5.6 *Fluorescein stock solution*, 0.125 g/100 mL: Dissolve 0.125 g fluorescein in 25 mL 0.1*N* NaOH and dilute to 100 mL with demineralized water. This solution is stable for one week if stored in a light-proof bottle.

5.7 *Fluorescein working solution*: Pipet 10 mL Fluorescein stock solution into a 100-mL volumetric flask; dilute to the mark with demineralized water. This solution must be prepared fresh daily.

5.8 *Sodium hydroxide solution*, 0.1*N*: Dissolve 4.0 g NaOH in demineralized water and dilute to 1 L with demineralized water.

5.9 *Potassium hydroxide solution*, 5.0*N*: CAUTIOUSLY dissolve 280 g KOH in demineralized water, cool, and dilute to 1 L with demineralized water.

6. Procedure

6.1 Set up manifold (fig. 18).

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

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 every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

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 peak reads full scale.

7. Calculations

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

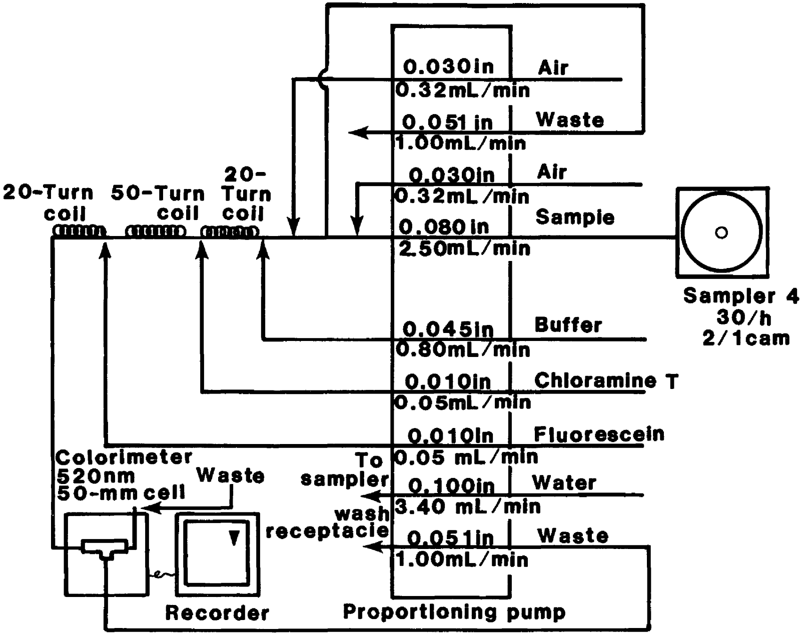

Figure 18.—Bromide, fluorescein manifold

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

7.3 Compute the iodide concentration of each sample in accordance with method I-2371.

7.4 Compute the bromide concentration as follows:

Br^{-1}(mg/L)=

mg/L apparent concentration−mg/L iodide concentration

8. Report

Report bromide, dissolved (71870), concentrations as follows: less than 0.1 mg/L, two decimals; 0.1 mg/L and above, two significant figures.

9. Precision

Single-operator precision for dissolved bromide for six samples expressed in terms of percent relative standard deviation is as follows:

Number of replicates	Concentration (mg/L)	Relative standard deviation (percent)
10	0.010	15.0
10	.050	10.0
10	.100	5.0
10	.350	2.0
10	.550	1.8
10	.860	2.0

References

Marti, V. C., and Arozarena, C. E., 1981, Automated determination of bromide in water: Proceedings Pittsburgh Conference, No. 734.

Thomas, L. C., and Chamberlin, G. J., 1980, Colorimetric chemical analytical methods, 9th: England, The Tintometer Ltd., p. 111-12.

Stenger, V. A., and Kolthorf, I. M., 1935, The detection and colorimetric estimation of micro quantities of bromide: Journal of the American Chemical Society, v. LV11, p. 831-3.

Zitomer, F. and Lambert, J. L., 1963, Spectrophotometric determination of bromide ion in water: Analytical Chemistry, v. 35, p. 1731-34.

Cadmium, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:

Cadmium, dissolved, I-1136-85 (μg/L as Cd): 01025
Cadmium, total recoverable, I-3136-85 (μg/L as Cd): 01027
Cadmium, suspended recoverable, I-7136-85 (μg/L as Cd): 01026

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 1 to 25 μg/L of cadmium. Sample solutions containing more than 25 μg/L need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption spectrometric direct method.

1.2 Suspended recoverable cadmium is calculated by subtracting dissolved cadmium from total recoverable cadmium.

1.3 Total-recoverable cadmium in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

1.4 If the iron concentration of the sample solution exceeds 25,000 μg/L, determine cadmium by the atomic absorption spectrometric direct method.

2. Summary of method

Cadmium is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the air-acetylene flame of the spectrometer.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by depressing the cadmium absorption.

4. Apparatus

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

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

Grating ------------ Ultraviolet
Wavelength -------- 228.8 nm
Source (hollow-cathode or electrodeless-discharge lamp) ----- Cadmium
Oxidant ------------ Air
Fuel --------------- Acetylene
Type of flame ------- Oxidizing

4.3 Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate solution*, 1 g/100 mL: Dissolve 1 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Cadmium standard solution I*, 1.00 mL= 100 μg Cd: Dissolve 0.1000 g Cd splatters in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1000 mL with demineralized water.

5.3 *Cadmium standard solution II*, 1.00 mL= 0.50 μg Cd: Dilute 5.0 mL cadmium standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.4 *Cadmium standard solution III*, 1.00 mL=0.05 μg Cd: Immediately before use, dilute 10.0 mL cadmium standard solution II to 100.0 mL with acidified water. This standard is used to prepare working standards at time of analysis.

5.5 *Citric acid-sodium citrate buffer solution*: Dissolve 126 g citric acid monohydrate and 44 g sodium citrate dihydrate in demineralized water and dilute to 1 L with demineralized water. See NOTE 3 before preparation.

5.6 *Methyl isobutyl ketone (MIBK).*

5.7 *Potassium hydroxide*, 10*M*: Dissolve 56 g KOH in demineralized water, cool, and dilute to 100 mL.

5.8 *Potassium hydroxide solution*, 2.5*M*: Dissolve 14 g KOH in demineralized water and dilute to 100 mL (NOTE 1).

NOTE 1. Alternately, a 2.5*M* NH_4OH solution may be used. Add 167 mL concentrated NH_4OH (sp gr 0.90) to 600 mL demineralized water. Cool and dilute to 1 L.

5.9 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+9) and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample solution containing less than 2.5 μg Cd (100 mL max) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.3 Prepare a blank of acidified water and sufficient standards, and adjust the volume of each to approx 100 mL with acidified water.

6.4 With a pH meter, adjust the pH of each solution to 2.7 (NOTES 2 and 3) with 2.5*M* KOH. Shake for 3 min.

NOTE 2. For water-suspended sediment samples which have been digested, add 1 to 2 mL 10*M* KOH or concentrated NH_4OH (sp gr 0.90) before pH adjustment.

NOTE 3. If an automated titration system is used to adjust the pH, add 2.5 mL citric acid-sodium citrate buffer solution prior to pH adjustment. This will prevent over-shooting the end point in poorly buffered samples.

6.5 Add 2.5 mL APDC solution and mix.

6.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.8 Aspirate the ketone layer within 1 h. Aspirate the ketone layer of the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable cadmium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing concentrations of cadmium that exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

7.2 To determine the micrograms per liter of suspended recoverable cadmium, subtract dissolved-cadmium concentration from total-recoverable-cadmium concentration.

8. Report

Report cadmium, dissolved (01025), total-recoverable (01027), and suspended-recoverable (01026), concentrations as follows: less than 10 μg/L, nearest microgram per liter, 10 μg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved cadmium for 22 samples within the range of 2 to 17 μg/L may be expressed as follows:

$$S_T = 0.213X - 0.111$$

where

S_T= overall precision, micrograms per liter, and

X= concentration of cadmium, micrograms per liter.

The correlation coefficient is 0.6914.

9.2 Precision for dissolved cadmium for four of the 22 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
6	2.0	32
11	4.6	24
6	10.2	17
12	17.2	34

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable cadmium will be greater than that reported for dissolved cadmium.

Cadmium, atomic absorption spectrometric, direct

Parameters and Codes:

Cadmium, dissolved, I-1135-85 (μg/L as Cd): 01025
Cadmium, total recoverable, I-3135-85 (μg/L as Cd): 01027
Cadmium, suspended recoverable, I-7135-85 (μg/L as Cd): 01026
Cadmium, recoverable-from-bottom-material, I-5135-85 (μg/g as Cd): 01028

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 10 μg/L of cadmium. Sample solutions containing more than 250 μg/L need either to be diluted or to be read on a less expanded scale. Sample solutions containing less than 10 μg/L need to be analyzed by the atomic absorption spectrometric chelation-extraction method, providing that the interference limits discussed in that method are not exceeded.

1.2 Suspended recoverable cadmium is calculated by subtracting dissolved cadmium from total recoverable cadmium.

1.3 This method may be used to analyze bottom material containing at least 1 μg/g of cadmium.

1.4 Total recoverable cadmium in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable cadmium in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

Cadmium is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment of the sample.

3. Interferences

3.1 Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), magnesium (4,500 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (100 mg/L), iron (4×10^6 μg/L), and cobalt, nickel, copper, zinc, lead, and chromium (10,000 μg/L each) do not interfere. Greater concentrations of each constituent were not investigated.

3.2 Calcium at concentrations greater than 1,000 mg/L suppresses the cadmium absorption. At 2,000 mg per liter of calcium, the suppression is approximately 19 percent.

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	228.8 nm
Source (hollow-cathode lamp)	Cadmium
Oxidant	Air
Fuel	Acetylene
Type of flame	Oxidizing

4.3 The Perkin-Elmer, flathead, single-slot burner allows a working range of 10 to 250 μg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Cadmium standard solution I*, 1.00 mL= 100 μg Cd: Dissolve 0.1000 g Cd splatters in a minimun of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Cadmium standard solution II*, 1.00 mL= 1.0 μg Cd: Dilute 10.0 mL cadmium standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.3 *Cadmium working standards*: Prepare a series of at least six working standards containing from 10 to 250 µg/L of cadmium by appropriate dilution of cadmium standard solutions I and II with acidified water. Prepare fresh daily.

5.4 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to a liter of demineralized water.

6. Procedure

Aspirate the blank (acidified water) to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable cadmium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing cadmium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per liter suspended recoverable cadmium, subtract dissolved-cadmium concentration from total-recoverable-cadmium concentration.

7.3 To determine micrograms per gram of cadmium in bottom-material samples, first determine the micrograms per liter of cadmium in each sample as in paragraph 7.1; then

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

8. Report

8.1 Report cadmium, dissolved (01025), total-recoverable (01027), and suspended-recoverable (01026), concentrations as follows: less than 1,000 µg/L, nearest 10 µg/L; 1,000 µg/L and above, two significant figures.

8.2 Report cadmium, recoverable-from-bottom-material (01028), concentrations as follows: less than 10 µg/g, nearest microgram per gram; 10 µg/g and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved cadmium within the range of 2.8 to 18.4 µg/L for 21 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 3.57 µg/L ranged from 3.24 to 3.95 µg/L.

9.2 Precision for dissolved cadmium for five of the 21 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
12	2.8	124
17	4.8	50
15	10.7	19
15	15.7	24
5	18.4	71

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable cadmium and for recoverable cadmium from bottom material will be greater than that reported for dissolved cadmium.

9.4 Precision for total recoverable cadmium expressed in terms of the percent relative standard deviation for two water-suspended sediment mixtures is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
13	5.4	43
9	15.8	25

Cadmium, atomic absorption spectrometric, graphite furnace

Parameter and Code:

Cadmium, dissolved, I-1137-85 (μg/L as Cd): 01025

1. Application

1.1 This method may be used to determine cadmium in low ionic-strength water and precipitation. With deuterium background correction and a 20-μL sample, the method is applicable in the range from 0.02 to 1.0 μg/L. With Zeeman background correction and a 20-μL sample, the method is applicable in the range from 0.1 to 3.0 μg/L. Sample solutions that contain cadmium concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric direct or chelation- extraction method or by the atomic emission spectrometric ICP method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Cadmium is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform and a matrix modifier is added. The sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (25 mg/L), magnesium (8 mg/L), sodium (20 mg/L), sulfate (34 mg/L), and chloride (25 mg/L) do not interfere. Greater concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of cadmium. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contribution from contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 228.8 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high-temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-μL sample with 5 μL of matrix modifier (NOTE 1).

NOTE 1. A 20-μL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms*. Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware*. Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Cadmium standard solution I*, 1.00 mL= 1,000 μg Cd: Dissolve 1.0000 g Cd splatters in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL high-purity concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with Type 1 water.

5.2 *Cadmium standard solution II*, 1.00 mL= 10.0 μg Cd: Dilute 10.0 mL cadmium standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified Type 1 water (paragraph 5.7) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.3 *Cadmium standard solution III*, 1.00 mL= 0.100 μg Cd: Dilute 10.0 mL cadmium standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.4 *Cadmium standard solution IV*, 1.00 mL= 0.001 μg Cd: Dilute 10.0 mL cadmium standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

5.5 *Matrix modifier solution*, 40g $NH_4H_2PO_4$/L: Add 40.0 g $NH_4H_2PO_4$ to 950 mL Type 1 water, mix, and dilute to 1,000 mL. Analyze 20 μL of matrix modifier for cadmium contamination. If the cadmium reading is more than 0.005 absorbance-seconds, purify the solution by chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK) (NOTE 3). Analyze 20 μL of the purified solution. Repeat extractions until the cadmium level is reduced to the acceptable level. **DO NOT ADD ACID TO THE PURIFIED MATRIX MODIFIER SOLUTION.**

NOTE 3. To purify matrix modifier solution, pour the solution into a Teflon or FEP container. Add 0.25g APDC for each liter of solution. While stirring, adjust the solution to pH 2.9 by dropwise addition of concentrated HNO_3 (sp gr 1.41). Transfer portions of the solution to a separatory funnel, add 100 mL MIBK/liter of solution, and shake vigorously for at least 5 min. Frequently, vent the funnel in a hood. Collect the extracted solution in the FEP container. Repeat the extraction with 50 mL MIBK/liter of solution. Because MIBK can dissolve some plastic autosampler cups, boil the solution for at least 10 min in a silicone-treated or acid-rinsed container covered with a watchglass to remove MIBK.

5.6 *Nitric acid, concentrated*, high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HNO_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for cadmium. Add an additional 1.5 mL of concentrated HNO_3/liter of water, and repeat analysis. The integrated signal should not increase by more than 0.001 absorbance-seconds.

5.7 *Water, acidified*, Type 1: Add 1.5 mL high-purity, concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water, Type 1*

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1+1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-μL aliquots of blank and working standards plus 5 μL of modifier each and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and/or platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of cadmium in each sample from the digital display or printer output. Dilute those samples containing concentrations of cadmium that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report cadmium, dissolved (01025), concentrations as follows: less than 1.0 μg/L, nearest 0.01 μg/L for deuterium background correction or nearest 0.1 μg/L for Zeeman background correction; 1.0 μg/L and above, two significant figures for both deuterium background correction and Zeeman background correction.

9. Precision

9.1 Analysis of five samples six times each by a single operator using deuterium background correction is as follows:

Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
0.030	0.004	6.9
.106	.004	4.0
.249	.009	3.4
.499	.010	2.0
1.005	.013	1.3

9.2 Analysis of four samples by a single operator using Zeeman background correction is as follows:

Number of replicates	Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
4	0.50	0.115	23
12	1.60	.060	3.8
6	2.10	.089	4.2
14	3.14	.074	2.4

9.3 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 μS/cm). A known amount of cadmium was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (μg/L)	Amount found (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
2.6	2.25	0.05	2.2	87
3.25	2.77	.05	1.8	85
5.0	4.53	.15	3.3	91
5.2	4.42	.17	3.8	85
6.5	5.63	.08	1.4	87
Tap water				
2.6	2.05	.08	3.9	79
3.25	2.55	.41	7.9	80
5.00	4.52	.12	2.7	90
5.2	3.90	.15	3.8	75
6.5	5.22	.41	7.9	80

9.4 The precision and bias for the deuterium background method were tested on deionized water and tap water (specific conductance 280 μS/cm). A known amount of cadmium was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (μg/L)	Amount found (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
2.6	2.55	0.31	12	98
3.25	2.72	.15	5.5	84
5.0	4.70	.30	6.4	94
5.2	4.97	.44	8.9	96
6.5	5.83	.33	5.6	90
Tap water				
2.6	3.03	1.0	33	117
3.25	2.83	.25	8.8	87
5.0	4.53	.27	6.0	91
5.2	4.23	.21	5.0	81
6.5	5.48	.15	2.7	84

9.5 Interlaboratory precision for dissolved cadmium for 16 samples within the range of

0.62 to 16.2 µg/L, without regard to type of background correction and use of matrix modifiers, if any, may be expressed as follows:

$$S_T = 0.282X + 0.022$$

where

S_T= overall precision, micrograms per liter, and

X= concentration of cadmium, micrograms per liter.

The correlation coefficient is 0.9157.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 39-41.

Cooksey, M., and Barnett, W. B., 1979, Matrix modification and the method of additions in flameless atomic absorption: Atomic Absorption Newsletter, v. 18, p. 101-5.

Fernandez, F. J., Beatty, M. M., and Barnett, W. B., 1981, Use of the L'vov platform for furnace atomic absorption applications: Atomic Spectroscopy, v. 2, p. 16-21.

Hinderberger, E. J., Kaiser, M. L., and Koirtyohann, S. R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1-11.

Manning, D. C., and Slavin, W., 1983, The determination of trace elements in natural waters using the stabilized temperature platform furnace: Applied Spectroscopy, v. 37, p. 1-11.

Ottaway, J. M., 1982, A revolutionary development in graphite furnace atomic absorption: Atomic Spectroscopy, v. 3, p. 89-92.

Slavin, W., Carnrick, G. R., and Manning, D. C., 1982, Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace: Analytical Chemistry, v. 54, p. 621-4.

Cadmium, atomic emission spectrometric, ICP

Parameter and Code:

Cadmium, dissolved, I-1472-85 (μg/L as Cd): 01025

2. Summary of method

Cadmium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Cadmium, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:

Cadmium, total, I-5474-85 (mg/kg as Cd): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200°C. Cadmium is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Calcium, atomic absorption spectrometric, direct

Parameters and Codes:

Calcium, dissolved, I-1152-85 (mg/L as Ca): 00915
Calcium, total recoverable, I-3152-85 (mg/L as Ca): none assigned
Calcium, suspended recoverable, I-7152-85 (mg/L as Ca): 81357
Calcium, recoverable-from-bottom-material, dry wt I-5152-85 (mg/kg as Ca): 00917

1. Application

1.1 This method may be used to analyze atmospheric precipitation, water, brines, and water-suspended sediment.

1.2 Two analytical ranges for calcium are included: from 0.01 to 5.0 mg/L and from 1.0 to 60 mg/L. Sample solutions containing calcium concentrations greater than 60 mg/L need to be diluted.

1.3 Suspended recoverable calcium is calculated by subtracting dissolved calcium from total recoverable calcium.

1.4 This method may be used to analyze bottom material containing at least 10 mg/kg of calcium.

1.5 Total recoverable calcium in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable calcium in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

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

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and a strip-chart recorder or printer or both (fig. 19).

3. Interferences

3.1 Phosphate, sulfate, and aluminum interfere but are masked by the addition of lanthanum. Silica also reportedly interferes. Because

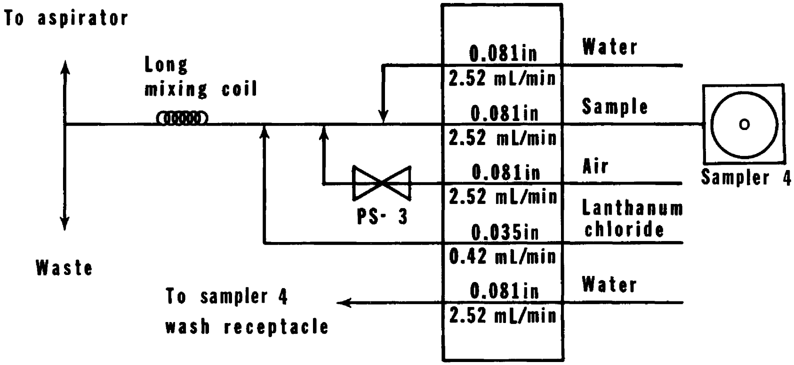

Figure 19.—Calcium manifold

low calcium values result if the pH of the sample is above 7, standards are prepared in hydrochloric acid solution and samples are preserved in the field with use of nitric acid solution. Concentrations of magnesium greater than 1,000 mg/L also cause low calcium values.

3.2 Nitrate interferes, but in the presence of lanthanum chloride-hydrochloric acid solution at least 2,000 mg/L can be tolerated. The addition of nitric acid to the sample causes no problem in the following procedure.

4. Apparatus

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

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

Grating	Visible
Wavelength	422.7 nm
Source (hollow-cathode lamp)	Calcium
Oxidant	Air
Fuel	Acetylene
Type of flame	Slightly reducing

4.3 The 50-mm (2-in.), flathead burner allows a working range of 0.01 to 5.0 mg/L. This burner, rotated 90°, allows a working range of 1.0 to 60 mg/L.

4.4 Different burners may be used according to manufacturers' instructions. A nitrous oxide-acetylene flame will provide two to five times greater analytical sensitivity and freedom from chemical interferences; however, sodium or potassium chloride must be added to control ionization of calcium.

5. Reagents

5.1 *Calcium standard solution*, 1.00 mL= 0.500 mg Ca: Suspend 1.250 g $CaCO_3$, dried at 180°C for 1 h before weighing, in demineralized water and dissolve *cautiously* with a minimum of dilute HCl. Dilute to 1,000 mL with demineralized water.

5.2 *Calcium working standards*: Prepare at least six working standards containing either from 0.01 to 5.0 mg/L or from 1.0 to 60 mg/L of calcium by diluting the calcium standard solution. To each working standard add 1.0 mL of $LaCl_3$ solution for each 10 mL of standard. Similarly, prepare a demineralized water blank.

5.3 *Lanthanum chloride solution*, 87 g/L: Mix 29 g of La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

6. Procedure

6.1 Add 1.0 mL of $LaCl_3$ solution per 10.0 mL of sample solution.

6.2 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analzyed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the milligrams per liter of dissolved or total recoverable calcium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing calcium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine milligrams per liter of suspended recoverable calcium, subtract dissolved-calcium concentration from total-recoverable-calcium concentration.

7.3 To determine milligrams per kilogram of calcium in bottom-material samples, first determine the milligrams per liter of calcium in each sample as in paragraph 7.1; then

$$\text{Ca (mg/kg)}=\frac{\text{mg/L Ca}\times\frac{\text{mL of original digest}}{1000}}{\text{wt of sample (kg)}}$$

8. Report

8.1 Report calcium, dissolved (00915), total-recoverable (none assigned), and suspended-recoverable (81357), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 to 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

8.2 Report calcium, recoverable-from-bottom-material (00917), concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

9.1 Precision for dissolved calcium for 37 samples within the range of 0.84 to 184 mg/L may be expressed as follows:

$$S_T = 0.087X - 0.249$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of calcium, milligrams per liter.

The correlation coefficient is 0.8632.

9.2 Precision for dissolved calcium for five of the 37 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
20	0.84	24
14	10.7	6
45	50.1	8
23	110	8
36	184	10

9.3 Precision for dissolved calcium within the range of 0.05 to 5.0 mg/L in terms of the percent relative standard deviation by a single operator is as follows:

Number of replicates	Mean (mg/L)	Relative standard deviation (percent)
8	0.052	40.4
8	1.02	5.9
8	1.85	10.3
8	5.05	1.0

9.4 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable calcium and for recoverable calcium from bottom material will be greater than that reported for dissolved calcium.

Reference

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

Calcium, atomic absorption spectrometric, direct-EPA

Parameter and Code:

Calcium, total recoverable, I-3153-85 (mg/L as Ca): 00916

1. Application

1.1 This method may be used to analyze water-suspended sediment. Sample solutions containing from 0.1 to 60 mg/L of calcium may be analyzed without dilution; whereas, those containing more than 60 mg/L need to be diluted.

1.2 For ambient water, analysis may be made on a measured portion of the acidified water-suspended sediment sample.

1.3 For all other waters, including domestic and industrial effluent, the atomic absorption procedure must be preceded by a digestion-solubilization as specified below. In cases where the analyst is uncertain about the type of sample, the digestion-solubilization procedure must be used.

2. Summary of method

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

2.2 Effluent samples must undergo a preliminary nitric acid digestion followed by a hydrochloric acid solubilization.

3. Interferences

3.1 Phosphate, sulfate, and aluminum interfere but are masked by the addition of lanthanum. Silica reportedly also interferes. Because low calcium values result if the pH of the sample is above 7, standards are prepared in hydrochloric acid solution and samples are preserved in the field with use of nitric acid solution. Concentrations of magnesium greater than 1,000 mg/L also cause low calcium values.

3.2 Nitrate interferes, but in the presence of lanthanum chloride-hydrochloric acid solution, at least 2,000 mg/L can be tolerated. The addition of nitric acid to the sample as a preservative at the time of collection causes no problem in the following procedure. Samples should be evaporated just to dryness following nitric acid digestion to avoid any possible nitrate interference.

4. Apparatus

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

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

Grating ------------	Visible
Wavelength --------	422.7 nm
Source (hollow-cathode lamp) ------------	Calcium
Oxidant ------------	Air
Fuel ---------------	Acetylene
Type of flame -------	Slightly reducing

4.3 Different burners may be used according to manufacturers' instructions. A nitrous oxide-acetylene flame provides 2 to 5 times greater sensitivity and freedom from chemical interferences; however, sodium or potassium chloride must be added to control ionization of calcium.

5. Reagents

5.1 *Calcium standard solution*, 1.00 mL= 0.500 mg Ca: Suspend 1.250 g $CaCO_3$, dried at 180 °C for 1 h before weighing, in demineralized water and dissolve *cautiously* with a minimum of dilute HCl. Dilute to 1,000 mL with demineralized water.

5.2 *Calcium working standards*: Prepare a series of at least six working standards containing from 0.1 to 60 mg/L of calcium by dilution of calcium standard solution. To each working standard add 1.0 mL of $LaCl_3$ solution for each 10 mL of standard.

5.3 *Hydrochloric acid*, 6*M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.4 *Hydrochloric acid*, 0.3*M*: Dilute 25 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.5 *Lanthanum chloride solution*, 87 g/L: Mix 29 g La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

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

6. Procedure

6.1 Transfer the entire sample to a beaker.

6.2 Rinse the sample bottle with 3 mL concentrated HNO_3 for each 100 mL of sample and add to the beaker. Prepare a blank using 3 mL concentrated HNO_3 per 100 mL demineralized water.

6.3 Evaporate samples and blank to dryness on a hotplate, making sure the samples do not boil.

6.4 Cool and add an additional 3 mL concentrated HNO_3 to the beaker. Cover with a watchglass, return to the hotplate, and gently reflux the sample.

6.5 Continue heating, adding additional acid as necessary, until the digestion is complete (indicated by a light-colored residue). Evaporate just to dryness.

6.6 Add 6 mL 6*M* HCl solution per 100 mL of original sample and warm the beaker to dissolve the residue.

6.7 Wash the watchglass and beaker with demineralized water and filter the sample (Whatman No. 41 or equivalent), rinsing the filter with hot, 0.3*M* HCl. Dilute to the original volume with demineralized water.

6.8 Add 1.0 mL lanthanum chloride solution per 10.0 mL of sample.

6.9 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

Determine the milligrams per liter of total recoverable calcium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing calcium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report calcium, total-recoverable (00916), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for total recoverable calcium over the range of the method will be greater than 8 percent.

References

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

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 215.1-1.

Calcium, atomic emission spectrometric, ICP

Parameter and Code:
Calcium, dissolved, I-1472-85 (mg/L as Ca): 00915

2. Summary of method

Calcium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Calcium, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:

Calcium, total, I-5473-85 (mg/kg as Ca): none assigned
Calcium, total, I-5474-85 (mg/kg as Ca): none assigned

2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The sample is then treated and analyzed by one of the following techniques.

2.1.1 The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1000 °C. The resulting bead is dissolved in acidified, boiling, demineralized water, and calcium is determined by atomic absorption spectrometry. See method I-5473, metals, major, total in sediment, atomic absorption spectrometric, direct.

2.1.2 The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Calcium is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Carbon dioxide, calculation

Parameter and Code:

Carbon dioxide, dissolved, I-1160-85 (mg/L as CO_2): 00405

1. Application

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

2. Summary of method

2.1 Carbon dioxide concentration is calculated from measured values of pH and bicarbonate ion. The pH is determined potentiometrically (method I-1586) and the bicarbonate ion by electrometric titration (method I-1030).

2.2 Gaseous carbon dioxide hydrolyzes slightly:

$$CO_2(aq) + H_2O \rightarrow H_2CO_3 \qquad (1)$$

The hydrolysis constant expression is:

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

The square brackets denote concentrations in moles per liter.

Carbonic acid is a weak acid and dissociates by steps:

$$H_2CO_3 \leftrightharpoons H^{+1} + HCO_3^{-1} \qquad (3)$$

$$HCO_3^{-1} \leftrightharpoons H^{+1} + CO_3^{-2} \qquad (4)$$

Only the two equilibria represented by equations (1) and (3), however, are usually of significance in determining CO_2 concentrations. When the pH of a water is sufficiently high to permit the existence of CO_3^{-2}, the concentration of free CO_2 that can coexist is negligibly small.

The CO_2 concentrations can, therefore, be calculated within experimental accuracy from equations (1) and (3) and their corresponding equilibrium-constant expressions as follows:

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

$$K_1 = \frac{[H^{+1}]\,[HCO_3^{-1}]}{[H_2CO_3]} = 1.7\times10^{-4} \qquad (6)$$

Multiply equations (5) and (6):

$$K_{hydr}\,K_1 = \frac{[H^{+1}]\,[HCO_3^{-1}]}{[CO_2]} = 4.4\times10^{-7} \qquad (7)$$

and solving for $[CO_2]$:

$$[CO_2] = \frac{[H^{+1}]\,[HCO_3^{-1}]}{4.4\times10^{-7}} \qquad (2)$$

This equation can then be used to determine the CO_2 concentration when $[HCO_3^{-1}]$ and $[H^{+1}]$, or pH, of the sample have been determined. Equation (8) can be rearranged to simplify the calculation, since both CO_2 and bicarbonate $[HCO_3^{-1}]$ concentrations are usually expressed in units of milligrams per liter rather than of moles per liter, and hydrogen-ion concentrations normally as pH units:

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

For convenience in making the calculations, the values of $1.60\times10^{(6.0-pH)}$ may be tabulated for a range of pH values (table 7).

2.3 For additional information on the theory of this method see De Martini (1938), Langelier

Table 7.—Values of $1.60 \times 10^{(6.0-\text{pH})}$

pH	$1.60 \times 10^{(6.0-\text{pH})}$	pH	$1.60 \times 10^{(6.0-\text{pH})}$
6.0	1.60	7.6	0.040
6.2	1.00	7.8	.025
6.4	.633	8.0	.016
6.6	.399	8.2	.010
6.8	.252	8.4	.006
7.0	.160	8.6	.004
7.2	.100	8.8	.003
7.4	.063	9.0	.002

(1936), Larson and Buswell (1942), and Moore (1939).

3. Interferences

3.1 The values of the constants K_{hydr} and K_1 vary with temperature and with both the concentration and nature of the dissolved solutes. Therefore, the accuracy of the calculation depends on the reliability of values of K_{hydr} and K_1 for a particular sample. For practical purposes and for most samples containing less than 800 mg/L of solutes, a value for $(K_{\text{hydr}} \times K_1)$ of 4.54×10^{-7} has been recommended and was used in calculating the constant factor of equation (9).

3.2 Carbon dioxide is easily lost from solution, and precautions must be taken to prevent or minimize such losses when collecting the sample. The pH and bicarbonate must be determined in the field at the time of collection.

7. Calculations

7.1 Calculate mg/L CO_2 as follows:

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

7.2 The calculated values of the variable $1.60 \times 10^{(6.0-\text{pH})}$ are shown in table 7.

8. Report

Report carbon dioxide, dissolved, calculation (00405), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

De Martini, F. E., 1938, Corrosion and the Langelier calcium carbonate saturation index: American Water Works Association Journal v. 30, p. 85.

Langelier, W. F., 1936, The analytical control of anticorrosion water treatment: American Water Works Association Journal, v. 28 p. 1500.

Larson, T. E., and Buswell, A. N., 1942, Calcium carbonate saturation and alkalinity interpretations: American Water Works Association Journal, v. 34, p. 1667.

Moore, E. W., 1939, Graphic determination of carbon dioxide and three forms of alkalinity: American Water Works Association Journal, v. 31, p. 51.

Chloride, colorimetric, ferric thiocyanate

Parameter and Code:

Chloride, dissolved, I-1187-85 (mg/L as Cl): 00940

1. Application

This method may be used to determine dissolved chloride in water containing from 0.1 to 10 mg/L of chloride ion. It is particularly useful for the analysis of low-dissolved- solids-content water when low chloride concentrations must be determined accurately.

2. Summary of method

2.1 Chloride is determined by measurement of the color developed by the displacement of the thiocyanate ion from mercuric thiocyanate by chloride ion in the presence of ferric ion; an intensely colored ferric thiocyanate complex is formed:

$$2Cl^{-1} + Hg(SCN)_2 + 2Fe^{+3} \rightarrow HgCl_2 + 2Fe(SCN)^{+2}$$

2.2 The color is stable for at least 2 h and is proportional to the chloride-ion concentration. The color has a maximum absorbance at 460 nm.

2.3 For additional information see ASTM Method D 512-81, "Standard Methods of Testing for Chloride Ion in Water" (American Society for Testing and Materials, 1984).

3. Interferences

Bromide, iodide, cyanide, thiosulfate, and nitrite interfere. Color, depending upon its spectral absorbance, may interfere with the photometric measurement.

4. Apparatus

4.1 *Spectrometer* for use at 460 nm.

4.2 Refer to manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Chloride standard solution I*, 1.00 mL= 1.00 mg Cl^{-1}: Dissolve 1.648 g primary standard NaCl crystals, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Chloride standard solution II*, 1.00 mL= 0.010 mg Cl^{-1}: Dilute 5.0 mL chloride standard solution I to 500.0 mL with demineralized water.

5.3 *Ferric ammonium sulfate solution*, 22.8 g/L: Dissolve 41.4 g $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 570 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1 L with demineralized water.

5.4 *Mercuric thiocyanate solution*, 3 g/L: Dissolve 3 g $Hg(SCN)_2$ in 1 L 95-percent ethanol (denatured alcohol formula No. 3A is also satisfactory). Stir for 1 h to saturate the solvent; allow undissolved thiocyanate to settle, and then filter through a Pyrex-wool plug or a 0.45-μm membrane filter.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.250 mg of Cl^{-1} (25.0 mL max) into a 50-mL beaker and adjust the volume to 25.0 mL with demineralized water.

6.2 Prepare a demineralized-water blank and at least five standards containing from 0.0025 to 0.250 mg Cl^{-1}, and adjust the volume of each to 25.0 mL.

6.3 Add 2.0 mL $FeNH_4(SO_4)_2$ solution and stir. The samples will be essentially colorless at this point.

6.4 Add 2.0 mL $Hg(SCN)_2$ solution and stir.

6.5 After at least 10 min, but within 2 h, read the absorbance of each standard and sample against the blank at 460 nm, and, when necessary, make corrections for water color.

7. Calculations

7.1 Determine the milligrams chloride from a plot of absorbances of standards containing known amounts of Cl^{-1}.

7.2 Determine the chloride concentration in milligrams per liter as follows:

$$Cl^{-1}\text{ (mg/L)}=\frac{1{,}000}{\text{mL sample}}\times \text{mg}Cl^{-1}$$

8. Report

Report chloride, dissolved (00940), concentrations of less than 10 mg/L to the nearest 0.1 mg/L.

9. Precision

9.1 Data published by the American Society for Testing and Materials (1984) indicate the overall precision of the method to be

$$S_T=0.054X$$

where

S_T=overall precision, milligrams per liter, and

X=concentration of Cl^{-1}, milligrams per liter.

9.2 Precision for one reference sample expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
6	1.4	33

Reference

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 392-400.

Chloride, colorimetric, ferric thiocyanate, automated-segmented flow

Parameter and Code:

Chloride, dissolved, I-2187-85 (mg/L as Cl): 00940

1. Application

This method may be used to determine concentrations of chloride in surface, domestic, and industrial water in the range of 10 to 100 mg/L or 0.1 to 10.0 mg/L. The latter range can be attained by interchanging the sample and diluent pump tubes.

2. Summary of method

This method is based on the displacement of thiocyanate from mercuric thiocyanate by chloride and on the subsequent reaction of the liberated thiocyanate ion with ferric ion to form the intensely colored ferric thiocyanate complex. The absorbance of this complex is then measured colorimetrically (O'Brien, 1962; Zall and others, 1956).

$$Hg(SCN)_2 + 2Cl^{-1} \rightarrow HgCl_2 + 2SCN^{-1}$$

$$SCN^{-1} + Fe^{+3} \rightarrow Fe(SCN)^{+2}$$

3. Interferences

Bromide, iodide, cyanide, thiosulfate, and nitrite interfere. Color, depending upon its spectral absorbance, may interfere with the photometric measurement.

4. Apparatus

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

4.2 With this equipment the following operating conditions have been found satisfactory for the ranges from 10 to 100 mg/L and from 0.1 to 10.0 mg/L:

Absorption cell -----	15 mm
Wavelength ---------	480 nm
Cam ----------------	60/h (6/1)

5. Reagents

5.1 *Chloride standard solution I*, 1.00 mL= 0.50 mg Cl^{-1}: Dissolve 0.8242 g primary standard NaCl crystals, dried at 180° C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Chloride working standards*; Prepare a blank and 500 mL each of a series of chloride working standards by appropriate quantitative dilution of the chloride standard solution I, as follows:

Chloride standard solution (mL)	Chloride concentration (mg/L)
0.0	0.0
5.0	5.0
10.0	10.0
20.0	20.0
30.0	30.0
50.0	50.0
60.0	60.0
80.0	80.0
100.0	100.0

5.3 *Ferric nitrate stock solution*, 121 g/L: Dissolve 202 g $Fe(NO_3)_3 \cdot 9H_2O$ in approx 500 mL demineralized water. Add 225 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1 L. Filter and store in an amber-colored container.

5.4 *Mercuric thiocyanate stock solution*, 4.17 g/L in methanol: Dissolve 4.17 g $Hg(SCN)_2$ in 500 mL methanol, dilute to 1 L with methanol, and filter.

5.5 *Chloride color reagent*: Add 150 mL ferric nitrate stock solution and 150 mL mercuric thiocyanate stock solution to demineralized water and dilute to 1 L. Add 1 mL/L of Brij-35 solution. Use amber bottle for storage.

6. Procedure

6.1 Set up manifold (fig. 20).

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

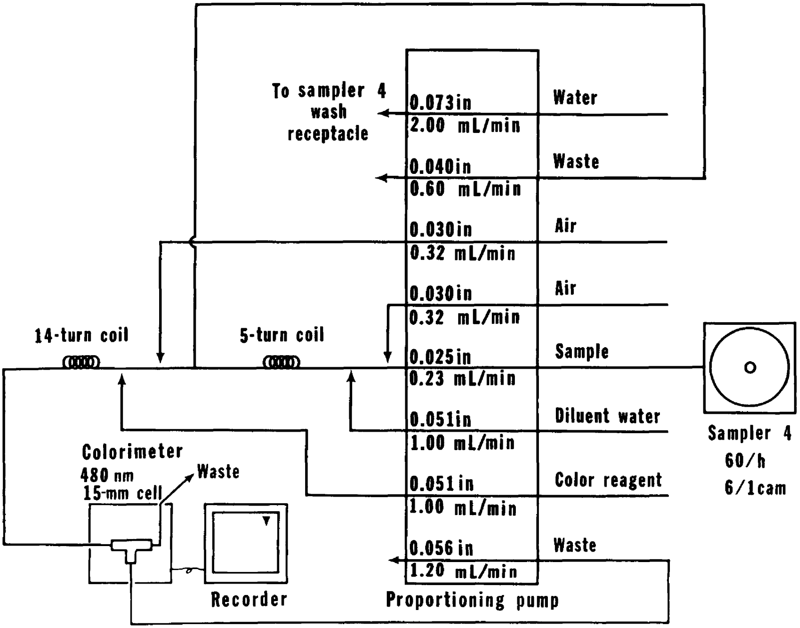

Figure 20.—Chloride, ferric thiocyanate manifold

6.3 Adjust 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).

NOTE 1. The sample cups should remain sealed in their packages until just prior to use to avoid contamination. Handle cups carefully to avoid contamination from perspiration on hands.

6.5 Begin analysis. When the peak from 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 chloride concentration.

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

8. Report

Report chloride, dissolved (00940), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for 20 samples within the range of 0.3 to 246 mg/L may be expressed as follows:

$$S_T = 0.027X + 0.786$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of chloride, milligrams per liter.

The correlation coefficient is 0.8935.

9.2 Precision for six of the 20 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
7	0.31	81
16	1.50	33
19	25.7	3
9	58.8	3
6	122	6
12	246	3

References

O'Brien, J. E., 1962, Automatic analysis of chlorides in sewage: Wastes Engineering, v. 33, p. 670-672.

Zall, D. M., Fisher, D., and Garner, M. Q., 1956, Photometric determination of chlorides in water: Analytical Chemistry, v. 28 p. 1665-1668.

Chloride, colorimetric, ferric thiocyanate, automated-discrete

Parameter and Code:

Chloride, dissolved, I-2188-85 (mg/L as Cl): 00940

1. Application

This method may be used to determine concentrations of chloride in surface, domestic, and industrial water in the ranges of 0.1 to 10.0 mg/L and 10.0 to 500 mg/L. Samples containing greater concentrations need to be diluted.

2. Summary of method

2.1 This method is based on the displacement of thiocyanate from mercuric thiocyanate by chloride and on the subsequent reaction of the liberated thiocyanate ion with ferric ion to form the intensely colored ferric thiocyanate complex. The absorbance of this complex is then measured colorimetrically (O'Brien, 1962; Zall and others, 1956).

$$Hg(SCN)_2 + 2Cl^{-1} \rightarrow HgCl_2 + 2SCN^{-1}$$

$$SCN^{-1} + Fe^{+3} \rightarrow Fe(SCN)^{+2}$$

2.2 For additional information see ASTM Method D512-81, "Standard Methods of Test for Chloride Ion in Water" (American Society for Testing and Materials, 1984).

3. Interferences

Bromide, iodide, cyanide, thiosulfate, and nitrite interfere. Color, depending upon its spectral absorbance, may interfere with the photometric measurement.

4. Apparatus

4.1 *Discrete analyzer system*, American Monitor IQAS or equivalent.

4.2 With this equipment the following operating conditions have been found satisfactory for the ranges from 0.1 to 10.0 mg/L and from 10.0 to 500 mg/L.

Wavelength -----	480 nm
Absorption cell --	1 cm_2, flow-through, temperature-controlled
Reaction temperature --------	37 °C or ambient
Sample volumes -	0.35 mL with 0.050 mL of diluent for 0.1 to 10.0 mg/L and 0.035 mL with 0.065 mL of diluent for 10.0 to 500 mg/L
Reagent volumes	0.90 mL color reagent for 0.1 to 10.0 mg/L and 1.4 mL color reagent for 10.0 to 500 mg/L (NOTE 1)

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each instrument according to manufacturer's specifications.

5. Reagents

5.1 *Chloride standard solution I*, 1.00 mL= 10.00 mg Cl^{-1}: Dissolve 16.485 g primary standard NaCl crystals, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Chloride standard solution II*, 1.00 mL= 0.10 mg Cl^{-1}: Dilute 10.0 mL chloride standard solution I to 1,000 mL with demineralized water.

5.3 *Chloride working standards*, low range: Prepare a blank and 1,000 mL each of a series of chloride working standards by appropriate dilution of the chloride standard solution II as follows:

Chloride standard solution II (mL)	Chloride concentration (mg/L)
0.0	0.00
1.00	.10
5.00	.50
10.0	1.00
50.0	5.00
100.0	10.00

5.4 *Chloride working standards*, high-range: Prepare 1,000 mL each of a series of chloride working standards by appropriate dilution of the chloride standard solution I, as follows:

Chloride standard solution II (mL)	Chloride concentration (mg/L)
4.0	40
8.0	80
30.0	300
50.0	500

5.5 *Ferric nitrate stock solution*, 121 g/L: Dissolve 202 g $Fe(NO_3)_3 \cdot 9H_2O$ in approx 500 mL demineralized water. Add 225 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1 L. Filter and store in an amber-colored container.

5.6 *Mercuric thiocyanate stock solution*, saturated: Add approx 5 g $Hg(SCN)_2$ to 1 L methanol. Mix thoroughly for 0.5 h and let stand. Remove excess $Hg(SCN)_2$ by filtration. **CAUTION—Poisonous.**

5.7 *Chloride color reagent*: Add 150 mL ferric nitrate stock solution and 150 mL mercuric thiocyanate stock solution to demineralized water and dilute to 1 L. Store in amber bottle. Prepare fresh daily.

6. Procedure

6.1 Set up analyzer and computer-card assignments according to manufacturer's instructions.

6.2 Place five standards and a blank, beginning with the lowest concentration, in the first positions on the sample turntable. For the low range use 0.10, 0.50, 1.00, 5.00, and 10.0 mg/L, and for the high range use 10, 40, 80, 300, and 500 mg/L. Fill remainder of turntable with samples.

6.3 Begin analysis. Printer will acknowledge parameter and concentration range selected, listing each sample-cup number and corresponding concentration. During each run the cathode-ray tube (CRT) display will identify a plot of standards and samples, and list blank and reagent optical densities with slope calculations.

7. Calculations

Obtain the milligrams per liter of chloride in each sample from the printer.

8. Report

Report chloride, dissolved (00940), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

Precision expressed in terms of the standard deviation and percent relative standard deviation for replicate analysis by a single operator is as follows:

Mean (mg/L)	Std. Deviation (mg/L)	Relative standard deviation (percent)
0.38	0.06	16
5.72	.07	1.2
15.0	.08	.5
21.4	1.0	4.7
177	1.3	.7

References

American Society for Testing and Materials, 1984, Annual book of ASTM Standards, section 11, water: Philadelphia, v. 11.01, p. 392-400.

O'Brien, J. E., 1962, Automatic analysis of chlorides in sewage: Wastes Engineering, v. 33, p. 670-672.

Zall, D. M., Fisher, D., and Garner, M. Q., 1956, Photometric determination of chlorides in water: Analytical Chemistry, v. 28, p. 1665-1668.

Chloride, titrimetric, mercurimetric

Parameter and Code:

Chloride, dissolved, I-1184-85 (mg/L as Cl): 00940

1. Application

This method may be used to determine chloride in water containing at least 0.1 mg/L of chloride. Samples containing lower concentrations need to be concentrated by evaporation.

2. Summary of method

2.1 Mercuric and chloride ions form a highly stable, soluble complex.

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

Thus, the chloride in a sample may be titrated with a standard solution of a soluble mercuric salt such as mercuric nitrate. The equivalence point is detected by adding a small amount of diphenylcarbazone to the sample. A slight excess of mercuric ions, above that required to complex all of the chloride, reacts with this indicator to form a blue-violet complex (Dubsky and Trtilek, 1933, 1934; Clarke, 1950).

2.2 The optimum pH range for the titration is between 3.0 and 3.6. If the titration is made in a solution whose pH is less than 3.0, the results will be high, and if in a solution of pH greater than 3.6, the results will be low (Clarke, 1950; Thomas, 1954). The proper pH for the titration is easily obtained by adding bromophenol blue indicator and carefully adding dilute nitric acid or sodium hydroxide to adjust the sample to the desired pH.

2.3 Two standard mercuric nitrate solutions are required. A dilute solution should be used to titrate samples containing less than 200 mg/L chloride; a more concentrated mercuric nitrate solution should be used to titrate samples containing more than 200 mg/L.

3. Interferences

The method is not subject to interference from any of the anions and cations normally found in natural waters; as much as 1,000 mg/L of nitrate, sulfate, phosphate, magnesium, and calcium and 1×10^6 μg/L of aluminum do not interfere. One thousand μg/L of zinc, lead, nickel, ferrous, and chromous ions affect the colors of the solution, but not the accuracy of the titration. Nickel ion at a concentration of 1×10^5 μg/L is purple in neutral solution, green in acid solution, but gray at the chloride end point. Copper ion is tolerable up to 50,000 μg/L. Chromate and ferric ions, if present at concentrations exceeding 10,000 μg/L, must be reduced to their lower valence state prior to titration. The addition of dilute fresh hydroquinone solution insures reduction of these ions. Sulfite ion interferes at concentrations above 10 mg/L; the addition of a small amount of 30-percent hydrogen peroxide eliminates sulfite interference. Bromide and iodide are titrated with the chloride.

4. Apparatus

4.1 *Buret*, 5-, 10-, or 25-mL capacity.

4.2 *Fluorescent lamp*, white.

4.3 *Stirrer*, magnetic.

5. Reagents

5.1 *Chloride standard solution*, 1.00 mL= 1.00 mg Cl^{-1}: Dissolve 1.648 g primary standard NaCl crystals, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Hydrogen peroxide*, 30-percent.

5.3 *Hydroquinone solution*, 1 g/100 mL: Dissolve 1.0 g purified hydroquinone in demineralized water and dilute to 100 mL.

5.4 *Mercuric nitrate standard solution I*, 1.00 mL ≎ 1.00 mg Cl^{-1}: Dissolve 4.832 g

$Hg(NO_3)_2 \cdot H_2O$ in 25 mL demineralized water acidified with 0.25 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL. Filter, if necessary, and standardize by titrating 10.00 mL chloride standard solution diluted to 50 mL with demineralized water.

5.5 *Mercuric nitrate standard solution II*, 1.00 mL ⦵ 0.500 mg Cl^{-1}: Dissolve 2.416 g $Hg(NO_3)_2 \cdot H_2O$ in 25 mL demineralized water acidified with 0.25 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL. Filter, if necessary, and standardize by titrating 10.00 mL chloride standard solution diluted to 50 mL with demineralized water.

5.6 *Mixed indicator solution*: Dissolve 0.5 g crystalline diphenylcarbazone (Eastman Kodak No. 4459) and 0.05 g bromophenol blue (Eastman Kodak No. 752) in 75 mL ethanol (methyl alcohol or specially denatured alcohol No. 3A are also suitable), and dilute to 100 mL with the alcohol. Store in a brown bottle; discard after 6 months.

5.7 *Nitric acid*, 0.05*M*: Dilute 3.0 mL concentrated HNO_3 (sp gr 1.41) to 1 L with demineralized water.

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

6. Procedure

6.1 Pipet a volume of sample containing less than 20 mg Cl^{-1} (50.0 mL max) into a 125-mL Erlenmeyer flask, and adjust the volume to approx 50 mL. If the sample contains less than 0.1 mg/L of Cl^{-1}, evaporate an appropriate volume to 50 mL.

6.2 Place the flask on a magnetic stirrer and add 10 drops mixed indicator solution.

6.3 If a blue, blue-violet, or red color develops, add 0.05*M* HNO_3 by drops until the color changes to yellow. Add 1.0 mL excess acid. If a yellow or orange color forms when the mixed indicator is added, add 0.05*M* NaOH solution by drops until the color changes to blue violet; then add 0.05*M* HNO_3 by drops until the color changes to yellow; then add 1 mL excess.

6.4 Titrate the solution with mercuric nitrate standard solution I or II until a blue-violet color persists throughout the solution.

6.5 Determine a blank correction by similarly titrating 50 mL demineralized water.

6.6 Alternatively, the end point of the titration may be determined spectrophotometrically, with attendant improvement in precision. Refer to specific manufacturer's manual for details. Reagents are identical to those specified for the visual determination using the mercurimetric method.

7. Calculations

$$Cl^{-1}\ (\text{mg/L}) = \frac{1{,}000}{\text{mL sample}} \times (\text{mL titrant} - \text{mL blank}) \times (\text{mg Cl per mL titrant})$$

8. Report

Report chloride, dissolved (00940), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for 36 samples within the range of 0.29 to 243 mg/L may be expressed as follows:

$$S_T = 0.045X + 0.581$$

where

S_T= overall precision, milligrams per liter,

and

X= concentration of chloride, milligrams per liter.

The correlation coefficient is 0.8862.

9.2 Precision for seven of the 36 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
7	0.29	59
11	1.92	40
17	9.25	18
20	26.4	7
16	58.0	5
15	120	4
18	243	5

References

Clarke, F. E., 1950, Determination of chloride in water: Analytical Chemistry, v. 22, p. 553-5, 1458.

Dubsky, J. V., and Trtilek, J., 1933, Microvolumetric analysis using diphenylcarbazide and diphenylcarbazone as indicators (mercurimetry): Mikrochemie, v. 12, p. 315.

———1934, Mercurimetric determination of iodide using diphenylcarbazone as indicator: Mikrochemie, v. 15, p. 95.

Thomas, J. F., 1954, Mercurimetric determination of chlorides: American Water Works Association Journal, v. 46, p. 257-62.

Chloride, titrimetric, Mohr

Parameter and Code:

Chloride, dissolved, I-1183-85 (mg/L as Cl): 00940

1. Application

1.1 This procedure is recommended for water containing concentrations of chloride between 10 and 2000 mg/L, although it can be used satisfactorily for measuring chloride concentrations up to 5,000 mg/L.

1.2 Two titrant solutions of different concentrations are recommended. The more dilute titrant is used when the chloride concentration is less than 200 mg/L. However, the end point is not as sharp as when a more concentrated titrant is used, and the latter is recommended when the chloride concentration of the sample exceeds 200 mg/L. In high-chloride waters, the voluminous precipitate tends to mask the end point, and the maximum amount of chloride that can be titrated satisfactorily is about 50 mg. Excessive sample dilution decreases both the precision and accuracy of the determination. Sample aliquots of less than 10 mL are not recommended.

2. Summary of method

2.1 In the well-known Mohr method for determination of chloride, the solution is saturated with silver chloride at the equivalence point and contains equal concentrations of silver and chloride ions. When potassium chromate is used as an indicator, a slight excess of silver precipitates as red-silver chromate. The following reactions occur:

$$Ag^{+1} + Cl^{-1} \rightarrow AgCl$$

$$2Ag^{+1} + CrO_4^{-2} \rightarrow Ag_2CrO_4$$

The pH for the titration should be between 7.0 and 10.5. In an acid medium, the sensitivity of the method is decreased; the second ionization constant of chromic acid is small, and, therefore, the chromate ion reacts with hydrogen ions.

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

The solution should not be too alkaline because of the limited solubility of silver hydroxide (Collins, 1928). Calcium carbonate can be used to adjust the pH of acidic waters without danger of making the solution too alkaline. Detection of the end point is facilitated by illuminating the titration with yellow light or by viewing the titration through yellow goggles or a filter.

2.2 Additional information on the principle of the determination is given by Kolthoff and others (1969).

3. Interferences

Iodide and bromide titrate stoichiometrically as chloride. Phosphate, sulfide, and cyanide interfere. Sulfide and cyanide can be removed by acidifying and boiling the sample, and then adjusting the pH with calcium carbonate. Hydrogen sulfide can often be removed by passing pure air through the sample. Sulfite interferes but can be oxidized readily to sulfate with hydrogen peroxide.

4. Apparatus

4.1 *Buret*, 25-mL capacity.

4.2 *Yellow light* (or filter).

5. Reagents

5.1 *Chloride standard solution*, 1.00 mL= 1.00 mg Cl^{-1}: Dissolve 1.648 g primary standard NaCl crystals, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Potassium chromate indicator solution*, 5 g/100 mL: Dissolve 5 g K_2CrO_4 in 100 mL demineralized water. Add silver standard solution II until a small amount of red Ag_2CrO_4 precipitates. Allow to stand overnight and filter to remove the Ag_2CrO_4.

5.3 *Silver standard solution I*, 1.00 mL ≎ 5.00 mg Cl^{-1}. Pulverize approx 30 g $AgNO_3$ crystals in a clean mortar and dry at 105 to 120°C. Discoloration of the crystals indicates decomposition caused by excessive drying temperature or impurities. Dissolve 23.96 g dried $AgNO_3$ in demineralized water and dilute to 950 mL. Standardize by titrating 25.00 mL chloride standard solution diluted to 50 mL. Store in a light-proof bottle.

5.4 *Silver standard solution II*, 1.00 mL ≎ 0.50 mg Cl^{-1}: Dilute 100 mL silver standard solution I with demineralized water to 1,000 mL. Check the titer of the reagent by titrating 10.00 mL chloride standard solution. Store in light-proof bottle.

6. Procedure

6.1 Pipet a volume of sample containing less than 50 mg Cl^{-1} (50.00 mL max) into a porcelain evaporating dish, and adjust the volume to approx 50 mL.

6.2 Add 10 drops K_2CrO_4 indicator solution.

6.3 With constant stirring, titrate with silver standard solution I or II until the pink-red Ag_2CrO_4 persists for 10 to 15 sec.

6.4 Determine a blank correction by similarly titrating 50 mL demineralized water. The normal blank correction with silver standard solution II is 0.05 or 0.10 mL. No blank correction is required with the more concentrated titrant.

7. Calculations

$$Cl^{-1}\ (\text{mg/L}) = \frac{1{,}000}{\text{mL sample}} \times (\text{mL titrant} - \text{mL blank}) \times (\text{mg } Cl^{-1} \text{ per mL titrant})$$

8. Report

Report chloride, dissolved (00940), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for 37 samples within the range of 0.22 to 244 mg/L may be expressed as follows:

$$S_T = 0.036X + 0.532$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of chloride, milligrams per liter.

The correlation coefficient is 0.8550.

9.2 Precision for seven of the 37 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
12	0.22	100
7	.29	72
10	8.59	13
21	46.0	4
13	95.8	3
12	123	6
16	244	5

References

Collins, W. D., 1928, Notes on practical water analysis: U.S. Geological Survey Water-Supply Paper 596-H, p. 235-266.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative chemical analysis [4th ed.]: New York, MacMillan, 1199 p.

Chloride, ion-exchange chromatographic, automated

Parameters and Codes:

Chloride, dissolved, I-2057-85 (mg/L as Cl): 00940
Chloride, dissolved, I-2058-85 (mg/L as Cl): 00940

2. Summary of method

Chloride is determined sequentially with six other anions by ion-exchange chromatography. Ions are separated based on their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical-conductivity cell. See method I-2057, anions, ion-exchange chromatographic, automated, and method I-2058, anions, ion-exchange chromatographic, precipitation, automated.

Chromium, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:

Chromium, dissolved, I-1238-85 (μg/L as Cr): 01030
Chromium, total recoverable, I-3238-85 (μg/L as Cr): 01034
Chromium, suspended recoverable, I-7238-85 (μg/L as Cr): 01031

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 1 to 25 μg/L of chromium. Samples containing more than 25 μg/L need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption spectrometric direct method.

1.2 Suspended recoverable chromium is calculated by subtracting dissolved chromium from total recoverable chromium.

1.3 Total recoverable chromium in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

1.4 If the iron concentration of the sample exceeds 5,000 μg/L, determine chromium by the atomic absorption spectrometric direct method.

2. Summary of method

2.1 Chromium is determined by atomic absorption spectrometry. Any trivalent chromium present is oxidized by potassium permanganate to the hexavalent state. The oxidized chromium, together with hexavalent chromium originally present, is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the air-acetylene flame of the spectrometer (Midgett and Fishman, 1967).

2.2 Excess permanganate is reduced with sodium azide, which must not be present in excess because it interferes with subsequent pH adjustment and chelation.

3. Interferences

3.1 The optimum pH for the extraction of the hexavalent chromium-APDC complex by methyl isobutyl ketone (MIBK) is 3.1. At this pH, however, manganese is also partially extracted. The manganese-APDC complex is unstable and decomposes to a fine suspension of manganese oxides that clogs the atomizer-burner. If the pH of the sample is adjusted to 2.4 prior to chelation and extraction, less manganese is extracted, and there is only a slight loss in extraction efficiency for chromium. If the extract is not clear after standing overnight, it must be centrifuged.

3.2 Concentrations of iron greater than 5,000 μg/L interfere by suppressing the chromium absorption.

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	357.9 nm
Source (hollow-cathode lamp)	Chromium
Oxidant	Air
Fuel	Acetylene
Type of flame	Reducing

4.3 Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate solution*, 1.0 g/100 mL: Dissolve 1.0 g APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.

5.2 *Bromophenol blue indicator solution*, 0.1

g/100 mL: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.

5.3 *Chromium standard solution I*, 1.00 mL=100 μg Cr^{+6}: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.4 *Chromium standard solution II*, 1.00 mL=2.00 μg Cr^{+3} Pipet 5.0 mL chromium standard solution I into an Erlenmeyer flask. Add approximately 15 mg Na_2SO_3 and 0.5 mL concentrated HNO_3 (sp gr 1.41). Gently evaporate just to dryness; strong heating reoxidizes the Cr. Add 0.5 mL concentrated HNO_3 and again evaporate to dryness to destroy any excess sulfite. Dissolve the residue in 1 mL concentrated HNO_3 with warming. Cool, transfer to a 250-mL volumetric flask, and dilute to the mark with demineralized water.

5.5 *Chromium standard solution III*, 1.00 mL=0.50 μg Cr^{+3}: Dilute 25.0 mL chromium standard solution II to 100 mL with demineralized water. Prepare immediately before use.

5.6 *Methyl isobutyl ketone* (MIBK).

5.7 *Potassium permanganate solution*, 0.32 g/100 mL: Dissolve 0.32 g $KMnO_4$ in demineralized water and dilute to 100 mL. Allow to stand several days and decant if necessary.

5.8 *Sodium azide solution*, 0.10 g/100 mL: Dissolve 0.10 g NaN_3 in 100 mL demineralized water.

5.9 *Sodium hydroxide solution*, 1*M*: Dissolve 40 g NaOH in demineralized water and dilute to 1 L.

5.10 *Sulfuric acid*, 0.12*M*: *Cautiously*, add 6.5 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1 + 9) and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample solution containing less than 2.5 μg Cr (100 mL max) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL. The pH must be 2.0 or less. Add concentrated HNO_3 if necessary.

6.3 Acidify a liter of demineralized water with 1.5 mL concentrated HNO_3 (sp gr 1.41). Prepare a blank and at least six standards, and adjust the volume of each to approx 100 mL with the acidified demineralized water.

6.4 Add $KMnO_4$ solution by drops to blank, standards, and samples until a faint-pink color persists.

6.5 Heat on a steam bath for 20 min. If the color disappears, add $KMnO_4$ solution by drops to maintain a slight excess.

6.6 While blanks, samples, and standards are still on the steam bath, add NaN_3 solution by drops until $KMnO_4$ color just disappears. Heat for about 2 min between each addition and avoid adding any excess. Continue heating for 5 min after adding the last drop of sodium azide solution.

6.7 Transfer to a water bath and cool to room temperature.

6.8 Remove from the water bath and filter through Whatman No. 40 filter paper any sample that has a brownish precipitate or coloration that may interfere with the pH adjustment.

6.9 Add 2.0 mL 1*M* NaOH and 2 drops bromophenol blue indicator solution. Continue the addition of 1*M* NaOH by drops to all samples and standards in which the indicator change from yellow to blue has not occurred. Add 0.12*M* H_2SO_4 by drops until the blue color just disappears; then add 2.0 mL in excess. The pH at this point should be 2.4 (NOTE 1).

NOTE 1. The pH adjustment in paragraph 6.9 may be made with a pH meter instead of with an indicator, in which case the filtration called for in paragraph 6.8 will not be necessary.

6.10 Add 5.0 mL APDC solution and shake for 3 min. The pH at this point should be 2.8.

6.11 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.12 Allow the layers to separate and then add demineralized water until the ketone layer is completely in the neck of the flask.

6.13 Stopper and allow to stand overnight. The Cr^{+6}-APDC complex is stable for at least 36 h.

6.14 Aspirate the ketone layer of the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable chromium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing chromium concentrations that exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

7.2 To determine the micrograms per liter of suspended recoverable chromium, subtract dissolved-chromium concentration from total-recoverable-chromium concentration.

8. Report

Report chromium, dissolved (01030), total-recoverable (01034), and suspended-recoverable (01031), concentrations as follows: less than 100 μg/L, the nearest microgram per liter; 100 μg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved chromium within the range of 5.8 to 47.8 μg/L for 14 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 13.2 μg/L ranged from 11.2 to 16.1 μg/L.

9.2 Precision for dissolved chromium for seven of the 14 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
4	5.75	66
3	9.67	6
12	12.9	113
11	18.7	66
3	20.0	39
3	44.3	9
9	47.8	55

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable chromium will be greater than that reported for dissolved chromium.

Reference

Midgett, M. R., and Fishman, M. J., 1967, Determination of total chromium in fresh waters by atomic absorption: Atomic Absorption Newsletter, v. 6, p. 128–131.

Chromium, atomic absorption spectrometric, direct

Parameters and Codes:

Chromium, dissolved, I-1236-85 (µg/L as Cr): 01030
Chromium, total recoverable, I-3236-85 (µg/L as Cr): 01034
Chromium, suspended recoverable, I-7236-85 (µg/L as Cr): 01031
Chromium, recoverable-from-bottom-material, I-5236-85 (µg/g as Cr): 01029

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 10 µg/L of chromium. Sample solutions containing more than 400 µg/L need to be diluted. Sample solutions containing less than 10 µg/L and brines need to be analyzed by the atomic absorption spectrometric chelation-extraction method, providing that the interference limits discussed in that method are not exceeded.

1.2 Suspended recoverable chromium is calculated by subtracting dissolved chromium from total recoverable chromium.

1.3 This method may be used to analyze bottom material containing at least 1 µg/g of chromium. Sample solutions containing more than 400 µg/L need to be diluted.

1.4 Total recoverable chromium in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable chromium in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

Chromium is determined by atomic absorption spectrometry by direct aspiration of the sample solution into an air-acetylene flame. Ammonium chloride is added to the sample to mask certain interferences.

3. Interferences

3.1 Iron, nickel, and cobalt at 100 µg/L and magnesium at 30 mg/L, in the prepared sample solution, interfere by suppressing the absorption of the chromium. These interferences are eliminated in solutions containing about 18,000 mg/L of ammonium chloride (Barnes, 1966, and Giammarise, 1966). Samples adjusted to this concentration of ammonium chloride show no interferences from 7×10^5 µg/L of iron and 10,000 µg/L each of nickel and cobalt, or from 1,000 mg/L of magnesium.

3.2 Individual concentrations of sodium (8,000 mg/L), calcium (4,000 mg/L), nitrate (100 mg/L), sulfate (8,000 mg/L), and chloride (10,000 mg/L) do not interfere. Greater concentrations of each constituent were not investigated.

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	357.9 nm.
Source (hollow-cathode lamp)	Chromium
Oxidant	Air
Fuel	Acetylene
Type of flame	Reducing

4.3 The 102-mm, flathead, single-slot burner allows a working range of 10 to 400 µg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ammonium chloride solution*, 200 g/L: Dissolve 200 g NH_4Cl in demineralized water and dilute to 1 L.

5.2 *Chromium standard solution I*, 1.00 mL= 100 µg Cr: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.3 *Chromium standard solution II*, 1.00 mL= 1.00 µg Cr: Dilute 10.0 mL chromium standard solution I to 1,000 mL with demineralized water.

5.4 *Chromium standard working solutions*: Prepare a series of at least six standard working solutions containing from 10 to 400 µg/L of chromium by diluting chromium standard solution II. To each standard working solution, add 1.0 mL of NH_4Cl solution for each 10 mL of standard. Similarly, prepare a demineralized water blank.

6. Procedure

6.1 Add 1.0 mL NH_4Cl solution to 10.0 mL sample solution and mix thoroughly.

6.2 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable chromium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing chromium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine the micrograms per liter of suspended recoverable chromium, subtract dissolved-chromium concentration from total-recoverable-chromium concentration.

7.3 To determine micrograms per gram of chromium in bottom-material samples first determine the micrograms per liter of chromium in each sample as in paragraph 7.1; then

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

8. Report

8.1 Report chromium, dissolved (01030), total-recoverable (01034), and suspended-recoverable (01031), concentrations as follows: less than 1,000 µg/L, nearest 10 µg/L: 1,000 µg/L and above, two significant figures.

8.2 Report chromium, recoverable-from-bottom-material (01029), concentrations as follows: less than 10 µg/g, nearest microgram per gram; 10 to 100 µg/g, nearest 10 µg/g; 100 µg/g and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved chromium within the range of 6.7 to 55 µg/L for 23 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 7.2 µg/L ranged from 6.7 to 7.9 µg/L.

9.2 Precision for dissolved chromium for five of the 23 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
6	6.7	77
23	10.9	54
23	18.7	46
13	30.2	19
6	55.0	19

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable chromium and for recoverable chromium from bottom material will be greater than that reported for dissolved chromium.

9.4 Precision for total recoverable chromium expressed in terms of percent relative standard deviation for two water-suspended sediment mixtures is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
8	31.6	22
11	27.3	38

References

Barnes, L., Jr., 1966, Determination of chromium in low alloy steels by atomic absorption spectrometry: Analytical Chemistry, v. 38, p. 1083–1085.

Giammarise, A., 1966, The use of ammonium chloride in analyses of chromium samples containing iron: Atomic Absorption Newsletter, v. 5, p. 113–115.

Chromium, atomic absorption spectrometric, graphite furnace

Parameter and Code:

Chromium, dissolved, I-1235-85 (μg/L as Cr): 01030

1. Application

1.1 This method may be used to determine chromium in low ionic-strength water and precipitation. With deuterium background correction and a 20-μL sample, the method is applicable in the range from 0.2 to 20 μg/L. With Zeeman background correction and a 20-μL sample, the method is applicable in the range from 0.5 to 25 μg/L. Sample solutions that contain chromium concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric direct or chelation-extraction method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Chromium is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform and a matrix modifier is added. The sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (25 mg/L), magnesium (8 mg/L), sodium (20 mg/L), sulfate (34 mg/L), and chloride (25 mg/L) do not interfere. Greater concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of chromium. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contribution from contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 357.9 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high-temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-μL sample with 5 μL of matrix modifier (NOTE 1).

NOTE 1. A 20-μL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms*. Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware*. Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Chromium standard solution I*, 1.00 mL=1,000 μg Cr: Dissolve 2.8290 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in Type 1 water. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with Type 1 water.

5.2 *Chromium standard solution II*, 1.00 mL=10.0 μg Cr: Dilute 10.0 mL chromium standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified Type 1 water (paragraph 5.7) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.3 *Chromium standard solution III*, 1.00 mL=1.00 μg Cr: Dilute 100.0 mL chromium standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.4 *Chromium standard solution IV*, 1.00 mL=0.01 μg Cr: Dilute 10.0 mL chromium standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

5.5 *Matrix modifier solution*, 4.0 g $Mg(NO_3)_2$/L, Suprapur MCB reagent or equivalent: Add 6.9 g $Mg(NO_3)_2 \cdot 6H_2O$ to 950 mL Type 1 water, mix, and dilute to 1,000 mL. DO NOT ADD ACID TO THE PURIFIED MATRIX MODIFIER SOLUTION.

5.6 *Nitric acid, concentrated*, high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HNO_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for chromium. Add an additional 1.5 mL of concentrated HNO_3/liter of water, and repeat analysis. Integrated signal should not increase by more than 0.001 absorbance-seconds.

5.7 *Water, acidified*, Type 1: Add 1.5 mL high-purity concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water, Type 1*

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1 + 1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-μL aliquots of blank and working standards plus 5 μL of modifier each and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and/or platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of chromium in each sample from the digital display or printer output. Dilute those samples containing concentrations of chromium that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report chromium, dissolved (01030), concentrations as follows: less than 10.0 μg/L, nearest 0.1 μg/L; 10 μg/L and above, two significant figures for both deuterium background correction and Zeeman background correction.

9. Precision

9.1 Analysis of one sample 15 times by a single operator using deuterium background correction is as follows:

Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
13.87	0.95	6.8

9.2 Analysis of four samples six times each by a single operator using Zeeman background correction is as follows:

Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
7.30	0.17	2.3
11.63	.18	1.5
17.53	.16	.9
23.63	.20	.8

9.3 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 μS/cm). A known amount of chromium was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (μg/L)	Amount found (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
2.2	2.43	0.29	11.9	110
4.4	5.08	.37	7.3	115
8.0	7.6	.42	5.5	95
8.5	7.93	.64	8.1	93
16	15.38	.34	2.2	96
Tap water				
2.2	2.37	.51	21.5	108
4.4	4.53	.96	21.2	103
8.0	7.17	1.43	19.9	90
8.5	7.53	1.17	7.0	89
16	13.90	2.13	15.3	87

9.4 The precision and bias for the deuterium background method were tested on deionized water and tap water (specific conductance 280 μS/cm). A known amount of chromium was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (μg/L)	Amount found (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
2.2	2.22	0.41	18.5	101
4.4	4.79	.28	5.8	109
8.0	8.09	.46	5.7	101
8.5	7.92	.56	7.1	93
16	15.45	.91	5.9	97
Tap water				
2.2	2.49	.30	12.0	113
4.4	4.64	.56	12.1	105
8.0	7.48	.41	5.5	94
8.5	8.36	.56	6.7	98
16	14.58	1.08	7.4	91

9.5 The standard deviation from interlaboratory data, without regard to type of background correction and use of matrix modifiers, if any, for dissolved chromium within the range of 4.6 to 30.8 μg/L for 16 samples, was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 5.0 μg/L ranged from 4.5 to 5.6 μg/L.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 39–41.

Cooksey, M., and Barnett, W. B., 1979, Matrix modification and the method of additions in flameless atomic absorption: Atomic Absorption Newsletter, v. 18, p. 101–5.

Fernandez, F. J., Beatty, M. M., and Barnett, W. B., 1981, Use of the L'vov platform for furnace atomic absorption applications: Atomic Spectroscopy, v. 2, p. 16–21.

Hinderberger, E. J., Kaiser, M. L., and Koirtyohann, S. R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1–11.

Manning, D. C., and Slavin, W., 1983, The determination of trace elements in natural waters using the stabilized temperature platform furnace: Applied Spectroscopy, v. 37, p. 1–11.

Ottaway, J. M., 1982, A revolutionary development in graphite furnace atomic absorption: Atomic Spectroscopy, v. 3, p. 89–92.

Slavin, W., Carnrick, G. R., and Manning, D. C., 1982, Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace: Analytical Chemistry, v. 54, p. 621–4.

Chromium, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:

Chromium, total I-5474-85 (mg/kg as Cr): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Chromium is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Chromium, hexavalent, atomic absorption spectrometric, chelation-extraction

Parameter and Code:

Chromium, hexavalent, dissolved, I-1232-85 (μg/L as Cr): 01032

1. Application

1.1 This method may be used to analyze water and brines containing from 1 to 25 μg/L of chromium. Samples containing more than 25 μg/L need to be diluted prior to chelation-extraction.

1.2 If the iron concentration of the sample exceeds 5,000 μg/L, determine hexavalent chromium by the colorimetric diphenylcarbazide method (I-1230).

2. Summary of method

Hexavalent chromium is determined by atomic absorption spectrometry. The element is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the air-acetylene flame of the spectrometer (Midgett and Fishman, 1967).

3. Interferences

Concentrations of iron greater than 5,000 μg/L interfere by suppressing the chromium absorption.

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	357.9 nm
Source (hollow-cathode lamp)	Chromium
Oxidant	Air
Fuel	Acetylene
Type of flame	Reducing

4.3 Different burners may be used according to manufacturers' instructions.

5. Reagents

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

5.2 *Chromium standard solution I*, 1.00 mL=100 μg Cr^{+6}: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.3 *Chromium standard solution II*, 1.00 mL=10.0 μg Cr^{+6}: Dilute 100 mL chromium standard solution I to 1,000 mL with demineralized water.

5.4 *Chromium standard solution III*, 1.00 mL=0.10 μg Cr^{+6}: Dilute 10.0 mL chromium standard solution II to 1,000 mL with demineralized water.

5.5 *Methyl isobutyl ketone* (MIBK).

5.6 *Sodium hydroxide solution*, 2.5*M*: Dissolve 100 g NaOH in demineralized water and dilute to 1 L. Alternately a 2.5*M* NH_4OH solution may be used. Add 167 mL concentrated NH_4OH (sp gr 0.90) to 600 mL demineralized water. Mix, cool,and dilute to 1 L with demineralized water.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+9) and rinse with demineralized water immediatley before use.

6.2 Pipet a volume of sample containing less than 2.5 μg Cr^{+6} (100 mL max) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.3 Acidify a liter of demineralized water with 1.5 mL concentrated HNO_3 (sp gr 1.41). Prepare a blank and at least six standards containing from 1 to 25 μg/L of Cr^{+6}, and adjust the volume of each to approx 100 mL with the acidified demineralized water.

6.4 With a pH meter, adjust the pH of each solution to 2.4 by dropwise addition of 2.5*M* NaOH or NH_4OH.

6.5 Add 5.0 mL APDC solution and mix.

6.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask. The Cr^{+6} -APDC complex is stable for at least 36 h.

6.8 Aspirate the ketone layer of the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

Determine the micrograms per liter of hexavalent chromium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing chromium concentrations that exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factor.

8. Report

Report chromium, dissolved, hexavalent (01032), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

It is estimated that the precision of this method for Cr^{+6} is equal to total chromium by the atomic absorption spectrometric chelation-extraction method.

Reference

Midgett, M. R., and Fishman, M. J., 1967, Determination of total chromium in fresh waters by atomic absorption: Atomic Absorption Newsletter, v. 6, p. 128-131.

Chromium, hexavalent, colorimetric, diphenylcarbazide

Parameter and Code:

Chromium, hexavalent, dissolved, I-1230-85 (μg/L as Cr^{+6}): 01032

1. Application

This method may be used to analyze most natural water containing from 50 to 4,000 μg/L hexavalent chromium. Samples containing higher concentrations must first be diluted.

2. Summary of method

2.1 This method determines only hexavalent chromium in solution.

2.2 In acid solution, diphenylcarbazide and hexavalent chromium form a soluble red- violet product that absorbs light at 540 nm. The pH of the reaction is not particularly critical; solutions differing in pH from 0.7 to 1.3 give identical colors. The color of the chromium-diphenylcarbazide product changes slightly with time, but for practical purposes it can be considered stable.

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

3. Interferences

For all practical purposes the reaction is specific for chromium; metallic interference almost never occurs. Iron, mercury, and molybdenum in concentrations as high as 100,000 μg/L show only a small effect. Vanadium should not be present in concentrations exceeding 4,000 μg/L. The effect of water color is small, and color as much as 50 color units (Hazen scale) is tolerable. The chromium color develops almost instantly and is stable; whereas, vanadium color develops instantly and then fades rapidly. If the original vanadium concentration is less than 4,000 μg/L, no vanadium color persists after 10 min.

4. Apparatus

4.1 *Spectrometer* for use at 540 nm.

4.2 Refer to the manufacturer's manual for optimizing instrument.

5. Reagents

5.1 *Chromium standard solution*, 1.00 mL= 100 μg Cr^{+6}: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.2 *Diphenylcarbazide reagent*: Dissolve 0.2 g diphenylcarbazide and 1.0 g phthalic anhydride in 200 mL ethanol. This reagent is stable for several weeks; a slight discoloration will not impair the usefulness of the reagent.

5.3 *Sulfuric acid*, 1.2*M*: CAUTIOUSLY, add 6.5 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 100 mL.

6. Procedure

6.1 Pipet a volume of sample containing less than 40 μg Cr^{+6} (10.0 mL max) into a 50-mL beaker, and adjust the volume to 10.0 mL with demineralized water.

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

6.3 Add 1.0 mL 1.2*M* H_2SO_4 and mix.

6.4 Add 0.5 mL diphenylcarbazide reagent and mix.

6.5 Allow to stand 10 min.

6.6 Determine the absorbance of the sample and standards against the blank, and when necessary make a correction for water color.

7. Calculations

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

7.2 Determine the hexavalent chromium concentration in micrograms per liter as follows:

$$Cr^{+6}\ (\mu g/L) = \frac{1{,}000 \times \mu g\ Cr^{+6}\ \text{in sample}}{\text{mL sample}}$$

8. Report

Report chromium, dissolved hexavalent (01032), concentrations as follows: 50 to 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

9. Precision

Precision expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
5	810	5

Reference

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

Cobalt, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:

Cobalt, dissolved, I-1240-85 (μg/L as Co): 01035
Cobalt, total recoverable, I-3240-85 (μg/L as Co): 01037
Cobalt, suspended recoverable, I-7240-85 (μg/L as Co): 01036

1. Application

1.1 This method may be used to analyze water, brines, and water-suspended sediment containing from 1 to 50 μg/L of cobalt. Sample solutions containing more than 50 μg/L need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption spectrometric direct method.

1.2 Suspended recoverable cobalt is calculated by subtracting dissolved cobalt from total recoverable cobalt.

1.3 Total recoverable cobalt in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

1.4 If the iron concentration of the sample solution exceeds 25,000 μg/L, determine cobalt by atomic absorption spectrometric direct method.

2. Summary of method

Cobalt is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer (Fishman and Midgett, 1968).

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the cobalt absorption.

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	240.7 nm
Source (hollow-cathode lamp)	Cobalt
Oxidant	Air
Fuel	Acetylene
Type of flame	Oxidizing

4.3 Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate solution*, 1 g/100 mL: Dissolve 1 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Citric acid-sodium citrate buffer solution*: Dissolve 126 g citric acid monohydrate and 44 g sodium citrate dihydrate in demineralized water and dilute to 1 L with demineralized water. See NOTE 3 before preparation.

5.3 *Cobalt standard solution I*, 1.00 mL= 100 μg Co: Dissolve 0.1407 g Co_2O_3 in a minimum amount of dilute HNO_3. Add 10 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1000 mL with demineralized water.

5.4 *Cobalt standard solution II*, 1.00 mL= 2.0 μg Co: Dilute 20.0 mL cobalt standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.5 *Cobalt standard solution III*, 1.00 mL= 0.2 μg Co: Immediately before use, dilute 10.0 mL cobalt standard solution II to 100.0 mL with acidified water. This standard is used to prepare working standards at the time of analysis.

5.6 *Methyl isobutyl ketone (MIBK).*

5.7 *Potassium hydroxide solution,* 10*M*: Dissolve 56 g KOH in demineralized water, cool, and dilute to 100 mL.

5.8 *Potassium hydroxide solution,* 2.5*M*: Dissolve 14 g KOH in demineralized water and dilute to 100 mL (NOTE 1).

NOTE 1. Alternatively, a 2.5*M* NH_4OH solution may be used. Add 167 mL concentrated NH_4OH (sp gr 0.90) to 600 mL demineralized water. Cool, and dilute to 1 L.

5.9 *Water, acidified:* Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1 + 9) and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample solution containing less than 5.0 µg Co (100 mL max) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.3 Prepare a blank of acidified water and sufficient standards, and adjust the volume of each to approx 100 mL with acidified water.

6.4 With a pH meter, adjust the pH of each solution to 2.7 with 2.5*M* KOH (NOTES 2 and 3). Shake for 3 min.

NOTE 2. For water-suspended sediment samples that have been digested, add 1 to 2 mL 10*M* KOH or concentrated NH_4OH (sp gr 0.90) before pH adjustment.

NOTE 3. If an automated titration system is used to adjust the pH, add 2.5 mL citric acid-sodium citrate buffer solution prior to pH adjustment. This will prevent over-shooting the end point in poorly buffered samples.

6.5 Add 2.5 mL APDC solution and mix.

6.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.8 Aspirate the ketone layer within 1 h. Aspirate the ketone layer of the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable cobalt in each sample from the digital display or printer. Dilute those samples containing cobalt concentrations that exceed the working range of the method; repeat the chelation-extraction, and multiply by the proper dilution factors.

7.2 To determine the micrograms per liter of suspended recoverable cobalt, subtract dissolved-cobalt concentration from total-recoverable-cobalt concentration.

8. Report

Report cobalt, dissolved (01035), total-recoverable (01037), and suspended-recoverable (01036), concentrations as follows: less than 100 µg/L, nearest microgram per liter; 100 µg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved cobalt within the range of 2.0 to 14.0 µg/L for 17 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 1.6 µg/L ranged from 1.4 to 1.9 µg/L.

9.2 Precision for dissolved cobalt for five of the 17 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
3	2.0	0
6	2.2	79
9	5.3	23
5	11.4	13
8	14.0	14

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable cobalt will be greater than that reported for dissolved cobalt.

Reference

Fishman, M. J., and Midgett, M. R., 1968, Extraction techniques for the determination of cobalt, nickel, and lead in fresh water by atomic absorption, *in* Trace inorganics in water: American Chemical Society, Advances in Chemistry Series, no. 73, p. 230-5.

Cobalt, atomic absorption spectrometric, direct

Parameters and Codes:

Cobalt, dissolved, I-1239-85 (μg/L as Co): 01035
Cobalt, total recoverable, I-3239-85 (μg/L as Co): 01037
Cobalt, suspended recoverable, I-7239-85 (μg/L as Co): 01036
Cobalt, recoverable-from-bottom-material, dry wt, I-5239-85, (μg/g as Co): 01038

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 50 μg/L of cobalt. Samples solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale. Sample solutions containing less than 50 μg/L need to be analyzed by the atomic absorption spectrometric chelation-extraction method, providing the interference limits discussed in that method are not exceeded.

1.2 Suspended recoverable cobalt is calculated by subtracting dissolved cobalt from total recoverable cobalt.

1.3 This method may be used to analyze bottom material containing at least 5 μg/g of cobalt.

1.4 Total recoverable cobalt in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable cobalt in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

Cobalt is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without additional treatment of the sample other than the addition of ammonium chloride to mask certain interferences.

3. Interferences

3.1 Nitrate at 1 mg/L interferes by suppressing the absorption of the cobalt. This interference is eliminated in solutions containing about 18,000 mg/L of ammonium chloride. Samples adjusted to this concentration of ammonium chloride show no interference from 800 mg/L of nitrate.

3.2 Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,500 mg/L), magnesium (4,500 mg/L), sulfate (9,000 mg/L), chloride (15,000 mg/L), iron (4×10^6 μg/L), and cadmium, nickel, copper, zinc, lead, and chromium (10,000 μg/L) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

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

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

Grating ------------ Ultraviolet
Wavelength -------- 240.7 nm
Source (hollow-cathode lamp) ------------ Cobalt
Oxidant ------------ Air
Fuel --------------- Acetylene
Type of flame ------- Oxidizing

4.3 The Perkin-Elmer, flathead, single-slot burner allows a working range of 50 to 1,000 μg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ammonium chloride solution*, 200 g/L: Dissolve 200 g NH_4Cl in demineralized water and dilute to 1 L with demineralized water.

5.2 *Cobalt standard solution I*, 1.00 mL= 100 μg Co: Dissolve 0.1407 g Co_2O_3 in a minimum amount of dilute HNO_3. Add 10 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1000 mL with demineralized water.

5.3 *Cobalt standard solution II*, 1.00 mL= 10 μg Co: Dilute 100.0 mL cobalt standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.4 *Cobalt standard working solutions*: Prepare a series of at least six standard working solutions containing from 50 to 1,000 μg/L cobalt by appropriate dilution of cobalt standard solution II with acidified water. Add 1.0 mL NH_4Cl solution for each 10 mL standard working solution. Similarly, prepare an acidified water blank. Prepare fresh daily.

5.5 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to a liter of demineralized water.

6. Procedure

6.1 Add 1.0 mL NH_4Cl solution to 10.0 mL sample solution and mix thoroughly.

6.2 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable cobalt in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing cobalt concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per liter suspended recoverable cobalt, subtract dissolved-cobalt concentration from total-recoverable-cobalt concentration.

7.3 To determine micrograms per gram of cobalt in bottom-material samples, first determine the micrograms per liter of cobalt in each sample as in paragraph 7.1; then

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

8. Report

8.1 Report cobalt, dissolved (01035), total-recoverable (01037), and suspended-recoverable (01036), concentrations to the nearest 50 μg/L.

8.2 Report cobalt, recoverable-from-bottom-material (01038), concentrations as follows: 50 to 100 μg/g, the nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved cobalt within the range of 6.2 to 19.3 μg/L (NOTE 1) for six samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 4.4 μg/L ranged from 3.4 to 6.4 μg/L.

NOTE 1. Precision data for cobalt are below the reporting level of 50 μg/L. Samples that contained greater cobalt concentrations were not available; however, precision should improve at greater concentrations.

9.2 Precision for dissolved cobalt for three of the six samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
5	6.2	57
4	15.8	27
3	19.3	11

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable cobalt and for recoverable cobalt in bottom material will be greater than that reported for dissolved cobalt.

Cobalt, atomic absorption spectrometric, graphite furnace

Parameter and Code:

Cobalt, dissolved, I-1241-85 (μg/L as Co): 01035

1. Application

1.1 This method may be used to determine cobalt in low ionic-strength water and precipitation. With deuterium background correction and a 20-μL sample, the method is applicable in the range from 0.5 to 100 μg/L. With Zeeman background correction and a 20-μL sample, the method is applicable in the range from 0.5 to 65 μg/L. Sample solutions that contain cobalt concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric direct or chelation-extraction method, or by the atomic emission spectrometric ICP method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Cobalt is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform, then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (60 mg/L), magnesium (14 mg/L), sodium (55 mg/L), sulfate (110 mg/L), and chloride (45 mg/L) do not interfere. Higher concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of cobalt. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 240.7 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-μL sample (NOTE 1).

NOTE 1. A 20-μL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms*. Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware*. Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Cobalt standard solution I*, 1.00 mL= 1,000 μg Co: Dissolve 1.4070 g Co_2O_3 in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with Type 1 water.

5.2 *Cobalt standard solution II*, 1.00 mL= 10.0 μg Co: Dilute 10.0 mL cobalt standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified Type 1 water (paragraph 5.6) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.3 *Cobalt standard solution III*, 1.00 mL= 1.00 μg Co: Dilute 100.0 mL cobalt standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.4 *Cobalt standard solution IV*, 1.00 mL=0.010 μg Co: Dilute 10.0 mL cobalt standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

5.5 *Nitric acid, concentrated*, high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HNO_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for cobalt. Add an additional 1.5 mL of concentrated HNO_3/liter of water, and repeat analysis. Integrated signal should not increase by more than 0.001 absorbance-seconds.

5.6 *Water, acidified*, Type 1: Add 1.5 mL high-purity, concentrated HNO_3(sp gr 1.41) to each liter of water.

5.7 *Water, Type 1.*

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1+1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-μL aliquots of blank and working standards and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and (or) platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of cobalt in each sample from the digital display or printer output. Dilute those samples containing concentrations of cobalt that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report cobalt, dissolved (01035), concentrations as follows: less than 10.0 μg/L, nearest 0.1 μg/L; 10 μg/L and above, two significant figures for both deuterium background correction and Zeeman background correction.

9. Precision

9.1 Analysis of one sample 13 times each by a single operator using deuterium background correction is as follows:

Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
9.05	0.67	7.4

9.2 Analysis of four samples six times each by a single operator using Zeeman background correction is as follows:

Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
5.75	0.24	4.2
20.52	.26	1.3
32.27	.38	1.2
64.20	.20	.3

9.3 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 μS/cm). A known amount of cobalt was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (μg/L)	Amount found (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
8.5	8.67	0.88	10.1	102
9.5	9.92	.97	9.8	104
15	15.00	1.10	7.3	100
17	17.00	1.52	8.9	100
30	29.50	1.41	4.8	98
Tap water				
8.5	8.58	1.07	12.5	101
9.5	9.58	.58	6.1	101
15	14.92	1.36	9.1	99
17	16.67	1.66	10.0	98
30	28.33	1.99	7.0	94

9.4 The precision and bias for the deuterium background method were tested on deionized water and tap water (specific conductance 280 μS/cm). A known amount of cobalt was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (μg/L)	Amount found (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
8.5	8.61	0.97	11.3	101
9.5	10.96	.58	5.3	115
15	14.34	.70	4.9	96
17	17.25	1.42	8.2	101
30	29.03	2.76	9.5	97
Tap water				
8.5	8.27	0.85	10.3	97
9.5	10.89	.86	7.9	115
15	15.12	1.73	11.7	101
17	15.88	.49	3.1	93
30	28.43	2.68	9.4	95

9.5 The standard deviation from interlaboratory data, without regard to type of background correction and use of matrix modifiers, if any, for dissolved cobalt within the range of 2.3 to 18.3 μg/L for 14 samples, was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 3.2 μg/L ranged from 2.7 to 3.8 μg/L.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 39–41.

Cooksey, M., and Barnett, W. B., 1979, Matrix modification and the method of additions in flameless atomic absorption: Atomic Absorption Newsletter, v. 18, p. 101–5.

Fernandez, F. J., Beatty, M. M., and Barnett, W. B., 1981, Use of the L'vov platform for furnace atomic absorption applications: Atomic Spectroscopy, v. 2, p. 16–21.

Hinderberger, E. J., Kaiser, M. L., and Koirtyohann, S. R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1–11.

Manning, D. C., and Slavin, W., 1983, The determination of trace elements in natural waters using the stabilized temperature platform furnace: Applied Spectroscopy, v. 37, p. 1–11.

Ottaway, J. M., 1982, A revolutionary development in graphite furnace atomic absorption: Atomic Spectroscopy, v. 3, p. 89–92.

Slavin, W., Carnrick, G. R., and Manning, D. C., 1982, Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace: Analytical Chemistry, v. 54, p. 621–4.

Cobalt, atomic emission spectrometric, ICP

Parameter and Code:

Cobalt, dissolved, I-1472-85 (μg/L as Co): 01035

2. Summary of method

Cobalt is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Cobalt, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:

Cobalt, total, I-5474-85 (mg/kg as Co): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200°C. Cobalt is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Color, electrometric, visual comparison

Parameter and Code:

Color, I-1250-85 (platinum-cobalt units): 00080

1. Application

This method may be used to measure the color of water whose color reasonably matches from 1 to 70 units of the Hazen scale (Hazen, 1892) and that contains no excessive amount of sediment. Samples that have a color unit value greater than 70 must first be diluted.

2. Summary of method

The color of the water is compared to that of colored glass disks that have been calibrated to correspond to the platinum-cobalt scale of Hazen (1892). The unit of color is that produced by 1 mg/L of platinum. A small amount of cobalt may be added to aid in color matching. The Hazen scale (platinum-cobalt units) is usually satisfactory for most waters, but the hues and shades of some waters may not easily be compared with standards. If the hue of the water does not compare with that of the standard, very little can be done except to visually compare the absorbances of the sample and standard. Highly colored waters should not be diluted more than necessary because the color of the diluted sample often is not proportional to the dilution.

3. Interferences

Turbidity generally causes the observed color value to be greater than the true color value, but there is some disagreement as to the magnitude of the effect of turbidity. The removal of turbidity is a recurrent problem in the determination of color. Color is removed by absorption on suspended material. Filtration of samples to remove turbidity frequently removes some of the color-imparting solutes by absorption on the sediments or on the filter medium. Centrifuging is preferable to filtration, but centrifuging may not be completely effective in removing very finely divided particles. Flocculation of the dispersed particles with a strong electrolyte has been proposed (Lamar, 1949) and is sometimes effective. The process of flocculation decolorizes some waters and is, therefore, not suitable in all cases.

4. Apparatus

Color comparator, with standard color disks, covering the range 0 to 70 color units.

5. Reagents

None required.

6. Procedure

6.1 Fill one instrument tube with the sample of water, level the tube, insert the glass plug, making sure that no air bubbles are trapped, and insert the tube into the comparator.

6.2 Use demineralized water as a blank in the second tube.

6.3 The color comparison is made by revolving the disk until the colors of the two tubes match. Samples having color values greater than 70 must first be diluted.

7. Calculations

Read the color directly from the matching color standard; apply the proper dilution if required.

8. Report

Report color (00080) (platinum-cobalt units) as follows:

Color unit	Record units to nearest
1-49	1
50-99	5
100-249	10
250-500	20

9. Precision

Precision data are not available for this method.

References

Hazen, Allen, 1892, A new color standard for natural waters: American Chemical Society Journal, v. 12, p. 427.

Lamar, W.L., 1949, Determination of color of turbid waters: Analytical Chemistry, v. 21, p. 726-27.

Copper, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:

Copper, dissolved, I-1271-85 (μg/L as Cu): 01040
Copper, total recoverable, I-3271-85 (μg/L as Cu): 01042
Copper, suspended recoverable, I-7271-85 (μg/L as Cu): 01041

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 1 to 50 μg/L of copper. Sample solutions containing more than 50 μg/L need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption spectrometric direct method.

1.2 Suspended recoverable copper is calculated by subtracting dissolved copper from total recoverable copper.

1.3 Total recoverable copper in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

1.4 If the iron concentration of the sample exceeds 25,000 μg/L, determine copper by the atomic absorption spectrometric direct method.

2. Summary of method

Copper is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the copper absorption.

4. Apparatus

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

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

Grating ------------	Ultraviolet
Wavelength --------	324.7 nm
Source (hollow-cathode lamp) ------------	Copper
Oxidant ------------	Air
Fuel ---------------	Acetylene
Type of flame -------	Oxidizing

4.3 Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate solution*, 1 g/100 mL: Dissolve 1 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Citric acid-sodium citrate buffer solution*: Dissolve 126 g citric acid monohydrate and 44 g sodium citrate dihydrate in demineralized water and dilute to 1 L with demineralized water. See NOTE 3 before preparation.

5.3 *Copper standard solution I*, 1.00 mL=100 μg Cu: Dissolve 0.1252 g CuO in a minimum amount of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

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

5.5 *Methyl isobutyl ketone (MIBK).*

5.6 *Potassium hydroxide*, 10*M*: Dissolve 56 g KOH in demineralized water, cool, and dilute to 100 mL.

5.7 *Potassium hydroxide*, 2.5*M*: Dissolve 14 g KOH in demineralized water and dilute to 100 mL (NOTE 1).

NOTE 1. Alternatively, a 2.5*M* NH_4OH solution may be used. Add 167 mL concentrated NH_4OH (sp gr 0.90) to 600 mL demineralized water. Cool, and dilute to 1 L.

5.8 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+9) and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample solution containing less than 5.0 μg Cu (100 mL max) into a 200-mL volumetric flask and adjust the volume to approx 100 mL.

6.3 Prepare a blank with 1.5 mL concentrated HNO_3 per liter of acidified water and sufficient standards, and adjust the volume of each to approx 100 mL with acidified water.

6.4 With a pH meter, adjust the pH of each solution to 2.4 with 2.5*M* KOH (NOTE 2 and NOTE 3). Shake for 3 min.

NOTE 2. For water-suspended sediment samples that have been digested, add 1 to 2 mL 10*M* KOH or concentrated NH_4OH (sp gr 0.90) before pH adjustment.

NOTE 3. If an automated titration system is used to adjust the pH, add 2.5 mL citric acid-sodium citrate buffer solution prior to pH adjustment. This will prevent over- shooting the end point in poorly buffered samples.

6.5 Add 2.5 mL APDC solution and mix.

6.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.8 Aspirate the ketone layer within 1 h. Aspirate the ketone layer of the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable copper in each sample from the digital display or printer. Dilute those samples containing copper concentrations that exceed the working range of the method; repeat the chelation-extraction, and multiply by the proper dilution factors.

7.2 To determine the micrograms per liter of suspended recoverable copper, subtract dissolved-copper concentration from total-recoverable-copper concentration.

8. Report

Report copper, dissolved (01040), total-recoverable (01042), and suspended-recoverable (01041), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved copper for eight samples within the range of 18.5 to 403 μg/L may be expressed as follows:

$$S_T = 0.084X + 2.57$$

where

S_T= overall precision, micrograms per liter, and

X= concentration of copper, micrograms per liter.

The correlation coefficient is 0.8156.

9.2 Precision for dissolved copper for four of the eight samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
4	18.5	14
3	100	0
3	153	21
3	403	8

9.3 It is estimated that the percent relative standard deviation for total-recoverable and suspended recoverable copper will be greater than that reported for dissolved copper.

Copper, atomic absorption spectrometric, direct

Parameters and Codes:

Copper, dissolved, I-1270-85 (μg/L as Cu): 01040
Copper, total recoverable, I-3270-85 (μg/L as Cu): 01042
Copper, suspended recoverable, I-7270-85 (μg/L as Cu): 01041
Copper, recoverable-from-bottom-material, dry wt, I-5270-85 (μg/g as Cu): 01043

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 10 μg/L of copper. Sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale. Brines need to be analyzed by the atomic absorption spectrometric chelation-extraction method, providing that the interference limits discussed in that method are not exceeded.

1.2 Suspended recoverable copper is calculated by subtracting dissolved copper from total recoverable copper.

1.3 This method may be used to analyze bottom material containing at least 1 μg/g of copper. Prepared sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale.

1.4 Total recoverable copper in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable copper in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

2.1 Copper is determined by atomic absorption spectrometry by direct aspiration of the sample solution into an air-acetylene flame (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer or both.

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), chloride (9,000 mg/L), nitrate (2,000 mg/L), iron (4×10^6 μg/L), lead, cadmium, zinc, and chromium (10,000 μg/L each) do not interfere. Higher concentrations of each constituent were not investigated. Nickel and cobalt concentrations greater than 8,000 μg/L suppress the copper absorption.

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	324.7 nm
Source (hollow-cathode lamp)	Copper
Oxidant	Air
Fuel	Acetylene
Type of flame	Oxidizing

4.3 The 100-mm (4-in.), flathead, single-slot burner allows a working range of 10 to 1,000 μg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Copper standard solution I*, 1.00 mL= 1000 μg Cu: Dissolve 1.252 g CuO in a minimum amount of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1000 mL with demineralized water.

5.2 *Copper standard solution II*, 1.00 mL= 5.00 μg Cu: Dilute 5.0 mL copper standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at time of analysis.

5.3 *Copper working standards*: Prepare a series of at least six working standards containing from 10 to 1,000 μg/L of copper by appropriate dilution of copper standard solution II with acidified water. Prepare fresh daily.

5.4 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

Aspirate the blank (acidified water) to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable copper in each sample solution from the digital display or printer while aspirating each sample. Dilute those samples containing copper concentrations that exceed the working range of the method and multiply by proper dilution factors.

7.2 To determine micrograms per liter suspended recoverable copper, subtract dissolved-copper concentration from total-recoverable-copper concentration.

7.3 To determine the micrograms per gram of copper in bottom-material samples, first determine the micrograms per liter of copper in each sample as in paragraph 7.1; then

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

8. Report

8.1 Report copper, dissolved (01040), total-recoverable (01042), and suspended- recoverable (01041), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

8.2 Report copper, recoverable-from-bottom-material (01043), concentrations as follows: less than 10 μg/g, nearest microgram per gram; 10 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved copper for 28 samples within the range of 10 to 595 μg/L may be expressed as follows:

$$S_T = 0.057X + 7.13$$

where

S_T= overall precision, micrograms per liter, and

X= concentration of copper, micrograms per liter.

The correlation coefficient is 0.8007.

9.2 Precision for dissolved copper for five of the 28 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
9	10.0	90
30	60.3	14
22	100	16
28	245	11
23	595	9

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable copper and for recoverable copper in bottom material will be greater than that reported for dissolved copper.

9.4 Precision for total recoverable copper expressed in terms of percent relative standard deviation for two water-suspended sediment mixtures is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
17	21.1	39
23	131	16

References

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 28-30.

Copper, atomic absorption spectrometric, graphite furnace

Parameter and Code:

Copper, dissolved, I-1272-85 (μg/L as Cu): 01040

1. Application

1.1 This method may be used to determine copper in low ionic-strength water and precipitation. With deuterium background correction and a 20-μL sample, the method is applicable in the range from 0.2 to 10 μg/L. With Zeeman background correction and a 20-μL sample, the method is applicable in the range from 0.5 to 35 μg/L. Sample solutions that contain copper concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric direct or chelation-extraction method, or by the atomic emission spectrometric ICP method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Copper is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform, and the sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (60 mg/L), magnesium (10 mg/L), sodium (50 mg/L), sulfate (100 mg/L), and chloride (40 mg/L) do not interfere. Higher concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of copper. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer,* for use at 324.7 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high-temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-μL sample (NOTE 1).

NOTE 1. A 20-μL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace,* capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms.* Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware.* Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Copper standard solution I*, 1.00 mL= 1,000 μg Cu: Dissolve 1.2518 g CuO in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41) Ultrex or equivalent and dilute to 1,000 mL with Type 1 water.

5.2 *Copper standard solution II*, 1.00 mL= 10.0 μg Cu: Dilute 10.0 mL copper standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified Type 1 water (paragraph 5.6) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.3 *Copper standard solution III*, 1.00 mL= 1.00 μg Cu: Dilute 100.0 mL copper standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.4 *Copper standard solution IV*, 1.00 mL= 0.010 μg Cu: Dilute 10.0 mL copper standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

5.5 *Nitric acid, concentrated*, high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HNO_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for copper. Add an additional 1.5 mL of concentrated HNO_3 per liter of water, and repeat analysis. The integrated signal should not increase by more than 0.001 absorbance-seconds.

5.6 *Water, acidified*, Type 1: Add 1.5 mL high-purity, concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.7 *Water, Type 1.*

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1+1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-μL aliquots of blank and working standards, and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and (or) platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of copper in each sample from the digital display or printer output. Dilute those samples containing concentrations of copper that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report copper, dissolved (01040), concentrations as follows: less than 10.0 μg/L, nearest 0.1 μg/L; 10 μg/L and above, two significant figures for both deuterium background correction and Zeeman background correction.

9. Precision

9.1 Analysis of six samples six times each by a single operator using deuterium background correction is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
0.60	0.04	7.2
1.38	.11	8.1
2.31	.10	4.2
4.11	.15	3.6
5.58	.25	4.4
10.25	.40	3.9

9.2 Analysis of four samples by a single operator using Zeeman background correction is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
3	3.93	0.55	14
4	12.85	1.23	9.6
9	17.76	.36	2.0
6	34.88	1.13	3.2

9.3 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of copper was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
4.35	4.57	0.29	6.3	105
8.0	8.23	.46	5.6	103
8.7	9.23	.57	6.2	106
9.0	8.40	.40	4.8	93
16	16.10	.98	6.1	101
Tap water (NOTE 3)				
4.35	6.45	4.00	7.0	148
8.0	8.28	3.47	5.9	103
8.7	12.97	4.15	6.6	149
9.0	9.49	1.73	5.0	105
16	14.17	4.43	6.9	89

NOTE 3. The tap water contained approx 50 µg/L of copper, and the standard deviation and percent relative standard deviation were calculated prior to subtraction of copper originally present.

9.4 The precision and bias for the deuterium background method were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of copper was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
4.35	4.38	0.13	3.0	101
8.0	7.45	.34	4.6	93
8.7	8.42	.52	6.2	97
9.0	8.68	.57	6.5	96
16	15	.75	5.0	94
Tap water (NOTE 3)				
4.35	9.40	.72	1.1	216
8.0	7.37	2.17	3.5	92
8.7	16.75	1.99	2.8	193
9.0	18.83	5.41	12	209
16	22.88	2.76	3.6	143

9.5 Interlaboratory precision for dissolved copper for 12 samples within the range of 21.8 to 490 µg/L without regard to type of background correction and use of matrix modifiers, if any, may be expressed as follows:

$$S_T = 0.184X + 2.04$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of copper, micrograms per liter.

The correlation coefficient is 0.9246.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 39-41.

Cooksey, M., and Barnett, W. B., 1979, Matrix modification and the method of additions in flameless atomic absorption: Atomic Absorption Newsletter, v. 18, p. 101-5.

Fernandez, F. J., Beatty, M. M., and Barnett, W. B., 1981, Use of the L'vov platform for furnace atomic absorption applications: Atomic Spectroscopy, v. 2, p. 16-21.

Hinderberger, E. J., Kaiser, M. L., and Koirtyohann, S. R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1-11.

Manning, D. C., and Slavin, W., 1983, The determination of trace elements in natural waters using the stabilized temperature platform furnace: Applied Spectroscopy, v. 37, p. 1-11.

Ottaway, J. M., 1982, A revolutionary development in graphite furnace atomic absorption: Atomic Spectroscopy, v. 3, p. 89-92.

Slavin, W., Carnrick, G. R., and Manning, D. C., 1982, Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace: Analytical Chemistry, v. 54, p. 621-4.

Copper, atomic emission spectrometric, ICP

Parameter and Code:

Copper, dissolved, I-1472-85 (μg/L as Cu): 01040

2. Summary of method

Copper is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Copper, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:

Copper, total, I-5474-85 (mg/kg as Cu): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Copper is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Cyanide, colorimetric, barbituric acid, automated-segmented flow

Parameters and Codes:

Cyanide, dissolved, I-2302-85 (mg/L as CN): 00723
Cyanide, total recoverable, I-4302-85 (mg/L as CN): 00720
Cyanide, recoverable-from-bottom-material, dry wt, I-6302-85 (mg/kg as CN): 00721

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 0.01 to 0.30 mg/L cyanide. Samples containing more than 0.30 mg/L need to be diluted.

1.2 Total recoverable cyanide in water-suspended sediment can be determined if each sample is shaken vigorously and a suitable aliquot of well-mixed sample withdrawn.

1.3 This method may be used to determine cyanide in bottom material containing at least 0.5 mg/kg.

2. Summary of method

This method is based on the chlorination of cyanide with chloramine-T and on the subsequent reaction with a pyridine-barbituric acid reagent (Goulden and others, 1972). This method detects simple cyanides only; therefore, any complex cyanides must first be broken down by passing the acidified sample solution through an ultraviolet digestion-distillation procedure. The distillation step also removes certain interferences.

3. Interferences

3.1 Chloride interferes if its concentration exceeds 3,000 mg/L.

3.2 Oxidizing agents may interfere.

3.3 Glycine and urea at the 10-mg/L level do not interfere.

3.4 A concentration of 10 mg/L sulfide increases the apparent cyanide concentration by approx 0.02 mg/L. Concentrations of sulfide greater than 10 mg/L interfere considerably.

3.5 Thiocyanate is broken down to cyanide and sulfide by this procedure and, therefore, interferes on an equimolar basis.

3.6 Sulfate concentrations of 4,000 mg/L do not interfere. Higher concentrations were not tested.

4. Apparatus

4.1 *Distillation train* (fig. 21). An efficient gas washer is essential to the proper operation of the distillation assembly. The Fisher-Milligan unit has been found satisfactory. This apparatus is for use only with bottom materials.

4.2 *Heating element* for Claisen flask.

4.3 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold with ultraviolet digestor, proportioning pump, heating bath with distillation head, voltage stabilizer, recorder, and printer.

4.4 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 0.30 mg/L CN:

Absorption cell ----- 15 mm
Wavelength -------- 570 nm
Cam --------------- 20/h (6/1)
Heating-bath temperature ------------ 155°C

5. Reagents

5.1 *Chloramine-T solution*, 4.0 g/L: Dissolve 2.0 g chloramine-T in demineralized water and dilute to 500 mL.

5.2 *Cyanide standard solution I*, 1.00 mL = 0.100 mg CN: Dissolve 0.2500 g KCN (NOTE 1) in 0.1*M* NaOH and dilute to 1,000 mL with 0.1*M* NaOH. Discard after 3 months.

NOTE 1. **CAUTION—POISON: May be fatal if swallowed or inhaled. Contact with acid liberates poisonous gas. Contact with KCN may burn eyes and irritate skin.**

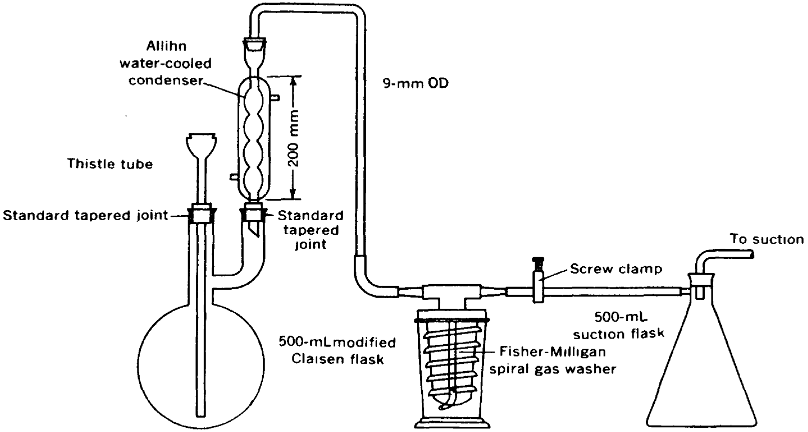

Figure 21.—Cyanide, distillation train

5.3 *Cyanide standard solution II*, 1.00 mL = 0.002 mg CN: Add 20 mL cyanide standard solution I to 800 mL 0.1*M* NaOH and dilute to 1,000 mL with 0.1*M* NaOH. Prepare fresh daily.

5.4 *Cyanide working standards*: Prepare fresh daily, a blank and 100 mL each of a series of cyanide working standards by appropriate quantitative dilution of cyanide standard solution II as follows:

Cyanide standard solution II (mL)	Cyanide concentration (mg/L)
1.0	0.020
2.0	.040
5.0	.100
10.0	.200
15.0	.300

5.5 *Magnesium chloride solution*, 24 g/100 mL: Dissolve 51 g $MgCl_2 \cdot 6H_2O$ in 100 mL demineralized water.

5.6 *Phosphate buffer solution*: Dissolve 13.6 g KH_2PO_4 and 0.28 g Na_2HPO_4 in demineralized water and dilute to 1 L. Add 0.5 mL Brij-35 solution and mix.

5.7 *Phosphoric acid-hypophosphorous acid distillation reagent*: Carefully add 250 mL concentrated H_3PO_4 (sp gr 1.69) and 50 mL hypophosphorous acid to approx 700 mL demineralized water. Dilute to 1 L with demineralized water.

5.8 *Pyridine-barbituric acid solution*: Place 15 g barbituric acid in a 1-L beaker and add enough demineralized water (about 100 mL) to wash the sides of the beaker and wet the barbituric acid. Add 75 mL pyridine and mix. Add 15 mL concentrated HCl (sp gr 1.19) and mix. Dilute to about 900 mL with demineralized water and mix until all the barbituric acid has dissolved. Transfer the solution to a 1,000-mL volumetric flask and dilute to volume with demineralized water.

5.9 *Sodium hydroxide*, 1*M*: Dissolve 4 g NaOH in 100 mL demineralized water.

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

6. Procedure

6.1 For water or water-suspended sediment proceed to paragraph 6.2. For bottom material proceed as follows:

6.1.1 Assemble the distillation train, consisting of Claisen flask, thistle tube, condenser, gas washer, screw clamp, suction flask, and aspirator (fig. 21).

6.1.2 Add a weighed portion (5 to 10 g) of bottom-material sample and 250 to 500 mL demineralized water to the boiling flask.

6.1.3 Add exactly 50 mL 1*M* NaOH and 100 mL demineralized water to the gas washer. Connect train and adjust suction so that 1 or 2 bubbles per second enter the boiling flask through the air inlet. Do not increase airflow beyond 2 bubbles per second.

6.1.4 Add 10 mL $MgCl_2$ solution through the thistle tube, and allow the airflow to mix for 3 min. Rinse air tube with demineralized water, then slowly add 20 mL concentrated H_2SO_4. Rinse the tube again.

6.1.5 Heat at a rate that provides rapid boiling, but not enough to flood the condenser inlet or permit the vapors to rise more than halfway into the condenser. Reflux for 1 h. Turn off heat, but permit airflow to continue for 15 min.

6.1.6 Transfer gas washer contents to a 200-mL volumetric flask. Wash the tube, from the condenser to the gas washer, and the gas washer with small amounts of demineralized water and add to contents of flask. Dilute contents of volumetric flask to 200 mL.

6.1.7 Refill the gas washer with NaOH and demineralized water, as in 6.1.3, and repeat reflux procedure. If only readily hydrolyzed cyanides are present, the absorber liquid from the first reflux period will contain all the available cyanide. If stable complex cyanides are present, a measurable yield will appear in the absorber liquid during the second and succeeding reflux periods, depending on the degree of stability of the compounds.

6.2 Set up manifold (fig. 22).

6.3 Allow the colorimeter, recorder, and heating bath to warm up for 30 min or until the heating-bath temperature has stabilized at 155 °C. Cold water must be flowing through the condensing jacket of the distillation head when heating bath is operating.

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

6.5 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. Each sample must be well mixed by vigorous shaking before transferring a portion to a sample cup.

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

7. Calculations

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

7.2 Compute the concentration of dissolved or total recoverable cyanide in milligrams per liter by comparing each sample peak height with the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 To determine milligrams per kilogram of cyanide in bottom-material samples, first determine the milligrams per liter of cyanide in each sample as in paragraph 7.2; then:

$$\text{CN(mg/kg)} = \frac{\text{mL distillate}}{\text{wt of sample (g)}} \times \text{mg/L CN}$$

8. Report

8.1 Report cyanide, dissolved (00723) and total-recoverable (00720), concentrations as follows: less than 1.00 mg/L, nearest 0.01 mg/L; 1.00 mg/L and above, two significant figures.

8.2 Report cyanide, total-recoverable-in-bottom-material (00721), concentrations as follows: less than 10 mg/kg, nearest 0.1 mg/kg; 10 mg/kg and above, two significant figures.

9. Precision

9.1 Precision for dissolved cyanide expressed in terms of the percent relative standard deviation for replicate analysis by a single operator is as follows:

Mean (mg/L)	Relative standard deviation (percent)
0.041	2
.125	1
.224	1

9.2 It is estimated that the percent relative standard deviation for total recoverable cyanide

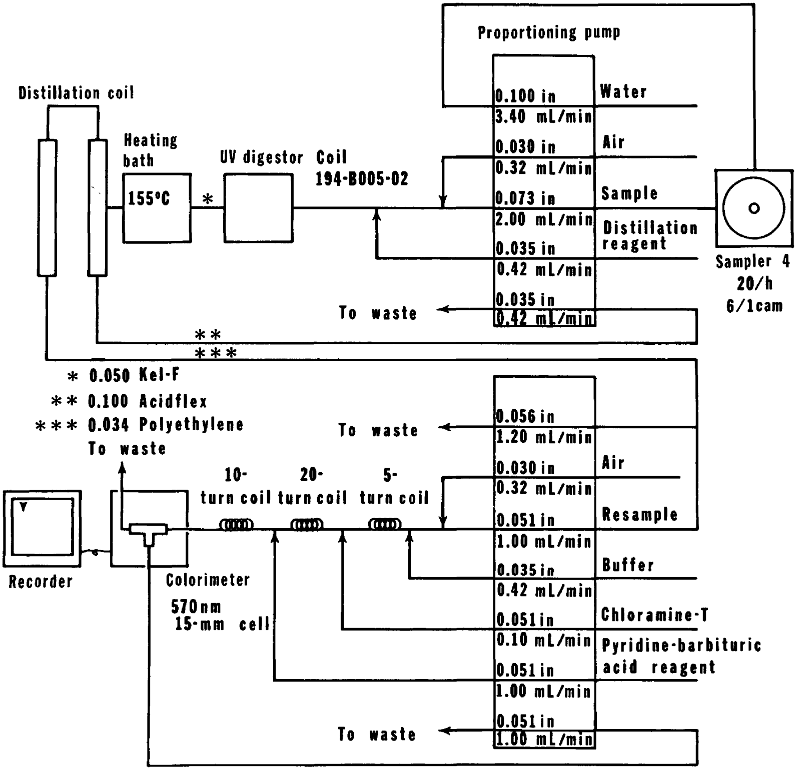

Figure 22.—Cyanide, barbituric acid manifold

and for recoverable cyanide in bottom material will be greater than that reported for dissolved cyanide.

References

Goulden, P. D., Afghan, B. K., and Brooksbank, Peter, 1972, Determination of nanogram quantities of simple and complex cyanides in water: Analytical Chemistry, v. 44, p. 1845–49.

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 353.3-1.

Cyanide, colorimetric, pyridine-pyrazolone

Parameters and Codes:

Cyanide, dissolved, I-1300-85 mg/L as CN): 00723
Cyanide, total, I-3300-85 (mg/L as CN): 00720
Cyanide, total-in-bottom-material, dry wt, I-5300-85 (mg/kg as CN): 00721

1. Application

1.1 The method may be used to determine cyanide in water and water-suspended sediment containing at least 0.01 mg/L of cyanide.

1.2 This method may be used to determine cyanide in bottom material containing at least 0.5 mg/kg.

1.3 Total cyanide in water-suspended sediment may be determined if each sample is shaken vigorously and a suitable aliquot of well-mixed sample withdrawn.

2. Summary of method

This method is based on the chlorination of cyanide and the subsequent reaction of the product with a mixed solution of pyridine-pyrazolone to form a stable complex dye. The method detects only simple cyanides; therefore, any complex cyanides present must be broken down. The decomposition of complex cyanides is accomplished by an acid reflux and distillation prior to the colorimetric procedure. The distillation also removes certain interferences from water samples.

3. Interferences

3.1 Common interferences include sulfide, heavy-metal ions, fatty acids, steam-distillable organic compounds, cyanate, thiocyanate, glycine, urea, oxidizing agents, and substances that may contribute color or turbidity to the sample.

3.2 These interferences may be removed or their effect minimized as follows:

3.2.1 Sulfide can be removed as lead sulfide by adding a slight excess of lead carbonate to 400 mL of the alkaline (pH 11.0 or above) sample. Filter the sample immediately, wash the precipitate with demineralized water, and add the washings to the filtrate.

3.2.2 Fatty acids can be removed by acidifying 400 mL of sample with acetic acid to a pH of between 6 and 7, and by extracting with 80 mL of either isooctane or hexane. A single extraction is usually sufficient.

3.2.3 Oxidizing agents can be removed by adding sodium sulfite solution to 400 mL of sample until a negative test with starch-iodide paper is obtained.

3.2.4 Most remaining interferences are removed by the distillation.

3.3 This method includes no provisions for removing these interferences or for minimizing their effects in water-suspended sediment and bottom material. The analyst must be aware that, when such interfering substances are present, the analytical result obtained may be in error, although distillation of the cyanide certainly separates it from some of the interfering substances.

4. Apparatus

4.1 *Distillation train* (fig. 23). An efficient gas washer is essential to the proper operation of the distillation assembly. The Fisher-Milligan unit has been found satisfactory.

4.2 *Heating element* for Claisen flask.

4.3 *Spectrometer* for use at 620 nm.

4.4 Refer to the manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Acetic acid*, 3*M*: Mix 172 mL glacial $HC_2H_3O_2$ (sp gr 1.06) with demineralized water and dilute to 1 L.

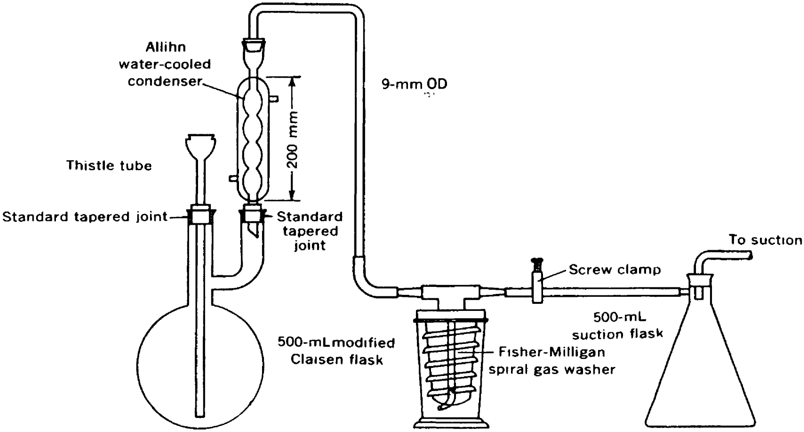

Figure 23.—Cyanide, distillation train

5.2 *Chloramine-T solution,* 1 g/100 mL: Dissolve 0.25 g chloramine-T in 25 mL demineralized water. This solution is unstable and must be prepared immediately before use. When a blank and standards are used, the chloramine-T solution may be used throughout a period of several hours, but each succeeding use results in lower absorbance readings for the same concentration of cyanide.

5.3 *Cyanide standard solution I,* 1.00 mL = 1.00 mg CN: Dissolve 2.50 g KCN (NOTE 1) in 1 L demineralized water. Standardize with silver nitrate standard solution, 1.00 mL = 1.00 mg CN, as follows: Adjust the pH of 5.0 mL cyanide standard solution I to 11.0 or above, and dilute to 250 mL with demineralized water. Add 0.5–1.0 mL 5-(p-dimethylaminobenzylidene)rhodamine indicator solution and titrate with standard silver nitrate solution to the first color change from canary yellow to salmon. Subtract the blank obtained by titrating an identical volume of water, alkali, and indicator. The cyanide solution is unstable and must be either restandardized weekly or prepared fresh when needed.

NOTE 1. **CAUTION—POISON: May be fatal if swallowed or inhaled. Contact with acid liberates poisonous gas. Contact with KCN may burn eyes and irritate skin.**

5.4 *Cyanide standard solution II,* 1.00 mL = 0.010 mg CN: Add 10.0 mL cyanide standard solution I to demineralized water and dilute to 1,000 mL. This solution must be prepared fresh before use.

5.5 *Cyanide standard solution III,* 1.00 mL = 0.001 mg CN: Add 10.0 mL cyanide standard solution II to demineralized water and dilute to 100 mL. This solution must be prepared fresh before use.

5.6 *Magnesium chloride solution,* 24 g/100 mL: Dissolve 51 g $MgCl_2 \cdot 6H_2O$ in 100 mL demineralized water.

5.7 *5-(p-Dimethylaminobenzylidene)rhodamine indicator solution,* 0.02 g/100 mL: Dissolve 0.02 g 5-(p-dimethylaminobenzylidene)rhodamine in 100 mL acetone. Eastman Kodak No. 2748 has been found satisfactory.

5.8 *Pyrazolone solution I*: Add 0.8 g 1-phenyl-3-methyl-5-pyrazolone to 150 mL demineralized water at 75°C. Cool to room temperature, with stirring; filter. Eastman Kodak No. 1397 has been found satisfactory.

5.9 *Pyrazolone solution II*: Dissolve 0.025 g bis-pyrazolone in 25 mL pyridine and filter. Eastman Kodak No. 6969 has been found satisfactory. Several minutes of mixing are usually required to effect solution.

5.10 *Pyridine-pyrazolone reagent*: Mix 125 mL pyrazolone solution I with 25 mL pyrazolone solution II. After standing, the mixed reagent develops a pink color which does not affect color development. Prepare this reagent fresh daily or before each use.

5.11 *Pyridine*.

5.12 *Silver nitrate standard solution*, 1.00 mL 1.00 mg CN: Crush approx 5 g of $AgNO_3$ crystals and dry to constant mass at 40°C. Dissolve 3.2647 g $AgNO_3$ in demineralized water and dilute to 1 L. This solution is needed only to standardize the cyanide standard solution I.

5.13 *Sodium hydroxide, 1M*: Dissolve 4 g NaOH in 100 mL demineralized water.

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

6. Procedure

6.1 *Distillation*: Follow instructions in paragraph 6.1.1 for water or water-suspended sediment and paragraph 6.1.2 for bottom material, after assembling the distillation train, consisting of Claisen flask, thistle tube, condenser, gas washer, screw clamp, suction flask, and aspirator.

6.1.1 Add 400 mL water or water-suspended sediment (or smaller aliquot diluted to 400 mL) to the boiling flask.

6.1.2 Add a weighed portion (5–10 g) of bottom-material and 250–500 mL demineralized water to the boiling flask.

6.2 Add exactly 50 mL 1*M* NaOH and 100 mL demineralized water to the gas washer. Connect train and adjust suction so that 1 or 2 bubbles per second enter the boiling flask through the air inlet. Do not increase airflow beyond 2 bubbles per second.

6.3 Add 10 mL $MgCl_2$ solution through the thistle tube, and allow the airflow to mix for 3 min. Rinse air tube with demineralized water, then slowly add 20 mL concentrated H_2SO_4. Rinse the tube again.

6.4 Heat at a rate that produces rapid boiling, but not enough to flood the condenser inlet or permit the vapors to rise more than halfway into the condenser. Reflux for 1 h. Turn off heat, but permit airflow to continue for 15 min.

6.5 Transfer gas washer contents to a 200-mL volumetric flask. Wash the tube, from the condenser to the gas washer, and the gas washer with small amounts of demineralized water and add to contents of flask. Dilute contents of volumetric flask to 200 mL.

6.6 Refill the gas washer with NaOH and demineralized water, as in 6.2, and repeat reflux procedure. If only readily hydrolyzed cyanides are present, the absorber liquid from the first reflux period will contain all the available cyanide. If stable complex cyanides are present, a measurable yield will appear in the absorber liquid during the second and succeeding reflux periods, depending on the degree of stability of the compounds.

6.7 *Colorimetric procedure*: The standards and many of the reagents used in this procedure are unstable and must be prepared immediately before use if maximum color development is to be obtained. The color development is also dependent on the presence of approximately equal total-salt concentrations in both samples and standards. If the final distillate volume is 200 mL, it will be about 0.25*M* in NaOH. For this reason 0.25*M* NaOH must be used for dilutions and for the standards and blank. Any substantial deviation in the quantity of 3*M* $HC_2H_3O_2$ required to neutralize blank and standards will require additional manipulation to bring these volumes into approximate agreement. The variation should be less than 0.3 mL.

6.8 Prepare a blank by pipetting 15 mL of 0.25*M* NaOH into a 23-mm absorption cell fitted with a rubber stopper. Prepare standards containing 0.0005 mg and 0.001 mg CN, each diluted to 15 mL with 0.25*M* NaOH in similar containers.

6.9 Take 15-mL aliquots (or smaller volumes diluted to 15 mL with 0.25*M* NaOH) of the distillates from the purification procedure and place in 23-mm stoppered absorption cells.

6.10 Neutralize each sample, blank, and standard with 3*M* $HC_2H_3O_2$ using phenolphthalein indicator solution.

6.11 To each sample, blank, and standard add 4 drops chloramine-T solution, stopper, and shake. Allow 2 min for the reaction to proceed.

6.12 Add 5.0 mL pyridine-pyrazolone reagent and mix well. Allow 20 min for color development.

6.13 Read absorbances at 620 nm. The color is stable for 30 min. The absorbance decreases slowly over a period of 3 h and can probably be read during this period with some decrease in accuracy.

7. Calculations

7.1 Determine the concentration of dissolved or total cyanide in milligrams per liter as follows:

$$\text{CN(mg/L)} = \frac{1000}{\text{mL original sample}} \times \frac{\text{mL distillate}}{\text{mL aliquot}} \times \frac{A_{\text{sample}}}{A_{\text{std.}}} \times \text{mg standard}$$

where

A_{sample} = absorbance of sample,

and

$A_{\text{std.}}$ = absorbance of standard.

7.2 Determine the concentration of cyanide in bottom-material samples in milligrams per kilogram as follows:

$$\text{CN(mg/L)} = \frac{1000}{\text{wt of sample (g)}} \times \frac{\text{mL distillate}}{\text{mL aliquot}} \times \frac{A_{\text{sample}}}{A_{\text{std.}}} \times \text{mg standard}$$

where

A_{sample} = absorbance of sample,

and

$A_{\text{std.}}$ = absorbance of standard.

8. Report

8.1 Report cyanide, dissolved (00723) and total (00720), concentrations as follows: less than 1.0 mg/L, nearest 0.01 mg/L; 1.0 mg/L and above, two significant figures.

8.2 Report cyanide, total-in-bottom-material (00721), concentrations as follows: less than 10 mg/kg, nearest 0.1 mg/kg; 10 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.

Density, gravimetric

Parameter and Code:

Density I-1312-85 (g/mL at 20°C): 71820

1. Application

This method may be used to determine the density of any water from which the suspended sediment has been satisfactorily removed.

2. Summary of method

The density determination is based on the weight of a carefully measured volume of filtered sample at a given temperature. Densities are determined at 20°C, the same temperature at which volumetric glassware is calibrated.

3. Interferences

The only significant interference with this method is suspended sediment, which may usually be removed by filtration, centrifugation, or flocculation. Precautions should be taken to minimize evaporation during removal of sediment.

4. Apparatus

4.1 *Pipet*, volumetric, 50 mL calibrated: The actual volume delivery of the pipet is determined by weighing a delivering volume of demineralized water at 20°C. The volume is obtained from relative-density tables in handbooks. Alternatively, 50-mL pycnometer can be used; it must also be calibrated.

4.2 *Water bath*, constant temperature, 20 + 0.5°C.

4.3 *Weighing bottle*, 50-mL capacity.

5. Reagents

None required.

6. Procedure

6.1 Adjust the temperature of the filtered sample to 20.0°C.

6.2 Using a previously calibrated 50-mL pipet, transfer the sample to a tared weighing bottle.

6.3 Stopper the bottle immediately to prevent water loss by evaporation.

6.4 Weigh the solution to the nearest 0.1 mg.

7. Calculations

7.1 Determine density as follows:

$$\text{Density} = \frac{\text{g sample}}{\text{mL sample}}$$

7.2 If a constant-temperature bath is not available, the determination can be made at the sample temperature and a correction applied for the departure from 20°C. The temperature is recorded with an accurate thermometer, and the relative density for that temperature obtained from a table. The density result is then corrected by the factor:

$$\frac{\text{Relative density (20°C)}}{\text{Relative density (test temperature in°C)}}$$

8. Report

Report density (71820) to three decimal places in terms of grams per millimeter at 20°C.

9. Precision

Precision data are not available for this method, but results are believed reproducible to + 0.005 g/mL.

Fluoride, colorimetric, zirconium-eriochrome cyanine R

Parameters and Codes:

Fluoride, dissolved, I-1325-85 (mg/L as F): 00950
Fluoride, total, I-3325-85 (mg/L as F): 00951
Fluoride, suspended total I-7325-85 (mg/L as F): 82299

1. Application

1.1 This method may be used to analyze water, brines, and water-suspended sediment containing from 0.1 to 3.0 mg/L of fluoride. Higher concentrations need to be reduced by dilution. If the fluoride concentration exceeds 30 mg/L, determine fluoride by the ion-selective electrode method (I-1327).

1.2 Suspended total fluoride is calculated by subtracting dissolved fluoride from total fluoride.

1.3 The total fluoride in water-suspended sediment is determined after each sample is shaken vigorously and a suitable aliquot of well-mixed sample is rapidly withdrawn and then distilled.

2. Summary of method

2.1 The zirconium-eriochrome cyanine R method given here is a modified version of the procedure of Megregian (1954).

2.2 In acid solution, zirconium reacts with eriochrome cyanine R to form a read complex ion. Fluoride forms a more stable complex with zirconium (ZrF_6^{-2}) and withdraws zirconium from the organic complex to produce a bleaching effect. Eriochrome cyanine R shows a decided specificity to zirconium.

2.3 The quality of the eriochrome cyanine R from different sources differs significantly, and it is necessary to test the reagent each time that it is prepared. The individual absorbance curves show corresponding differences, and the sensitivity of fluoride between reagents may differ by 20 percent.

2.4 The method includes a distillation step to decompose organic fluoride compounds and attack minerals such as fluorspar in water-suspended sediment. Samples that contain a high concentration of dissolved solids need to be distilled. The method also eliminates interferences noted below. A fixed volume of sample is added to a sulfuric acid solution having a specific boiling point and is distilled until an identical volume is recovered (Bellack, 1958). The fluoride is distilled as fluosilicic acid.

3. Interferences

3.1 Under the experimental conditions, the dye does not give a color with titanium or beryllium, two metals that react with many other zirconium agents. Aluminum decreases the apparent fluoride concentration. This interference is eliminated by allowing the solution to stand for at least 2 h before measuring the absorbance. As much as 10,000 μg/L of aluminum can be tolerated.

3.2 Analytical conditions are not overly critical. The pH is controlled at a highly acid level by the addition of 1.7 mL of concentrated hydrochloric acid to each sample. This assures that high concentrations of bicarbonate or other alkaline ions will not affect the pH significantly. Sulfate interferes but is removed by precipitation as barium sulfate. Overnight standing is usually required to ensure complex settling of barium sulfate before measuring the absorbance. The clarification of the sample can be accelerated by centrifuging if immediate results are required. Filtration should not be used because of loss of color by adsorption on the filter medium.

3.3 Residual chlorine, chromate, and probably other strong oxidants attack the dye.

Stannous chloride is used to eliminate chromate and chlorine interference. Chromium, cadmium, and nickel, in concentrations of less than 5,000 μg/L, do not interfere. When the fluoride concentration exceeds 1.0 mg/L, larger quantities of these metals can be tolerated. Ten mg/L of cyanide or phosphate and 10,000 μg/L of iron, or zinc, or lead cause no appreciable interference if the sample is allowed to stand overnight.

3.4 The determination shows "salt effect"; the sensitivity is depressed by 5–10 percent at a dissolved-solids concentration of 10,000 mg/L. The effect of the usual type of color is not serious. A color of 70 on the platinum-cobalt scale is equivalent to an absorbance error of only 0.005 in the spectrophotometric measurement. Thus, it appears that color correction will not often be necessary. Highly colored or highly mineralized samples need to be distilled.

3.5 The method has rather good tolerance for temperature differences. For most purposes, operating at room temperature without other precautions is satisfactory.

4. Apparatus

4.1 *Distillation assembly* (fig. 24), consisting of a round-bottom distilling flask, adapter, connecting tube, condenser, receiving flask, and thermometer, 250 °C.

4.2 *Spectrometer*, for use at 540 nm, and cells with a mimimum light-path length of 4 cm.

5. Reagents

5.1 *Eriochrome cyanine R solution*, 0.90 g/100 mL: Dissolve 1.80 g tested eriochrome cyanine R in water and dilute to 200 mL. The National Aniline Co. product labeled "alizarol cyanine RC" has been used successfully. A precipitate sometimes forms when the solution is prepared, but the solution may be filtered prior to use.

5.2 *Fluoride standard solution I*, 1.00 mL = 0.10 mg F^{-1}: Dissolve 0.2210 g NaF in demineralized water and dilute to 1,000 mL.

5.3 *Fluoride standard solution II*, 1.00 mL = 0.01 mg F^{-1}: Dilute 100 mL fluoride standard solution I to 1,000 mL with demineralized water.

5.4 *Hydrochloric acid*, 6*M*: Mix 50 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 100 mL.

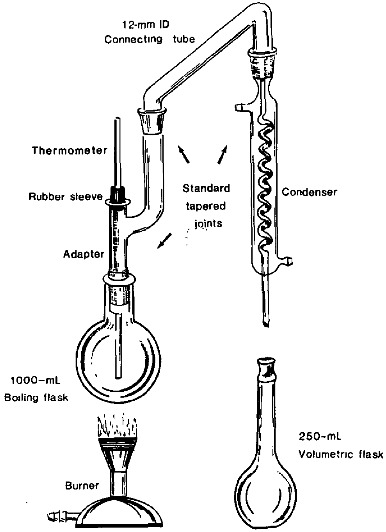

Figure 24.—Fluoride, distillation assembly

5.5 *Mixed indicator solution*: To about 300 mL demineralized water, add 20.0 mL eriochrome cyanine R solution and 10.0 mL $ZrO(NO_3)_2 \cdot 2H_2O$ solution. Add 70 mL concentrated HCl (sp gr 1.19) and 4 g $BaCl_2$. Dissolve and dilute to 1,000 mL with demineralized water.

NOTE 1. It is practical to prepare more than 1 L of mixed indicator solution at a time. Eighteen liters, contained in a 5-gallon reagent bottle, seems to be a practical volume. If this volume is prepared, the component solutions must be prepared in correspondingly larger volumes.

NOTE 2. Once prepared, the mixed indicator solution should be allowed to stand for about 1 week in order to permit any precipitate to settle to the bottom of the bottle. The reagent is then used without disturbing the precipitate.

5.6 *Silver sulfate*, powder.

5.7 *Stannous chloride solution*, 1.7 g/100 mL: Dissolve 1.0 g $SnCl_2 \cdot 2H_2O$ in 10 mL concentrated HCl (sp gr 1.19) and dilute to 50 mL with demineralized water. This solution is unstable. Prepare fresh daily.

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

5.9 *Zirconyl nitrate solution*, 0.21 g/100 mL: Dissolve 0.49 g $ZrO(NO_3)_2 \cdot 2H_2O$ in 200 mL 6*M* HCl.

6. Procedure

6.1 *Distillation*:

6.1.1 Place 400 mL demineralized water in a 1-L distilling flask containing a few glass beads. *Cautiously*, and with constant swirling, add 200 mL concentrated H_2SO_4. Connect the flask to the condenser assembly and distill until the temperature of the acid mixture reaches 180 °C. At this point the proper acid concentration has been reached. The acid need not be replaced until the accumulation of nonvolatile material is sufficient to cause interference. An occasional recovery check with a standard fluoride sample will indicate the need for replacement.

6.1.2 Cool to room temperature.

6.1.3 *Cautiously*, and with constant swirling, add 250 mL well-mixed sample to the acid mixture in the distillation flask.

6.1.4 Distill until 250 mL of distillate has been collected, and the temperature of the acid mixture has returned to 180 °C. When the temperature of the acid mixture at the completion of the distillation exceeds 183 °C, add 50 mL demineralized water and distill the mixture until the temperature again reaches 180 °C. After distilling a high-fluoride sample (3 mg/L or more), clean the apparatus by distilling 250 mL of water. This prevents a carryover of fluoride in subsequent samples. When samples with high-chloride content are to be distilled, Ag_2SO_4 should be added to the distilling flask in proportion of 5 mg per milligram of Cl^{-1}.

6.2 *Colorimetric procedure*:

6.2.1 Pipet a volume of filtered sample or a volume of the cooled distillate (step 6.1.4) containing less than 0.03 mg F^{-1} (10.0 mL max) into a 50-mL centrifuge tube or test tube.

6.2.2 Prepare a blank and sufficient standards, and adjust the volume of each to 10.0 mL.

6.2.3 If chromate, residual chlorine, or other strong oxidizing agents are present in the sample, add 0.1 mL $SnCl_2$ solution and let the solution stand for 10 minutes.

6.2.4 Add 25.0 mL mixed indicator solution.

6.2.5 Allow the solution to stand overnight for barium sulfate to settle.

6.2.6 Decant approximately 25 mL clear supernatant solution, taking care not to disturb the precipitate.

6.2.7 Determine the absorbance of each sample and standard against the blank, which is set at an absorbance of 1.50 (NOTE 3); when necessary, make correction for water color.

NOTE 3. Alternatively, measurement of transmittance may allow some instruments to be calibrated so that concentration can be read directly.

7. Calculations

7.1 Determine milligrams of fluoride in each sample solution from a plot of absorbances of standards.

7.2 Determine the dissolved or total-fluoride concentration in milligrams per liter as follows:

$$F\ (\mathrm{mg/L}) = \frac{1{,}000}{\mathrm{mL\ sample}} \times \mathrm{mg\ F\ in\ sample}$$

7.3 To determine milligrams per liter of suspended total fluoride, subtract dissolved-fluoride concentration from total-fluoride concentration.

8. Report

Report fluoride, dissolved (00950), total (00951), and suspended-total (82299), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved fluoride for 30 samples within the range of 0.3 to 3.7 mg/L may be expressed as follows:

$$S_T = 0.118X + 0.006$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of fluoride, milligrams per liter.

The correlation coefficient is 0.8048.

9.2 Precision for dissolved fluoride for four of the 30 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
34	0.30	17
17	1.06	7
3	2.00	15
9	3.69	13

9.3 It is estimated that the percent relative standard deviation for total and suspended total fluoride will be greater than that reported for dissolved fluoride.

References

Bellack, Ervin, 1958, Simplified fluoride distillation method: American Water Works Association Journal, v. 50, p. 530–5.

Megregian, Stephen, 1954, Rapid spectrophotometric determination of fluoride with zirconium-eriochrome cyanine R lake: Analytical Chemistry, v. 26, p. 1161–66.

Fluoride, electrometric, ion-selective electrode

Parameter and Code:

Fluoride, dissolved, I-1327-85 (mg/L as F): 00950

1. Application

This method is applicable to the measurement of dissolved fluoride in finished water, natural water, brines, and industrial wastewater. Concentrations of at least 0.1 mg/L can be determined. Samples containing more than 3 mg/L of fluoride need to be diluted.

2. Summary of method

2.1 Fluoride is determined potentiometrically in a buffered sample with use of an ion-selective (fluoride) electrode in conjunction with a standard calomel reference electrode (SCE), and a pH meter having an expanded millivolt scale (Frant and Ross, 1968).

2.2 The fluoride electrode consists of a laser-type doped lanthanum fluoride crystal, across which a potential is developed by fluoride ions. The cell may be represented by:

$$\text{Ag/AgCl, Cl}^{-1}\ (0.3M),$$

$$\text{F}^{-1}\ (0.001M)/\text{LaF}_3/\text{test solution/SCE}.$$

3. Interferences

3.1 The ion-selective electrode measures fluoride-ion activity, so that high concentrations of dissolved solutes (which lower the ion-activity coefficient) cause an error in the determination. Addition of the buffer solution, which contains a high concentration of dissolved solutes, effectively masks minor variations in the salt content of the samples and, therefore, minimizes this error.

3.2 The optimum pH for measurement is between 5.0 and 8.5. Below this range, hydrofluoric acid is only slightly dissociated, and above a pH of 8.5, hydroxyl ion interferes. The addition of the buffer solution will adjust the pH of most samples to between 5.0 and 5.5.

3.3 Several polyvalent cations capable of complexing fluoride ion interfere. These include iron(III), aluminum(III), and silicon dioxide. The extent of their interference is proportional to their concentration, so that dilution of the sample with an equal volume of buffer solution reduces the interference. The (1,2-cyclohexylenedinitrilo)tetraacetic acid (CDTA) in the buffer solution complexes as much as to 10,000 μg iron(III), 2,000 μg aluminum(III), and 100 mg silicon dioxide.

3.4 Orthophosphate-phosphorus concentrations of 25 mg/L and sulfate and chloride concentrations of 3,000 mg/L do not interfere (Harwood, 1969).

4. Apparatus

4.1 *Fluoride ion-selective electrode.*

4.2 *pH meter*, with expanded scale.

4.3 *Reference electrode*, standard calomel, sleeve-type.

4.4 *Stirrer*, magnetic, Teflon-coated stirring bar.

5. Reagents

5.1 *Buffer solution*, pH 5.0 to 5.5: To approx 500 mL demineralized water in a 1-L beaker, add 57 mL glacial $HC_2H_3O_2$, 58 g NaCl, and 4.5 g (1,2-cyclohexylenedinitrilo) tetraacetic acid (CDTA). Stir to dissolve and cool to room temperature. Adjust the pH of the solution to between 5.0 and 5.5 with 5*M* NaOH (about 170 mL will be required). Dilute to 1 L with demineralized water.

5.2 *Fluoride standard solution I*, 1.00 mL = 0.10 mg F^{-1}: Dissolve 0.2210 g NaF in demineralized water and dilute to 1,000 mL.

5.3 *Fluoride standard solution II*, 1.00 mL = 0.01 mg F^{-1}: Dilute 100 mL fluoride standard solution I to 1,000 mL with demineralized water.

6. Procedure

6.1 Adjust pH meter according to manufacturer's instructions.

6.2 Pipet 25.0 mL sample into 100-mL beaker.

6.3 Prepare a series of four standards containing 0.1, 1.0, 2.0, and 3.0 mg/L F^{-1}, and pipet 25.0 mL of each into 100-mL beakers.

6.4 Add 25.0 mL buffer solution to each sample and standard.

6.5 Place beaker on magnetic stirrer, immerse electrodes, and measure potential while mixing. The electrodes must remain in the solution until reading has stabilized. This may require 5 min or more.

7. Calculations

7.1 Construct a graph of potential in millivolts (mV) versus concentration of standards (mg/L) on semilog paper, with the concentrations plotted on the logarithmic axis.

7.2 From the graph, determine the milligrams per liter of fluoride in each sample.

8. Report

Report fluoride, dissolved (00950), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved fluoride within the range of 0.03 to 2.14 mg/L for 27 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 0.14 mg/L ranged from 0.135 to 0.153 mg/L.

9.2 Precision for dissolved fluoride for five of the 27 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
16	0.03	167
6	.32	41
13	.55	35
16	1.01	15
17	2.14	11

References

Frant, M. S., and Ross, J. W., Jr., 1968, Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water samples: Analytical Chemistry, v. 40, p. 1169–71.

Harwood, J. E., 1969, The use of an ion-selective electrode for routine fluoride analysis on water samples: Water Research, v. 3, p. 273–80.

Fluoride, electrometric, ion-selective electrode, automated-segmented flow

Parameters and Codes:

Fluoride, dissolved, I-2327-85 (mg/L as F): 00950
Fluoride, total, I-4327-85 (mg/L as F): 00951
Fluoride, suspended total, I-7327-85 (mg/L as F): 82299

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 0.1 to 3.0 mg/L of fluoride with conductivities less than 20,000 μS/cm. Samples with higher conductivities need to be distilled.

1.2 Suspended total fluoride is calculated by subtracting dissolved fluoride from total fluoride.

1.3 Total fluoride in water-suspended sediment is determined after each sample is shaken vigorously and a suitable aliquot of well-mixed sample is rapidly withdrawn and then distilled.

2. Summary of method

2.1 Fluoride is determined potentiometrically in a buffered sample with use of an ion-selective (fluoride) electrode in conjunction with a standard calomel reference electrode (SCE) and with a pH meter having an expanded millivolt scale (Frant and Ross, 1968; Harwood, 1969; Bellack, 1958).

2.2 The fluoride electrode consists of a laser-type, doped lanthanum fluoride crystal, across which a potential is developed by fluoride ions. The cell may be represented by:

$$\mathrm{Ag/AgCl,\ Cl^{-1}\ (0.3}M\mathrm{),}$$

$$\mathrm{F^{-1}\ (0.001}M\mathrm{)/LaF_3/test\ solution/SCE.}$$

This electrode deteriorates in time and must be replaced when results become erratic.

2.3 The method includes a distillation step to decompose organic fluoride compounds and attack minerals such as fluorspar in water-suspended sediment. A fixed volume of sample is added to a sulfuric acid solution having a specific boiling point and is distilled until an identical volume is recovered (Bellack, 1958). The fluoride is distilled as fluosilicic acid.

3. Interferences

3.1 The ion-selective electrode measures fluoride-ion activity; thus, high concentrations of dissolved solutes (which lower the ion-activity coefficient) cause an error in the determination. Addition of a buffer solution that contains a high concentration of dissolved solutes effectively masks minor variations in the salt content of the samples and, therefore, minimizes this error.

3.2 The optimum pH for measurement is between 5.0 and 8.5. Below this range, hydrofluoric acid is only slightly dissociated, and above a pH of 8.5, hydroxyl ion interferes. The addition of the buffer solution will adjust the pH of most samples to between 5.0 and 5.5.

3.3 Several polyvalent cations capable of complexing fluoride ion interfere. These include iron(III), aluminum(III), and silicon dioxide. The extent of their interference is proportional to their concentration, so that dilution of the sample with an equal volume of buffer solution reduces the interference. The (1,2-cyclohexylenedinitrilo)tetraacetic acid (CDTA) in the buffer solution complexes up to 10,000 μg iron(III), 2,000 μg aluminum(III), and 100 mg silicon dioxide.

3.4 Orthophosphate-phosphorus concentrations of 25 mg/L and sulfate and chloride concentrations of 3,000 mg/L do not interfere (Harwood, 1969).

4. Apparatus

4.1 *Distillation assembly,* (fig. 25), consisting of a round-bottom distilling flask, adapter, connecting tube, condenser, receiving flask, and thermometer (250 °C).

4.2 *Technicon AutoAnalyzer II,* consisting of a sampler, proportioning pump, cartridge manifold, heating bath, recorder, potentiometer, and printer.

4.3 *Fluoride ion-selective electrode.*

4.4 *Reference electrode,* standard calomel.

4.5 With this equipment a 40/h (2/1) cam has been found satisfactory for the range from 0.1 to 3.0 mg/L.

5. Reagents

5.1 *Brij-35 solution:* 30-percent aqueous solution (Baker Cat. No. C 706 or equivalent).

5.2 *Buffer solution,* 0.33 mg/L, pH 5.0 to 5.5: To approx 500 mL demineralized water in a 1-L beaker, add 57 mL glacial $HC_2H_3O_2$, 58 g NaCl, and 4.5 g (1,2-cyclohexylenedinitrilo) tetraacetic acid (CDTA). Stir to dissolve and cool to room temperature. Adjust the pH of the solution between 5.0 and 5.5 with 5*M* NaOH (about 170 mL will be required). Filter if necessary and add 33 mL of fluoride standard solution II and 0.5 mL of Brij-35 solution. Dilute to 1,000 mL with demineralized water.

5.3 *Fluoride standard solution I,* 1.00 mL = 1.00 mg F: Dissolve 2.2101 g NaF in demineralized water and dilute to 1,000 mL.

5.4 *Fluoride standard solution II,* 1.00 mL = 0.01 mg F: Dilute 10.0 mL fluoride standard solution I to 1,000 mL with demineralized water.

5.5 *Fluoride working standards:* Prepare a blank and 500 mL each of a series of fluoride working standards by appropriate quantitative dilution of fluoride standard solution II as follows:

Fluoride standard solution (mL)	Fluoride concentration (mg/L)
0.0	0.0
10.0	.20
25.0	.50
50.0	1.00
75.0	1.50
100.0	2.00
125.0	2.50
150.0	3.00

5.6 *Silver sulfate,* powder.

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

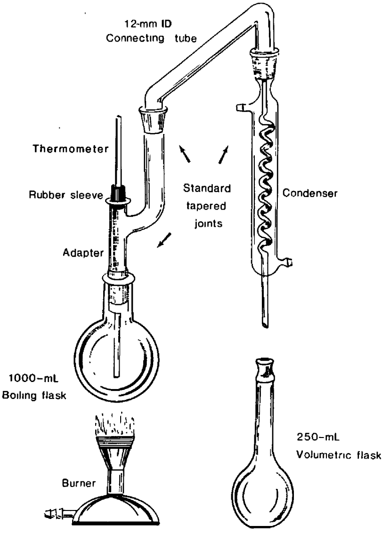

Figure 25.—Fluoride, distillation assembly

6. Procedure

6.1 *Distillation procedure:* Water-suspended sediment needs to be distilled. The distillation may be omitted for samples for determining dissolved fluoride if the specific conductance is less than 20,000 μS/cm.

6.1.1 Place 400 mL demineralized water in a 1-L distilling flask containing a few glass beads. *Cautiously,* and with constant swirling, add 200 mL concentrated H_2SO_4. Connect the flask to the condenser assembly and distill until the temperature of the acid mixture reaches 180 °C. At this point the proper acid concentration has been reached. The acid need not be replaced until the accumulation of nonvolatile material is sufficient to cause interference. An occasional recovery check with a standard fluoride sample will indicate the need for replacement.

6.1.2 Cool to room temperature.

6.1.3 *Cautiously,* and with constant swirling, add 250 mL of well-mixed sample to the acid mixture in the distillation flask.

6.1.4 Distill until 250 mL distillate has been collected and the temperature of the acid mixture has returned to 180°C. When the temperature of the acid mixture at the completion of the distillation exceeds 183°C, add 50 mL distilled water and distill the mixture until the temperature again reaches 180°C. After distilling a high fluoride sample (3 mg/L or more), clean the apparatus by distilling 250 mL water. This prevents a carryover of fluoride in subsequent samples. When samples with high chloride content are to be distilled, $AgSO_4$ should be added to the distilling flask in proportion of 5 mg per milligram of Cl^{-1}.

6.2 *Electrometric procedure*:

6.2.1 Set up manifold (fig. 26).

6.2.2 Allow potentiometer, recorder, and heating bath to warm up for at least 30 min or until the temperature of the heating bath reaches 37°C.

6.2.3 Calibrate the potentiometer according to the manufacturer's instructions.

6.2.4 Adjust the baseline to read 10 scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.2.5 Place a complete set of standards in the first positions of the first sample tray, beginning with the most concentrated working standard (the first two positions should both contain 3-mg/L standards). Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.2.6 Begin analysis. When the peak from the second 3-mg/L standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads 100 scale divisions.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective fluoride concentration. This curve should be linear or very nearly linear.

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

7.3 To determine milligrams per liter of suspended total fluoride, subtract dissolved-fluoride concentration from total-fluoride concentration.

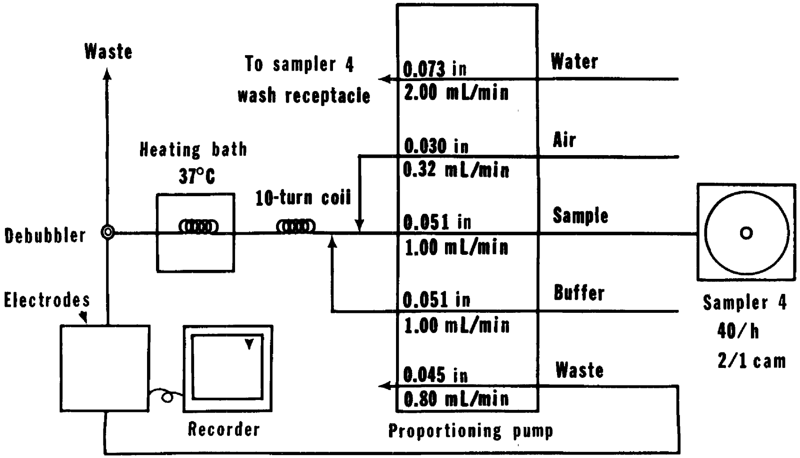

Figure 26.—Fluoride, ion-selective electrode manifold

8. Report

Report fluoride, dissolved (00950), total (00951), and suspended-total (82299), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved fluoride within the range of 0.33 to 1.28 mg/L for nine samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 0.07 mg/L ranged from 0.05 to 0.09 mg/L.

9.2 Precision for dissolved fluoride for three of the nine samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
3	0.33	18
8	1.09	6
4	1.28	7

9.3 It is estimated that the percent relative standard deviation for total and suspended total fluoride will be greater than that reported for dissolved fluoride.

References

Bellack, Ervin, 1958, Simplified fluoride distillation method: American Water Works Association Journal, v. 50, p. 530-5.

Erdmann, D.E., 1975, Automated ion-selective method for determining fluoride in natural waters: Environmental Science and Technology, v. 9, p. 252-3.

Frant, M. S., and Ross, J. W., Jr., 1968, Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water supplies: Analytical Chemistry, v. 40, p. 1169-71.

Harwood, J. E., 1969, The use of an ion-selective electrode for routine fluoride analysis on water samples: Water Research, v. 3, p. 273-80.

Fluoride, ion-exchange chromatographic, automated

Parameters and Codes:

Fluoride, dissolved, I-2057-85 (mg/L as F): 00950
Fluoride, dissolved, I-2058-85 (mg/L as F): 00950

2. Summary of method

Fluoride is determined sequentially with six other anions by ion-exchange chromatography. Ions are separated based on their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical-conductivity cell. See method I-2057, anions, ion-exchange chromatographic, automated, and method I-2058 anions, ion-exchange chromatographic, precipitation, automated.

Hardness, calculation

Parameter and Code:

Hardness, I-1340-85 (mg/L as $CaCO_3$): 00900

1. Application

This method may be used to calculate hardness for any sample for which determined values for barium, calcium, strontium, and magnesium are available.

2. Summary of method

Hardness is computed from the individual determinations of the alkaline earths. This is best accomplished by summing the milliequivalents per liter of calcium, magnesium, strontium, and barium. In many cases the contributions of strontium and barium are insignificant compared to those of calcium and magnesium and can safely be ignored.

7. Calculations

$$\text{Hardness as mg/L } CaCO_3 = \Sigma\text{me/L}(Ca + Mg + Ba + Sr) \times 50.05.$$

8. Report

Report hardness, calculated, as $CaCO_3$ (00900), concentrations as follows: less than 10 mg/L, whole numbers, 10 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method, but reproducibility should be comparable to those of the individual determinations.

Hardness, titrimetric, complexometric

Parameter and Code:

Hardness I-1338-85 (mg/L as $CaCO_3$): 00900

1. Application

This procedure is applicable to most natural and treated water, but the method fails conspicuously at times with acidic or polluted water that contains excessive amounts of heavy metals.

2. Summary of method

2.1 Disodium dihydrogen ethylenediaminetetraacetate (Na_2EDTA) forms a slightly ionized, colorless, stable complex with alkaline-earth ions. The indicator Eriochrome Black T is bright blue in the absence of alkaline earths, but with them forms a deep-red complex that has a higher ionization constant than that of the Na_2EDTA complex. Hence, with Eriochrome Black T as an indicator, the alkaline earth can be titrated with Na_2EDTA.

2.2 All alkaline earths titrate approximately stoichiometrically. The titration should proceed immediately upon addition of the indicator, because the color of the solution fades after standing. The optimum pH of the titration is 10.4 or above.

2.3 Additional information on the principle of the determination is given by Goetz and others (1950), and by Botha and Webb (1952).

3. Interferences

3.1 The salt Na_2EDTA also forms stable complexes with iron, manganese, copper, lead, cobalt, zinc, and nickel. Heavy-metal interferences can usually be eliminated by complexing the metals with cyanide. In the presence of cyanide, the procedure can be used to analyze undiluted samples having iron, copper, zinc, or lead concentrations as high as 10 mg/L.

3.2 The higher oxidation states of manganese than manganese(II) react rapidly with the indicator to form discolored oxidation products. Hydroxylamine hydrochloride reagent is used to reduce manganese to the divalent state. The divalent manganese interference can be removed by addition of one or two small crystals of potassium ferrocyanide.

3.3 In the presence of high aluminum concentrations, a characteristic effect will be observed as the end point is approached. The blue color that indicates the end point will appear and then, after short standing, will revert to red. The reversion should not be confused with the gradual change that normally takes place in the titrated sample several minutes after the titration has been completed.

4. Apparatus

Visual-titration assembly: Some analysts prefer to use conventional lighting and hand stirring. Others report better results by using a visual-titration assembly consisting of a motor-driven stirrer, 25-mL buret, white-porcelain-base buret holder, and shaded incandescent lamp. The sample beaker is placed near the front of the porcelain base, and the reaction is viewed diagonally downward through the side of the beaker and against the white background. Illumination is from behind the beaker.

5. Reagents

5.1 *Ammonium hydroxide, concentrated* (sp gr 0.900).

5.2 *Calcium standard solution*, 1.00 mL = 1.00 mg $CaCO_3$: Suspend 1.000 g $CaCO_3$, dried at 180 °C for 1.0 h, in approx 600 mL demineralized water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 mL with demineralized water.

5.3 *Eriochrome Black T indicator solution*, 0.4 g/L: Dissolve 0.40 g Eriochrome Black T in 100 mL demineralized water and dilute to 1 L with 95-percent ethanol. This indicator is stable for at least 2 months. The Eastman Kodak Co. reagent has been found to be satisfactory.

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

5.5 *Potassium ferrocyanide*, crystals.

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

5.7 *Na_2EDTA standard solution*, 1.00 mL ≎ 1.00 mL mg $CaCO_3$: Dissolve 3.72 g $Na_2EDTA{\cdot}2H_2O$, dried overnight in a H_2SO_4 desiccator, in demineralized water and dilute to 1,000 mL. The reagent is stable for several weeks and a larger volume is usually prepared. Check the titer of the reagent by titrating 25.0 mL calcium standard solution as described in the procedure for sample analysis.

6. Procedure

6.1 Pipet a volume of sample containing less than 25 mg hardness (50.0 mL max) into a 150-mL beaker, and adjust the volume to approx 50 mL.

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

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

6.4 Add 1 mL concentrated NH_4OH. (If not tightly stoppered, it tends to lose strength, and 1 mL of weak NH_4OH will not buffer the solution to the desired pH).

6.5 Add 2 mL NaCN solution—CAUTION: **deadly poison.** The addition of NaCN may be omitted if copper, zinc, lead, cobalt, and nickel are entirely absent, and if the sample contains less than 0.25 mg Fe and 0.025 mg Mn.

6.6 If manganese is present, add one or two small crystals of $K_4Fe(CN)_6{\cdot}3H_2O$. Stir and wait at least 5 min until the $Mn_2Fe(CN)_6$ precipitates.

6.7 Add 2.0 mL Eriochrome Black T indicator solution.

6.8 Titrate with Na_2EDTA standard solution until blue or purple swirls begin to show. The end point is reached when all traces of red and purple have disappeared and the solution is clear blue. The change in color occurs rapidly; so the end point of the titration must be approached cautiously.

7. Calculations

Hardness,

$$\text{as } CaCO_3\ (\text{mg/L}) = \frac{1{,}000}{\text{mL sample}} \times \text{mL titrant}$$

8. Report

Report hardness, as $CaCO_3$ (00900), as follows: less than 10 mg/L, whole numbers; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for hardness for 37 samples within the range of 3.2 to 312 mg/L may be expressed as follows:

$$S_T = 0.041X + 0.310$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of hardness, milligrams per liter as $CaCO_3$.

The correlation coefficient is 0.8105.

9.2 Precision for hardness for six of the 31 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
14	3.22	90
11	4.50	7
8	50.5	3
14	105	3
8	232	3
11	312	4

References

Botha, C. R., and Webb, M. M., 1952, The versenate method for the determination of calcium and magnesium in mineralized waters containing large concentrations of interfering ions: Institute of Water Engineers Journal, v. 6.

Goetz, A., Loomis, T. C., and Diehl, H., 1950, Total hardness in water—the stability of standard disodium dihydrogen ethylenediamine tetraacetate solutions: Analytical Chemistry, v. 22, p. 798–9.

Hardness, noncarbonate, calculation

Parameter and Code:

Hardness, noncarbonate I-1344-85 (mg/L as $CaCO_3$): 00902

1. Application

This method may be used to compute noncarbonate hardness for any water for which determined values are available for hardness and alkalinity.

2. Summary of method

Noncarbonate hardness is computed from the hardness and alkalinity determinations (methods I-1340 and I-1030 or I-2030). No negative values are reported. However, "negative noncarbonate hardness" will counteract "positive noncarbonate hardness" in a mixture of two or more waters. Hence, in all calculations of averages concerned with a mixture of waters for which two or more analyses are available, noncarbonate hardness of the resulting mixtures must be computed from the average hardness and average alkalinity and not from the average of the noncarbonate hardnesses of the individual samples.

7. Calculations

Hardness, noncarbonate, as mg/L $CaCO_3$ = (me/L hardness–me/L alkalinity) × 50.05

8. Report

Report hardness, noncarbonate, calculated as $CaCO_3$ (00902), concentrations as follows: less than 10 mg/L, whole numbers; 10 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method, but reproducibility should be comparable to that of the individual determinations.

Iodide, colorimetric, ceric-arsenious oxidation

Parameter and Code:

Iodide, dissolved, I-1371-85 (mg/L as I): 71865

1. Application

This method may be used to determine iodide in fresh water and brines containing from 0.001 to 0.060 mg/L of iodide. Greater concentrations need to be reduced by dilution; however, samples containing concentrations greater than 1 mg/L need to be analyzed by the bromine oxidation method (method I-1370).

2. Summary of method

This method is based on the catalytic effect of iodide on the ceric-arsenious oxidation reaction in acid solution. In the presence of a small amount of iodide, the reaction follows first-order reaction-rate kinetics—and at a given temperature and for a given reaction time, the extent of reduction of ceric ion is directly proportional to the iodide concentration. The reaction may be stopped completely at any time by the addition of silver ion. Photometric measurement of the absorbance of the solution permits evaluation of the extent of the reaction (Mitchell, 1966).

3. Interferences

3.1 Most substances normally present in natural water do not interfere.

3.2 Low values for iodide may result if the reaction test tubes are not clean. Rinsing each sample tube with hydrochloric acid, followed by deionized water immediately before use, removes possible contaminants.

3.3 Bromide ion does not interfere, and any substance that oxidizes iodide to iodine has no effect on the reaction.

3.4 Certain phosphate compounds used in water treatment, such as Calgon, have an inhibiting effect on the reaction. This effect can be eliminated by adding 3 drops concentrated nitric acid at step 6.1 in the procedure. The nitric acid should be aerated to remove nitrogen oxides.

4. Apparatus

4.1 *Stirring rods*, glass.

4.2 *Water bath*, constant-temperature (30 ± 0.5°C).

4.3 *Spectrometer* for use at 450 nm.

4.4 Refer to manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Arsenious acid standard solution*, 0.3*N* H_3AsO_3: Add 14.84 g primary standard As_2O_3 to 500 mL demineralized water in a 1,000-mL beaker. Next, add slowly 28 mL concentrated H_2SO_4 (sp gr 1.84); stir and warm the mixture until the As_2O_3 is dissolved. Cool, transfer to a 1,000-mL volumetric flask, and dilute to volume with demineralized water. Add a small piece of metallic arsenic to stabilize the solution.

5.2 *Ceric sulfate standard solution*, 0.1*N* $Ce(HSO_4)_4$: Dissolve 52.80 g anhydrous $Ce(HSO_4)_4$ in 600 mL 2.5*M* H_2SO_4 contained in a 1000-mL volumetric flask. Warm the mixture and stir occasionally until a clear solution is obtained. Cool and dilute to volume with 2.5*M* H_2SO_4.

5.3 *Iodide standard solution I*, 1.00 mL = 0.100 mg I^{-1}: Dissolve 0.1308 g KI crystals, dried overnight in a sulfuric acid desiccator, in demineralized water and dilute to 1,000 mL.

5.4 *Iodide standard solution II*, 1.00 mL = 0.010 mg I^{-1}: Dilute 100 mL iodide standard solution I to 1,000 mL with demineralized water.

5.5 *Iodide standard solution III*, 1.00 mL = 0.0001 mg I^{-1}: Dilute 10.0 mL iodide standard solution II to 1,000 mL with demineralized water.

5.6 *Silver nitrate solution*, 0.10 g/L: Dissolve 0.10 g $AgNO_3$ in 1 L demineralized water. Store in a dark bottle.

5.7 *Sulfuric acid*, 2.5*M*: *Cautiously* add 139 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water, cool, and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.0012 mg I^{-1} (20.0 mL max) into a 23-mm absorption cell.

6.2 Prepare a demineralized water blank to be used as a control and sufficient standards containing less than 0.0012 mg I^{-1} in 23-mm absorption cells.

6.3 Dilute each sample, blank, and standard to 20.0 mL with demineralized water; add 0.5 mL concentrated H_2SO_4 to each and mix.

6.4 Add 1.0 mL H_3AsO_3 standard solution to each absorption cell and mix.

6.5 Place all absorption cells in a constant-temperature bath at 30 °C. Allow 30 to 45 min for the contents to reach temperature equilibrium.

6.6 At zero time, add 1.0 mL $Ce(HSO_4)_4$ standard solution (temperature equilibrated) and mix.

6.7 After exactly 10 min add, with stirring, 1 drop (0.05 mL) $AgNO_3$ solution (NOTE 1).

NOTE 1. The addition of $AgNO_3$ solution may be omitted if the ceric sulfate solution is added at intervals of 30 sec or longer and the absorbance of each sample, blank, and standard measured exactly 10.0 min after the addition of the $Ce(HSO_4)_4$ solution.

6.8 Measure the absorbance of each blank, standard, and sample at 450 nm, using demineralized water as a reference.

7. Calculations

7.1 Construct an analytical curve by plotting the ratio A_s/A_c against milligrams of iodide on semilog paper (A_s = absorbance of standard and A_c = absorbance of control).

7.2 From the curve, determine the milligrams of iodide corresponding to the absorbance ratio obtained for each sample.

7.3 Determine iodide concentration in milligrams per liter as follows:

$$I^{-1}\ (\text{mg/L}) = \frac{1{,}000}{\text{mL sample}} \times \text{mg } I^{-1}$$

8. Report

Report iodide, dissolved (71865), concentrations as follows: less than 0.1 mg/L, three decimals; 0.1 mg/L and above, two significant figures.

9. Precision

Precision expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
3	0.023	91
3	.034	91
3	.117	55

Reference

Mitchell, C. G., 1966, Semimicroanalytical method for the determination of iodide in water: U.S. Geological Survey Water-Supply Paper 1822, p. 77-83.

Iodide, colorimetric, ceric-arsenious oxidation, automated-segmented flow

Parameter and Code:

Iodide, dissolved, I-2371-85 (mg/L as I): 71865

1. Application

This method may be used to determine iodide in fresh water and brines containing from 0.001 to 0.060 mg/L of iodide. Greater concentrations need to be reduced by dilution; however, samples containing concentrations greater than 1 mg/L need to be analyzed by the bromine oxidation method (method I-1370).

2. Summary of method

The method is based on the catalytic effect of iodide on the ceric-arsenious oxidation reaction in acid solution. In the presence of a small amount of iodide, the reaction follows first-order reaction-rate kinetics—and at a given temperature and for a given reaction time, the extent of reduction of ceric ion is directly proportional to the iodide concentration. Photometric measurement of the absorbance of the solution permits evaluation of the extent of the reaction (Mitchell, 1966).

3. Interferences

3.1 Most substances normally present in natural water do not interfere.

3.2 Bromide ion does not interfere.

3.3 Low iodide values will be obtained if the pH of the water samples is less than 3 or if the iron concentration exceeds 500 µg/L.

4. Apparatus

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

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.001 to 0.060 mg/L:

Absorption cell -----	15 mm
Wavelength --------	410 nm
Cam --------------	30/h (2/1)

5. Reagents

5.1 *Arsenious acid solution*, 2.782 g/L: Add 2.782 g primary standard As_2O_3 to approx 500 mL demineralized water in a 1,000-mL volumetric flask. Slowly add 3 mL concentrated H_2SO_4 (sp gr 1.84). Warm the mixture until the As_2O_3 is dissolved. Cool and dilute to 1,000 mL with demineralized water. Add a small piece of metallic arsenic to stabilize the solution.

5.2 *Ceric sulfate solution*, 1.584 g/L: Add 600 mL 2.5*M* H_2SO_4 and 1.584 g anhydrous $Ce(HSO_4)_4$ to a 1,000-mL volumetric flask. Warm the mixture and stir occasionally until a clear solution is obtained. Cool and dilute to volume with 2.5*M* H_2SO_4.

5.3 *Iodide standard solution I*, 1.00 mL = 0.100 mg I^{-1}: Dissolve 0.1308 g KI crystals, dried overnight in a sulfuric acid desiccator, in demineralized water and dilute to 1,000 mL.

5.4 *Iodide standard solution II*, 1.00 mL = 0.010 mg I^{-1}: Dilute 100 mL iodide standard solution I to 1,000 mL with demineralized water.

5.5 *Iodide standard solution III*, 1.00 mL = 0.0005 mg I^{-1}: Dilute 50.0 mL iodide standard solution II to 1,000 mL with demineralized water.

5.6 *Iodide working standards*: Prepare a blank and 500 mL each of a series of iodide working standards by appropriate quantitative dilution of the iodide standard solution III as follows:

Iodide standard solution III (mL)	Iodide concentration (mg/L)
0.0	0.000
2.0	.002
5.0	.005
10.0	.010
20.0	.020
40.0	.040
60.0	.060

5.6 *Sulfuric acid*, 2.5*M*: *Cautiously* add 139 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water, cool, and dilute to 1 L.

6. Procedure

6.1 Set up manifold (fig. 27).

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

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

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 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 peak reads full scale.

7. Calculations

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

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

8. Report

Report iodide, dissolved (71865), concentrations as follows: less than 0.1 mg/L, three decimals; 0.1 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

Reference

Mitchell, C. G., 1966, Semimicroanalytical method for the determination of iodide in water: U.S. Geological Survey Water-Supply Paper 1822, p. 77-83.

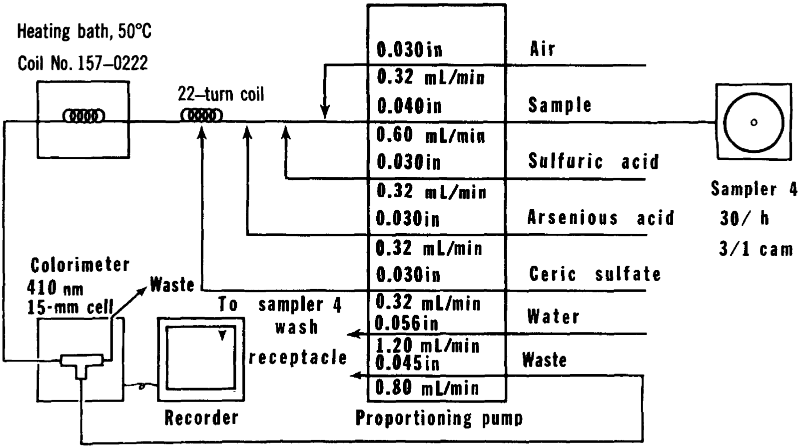

Figure 27.—Iodide, ceric-arsenious oxidation manifold

Iodide, titrimetric, bromine oxidation

Parameter and Code:

Iodide, dissolved I-1370-85 (mg/L as I): 71865

1. Application

This method may be used to analyze any natural or treated water or brine containing at least 1.0 mg/L of iodide, from which interfering substances have been removed.

2. Summary of method

Iodide in a buffered solution is oxidized by bromine to iodate; the excess bromine is subsequently removed by adding sodium formate (Kolthoff and others, 1969):

$$I^{-1} + 3Br_2 + 3H_2O \rightarrow IO_3^{-1} + 6HBr$$

Iodine equivalent to the iodate is then liberated by addition of potassium iodide to an acid solution:

$$IO_3^{-1} + 5I^{-1} + 6H^{+1} \rightarrow 3I_2 + 3H_2O$$

Finally the liberated iodine is titrated with standard thiosulfate solution with starch used as the indicator:

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

3. Interferences

Iron, manganese, and organic material interfere with the basic reactions of the method, but their interferences are removed by preliminary treatment with calcium oxide.

4. Apparatus

4.1 *Buret*, 10-mL capacity.

4.2 *Flasks*, 250-mL capacity.

5. Reagents

5.1 *Acetic acid*, 2.2*M*: Mix 125 mL glacial *CH_3COOH* (sp gr 1.06) with demineralized water and dilute to 1 L.

5.2 *Bromine water*, saturated: Add to approx 250 mL demineralized water slightly more liquid Br_2 than will dissolve when mixed. Store in a glass-stoppered, actinic-glass bottle.

5.3 *Calcium oxide*, CaO, anhydrous powder.

5.4 *Methyl red indicator solution*, 0.01 g/100 mL: Dissolve 0.01 g water-soluble methyl red in 100 mL demineralized water.

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

5.6 *Potassium iodide*, crystals, IO_3^{-1}-free: The KI can be tested for IO_3^{-1} by dissolving 0.1 g in 5 mL water, acidifying with 1 or 2 drops concentrated H_2SO_4 (sp gr 1.84), and adding 2 or 3 mL starch indicator. Immediate appearance of a blue color indicates the presence of IO_3^{-1}; slow color formation is due to atmospheric oxidation.

5.7 *Sodium acetate solution*, 165 g/L: Dissolve 274 g $CH_3COONa \cdot 3H_2O$ in demineralized water and dilute to 1 L.

5.8 *Sodium formate solution*, 50 g/100 mL: Dissolve 50 g HCOONa in hot demineralized water and dilute to 100 mL. Prepare fresh daily.

5.9 *Sodium thiosulfate solution*, 0.10*N*: Dissolve 25 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free demineralized water. Add 1 g Na_2CO_3 and dilute to 1 L.

5.10 *Sodium thiosulfate standard solution*, 0.010*N*: Dilute 100 mL 0.10*N* $Na_2S_2O_3$ solution to 950 mL with carbon dioxide-free demineralized water and standardize against KIO_3 as follows: Dry approx 0.5 g KIO_3 for 2 h at 180°C. Cool and dissolve 0.3567 g in demineralized water; dilute to 1,000 mL. Pipet 25.0 mL of the KIO_3 solution into a 250 mL flask; then add successively 75 mL demineralized water and 0.5 g KI crystals. After solution is complete, add 10 mL 3.6*M* H_2SO_4. Allow the stoppered flask to stand 5 min in the dark, then titrate with standard $Na_2S_2O_3$ solution, adding 2 to 3 mL starch indicator solution as the end point is approached (light-straw color).

$$\text{Normality of } Na_2S_2O_3 = \frac{0.25}{\text{mL } Na_2S_2O_3}$$

5.11 *Starch indicator solution*, stable or "thyodene," powdered (Fisher No. T138 or equivalent).

5.12 *Sulfuric acid*, 3.6*M*: *Cautiously* add 200 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water, cool, and dilute to 1 L.

6. Procedure

6.1 Remove soluble iron, manganese, and organic matter by adding a slight excess of CaO to approx 400 mL of sample; shake, let stand approx 1 h, and filter through a dry, moderately retentive filter paper. Discard the first 75 mL of filtrate.

6.2 Pipet a volume of the filtrate containing less than 5.0 mg I^{-1} (100.0 mL max) into a 250-mL flask, and adjust the volume to 100 mL.

6.3 Prepare a blank of 100 mL demineralized water and carry it through the procedure along with the sample.

6.4 Add 1 drop methyl red indicator solution and make the solution just acid with 3.6*M* H_2SO_4.

6.5 Add 15.0 mL CH_3COONa solution and 5.0 mL 2.2*M* CH_3COOH.

6.6 Add sufficient Br_2 water to produce a light-yellow color, mix, and allow to stand 5 min.

6.7 Reduce the excess Br_2 by adding HCOONa solution until the yellow tinge in the sample disappears; then add 1 mL excess.

6.8 Wash the sides of the flask with a small amount of water, and expel Br_2 vapors with a syringe and a glass tube inserted through the mouth of the flask.

6.9 If any iron precipitates at this point, add 0.5 g $KF{\cdot}2H_2O$.

6.10 Add approx 1 g KI and 10 mL 3.6*M* H_2SO_4; mix and let stand 5 min in the dark.

6.11 Titrate the liberated I_2 with standard $Na_2S_2O_3$ solution, adding 2 to 3 mL starch indicator solution as the end point is approached (light-straw color). Disregard a return of the blue color after the end point has been reached.

7. Calculations

$$I^{-1}, \text{ mg/L} = \frac{1{,}000}{\text{mL sample}} \times 21.15 \times$$

$$[(\text{mL titrant} - \text{mL blank}) \times N]$$

where

N = normality of standard thiosulfate solution,

and

21.15 = equivalent weight of iodide.

8. Report

Report iodide, dissolved (71865), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

Single-operator precision of this method (American Society for Testing and Materials, 1984) may be expressed as follows:

$$S_o = 0.009X$$

where

S_o = single-operator precision, milligrams per liter,

and

X = concentration of iodide, milligrams per liter.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 476–84.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative Chemical Analysis (4th ed.): New York, Macmillan, 1199 p.

Iron, atomic absorption spectrometric, direct

Parameters and Codes:

Iron, dissolved, I-1381-85 (μg/L as Fe): 01046
Iron, total recoverable, I-3381-85 (μg/L as Fe): 01045
Iron, suspended recoverable, I-7381-85 (μg/L as Fe): 01044
Iron, recoverable-from-bottom-material, dry wt I-5381-85 (μg/g as Fe): 01170

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 10 μg/L of iron. Sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale.

1.2 Suspended recoverable iron is calculated by subtracting dissolved iron from total recoverable iron.

1.3 This method may be used to analyze bottom material containing at least 1 μg/g of iron. Prepared sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale.

1.4 Total recoverable iron in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable iron in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

2.1 Iron is determined by atomic absorption spectrometry by direct aspiration of the sample solution into an air-acetylene flame.

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer or both.

3. Interferences

Individual concentrations of sodium, potassium, chloride, and sulfate (5,000 mg/L each), calcium and magnesium (1,000 mg/L each), nitrate (100 mg/L), chromium, manganese, cobalt, nickel, copper, zinc, silver, cadmium, tin, lead, lithium, mercury, selenium, aluminum, antimony, arsenic, vanadium, boron, and molybdenum (1×10^5 μg/L each) do not interfere. Greater concentrations of each constituent were not investigated.

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	248.3 nm
Source (hollow-cathode lamp)	Iron
Oxidant	Air
Fuel	Acetylene
Type of flame	Oxidizing

4.3 Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Iron standard solution I*, 1.00 mL = 400 μg Fe: Weigh 0.400 g analytical grade Fe wire that has been cleaned in dilute HCl, rinsed, and dried. Dissolve in 5 mL concentrated HNO_3 (sp gr 1.41), warming if necessary, and dilute to 1,000 mL with demineralized water.

5.2 *Iron standard solution II*, 1.00 mL = 4.00 μg Fe: Dilute 10.0 mL iron standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at time of analysis.

5.3 *Iron working standards*: Prepare a series of at least six working standards containing from 10 to 1,000 μg/L of iron by appropriate dilution of iron standard solution II with acidified water. Prepare fresh daily.

5.4 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 liter of demineralized water.

6. Procedure

Aspirate the blank (acidified water) to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable iron in each sample solution from the digital display or printer while aspirating each sample. Dilute those samples containing iron concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per liter suspended recoverable iron, subtract dissolved-iron concentration from total-recoverable-iron concentration.

7.3 To determine micrograms per gram of iron in bottom-material samples, first determine the micrograms per liter of iron as in paragraph 7.1; then

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

8. Report

8.1 Report iron, dissolved (01046), total-recoverable (01045), and suspended-recoverable (01044), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

8.2 Report iron, recoverable-from-bottom-material (01170), concentrations as follows: less than 100 μg/g, nearest microgram per gram; 100 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved iron for 26 samples within the range of 38 to 996 μg/L may be expressed as follows:

$$S_T = 0.066X + 18.58$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of iron, micrograms per liter.

The correlation coefficient is 0.8305.

9.2 Precision for dissolved iron for six of the 26 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
18	38	42
29	110	25
22	277	12
16	445	10
33	750	8
13	996	6

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable iron and recoverable iron in bottom material will be greater than that reported for dissolved iron.

9.4 Precision for total recoverable iron expressed in terms of percent relative standard deviation for two water-suspended sediment mixtures is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
24	7376	49
19	7680	38

Iron, atomic emission spectrometric, ICP

Parameter and Code:

Iron, dissolved, I-1472-85 (μg/L as Fe): 01046

2. Summary of method

Iron is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Iron, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:

Iron, total, I-5473-85 (mg/kg as Fe): none assigned
Iron, total, I-5474-85 (mg/kg as Fe): none assigned

2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The sample is then treated and analyzed by one of the following techniques.

2.1.1 The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1000 °C. The resulting bead is dissolved in acidified, boiling, demineralized water; iron is then determined by atomic absorption spetrometry. See method I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

2.1.2 The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Iron is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Lead, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:

Lead, dissolved, I-1400-85 (μg/L as Pb): 01049
Lead, total recoverable, I-3400-85 (μg/L as Pb): 01051
Lead, suspended recoverable, I-7400-85 (μg/L as Pb): 01050

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 5 to 100 μg/L of lead. Sample solutions containing more than 100 μg/L need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption spectrometric direct method.

1.2 Suspended recoverable lead is calculated by subtracting dissolved lead from total recoverable lead.

1.3 Total recoverable lead in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

1.4 If the iron concentration of the sample exceeds 25,000 μg/L, determine lead by the atomic absorption spectrometric direct method.

2. Summary of method

Lead is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer (Fishman and Midgett, 1968).

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the lead absorption.

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	283.3 nm
Source (hollow-cathode lamp or electrodeless-discharge lamp)	Lead
Oxidant	Air
Fuel	Acetylene
Type of flame	Oxidizing

4.3 Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate solution*, 1 g/100 mL: Dissolve 1 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Citric acid-sodium citrate buffer solution*: Dissolve 126 g citric acid monohydrate and 44 g sodium citrate dihydrate in demineralized water and dilute to 1 L with demineralized water. See NOTE 3 before preparation.

5.3 *Lead standard solution I*, 1.00 mL = 200 μg Pb: Dissolve 0.2000 g Pb shot in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.4 *Lead standard solution II*, 1 mL = 2.00 μg Pb: Dilute 10.0 mL lead standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.5 *Methyl isobutyl ketone* (MIBK).

5.6 *Potassium hydroxide*, 10 *M*: Dissolve 56 g KOH in demineralized water, cool, and dilute to 100 mL.

5.7 *Potassium hydroxide*, 2.5*M*: Dissolve 14 g KOH in demineralized water and dilute to 100 mL (NOTE 1).

NOTE 1. Alternatively, a 2.5*M* NH_4OH solution may be used. Add 167 mL concentrated NH_4OH (sp gr 0.90) to 600 mL demineralized water. Cool, and dilute to 1 L.

5.8 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+9) and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample solution containing less than 10.0 μg Pb (100 mL max) into a 200-mL volumetric flask and adjust the volume to approx 100 mL.

6.3 Prepare a blank of acidified water and sufficient standards, and adjust the volume of each to approx 100 mL with acidified water.

6.4 With a pH meter, adjust the pH of each solution to 2.4 with 2.5*M* KOH (NOTES 2 and 3). Shake for 3 min.

NOTE 2. For water-suspended sediment samples that have been digested, add 1 to 2 mL 10*M* KOH or concentrated NH_4OH (sp gr 0.90) before pH adjustment.

NOTE 3. If an automated titration system is used to adjust the pH, add 2.5 mL citric acid-sodium citrate buffer solution prior to pH adjustment. This will prevent over-shooting the end point in poorly buffered samples.

6.5 Add 2.5 mL APDC solution and mix.

6.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.8 Aspirate the ketone layer within 1 h. Aspirate the ketone layer of the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable lead in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing lead concentrations that exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

7.2 To determine the micrograms per liter of suspended recoverable lead, subtract dissolved-lead concentration from total-recoverable-lead concentration.

8. Report

Report lead (Pb), dissolved (01049), total-recoverable (01051), and suspended-recoverable (01050), concentrations as follows: 5 to 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved lead for 23 samples within the range of 3.8 to 73 μg/L may be expressed as follows:

$$S_T = 0.231X + 0.458$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of lead, micrograms per liter.

The correlation coefficient is 0.8702.

9.2 Precision for dissolved lead for five of the 23 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
6	3.83	76
7	4.00	38
14	13.9	30
14	26.5	29
17	72.9	28

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable lead will be greater than that reported for dissolved lead.

Reference

Fishman, M. J., and Midgett, M. R., 1968, Extraction techniques for the determination of cobalt, nickel, and lead in fresh water by atomic absorption, *in* Trace inorganics in water: American Chemical Society, Advances in Chemistry Series, no. 73, p. 230-5.

Lead, atomic absorption spectrometric, direct

Parameters and Codes:
Lead, dissolved, I-1399-85 (µg/L as Pb): 01049
Lead, total recoverable, I-3399-85 (µg/L as Pb): 01051
Lead, suspended recoverable, I-7399-85 (µg/L as Pb): 01050
Lead, recoverable-from-bottom-material, dry wt, I-5399-85 (µg/g as Pb): 01052

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 100 µg/L of lead. Sample solutions containing more than 4,000 µg/L need either to be diluted or to be read on a less expanded scale. Sample solutions containing less than 100 µg/L need to be analyzed by the atomic absorption spectrometric chelation-extraction method, providing that the interference limits discussed in that method are not exceeded.

1.2 Suspended recoverable lead is calculated by subtracting dissolved lead from total recoverable lead.

1.3 This method may be used to analyze bottom material containing at least 10 µg/g of lead. Prepared sample solutions containing more than 4,000 µg/L need either to be diluted or to be read on a less expanded scale.

1.4 Total recoverable lead in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable lead in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

Lead is determined by atomic absorption spectrometry by direct aspiration of the sample solution into an air-acetylene flame.

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), nitrate (900 mg/L), iron (4×10^6 µg/L), and cadmium, nickel, copper, zinc, cobalt, and chromium (10,000 µg/L) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	283.3 nm
Source (hollow-cathode or electrodeless-discharge lamp)	Lead
Oxidant	Air
Fuel	Acetylene
Type of flame	Slightly oxidizing

4.3 The 100-mm (4-in.), flathead, single-slot burner allows a working range of 100 to 4,000 µg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Lead standard solution I*, 1.00 mL = 200 µg Pb: Dissolve 0.2000 g Pb shot in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Lead standard solution II*, 1.00 mL = 20 µg Pb: Dilute 100.0 mL lead standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.3 *Lead working standards*: Prepare a series of at least six working standards containing from 100 to 4,000 µg/L of lead by appropriate dilution of lead standard solution II with acidified water. Prepare fresh daily.

5.4 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

Aspirate the blank (acidified water) to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable lead in each sample solution from the digital display or printer while aspirating each sample. Dilute those samples containing lead concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per liter suspended recoverable lead, subtract dissolved-lead concentration from total-recoverable-lead concentration.

7.3 To determine micrograms per gram of lead in bottom-material samples, first determine the micrograms per liter of lead as in paragraph 7.1; then

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

8. Report

8.1 Report lead, dissolved (01049), total-recoverable (01051), and suspended-recoverable (01050), concentrations to the nearest 100 µg/L.

8.2 Report lead, recoverable-from-bottom-material (01052), concentrations as follows: less than 100 µg/g, nearest 10 µg/g; 100 µg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved lead for 15 samples within the range of 6.70 to 80.3 µg/L (NOTE 1) may be expressed as follows:

$$S_T = 0.498X - 0.509$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of lead, micrograms per liter.

The correlation coefficient is 0.9118.

NOTE 1. Precision data are given for lead concentrations below the reporting level of 100 µg/L. Samples were not available that contained greater lead concentrations; however, precision should improve at greater concentrations.

9.2 Precision for dissolved lead for four of the 15 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
7	6.70	75
8	25.5	56
13	46.4	51
18	80.3	55

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable lead and for recoverable lead in bottom material will be greater than that reported for dissolved lead.

9.4 Precision for total recoverable lead expressed in terms of percent relative standard deviation for two water-suspended sediments is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
9	44.1	54
7	51.9	38

Lead, atomic absorption spectrometric, graphite furnace

Parameter and Code:

Lead, dissolved, I-1401-85 (µg/L as Pb): 01049

1. Application

1.1 This method may be used to determine lead in low ionic-strength water and precipitation. With deuterium background correction and a 20-µL sample, the method is applicable in the range from 0.3 to 20 µg/L. With Zeeman background correction and a 20-µL sample, the method is applicable in the range from 0.5 to 50 µg/L. Sample solutions that contain lead concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric direct or chelation-extraction method, or by the atomic emission spectrometric ICP method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Lead is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform and a matrix modifier is added. The sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (25 mg/L), magnesium (8 mg/L), sodium (20 mg/L), sulfate (34 mg/L), and chloride (25 mg/L) do not interfere. Higher concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of lead. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contribution from contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 283.3 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high-temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-µL sample with 5 µL of matrix modifier (NOTE 1).

NOTE 1. A 20-µL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms*. Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware*. Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Lead standard solution I*, 1.00 mL = 1,000 µg Pb: Dissolve 1.0000 g Pb shot in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41) Ultrex or equivalent and dilute to 1,000 mL with Type 1 water.

5.2 *Lead standard solution II*, 1.00 mL = 10.0 µg Pb: Dilute 10.0 mL lead standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified Type 1 water (paragraph 5.7) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.3 *Lead standard solution III*, 1.00 mL = 1.00 µg Pb: Dilute 100.0 mL lead standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.4 *Lead standard solution IV*, 1.00 mL = 0.010 µg Pb: Dilute 10.0 mL lead standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

5.5 *Matrix modifier solution*, 40 g $NH_4H_2PO_4$/L: Add 40.0 g $NH_4H_2PO_4$ to 950 mL Type 1 water, mix, and dilute to 1,000 mL. Analyze 20 µL of matrix modifier for lead contamination. If the lead reading is more than 0.005 absorbance-seconds, purify the solution by chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK) (NOTE 3). Analyze 20 µL of the purified solution. Repeat extractions until the lead level is reduced to the acceptable level. **DO NOT ADD ACID TO THE PURIFIED MATRIX MODIFIER SOLUTION.**

NOTE 3. To purify matrix modifier solution, pour the solution into a Teflon or FEP container. Add 0.25g APDC for each liter of solution. While stirring, adjust the solution to pH 2.9 by dropwise addition of concentrated HNO_3 (sp gr 1.41). Transfer portions of the solution to a separatory funnel, add 100 mL MIBK/liter of solution, and shake vigorously for at least 5 min. Frequently, vent the funnel in a hood. Collect the extracted solution in the FEP container. Repeat the extraction with 50 mL MIBK/liter of solution. Because MIBK can dissolve some plastic autosampler cups, boil the solution for at least 10 min in a silicone-treated or acid-rinsed container covered with a watchglass to remove MIBK.

5.6 *Nitric acid, concentrated*, high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HNO_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for lead. Add an additional 1.5 mL of concentrated HNO_3/liter of water, and repeat analysis. The integrated signal should not increase by more than 0.003 absorbance-seconds.

5.7 *Water, acidified*, Type 1: Add 1.5 mL high-purity, concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water, Type 1.*

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1+1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-μL aliquots of blank and working standards plus 5 μL of modifier each and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and (or) platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of lead in each sample from the digital display or printer output. Dilute those samples containing concentrations of lead that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report lead, dissolved (01049), concentrations as follows: less than 10.0 μg/L, nearest 0.1 μg/L; 10 μg/L and above, two significant figures for both deuterium background correction and Zeeman background correction.

9. Precision

9.1 Analysis of six samples six times each by a single operator using deuterium background correction is as follows:

Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
1.13	0.13	12
2.06	.12	5.7
3.95	.16	4.1
6.02	.22	3.6
10.41	.32	3.1
20.21	.35	1.7

9.2 Analysis of five samples by a single operator using Zeeman background correction is as follows:

Number of replicates	Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
4	0.62	0.17	27
4	1.80	.27	15
4	5.68	.05	.9
10	24.00	.77	3.2
14	48.31	.79	1.6

9.3 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 μS/cm). A known amount of lead was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (μg/L)	Amount found (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
11	10.63	0.48	4.5	97
13.5	13.30	.78	5.9	98
15	15.27	.96	6.3	102
22	21.40	.58	2.7	97
30	29.37	.54	1.8	98
Tap water (NOTE 4)				
11	10.15	1.19	10	92
13.5	15.37	2.40	15	114
15	15.18	.92	5.6	101
22	20.88	.83	3.7	95
30	30.81	1.70	5.3	103

NOTE 4. The tap water contained 1.3 μg/L of lead, and the standard deviation and percent relative standard deviation were calculated prior to subtraction of lead originally present.

9.4 The precision and bias for the deuterium background method were tested on deionized water and tap water (specific conductance 280 μS/cm). A known amount of lead was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (μg/L)	Amount found (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
11	10.70	0.81	7.6	97
13.5	12.63	1.18	9.3	94
15	13.82	.76	5.5	92
22	21.18	.86	4.1	96
30	30.60	1.72	5.6	102
Tap water (NOTE 4)				
11	10.64	.63	5.3	97
13.5	15.37	1.59	9.9	114
15	17.78	3.70	19.4	119
22	21.49	1.97	8.6	98
30	29.68	1.13	3.7	99

9.5 Interlaboratory precision for dissolved lead for 16 samples within the range of 3.4 to 37.4 μg/L, without regard to type of background correction and use of matrix modifiers, if any, may be expressed as follows:

$$S_T = 0.448X + 1.478$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of lead, micrograms per liter.

The correlation coefficient is 0.8247.

References

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Hinderberger, E. J., Kaiser, M. L., and Koirtyohann, S. R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1-11.

Manning, D. C., and Slavin, W., 1983, The determination of trace elements in natural waters using the stabilized temperature platform furnace: Applied Spectroscopy, v. 37, p. 1-11.

Ottaway, J. M., 1982, A revolutionary development in graphite furnace atomic absorption: Atomic Spectroscopy, v. 3, p. 89-92.

Slavin, W., Carnrick, G. R., and Manning, D. C., 1982, Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace: Analytical Chemistry, v. 54, p. 621-4.

Lead, atomic emission spectrometric, ICP

Parameter and Code:

Lead, dissolved, I-1472-85 (μg/L as Pb): 01049

2. Summary of method

Lead is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Lead, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:

Lead, total, I-5474-85 (mg/kg as Pb): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200°C. Lead is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Lithium, atomic absorption spectrometric, direct

Parameters and Codes:

Lithium, dissolved, I-1425-85 (μg/L as Li): 01130
Lithium, total recoverable, I-3425-85 (μg/L as Li): 01132
Lithium, suspended recoverable, I-7425-85 (μg/L as Li): 01131
Lithium, recoverable-from-bottom-material, dry wt, I-5425-85 (μg/g as Li): 01133

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 10 μg/L of lithium. Sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale.

1.2 Brines need to be diluted to eliminate interference from other elements. (See section 3, "Interferences.") If the lithium concentrations in the diluted samples are below detection, the undiluted samples need to be analyzed by the standard-addition method.

1.3 Suspended recoverable lithium is calculated by subtracting dissolved lithium from total recoverable lithium.

1.4 This method may be used to analyze bottom material containing at least 1 μg/g of lithium. Prepared sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale.

1.5 Total recoverable lithium in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable lithium in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

2.1 Lithium is determined by atomic absorption spectrometry by direct aspiration of the sample solution into an air-acetylene flame (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer or both.

3. Interferences

The following elements interfere when the indicated concentrations are exceeded: sodium, 1,000 mg/L; potassium, 100 mg/L; magnesium, 200 mg/L; calcium, 200 mg/L; chloride, 1,000 mg/L; sulfate, 2,000 mg/L; nitrate, 100 mg/L; and strontium, 5,000 μg/L.

4. Apparatus

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

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

Grating	Visible
Wavelength	670.8 nm
Source (hollow-cathode lamp)	Lithium
Oxidant	Air
Fuel	Acetylene
Type of flame	Oxidizing

4.3 The 50-mm (2-in.), flathead, single-slot burner allows a working range of 10 to 1,000 μg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Lithium standard solution I*, 1.00 mL = 1,000 μg Li: Dissolve 9.936 g $LiNO_3$ in demineralized water and dilute to 1,000 mL.

5.2 *Lithium standard solution II*, 1.00 = 10.0 μg Li: Dilute 10.0 mL lithium standard solution I to 1,000 mL with demineralized water. This solution is used to prepare working standards at time of analysis.

5.3 *Lithium working standards*: Prepare a series of at least six working standards containing from 10 to 1,000 μg/L of lithium by appropriate dilution of lithium standard solution II. Prepare fresh daily.

6. Procedure

Aspirate the blank (demineralized water) to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable lithium in each sample solution from the digital display or printer while aspirating each sample. Dilute those samples containing lithium concentrations that exceed working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per liter suspended recoverable lithium, subtract dissolved-lithium concentration from total-recoverable-lithium concentration.

7.3 To determine micrograms per gram of lithium in bottom-material samples, first determine micrograms per liter of lithium as in paragraph 7.1; then

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

8. Report

8.1 Report lithium, dissolved (01130), total-recoverable (01132), and suspended-recoverable (01131), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

8.2 Report lithium, recoverable-from-bottom-material (01133), concentrations as follows: less than 10 μg/g, nearest microgram per gram; 10 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved lithium for 19 samples within the range of 32 to 632 μg/L may be expressed as follows:

$$S_T = 0.080X + 1.13$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of lithium, micrograms per liter.

The correlation coefficient is 0.8270.

9.2 Precision for dissolved lithium for five of the 19 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
13	32	12
10	113	9
12	215	7
10	395	4
12	632	7

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable lithium and for recoverable lithium in bottom material will be greater than that reported for dissolved lithium.

9.4 Precision for total recoverable lithium expressed in terms of percent relative standard deviation for one water-suspended sediment is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
7	116	17
6	222	9

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 30-5.

Lithium, atomic emission spectrometric, ICP

Parameter and Code:

Lithium, dissolved, I-1472-85 (µg/L as Li): 01130

2. Summary of method

Lithium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Lithium, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:

Lithium, total, I-5474-85 (mg/kg as Li): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Lithium is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Magnesium, atomic absorption spectrometric, direct

Parameters and Codes:

Magnesium, dissolved, I-1447-85 (mg/L as Mg): 00925
Magnesium, total recoverable, I-3447-85 (mg/L as Mg): none assigned
Magnesium, suspended recoverable, I-7447-85 (mg/L as Mg): 00926
Magnesium, recoverable-from-bottom-material, dry wt, I-5447-85 (mg/kg as Mg): 00924

1. Application

1.1 This method may be used to analyze atmospheric precipitation, water, brines, and water-suspended sediment.

1.2 Two analytical ranges for magnesium are included: from 0.01 to 5.0 mg/L and from 2.5 to 50 mg/L. Sample solutions containing magnesium concentrations greater than 50 mg/L need to be diluted.

1.3 Suspended recoverable magnesium is calculated by subtracting dissolved magnesium from total recoverable magnesium.

1.4 This method may be used to analyze bottom material containing at least 10 mg/kg of magnesium. Prepared sample solutions containing more than 50 mg/L to be diluted.

1.5 Total recoverable magnesium in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable magnesium in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

2.1 Magnesium is determined by atomic absorption spectrometry (Fishman and Downs, 1966). Lanthanum chloride is added to mask interferences.

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer or both (fig. 28).

3. Interferences

3.1 The interference caused by aluminum concentrations greater than 2,000 μg/L is masked by addition of lanthanum. Because low magnesium values result if the pH of the sample is above 7, standards are prepared in hydrochloric acid solution and samples are preserved in the field with use of nitric acid solution.

3.2 Nitrate, sulfate, and silica interfere, but in the presence of lanthanum chloride-hydrochloric acid solution at least 2,000 mg/L, 1,000 mg/L, and 200 mg/L, respectively, can be tolerated. The addition of nitric acid at the time of collection to preserve the samples causes no problem in the following procedure.

3.3 Sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/L.

4. Apparatus

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

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

Grating ------------	Ultraviolet
Wavelength --------	285.2 nm
Source (hollow-cathode lamp) ------------	Magnesium
Oxidant ------------	Air
Fuel ---------------	Acetylene
Type of flame -------	Slightly reducing

4.3 The 50-mm (2-in.), flathead, single-slot burner allows a working range of 0.01 to 5.0 mg/L. This burner, rotated 90°, allows a working range of 2.5 to 50 mg/L. Different burners may be used according to manufacturers' instructions.

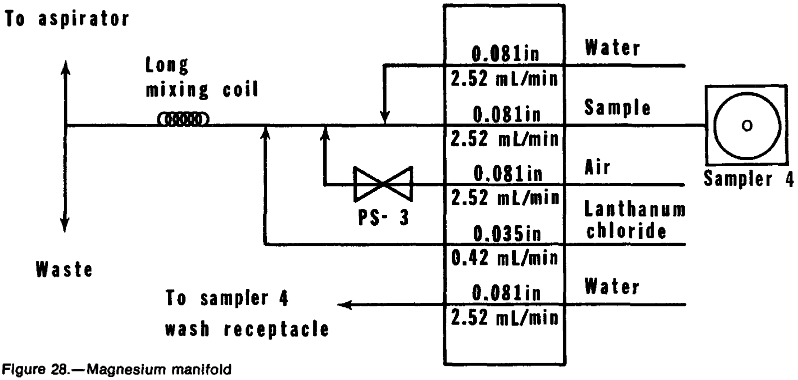

Figure 28.—Magnesium manifold

5. Reagents

5.1 *Lanthanum chloride solution*, 87 g/L: Mix 29 g La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

5.2 *Magnesium standard solution I*, 1.00 mL = 0.50 mg Mg: Dissolve 0.500 g pure metallic Mg in a minimum amount of dilute HCl, and dilute to 1,000 mL with demineralized water.

5.3 *Magnesium working standards*: Prepare a series of at least six working standards containing either from 0.01 to 5.0 mg/L or from 2.5 to 50 mg/L magnesium by appropriate dilution of magnesium standard solution I. Add 1.0 mL $LaCl_3$ solution for each 10 mL of working standard. Similarly, prepare a demineralized water blank.

6. Procedure

6.1 Add 1.0 mL lanthanum chloride solution to 10.0 mL of sample solution.

6.2 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the milligrams per liter of dissolved or total recoverable magnesium in each sample solution from the digital display or printer while aspirating each sample. Dilute those samples containing magnesium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine milligrams per liter suspended recoverable magnesium, subtract dissolved-magnesium concentration from total-recoverable-magnesium concentration.

7.3 To determine milligrams per kilogram of magnesium in bottom-material samples, first determine the milligrams per liter of magnesium in each sample as in paragraph 7.1; then

$$\text{Mg (mg/kg)} = \frac{\text{mg/L Mg} \times \dfrac{\text{mL of original digest}}{1000}}{\text{wt of sample (kg)}}$$

8. Report

8.1 Report magnesium, dissolved (00925), total-recoverable (none assigned), and suspended-recoverable (00926), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 to 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

8.2 Report magnesium, recoverable-from-bottom-material (00924), concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

9.1 Precision for dissolved magnesium for 35 samples within the range of 0.1 to 120 mg/L may be expressed as follows:

$$S_T = 0.062X + 0.003$$

where

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

The correlation coefficient is 0.9823.

9.2 Precision for dissolved magnesium for five of the 35 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
20	0.10	50
23	1.98	9
38	11.1	7
40	54.7	7
39	120	7

9.3 Precision for dissolved magnesium within the range of 0.03 to 5.2 mg/L in terms of the percent relative standard deviation by a single operator is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
8	0.033	21.2
8	.315	1.6
7	.993	2.6
6	5.18	4.2

9.4 It is estimated that the percent relative standard deviation for total and suspended recoverable magnesium and for recoverable magnesium in bottom material will be greater than that reported for dissolved magnesium.

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 30-5.

Magnesium, atomic absorption spectrometric, direct-EPA

Parameter and Code:

Magnesium, total recoverable, I-3448-85 (mg/L as Mg): 00927

1. Application

1.1 This method may be used to analyze water-suspended sediment.

1.2 For ambient water, analysis may be made on a measured portion of the acidified water-suspended sediment sample.

1.3 For all other waters, including domestic and industrial effluent, the atomic absorption procedure must be preceded by a digestion-solubilization as specified below. In cases where the analyst is uncertain about the type of sample, the digestion-solubilization procedure must be used.

1.4 Two analytical ranges are provided: from 0.1 to 10 mg/L of Mg and from 2.5 to 50 mg/L. Samples containing magnesium at concentrations greater than 50 mg/L need to be diluted.

2. Summary of method

2.1 Magnesium is determined by atomic absorption spectrometry (Fishman and Downs, 1966). Lanthanum chloride is added to mask interferences.

2.2 Effluent samples must undergo a preliminary nitric acid digestion followed by a hydrochloric acid solubilization.

3. Interferences

3.1 The interference caused by aluminum at concentrations greater than 2,000 μg/L is masked by addition of lanthanum. Because low magnesium values result if the pH of the sample is above 7, standards are prepared in hydrochloric acid solution and samples are preserved in the field using a nitric acid solution.

3.2 Nitrate, sulfate, and silica interfere, but in the presence of lanthanum chloride-acid solution at least 2,000 mg/L, 1,000 mg/L, and 200 mg/L, respectively, can be tolerated. The addition of nitric acid to the sample as a preservative at the time of collection causes no problem in the following procedure. Samples should be evaporated just to dryness following HNO_3 digestion to avoid any possible nitrate interference.

3.3 Sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/L.

4. Apparatus

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

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

Grating ------------	Ultraviolet
Wavelength --------	285.2 nm
Source (hollow-cathode lamp) ------------	Magnesium
Oxidant ------------	Air
Fuel ----------------	Acetylene
Type of flame -------	Slightly reducing

4.3 The 50-mm (2-in.), flathead, single-slot burner allows a working range of 0.1 to 10 mg/L. This burner, rotated 90°, allows a range of 2.5 to 50 mg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Hydrochloric acid, 6M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.2 *Hydrochloric acid,* 0.3*M*: Dilute 25 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.3 *Lanthanum chloride solution,* 87 g/L: Mix 29 g La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

5.4 *Magnesium standard solution I*, 1.00 mL = 0.50 mg Mg: Dissolve 0.500 g pure metallic Mg in a minimum amount of dilute HCl, and dilute to 1,000 mL with demineralized water.

5.5 *Magnesium working standards*: Prepare a series of at least six working standards containing from 0.1 to 50 mg/L magnesium by diluting magnesium standard solution I. Add 1.0 mL $LaCl_3$ solution for each 10 mL of working standard.

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

6. Procedure

6.1 Transfer the entire sample to a beaker.

6.2 Rinse the sample bottle with 3 mL concentrated HNO_3 for each 100 mL of sample and add to the beaker. Prepare a blank using 3 mL concentrated HNO_3 per 100 mL of demineralized water.

6.3 Evaporate samples and blank to dryness on a hotplate, making sure the samples do not boil.

6.4 Cool and add an additional 3 mL concentrated HNO_3 to the beaker. Cover with a watchglass, return to the hotplate, and gently reflux the sample.

6.5 Continue heating, adding additional acid as necessary, until digestion is complete (indicated by a light-colored residue). Evaporate just to dryness.

6.6 Add 6 mL 6*M* HCl solution per 100 mL of original sample and warm the beaker to dissolve the residue.

6.7 Wash the watchglass and beaker with demineralized water and filter the sample (Whatman No. 41 or equivalent), rinsing the filter with hot, dilute 0.3*M* HCl. Dilute to the original volume with demineralized water.

6.8 Add 1.0 mL lanthanum chloride solution per 10.0 mL of sample.

6.9 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

Determine the milligrams per liter of magnesium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing magnesium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report magnesium, total-recoverable (00927), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for total recoverable magnesium over the range of the method will be greater than 9 percent.

References

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 30-5.

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 215.1-1.

Magnesium, atomic emission spectrometric, ICP

Parameter and Code:

Magnesium, dissolved, I-1472-85 (mg/L as Mg): 00925

2. Summary of method

Magnesium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Magnesium, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:

Magnesium, total, I-5473-85 (mg/kg as Mg): none assigned
Magnesium, total, I-5474-85 (mg/kg as Mg): none assigned

2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The sample is then treated and analyzed by one of the following techniques.

2.1.1 The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1000 °C. The resulting bead is dissolved in acidified, boiling, demineralized water and magnesium determined by atomic absorption spectrometry. See method I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

2.1.2 The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Magnesium is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Manganese, atomic absorption spectrometric, chelation-extraction

Parameter and Code:

Manganese, dissolved, I-1456-85 (μg/L as Mn): 01056

1. Application

This method may be used to analyze water and brines containing from 1 to 100 μg/L of manganese. Brines containing more than 100 μg/L need either to be diluted or to be read on a less expanded scale. Samples containing more than 100 μg/L need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption spectrometric direct method, providing that the interference limits discussed in that method are not exceeded.

2. Summary of method

Manganese is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with chloroform. The extract is evaporated to dryness, treated with hot nitric acid to destroy organic matter, dissolved in hydrochloric acid, and diluted to a specified volume with demineralized water. The resulting solution is aspirated into the air-acetylene flame of the spectrometer.

3. Interferences

Concentrations of iron to 4 × 106 μg/L do not interfere; higher concentrations were not tested.

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	279.5 nm
Source (hollow-cathode lamp)	Manganese
Oxidant	Air
Fuel	Acetylene
Type of flame	Oxidizing

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate solution*, 4 g/100 mL: Dissolve 4 g APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.

5.2 *Bromocresol green indicator solution*, 0.1 g/100 mL: Dissolve 0.1 g bromocresol green in 100 mL 20-percent ethanol.

5.3 *Chloroform.*

5.4 *Hydrochloric acid*, *4M*: Mix 333 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.5 *Manganese standard solution I*, 1.00 mL = 100 μg Mn: Dissolve 0.1000 g 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.

5.6 *Manganese standard solution II*, 1.00 mL = 1.00 μg Mn: Immediately before use, dilute 10.0 manganese standard solution I to 1,000 mL with demineralized water. This solution is used to prepare working standards at time of analysis.

5.7 *Sodium hydroxide*, 0.25*M*: Dissolve 10 g NaOH in demineralized water and dilute to 1 L.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+9) and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample containing less than 5 μg Mn (50 mL max) into a 125-mL separatory funnel. Adjust the volume to approx 50 mL.

6.3 Prepare a blank and at least six standards, and adjust the volume of each to approx 50 mL with demineralized water.

6.4 Add 2 drops bromocresol green indicator solution and adjust the pH of each sample, standard, and blank to 4.0 (light olive-green color) with the addition of 0.25*M* NaOH.

6.5 Add 5.0 mL APDC solution and mix.

6.6 Add 10 mL chloroform and shake for 2 min.

6.7 Allow the phases to separate and drain the chloroform phase into a 100-mL beaker.

6.8 Repeat the extraction with an additional 10 mL chloroform and drain the chloroform phase into the same beaker.

6.9 Place the beaker on a steam bath and evaporate just to dryness.

6.10 Hold the beaker at a 45° angle, and slowly add 2 mL concentrated HNO_3 (sp gr 1.41), rotating the beaker to effect thorough contact of the acid with the residue (CAUTION—NOTE 1).

NOTE 1. If acid is added to the beaker in a vertical position, a violent reaction may occur accompanied by high heat and spattering.

6.11 Place the beaker on a hotplate at low heat and evaporate just to dryness.

6.12 Add 2 mL 4*M* HCl and heat, while swirling, for 1 min.

6.13 Cool and transfer the solution to a 10-mL volumetric flask and dilute to volume with demineralized water.

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

7. Calculations

Determine the micrograms per liter of dissolved manganese in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing concentrations of manganese that exceed the working range of the method. Repeat those analyses and multiply by the proper dilution factors.

8. Report

Report manganese, dissolved (01056), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

Precision for dissolved manganese for three samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
6	22.2	16
6	121	7
6	291	5

Manganese, atomic absorption spectrometric, direct

Parameters and Codes:

Manganese, dissolved, I-1454-85 (μg/L as Mn): 01056
Manganese, total recoverable, I-3454-85 (μg/L as Mn): 01055
Manganese, suspended recoverable, I-7454-85 (μg/L as Mn): 01054
Manganese, recoverable-from-bottom-material, dry wt, I-5454-85 (μg/g as Mn): 01053

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 10 μg/L of manganese. Sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale. Brines need to be analyzed by the atomic absorption spectrometric, chelation-extraction method, providing that the interferences discussed in that method are not exceeded.

1.2 Suspended recoverable manganese is calculated by subtracting dissolved manganese from total recoverable manganese.

1.3 This method may be used to analyze bottom material containing at least 1 μg/g of manganese. Prepared sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale.

1.4 Total recoverable manganese in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable manganese in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

2.1 Manganese is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment.

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer or both.

3. Interferences

Magnesium (100 mg/L) and silica (100 mg/L) do not interfere. Magnesium in excess of 100 mg/L may present some interference, especially when the manganese concentration exceeds 500 μg/L. Silica interferes above 100 mg/L. Iron concentration to 4 × 106 μg/L does not interfere.

4. Apparatus

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

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

Grating ------------	Ultraviolet
Wavelength --------	279.5 nm
Source (hollow-cathode lamp) ------------	Manganese
Oxidant ------------	Air
Fuel ----------------	Acetylene
Type of flame -------	Oxidizing

4.3 The 100-mm (4-in.), flathead, single-slot burner allows a working range from 10 to 1,000 μg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Manganese standard solution I*, 1.00 mL = 100 μg Mn: Dissolve 0.1000 g 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 *Manganese standard solution II*, 1.00 mL = 10.0 μg Mn: Immediately before use, dilute 10.0 mL manganese standard solution I to 100 mL with demineralized water.

5.3 *Manganese working standards*: Prepare at least six working standards containing from 10 to 1,000 µg/L manganese by appropriate dilution of manganese standard solution II with acidified water. Prepare fresh daily.

5.4 *Water*, acidified: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

Aspirate the blank (acidified water) to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable manganese in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing manganese concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per liter of suspended recoverable manganese, subtract dissolved-manganese concentration from total-recoverable-manganese concentration.

7.3 To determine micrograms per gram of manganese in bottom-material samples, first determine the micrograms per liter of manganese as in paragraph 7.1; then

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

8. Report

8.1 Report manganese, dissolved (01056), total-recoverable (01055), and suspended-recoverable (01054), concentrations as follows: less than 100 µg/L, nearest 10 µg/L; 100 µg/L and above, two significant figures.

8.2 Report manganese, recoverable-from-bottom-material (01053), concentrations as follows: less than 10 µg/g, nearest microgram per gram; 10 µg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved manganese for 30 samples within the range of 3.0 to 568 µg/L may be expressed as follows:

$$S_T = 0.056X + 8.28$$

where

S_T = overall precision, micrograms per liter, and

X=concentration of manganese, micrograms per liter.

The correlation coefficient is 0.9003.

9.2 Precision for dissolved manganese for six of the 30 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
6	3.0	267
6	12	83
27	60	17
25	106	12
34	256	9
36	568	7

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable manganese and for recoverable manganese in bottom material will be greater than that reported for dissolved manganese.

9.4 Precision for total recoverable manganese expressed in terms of percent relative standard deviation for two water-suspended sediment samples is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
21	52	44
22	317	6

Manganese, atomic absorption spectrometric, graphite furnace

Parameter and Code:

Manganese, dissolved, I-1455-85 (µg/L as Mn): 01056

1. Application

1.1 This method may be used to determine manganese in low ionic-strength water and precipitation. With deuterium background correction and a 20-µL sample, the method is applicable in the range from 0.2 to 12 µg/L. With Zeeman background correction and a 20-µL sample, the method is applicable in the range from 0.2 to 20 µg/L. Sample solutions that contain manganese concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric direct or chelation-extraction method, or by the atomic emission spectrometric ICP method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Manganese is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform and a matrix modifier is added. The sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (60 mg/L), magnesium (14 mg/L), sodium (56 mg/L), sulfate (110 mg/L), and chloride (45 mg/L) do not interfere. Higher concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of manganese. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 279.5 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high-temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-µL sample with 5 µL of matrix modifier (NOTE 1).

NOTE 1. A 20-µL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms*. Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware*. Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Matrix modifier solution*, 10 g $Mg(NO_3)_2$/L, Suprapur MCB reagent or equivalent: Add 16.8 g $Mg(NO_3)_2 \cdot 6H_2O$ to 950 mL Type 1 water, mix, and dilute to 1,000 mL. DO NOT ADD ACID TO THE MATRIX MODIFIER SOLUTION.

5.2 *Manganese standard solution I*, 1.00 mL = 1,000 μg Mn: Dissolve 1.0000 g Mn flakes in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with Type 1 water.

5.3 *Manganese standard solution II*, 1.00 mL = 10.0 μg Mn: Dilute 10.0 mL manganese standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified Type 1 water (paragraph 5.7) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.4 *Manganese standard solution III*, 1.00 mL = 1.00 μg Mn: Dilute 100.0 mL manganese standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.5 *Manganese standard solution IV*, 1.00 mL = 0.01 μg Mn: Dilute 10.0 mL manganese standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

5.6 *Nitric acid, concentrated*, high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HNO_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for manganese. Add an additional 1.5 mL of concentrated HNO_3/liter of water, and repeat analysis. The integrated signal should not increase by more than 0.001 absorbance-seconds.

5.7 *Water*, acidified, Type 1: Add 1.5 mL high-purity, concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water*, Type 1.

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1+1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-μL aliquots of blank and working standards plus 5 μL of modifier each and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and/or platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of manganese in each sample from the digital display or printer output. Dilute those samples containing concentrations of manganese that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report manganese, dissolved (01056), concentrations as follows: less than 10.0 µg/L, nearest 0.1 µg/L; 10 µg/L and above, two significant figures for both deuterium background correction and Zeeman background correction.

9. Precision

9.1 Analysis of four rainwater samples six times each by a single operator using deuterium background correction is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
0.53	0.07	13.7
1.14	.05	4.8
1.53	.04	2.8
1.79	.05	3.0

9.2 Analysis of four samples by a single operator using Zeeman background correction is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
7	3.94	0.38	9.6
11	9.92	.60	6.0
4	15.48	.25	1.6
12	19.06	.51	2.7

9.3 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of manganese was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
3.95	4.38	0.35	8.0	111
7.9	8.13	.77	9.5	103
13	13.43	.64	4.8	103
15.5	16.03	.77	4.8	103
26	25.45	1.29	5.1	98
Tap water (NOTE 3)				
3.95	3.11	1.11	6.4	79
7.9	6.63	.66	3.2	84
13	9.67	1.48	6.2	74
15.5	14.83	1.59	7.2	96
26	24.94	2.11	5.4	96

NOTE 3. The tap water contained approx 14.4 µg/L of manganese, and the standard deviation and percent relative standard deviation were calculated prior to subtraction of manganese originally present.

9.4 The precision and bias for the deuterium background method were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of manganese was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
3.95	3.89	0.23	5.9	98
7.9	8.12	.57	7.0	103
13	13.32	.58	4.4	102
15.5	14.76	1.17	7.9	95
26	26.12	.72	2.8	100
Tap water (NOTE 3)				
3.95	6.61	2.19	10.3	167
7.9	9.07	1.43	6.1	115
13	12.16	1.99	7.4	94
15.5	17.53	1.34	5.4	113
26	23.85	3.07	8.0	92

9.5 Interlaboratory precision for dissolved manganese for 9 samples within the range of 40 to 547 µg/L, without regard to type of background correction and use of matrix modifiers, if any, may be expressed as follows:

$$S_T = 0.144X + 5.023$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of manganese, micrograms per liter.

The correlation coefficient is 0.8074.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 39-41.

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Fernandez, F. J., Beatty, M. M., and Barnett, W. B., 1981, Use of the L'vov platform for furnace atomic absorption applications: Atomic Spectroscopy, v. 2, p. 16-21.

Hinderberger, E. J., Kaiser, M. L., and Koirtyohann, S. R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1-11.

Manning, D. C., and Slavin, W., 1983, The determination of trace elements in natural waters using the stabilized temperature platform furnace: Applied Spectroscopy, v. 37, p. 1-11.

Ottaway, J. M., 1982, A revolutionary development in graphite furnace atomic absorption: Atomic Spectroscopy, v. 3, p. 89-92.

Slavin, W., Carnrick, G. R., and Manning, D. C., 1982, Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace: Analytical Chemistry, v. 54, p. 621-4.

Manganese, atomic emission spectrometric, ICP

Parameter and Code:
Manganese, dissolved, I-1472-85 (μg/L as Mn): 01056

2. Summary of method

Manganese is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Manganese, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:

Manganese, total, I-5473-85 (mg/kg as Mn): none assigned
Manganese, total, I-5474-85 (mg/kg as Mn): none assigned

2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The sample is then treated and analyzed by one of the following techniques.

2.1.1 The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1000°C. The resulting bead is dissolved in acidified, boiling, demineralized water; manganese is then determined by atomic absorption spectrometry. See method I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

2.1.2 The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200°C. Manganese is determined on the resulting solution by atomic absorption spectrometry. See method I- 5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Mercury, atomic absorption spectrometric, flameless

Parameters and Codes:

Mercury, dissolved, I-1462-85 (μg/L as Hg): 71890
Mercury, total recoverable, I-3462-85 (μg/L as Hg): 71900
Mercury, suspended recoverable, I-7462-85 (μg/L as Hg): 71895
Mercury, recoverable-from-bottom-material, dry wt, I-5462-85 (μg/g as Hg): 71921

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 0.5 μg/L of mercury. Samples containing mercury concentrations greater than 10 μg/L need to be diluted. Industrial and sewage effluent may be analyzed, as well as samples of fresh and saline water.

1.2 Suspended recoverable mercury is calculated by subtracting dissolved mercury from total recoverable mercury.

1.3 This method may be used to analyze bottom material containing at least 0.01 μg/g of mercury. Usually, a 5-g sample of prepared material (method P-0520) is taken for analysis. For samples containing more than 1.0 μg/g, use less sediment.

1.4 Total recoverable mercury in water-suspended sediment may be determined after each sample has been thoroughly mixed by vigorous shaking and a suitable sample portion has been rapidly withdrawn from the mixture.

2. Summary of method

2.1 The cold-vapor, flameless, atomic absorption procedure is based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds, if present, are decomposed by hot (95 °C) digestion with potassium permanganate and potassium persulfate in acid solution. The mercuric ions are then reduced to the elemental state with stannous chloride, and the mercury vapor is subsequently removed from solution by aeration and passed through a cell positioned in the light path of an atomic absorption spectrometer.

2.2 This method is based on a procedure described by Hatch and Ott (1968) and is similar in substance to the flameless atomic absorption method in "Methods for Chemical Analysis of Water and Wastes," published by the Water Quality Office of the Environmental Protection Agency (1979).

3. Interferences

3.1 Some samples may contain volatile organic compounds that absorb radiation at 253.7 nm and that may be swept from the solution along with the mercury vapor. These constitute a positive interference, and the possibility of their presence must not be overlooked.

3.2 Selenium concentrations, either as selenate or selenite, up to 10,000 μg/L do not interfere; higher concentrations were not tested.

4. Apparatus

4.1 *Absorption cell* (fig. 29). Mount and align an absorption cell (10- to 20-cm path length) in the light path of the spectrometer. Position a 60-watt lamp over the cell (10 to 15 cm) to prevent condensation of water vapor. Attach a sufficient length of tubing to the outlet of the cell and vent to a hood. Connect the inlet of the cell to the aerator with a minimum length of plastic tubing. Attach a water aspirator to the outlet of the stopcock (NOTE 1). Alternately, a forced-air pump may be used.

NOTE 1. The stopcock must remain closed during analysis and be opened only briefly between samples to remove residual mercury vapor from the absorption cell.

4.2 *Aerator* (fig. 29).

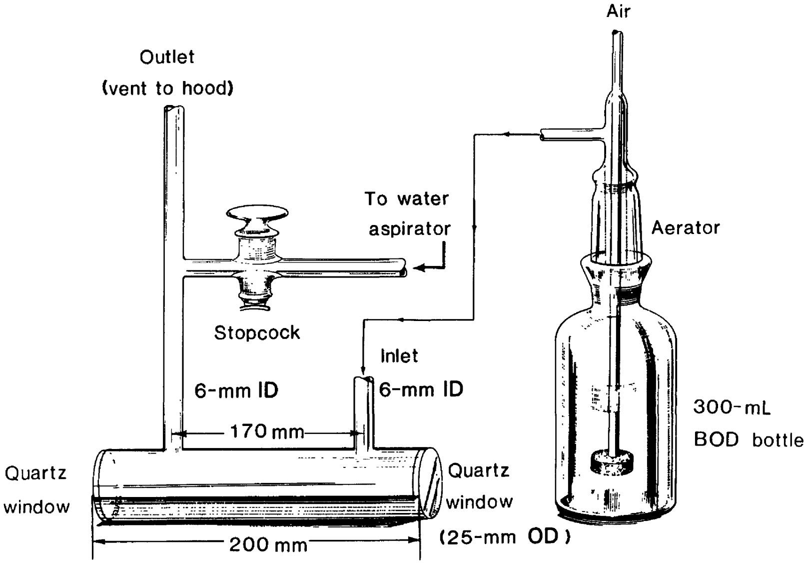


Figure 29.—Absorption cell and aerator

4.3 *Atomic absorption spectrometer and recorder* or a commerical mercury analyzer.

4.4 Refer to the manufacturer's manual to optimize instrument for the following:

Grating	Ultraviolet
Wavelength ..	253.7 nm
Source	Mercury-vapor discharge, hollow-cathode, or electrodeless-discharge lamp

4.5 *BOD bottle*, 300-mL capacity.

4.6 *Water bath* or controlled-temperature oven, 95°C.

5. Reagents

5.1 *Hydroxylamine hydrochloride-sodium chloride solution*: Dissolve 10 g $NH_2OH{\cdot}HCl$ and 12 g NaCl in demineralized water and dilute to 100 mL (NOTE 2). Prepare fresh daily. Alternatively, 12 g hydroxylamine sulfate may be used instead of the hydroxylamine hydrochloride.

NOTE 2. A larger volume of this reagent can be prepared if it is kept refrigerated.

5.2 *Mercury standard solution I*, 1.00 mL = 100 μg Hg: Dissolve 0.1712 g $Hg(NO_3)_2{\cdot}H_2O$ in demineralized water. Add 1.5 mL concentrated HNO_3 and dilute to 1,000 mL with demineralized water.

5.3 *Mercury standard solution II*, 1.00 mL = 1.00 μg Hg: Dilute 5.00 mL mercury standard solution I and 1.5 mL concentrated HNO_3 to 500 mL with demineralized water. This and the following mercury standard solutions must be prepared fresh daily.

5.4 *Mercury standard solution III*, 1.00 mL = 0.050 μg Hg: Dilute 10.0 mL mercury standard solution II and 1.5 mL concentrated HNO_3 to 200 mL with demineralized water. Use this solution to prepare working standards at the time of analysis.

5.5 *Nitric acid*, concentrated (sp gr 1.41), with low mercury content: duPont, reagent-grade acid has been found satisfactory.

5.6 *Potassium permanganate solution*, 50 g/L: Dissolve 5 g $KMnO_4$ in demineralized water and dilute to 100 mL. Prepare fresh weekly. Store in brown glass bottle.

5.7 *Potassium persulfate solution*, 50 g/L: Dissolve 5 g $K_2S_2O_8$ in demineralized water and dilute to 100 mL.

5.8 *Stannous chloride solution*, 74 g/L: Add 22 g $SnCl_2 \cdot 2H_2O$ to 250 mL 0.25*M* H_2SO_4. This solution is unstable. Prepare fresh daily.

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

5.10 *Sulfuric acid*, 0.25*M*: *Cautiously* add 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

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

6.2 Follow instructions in paragraphs 6.2.1 through 6.2.5 for dissolved mercury.

6.2.1 Pipet a volume of sample containing less than 1.0 μg Hg (100 mL max) into a 300-mL capacity BOD bottle and adjust the volume to approx 100 mL.

6.2.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.2.3 Add 5 mL concentrated H_2SO_4 and 2.5 mL concentrated HNO_3, mixing after each addition.

6.2.4 Add 5 mL $KMnO_4$ solution and shake. Add additional small amounts of $KMnO_4$ solution, if necessary, until the purple color persists for at least 15 min.

6.2.5 Add 2 mL $K_2S_2O_8$ solution, mix, and heat for 2 h in a boiling-water bath or for 3 h in an oven at 95 °C. Proceed to paragraph 6.5.

6.3 Follow instructions in paragraph 6.3.1 through 6.3.5 for total recoverable mercury.

6.3.1 Pipet a volume of well-mixed sample containing less than 1.0 μg Hg (100 mL max) into a 300-mL capacity BOD bottle and adjust the volume to approx 100 mL.

6.3.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.3.3 Add 5 mL concentrated H_2SO_4 and 2.5 mL concentrated HNO_3, mixing after each addition.

6.3.4 Add 15 mL $KMnO_4$ solution and shake. Add additional small amounts of $KMnO_4$ solution, if necessary, until the purple color persists for at least 15 min.

6.3.5 Add 8 mL $K_2S_2O_8$ solution, mix, and heat for 2 h in a boiling-water bath or for 3 h in an oven at 95 °C. Proceed to paragraph 6.5.

6.4 Follow instructions in paragraphs 6.4.1 through 6.4.5 for recoverable mercury from bottom material.

6.4.1 Place a weighed portion of sample containing less than 1.0 μg Hg (5 g max) into a 300-mL capacity BOD bottle and add approx 100 mL demineralized water.

6.4.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.4.3 Add 5 mL concentrated H_2SO_4 and 2.5 mL concentrated HNO_3, mixing after each addition.

6.4.4 Add 15 mL $KMnO_4$ solution and shake. Add additional small amounts of $KMnO_4$ solution, if necessary, until the purple color persists for at least 15 min.

6.4.5 Add 8 mL $K_2S_2O_8$ solution, mix, and heat for 2 h in a boiling-water bath or for 3 h in an oven at 95 °C. Proceed to paragraph 6.5.

6.5 Remove from water bath, cool, and add $NH_2OH \cdot HCl$-$NaCl$ solution in 2-mL increments to reduce the excess permanganate, as evidenced by the disappearance of the permanganate color.

6.6 Add 5 mL $SnCl_2$ solution to one sample and immediately attach the bottle to the aerator (NOTE 3). Record the maximum absorbance. After maximum absorbance has been recorded, remove the BOD bottle and open the stopcock to the vacuum. Momentarily pinch off the vent tube in order to remove residual mercury vapor from the absorption cell. Treat each succeeding sample, blank, and standard in a like manner.

NOTE 3. Use the atomic absorption compressed-air supply or a peristaltic pump to aerate the sample. Adjust the rate of air flow to approx 2 L/min.

7. Calculations

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

7.2 Determine the concentration of dissolved or total recoverable mercury in each sample as follows:

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

7.3 To determine the concentration of suspended recoverable mercury, subtract dissolved-mercury concentration from total-recoverable-mercury concentration.

7.4 Determine the concentration of mercury in air-dried bottom material as follows:

$$\text{Hg } (\mu\text{g/g}) = \frac{\mu\text{g Hg in sample}}{\text{wt of sample (g)}}$$

8. Report

8.1 Report mercury, dissolved (71890), total-recoverable (71900), and suspended- recoverable (71895), concentrations as follows: less than 10 μg/L and greater than or equal to 0.5 μg/L, nearest 0.1 μg/L; 10 μg/L and above, two significant figures.

8.2 Report mercury, recoverable-from-bottom-material (71921), concentrations as follows: less than 1.00 μg/g, nearest 0.01 μg/g; 1.0 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved mercury for 23 samples within the range of 0.3 to 15.5 μg/L may be expressed as follows:

$$S_T = 0.152X + 0.164$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of mercury, micrograms per liter.

The correlation coefficient is 0.9229.

9.2 Precision for dissolved mercury for six of the 23 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
22	0.33	50
15	.60	46
27	1.69	32
7	3.46	30
7	6.54	18
26	15.5	16

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable mercury and for recoverable mercury in bottom material will be greater than that reported for dissolved mercury.

9.4 Precision for total recoverable mercury expressed in terms of percent relative standard deviation for two water-suspended sediment samples is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
19	9.2	32
18	11.4	38

References

Fishman, M. J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of wastewaters: U.S. Geological Survey Open-File Report 76-177, p. 51-60.

Hatch, W. R., and Ott, W. L., 1968, Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry: Analytical Chemistry, v. 40, p. 2085-90.

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 245.1-1.

Mercury, atomic absorption spectrometric, flameless automated-sequential

Parameter and Code:

Mercury, dissolved, I-2462-85 (μg/L as Hg): 71890

1. Application

This method may be used to analyze water and wastewater containing at least 0.1 μg/L mercury. Samples containing mercury concentrations greater than 8.0 μg/L need to be diluted.

2. Summary of method

2.1 The cold-vapor, flameless, atomic absorption procedure is based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds, if present, are decomposed by hot (95 °C) digestion with potassium dichromate and potassium persulfate in acid solution. Mercuric ions are then reduced to the elemental state with stannous chloride, and mercury vapor is subsequently removed from solution by aeration and passed through a cell positioned in the light path of an atomic absorption spectrometer.

2.2 The method is based on a procedure described by El-Awady and others (1976).

3. Interferences

3.1 Chloride concentrations up to 5,000 mg/L do not interfere; higher concentrations were not tested.

3.2 Hydroxylamine hydrochloride-sodium chloride solution is added to prevent interference from residual chlorine.

3.3 El-Awady and others (1976) reported that copper sulfate (1,000 mg/L) does not interfere and that chemical-oxygen-demand (COD) concentrations of less than 700 mg/L can be tolerated. Ethyl alcohol, methyl alcohol, glycerol, chloroform, and carbon tetrachloride did not interfere when added in concentrations as high as 0.5 percent. Major interferences were observed from benzene and toluene. A maximum tolerance of 500 μg/L was obtained for these compounds.

3.4 Selenate concentrations up to 10,000 μg/L do not interfere; higher concentrations were not tested. Concentrations of selenite greater than 100 μg/L interfere by suppressing the mercury absorption.

4. Apparatus

4.1 *Absorption cell*, 100-mm long, 10-mm diameter, with quartz windows.

4.2 *Atomic absorption spectrometer and recorder* or a commercial mercury analyzer.

4.3 Refer to manufacturer's manual to optimize instrument for the following:

Grating	Ultraviolet
Wavelength counter	253.7 nm
Source	Mercury-vapor, hollow-cathode, or electrodeless-discharge lamp
Carrier	Nitrogen (flow approx 20 mL/min; adjust for maximum sensitivity with use of a standard)

4.4 *Technicon Autoanalyzer*, consisting of sampler, manifold (fig. 30), proportioning pump, and high-temperature heating bath (NOTE 1).

NOTE 1. Nitrogen gas may be used instead of air in manifold (fig. 30).

4.5 *Vapor-liquid separator* (fig. 31).

5. Reagents

5.1 *Hydroxylamine hydrochloride-sodium chloride solution*: Dissolve 30 g $NH_2OH \cdot HCl$ and 30 g NaCl in demineralized water and dilute to 1 L.

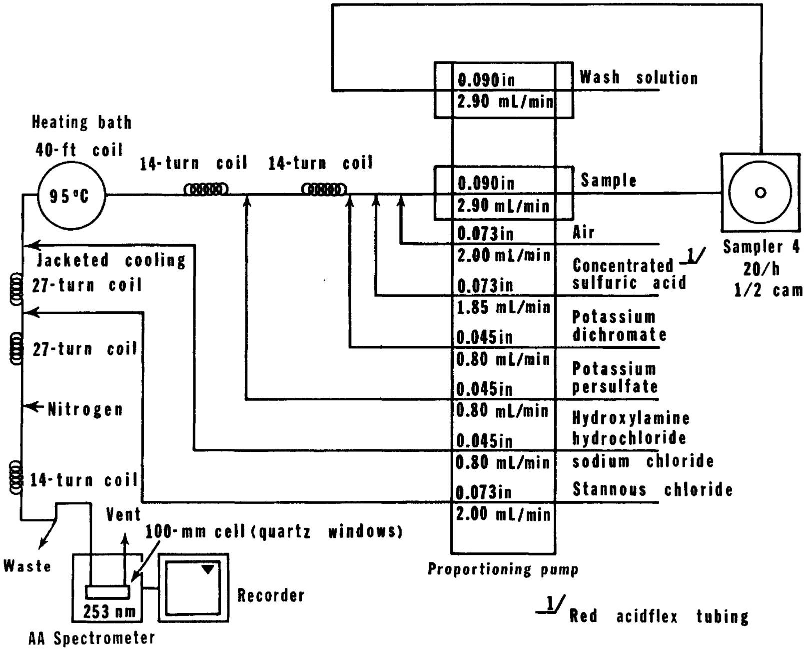


Figure 30.—Mercury manifold

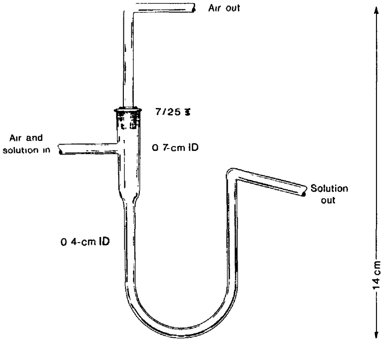


Figure 31.—Vapor-liquid separator

5.2 *Mercury standard solution I*, 1.00 mL = 100 µg Hg: Dissolve 0.1712 g $Hg(NO_3)_2 \cdot H_2O$ in demineralized water. Add 1.5 mL concentrated HNO_3 (sp gr 1.41) and 25 mL $K_2Cr_2O_7$ solution, and dilute to 1,000 mL with demineralized water.

5.3 *Mercury standard solution II*, 1.00 mL = 1.00 µg Hg: Dilute 10.0 mL mercury standard solution I, 5 mL concentrated HNO_3, and 25 mL $K_2Cr_2O_7$ solution to 1,000 mL with demineralized water.

5.4 *Mercury standard solution III*, 1.00 mL = 0.100 µg Hg: Dilute 100.0 mL mercury standard solution II, 5 mL concentrated HNO_3, and 25 mL $K_2Cr_2O_7$ solution to 1,000 mL with demineralized water. Use this solution to prepare working standards. The working standards should also contain 5 mL/L of concentrated HNO_3 and 25 mL/L of $K_2Cr_2O_7$ solution. The working standards are stable for at least 3 weeks.

5.5 *Nitric acid,* concentrated (sp gr 1.41), with low mercury content: Both duPont and Baker reagent-grade acids have been found satisfactory.

5.6 *Nitric acid (1+99),* wash solution: Dilute 10 mL of concentrated HNO_3 (sp gr 1.41) to 1 L with demineralized water.

5.7 *Potassium dichromate solution,* 20 g/L: Dissolve 20 g $K_2Cr_2O_7$ in demineralized water and dilute to 1 L.

5.8 *Potassium persulfate solution,* 40 g/L: Dissolve 40 g $K_2S_2O_8$ in demineralized water and dilute to 1 L. Prepare fresh each week.

5.9 *Stannous chloride solution,* 84 g/L: Dissolve 100 g $SnCl{\cdot}2H_2O$ in 100 mL concentrated hydrochloric acid (sp gr 1.19) and dilute to 1 L with demineralized water. This solution is unstable. Prepare fresh daily.

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

6. Procedure

6.1 Set up manifold (fig. 30).

6.2 Prepare a blank of demineralized water and sufficient standards to 8.0 μg/L by appropriate dilutions of mercury standard solution III.

6.3 Initially feed all reagents through the system using the nitric acid wash solution in the sample line. Allow the heating bath to warm to 95°C.

6.4 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 Remove the sample line from the nitric acid wash solution when the baseline stabilizes and begin analysis.

7. Calculations

7.1 Prepare an analytical curve by plotting the absorbance of each standard versus its respective mercury concentration.

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

8. Report

Report mercury, dissolved (71890), concentrations as follows: less than 10 μg/L, nearest 0.1 μg/L; 10 μg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved mercury for 11 samples within the range of 0.3 to 16.4 μg/L may be expressed as follows:

$$S_T = 0.134X + 0.106$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of mercury, micrograms per liter.

The correlation coefficient is 0.9722.

9.2 Precision for dissolved mercury for five of the 11 samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
3	0.33	17
4	.58	54
3	1.87	32
3	2.80	27
5	16.4	14

Reference

El-Awady, A. A., Miller, R. B., and Carter, M. J., 1976, Automated method for the determination of total and inorganic mercury in water and waste-water samples: Analytical Chemistry, v. 48, p. 110-16.

Molybdenum, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:

Molybdenum, dissolved, I-1490-85 (µg/L as Mo): 01060
Molybdenum, total recoverable, I-3490-85 (µg/L as Mo): 01062
Molybdenum, suspended recoverable, I-7490-85 (µg/L as Mo): 01061
Molybdenum, recoverable-from-bottom-material, dry wt, I-5490-85 (µg/g as Mo): 01063

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 1 to 50 µg/L of molybdenum. Samples containing more than 50 µg/L need to be diluted prior to chelation-extraction.

1.2 Suspended recoverable molybdenum is calculated by subtracting dissolved molybdenum from total recoverable molybdenum.

1.3 This method may be used to analyze bottom material containing at least 0.05 µg/g of molybdenum. Prepared sample solutions containing more than 50 µg/L of molybdenum need to be diluted.

1.4 Total recoverable molybdenum in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable molybdenum in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

Molybdenum is determined by atomic absorption spectrometry following chelation with 8-hydroxyquinoline and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into a nitrous oxide-acetylene flame of the spectrometer (Chau and Lum-Shue- Chan, 1969).

3. Interferences

The method is free from interference from most elements commonly found in fresh water. Vanadium(V) and iron(III) enhance the absorption, and chromium(VI) and tungsten(VI) suppress it. With the addition of ascorbic acid, up to 50,000 µg/L of iron(III), 1,000 µg/L of vanadium(V), and 10,000 µg/L of chromium(VI) or tungsten(VI) can be tolerated (Chau and Lum-Shue-Chan, 1969).

4. Apparatus

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

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

Grating ------------ Ultraviolet
Wavelength -------- 313.3 nm
Source (hollow-cathode lamp) ------------ Molybdenum
Oxidant ------------ Nitrous oxide
Fuel --------------- Acetylene
Type of flame ------- Fuel-rich

4.3 Different nitrous oxide burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ascorbic acid solution,* 1 g/100 mL: Dissolve 1 g ascorbic acid in 100 mL demineralized water.

5.2 *Bromophenol blue indicator solution,* 0.1 g/100 mL: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.

5.3 *Hydrochloric acid,* 0.3*M*: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.4 *8-Hydroxyquinoline-methyl isobutyl ketone solution,* 1 g/100 mL: Dissolve 1 g 8-hydroxyquinoline in 100 mL MIBK. Prepare fresh daily.

5.5 *Methyl isobutyl ketone (MIBK).*

5.6 *Molybdenum standard solution I*, 1.00 mL = 100 μg Mo: Dissolve 0.1500 g reagent-grade MoO_3 in 10 mL 0.1*M* NaOH (warm if necessary). Make just acidic with 0.1*M* HCl and dilute to 1,000 mL with demineralized water.

5.7 *Molybdenum standard solution II*, 1.00 mL = 1.0 μg Mo: Dilute 10.0 mL molybdenum standard solution I to 1,000 mL with demineralized water.

5.8 *Molybdenum standard solution III*, 1.0 mL = 0.10 μg Mo: Immediately before use, dilute 10.0 mL molybdenum standard solution II to 100 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.9 *Sodium hydroxide solution*, 2.5*M*: Dissolve 100 g NaOH in demineralized water and dilute to 1 L.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+9), and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample or prepared sample solution containing less than 5.0 μg Mo (100 mL max) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.3 Prepare a demineralized-water blank with 1.5 mL concentrated. HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.4 Add 5 mL ascorbic acid solution and mix.

6.5 Add 2 drops bromophenol blue indicator solution and mix.

6.6 Adjust the pH by addition of 2.5*M* NaOH until a blue color persists. Add 0.3*M* HCl by drops until the blue color just disappears; then add 2.0 mL 0.3*M* HCl in excess. The pH at this point should be 2.3 (NOTE 1).

NOTE 1. The pH adjustment in paragraphs 6.5 and 6.6 may be made using a pH meter instead of using indicator. Add 2.5*M* NaOH to the solution until the pH is 2.3.

6.7 Add 5.0 mL 8-hydroxyquinoline-MIBK solution and shake vigorously for 15 min.

6.8 Allow the layers to separate; then add demineralized water until the ketone layer is completely in the neck of the flask.

6.9 While aspirating the ketone layer of the blank, use the automatic zero control to set the digital display to read zero concentration. While aspirating standards, use the automatic concentration control to set the digital display to read the concentration of the standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable molybdenum in each sample from the digital display or printer. Dilute those samples containing molybdenum concentrations that exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

7.2 To determine micrograms per liter of suspended recoverable molybdenum, subtract dissolved-molybdenum concentration from total-recoverable-molybdenum concentration.

7.3 To determine micrograms per gram of molybdenum in bottom-material samples, first determine the micrograms per liter of molybdenum as in paragraph 7.1; then

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

8. Report

8.1 Report molybdenum, dissolved (01060), total recoverable (01062), and suspended recoverable (01061), concentrations as follows: less than 100 μg/L, nearest microgram per liter; 100 μg/L and above, two significant figures.

8.2 Report molybdenum, recoverable-from-bottom-material (01063), concentrations as follows: less than 10 μg/g, nearest 0.1 μg/g; 10 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved molybdenum for seven samples within the range of 1.3 to 56.7 μg/L may be expressed as follows:

$$S_T = 0.068X + 1.320$$

where

S_T = overall precision, micrograms per liter, and,

X = concentration of molybdenum, micrograms per liter.

The correlation coefficient is 0.8718.

9.2 Precision for dissolved molybdenum for four of the seven samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
3	1.3	115
5	2.0	35
4	25.2	17
3	56.7	8

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable molybdenum and for recoverable molybdenum in bottom material will be greater than that reported for dissolved molybdenum.

Reference

Chau, Y. K., and Lum-Shue-Chan, K., 1969, Atomic absorption determination of microgram quantities of molybdenum in lake waters: Analytical Chimica Acta, v. 48, p. 205.

Molybdenum, atomic emission spectrometric, ICP

Parameter and Code:

Molybdenum, dissolved, I-1472-85 (μg/L as Mo): 01060

2. Summary of method

Molybdenum is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Nickel, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:
Nickel, dissolved, I-1500-85 (μg/L as Ni): 01065
Nickel, total recoverable, I-3500-85 (μg/L as Ni): 01067
Nickel, suspended recoverable, I-7500-85 (μg/L as Ni): 01066

1. Application

1.1 This method may be used to analyze water, brines, and water-suspended sediment containing from 1 to 100 μg/L of nickel. Sample solutions containing more than 100 μg/L need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption direct method.

1.2 Suspended recoverable nickel is calculated by subtracting dissolved nickel from total recoverable nickel.

1.3 Total recoverable nickel in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

1.4 If the iron concentration of the sample solution exceeds 25,000 μg/L, determine nickel by the atomic absorption spectrometric direct method.

2. Summary of method

Nickel is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the air-acetylene flame of the spectrometer (Fishman and Midgett, 1968).

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the nickel absorption.

4. Apparatus

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

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

Grating ------------	Ultraviolet
Wavelength --------	232.0 nm (NOTES 1 and 2)
Source (hollow-cathode lamp) ------------	Nickel
Oxidant ------------	Air
Fuel ----------------	Acetylene
Type of flame -------	Oxidizing

NOTE 1. Setting the proper wavelength for nickel is critical because of the presence of an ion line at 231.6 nm. By aspirating a standard that gives approx 50-percent absorption, the 232.0-nm absorption line can easily be set.

NOTE 2. The 352.4-nm wavelength, less susceptible to nonatomic absorbance, may be used. The resulting analytical curve is more nearly linear; however, the procedure reduces sensitivity.

4.3 Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate solution*, 1 g/100 mL: Dissolve 1 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Citric acid-sodium citrate buffer solution*: Dissolve 126 g citric acid monohydrate and 44 g sodium citrate dihydrate in demineralized water and dilute to 1 L with demineralized water. See NOTE 5 before preparation.

5.3 *Methyl isobutyl ketone* (MIBK).

5.4 *Nickel standard solution I*, 1.00 mL = 200 μg Ni: Dissolve 0.2000 g nickel powder in a minimum amount of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.5 *Nickel standard solution II*, 1.00 mL = 2.00 µg Ni: Dilute 10.0 mL nickel standard solution I and 1 mL concentrated HNO_3 to 1,000 mL with demineralized water. This solution is used to prepare working standards at the time of analysis.

5.6 *Potassium hydroxide*, 10*M*: Dissolve 56 g KOH in demineralized water, cool, and dilute to 100 mL.

5.7 *Potassium hydroxide*, 2.5*M*: Dissolve 14 g KOH in demineralized water and dilute to 100 mL (NOTE 3).

NOTE 3. Alternatively, a 2.5*M* NH_4OH solution may be used. Add 167 mL concentrated NH_4OH (sp gr 0.90) to 600 mL demineralized water. Cool, and dilute to 1 L.

5.8 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+9) and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample solution containing less than 10 µg Ni (100 mL max) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.3 Prepare a blank of acidified water and sufficient standards, and adjust the volume of each to approx 100 mL with acidified water.

6.4 With a pH meter, adjust the pH of each solution to 2.4 with 2.5*M* KOH (NOTES 4 and 5). Shake for 3 min.

NOTE 4. For water-suspended sediment samples that have been digested, add 1 to 2 mL 10*M* KOH or concentrated NH_4OH (sp gr 0.90) before pH adjustment.

NOTE 5. If an automated titration system is used to adjust the pH, add 2.5 mL citric acid-sodium citrate buffer solution prior to pH adjustment. This will prevent over-shooting the end point in poorly buffered samples.

6.5 Add 2.5 mL APDC solution and mix.

6.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.8 Aspirate the ketone layer within 1 h. Aspirate the ketone layer of the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable nickel in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing concentrations of nickel that exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

7.2 To determine the micrograms per liter of suspended recoverable nickel, subtract dissolved-nickel concentration from total-recoverable-nickel concentration.

8. Report

Report nickel, dissolved (01065), total-recoverable (01067), and suspended-recoverable (01066), concentrations as follows: less than 10 µg/L, nearest microgram per liter; 10 µg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved nickel within the range of 3.8 to 23.2 µg/L for 20 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 4.3 µg/L ranged from 3.8 to 5.0 µg/L.

9.2 Precision for dissolved nickel for five of the 20 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
5	3.8	11
5	4.4	61
4	10.2	38
8	10.5	16
13	23.2	23

9.3 It is estimated that the percent relative standard deviation for total-recoverable and suspended recoverable nickel will be greater than that reported for dissolved nickel.

Reference

Fishman, M. J., and Midgett, M. R., 1968, Extraction techniques for the determination of cobalt, nickel, and lead in fresh water by atomic absorption, *in* Trace inorganics in water: American Chemical Society Advances in Chemistry Series, no. 73, p. 230–5.

Nickel, atomic absorption spectrometric, direct

Parameters and Codes:

Nickel, dissolved, I-1499-85 (µg/L as Ni): 01065
Nickel, total recoverable, I-3499-85 (µg/L as Ni): 01067
Nickel, suspended recoverable, I-7499-85 (µg/L as Ni): 01066
Nickel, recoverable-from-bottom-material, dry wt, I-5499-85 (µg/g as Ni): 01068

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 100 µg/L of nickel. Sample solutions containing more than 1,000 µg/L need either to be diluted or to be read on a less expanded scale. Sample solutions containing less than 100 µg/L and brines need to be analyzed by the atomic absorption spectrometric chelation-extraction method, providing that the interference limits discussed in that method are not exceeded.

1.2 Suspended recoverable nickel is calculated by subtracting dissolved nickel from total recoverable nickel.

1.3 This method may be used to analyze bottom material containing at least 5.0 µg/g of nickel. Sample solutions containing more than 1,000 µg/L need either to be diluted or to be read on a less expanded scale.

1.4 Total recoverable nickel in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable nickel in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

Nickel is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment.

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), sulfate (9,000 mg/L), and cadmium, lead, copper, zinc, cobalt, and chromium (10,000 µg/L each) do not interfere. Higher concentrations of each constituent were not investigated.

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	232.0 nm (NOTES 1 and 2)
Source (hollow-cathode lamp)	Nickel
Oxidant	Air
Fuel	Acetylene
Type of flame	Oxidizing

NOTE 1. Setting the proper wavelength for nickel is critical because of the presence of an ion line at 231.6 nm. By aspirating a standard that gives approx 50-percent absorption, the 232.0 nm-absorption line can easily be set.

NOTE 2. The 352.4-nm wavelength, less susceptible to nonatomic absorbance, may be used. The resulting analytical curve is more nearly linear; however, the procedure reduces sensitivity.

5. Reagents

5.1 *Nickel standard solution I,* 1.00 mL = 200 µg Ni: Dissolve 0.2000 g Ni powder in a minimum amount of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Nickel standard solution II*, 1.00 mL = 20 μg Ni: Dilute 100 mL nickel standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water.

5.3 *Nickel standard working solutions*: Prepare a series of at least six standard working solutions containing from 100 to 1,000 μg/L of nickel by appropriate dilution of nickel standard solution II with acidified water. Prepare fresh daily.

5.4 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

Aspirate the blank (acidified water) to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable nickel in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing concentrations of nickel that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per liter of suspended recoverable nickel, subtract dissolved-nickel concentration from total-recoverable-nickel concentration.

7.3 To determine micrograms per gram of nickel in bottom-material samples, first determine the micrograms per liter of nickel as in paragraph 7.1; then

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

8. Report

8.1 Report nickel, dissolved (01065), total-recoverable (01067), and suspended- recoverable (01066), concentrations to the nearest 100 μg/L.

8.2 Report nickel, recoverable-from-bottom-material (01068), concentrations as follows: less than 100 μg/g, nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved nickel for 16 samples within the range of 6.2 to 36.2 μg/L (NOTE 3) may be expressed as follows:

$$S_T = 0.431X + 2.88$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of nickel, micrograms per liter.

The correlation coefficient is 0.7593.

NOTE 3. Precision data for nickel are below the reporting level of 100 μg/L. Samples were not available that contained greater nickel concentrations; however, precision should improve at greater concentrations.

9.2 Precision for dissolved nickel for five of the 16 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
5	6.2	18
11	10.5	80
6	10.8	15
6	20.0	46
19	36.2	47

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable nickel and for nickel in bottom material will be greater than that reported for dissolved nickel.

9.4 Precision for total recoverable nickel expressed in terms of the percent relative standard for two water-suspended sediments is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
10	26.2	58
10	35.9	53

Nickel, atomic absorption spectrometric, graphite furnace

Parameter and Code:

Nickel, dissolved, I-1501-85 (µg/L as Ni): 01065

1. Application

1.1 This method may be used to determine nickel in low ionic-strength water and precipitation. With deuterium background correction and a 20-µL sample, the method is applicable in the range from 1 to 100 µg/L. With Zeeman background correction and a 20-µL sample, the method is applicable in the range from 1 to 80 µg/L. Sample solutions that contain nickel concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric direct or chelation-extraction method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Nickel is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform, and the sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation,normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (25 mg/L), magnesium (8 mg/L), sodium (20 mg/L), sulfate (34 mg/L), and chloride (25 mg/L) do not interfere. Higher concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of nickel. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 232.0 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high-temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-µL sample (NOTE 1).

NOTE 1. A 20-µL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms*. Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware*. Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil

(Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Nickel standard solution I*, 1.00 mL = 1,000 µg Ni: Dissolve 1.0000 g Ni powder in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with Type 1 water.

5.2 *Nickel standard solution II*, 1.00 mL = 10.0 µg Ni: Dilute 10.0 mL nickel standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified Type 1 water (paragraph 5.6) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.3 *Nickel standard solution III*, 1.00 mL = 1.00 µg Ni: Dilute 100.0 mL nickel standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.4 *Nickel standard solution IV*, 1.00 mL = 0.010 µg Ni: Dilute 10.0 mL nickel standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

5.5 *Nitric acid, concentrated*, high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HNO_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for nickel. Add an additional 1.5 mL of concentrated HNO_3/liter of water, and repeat analysis. The integrated signal should not increase by more than 0.001 absorbance-seconds.

5.6 *Water, acidified*, Type 1: Add 1.5 mL high purity concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.7 *Water*, Type 1.

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1+1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-µL aliquots of blank and working standards, and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and (or) platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of nickel in each sample from the digital display or printer output. Dilute those samples containing concentrations of nickel that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report nickel, dissolved (01065), concentrations as follows: less than 10 µg/L, nearest 1 µg/L; 10 µg/L and above, two significant figures for both deuterium background correction and Zeeman background correction.

9. Precision

9.1 Analysis of two samples by a single operator using deuterium background correction is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
10	5.8	0.6	10.3
5	9.8	.8	8.2

9.2 Analysis of three samples six times each by a single operator using Zeeman background correction is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
14.5	0.6	4.1
48.3	.5	1.0
79.7	.5	.6

9.3 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of nickel was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
4.35	4.0	0.6	16	92
8.7	9.3	.5	5	107
13	12.3	.8	7	95
26	24.5	1.6	6	94
27.5	22.8	1.5	7	83
Tap water (NOTE 3)				
4.35	4.2	.8	15	97
8.7	9.6	.8	7	110
13	12.0	1.0	7	92
26	21.5	1.5	7	83
27.5	24.1	1.9	8	88

NOTE 3. The tap water contained 1.2 µg/L of nickel, and the standard deviation and percent relative standard deviation were calculated prior to subtraction of nickel originally present.

9.4 The precision and bias for the deuterium background method were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of nickel was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
4.35	3.8	1.0	26.3	87
8.7	9.0	.6	6.7	103
13	13.2	1.2	9.1	102
26	25.5	3.1	12.2	98
27.5	23.2	1.7	7.3	84
Tap water (NOTE 3)				
4.35	5.7	.8	11.6	131
8.7	9.8	.6	5.5	113
13	12.8	1.3	9.3	98
26	22.5	3.1	13.0	87
27.5	24.1	2.7	10.9	88

9.5 The standard deviation from interlaboratory data, without regard to type of background correction and use of matrix modifiers, if any, for dissolved nickel within the range of 3.8 to 22.5 µg/L for 16 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 5.2 µg/L ranged from 4.5 to 6.1 µg/L.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 39–41.

Cooksey, M., and Barnett, W. B., 1979, Matrix modification and the method of additions in flameless atomic absorption: Atomic Absorption Newsletter, v. 18, p. 101–5.

Fernandez, F. J., Beatty, M. M., and Barnett, W. B., 1981, Use of the L'vov platform for furnace atomic absorption applications: Atomic Spectroscopy, v. 2, p. 16–21.

Hinderberger, E. J., Kaiser, M. L., and Koirtyohann, S. R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1–11.

Manning, D. C., and Slavin, W., 1983, The determination of trace elements in natural waters using the stabilized temperature platform furnace: Applied Spectroscopy, v. 37, p. 1–11.

Ottaway, J. M., 1982, A revolutionary development in graphite furnace atomic absorption: Atomic Spectroscopy, v. 3, p. 89–92.

Slavin, W., Carnrick, G. R., and Manning, D. C., 1982, Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace: Analytical Chemistry, v. 54, p. 621–4.

Nickel, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:

Nickel, total, I-5474-85 (mg/kg as Ni): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Nickel is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Nitrogen, titrimetric, digestion-distillation

Parameter and Code:

Nitrogen, total-in-bottom-material, dry wt, I-5554-85 (mg/kg as N): 00603

1. Application

This method may be used to determine the total nitrogen concentration of any sample of bottom material containing at least 20 mg/kg. Only that portion of bottom material that passes a 2-mm sieve is taken for analysis.

2. Summary of method

Salicylic acid in concentrated sulfuric acid is added to the sample of bottom material. The sample is then subjected to a digestion whereby all nitrogen-containing compounds are converted to ammonium salts. The resulting mixture is then made strongly alkaline, and the ammonia so formed is distilled from the mixture into a solution of boric acid and subsequently determined by titration with standard sulfuric acid solution.

3. Interferences

There are no known interferences with this method.

4. Apparatus

Kjeldahl distillation apparatus, 500-mL flasks.

5. Reagents

5.1 *Ammonium chloride*, crystals.

5.2 *Boric acid solution*, 20 g/L: Dissolve 20 g H_3BO_3 crystals in 800 mL ammonia-free water and dilute to 1 L.

5.3 *Digestion catalyst*: Tablets containing 3.5 g K_2SO_4 and 0.175 g HgO (Scientific Chemical Sales Inc., Kel-catalyst No. KC-M3 or equivalent).

5.4 *Mixed indicator solution*: Dissolve 20 mg methyl red and 100 mg bromocresol green in 100 mL 95-percent ethanol. Store in a well-sealed bottle.

5.5 *Salicylic acid*, crystals.

5.6 *Sodium carbonate solution*, 0.0357*N*: Dissolve 1.892 g primary standard Na_2CO_3 in carbon dioxide-free water and dilute to 1,000 mL.

5.7 *Sodium hydroxide-thiosulfate solution*: With care, dissolve 500 g NaOH in 600 mL ammonia-free water. Add 80 g $Na_2S_2O_3 \cdot 5H_2O$ and dilute to 1 L.

5.8 *Sodium thiosulfate*, crystals $Na_2S_2O_3 \cdot 5H_2O$.

5.9 *Sucrose*.

5.10 *Sulfuric acid*, concentrated, sp gr 1.84.

5.11 *Sulfuric acid standard solution*, approx 0.036*N*: *Cautiously* add 1.0 mL concentrated H_2SO_4 (sp gr 1.84) to 800 mL ammonia-free water and dilute to 1 L. Standardize by titrating 25.0 mL 0.035*N* Na_2CO_3 to pH 4.5. Compute normality of sulfuric acid standard solution to four decimal places.

6. Procedure

6.1 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent—**CAUTION: deadly poison.** (See nitrogen, ammonia, colorimetric, distillation-nesslerization method.)

6.2 Weigh, to the nearest milligram, 3 g of bottom-material sample, prepared as directed in method P-0810 (subsampling, bottom-material, coring), and transfer to the digestion flask.

6.3 Prepare a blank and standard, using 2.0 g sucrose for the blank and 0.1000 g NH_4Cl plus 2.0 sucrose for the standard.

6.4 *Cautiously*, add 25 mL concentrated H_2SO_4 (sp gr 1.84), and then add 1.0 g salicylic acid. Under a hood, swirl the contents of each flask until thoroughly mixed. Allow to stand for at least 30 min.

6.5 Under a hood, add 5 g $Na_2S_2O_3 \cdot 5H_2O$ and heat gently over a Bunsen burner. Let stand for about 5 min or until any frothing ceases.

6.6 Add three digestion-catalyst tablets and mix well. Add a few glass beads and begin the digestion. Continue the digestion until a clear solution is obtained, and then continue fuming 1 h.

6.7 Cool the flask until crystals appear. (Do not cool completely). Add 150 mL ammonia-free water; mix and allow to cool.

6.8 To avoid bumping during the subsequent distillation, transfer the entire solution from the digestion flask to a clean Kjeldahl flask. Rinse the digestion flask with a minimum of ammonia-free water and add to the contents of the clean flask.

6.9 Add 100 mL NaOH-$Na_2S_2O_3$ solution. Immediately connect the flask to the distillation apparatus and *cautiously* mix the contents by swirling.

6.10 Distill at a rate of not more than 10 mL/min or less than 6 mL/min; collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.11 Collect approx 200 mL of distillate, dilute to 250 mL with ammonia-free water, and mix.

6.12 Add 3 drops mixed indicator solution to the distillate and titrate with standard H_2SO_4 until the solution changes from yellow to red.

7. Calculations

$$\text{Nitrogen, total, mg/kg} = \frac{V_a \times N_a \times 14{,}000}{Wt_s}$$

where

V_a =volume of standard H_2SO_4 used to titrate sample, milliliters, minus volume used to titrate blank, milliliters,

N_a = normality of standard H_2SO_4 solution, and

Wt_s = weight of sample, grams.

8. Report

Report nitrogen, total in bottom material (00603), as follows: less than 100 mg/kg, nearest 10 mg/kg; 100 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.

Nitrogen, ammonia, colorimetric, distillation-nesslerization

Parameters and Codes:

Nitrogen, ammonia, dissolved, I-1520-85 (mg/L as N): 00608
Nitrogen, ammonia, total, I-3520-85 (mg/L as N): 00610

1. Application

This method may be used to analyze water and water-suspended sediment containing from 0.01 to 2 mg/L of ammonia-nitrogen. Samples containing more than 2 mg/L need either to be diluted or to be analyzed by an alternative titration procedure.

2. Summary of method

2.1 The sample is buffered to a pH of 9.5 to minimize hydrolysis of organic nitrogen compounds. Ammonia is distilled from the buffered solution, and an aliquot of the distillate then is nesslerized. Essentially, nesslerization is the reaction between potassium mercuric iodide and ammonia to form a red-brown colloidal complex of mercuric ammono-basic iodide:

$$2(HgI_2{\cdot}2KI) + 2NH_3 \rightarrow NH_2Hg_2I_3 + 4KI + NH_4I$$

Concentrations of ammonia are then determined by standard spectrometric measurements. Alternatively, the distillate may be titrated with standard sulfuric acid solution.

2.2 Additional information on the principle of the determination was given by Blaedel and Meloche (1963).

3. Interferences

3.1 Calcium, magnesium, iron, and sulfide interfere with the nesslerization, but the interference of the metals is eliminated by the distillation, and sulfide can be precipitated in the distillation flask by lead carbonate.

3.2 Some organic compounds may distill with the ammonia and form colors with nessler reagent, which cannot satisfactorily be read with the spectrophotometer. Under such conditions, the sample should be titrated with standard sulfuric acid solution.

4. Apparatus

4.1 *Cylinder, graduated, with ground-glass stopper*, 50-mL capacity (Corning No. 3002 or equivalent).

4.2 *Kjeldahl distillation apparatus*, 500-mL flasks.

4.3 *Spectrophotometer*, for use at 425 nm.

4.4 Refer to the manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.010 mg NH_3-N: Dilute 10.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Borate buffer solution*: Dissolve 9.54 g $Na_2B_4O_7{\cdot}10H_2O$ in ammonia-free water. Adjust the pH to 9.5 with 1*M* NaOH (approx 15 mL) and dilute to 1 L with ammonia-free water.

5.4 *Boric acid solution*, 20 g/L: Dissolve 20 g H_3BO_3 in 800 mL ammonia-free water and dilute to 1 L.

5.5 *Nessler reagent*—CAUTION: **HgI_2 is a deadly poison, and the reagent must be so marked:** Dissolve 100 g HgI_2 and 70 g KI in a small volume of ammonia-free water. Add this mixture slowly, with stirring, to a cooled solution of 160 g NaOH in 500 mL ammonia- free water and dilute to 1 L. Allow the reagent to stand at least overnight and filter through a fritted-glass crucible.

5.6 *Sodium hydroxide solution, 1M*: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 L.

6. Procedure

6.1 Rinse all glassware with ammonia-free water before beginning this determination.

6.2 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent—**CAUTION: deadly poison.**

6.3 Pipet a volume of well-mixed sample containing less than 1.0 mg ammonia-nitrogen (250 mL max) into a 500-mL distillation flask, and adjust the volume to approx 250 mL with ammonia-free water (NOTE 1).

NOTE 1. For water-suspended sediment mixtures, rinse the pipet with ammonia-free water to remove adhering particles and combine with sample.

6.4 Add 12.5 mL borate buffer solution, and adjust the pH to 9.5 with 1*M* NaOH, if necessary.

6.5 Immediately distill at a rate of not more than 10 mL or less than 6 mL per min; collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.6 Collect approx 200 mL of distillate, dilute to 250 mL with ammonia-free water, and mix.

6.7 Pipet an aliquot of distillate containing less than 0.1 mg ammonia-nitrogen (50.0 mL maximum) into a glass-stoppered, graduated mixing cylinder, and adjust the volume to 50.0 mL with ammonia-free water.

6.8 Prepare a blank of ammonia-free water and a series of standards in glass-stoppered, graduated mixing cylinders. Add 5 mL boric acid solution to each, and adjust the volume of each to 50.0 mL.

6.9 Add 1.0 mL nessler reagent—**CAUTION: deadly poison**—to each blank, standard, and sample. Stopper and invert several times to mix thoroughly.

6.10 Allow the solutions to stand at least 10 min, but not more than 30 min.

6.11 Determine the absorbance of each test sample and standard against the blank.

7. Calculations

7.1 Determine milligrams of ammonia-nitrogen in each sample from a plot of absorbances of standards.

7.2 Determine the ammonia-nitrogen concentration in milligrams per liter as follows:

Ammonia-nitrogen as N, (mg/L) =

$$\frac{1{,}000}{\text{mL sample}} \times \frac{250}{\text{mL aliquot}} \times \text{mg N in aliquot}$$

8. Report

Report nitrogen, ammonia, dissolved (00608), and total (00610), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved ammonia-nitrogen for nine samples within the range of 0.10 to 2.0 mg/L may be expressed as follows:

$$S_T = 0.465X + 0.0001$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of ammonia-nitrogen, milligrams per liter.

The correlation coefficient is 0.8140.

9.2 Precision for dissolved ammonia-nitrogen for four of the nine samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
11	0.104	73
4	.600	33
8	1.51	44
7	2.04	63

9.3 It is estimated that the percent relative standard deviation for total ammonia- nitrogen will be greater than that reported for dissolved ammonia-nitrogen.

Reference

Blaedel, W. J., and Meloche, V. W., 1963, Elementary quantitative analysis: theory and practice (2d ed.): New York, Harper and Row, 826 p.

Nitrogen, ammonia, colorimetric, salicylate-hypochlorite, automated-segmented flow

Parameters and Codes:

Nitrogen, ammonia, dissolved, I-2522-85 (mg/L as N): 00608
Nitrogen, ammonia, total, I-4522-85 (mg/L as N): 00610
Nitrogen, ammonia, total-in-bottom-material, I-6522-85 (mg/kg as N): 00611

1. Application

1.1 This method may be used to analyze surface, domestic, and industrial water, brines, and water-suspended sediment containing from 0.01 to 1.5 mg/L of ammonia-nitrogen. Concentrations greater than 1.5 mg/L need to be diluted.

1.2 This method may also be used to determine concentrations of ammonia-nitrogen in bottom material containing at least 0.2 mg/kg NH_3–N. Prepared sample solutions containing more than 1.5 mg/L NH_3–N must first be diluted.

1.3 Sodium ion is a good replacement ion for ammonium in the slow-exchange positions of soil minerals (Jackson, 1958). The water-suspended sediment is treated and preserved in the field with mercury chloride and sodium chloride. The resulting mixture, prior to analysis in the laboratory, is either centrifuged or decanted to obtain a clear supernatent solution. Similarly, bottom material is treated with an acidified sodium chloride solution and the resulting mixture centrifuged to obtain a clear supernatant solution for analysis.

2. Summary of method

Ammonia reacts with sodium salicylate, sodium nitroprusside, and sodium hypochlorite, in an alkaline medium, to form an intensely colored compound. The resulting color is directly proportional to the concentration of ammonia present.

3. Interferences

3.1 No substance found in natural waters appears to interfere with this method.

3.2 The samples are easily contaminated by ammonia in the laboratory atmosphere; therefore, sample handling and analysis should be performed where there is no possibility of ammonia contamination.

4. Apparatus

4.1 *Centrifuge.*

4.2 *Shaker*, wrist-action.

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

4.4 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 1.5 mg/L ammonia-nitrogen:

Absorption cell -----	50 mm
Wavelength --------	660 nm
Cam ---------------	50/h (2/1)
Heating-bath temperature -------------	37 °C

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 0.50 mg NH_3–N: Dissolve 1.9095 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1000 mL. Refrigerate.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.0025 mg NH_3–N: Dilute 5.0 mL ammonia standard solution I to 1000 mL with ammonia-free water. Prepare fresh weekly and refrigerate.

5.2.1 *Ammonia working standards*, bottom materials: Prepare an ammonia-free blank and at least 250 mL each of a series of ammonia working standards by appropriate quantitative dilution of ammonia standard solution II with acidified sodium chloride solution (5.8) as follows:

Ammonia standard solution II (mL)	Ammonia-nitrogen concentration (mg/L)
0.0	0.0
2.0	.02
10	.10
25	.25
50	.50
100	1.0
125	1.5

Prepare fresh weekly and refrigerate.

5.2.2 *Ammonia working standards*, water and water suspended-sediment: Prepare an ammonia-free blank and at least 250 mL each of a series of ammonia working standards by dilution of ammonia standard solution II with diluent solution (5.5) as follows:

Ammonia standard solution II (mL)	Ammonia-nitrogen concentration (mg/L)
0.0	0.0
2.0	.02
10	.10
25	.25
50	.50
100	1.0
125	1.5

Prepare fresh weekly and refrigerate.

5.3 *Buffer stock solution*, 71 g/L: Dissolve 134 g $Na_2HPO_4 \cdot 7H_2O$ in 800 mL ammonia-free water. Add 100 mL 5*M* NaOH, dilute to 1 L with ammonia-free water, and mix thoroughly.

5.4 *Buffer working solution*: Add, with stirring, 250 mL stock potassium sodium tartrate solution to 200 mL stock buffer solution. Slowly, with stirring, add 120 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water, add 1 mL Brij-35 solution, and mix thoroughly.

5.5 *Diluent solution*: Dissolve 52 mg mercuric chloride ($HgCl_2$) and 600 mg sodium chloride (NaCl) in approximately 800 mL ammonia-free water, mix thoroughly, and dilute to 1 L with ammonia-free water.

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

5.7 *Potassium sodium tartrate solution*, 149 g/L: Dissolve 200 g $NaKC_4H_4O_6 \cdot 4H_2O$ in approximately 600 mL ammonia-free water. Dilute to 1 L.

5.8 *Sodium chloride solution*, 100 g/L: Dissolve 100 g NaCl in 800 mL ammonia-free water, mix thoroughly, and dilute to 1 L. Adjust the pH to 2.5 using concentrated HCl (sp gr 1.19).

5.9 *Sodium hydroxide solution*, 5*M*: Add, with cooling and stirring, 200 g NaOH to approximately 800 mL ammonia-free water. Cool and dilute to 1 L.

5.10 *Sodium hypochlorite solution*: Dilute 50 mL sodium hypochlorite solution (a commercial bleach solution containing 5.25-percent available chlorine is satisfactory) to 500 mL with ammonia-free water. Add 1.0 mL Brij-35 solution. Prepare fresh daily.

5.11 *Sodium salicylate-sodium nitroprusside solution*: Dissolve 150 g sodium salicylate and 0.30 g sodium nitroprusside, ($Na_2Fe(CN)_5NO \cdot 2H_2O$), in approximately 600 mL ammonia-free water. Filter through Whatman 41 filter paper or equivalent, and dilute to 1 L. Add 1.0 mL Brij-35 solution and store in a light-resistant container.

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

5.13 *Sulfuric acid*, 2.5*M*: *Cautiously* add 138 mL concentrated H_2SO_4 (sp gr 1.84) to approximately 700 mL ammonia-free water. Cool and dilute to 1 L with ammonia-free water.

6. Procedure

6.1 Proceed to paragraph 6.2 for waters or water-suspended sediments. For bottom materials begin with paragraph 6.1.1.

6.1.1 Weigh, to the nearest milligram, approximately 5 g of sample prepared as directed in either method P-0520 or P-0810, and transfer to a 250-mL Erlenmeyer flask.

6.1.2 Add 50 mL of the acidic sodium chloride solution (5.8) and shake on the wrist-action shaker for 30 min.

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

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

6.1.5 Wash the sediment in the centrifuge tube with 20 mL acidic sodium chloride solution (5.8), recentrifuge, and transfer the clear wash solution to the volumetric flask. Adjust to volume with acidic sodium chloride solution (5.8). Proceed to paragraph 6.2.

6.2 Set up the manifold (fig. 32). If the laboratory air is contaminated with ammonia, the air must be passed through a scrubber containing 2.5*M* H_2SO_4 before the air enters the air-manifold tube.

6.3 Allow the colorimeter, recorder, and heating bath to warm for at least 30 min, or until the temperature of the heating bath reaches 37°C.

6.4 Adjust the baseline to read zero scale divisions on the recorder with all reagents (NOTE 1), but with either the acidic sodium chloride (paragraph 5.8, for bottom material analysis) or the diluent (paragraph 5.5, for water or water-suspended sediment analysis) in the sample line. The solution remaining in the wash reservoir from previous determinations may have become contaminated; therefore, this reservoir should be emptied and rinsed, and then refilled with fresh solution before proceeding.

NOTE 1. Place each reagent line except salicylate into its respective container; allow at least 5 min for the introduction of these reagents, and then place the salicylate line into its reagent container. If a precipitate forms after the addition of the salicylate, the pH of the solution stream is too low; check for contaminated reagents and (or) remake them, and start again using the procedure outlined above.

6.5 Place a complete set of standards and a blank (NOTE 2) in the first positions of the first sample tray, beginning with the most concentrated standard (NOTE 3). Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill the remainder of each tray with unknown samples.

NOTE 2. For analysis of bottom materials use blank and working standards prepared in paragraph 5.2.1. For analysis of waters and water-suspended-sediment mixtures, use blank and working standards prepared in paragraph 5.2.2.

NOTE 3. To avoid possible contamination of the sample cups, keep them sealed in their packages until just prior to use. Rinse each sample cup with sample prior to filling.

6.6 Begin analysis. When the peak from the most concentrated working standard appears on

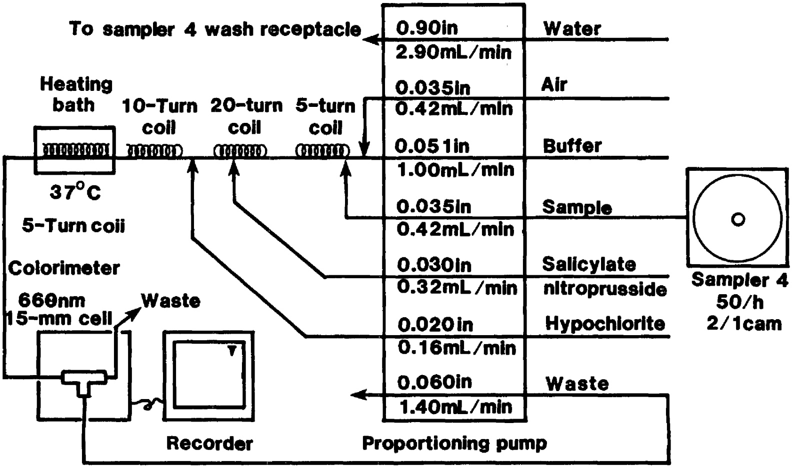


Figure 32.—Nitrogen, ammonia, salicylate-hypochlorite manifold

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 ammonia-nitrogen concentration.

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

7.3 Compute the concentration of ammonia-nitrogen in each bottom-material sample as follows:

$$NH_3N \text{ (mg/kg)} = \frac{C_N \times 100}{\text{wt of sample (g)}}$$

where

C_N = NH_3-N concentration in sample, milligrams per liter.

8. Report

8.1 Report nitrogen, ammonia, dissolved (00608), and total (00610), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

8.2 Report nitrogen, ammonia, total in bottom material (00611), concentrations as follows: less than 10 mg/kg, one decimal; 10 mg/kg and above, two significant figures.

9. Precision

9.1 Single-operator precision for dissolved ammonia-nitrogen, as determined on synthetic, deionized water-matrix samples, expressed in terms of the percent relative standard deviation, is as follows:

Number of determinations	Mean (mg/L)	Relative standard deviation (percent)
77	0.20	13
77	1.25	3
77	2.00	2

9.2 It is estimated that the percent relative standard deviation for total ammonia-nitrogen and for total ammonia-nitrogen in bottom material will be greater than that reported for dissolved ammonia-nitrogen.

Reference

Jackson, M. L., 1958, Soil chemical analysis: Englewood Cliffs, N.J., Prentice-Hall, p. 193.

Nitrogen, ammonia, colorimetric, salicylate-hypochlorite, automated-discrete

Parameters and Codes:

Nitrogen, ammonia, dissolved, I-2521-85 (mg/L as N): 00608
Nitrogen, ammonia, total, I-4521-85 (mg/L as N): 00610

1. Application

This method may be used to analyze water, wastewater, water-suspended sediment, and brines containing 0.05 to 5.0 mg/L ammonia-nitrogen. Samples containing concentrations greater than 5.0 mg/L need to be diluted.

2. Summary of method

Ammonia reacts with sodium salicylate, sodium nitroprusside, and sodium hypochlorite to form an intensely colored compound in an alkaline medium. The resulting color is directly proportional to the concentration of the ammonia present.

3. Interferences

3.1 A comparison study of the results obtained by this method and those from the colorimetric, salicylate-hypochlorite, automated-segmented flow method (methods I-2522 and 4522) indicate the absence of interferences.

3.2 Samples are easily contaminated by ammonia in the laboratory atmosphere; therefore, sample handling and analysis should be performed where there is no possibility of ammonia contamination.

4. Apparatus

4.1 *Discrete chemical and analyzer system*, American Monitor IQAS or equivalent.

4.2 With this equipment, the following operating conditions have been found satisfactory for the range 0.01 to 5.00 mg/L.

Wavelength ----	620 nm
Absorption cell -	1 cm square, temperature-controlled, flow-through, quartz cuvette
Reaction temperature --------	37 °C
Sample volume -	0.150 mL with 0.100 mL diluent (NOTE 1)
Reagent volumes	0.5 mL buffer solution, 0.50 mL sodium salicylate-sodium nitroprusside solution, 0.2 mL sodium hypochlorite solution, and 0.80 mL demineralized water (NOTE 1)

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each individual instrument according to manufacturer's specifications.

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over concentrated sulfuric acid (sp gr 1.84), in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.100 mg NH_3-N: Dilute 100.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water.

5.3 *Ammonia working standards*: Prepare a blank and 1,000 mL each of a series of working standards by dilution of ammonia standard solution II. Dissolve 52 mg mercuric chloride and 600 mg sodium chloride in each working standard. For example:

Standard solution II (mL)	Ammonia-nitrogen concentration (mg/L)
0.0	0.00
2.5	.25
5.0	.50
10.0	1.00
50.0	5.00

5.4 *Buffer solution*: Add, with stirring, 250 mL potassium sodium tartrate solution to 200 mL sodium phosphate solution. Slowly, with stirring, add 120 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water.

5.5 *Sodium hydroxide solution*, 5*M*: Add, with cooling and stirring, 200 g NaOH to approx 800 mL ammonia-free water. Cool and dilute to 1 L.

5.6 *Sodium hypochlorite solution*: Dilute 6.0 mL sodium hypochlorite solution (a commercial bleach solution containing 5.25-percent available chlorine is satisfactory) to 100 mL with ammonia-free water.

5.7 *Sodium phosphate, diabasic solution*, 71 g/L: Dissolve 71 g anhydrous Na_2HPO_4 in approx 800 mL ammonia-free water. Add 100 mL 5*M* NaOH, dilute to 1 L with ammonia-free water, and mix thoroughly.

5.8 *Sodium potassium tartrate solution*, 149 g/L: Dissolve 200 g $NaKC_4H_4O_6 \cdot 4H_2O$ in approx 600 mL ammonia-free water. Dilute to 1 L.

5.9 *Sodium salicylate-sodium nitroprusside solution*: Dissolve 150 g sodium salicylate and 0.30 g sodium nitroprusside in approx 600 mL ammonia-free water. Filter through Whatman 41 filter paper or equivalent, and dilute to 1 L. Store in a light-resistant container.

6. Procedure

6.1 Rinse all glassware with ammonia-free water before each use.

6.2 Set up analyzer and computer-card assignments according to manufacturer's instructions.

6.3 Place standards, beginning with the lowest concentrations, in ascending order (computer-calibration curve) in the first five positions on the sample turntable. Place samples and quality-control standards in the remainder of the sample turntable.

6.4 Begin analysis. The cathode-ray tube (CRT) will acknowledge the parameter and concentration range listing each sample-cup number and corresponding concentrations calculated from the working curve. During each run, the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from the printer.

7. Calculations

Determine the concentration in milligrams per liter of dissolved or total ammonia-nitrogen in each sample from either the CRT display or the printer output.

8. Report

Report nitrogen, ammonia, dissolved (00608), and total (00610), concentrations as follows: less than 1.00 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the standard deviation and percent relative standard deviation for replicate analysis of reference materials by a single operator is as follows:

Mean (mg/L)	Number of replicates	Standard deviation (mg/L)	Relative standard deviation (percent)
0.014	39	0.002	14.3
.030	39	.003	10.0
.186	30	.012	6.4
.651	22	.010	1.5
1.27	30	.020	1.6
2.48	22	.018	.7
3.38	22	.093	2.8
4.99	30	.027	.5

Nitrogen, ammonia, colorimetric, indophenol, automated-segmented flow

Parameters and Codes:

Nitrogen, ammonia, dissolved, I-2523-85 (mg/L as N): 00608
Nitrogen, ammonia, total, I-4523-85 (mg/L as N): 00610
Nitrogen, ammonia, total-in-bottom-material, I-6523-85 (mg/kg as N): 00611

1. Application

1.1 This method may be used to analyze surface, domestic, and industrial water, and brines and water-suspended sediment containing from 0.01 to 5.0 mg/L of ammonia-nitrogen. The range may be extended if the nitroprusside is omitted.

1.2 This method may be used to determine concentrations of ammonia-nitrogen in bottom material containing at least 0.2 mg/kg NH_3–N. Prepared sample solutions containing more than 5.0 mg/L NH_3–N must first be diluted. The range may be extended to 10.0 mg/L NH_3–N if the nitroprusside is omitted.

1.3 Sodium ion is a good replacement ion for ammonium in the slow-exchange positions of soil minerals (Jackson, 1958). Water-suspended sediment is treated and preserved in the field with mercury chloride and sodium chloride. The resulting mixture, prior to analysis in the laboratory, is either centrifuged or decanted to obtain clear supernatant solution. Similarly, bottom material is treated with an acidified sodium chloride solution, and the resulting mixture centrifuged to obtain a clear supernatant solution for analysis.

2. Summary of method

Ammonia reacts with hypochlorite and alkaline phenol to form an intensely colored indophenol compound, the absorbance of which is directly proportional to the ammonia concentration. Sodium nitroprusside may be added to improve the sensitivity of this determination (Bolleter and others, 1961; O'Brien and Fiore, 1962; Tetlow and Wilson, 1964; Van Slyke and Hiller, 1933).

3. Interferences

A complexing reagent consisting of sodium potassium tartrate and sodium citrate is added to remove interferences from several metal ions, including calcium, magnesium, and iron. The color development is pH dependent; therefore, samples whose pH values lie outside of the range from 4 to 10 must be analyzed with standards and a wash solution of approximately the same pH. Aromatic amines may interfere.

4. Apparatus

4.1 *Centrifuge.*

4.2 *Shaker*, wrist-action.

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

4.4 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 5.0 mg/L ammonia-nitrogen.

Absorption cell -----	15 mm
Wavelength --------	630 nm
Cam ---------------	60/h (6/1)
Heating-bath temperature -------------	50°C

5. Reagents

5.1 *Alkaline phenol solution*: Mix 89 mL liquid phenol (approx 90 percent) in 50 mL ammonia-free water. *Cautiously* add, while cooling, in small increments with agitation, 180 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water (NOTE 1). Keep refrigerated in an amber bottle.

5.2 *Ammonia standard solution I,* 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL. Refrigerate.

5.3 *Ammonia standard solution II,* 1.00 mL = 0.025 mg NH_3-N: Dilute 25.0 mL ammonia standard solution I to 1,000 mL with diluent solution (paragraph 5.6). Prepare fresh weekly and refrigerate.

5.4 *Ammonia working standards*: Prepare a blank and 250 mL each of a series of ammonia working standards by appropriate quantitative dilution of ammonia standard solution II with diluent solution (paragraph 5.6) as follows (NOTE 1):

Ammonia standard solution II (mL)	Ammonia-nitrogen concentration (mg/L)
0.0	0.0
10	1.0
20	2.0
30	3.0
40	4.0
50	5.0

Prepare fresh weekly and refrigerate.

NOTE 1. If ammonia-nitrogen in bottom material is being determined, the working standards are diluted with sodium chloride solution (paragraph 5.9).

5.5 *Brij-35 solution*: 30-percent aqueous solution (Baker Cat. No. C706 or equivalent).

5.6 *Diluent solution*: Dissolve 52 mg mercuric chloride and 600 mg sodium chloride in 800 mL ammonia-free water, mix thoroughly, and dilute to 1 L with ammonia-free water.

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

5.8 *Potassium sodium tartrate-sodium citrate solution*: Dissolve 33 g $KNaC_4H_4O_6 \cdot 4H_2O$ and 24 g sodium citrate in 950 mL ammonia-free water. Adjust the pH of this solution to 5.0 with concentrated H_2SO_4 (sp gr 1.84) and dilute to 1 L with ammonia-free water. Add 0.5 mL Brij-35 solution.

5.9 *Sodium chloride solution,* 100 g/L: Dissolve 100 g NaCl in 800 mL ammonia-free water, mix thoroughly, and dilute to 1 L. Adjust the pH to 2.5 using concentrated HCl (sp gr 1.19).

5.10 *Sodium hydroxide solution, 5M: Cautiously,* dissolve 200 g NaOH in ammonia-free water. Cool and dilute to 1 L. Store in a plastic container.

5.11 *Sodium hypochlorite stock solution*: Clorox or any other good commercial household bleach having approx 5-percent available chlorine.

5.12 *Sodium hypochlorite working solution*: Dilute 200 mL of stock sodium hypochlorite to 1 L with ammonia-free water.

5.13 *Sodium nitroprusside solution,* 0.44 g/L: Dissolve 0.5 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ in ammonia-free water and dilute to 1 L.

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

5.15 *Sulfuric acid, 2.5M: Cautiously,* add 138 mL concentrated (sp gr 1.84) to 500 mL ammonia-free water, cool, and dilute to 1 L.

6. Procedure

6.1 Proceed to paragraph 6.2 for waters or water-suspended sediments. For bottom materials begin with paragraph 6.1.1.

6.1.1 Weigh, to the nearest milligram, approx 5 g of sample, prepared as directed in either method P-0520 or P-0810, and transfer to a 250-mL Erlenmeyer flask.

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

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

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

6.1.5 Wash the sediment in the centrifuge tube with 20 mL NaCl solution, recentrifuge, and transfer the clear wash solution to the volumetric flask. Adjust to volume with NaCl solution. Proceed to paragraph 6.2.

6.2 Set up manifold (fig. 33). If the laboratory air is contaminated with ammonia, the air must be passed through a scrubber containing 2.5*M* H_2SO_4 before the air enters the air-manifold tube.

6.3 Allow the colorimeter, recorder, and heating bath to warm for at least 30 min, or until the temperature of the heating bath reaches 50 °C.

6.4 Adjust the baseline to read zero scale divisions on the recorder with all reagents,

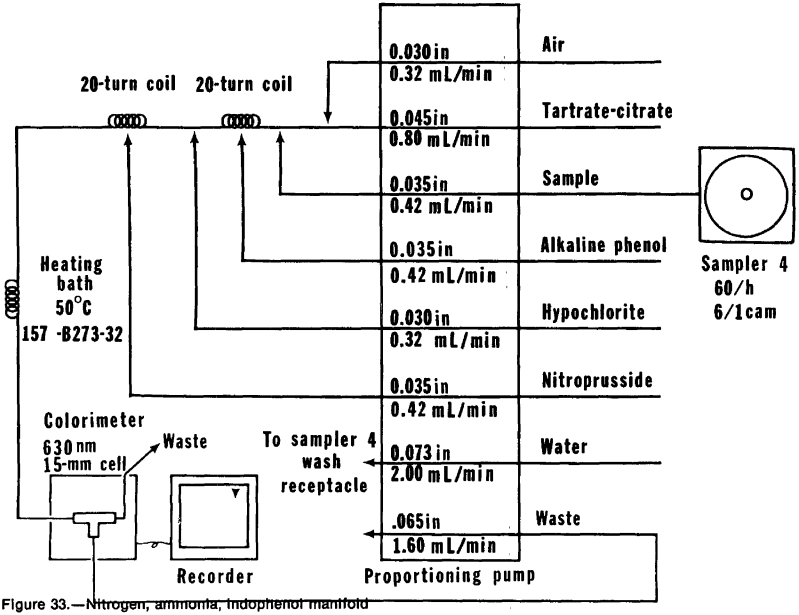


Figure 33.—Nitrogen, ammonia, indophenol manifold

but with ammonia-free water in the sample line.

6.5 Place a complete set of standards and a blank in the first positions of the first sample tray, beginning with the most concentrated standard (NOTE 2). 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 2. To avoid possible contamination of the sample cups, keep them sealed in their packages until just prior to use. Rinse each sample cup with sample prior to filling.

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

7. Calculations

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

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

7.3 Compute ammonia-nitrogen concentrations in each bottom material sample as follows:

$$NH_3\text{-N (mg/kg)} = \frac{C_N \times 100}{\text{wt of sample (g)}}$$

where

C_N = NH_3-N concentration in sample, milligrams per liter.

8. Report

8.1 Report nitrogen, ammonia, dissolved (00608), and total (00610), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

8.2 Report nitrogen, ammonia, total-in-bottom-material (00611), concentrations as follows: less than 10 mg/kg, one decimal; 10 mg/kg and above, two significant figures.

9. Precision

9.1 Precision for dissolved ammonia-nitrogen for nine samples within the range of 0.126 to 3.25 mg/L may be expressed as follows:

$$S_T = 0.098X + 0.079$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of ammonia-nitrogen, milligrams per liter.

The correlation coefficient is 0.9085.

9.2 Precision for dissolved ammonia-nitrogen for four of the nine samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
8	0.126	17
21	.665	13
20	1.20	17
23	3.25	12

9.3 It is estimated that the percent relative standard deviation for total ammonia-nitrogen and for total ammonia-nitrogen in bottom material will be greater than that reported for dissolved ammonia-nitrogen.

References

Bolleter, W. T., Bushman, C. J., and Tidwell, P. W., 1961, Spectrophotometric determination of ammonia as indophenol: Analytical Chemistry, v. 33, p. 592–3.

Jackson, M. L., 1958, Soil chemical analysis: Englewood Cliffs, N.J., Prentice-Hall, p. 193.

O'Brien, J. E., and Fiore, J., 1962, Ammonia determination by automatic analysis: Wastes Engineering, v. 33, p. 352.

Tetlow, J. A., and Wilson, A. L., 1964, An absorptiometric method for determining ammonia in boiler-feed water: Analyst, v. 89, p. 453–65.

Van Slyke, D. D., and Hiller, A. J., 1933, Determination of ammonia in blood: Biological Chemistry Journal, v. 102, p. 499.

Nitrogen, ammonia, electrometric, ion-selective electrode

Parameters and Codes:

Nitrogen, ammonia, dissolved, I-1524-85 (mg/L as N): 00608
Nitrogen, ammonia, total, I-3524-85 (mg/L as N): 00610

1. Application

This method may be used to analyze water, brines, and water-suspended sediment containing at least 0.10 mg/L ammonia-nitrogen. Samples containing less than 0.10 mg/L need to be analyzed by the single standard addition technique (paragraph 6.6).

2. Summary of method

Ammonia is determined potentiometrically in an alkaline medium by using an ammonia gas-detecting electrode. The internal solution of the electrode is separated from the sample solution by a gas-permeable membrane. Dissolved ammonia in the sample diffuses through the membrane until the partial pressure of ammonia is the same on both sides. The change in partial pressure is proportional to the ammonia concentration and is measured as a potential with an internal chloride-sensing reference electrode and a glass electrode.

3. Interferences

3.1 Color and turbidity do not affect the measurements. Significant quantities of inorganic cations and anions cannot penetrate the nonwettable, gas-permeable membrane and do not interfere directly. However, as the salinity of the sample increases, there is an increase in the observed ammonia concentration. Samples containing dissolved substances at a total concentration greater than 1*M* should be analyzed by standard addition or, if the ammonia concentration is sufficiently high, be analyzed after appropriate dilution.

3.2 Certain gases do present a potential interference; however, common gases such as CO_2, HCN, SO_2, and Cl_2 do not interfere (Orion Research Inc., 1971).

4. Apparatus

4.1 *Ammonia electrode*, Orion Model No. 95-10 or equivalent.

4.2 *pH/millivolt meter*, with expanded scale.

4.3 *Stirrer*, magnetic, battery-operated, with Teflon-coated stirring bar.

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 1.00 mg NH_3–N: Dissolve 3.819 g ammonium chloride (NH_4Cl), dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.010 mg N: Dilute 10.0 mL of ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Ammonia working standards*: Prepare a series of three standard solutions containing 0.1, 1.0, and 5.0 mg/L NH_3–N by appropriate dilution of either ammonia standard solution I or II with ammonia-free water.

5.4 *Sodium hydroxide solution*, 10*M*. Dissolve *with caution* 400 g NaOH in ammonia-free water and dilute to 1 L.

6. Procedure

6.1 Rinse all glassware with ammonia-free water before beginning this determination.

6.2 Adjust the pH/millivolt meter according to the manufacturer's instructions.

6.3 Pipet 50.0 mL of each ammonia chloride working standard (0.1, 1.0, and 5.0 mg/L NH_3–N, respectively) into 100-mL beakers.

6.4 Pipet 50.0 mL of well-mixed sample into a 100-mL beaker.

6.5 Place each standard and sample consecutively on a magnetic stirrer (NOTE 1), immerse the electrode, and then add 0.5 mL 10*M*

NaOH solution. Start the stirrer and record the potential (mV) reading after it has stabilized (2 to 5 min). Rinse the electrode thoroughly with distilled water between samples and blot with a damp tissue.

NOTE 1. Insulate the top of the stirrer with an asbestos sheet and an air space to avoid raising the temperature of the solution.

6.6 If the millivolt reading from the analytical curve (paragraph 7) indicates a concentration of less than 0.10 mg/L, determine NH_3-N in the sample by single standard addition (paragraph 6.7).

6.7 Add 0.5 mL ammonia chloride standard solution II to the sample (paragraph 6.5), equivalent to an increase in concentration of 0.10 mg/L NH_3-N, and record the new potential. Approx 5 min is required for the potential to stabilize.

7. Calculations

Construct an analytical curve of potential (mV) versus concentration of standards on semilog paper, with concentrations plotted on the logarithmic axis. Determine the milligrams per liter ammonia-nitrogen in each sample from the analytical curve. When standard addition is used to determine NH_3-N (paragraph 6.7), subtract 0.10 mg/L NH_3-N from the concentration obtained from the analytical curve.

8. Report

Report nitrogen, ammonia, dissolved (00608), and total (00610), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved ammonia-nitrogen for seven samples within the range of 0.339 to 3.48 mg/L may be expressed as follows:

$$S_T = 0.140X + 0.083$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of ammonia-nitrogen, milligrams per liter.

The correlation coefficient is 0.8331.

9.2 Precision for dissolved ammonia-nitrogen for four of the seven samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
7	0.339	45
4	.620	13
7	1.01	29
6	3.48	17

9.3 It is estimated that the percent relative standard deviation for total ammonia-nitrogen will be greater than that reported for dissolved ammonia-nitrogen.

Reference

Orion Research, Inc., 1971, Instruction manual, ammonia ammonia electrode, Model 95-10: Cambridge, Mass.

Nitrogen, ammonia plus organic, colorimetric, block digestor–salicylate-hypochlorite, automated-segmented flow

Parameters and Codes:

Nitrogen, ammonia plus organic, dissolved, I-2552-85 (mg/L as N): 00623
Nitrogen, ammonia plus organic, total, I-4552-85 (mg/L as N): 00625
Nitrogen, ammonia plus organic, suspended-total, I-7552-85 (mg/L as N): 00624
Nitrogen, ammonia plus organic, total-in-bottom-material, dry wt, I-6552-85 (mg/kg as N): 00626

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing 0.2 to 10 mg/L total ammonia plus organic nitrogen. Samples containing concentrations greater than 10 mg/L need to be diluted.

1.2 Suspended total ammonia plus organic nitrogen is calculated by subtracting dissolved ammonia plus organic nitrogen from total ammonia plus organic nitrogen.

1.3 This method may be used to analyze samples of bottom material containing at least 10 mg/kg total ammonia plus organic nitrogen. Concentration ranges for determining 10 to 120 mg/kg and 80 to 400 mg/kg of nitrogen are used.

2. Summary of method

Organic nitrogen compounds are reduced to the ammonium ion by digestion with sulfuric acid in the presence of mercuric sulfate, which acts as a catalyst, and potassium sulfate. The ammonium ion produced by this digestion, as well as the ammonium ion originally present, is determined by reaction with sodium salicylate, sodium nitroprusside, and sodium hypochlorite in an alkaline medium. The resulting color is directly proportional to the concentration of ammonia present.

3. Interferences

3.1 A comparison study of results obtained by this method with those from the colorimetric, digestion-distillation-nesslerization method, and the colorimetric, digestion-distillation-indophenol, automated method (methods I-1550 and I-2551, respectively) indicated the absence of interferences.

3.2 The samples are easily contaminated by ammonia in the laboratory atmosphere. The digestion process should be performed in a fume hood that is operating properly and that is located in an ammonia-free area of the laboratory. Other laboratory procedures may be performed outside or near this hood only if there is no possibility of ammonia contamination.

4. Apparatus

4.1 *Technicon block digestor*, Model BD-40 with 75-mL digestion tubes or equivalent.

4.2 With this equipment, the following operating conditions have been found satisfactory:

Modeswitch -------- Automatic
Low-temperature regulator ------------ 160 °C
High-temperature regulator ------------ 370 °C
Low-temperature timer 1.5 h
Total cycle time ----- 3.5 h

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

4.4 With this equipment, the following operating conditions have been found satisfactory (NOTE 1):

Absorption cell ----- 15 mm
Wavelength -------- 660 nm
Cam ---------------- 60/h (6/1)
Water-bath temperature ------------- 37 °C

NOTE 1. Two concentration ranges—0.2 to 3 mg/L and 2 to 10 mg/L N—are obtained by using different STD CAL settings.

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.010 mg NH_3-N: Dilute 10.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Buffer stock solution*, 71 g/L: Dissolve 71 g anhydrous Na_2HPO_4 in approx 800 mL ammonia-free water. Add 100 mL 5*M* NaOH, dilute to 1 L with ammonia-free water, and mix thoroughly.

5.4 *Buffer working solution*: Add, with stirring, 250 mL stock potassium sodium tartrate solution to 200 mL stock buffer solution. Slowly, with stirring, add 120 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water, add 1 mL Brij-35 solution, and mix thoroughly.

5.5 *Mercuric sulfate solution*, 11 g/100 mL: Dissolve 8 g red HgO in 50 mL 3.6*M* H_2SO_4 and dilute to 100 mL with ammonia-free water.

5.6 *Potassium sodium tartrate solution*, 149 g/L: Dissolve 200 g $NaKC_4H_4O_6 \cdot 4H_2O$ in approx 600 mL ammonia-free water. Dilute to 1 L.

5.7 *Sodium hydroxide solution*, 5*M*: Add, with cooling and stirring, 200 g NaOH to approx 800 mL ammonia-free water. Cool and dilute to 1 L.

5.8 *Sodium hypochlorite solution*: Dilute 6.0 mL sodium hypochlorite solution (a commercial bleach solution containing 5.25-percent available chlorine is satisfactory) to 100 mL with ammonia-free water. Add 0.1 mL Brij-35 solution. Prepare fresh daily.

5.9 *Sodium salicylate-sodium nitroprusside solution*: Dissolve 150 g sodium salicylate and 0.30 g sodium nitroprusside, ($Na_2Fe(CN)_5NO \cdot 2H_2O$), in approx 600 mL ammonia-free water. Filter through Whatman 41 filter paper or equivalent, and dilute to 1 L. Add 1.0 mL Brij-35 solution and store in a light-resistant container.

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

5.11 *Sulfuric acid*, 0.20*M*: *Cautiously*, add 11 mL concentrated H_2SO_4 (sp gr 1.84) to ammonia-free water and dilute to 1 L.

5.12 *Sulfuric acid*, 3.6*M*: *Cautiously*, add 200 mL concentrated H_2SO_4 (sp gr 1.84) to approx 700 mL ammonia-free water. Cool and dilute to 1 L with ammonia-free water.

5.13 *Sulfuric acid-mercuric sulfate-potassium sulfate solution*: Dissolve 267 g K_2SO_4 in approx 1,300 mL ammonia-free water. *Cautiously*, add 400 mL concentrated H_2SO_4 (sp gr 1.84) and 50 mL mercuric sulfate solution. Cool and dilute to 2 L with ammonia-free water.

6. Procedure

6.1 Rinse all glassware with ammonia-free water before each use.

6.2 Follow instructions in paragraph 6.2.1 for waters or water-suspended sediments and in paragraph 6.2.2 for bottom materials.

6.2.1 Pipet a volume (20.0 mL max) of well-mixed sample (NOTE 2) containing less than 0.2 mg ammonia plus organic nitrogen (as N) into a digestion tube and adjust the volume to 20 mL with ammonia-free water.

NOTE 2. For water-suspended sediment, rinse the pipet with a small amount of ammonia-free water to remove adhering particles, and combine with sample.

6.2.2 Weigh, to the nearest milligram, an amount of wet sample (500 mg max) containing less than 0.2 mg total ammonia plus organic nitrogen. Transfer the weighed sample to a digestion tube, rinsing the weighing container with ammonia-free water as needed. Add additional ammonia-free water as necessary to bring the liquid volume in the digestion tube to approximately 20 mL.

6.3 Prepare an ammonia-free water blank and at least five standards containing either from 0.004 to 0.06 mg or from 0.04 to 0.20 mg ammonia-nitrogen, depending upon use of 0.2- to 3-mg/L or 2- to 10-mg/L concentration range of interest (NOTE 3). The standards and blank must also undergo the digestion process.

NOTE 3. The blank and standards must contain mercuric chloride fortified with sodium chloride. For example, if 250 mL is prepared, dissolve 13 mg $HgCl_2$ and 150 mg NaCl in each standard.

6.4 Add 4.0 mL sulfuric acid-mercuric sulfate-potassium sulfate solution and two boiling chips. CAUTION: **Hazardous.** Mix well before placing in digestor (NOTES 4 and 5).

NOTE 4. Protective eyeglasses and clothing are mandatory for this procedure because sulfuric acid and high-temperature solutions are very hazardous.

NOTE 5. Teflon boiling chips, available from Cole-Parmer Instrument Co., are preferable. Before use they should be soaked in dilute HCl (approx 6*M*), rinsed several times in ammonia-free water, and dried at 180 °C. In order to avoid contamination by laboratory fumes, store them in a tightly stoppered container in an ammonia-free area of the laboratory.

6.5 Digest under a hood for 3½ h using the listed conditions. It is imperative that the heating block cool to 150 °C before subsequent batches of samples are placed in the digestor or extreme spattering will occur.

6.6 *Cautiously* remove tubes from the digestor and allow to cool for approx 15 min in a hood. Quickly add approx 50 mL ammonia-free water to each tube with vigorous agitation and *extreme caution* (NOTE 6). Allow to cool briefly before making the final dilution to the calibration mark. Stopper the tubes and invert several times until well mixed (NOTE 7). If a portion of this solution must be diluted to remain within the designated concentration range, this dilution must be made with 0.20*M* H_2SO_4.

NOTE 6. The precipitation of salts is minimized by this procedure. A vortex mixer is useful for agitating the water-acid mixture.

NOTE 7. Allow any precipitate that has formed or any boiling chip flakes to settle before filling the sample cups as described in paragraph 6.10.

6.7 Set up manifold (fig. 34). If the laboratory air is contaminated with ammonia, the air must be passed through a scrubber containing 2.5*M* H_2SO_4 before the air enters the air-manifold tube.

6.8 Allow the colorimeter, recorder, and heating bath to warm for at least 30 min.

6.9 Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with 0.20*M* H_2SO_4 in the sample line. The solution remaining in the wash reservoir from previous analyses may have become contaminated; therefore, this reservoir should be emptied and rinsed, and filled with fresh wash solution before proceeding. Place each reagent line except salicylate into its respective container; allow at least 5 min for the introduction of these reagents, and then place the salicylate

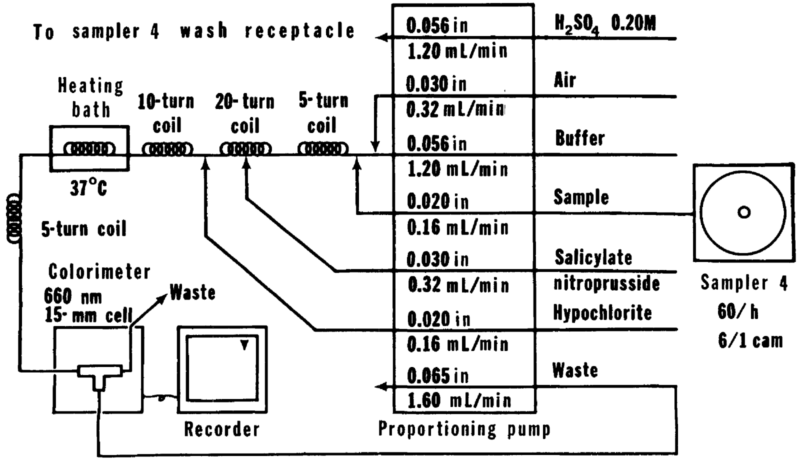


Figure 34.—Nitrogen, ammonia plus organic, salicylate-hypochlorite manifold

line into its reagent container. If a precipitate forms after the addition of the salicylate, the pH of the solution stream is too low.

6.10 Place a complete set of standards and a blank in the first positions of the first sample tray, beginning with the most concentrated standard (NOTE 8). 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 8. To avoid possible contamination of the sample cups, keep them sealed in their packages until just prior to use. Rinse each sample cup with sample prior to filling.

6.11 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 Determine the milligrams of ammonia-nitrogen in each sample from a plot of peak heights of standards. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak. Likewise, the amount of NH_3-N present from the addition of H_2SO_4, as indicated by the concentration of NH_3-N in the blank, must be subtracted from the total milligrams of NH_3-N in each sample.

7.2 Determine the concentration of dissolved or total ammonia plus organic nitrogen as follows:

$$\text{Nitrogen, ammonia plus organic (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times \text{mg } NH_3\text{-N in sample}$$

7.3 To determine the concentration of suspended total ammonia plus organic nitrogen, subtract dissolved ammonia-plus-organic nitrogen concentration from total ammonia-plus-organic nitrogen concentration.

7.4 Determine the concentration of total ammonia plus organic nitrogen in bottom material as follows:

$$\text{Nitrogen, ammonia plus organic (mg/kg)} = \frac{\text{mg } NH_3\text{-N in sample}}{\text{ample dry wt (g)}} \times 1000$$

8. Report

8.1 Report nitrogen, ammonia plus organic, dissolved (00623), total (00625), suspended-total (00624), concentrations as follows: 0.2 to 1.0 mg/L, one decimal; 1.0 mg/L and above, two significant figures.

8.2 Report nitrogen, ammonia plus organic, total-in-bottom-material (00626), in milligrams per kilogram of dry-weight sample, concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved ammonia plus organic nitrogen within the range of 0.68 to 1.41 mg/L for seven samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 0.577 mg/L ranged from 0.486 to 0.750 mg/L.

9.2 Precision for dissolved ammonia plus organic nitrogen for three of the seven samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
8	0.675	63
8	1.14	54
8	1.41	54

9.3 It is estimated that the percent relative standard deviation for total and suspended total ammonia plus organic nitrogen and for total ammonia plus organic nitrogen in bottom material will be greater than that reported for dissolved ammonia plus organic nitrogen.

Nitrogen, ammonia plus organic, colorimetric, block digestor–salicylate-hypochlorite, automated-discrete

Parameters and Codes:

Nitrogen, ammonia plus organic, dissolved, I-2558-85 (mg/L as N): 00623
Nitrogen, ammonia plus organic, total, I-4558-85 (mg/L as N): 00625
Nitrogen, ammonia plus organic, suspended total, I-7558-85 (mg/L as N): 00624

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 0.2 to 5.0 mg/L ammonia plus organic nitrogen. Samples containing concentrations greater than 5.0 mg/L need to be diluted.

1.2 Suspended total ammonia plus organic nitrogen is calculated by subtracting dissolved ammonia plus organic nitrogen from total ammonia plus organic nitrogen.

2. Summary of method

Organic nitrogen compounds are reduced to the ammonium ion by digestion with sulfuric acid in the presence of mercuric sulfate, which acts as a catalyst, and potassium sulfate. The ammonium ion produced by this digestion, as well as the ammonium ion originally present, is determined by reaction with sodium salicylate, sodium nitroprusside, and sodium hypochlorite in an alkaline medium. The resulting color is directly proportional to the concentration of ammonia present.

3. Interferences

3.1 A comparision study of results obtained by this method with those from the colorimetric, block-digestor salicylate-hypochlorite, automated-segmented-flow method (method I-2552) indicates the absence of interferences.

3.2 The samples are easily contaminated by ammonia in the laboratory atmosphere. The digestion process should be performed in a fume hood that is operating properly and that is located in an ammonia-free area of the laboratory. Other laboratory procedures may be performed outside or near this hood only if there is no possibility of ammonia contamination.

4. Apparatus

4.1 *Block digestor*, Technicon Model BD-40 with 75-mL digestion tubes or equivalent.

4.2 With this equipment, the following operating conditions have been found satisfactory:

Modeswitch ---	Automatic
Low-temperature regulator ---	160°C
High-temperature regulator	370°C
Low-temperature timer ------	1.5 h
Total cycle time	3.5 h

4.3 *Discrete analyzer system*, American Monitor IQAS or equivalent.

4.4 With this equipment, the following operating conditions have been found satisfactory:

Wavelength ---	620 nm
Absorption cell	1 cm square, temperature-controlled, flow-through quartz cuvette
Reaction temperature ---------	40°C
Sample volume	0.375 mL with 0.075 mL diluent
Reagent volumes	1.0 mL buffer solution, 0.45 mL sodium salicylate-sodium nitroprusside solution, and 0.25 mL sodium hypochlorite solution

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each instrument according to manufacturer's specifications.

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.10 mg NH_3-N: Dilute 100.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water.

5.3 *Ammonia working standards*: Prepare a blank and 1,000 mL each of a series of working standards by dilution of ammonia standard solution II. Dissolve 52 mg mercuric chloride and 600 mg sodium chloride in each working standard.

'Standard solution II (mL)	Nitrogen concentration (mg/L)
2.0	0.2
5.0	0.5
10	1
30	3
50	5

5.4 *Buffer solution*: Add, with stirring, 250 mL potassium sodium tartrate solution to 200 mL sodium phosphate solution. Slowly, with stirring, add 120 mL 5 *M* NaOH. Dilute to 1 L with ammonia-free water.

5.5 *Mercuric sulfate solution*, 11 g/100 mL: Dissolve 40 g red HgO in 250 mL 3.6 *M* H_2SO_4 and dilute to 500 mL with ammonia-free water.

5.6 *Sodium hydroxide solution*, 5 *M*: Add, with cooling and stirring, 200 g NaOH to approx 800 mL ammonia-free water. Cool and dilute to 1 L.

5.7 *Sodium hypochlorite solution*: Dilute 6.0 mL sodium hypochlorite solution (a commercial bleach solution containing 5.25-percent available chlorine is satisfactory) to 100 mL with ammonia-free water.

5.8 *Sodium phosphate, dibasic, solution*, 71 g/L: Dissolve 134 g $Na_2HPO_4 \cdot 7H_2O$ in approx 800 mL ammonia-free water. Add 100 mL 5 *M* NaOH, dilute to 1 L with ammonia-free water, and mix thoroughly.

5.9 *Sodium potassium tartrate solution*, 149 g/L: Dissolve 200 g $NaKC_4H_4O_6 \cdot 4H_2O$ in approx 600 mL ammonia-free water. Dilute to 1 L.

5.10 *Sodium salicylate-sodium nitroprusside solution*: Dissolve 150 g sodium salicylate and 0.50 g sodium nitroprusside in approx 600 mL ammonia-free water. Dilute to 1 L with ammonia-free water, and store in a light-resistant container.

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

5.12 *Sulfuric acid*, 0.20 *M*: *Cautiously*, add 11 mL concentrated H_2SO_4 (sp gr 1.84) to ammonia-free water and dilute to 1 L with ammonia-free water.

5.13 *Sulfuric acid*, 3.6 *M*: *Cautiously*, add 200 mL concentrated H_2SO_4 (sp gr 1.84) to approx 700 mL ammonia-free water. Cool and dilute to 1 L with ammonia-free water.

5.14 *Sulfuric acid-mercuric sulfate-potassium sulfate solution*: Dissolve 267 g K_2SO_4 in approx 1,300 mL ammonia-free water. *Cautiously*, add 400 mL concentrated H_2SO_4 (sp gr 1.84) and 50 mL mercuric sulfate solution. Cool and dilute to 2 L with ammonia-free water.

6. Procedure

Rinse all glassware with ammonia-free water before each use.

6.1 Pipet a volume (20.0 mL max) of well-mixed sample containing less than 0.1 mg ammonia plus organic nitrogen (as N) into a digestion tube and adjust the volume to 20 mL with ammonia-free water. For water-suspended sediment mixtures, rinse the pipet with a small amount of ammonia-free water to remove adhering particles, and combine with sample.

6.2 Prepare a blank and four standards in a similar manner. The blank and standards must also undergo the digestion process.

6.3 Add 4.0 mL sulfuric acid-mercuric sulfate-potassium sulfate solution and two boiling chips. **CAUTION: Hazardous.** Mix well before placing in digestor (NOTES 2 and 3).

NOTE 2. Protective eyeglasses and clothing are mandatory for this procedure because sulfuric acid and high-temperature solutions are very hazardous. The addition of the above mixture must be carried out in a hood.

NOTE 3. Teflon boiling chips, available from Cole-Parmer Instrument Co., are preferable. Before use they should be soaked in dilute HCl (approx 6*M*), rinsed several times in ammonia-free water, and dried at 180 °C. In order to avoid contamination by laboratory fumes, store them in a tightly stoppered container in an ammonia-free area of the laboratory.

6.4 Digest under a hood for 3½ h using the listed conditions. It is imperative that the heating block cool to 150 °C before subsequent batches of samples are placed in the digestor or extreme spattering will occur.

6.5 *Cautiously*, remove tubes from the digestor and allow to cool for approx 15 min in a hood. Quickly add approx 50 mL ammonia-free water to each tube with vigorous agitation and *extreme caution* (NOTE 4). Allow to cool briefly before making the final dilution to the calibration mark. Stopper the tubes and invert several times until well mixed (NOTE 5). If a portion of this solution must be diluted to remain within the designated concentration range, this dilution must be made with 0.20*M* H_2SO_4.

NOTE 4. The precipitation of salts is minimized by this procedure. A vortex mixer is useful for agitating the water-acid mixture.

NOTE 5. Allow any precipitate that has formed or any boiling chip flakes to settle before filling the sample cups as described in paragraph 6.8.

6.6 Set up analyzer and computer-card assignments according to the manufacturer's instructions.

6.7 Place standards, beginning with the lowest concentration, in ascending order (computer-calibration curve) in the first five positions on the sample turntable. These standards should be 0.2, 0.5, 1.0, 3.0, and 5.0 mg/L NH_3-N. Place samples and quality-control standards in the remainder of the sample turntable.

6.8 Begin analysis. The cathode-ray tube (CRT) will acknowledge the parameters and concentration range, listing each sample-cup number and corresponding concentrations calculated from the working curve. During each run, the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from printer.

7. Calculations

Determine the concentration in milligrams per liter of dissolved or total ammonia plus organic nitrogen in each sample from either the CRT display or the printer output.

7.2 To determine concentration of suspended total ammonia plus organic nitrogen, subtract dissolved-ammonia-plus-organic nitrogen concentration from total ammonia-plus-organic nitrogen concentration.

8. Report

Report nitrogen, ammonia plus organic, dissolved (00623), total (00625), and suspended-total (00624), concentrations as follows: 0.2 to 1.0 mg/L, one decimal; 1.0 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the standard deviation and percent relative standard deviation for replicate analysis of reference materials by a single operator is as follows:

Mean (mg/L)	Number of replicates	Standard deviation (mg/L)	Relative standard deviation (percent)
0.11	10	0.04	36.4
.42	34	.09	21.4
4.2	35	.08	1.9
5.0	26	.08	1.6

Nitrogen, ammonia plus organic, colorimetric, digestion-distillation-nesslerization

Parameter and Code:

Nitrogen, ammonia plus organic, dissolved, I-1550-85 (mg/L as N): 00623

1. Application

This method, is recommended for analysis of water containing from 0.01 to 2.0 mg/L of dissolved ammonia plus organic nitrogen. Samples with greater concentrations need either to be diluted or to be analyzed by a titrimetric procedure.

2. Summary of method

2.1 Organic nitrogen-containing compounds are degraded to ammonium salts by digestion with sulfuric acid in the presence of copper sulfate, which acts as a catalyst. The solution is then made alkaline with sodium hydroxide, and the resulting free ammonia is distilled and nesslerized. The color developed is proportional to the ammonia-plus-organic nitrogen content of the sample.

2.2 Additional information on the principle of the determination is given in Kolthoff and others (1969).

3. Interferences

3.1 Nitrate and nitrite do not interfere.

3.2 Calcium, magnesium, iron, and sulfide interfere with the nesslerization, but the distillation eliminates interference of the metals, and sulfides are completely destroyed during the digestion.

4. Apparatus

4.1 *Cylinder*, graduated, with ground-glass stopper, 50-mL capacity (Corning No. 3002 or equivalent).

4.2 *Kjeldahl distillation apparatus*, 800-mL flasks.

4.3 *Spectrometer*, for use at 425 nm.

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 1.00 mg N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.010 mg N: Dilute 10.00 mL ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Borate buffer solution*: Dissolve 9.54 g $Na_2B_4O_7 \cdot 10H_2O$ in ammonia-free water. Adjust the pH to 9.5 with $1M$ NaOH (approx 15 mL), and dilute to 1 L with ammonia-free water.

5.4 *Boric acid solution*, 20 g/L: Dissolve 20 g H_3BO_3 in ammonia-free water and dilute to 1 L.

5.5 *Copper sulfate solution*, 6.5 g/100 mL: Dissolve 6.5 g $CuSO_4$ (anhydrous) in ammonia-free water and dilute to 100 mL.

5.6 *Methyl red indicator solution*, 0.1 g/100 mL: Dissolve 0.1 g methyl red indicator in 100 mL 95-percent ethanol.

5.7 *Nessler reagent*— **CAUTION: HgI_2 is a deadly poison, and the reagent must be so marked:** Dissolve 100 g HgI_2 and 70 g KI in a small volume of ammonia-free water. Add this mixture slowly, with stirring, to a cooled solution of 160 g NaOH in 500 mL ammonia-free water and dilute to 1 L. Allow the reagent to stand at least overnight and filter through a fritted-glass crucible.

5.8 *Sodium hydroxide solution*, $10M$: Dissolve 400 g NaOH in ammonia-free water and dilute to 1 L.

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

6. Procedure

6.1 Rinse all glassware with ammonia-free water before use.

6.2 Free the Kjeldahl distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent—**CAUTION: deadly poison.**

6.3 Pipet a volume of sample containing less than 1.0 mg ammonia plus organic nitrogen (250 mL max) into a 800-mL Kjeldahl digestion flask.

6.4 Add 5.0 mL concentrated H_2SO_4 and 0.5 mL $CuSO_4$ solution, and mix.

6.5 Digest under a hood until copious fumes are given off. Continue heating until the fumes have subsided and the liquid becomes colorless or pale yellow. Continue digestion an additional 30 min.

6.6 Cool and dilute to approx 150 mL with ammonia-free water.

6.7 Add 25 mL 10*M* NaOH *cautiously* down the side of the flask.

6.8 Immediately connect the flask to the distillation apparatus, and *cautiously* mix the contents by gentle swirling.

6.9 Distill at a rate of no more than 10 and no less than 6 mL/min: collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.10 Collect approx 150 mL distillate, dilute to the mark with ammonia-free water, and mix.

6.11 Pipet an aliquot of distillate containing less than 0.1 mg ammonia-nitrogen (50.0 mL max) into a glass-stoppered, graduated mixing cylinder, and adjust the volume to 50.0 mL with ammonia-free water.

6.12 Prepare a blank of ammonia-free water and a series of standards in glass-stoppered, graduated mixing cylinders. Add 5 mL boric acid solution to each, and adjust the volume of each to 50.0 mL.

6.13 Add 1.0 mL nessler reagent—**CAUTION: deadly poison**—to each blank, standard, and sample. Stopper and invert several times to mix thoroughly.

6.14 Allow the solutions to stand at least 10 min, but not more than 30 min.

6.15 Determine the absorbance of each test sample and standard against that of the blank.

7. Calculations

7.1 Determine a reagent blank for each new batch of H_2SO_4 by taking 250 mL ammonia-free water through the entire procedure:

$$\text{mg reagent blank} = \left(\begin{array}{c}\text{mg ammonia}\\ \text{plus organic N}\\ \text{per 5.0 mL } H_2SO_4\end{array}\right) \times \frac{\text{mL aliquot}}{\text{mL distillate}}$$

7.2 Determine the milligrams of ammonia plus organic nitrogen in each sample aliquot from a plot of absorbances of standards.

7.3 Determine the ammonia-plus-organic nitrogen concentration in milligrams per liter as follows:

$$\text{Ammonia plus organic nitrogen, mg/L} = \frac{1{,}000}{\text{mL sample}} \times \frac{250}{\text{mL aliquot}} \times [(\text{mg ammonia plus organic N in aliquot}) - (\text{mg reagent blank})].$$

8. Report

Report nitrogen, ammonia plus organic, dissolved (00623), concentrations as follows: less than 1.0 mg/L, two decimals; 1 mg/L and above, two signifcant figures.

9. Precision

9.1 The standard deviation for dissolved ammonia plus organic nitrogen within the range of 0.43 to 1.81 mg/L for nine samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 0.682 mg/L ranged from 0.603 to 0.786 mg/L.

9.2 Precision for dissolved ammonia plus organic nitrogen for four of the nine samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
11	0.434	58
13	.957	79
15	1.003	53
8	1.807	72

Reference

Kolthoff, I. M., Sandell, E. B., Meehen, E. J., and Bruckenstein, S., 1969, Quantitative chemical analysis (4th ed.): New York, Macmillan, 1199 p.

Nitrogen, ammonia plus organic, titrimetric, digestion-distillation

Parameter and Code:

Nitrogen, ammonia plus organic, total-in-bottom-material, dry wt, I-5553-85 (mg/kg as N): 00626

1. Application

This method may be used for analysis of bottom material containing at least 10 mg/kg of total ammonia plus organic nitrogen. Only that portion of bottom material that passes a 2-mm sieve is taken for analysis (method P-0810, subsampling, bottom material, coring).

2. Summary of method

The sample is subjected to a digestion whereby all organic nitrogen-containing compounds are converted to ammonium salts. The resulting mixture is then made strongly alkaline, and the ammonia so formed is distilled from the mixture into a solution of boric acid and subsequently determined by titration with standard sulfuric acid solution.

3. Interferences

There are no known interferences with this method.

4. Apparatus

Kjeldahl distillation apparatus, 500-mL flasks.

5. Reagents

5.1 *Ammonium chloride*, crystals.

5.2 *Boric acid solution*, 20 g/L: Dissolve 20 g H_3BO_3 crystals in 800 mL ammonia-free water and dilute to 1 L.

5.3 *Digestion catalyst*: Tablets containing 3.5 g K_2SO_4 and 0.175 g HgO (Scientific Chemical Technical Sales Inc., SCT Kel-catalyst No. KC-M3, or equivalent).

5.4 *Mixed indicator solution*: Dissolve 20 mg methyl red and 100 mg bromocresol green in 100 mL 95-percent ethanol. Store in a well-sealed bottle.

5.5 *Sodium carbonate solution*, 0.0357*N*: Dissolve 1.892 g primary standard Na_2CO_3 in carbon dioxide-free water and dilute to 1,000 mL.

5.6 *Sodium hydroxide-thiosulfate solution*: *Cautiously*, dissolve 500 g NaOH in 600 mL ammonia-free water. Add 80 g $Na_2S_2O_3 \cdot 5H_2O$ and dilute to 1 L.

5.7 *Sodium thiosulfate*, crystals, $Na_2S_2O_3 \cdot 5H_2O$.

5.8 *Sucrose.*

5.9 *Sulfuric acid*, concentrated, sp gr 1.84.

5.10 *Sulfuric acid standard solution*, approx 0.036*N*: *Cautiously*, add 1.0 mL concentrated H_2SO_4 (sp gr 1.84) to 800 mL ammonia-free water and dilute to 1 L. Standardize by titrating 25.0 mL 0.0357*N* Na_2CO_3 to pH 4.5. Compute normality of sulfuric acid standard solution to four decimal places.

6. Procedure

6.1 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent—**CAUTION: deadly poison.**

6.2 Weigh to the nearest milligram, 3 g of bottom-material sample, prepared as directed in method P-0810, and transfer to the digestion flask.

6.3 In the same manner prepare a blank, using 2.0 g sucrose. Analyze the blank and each sample as directed in paragraphs 6.4 to 6.10.

6.4 *Cautiously*, add 25 mL concentrated H_2SO_4 (sp gr 1.84), and under a hood, swirl the contents of the flask until thoroughly mixed.

6.5 Add three digestion-catalyst tablets and mix well. Add a few glass beads and begin the digestion. Continue the digestion until a clear solution is obtained, and then continue fuming 1 h.

6.6 Cool the flask until crystals appear (do not cool completely). Add 150 mL ammonia-free water; mix and allow to cool.

6.7 Add 100 mL NaOH-$Na_2S_2O_3$ solution. Immediately connect the flask to the distillation apparatus and *cautiously* mix the contents by swirling.

6.8 Distill at a rate of not more than 10 mL/min and no less than 6 mL/min; collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.9 Collect approx 200 mL of distillate, dilute to 250 mL with ammonia-free water, and mix.

6.10 To the distillate, add 3 drops mixed indicator solution, and titrate with sulfuric acid standard solution until the color of the solution changes from yellow to red.

7. Calculations

Nitrogen, ammonia plus organic (mg/kg) =

$$\frac{V_a \times N_a \times 14{,}000}{Wt_s}$$

where

V_a = volume of standard H_2SO_4 used to titrate sample, milliliters, minus volume used to titrate blank, milliliters,

N_a = normality of standard H_2SO_4 solution, and

Wt_s = weight of sample, grams.

8. Report

Report nitrogen, ammonia plus organic, total-in-bottom-material (00626), concentrations as follows: 10 to 100 mg/kg, nearest 1 mg/kg; 100 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.

Nitrogen, nitrate, ion-exchange chromatographic, automated

Parameters and Codes:

Nitrogen, nitrate, dissolved, I-2057-85 (mg/L as N): 00618
Nitrogen, nitrate, dissolved, I-2058-85 (mg/L as N): 00618

2. Summary of method

Nitrate is determined sequentially with six other anions by ion-exchange chromatography. Ions are separated based on their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical-conductivity cell. See method I-2057, anions, ion-exchange chromatographic, automated, and method I-2058, anions, ion-exchange chromatographic, precipitation, automated.

Nitrogen, nitrite, colorimetric, diazotization

Parameter and Code:

Nitrogen, nitrite, dissolved, I-1540-85 (mg/L as N): 00613

1. Application

This method may be used to analyze water containing between 0.01 and 0.6 mg/L of nitrite-nitrogen; samples containing greater concentrations need to be diluted.

2. Summary of method

Nitrite is diazotized with sulfanilamide, and the resulting diazo compound is coupled with N-1-naphthylethylenediamine dihydrochloride to form an intensely colored red compound, which is determined spectrometrically at 540 nm. Sulfanilamide and N-1-naphthylethylenediamine dihydrochloride are combined with a sodium acetate buffer to form a single reagent solution.

3. Interferences

Oxidizing agents interfere by oxidizing nitrite to nitrate. Sulfide also interferes. No other substance commonly occurring in natural water interferes with this method.

4. Apparatus

4.1 Spectrometer for use at 540 nm.

4.2 Refer to manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Color-buffer solution*: Add 105 mL concentrated HCl (sp gr 1.19), 5.0 g sulfanilamide, and 0.5 g N-1-naphthylethylenediamine dihydrochloride to 250 mL demineralized water. Stir until dissolved. Add 136 g $CH_3COONa{\cdot}3H_2O$ or 82 g CH_3COONa and stir until dissolved. Dilute to 500 mL with demineralized water. When 2 mL of this solution is added to 50 mL demineralized water, the resultant solution should have a pH of 1.8. Store the color-buffer solution in the dark and protect from nitrogen oxides that may be in the atmosphere. The solution is stable for several months.

5.2 *Nitrite-nitrogen standard solution I*, 1.00 mL = 0.50 mg NO_2-N: Dissolve 3.038 g KNO_2 in demineralized water and dilute to 1,000 mL. This and the following nitrite standard solution are not stable indefinitely; their concentrations must be checked frequently.

5.3 *Nitrite-nitrogen standard solution II*, 1.00 mL = 0.05 mg NO_2-N: Dilute 100.0 mL nitrite-nitrogen standard solution I to 1,000 mL with demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.03 mg NO_2-N (50.0 mL max) into a 100-mL beaker and adjust the volume to 50.0 mL with demineralized water (NOTE 1).

NOTE 1. If the sample has a pH greater than 10 or less than 4 (or greater than 600 mg/L alkalinity or acidity), adjust to approx pH 6 with 3*M* HCl or 2.5*M* NaOH.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 mL (NOTE 2).

NOTE 2. If the samples were preserved with mercuric chloride fortified with sodium chloride, add an equivalent amount to the blank and standards.

6.3 Add 2.0 mL color-buffer solution and mix.

6.4 Allow the color to develop for at least 15 min and measure the absorbances of the sample and standards against that of the blank.

7. Calculations

7.1 Determine milligrams of nitrite-nitrogen in each test sample from a plot of absorbances of standards.

7.2 Determine the nitrite-nitrogen concentration in milligrams per liter as follows:

$$NO_2\text{-N (mg/L)} = \frac{1{,}000}{\text{mL aliquot}} \times \text{mg } NO_2\text{-N in sample}$$

8. Report

Report nitrogen, nitrite dissolved (00613), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved nitrite-nitrogen for 19 samples within the range of 0.005 to 2.17 mg/L may be expressed as follows:

$$S_T = 0.096X + 0.006$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of nitrite-nitrogen, milligrams per liter.

The correlation coefficient is 0.9094.

9.2 Precision for dissolved nitrite-nitrogen for five of the 19 samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
11	0.005	100
11	.050	20
14	.556	9
17	1.48	8
10	2.17	12

Nitrogen, nitrite, colorimetric, diazotization, automated-segmented flow

Parameters and Codes:

Nitrogen, nitrite, dissolved, I-2540-85 (mg/L as N): 00613
Nitrogen, nitrite, total, I-4540-85 (mg/L as N): 00615

1. Application

1.1 This method may be used to analyze surface, domestic and industrial water, and brines and water-suspended sediment containing from 0.01 to 1.0 mg/L of nitrite-nitrogen. Samples containing greater concentrations need to be diluted.

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

2. Summary of method

Nitrite ion reacts with sulfanilamide under acidic conditions to form a diazo compound, which then couples with N-1-naphthylethylenediamine dihydrochloride to form a red compound, the absorbance of which is measured colorimetrically (Kamphake and others, 1967).

3. Interferences

Oxidizing agents interfere by oxidizing nitrite to nitrate. Sulfide also interferes. No other substance commonly occurring in natural water interferes with this method.

4. Apparatus

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

4.2 With this equipment the following operating conditions have been found satisfactory:

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

5. Reagents

5.1 *Color reagent*: Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to approx 1,500 mL demineralized water. Dissolve completely (warm if necessary). Add 1.0 g N-1-naphthylethylenediamine dihydrochloride and dissolve completely. Dilute to 2 L with demineralized water. Store in an amber bottle and refrigerate; however, the reagent must be at room temperature when it is used. The reagent is stable for approx 1 month.

5.2 *Nitrite-nitrogen standard solution I*, 1.00 mL = 0.100 mg NO_2-N: Dissolve 0.6076 g KNO_2 in demineralized water and dilute to 1,000 mL. This and the following nitrite standard solutions are not stable indefinitely; their concentrations must be checked frequently.

5.3 *Nitrite-nitrogen standard solution II*, 1.00 mL = 0.010 mg NO_2-N: Quantitatively dilute 100.0 mL nitrite-nitrogen standard solution I to 1,000 mL with demineralized water.

5.4 *Nitrite-nitrogen working standards*: Prepare a blank and 100 mL each of a series of nitrite-nitrogen working standards by appropriate quantitative dilution of nitrite-nitrogen standard solution II. Dissolve 5.2 mg mercuric chloride and 60 mg sodium chloride in each working standard. For example:

Nitrite-nitrogen standard solution II (mL)	Nitrite-nitrogen concentration (mg/L)
0.0	0.00
.5	.05
2.0	.2
5.0	.5
10.0	1.0

6. Procedure

6.1 Set up manifold (fig. 35).

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

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

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 peak reads full scale.

7. Calculations

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

7.2 Compute the concentration of dissolved or total nitrite-nitrogen in each sample by comparing its 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, dissolved (00613), and total (00615), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved nitrite-nitrogen for 19 samples within the range of 0.006 to 2.22 mg/L may be expressed as follows:

$$S_T = 0.093X + 0.004$$

where

S_T = overall precision, milligrams per liter, and

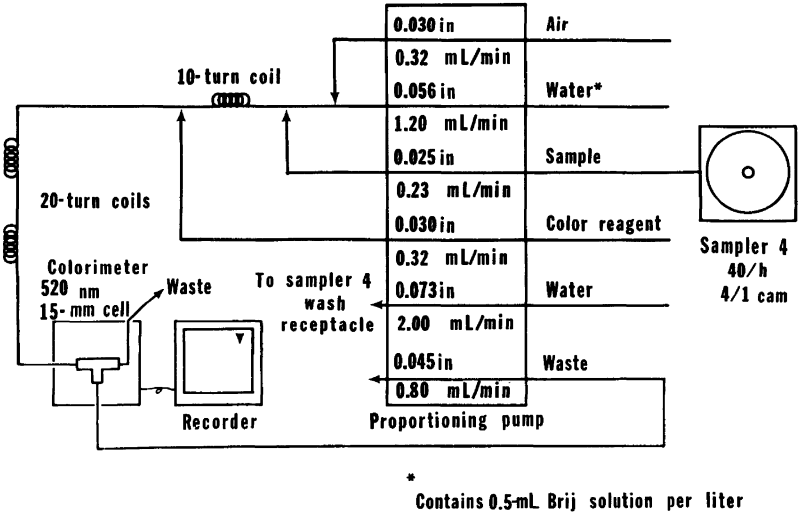


Figure 35.—Nitrogen, nitrite, diazotization manifold

X = concentration of nitrite-nitrogen, milligrams per liter.

The correlation coefficient is 0.9445.

9.2 Precision for dissolved nitrite-nitrogen for six of the 19 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
13	0.006	133
14	.010	60
20	.050	16
20	.540	6
21	1.40	13
19	2.22	9

9.3 It is estimated that the percent relative standard deviation for total nitrite-nitrogen will be greater than that reported for dissolved nitrite-nitrogen.

Reference

Kamphake, L., Hannah, S., and Cohen, J., 1967, Automated analysis for nitrite by hydrazine reduction: Water Research, v. 1, p. 205-16.

Nitrogen, nitrite, colorimetric, diazotization, automated-discrete

Parameters and Codes:

Nitrogen, nitrite, dissolved, I-2539-85 (mg/L as N): 00613
Nitrogen, nitrite, total, I-4539-85 (mg/L as N): 00615

1. Application

1.1 This method may be used to analyze surface, domestic, and industrial water, and water-suspended sediment containing from 0.01 to 1.00 mg/L of nitrite-nitrogen. Samples containing concentrations greater than 1.0 mg/L need to be diluted.

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

2. Summary of method

Nitrite ion reacts with sulfanilamide under acidic conditions to form a diazo compound, which then couples with N-1-naphthylethylenediamine dihydrochloride to form a red-colored compound, the absorbance of which is measured colorimetrically (Kamphake and others, 1967).

3. Interferences

3.1 Oxidizing agents interfere by oxidizing nitrite to nitrate. Sulfide also interferes. No other substance commonly occurring in natural water interferes.

4. Apparatus

4.1 *Discrete chemical analyzer system*, American Monitor IQAS or equivalent.

4.2 With this equipment, the following operating conditions have been found satisfactory for the range 0.01 to 1.00 mg/L:

Wavelength --	547 nm
Absorption cell	1 cm square, temperature-controlled, flow-through quartz cuvette
Reaction temperature ---	37°C
Sample volume	0.125 mL with 0.100 mL diluent (NOTE 1)
Reagent volume	1.0 mL color reagent (NOTE 1)

NOTE 1. Sample-to-diluent ratio and reagent volume must be optimized for each instrument according to manufacturer's specifications.

5. Reagents

5.1 *Color reagent*: Add 100 mL concentrated phosphoric acid (sp gr 1.69) and 10 g sulfanilamide to approx 750 mL demineralized water. Dissolve completely (warm if necessary). Add 0.5 g N-1-naphthylethylenediamine dihydrochloride and dissolve completely. Dilute to 1000 mL with demineralized water. Store in an amber bottle and refrigerate. Solution is stable for approx 1 month.

5.2 *Nitrite-nitrogen standard solution I*, 1.00 mL = 1.00 mg NO_2-N: Dissolve 6.076 g KNO_2 in demineralized water and dilute to 1000 mL. This and the following nitrite standard solutions are not stable indefinitely; their concentrations must be checked frequently.

5.3 *Nitrite-nitrogen standard solution II*, 1.00 mL = 0.01 mg NO_2-N: Quantitatively dilute 10.0 mL nitrite-nitrogen standard solution I to 1000 mL with demineralized water.

5.4 *Nitrite-nitrogen working standards*: Prepare a blank and 1000 mL each of a series of nitrite-nitrogen working standards by dilution of nitrite-nitrogen standard solution II. Dissolve 52 mg mercuric chloride and 600 mg sodium chloride in each working standard. For example:

Nitrite-nitrogen standard solution II (mL)	Nitrite-nitrogen concentration (mg/L)
0.0	0.00
2.0	.02
5.0	.05
30.0	.30
100.0	1.00

6. Procedure

6.1 Set up the analyzer and computer-card assignments according to manufacturer's instructions.

6.2 Place standards, beginning with the lowest concentrations, in ascending order (computer-calibration curve) in the first five positions on the sample turntable. Place samples and quality-control standards in the remainder of the sample turntable.

6.3 Begin analysis. The cathode-ray tube (CRT) will acknowledge the parameter and concentration range, listing each sample-cup number and corresponding concentrations calculated from the working curve. During each run, the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from printer.

7. Calculations

Determine the concentration in milligrams per liter of dissolved or total nitrite-nitrogen in each sample from either the CRT display or the printer output.

8. Report

Report nitrogen, nitrite, dissolved (00613), and total (00615), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the standard deviation and percent relative standard deviation for replicate analysis of reference materials by a single operator is as follows:

Mean (mg/L)	Number of replicates	Standard deviation (mg/L)	Relative standard deviation (percent)
0.019	11	0.002	10.5
.051	14	.004	7.8
.156	14	.004	2.6
.243	14	.003	1.2
.470	14	.006	1.3
.822	14	.016	2.0

Nitrogen, nitrite, ion-exchange chromatographic, automated

Parameter and Code:

Nitrogen, nitrite, dissolved, I-2057-85 (mg/L as N): 00613

2. Summary of method

Nitrite is determined sequentially with six other anions by ion-exchange chromatography. Ions are separated based on their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical-conductivity cell. See method I-2057, anions, ion-exchange chromatographic (IC), automated.

Nitrogen, nitrite plus nitrate, colorimetric, cadmium reduction-diazotization, automated-segmented flow

Parameters and Codes:

Nitrogen, nitrite plus nitrate, dissolved, I-2545-85 (mg/L as N): 00631
Nitrogen, nitrite plus nitrate, total, I-4545-85 (mg/L as N): 00630
Nitrogen, nitrite plus nitrate, total-in-bottom-material, dry wt, I-6545-85 (mg/kg as N): 00633

1. Application

1.1 This method may be used to analyze surface, domestic, and industrial water, and brines and water-suspended sediment containing from 0.1 to 5.0 mg/L of nitrite- plus nitrate-nitrogen. Samples containing greater concentrations need to be diluted.

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

1.3 This method may be used to determine the sum of nitrite- plus nitrate-nitrogen concentrations in bottom material containing at least 2 mg/kg.

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 Ehrlich and MacDonald, written commun., 1969).

2.3 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 (1984) 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 more than 2 mg/L 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 1*M* HCl followed by demineralized water. Allow to air-dry. Shake the dry powder with copper sulfate solution (20 g/L). The weight of the solution should be approx 10 times that of the cadmium. Wash thoroughly with demineralized water to remove colloidal copper, 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*, 1.0*M*: Add 83.3 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

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

5.8 *Nitrate-nitrogen standard solution II*, 1.00 mL = 0.025 mg NO_3-N: 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 (NOTE 1). Dissolve 26 mg mercuric chloride and 300 mg sodium chloride in each working standard. For example:

Nitrite-nitrogen standard solution II (mL)	Nitrite-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

NOTE 1. If nitrate-nitrogen in bottom material is being determined, the working standards are diluted with sodium chloride solution (5.10). Mercuric chloride is not added.

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 Proceed to paragraph 6.2 for waters or water-suspended sediment mixtures. For bottom materials begin with paragraph 6.1.1.

6.1.1 Weigh approx 5 g of sample, prepared as directed in either method P-0520 or P-0810, 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 (5.10). Proceed to paragraph 6.2.

6.2 Set up manifold (fig. 36).

6.3 Allow the color reagent to come to room temperature.

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

6.5 Fill the reduction column, which is a U-shaped, 36-cm length of 2.0-mm ID glass tubing

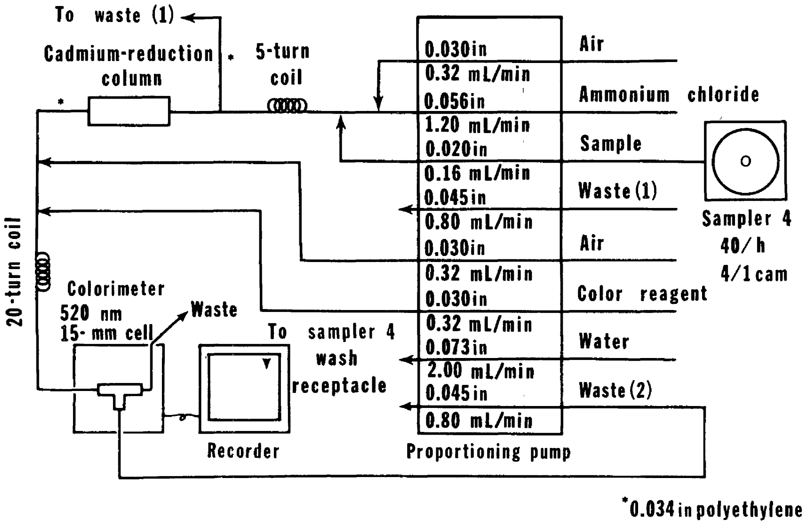


Figure 36.—Nitrogen, nitrite plus nitrate, cadmium reduction-diazotization, manifold

(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 filling is completed, insert borosilicate glass wool in the exit end of the tube. This column should function for several hundred samples before it needs to be refilled (NOTE 2).

NOTE 2. 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 heights. Replace the column if the efficiency falls below 90 percent.

6.6 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 3).

NOTE 3. 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.

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

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

6.9 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.

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

7. Calculations

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

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

7.3 Compute the concentration of nitrite- plus nitrate-nitrogen in bottom material samples 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.

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

where

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

8. Report

8.1 Report nitrogen, nitrite plus nitrate, dissolved (00631), and total (00630), concentrations as follows: 0.1 to 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

8.2 Report nitrogen, nitrite plus nitrate, total-in-bottom-material (00633), concentrations as follows: less than 10 mg/kg, one decimal; 10 mg/kg and above, two significant figures.

9. Precision

9.1 Precision for dissolved nitrite- plus nitrate-nitrogen for 18 samples within the range of 0.62 to 5.0 mg/L may be expressed as follows:

$$S_T = 0.120X + 0.009$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of nitrogen, milligrams per liter.

The correlation coefficient is 0.6826.

9.2 Precision for dissolved nitrite- plus nitrate-nitrogen for five of the 18 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
24	0.62	8
4	1.05	4
9	1.27	16
16	2.38	16
24	5.05	8

9.3 It is estimated that the percent relative standard deviation for total nitrite- plus nitrate-nitrogen and for total nitrite- plus nitrate-nitrogen in bottom material will be greater than that reported for dissolved nitrite- plus nitrate-nitrogen.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 559-71.

Brewer, P. G., and Riley, J. P., 1965, The automatic determination of nitrate in sea water: Deep Sea Research, v. 12, p. 765-72.

Kamphake, L., Hannah, S., and Cohen, J., 1967, Automated analysis for nitrate by hydrazine reduction: Water Research, v. 1, p. 205-16.

Morris, A. W., and Riley, J. P., 1963, The determination of nitrate in sea water: Analytica Chimica Acta, v. 29, p. 272-9.

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

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

Nitrogen, nitrite plus nitrate, colorimetric, hydrazine reduction-diazotization, automated-discrete

Parameters and Codes:

Nitrogen, nitrite plus nitrate, dissolved, I-2543-85 (mg/L as N): 00631
Nitrogen, nitrite plus nitrate, total, I-4543-85 (mg/L as N): 00630

1. Application

1.1 This method may be used to determine the concentration of the sum of nitrite- plus nitrate-nitrogen in surface, ground, domestic, and industrial water, and water-suspended sediment in the range from 0.01 to 3.0 mg/L. Samples containing greater concentrations need to be diluted.

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

2. Summary of method

Nitrate is reduced to nitrite with hydrazine sulfate in alkaline solution. The nitrite (that originally present plus reduced nitrate) is then treated with sulfanilamide under acidic conditions to yield a diazo compound, which is coupled with N-1-napthylethylenediamine dihydrochloride to form a red azo dye. The absorbance of this dye is measured colorimetrically at 520 nm (Kamphake and others, 1967; U.S. Environmental Protection Agency, 1979).

3. Interferences

3.1 Sample color that absorbs at the spectrophotometric wavelength used for analysis will interfere and must be corrected if the color exceeds 50 platinum cobalt units.

3.2 Samples containing concentrations greater than 5000 mg/L sulfate, 1000 mg/L calcium, sodium, potassium, or chloride, 150 mg/L magnesium, 30 mg/L phosphate, and 2 mg/L sulfide interfere.

4. Apparatus

4.1 *Discrete analyzer system*, American Monitor IQAS or equivalent.

4.2 With this equipment, the following operating conditions have been found satisfactory for the range 0.01 to 3.0 mg/L:

Wavelength ---	520 nm
Absorption cell	1 cm square, temperature-controlled, flow-through quartz cuvette
Reaction temperature ------	37 °C
Sample volume	0.13 mL with 0.27 mL of diluent (NOTE 1)
Reagent volumes	0.25 mL NaOH, 0.25 mL working reductant solution, and 0.80 mL color reagent (NOTE 1)

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each instrument according to manufacturer's specifications.

5. Reagents

5.1 *Color reagent*: Add 100 mL concentrated H_3PO_4 (sp gr 1.69) and 10 g sulfanilamide to 750 mL demineralized water and warm if necessary for complete dissolution. Add 0.5 g N-1-napthylethylenediamine dihydrochloride and dissolve completely. Dilute to 1000 mL with demineralized water. Store in a dark bottle in a refrigerator. Solution must be at room temperature before use. Solution is stable for approximately one month.

5.2 *Copper sulfate solution*, 4 g/L: Dissolve 4 g $CuSO_4$ (anhydrous) in 500 mL demineralized water and dilute to 1000 mL.

5.3 *Hydrazine sulfate solution*, 27.5 g/L: Dissolve 13.75 g $N_2H_4 \cdot H_2SO_4$ in 400 mL demineralized water and dilute to 500 mL—**CAUTION: Poisonous.**

5.4 *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.

5.5 *Nitrate-nitrogen standard solution II*, 1.00 mL = 0.025 mg NO_3-N: Dilute 50.0 mL nitrate-nitrogen standard solution I to 1000 mL with demineralized water.

5.6 *Nitrate-nitrogen working standards*: Prepare a blank and 500 mL each of a series of nitrate-nitrogen working standards by appropriate dilution of the nitrate standard solution II. Dissolve 26 mg mercuric chloride and 300 mg sodium chloride in each working standard. For example:

Nitrite-nitrogen standard solution II (mL)	Nitrite-nitrogen concentration (mg/L)
0.0	0.00
1.0	.05
2.0	.10
10.0	.50
20.0	1.0
60.0	3.0

5.7 *Sodium hydroxide solution*, 0.3*M*: Dissolve 12 g NaOH in 500 mL demineralized water and dilute to 1000 mL.

5.8 *Working reductant solution*: Add 13.5 mL hydrazine sulfate solution plus 8 mL copper sulfate solution to 500 mL demineralized water and dilute to 1000 mL. Prepare fresh daily.

6. Procedure

6.1 Set up the analyzer and computer-card assignments according to the manufacturer's instructions. Add the 0.3*M* NaOH solution from the first available dispensing station and the working reductant solution from the last available dispensing station. The color reagent is added from a dispensing station during a second cycle of the turntable (NOTE 2).

NOTE 2. This second cycle of the turntable is necessary to ensure complete reduction of nitrate to nitrite prior to the formation of the red-colored azo dye.

6.2 Place four standards (0.1, 0.5, 1.0, and 3.0 mg/L NO_3-N, respectively) and blank, beginning with the lowest concentration in the first positions, on the sample turntable. Fill remainder of turntable with samples.

6.3 Begin analysis. The cathode-ray tube (CRT) will acknowledge the parameter and concentration range, listing each sample-cup number and corresponding concentrations calculated from the working curve. During each run the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from printer.

7. Calculations

Determine the concentration in milligrams per liter of dissolved or total nitrite plus nitrate-nitrogen in each sample from either the printer output or the CRT display.

8. Report

Report nitrogen, nitrite plus nitrate, dissolved (00631) and total (00630), concentrations as follows: less than 1.0 mg/L, nearest 0.01 mg/L; 1.0 mg/L and above, two significant figures.

9. Precision

Precision expressed in terms of the standard deviation and percent relative standard deviation for replicate analyses of reference materials by a single operator are as follows:

Number of replicates	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
40	0.10	0.01	10
40	.24	.02	8
17	.31	.03	10
40	.50	.02	4
40	1.01	.02	2
16	1.63	.08	5
57	3.05	.09	3

References

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

U.S. Environmental Protection Agency, 1979, Methods for chemical analyses of water and wastes: Cincinnati, p. 353.1-1.

Oxygen demand, chemical (COD), colorimetric, dichromate oxidation

Parameter and Code:

Oxygen demand, chemical, total, I-3561-85 (COD in mg/L): 00340

1. Application

This method may be used to analyze water-suspended sediment containing between 10 and 500 mg/L chemical oxygen demand (COD).

2. Summary of method

2.1 Organic and other oxidizable materials are oxidized by digestion with an acid-dichromate solution in the presence of silver sulfate catalyst. The COD concentration is determined spectrometrically by measuring the absorbance of the Cr^{+3} that is formed.

2.2 Additional information about the principles of the method may be found in Jirka and Carter (1975).

3. Interferences

3.1 Reducing substances such as ferrous iron and chloride interfere, because they are oxidized by dichromate in acid solution. Chlorides constitute the largest and most common interference, with 1 mg/L Cl^{-1} equivalent to 0.226 mg/L COD. To eliminate chloride interference as great as 2,000 mg/L, add mercuric sulfate to the acid-dichromate digestion solution.

3.2 Chromium(III) interferes. One milligram per liter is equivalent to 0.719 mg/L COD. Levels great enough to have significant effect on the accuracy are unlikely in natural water samples.

3.3 Ferric iron concentrations less than 5000 mg/L do not interfere.

4. Apparatus

4.1 *Ampules*, glass, 10-mL capacity.

4.2 *Centrifuge*, Sorvall SS-3 Automatic Superspeed or equivalent.

4.3 *Spectrometer* for use at 600 nm: Refer to the manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Potassium acid phthalate standard solution I*, 1.0 mL = 10.0 mg COD: Dissolve 8.500 g potassium acid phthalate, which has been dried for 2 h at 110°C, in demineralized water and dilute to 1,000 mL.

5.2 *Potassium acid phthalate standard solution II*, 1.0 mL = 1.0 mg COD: Dilute 100 mL potassium acid phthalate standard solution I to 1,000 mL with demineralized water. This solution is used to prepare working standards at time of analysis.

5.3 *Potassium dichromate-mercuric sulfate digestion solution*: To approx 700 mL demineralized water, add 10.216 g $K_2Cr_2O_7$ and 33.0 g $HgSO_4$. **CAUTION: Hazardous.** Slowly, and with constant stirring, add 167 mL concentrated H_2SO_4 (sp gr 1.84). Mix until dissolved. After the solution cools, dilute to 1 L with demineralized water.

5.4 *Silver sulfate solution*: Dissolve 22 g Ag_2SO_4 in a 9-pound bottle of concentrated H_2SO_4 (sp gr 1.84).

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

6. Procedure

6.1 Heat the ampules at 500°C for 6 h, and cool.

6.2 Pipet 2.5 mL of a well-mixed sample into an ampule.

6.3 Prepare a blank and sufficient standards containing from 10 to 500 mg/L COD using potassium acid phthalate standard solution II. Pipet 2.5 mL of each into ampules.

6.4 Add 1.5 mL potassium dichromate-mercuric sulfate digestion solution to each ampule (NOTE 1).

NOTE 1. Protective eyeglasses and clothing are mandatory for this entire procedure, because sulfuric acid and potassium dichromate solutions at high temperatures are especially hazardous.

6.5 Add 3.5 mL silver sulfate solution to each ampule.

6.6 Heat-seal the ampules and shake vigorously.

6.7 Heat the ampules in an oven at 150°C for 2 h.

6.8 Cool the ampules to room temperature in a cold-water bath.

6.9 Centrifuge the solutions at 5,000 rpm for 15 min.

6.10 Set the spectrophotometer at 600 nm and adjust the absorbance to 0.000 with the digested blank.

6.11 Individually transfer each standard and sample to the sample cuvette, preferably using an automated flow-through cell, and read and record each absorbance value. Care must be taken not to disturb any precipitate when pouring the sample into the cuvette (NOTE 2).

NOTE 2. A Technicon AutoAnalyzer system, consisting of a sampler, proportioning pump, cartridge manifold, colorimeter, recorder, and printer, may be used in place of the spectrophotometer to measure the absorbance of the digested solution (Jirka and Carter, 1975). Steps 6.2 to 6.9 remain unchanged.

7. Calculations

Determine the milligrams per liter of COD in each sample from a plot of absorbances of standards.

8. Report

Report oxygen demand, chemical (COD), total (00340), concentrations as follows: less than 10 mg/L, as <10 mg/L; 10 mg/L and above, two significant figures.

9. Precision

For potassium acid phthalate standards, the precision for a single operator expressed in terms of the percent relative standard deviation is as follows:

Mean (mg/L)	Relative standard deviation (percent)
50	14
400	2

Reference

Jirka, A. M., and Carter, M. J., 1975, Micro semiautomated analysis of surface and wastewaters for chemical oxygen demand: Analytical Chemistry, v. 47, no. 8, p. 1397-1402.

Oxygen demand, chemical (COD), titrimetric, dichromate oxidation

Parameters and Codes:

Oxygen demand, chemical, total, 0.025*N* dichromate, I-3562-85 (COD in mg/L): 00335
Oxygen demand, chemical, total, 0.25*N* dichromate, I-3560-85 (COD in mg/L): 00340
Oxygen demand, chemical, total-in-bottom-materials, dry wt, I-5560-85 (COD in mg/kg): 00339

1. Application

1.1 This method may be used to analyze natural water and industrial waste containing more than 50 mg/L chemical oxygen demand (COD) and less than 2,000 mg/L of chloride. Samples containing less than 50 mg/L COD need to be analyzed as directed in paragraph 6.10. COD values for samples containing more than 2,000 mg/L of chloride need to be corrected as indicated in paragraph 6.11.

1.2 This method may be used to analyze samples of bottom material containing more than 100 mg/kg chemical oxygen demand (COD). Samples containing less than 1,000 mg/kg COD need to be analyzed as directed in paragraph 6.10.

1.3 Bottom material may be analyzed by the procedure after it has been prepared as directed in method P-0810 or P-0811.

2. Summary of method

2.1 Organic and other oxidizable material is oxidized by refluxing with standard acid-dichromate solution in the presence of silver sulfate catalyst. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as indicator.

2.2 For additional information, see American Society for Testing and Materials, (1984).

3. Interferences

Reducing substances such as ferrous iron, nitrites, and chlorides interfere, because they are oxidized. Chlorides constitute by far the greatest and most common interference, being quantitatively oxidized by dichromate in acid solution. One milligram of chloride per liter is equivalent to 0.226 mg/L COD. To eliminate chloride interference, add mercuric sulfate to the sample to form a soluble mercuric chloride complex. Nitrite interference may be eliminated by incorporating in the standard dichromate solution 10 mg of sulfamic acid for each milligram of nitrite in the reflux flask.

4. Apparatus

4.1 *Reflux apparatus*, consisting of 500-mL Erlenmeyer flask and water-cooled condenser, with ground-glass joints and made of heat-resistant glass.

4.2 *Hotplate* or heating mantle.

5. Reagents

5.1 *Ferrous ammonium sulfate standard solution I*, appprox 0.250*N*: Dissolve 98.0 g $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in demineralized water. Add 20 mL concentrated H_2SO_4 (sp gr 1.84), cool, and dilute to 1 L with demineralized water. To standardize: Dilute 25.0 mL standard 0.2500*N* $K_2Cr_2O_7$ solution to 250 mL. Add 20 mL concentrated H_2SO_4 (sp gr 1.84) and cool. Titrate with the ferrous ammonium sulfate solution, using 8 to 10 drops ferroin indicator. Compute normality of the ferrous ammonium sulfate standard solution to four decimal places. The solution must be standardized daily or before use.

5.2 *Ferrous ammonium sulfate standard solution II*, 0.025*N*: Dilute 100 mL of ferrous ammonium sulfate standard solution I to 1,000 mL with demineralized water. The normality of this solution is dependent upon the standardized normality of solution I.

5.3 *Mercuric sulfate*, powdered $HgSO_4$.

5.4 *Orthophenanthroline ferrous sulfate (ferroin) indicator solution*: Dissolve 1.48 g 1,10-(ortho)-phenanthroline monohydrate and 0.70 g $FeSO_4 \cdot 7H_2O$ in 100 mL water. The prepared indicator is available commercially.

5.5 *Potassium dichromate standard solution I*, 0.2500*N*: Dissolve 12.2588 g $K_2Cr_2O_7$ primary standard, dried for 2 h at 110°C, in demineralized water and dilute to 1,000 mL.

5.6 *Potassium dichromate standard solution II*, 0.0250*N*: Dilute 100 mL of potassium dichromate standard solution I to 1,000 mL with demineralized water.

5.7 *Silver sulfate*, powder, Ag_2SO_4.

5.8 *Sulfamic acid*, crystals.

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

6. Procedure

6.1 Follow instructions in paragraph 6.1.1 for natural waters and industrial wastes, and in paragraph 6.1.2 for bottom materials.

6.1.1 Pipet 50.0 mL of a well-mixed sample or of a smaller volume diluted to 50.0 mL into the reflux flask.

6.1.2 Weigh, to the nearest milligram, an amount of wet sample (1.0 g max) that will consume approx one-half of the 0.2500*N* $K_2Cr_2O_7$ solution added in paragraph 6.5. Transfer the sample to the reflux flask and add 50 mL demineralized water.

6.2 Add slowly, over a period of 2 to 3 min, 1 g $HgSO_4$; allow to stand 5 min, swirling frequently.

6.3 Add 1 g Ag_2SO_4 and a few glass beads that have been ignited at 600°C for 1 h.

6.4 Cool in ice water and add 75 mL concentrated H_2SO_4 (sp gr 1.84) slowly enough, with mixing, to prevent appreciable solution heating.

6.5 Add 25.0 mL 0.2500*N* $K_2Cr_2O_7$ solution and mix thoroughly by swirling (NOTE 1).

NOTE 1. If contents are not well mixed, superheating may result, and the contents of the flask may be expelled from the open end of the condenser.

6.6 Attach flask to condenser, start water flow, and reflux for 2 h.

6.7 Allow flask to cool and wash condenser with 25 mL demineralized water.

6.8 Dilute to 300 mL with demineralized water, cool to room temperature, and titrate the excess dichromate with ferrous ammonium sulfate standard solution I, using 8 to 10 drops ferroin indicator solution. The end point is a sharp change from blue green to reddish brown.

6.9 A demineralized-water blank is carried through all steps of the procedure with each group of samples.

6.10 Samples containing less than 50 mg/L COD or 1,000 mg/kg COD should be reanalyzed, using 0.025*N* solutions of potassium dichromate and ferrous ammonium sulfate. A sample size should be selected so that no more than half the dichromate is reduced.

6.11 To determine COD on samples containing more than 2,000 mg/L of chloride, the following treatment should be used (Burns and Marshall, 1965). Add 10 mg $HgSO_4$ for each milligram of chloride ion in the sample aliquot. Prepare a series of chloride solutions containing from 2,000 to 20,000 mg/L with the concentration interval not exceeding 4,000 mg/L, and add 10 mg $HgSO_4$ to each solution for each milligram of chloride ion present. Determine the COD of the sample and chloride solution, starting with paragraph 6.2. Plot the COD values obtained versus milligrams per liter chloride. From this curve, COD values may be obtained for any desired chloride concentration. This value is subtracted as a correction factor to obtain the COD value of a sample.

7. Calculations

7.1 For natural waters and industrial wastes not requiring chloride correction:

$$COD\ (\text{mg/L}) = \frac{(A-B)N \times 8{,}000}{\text{mL sample}}$$

7.2 For natural waters and industrial wastes requiring chloride correction:

$$COD\ (\text{mg/L}) = \left[\frac{(A-B)N \times 8{,}000}{\text{mL sample}} - C\right] \times 1.20$$

where

COD = chemical oxygen demand from dichromate,

A = amount of ferrous ammonium sulfate for blank, milliliters,

B = amount of ferrous ammonium sulfate for sample, milliliters,

N = normality ferrous ammonium sulfate,

C = chloride-correction value from graph of chloride concentration versus COD,

and

1.20 = empirical compensation factor.

7.3 Compute the dry weight of the bottom-material samples as follows:

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

where

W = wet weight of the sample, grams,

and

M = percentage moisture.

7.4 Determine the chemical oxygen demand in each bottom-material sample as follows (NOTE 2):

NOTE 2. Most bottom-material samples contain low concentrations of chloride; therefore, a chloride correction is not necessary.

$$COD \text{ (mg/kg)} = \frac{(A-B)N \times 8{,}000}{\text{sample, dry weight (g)}}$$

where

COD = chemical oxygen demand from dichromate,

A = amount of ferrous ammonium sulfate for blank, milliliters,

B = amount of ferrous ammonium sulfate for sample, milliliters,

and

N = normality ferrous ammonium sulfate.

8. Report

8.1 Report COD, total, 0.025N dichromate (00335), as follows: less than 50 mg/L, whole numbers.

8.2 Report COD, total, 0.25N dichromate (00340), as follows: 50 mg/L and above, two significant figures.

8.3 Report COD, total-in-bottom-material, dry-weight (00339), as follows: less than 10,000 mg/kg, to the nearest 100 mg/kg; 10,000 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 62-8.

Burns, E. R., and Marshall, C., 1965, Correction for chloride interference in the chemical oxygen demand test: Water Pollution Control Federation Journal, v. 37, p. 1716-21.

pH, electrometric, glass-electrode

Parameters and Codes:

pH lab, I-1586-85 (units): 00403
pH lab, automated, I-2587-85 (units): 00403

1. Application

This method may be used to determine the pH of any natural or treated water and any industrial or other wastewater.

2. Summary of method

2.1 See the introduction to electrometry in this chapter for the principles of pH-meter operation. See also Barnes (1964), Bates (1964), and Willard and others (1965).

2.2 This procedure may be automated with commercially available instrumentation.

3. Interferences

3.1 The determination is not affected by the presence of color or turbidity, or of organic or colloidal material. Oxidizing and reducing substances do not impair the accuracy of method.

3.2 The pH measurement is temperature dependent, and a significant error results if the temperatures of the buffers and samples differ appreciably. However, a variation of less than 5 °C has no significant effect except in the most exacting work.

3.3 For samples having abnormally high sodium levels, corrections may be necessary. This correction varies with the type of electrodes used; hence, see the manufacturer's instructions for the necessary computations.

4. Apparatus

4.1 *pH meter*, with glass and reference electrodes or combination pH electrode.

4.2 Several types of pH meters are available, including digital and expanded-scale models. Unless a different type is needed for special purposes, an ordinary laboratory, line-operated, pH meter—capable of a reproducibility of 0.05 of a pH unit—is adequate.

4.3 A new glass electrode or one that has dried completely may require several hours of soaking in water or buffer solution before it produces stable, reliable readings. The tip of the glass electrode must be kept immersed in water when not in use. Although the glass tip is reasonably durable, it can be damaged, and should never be cleaned or wiped with an abrasive or dirty tissue or cloth.

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 After an appropriate warmup period, standardize the instrument with the buffer solutions, bracketing the pH values of the samples. Samples and buffers must be at the same temperature.

6.2 With a minimum of aeration or agitation, measure the pH of samples in accordance with the manufacturer's instructions.

7. Calculations

The pH is read directly from the meter.

8. Report

Report pH values (00403) to the nearest 0.1 pH unit.

9. Precision

9.1 Precision for pH for five of the 36 samples expressed in terms of standard deviation is as follows:

Number of laboratories	Mean (pH units)	Relative standard deviation (pH units)
27	6.21	0.26
59	7.14	.32
33	7.52	.15
48	8.00	.21
60	8.54	.15

9.2 Using automated instrumentation, 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.

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 and Sons, 435 p.

Willard, H. H., Merritt, L. L., Jr., and Dean, J. A., 1974, Instrumental methods of analysis (5th ed.): New York, D. Van Nostrand, 860 p.

Phosphorus, colorimetric, phosphomolybdate

Parameter and Code:

Phosphorus, dissolved, I-1600-85 (mg/L as P): 00666

1. Application

This method may be used to analyze most water and wastewater containing between 0.02 and 0.4 mg/L of dissolved phosphorus. Samples containing greater concentrations need to be diluted.

2. Summary of method

2.1 As far as is known, the phosphomolybdate method is specific for the orthophosphate form of phosphorus. Weak tests are reported with pyrophosphate and polyphosphate, but these positive tests may well result from orthophosphate contamination of the material.

2.2 Acid hydrolyzable and organic forms of phosphorus are decomposed to orthophosphate by sulfuric acid-ammonium persulfate digestion. Orthophosphate is then converted to phosphomolybdate by acidified ammonium molybdate reagent:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21H^{+1} \rightarrow$$

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^{+1} + 12H_2O$$

2.3 When phosphomolybdate is reduced with ascorbic acid in the presence of antimony (Murphy and Riley, 1962), an intense blue complex is developed that absorbs light at 882 nm. The reduction is not instantaneous, nor is the developed blue color stable. The full color develops in 6 to 10 min and fades gradually thereafter.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. Silica produces a pale-blue color that is additive to the phosphate color and may require correction. The effect of silica is somewhat dependent on the reagents; therefore, an appropriate silica correction should be determined for each batch of reagents. Nitrite interferes, but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples are fortified with a minimum of 85 mg/L NaCl to overcome this interference.

3.3 Arsenic as arsenate (AsO_4^{-3}) produces a color similar to that of phosphate (Murphy and Riley, 1962) and may cause a positive interference. Arsenic concentrations up to 100 μg/L do not interfere. Greater concentrations were not investigated.

4. Apparatus

Spectrometer for use at 700 or 882 nm.

5. Reagents

5.1 *Ammonium persulfate*, $(NH_4)_2S_2O_8$.

5.2 *Antimony tartrate-ammonium molybdate solution*: Dissolve 0.13 g antimony potassium tartrate, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, in about 700 mL demineralized water contained in a 1-L volumetric flask. Add 5.6 g ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and shake flask until dissolved. *Cautiously* add 70 mL concentrated H_2SO_4 (sp gr 1.84) while swirling the contents of the flask. Cool and dilute to volume. Mix thoroughly by repeated inversion and swirling. This solution is stable for at least 1 year if stored in a polyethylene bottle away from heat.

5.3 *Combined reagent solution*: Dissolve 0.50 g ascorbic acid in 100 mL antimony tartrate-ammonium molybdate solution. This reagent is stable for at least 1 week if stored at 4 °C; otherwise prepare fresh daily.

5.4 *Phenolphthalein indicator solution*, 0.5 g/100 mL: Dissolve 0.5 g phenolphthalein in 100 mL 50-percent ethanol.

5.5 *Phosphate standard solution I*, 1.00 mL = 0.050 mg P: Dissolve 0.2197 g KH_2PO_4, dried overnight over H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate standard solution II*, 1.00 mL = 0.001 mg P: Dilute 20.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Sodium hydroxide*, 3*M*: *Carefully*, with cooling, dissolve 120 g NaOH in demineralized water and dilute to 1 L.

5.8 *Sulfuric acid*, 6*M*: *Cautiously*, add slowly, with constant stirring and cooling, 330 mL concentrated H_2SO_4 (sp gr 1.84) to 600 mL demineralized water and dilute to 1 L.

5.9 *Sulfuric acid*, 0.25*M*: *Cautiously*, add slowly, with constant stirring and cooling, 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.020 mg P (50.0 mL max) into a 125-mL Erlenmeyer flask, and adjust the volume to 50.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 mL (NOTE 1).

NOTE 1. If the samples were preserved with mercuric chloride fortified with sodium chloride, add an equivalent amount to the blank and standards.

6.3 Add 1.0 mL 6*M* H_2SO_4 and 0.4 g $(NH_4)_2S_2O_8$. Boil gently on a hotplate until the volume is reduced to about 10 mL.

6.4 Cool. Add 2 drops phenolphthalein indicator solution and neutralize with 3*M* NaOH, and then *carefully* add 0.25*M* H_2SO_4 until the pink color just disappears. Transfer to a 50-mL volumetric flask and dilute to the mark with demineralized water.

6.5 Add 10 mL combined reagent solution to each sample, blank, and standard, and mix.

6.6 After 10 min, measure absorbance of each sample and standard against that of the blank at either 882 or 700 nm.

7. Calculations

7.1 Determine the milligrams of phosphorus in each sample from a plot of absorbances of standards.

7.2 Determine the phosphorus concentration in milligrams per liter as follows:

$$\text{P in mg/L} = \frac{1{,}000}{\text{mL sample}} \times \text{mg P in sample}$$

8. Report

Report phosphorus, dissolved (00666), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved phosphorus within the range of 0.138 to 3.14 mg/L for 21 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 0.272 mg/L ranged from 0.252 to 0.296 mg/L.

9.2 Precision for dissolved phosphorus for six of the 21 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
13	0.138	48
15	.573	27
14	.867	5
16	.887	49
18	1.52	30
15	3.20	5

Reference

Murphy, J., and Riley, J. P., 1962, A modified single-solution method for the determination of phosphate in natural waters: Analytica Chemica Acta, v. 27, p. 31–6.

Phosphorus, colorimetric, phosphomolybdate, automated-segmented flow

Parameters and Codes:

Phosphorus, dissolved, I-2600-85 (mg/L as P): 00666
Phosphorus, total, I-4600-85 (mg/L as P): 00665
Phosphorus, total-in-bottom-material, dry wt, I-6600-85 (mg/kg as P): 00668

1. Application

1.1 This method may be used to analyze most water, wastewater, brines, and water-suspended sediment containing from 0.01 to 1.0 mg/L of phosphorus. Samples containing greater concentrations need to be diluted.

1.2 This method may be used to analyze bottom material containing from 40 to 4,000 mg/kg of phosphorus. This range may be extended by using a 0.1-g subsample rather than the 1-g subsample specified.

2. Summary of method

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

2.2 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 and others, 1966).

2.3 Mercuric chloride-preserved water samples and water-suspended sediment mixtures are fortified with a minimum of 85 mg/L NaCl to overcome the interference from mercury in the analysis.

2.4 Digested and centrifuged bottom-material samples are diluted to reduce the acid and phosphorus concentrations before final analysis.

3. Interferences

3.1 The color of the molybdate blue complex is strongly affected by pH. The method incorporates a dilution step for bottom-material samples to reduce the hydrogen-ion concentrations of all samples.

3.2 Barium, lead, and silver interfere by forming a phosphate precipitate, but the effect is usually 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 Arsenic as arsenate (AsO_4^{-3}) produces a color similar to that of phosphate (Murphy and Riley, 1962) and may cause a positive interference. Arsenic concentrations as much as 100 μg/L do not interfere. Greater concentrations were not investigated.

4. Apparatus

4.1 *Autoclave.*

4.2 *Centrifuge.*

4.3 *Centrifuge tubes*, 50-mL capacity.

4.4 *Glass tubes with plastic caps*, disposable, 18×150 mm.

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

4.6 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 1.0 mg/L P:

Absorption cell ----- 50 mm
Wavelength -------- 880 nm or 660 nm
Cam --------------- 40/h (5/1)
Heating-bath temperature ------------- 37.5°C

5. Reagents

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

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

5.3 *Antimony potassium tartrate solution*, 3 g/L: Dissolve 3.0 g antimony potassium tartrate $K(SbO)C_4H_4O_6\cdot ½H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent*: Combine reagents in order and volumes 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 V solution* or equivalent.

5.6 *Phosphate standard solution I*, 1.00 mL = 0.100 mg P: Dissolve 0.4394 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: 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 with demineralized water. Dissolve 10 mg mercuric chloride and 120 mg sodium chloride in each working standard. For example:

Phosphate standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
1.0	.05
2.0	.10
5.0	.25
10	.50
20	1.00

5.9 *Potassium persulfate*, crystals.

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

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

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

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

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

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

6. Procedure

6.1 Follow instructions in paragraphs 6.1.1 through 6.1.4 for water or water-suspended sediment and in paragraphs 6.1.5 through 6.1.12 for bottom material.

6.1.1 Pipet a volume of well-mixed sample containing less than 0.01 mg total P (10.0 mL max) into a disposable glass tube, and adjust the volume to 10.0 mL.

6.1.2 Pipet 10.0 mL of blank and each working standard into disposable glass tubes.

6.1.3 Add 4.0 mL sulfuric acid-persulfate reagent.

6.1.4 Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 min at 15 lbs pressure. Cool and filter those samples containing sediment through a 0.45-μm membrane filter. Proceed to paragraph 6.2.

6.1.5 Accurately weigh a portion of as-received sample having a dry weight of approx 1 g. The sample must first be prepared as directed in method P-0810. Transfer the weighed sample to a 50-mL centrifuge tube and add 10 mL demineralized water.

6.1.6 On a separate portion, determine the dry weight of the sample (method P-0590).

6.1.7 Add 1.0 mL concentrated H_2SO_4 and 1.0 g potassium persulfate to each centrifuge tube.

6.1.8 Autoclave for 30 min at 15 psi pressure.

6.1.9 Centrifuge for 5 to 10 min at 5,000 rpm.

6.1.10 Transfer the supernatant solution to a 200-mL volumetric flask, taking care not to disturb the residue in the bottom of the centrifuge tube.

6.1.11 Wash the residue several times with demineralized water, adding the washings to the volumetric flask. Dilute to 200 mL with demineralized water.

6.1.12 Pipet 5.0 mL of sample, into a 100-mL volumetric flask and dilute to volume with demineralized water. Proceed to paragraph 6.2 (NOTE 1).

NOTE 1. Use blank and standards as prepared in paragraphs 6.1.2 through 6.1.4.

6.2 Set up manifold (fig. 37).

6.3 Allow colorimeter, recorder, and heating bath to warm for at least 30 min or until the temperature of the heating bath is 37.5 °C.

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

6.5 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.

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

7.3 Compute total phosphorus concentrations in each bottom-material sample as follows:

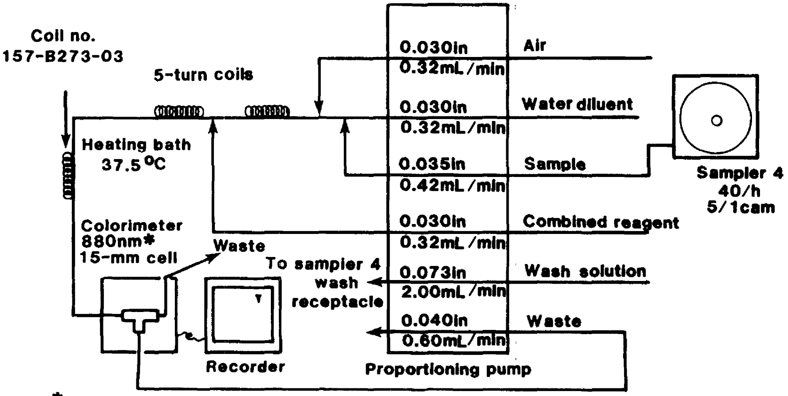
$$\text{Phosphorus (mg/kg)} = \frac{P}{5} \times \frac{20}{W} \times 1{,}000$$

where

P = concentration of phosphorus, milligrams per liter, in the sample,

and

W = dry weight, grams, of the sample.



* Alternatively 660 nm

Figure 37.—Phosphorus, phosphomolybdate manifold

8. Report

8.1 Report phosphorus, dissolved (00666), and total (00665), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

8.2 Report phosphorus, total-in-bottom-material (00668), in milligrams per kilogram, to two significant figures.

9. Precision

9.1 Precision for dissolved phosphorus for 20 samples within the range of 0.183 to 3.59 mg/L may be expressed as follows:

$$S_T = 0.189X - 0.062$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of phosphorus, milligrams per liter.

The correlation coefficient is 0.9260.

9.2 Precision for dissolved phosphorus for four of the 20 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
3	0.183	12
13	.572	8
18	1.411	9
15	3.59	19

9.3 It is estimated that the percent relative standard deviation for total phosphorus and for total phosphorus in bottom material will be greater than that reported for dissolved phosphorus.

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. 1363-8.

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. 31-6.

Phosphorus, colorimetric, phosphomolybdate, automated-discrete

Parameters and Codes:
Phosphorus, dissolved, I-2599-85 (mg/L as P): 00666
Phosphorus, total, I-4599-85 (mg/L as P): 00665

1. Application

This method may be used to analyze water, wastewater, water-suspended sediment, and brines containing from 0.01 to 2.0 mg/L phosphorus. Samples containing concentrations greater than 2.0 mg/L need to 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 and others, 1966).

2.3 Mercuric chloride-preserved samples are fortified with a minimum of 85 mg/L NaCl to overcome the interference from mercury in the analysis.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. The interference from silica, which forms a pale-blue complex, is slight 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 Arsenic as arsenate (AsO_4^{-3}) produces a color similar to that of (Murphy and Riley, 1962) and may cause a positive interference. Arsenic concentrations as much as 100 μg/L do not interfere. Greater concentrations were not investigated.

3.3 The blue color produced will coat the flow cell, causing a small but significant high bias. A 0.1-mg/L P spike is dispensed into the four leading wash tubes with the color reagent. The resulting blue color then coats the flow cell prior to the introduction of the working standards. By this action, the high bias is effectively eliminated.

4. Apparatus

4.1 *Discrete chemical analyzer system,* American Monitor IQAS or equivalent.

4.2 With this equipment, the following operating conditions have been found satisfactory:

Wavelength ---	880 nm
Absorption cell	1 cm square, temperature-controlled, flow-through quartz cuvette
Reaction temperature ---	37°C
Sample volume	0.400 mL with 0.050 mL diluent (NOTE 1)
Reagent volumes ---	0.25 mL color reagent and 0.80 mL demineralized water (NOTE 1)

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each instrument according to manufacturer's specifications.

4.3 *Autoclave.*

4.4 *Glass tubes with plastic caps,* disposable, 18 by 150 mm.

5. Reagents

5.1 *Ammonium molybdate solution,* 35.6 g/L: Dissolve 40 g ammonium molybdate,

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in 800 mL demineralized water and dilute to 1 L.

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

5.3 *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.

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

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

5.5 *Phosphate standard solution I*, 1.00 mL = 1.00 mg P: Dissolve 4.394 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate standard solution II*, 1.00 mL = 0.05 mg P: Dilute 50.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphate working standards*: Prepare a blank and 1,000 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solution II with demineralized water. Dissolve 52 mg mercuric chloride and 600 mg sodium chloride in each working standard. For example:

Standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
1.0	.05
5.0	.25
10.0	.50
20.0	1.00
40.0	2.00

5.8 *Phosphate standard solution III (spike)*, 1.00 mL = 0.0001 mg P: Dilute 2.0 mL phosphate standard solution II to 1,000 mL with demineralized water.

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

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

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

6. Procedure

6.1 Pipet a volume of well-mixed sample containing less than 0.02 mg total P (10.0 mL max) into a disposable glass tube, and adjust the volume to 10.0 mL.

6.2 Pipet 10.0 mL of blank and each working standard into disposable glass tubes.

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. Cool and filter those samples containing sediment through a 0.45-μm membrane filter.

6.5 Set up analyzer and computer-card assignments according to manufacturer's instructions.

6.6 Place standards, beginning with the lowest concentrations, in ascending order (computer-calibration curve) in the first five positions on the sample turntable. Place samples and quality-control standards in the remainder of the sample turntable.

6.7 Begin analysis. The cathode-ray tube (CRT) will acknowledge the parameter and concentration range, listing each sample-cup number and the corresponding concentrations calculated from the working curve. During each run, the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from printer.

7. Calculations

Determine the concentration in milligrams per liter of dissolved or total phosphorus in each sample from either the CRT display or the printer output.

8. Report

Report phosphorus, dissolved (00666), and total (00665), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the standard deviation and percent relative standard deviation for replicate analysis of reference materials by a single operator is as follows:

Mean (mg/L)	Number of replicates	Standard deviation (mg/L)	Relative standard deviation (percent)
0.142	27	0.009	6.34
.551	25	.009	1.63
.750	25	.009	1.20
1.00	25	.015	1.50
1.72	22	.007	.41
2.00	25	.027	1.35

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. 1363-8.

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. 31-6.

Phosphorus, orthophosphate plus hydrolyzable, colorimetric, phosphomolybdate

Parameter and Code:

Phosphorus, orthophosphate plus hydrolyzable, dissolved, I-1602-85 (mg/L as P): 00677

1. Application

This method may be used to analyze most water and wastewater containing between 0.02 and 0.4 mg/L of dissolved orthophosphate plus hydrolyzable phosphorus. Samples containing greater concentrations need to be diluted.

2. Summary of method

2.1 As far as is known, the phosphomolybdate method is specific for the orthophosphate form of phosphorus. Weak tests are reported with pyrophosphate and polyphosphates, but these positive tests may well result from orthophosphate contamination of the material.

2.2 Acid hydrolyzable phosphorus is decomposed to orthophosphate by sulfuric acid digestion. Orthophosphate is then converted to phosphomolybdate by acidified ammonium molybdate reagent:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21H^{+1} \rightarrow$$

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^{+1} + 12H_2O$$

2.3 When phosphomolybdate is reduced with ascorbic acid in the presence of antimony (Murphy and Riley, 1962), an intense blue complex is developed that absorbs light at 882 nm. The reduction is not instantaneous, nor is the developed color stable. The full color develops in 6 to 10 min and fades gradually thereafter.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. Silica gives a pale-blue color that is additive to the phosphate color and may require correction. The effect of silica is somewhat dependent on the reagents; therefore, an appropriate silica correction should be determined for each batch of reagents. Nitrite interferes, but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples are fortified with a minimum of 85 mg/L NaCl to overcome this interference.

3.3 Arsenic as arsenate (AsO_4^{-3}) produces a color similar to that of phosphate (Murphy and Riley, 1962) and may cause a positive interfere. Arsenic concentrations as much as 100 μg/L do not interfere. Greater concentrations were not investigated.

4. Apparatus

Spectrometer for use at 700 or 882 nm.

5. Reagents

5.1 *Antimony tartrate-ammonium molybdate solution*: Dissolve 0.13 g antimony potassium tartrate, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, in about 700 mL demineralized water contained in a 1-L volumetric flask. Add 5.6 g ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and shake flask until dissolved. *Cautiously*, add 70 mL concentrated H_2SO_4 (sp gr 1.84) while swirling the contents of the flask. Cool and dilute to volume. Mix thoroughly by repeated inversion and swirling. This solution is stable for at least 1 year if stored in a polyethylene bottle away from heat.

5.2 *Combined reagent solution*: Dissolve 0.50 g ascorbic acid in 100 mL antimony tartrate-ammonium molybdate solution. This reagent is stable for at least 1 week if stored at 4 °C; otherwise prepare fresh daily.

5.3 *Phenolphthalein indicator solution*, 0.5 g/100 mL: Dissolve 0.5 g phenolphthalein in 100 mL 50-percent ethanol.

5.4 *Phosphate standard solution I*, 1.00 mL = 0.050 mg P: Dissolve 0.2197 g KH_2PO_4, dried overnight over H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.5 *Phosphate standard solution II*, 1.00 mL = 0.001 mg P: Dilute 20.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.6 *Sodium hydroxide*, 3*M*: *Carefully*, with cooling, dissolve 120 g NaOH in demineralized water and dilute to 1 L.

5.7 *Sulfuric acid*, 6*M*: *Cautiously*, add slowly, with constant stirring and cooling, 330 mL concentrated H_2SO_4 (sp gr 1.84) to 600 mL demineralized water and dilute to 1 L.

5.8 *Sulfuric acid*, 0.25*M*: *Cautiously*, add slowly, with constant stirring and cooling, 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.020 mg P (50.0 mL max) into a 125-mL Erlenmeyer flask, and adjust the volume to 50.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 mL (NOTE 1).

NOTE 1. If the samples were preserved with mercuric chloride fortified with sodium chloride, add an equivalent amount to the blank and standards.

6.3 Add 1.0 mL 6*M* H_2SO_4. Boil gently on a hotplate until the volume is reduced to about 10 mL.

6.4 Cool. Add 2 drops phenolphthalein indicator solution and neutralize with 3*M* NaOH, and then *carefully* add 0.25*M* H_2SO_4 until the pink color just disappears. Transfer to a 50-mL volumetric flask and dilute to the mark with demineralized water.

6.5 Add 10 mL combined reagent to each sample, blank, and standard, and mix.

6.6 After 10 min measure absorbance of each sample and standard against that of the blank at either 882 or 700 nm.

7. Calculations

7.1 Determine the milligrams of phosphorus in each sample from a plot of absorbances of standards.

7.2 Determine the phosphorus concentration in milligrams per liter as follows:

$$\text{P in mg/L} = \frac{1{,}000}{\text{mL sample}} \times \text{mg P in sample}$$

8. Report

Report phosphorus, orthophosphate plus hydrolyzable, dissolved (00677), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for dissolved orthophosphate plus hydrolyzable phosphorus will be equal to that reported for dissolved phosphorus.

Reference

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. 31-6.

Phosphorus, orthophosphate plus hydrolyzable, colorimetric, phosphomolybdate, automated-segmented flow

Parameters and Codes:

Phosphorus, orthophosphate plus hydrolyzable, dissolved, I-2602-85 (mg/L as P): 00677
Phosphorus, orthophosphate plus hydrolyzable, total, I-4602-85 (mg/L as P): 00678

1. Application

This method may be used to analyze most water, brines, and water-suspended sediment containing between 0.01 and 1.0 mg/L combined acid hydrolyzable and orthophosphate-phosphorus. Samples containing greater concentrations need to 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 and others, 1966).

2.3 Mercuric chloride-preserved samples are fortified with a minimum of 85 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 usually negligible in natural waters. The interference from silica, which forms a pale-blue complex, is slight 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 color similar to that of phosphate (Murphy and Riley, 1962) and may cause a positive interference. Arsenic concentrations as much as 100 µg/L do not interfere. Greater concentrations were not investigated.

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 1.0 mg/L combined hydrolyzable and orthophosphate-phosphorus:

Absorption cell -----	50 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 × 150 mm.

5. Reagents

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

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

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

5.4 *Combined working reagent*: Combine reagents in order and volumes 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 V solution* or equivalent.

5.6 *Phosphate standard solution I*, 1.00 mL = 0.100 mg P: Dissolve 0.4394 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: 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 10 mg mercuric chloride and 120 mg sodium chloride in each working standard. For example:

Phosphate standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
1.0	.05
2.0	.10
5.0	.25
10	.50
20	1.00

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

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

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

6. Procedure

6.1 Pipet a volume of well-mixed sample containing less than 0.01 mg combined hydrolyzable and orthophosphate-phosphorus (10.0 mL max) into a disposable glass tube and adjust the volume to 10.0 mL.

6.2 Pipet 10.0 mL of blank and each working standard into disposable glass tubes.

6.3 Add 2.0 mL 0.45*M* sulfuric acid.

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

6.5 Set up manifold (fig. 38).

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

6.7 Adjust the baseline to read zero scale divisions on the recorder for 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.

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

8. Report

Report phosphorus, orthophosphate plus hydrolyzable, dissolved (00677), and total (00678), concentrations as follows: less than 1

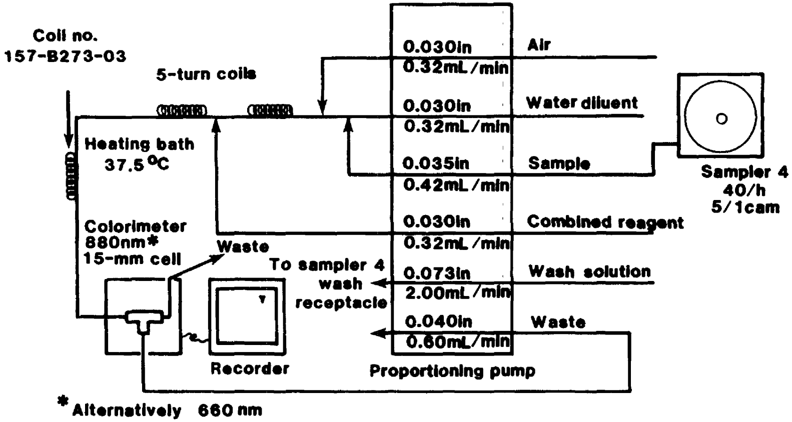


Figure 38.—Phosphorus, phosphomolybdate manifold

mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for dissolved and total orthophosphate plus hydrolyzable phosphorus will be equal to that reported for phosphorus by the automated phosphomolybdate method.

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. 1363-8.

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. 31-6.

Phosphorus, orthophosphate, colorimetric, phosphomolybdate

Parameter and Code:

Phosphorus, orthophosphate, dissolved, I-1601-85 (mg/L as P): 00671

1. Application

This method may be used to analyze most water and wastewater containing between 0.02 and 0.4 mg/L of orthophosphate-phosphorus. Samples containing greater concentrations need to be diluted.

2. Summary of method

2.1 As far as is known, the phosphomolybdate method is specific for the orthophosphate form of phosphorus. Weak tests are reported with pyrophosphate and polyphosphates, but these positive tests may well result from orthophosphate contamination of the material.

2.2 Orthophosphate is converted to phosphomolybdate by acidified ammonium molybdate reagent:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21H^{+1} \rightarrow$$

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^{+1} + 12H_2O$$

2.3 When phosphomolybdate is reduced with ascorbic acid in the presence of antimony (Murphy and Riley, 1962), an intense blue complex is developed that absorbs light at 882 nm. The reduction is not instantaneous, nor is the developed blue color stable. The full color develops in 6 to 10 min and fades gradually thereafter.

3. Interferences

3.1 Barium, lead, and silver interfere by forming a precipitate. Silica produces a pale-blue color that is additive to the phosphate color, and may require correction. The effect of silica is somewhat dependent on the reagents; therefore, an appropriate silica correction should be determined for each batch of reagents. Nitrite interferes but can be oxidized to nitrate with hydrogen peroxide before analysis. Residual chlorine must be removed by boiling the sample.

3.2 Mercuric chloride interferes when the chloride concentration is less than 50 mg/L. Mercuric chloride-preserved samples are fortified with a minimum of 85 mg/L NaCl to overcome this interference.

3.3 Arsenic as arsenate (AsO_4^{-3}) produces a color similar to that of phosphate (Murphy and Riley, 1962) and may cause a positive interference. Arsenic concentrations as much as 100 μg/L do not interfere. Greater concentrations were not investigated.

4. Apparatus

Spectrometer for use at 700 or 882 nm.

5. Reagents

5.1 *Antimony tartrate-ammonium molybdate solution*: Dissolve 0.13 g antimony potassium tartrate, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, in about 700 mL demineralized water contained in a 1-L volumetric flask. Add 5.6 g ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and shake flask until dissolved. *Cautiously*, add 70 mL concentrated H_2SO_4 (sp gr 1.84) while swirling the contents of the flask. Cool and dilute to volume. Mix thoroughly by repeated inversion and swirling. This solution is stable for at least 1 year if stored in a polyethylene bottle away from heat.

5.2 *Combined reagent solution*: Dissolve 0.50 g ascorbic acid in 100 mL antimony tartrate-ammonium molybdate solution. This reagent is stable for at least 1 week if stored at 4°C; otherwise prepare fresh daily.

5.3 *Phosphate standard solution I*, 1.00 mL = 0.050 mg P: Dissolve 0.2197 g KH_2PO_4, dried overnight over H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.4 *Phosphate standard solution II*, 1.00 mL = 0.001 mg P: Dilute 20.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.020 mg P (50.0 mL max) into a 100-mL beaker, and adjust the volume to 50.0 mL.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 mL (NOTE 1).

NOTE 1. If the samples were preserved with mercuric chloride fortified with sodium chloride, add an equivalent amount to the blank and standards.

6.3 Add 10 mL combined reagent solution to each sample, blank, and standard, and mix.

6.4 After 10, but before 30, min measure absorbance of each sample and standard against that of the blank at either 882 or 700 nm.

7. Calculations

7.1 Determine the milligrams of phosphorus in each sample from a plot of absorbances of standards.

7.2 Determine the phosphorus concentration in milligrams per liter as follows:

$$\text{P (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times \text{mg P in sample}$$

8. Report

Report phosphorus, orthophosphate, dissolved (00671), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved orthophosphate-phosphorus for nine samples within the range of 0.000 to 1.70 mg/L may be expressed as follows:

$$S_T = 0.114\,X + 0.004$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of orthophosphate-phosphorus, milligrams per liter.

The correlation coefficient is 0.9067.

9.2 Precision for dissolved orthophosphate-phosphorus for five of the nine samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
11	0.000	0
12	.008	62
15	.406	11
11	1.02	8
14	1.70	13

Reference

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. 31–6.

Phosphorus, orthophosphate, colorimetric, phosphomolybdate, automated-segmented flow

Parameters and Codes:

Phosphorus, orthophosphate, dissolved, I-2601-85 (mg/L as P): 00671
Phosphorus, orthophosphate, total, I-4601-85 (mg/L as P): 70507

1. Application

1.1 This method may be used to analyze most water, wastewater, brines, and water-suspended sediment containing between 0.01 and 1.0 mg/L orthophosphate-phosphorus.

1.2 Total orthophosphate-phosphorus is determined by allowing the suspended sediment in an unfiltered, unacidified sample to settle in the sample bottle and by decanting a portion of the clear supernatant solution 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 and others, 1966).

2.2 Mercuric chloride-preserved samples are fortified with a minimum of 85 mg/L NaCl to overcome the interference from mercury in the analysis.

3. Interferences

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

3.2 Barium, lead, and silver interfere by forming a phosphate precipitate, but the effect is usually negligible in natural waters. The interference from silica, which forms a pale-blue complex, is slight 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 color similar to that of phosphate (Murphy and Riley, 1962) and may cause a positive interference. Arsenic concentrations as much as 100 μg/L do not interfere. Greater concentrations were not investigated.

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 1.0 mg/L P:

Absorption cell -----	50 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, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent:* Combine reagents together in order and volumes listed below. This reagent is stable for about 8 hr:

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 V solution* or equivalent.

5.6 *Phosphate* standard solution I, 1.00 mL = 0.100 mg P: Dissolve 0.4394 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: 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 10 mg mercuric chloride and 120 mg sodium chloride in each working standard. For example:

Phosphate standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
1.0	.05
2.0	.10
5.0	.25
10	.50
20	1.00

5.9 *Sulfuric acid,* 2.45*M*: *Cautiously,* add slowly, with constant stirring and cooling, 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 V and dilute to 1 L with demineralized water.

6. Procedure

6.1 Set up manifold (fig. 39).

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

6.3 Adjust the baseline to read zero scale divisions on the recorder for 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

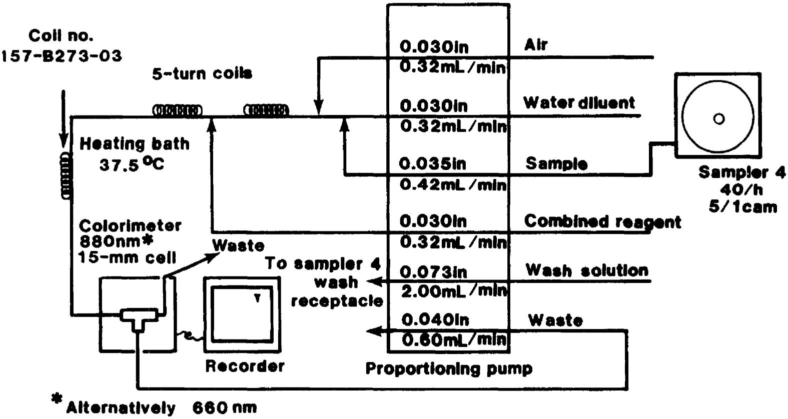


Figure 39.—Phosphorus, phosphomolybdate manifold

concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples (NOTE 1).

NOTE 1. For water-suspended sediment, 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 dissolved or total 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, orthophosphate, dissolved (00671), and total (70507), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved orthophosphate-phosphorus for 9 samples within the range of 0.007 to 1.93 mg/L may be expressed as follows:

$$S_T = 0.106X + 0.015$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of orthophosphate-phosphorus, milligrams per liter.

The correlation coefficient is 0.8580.

9.2 Precision for dissolved orthophosphate-phosphorus for four of the nine samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
3	0.007	86
20	.404	11
18	1.07	10
17	1.93	13

9.3 It is estimated that the percent relative standard deviation for total orthophosphate-phosphorus will be equal to or greater than that reported for dissolved orthophosphate-phosphorus.

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. 1363-8.

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. 31-6.

Phosphorus, orthophosphate, colorimetric, phosphomolybdate, automated-discrete

Parameters and Codes:

Phosphorus, orthophosphate, dissolved, I-2598-85 (mg/L as P): 00671
Phosphorus, orthophosphate, total, I-4598-85 (mg/L as P): 70507

1. Application

1.1 This method may be used to analyze water, wastewater, brines, and water-suspended sediment containing from 0.01 to 2.0 mg/L orthophosphate-phosphorus. Samples containing concentrations greater than 2.0 mg/L need to be diluted.

1.2 To determine total orthophosphate-phosphorus, 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 and others, 1966).

2.2 Mercuric chloride-preserved samples are fortified with a minimum of 85 mg/L NaCl to overcome the interference from mercury in the analysis.

3. Interferences

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

3.2 Barium, lead, and silver interfere by forming a precipitate. The interference from silica, which forms a pale-blue complex, is slight 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 Arsenic as arsenate (AsO_4^{-3}) produces a color similar to that of phosphate (Murphy and Riley, 1962) and may cause a positive interference. Arsenic concentrations up to 100 µg/L do not interfere. Greater concentrations were not investigated.

3.4 The blue color produced will coat the flow cell, causing a small but significant high bias. A 0.10-mg/L P spike is dispensed into the four leading wash tubes with the color reagent. The resulting blue color then coats the flow cell prior to the introduction of the working standards. By this action, the high bias is effectively eliminated.

4. Apparatus

4.1 *Discrete chemical analyzer system*, American Monitor IQAS or equivalent.

4.2 With this equipment, the following operating conditions have been found satisfactory:

Wavelength --	880 nm
Absorption cell	1-cm square, temperature-controlled, flow-through quartz cuvette
Reaction temperature	37 °C
Sample volume	0.300 mL with 0.050 mL of diluent (NOTE 1)

Reagent volumes	0.25 mL color reagent and 0.80 mL demineralized water (NOTE 1)

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each instrument according to manufacturer's specifications.

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

5.3 *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.

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

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

5.5 *Phosphate standard solution I*, 1.00 mL = 1.00 mg P: Dissolve 4.394 g KH_2PO_4, dried overnight over concentrated H_2SO_4 (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.6 *Phosphate standard solution II*, 1.00 mL = 0.05 mg P: Dilute 50.0 mL phosphate standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphate working standards*: Prepare a blank and 1,000 mL each of a series of phosphate working standards by appropriate quantitative dilution of phosphate standard solution II with demineralized water. Dissolve 52 mg mercuric chloride and 600 mg sodium chloride in each working standard. For example:

Standard solution II (mL)	Orthophosphate-phosphorus concentration (mg/L)
0.0	0.00
1.0	.05
5.0	.25
10.0	.50
20.0	1.00
40.0	2.00

5.8 *Phosphate standard solution III (spike)*, 1.00 mL = 0.0001 mg P: Dilute 2.0 mL of phosphate standard solution II to 1,000 mL with demineralized water.

6. Procedure

6.1 Set up analyzer and computer-card assignments according to manufacturer's instructions.

6.2 Place standards, beginning with the lowest concentrations, in ascending order (computer-calibration curve) in the first five positions on the sample turntable. Place samples and quality-control standards in the remainder of the sample turntable.

6.3 Begin analysis. The cathode-ray tube (CRT) will acknowledge the parameter and concentration range, listing each sample-cup number and the corresponding concentration calculated from the working curve. During each run, the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from printer.

7. Calculations

Determine the concentration in milligrams per liter of dissolved or total orthophosphate-phosphorus in each sample from either the CRT display or the printer output.

8. Report

Report phosphorus, orthophosphate, dissolved (00671), and total (70507), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the standard deviation and percent relative standard deviation for replicate analysis of reference materials by a single operator is as follows:

Mean (mg/L)	Number of replicates	Standard deviation (mg/L)	Relative standard deviation (percent)
0.030	30	0.004	13.3
.152	30	.004	2.63
.737	24	.013	1.76
1.71	24	.009	.53
2.01	30	.017	.84

Phosphorus, orthophosphate, ion-exchange chromatographic, automated

Parameters and Codes:

Phosphorus, orthophosphate, dissolved, I-2057-85 (mg/L as P): 00671
Phosphorus, orthophosphate, dissolved, I-2058-85 (mg/L as P): 00671

2. Summary of method

Orthophosphate is determined sequentially with six other anions by ion-exchange chromatography. Ions are separated based on their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical-conductivity cell. See method I-2057, anions, ion-exchange chromatographic, automated, and I-2058, anions, ion-exchange chromatographic, precipitation, automated.

Phosphorus, hydrolyzable and organic, calculation

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

1. Application

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

Parameters	Method No.
Phosphorus, orthophosphate, dissolved	I-1601 or I-2601 or I-2598
Phosphorus, orthophosphate, total	I-4601 or I-4598
Phosphorus, orthophosphate plus hydrolyzable, dissolved	I-1602 or I-2602
Phosphorus, orthophosphate plus hydrolyzable, total	I-4602
Phosphorus, dissolved	I-1600 or I-2600 or I-2599
Phosphorus, total	I-4600 or I-4599

2. Summary of method

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

7. Calculations

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

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

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

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

8. Report

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

9. Precision

See the individual methods: phosphorus, orthophosphate, dissolved or total; phosphorus, orthophosphate plus hydrolyzable, dissolved or total; and phosphorus, dissolved or total. Precision will depend on the precision obtained for each method.

Potassium, atomic absorption spectrometric, direct

Parameters and Codes:

Potassium, dissolved, I-1630-85 (mg/L as K): 00935
Potassium, total recoverable, I-3630-85 (mg/L as K): none assigned
Potassium, recoverable-from-bottom-material, dry wt, I-5630-85 (mg/kg as K): 00938

1. Application

1.1 This method may be used to analyze atmospheric precipitation, water, brines, and water-suspended sediment.

1.2 Two analytical ranges for potassium are included: from 0.01 to 1.0 mg/L and from 0.10 to 10.0 mg/L. Sample solutions containing potassium concentrations greater than 10 mg/L need to be diluted.

1.3 This method may be used to analyze bottom material containing at least 10 mg/kg of potassium.

1.4 Total recoverable potassium in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485 and recoverable potassium in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

2.1 Potassium is determined by atomic absorption spectrometry by direct aspiration of the sample solution into an air-acetylene flame (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer.

3. Interferences

3.1 Of the substances commonly occurring in water, only sodium has been found to interfere, and its interference is greatly minimized if a reducing flame is used and the burner is raised to approximately 0.05 cm below the optical light path. The following data are indicative of the magnitude of sodium interference under these conditions:

Potassium added (mg/L)	Sodium added (mg/L)	Potassium found (mg/L)
1.00	0.0	1.00
1.00	100	1.03
1.00	500	1.05
1.00	1,000	1.07

3.2 Alternatively, an excess of sodium or cesium may be added to all samples and standards. Such additions essentially eliminate the effects of the then comparatively minor contributions of sodium present in the samples.

4. Apparatus

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

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

Grating ------------	Visible
Wavelength --------	766.5 nm
Source (hollow-cathode lamp) ------------	Potassium
Oxidant ------------	Air
Fuel ----------------	Acetylene
Type of flame -------	Slightly reducing

4.3 The 50-mm (2-in.), flathead, single-slot burner allows working ranges of 0.01 to 1.0 mg/L and 0.1 to 10 mg/L. The burner, rotated 90°, extends the range to 100 mg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Potassium standard solution I*, 1.00 mL = 0.100 mg K: Dissolve 0.1907 g KCl, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Potassium working standards*: Prepare a series of at least six working standards containing either from 0.01 to 1.0 mg/L or from 0.1 to 10.0 mg/L of potassium by appropriate dilution of potassium standard solution I.

6. Procedure

While aspirating the blank use the automatic zero control to set the digital display to read zero concentration. While aspirating standards use the automatic concentration control to set the digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the milligrams per liter of dissolved or total recoverable potassium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing potassium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine milligrams per kilogram of potassium in bottom-material samples, first determine the milligrams per liter of potassium as in paragraph 7.1; then:

$$\text{K (mg/kg)} = \frac{\text{mg/L K} \times \dfrac{\text{mL original digest}}{1000}}{\text{wt of sample (kg)}}$$

8. Report

8.1 Report potassium, dissolved (00935), and total recoverable (none assigned), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 to 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

8.2 Report potassium, recoverable-from-bottom-material (00938), concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

9.1 Precision for dissolved potassium for 36 samples within the range of 0.09 to 26.1 mg/L may be expressed as follows:

$$S_T = 0.113X - 0.050$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of potassium, milligrams per liter.

The correlation coefficient is 0.9350.

9.2 Precision for dissolved potassium for five of the 36 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
24	0.09	55
17	2.48	10
32	5.20	11
23	11.7	8
19	26.1	13

9.3 Precision for dissolved potassium within the range of 0.01 to 1.0 mg/L in terms of the percent relative standard deviation by a single operator is as follows:

Number of replicates	Mean (mg/L)	Relative standard deviation (percent)
18	0.023	38.9
12	.078	9.7
11	.358	2.7
10	.585	1.8
11	1.02	4.6

9.4 It is estimated that percent relative standard deviation for total recoverable potassium and for recoverable potassium from bottom material will be greater than that reported for dissolved potassium.

Reference

Fishman, M. J., and Downs, S. C., 1966, Method for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 36-8.

Potassium, atomic absorption spectrometric, direct-EPA

Parameter and Code:

Potassium, total recoverable, I-3631-85 (mg/L as K): 00937

1. Application

1.1 This method may be used to analyze water-suspended sediment. Sample solutions containing from 0.1 to 100 mg/L of potassium may be analyzed without dilution, but those containing more than 100 mg/L need to be diluted.

1.2 For ambient water, analysis may be made on a portion of the acidified water-suspended sediment sample.

1.3 For all other water, including domestic and industrial effluent, the atomic absorption procedure must be preceded by a digestion-solubilization as specified below. In cases where the analyst is uncertain about the type of sample, the digestion-solubilization procedure must be used.

2. Summary of method

2.1 Potassium is determined by atomic absorption spectrometry by direct aspiration of the filtered or digested and filtered sample into an air-acetylene flame (Fishman and Downs, 1966).

2.2 Effluent samples must undergo a preliminary nitric acid digestion followed by a hydrochloric acid solubilization.

3. Interferences

3.1 Of the substances commonly occurring in water, only sodium has been found to interfere, and its interference is greatly minimized if a reducing flame is used and the burner is raised to approximately 0.05 cm below the optical light path. The following data are indicative of the magnitude of sodium interference under these conditions:

Potassium added (mg/L)	Sodium added (mg/L)	Potassium found (mg/L)
1.00	0.0	1.00
1.00	100	1.03
1.00	500	1.05
1.00	1,000	1.07

3.2 Alternatively, an excess of sodium or cesium may be added to all samples and standards. Such additions essentially eliminate the effects of the then comparatively minor contributions of sodium present in the samples.

4. Apparatus

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

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

Grating ------------	Visible
Wavelength ---------	766.5 nm
Source (hollow-cathode lamp) ------------	Potassium
Oxidant ------------	Air
Fuel ----------------	Acetylene
Type of flame -------	Slightly reducing

4.3 The 50-mm (2-in.), flathead, single-slot burner allows a working range of 0.1 to 10 mg/L. The burner, rotated 90°, extends the range to 100 mg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Hydrochloric acid, 6M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.2 *Hydrochloric acid, 0.3M*: Dilute 25 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

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

5.4 *Potassium standard solution I*, 1.00 mL = 0.100 mg K: Dissolve 0.1907 g KCl, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.5 *Potassium working standards*: Prepare a series of at least six working standards containing from 0.1 to 100 mg/L of potassium by appropriate dilution of potassium standard solution.

6. Procedure

6.1 Transfer the entire sample to a beaker.

6.2 Rinse the sample bottle with 3 mL concentrated HNO_3 for each 100 mL of sample and add to the beaker. Prepare a blank using 3 mL concentrated HNO_3 per 100 mL demineralized water.

6.3 Evaporate samples and blank to dryness on a hotplate, making sure the samples do not boil.

6.4 Cool and add an additional 3 mL concentrated HNO_3 to each beaker. Cover with a watchglass, return to the hotplate, and gently reflux the samples.

6.5 Continue heating, adding additional acid as necessary, until the digestion is complete (indicated by a light-colored residue). Evaporate just to dryness.

6.6 Add 6 mL 6*M* HCl solution per 100 mL original sample and warm the beaker to dissolve the residue.

6.7 Wash the watchglass and beaker with demineralized water and filter the sample (Whatman No. 41 or equivalent), rinsing the filter with hot 0.3*M* HCl. Dilute to the original volume with demineralized water.

6.8 While aspirating the blank use the automatic zero control to set the digital display to read zero concentration. While aspirating standards use the automatic concentration control to set the digital display to read the concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

Determine the milligrams per liter of total recoverable potassium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing potassium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report potassium, total-recoverable (00937), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for total recoverable potassium over the range of the method will be greater than 13 percent.

References

Fishman, M. J., and Downs, S. C., 1966, Method for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 36-8.

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 258.1-1.

Potassium, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:

Potassium, total, I-5473-85 (mg/kg as K): none assigned
Potassium, total, I-5474-85 (mg/kg as K): none assigned

2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The sample is then treated and analyzed by one of the following techniques.

2.1.1 The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1000°C. The resulting bead is dissolved in acidified, boiling, demineralized water, and potassium is determined by atomic absorption spectrometry. See method I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

2.1.2 The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hot plate at 200°C. Potassium is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Selenium, atomic absorption spectrometric, hydride

Parameters and Codes:

Selenium, dissolved, I-1667-85 (μg/L as Se): 01145
Selenium, total, I-3667-85 (μg/L as Se): 01147
Selenium, suspended total, I-7667-85 (μg/L as Se): 01146
Selenium, total-in-bottom-material, dry wt, I-5667-85 (μg/g as Se): 01148

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 1 μg/L of selenium. Samples containing more than 20 μg/L need to be diluted.

1.2 Suspended total selenium is calculated by subtracting dissolved selenium from total selenium.

1.3 This method may be used to analyze bottom material containing at least 1 μg/g of selenium. Usually a 100-mg sample of prepared bottom material (method P-0520) is taken for analysis. However, if the sample contains more than 20 μg/g of selenium, a smaller sample needs to be used.

1.4 Total selenium in water-suspended sediment may be determined after each sample has been thoroughly mixed by vigorous shaking and a suitable sample portion has been rapidly withdrawn from the mixture.

2. Summary of method

Organic selenium compounds, if present, are first decomposed by digestion with potassium permanganate in hot acidic solution. The solution is then made basic and evaporated to dryness in the presence of calcium chloride to prevent loss of selenate during the evaporation. Hydrochloric acid is added to the residue to reduce the selenate to selenite. Quantitative reduction without loss of selenium requires control of the temperature, time, and acid concentration. All selenium must be in the selenite form prior to its final reduction with stannous chloride in 6*M* hydrochloric acid solution. The selenium hydride so formed is subsequently removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame where it is determined by atomic absorption at 196.0 nm (Freeman and Uthe, 1974; Lansford and others, 1974).

3. Interferences

3.1 Arsenic interferes by suppressing the selenium absorption if an excess of stannous chloride is used. This interference can be avoided by carefully controlling the amount of stannous chloride added. If 42 mg stannous chloride is added, as much as 150 μg/L of arsenic can be tolerated. At least this amount must be added, however, to ensure efficient reduction of selenite to the hydride.

3.2 Mercury interferes when its concentration exceeds 25 μg/L.

4. Apparatus

4.1 *Atomic absorption spectrometer.*

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

Grating ------------	Ultraviolet
Wavelength --------	196.0 nm
Source (electrodeless discharge lamp) ---	Selenium
Burner ------------	Three-slot
Fuel ---------------	Hydrogen
Diluent ------------	Nitrogen
Carrier ------------	Nitrogen

4.3 *Selenium hydride vapor analyzer* (fig. 40) consisting of —

4.3.1 *Fleaker*, 300-mL capacity, or beaker, Berzelius, 200-mL capacity.

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

4.3.3 *Medicine dropper*, 2-mL capacity min.

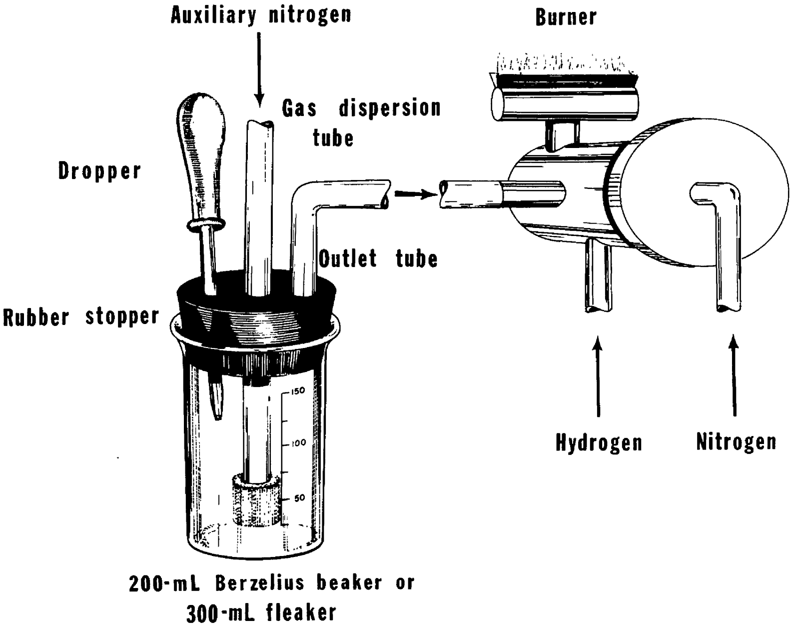


Figure 40.—Selenium hydride vapor analyzer

5. **Reagents**

5.1 *Ammonium chloride solution*, 250 g/L: Dissolve 250 g NH_4Cl in demineralized water and dilute to 1 L.

5.2 *Calcium chloride solution*, 22.6 g/L: Dissolve 30 g $CaCl_2 \cdot 2H_2O$ in demineralized water and dilute to 1 L.

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

5.4 *Hydrochloric acid*, 6*M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.5 Hydrochloric acid, 0.1*M*: Dilute 8 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.6 *Methyl orange indicator solution*, 50 mg/100 mL: Dissolve 50 mg methyl orange in 100 mL demineralized water.

5.7 *Potassium permanganate solution*, 0.3 g/L: Dissolve 0.3 g $KMnO_4$ in 1 L demineralized water.

5.8 *Selenium standard solution I*, 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 1000 mL with demineralized water.

5.9 *Selenium standard solution II*, 1.00 mL = 10.0 µg Se: Dilute 10.0 mL selenium standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 1000 mL with demineralized water. Discard after 3 months.

5.10 *Selenium standard solution III*, 1.00 mL = 0.100 µg 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.

5.11 *Sodium hydroxide solution*, 0.1*M*: Dissolve 4 g NaOH in demineralized water and dilute to 1 L.

5.12 *Stannous chloride solution*, 4.2 g/100 mL concentrated HCl: Dissolve 5 g $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl (sp gr 1.19). This solution is unstable. Prepare fresh daily.

6. Procedure

6.1 Follow instructions in paragraph 6.1.1 for waters and water-suspended sediment mixtures and in paragraph 6.1.2 for bottom materials.

6.1.1 Pipet a volume of well-mixed sample containing less than 2.0 μg Se (100 mL max) into a 300-mL fleaker and dilute to 100 mL.

6.1.2 Weigh a portion of prepared bottom-material sample containing less than 2.0 μg Se (100 mg max); transfer to a 300-mL fleaker and add 100 mL demineralized water (NOTE 1). Stir to mix thoroughly and allow to settle.

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

6.2 Prepare, in 300-mL fleakers, a blank and sufficient standards containing from 0.1 to 2.0 μg Se by diluting 1.0- to 20.0-mL portions of selenium standard solution III. Dilute each to approx 100 mL.

6.3 To each fleaker add 1 drop methyl orange, 0.5 mL $CaCl_2$ solution, and a boiling chip or several glass beads.

6.4 To the fleakers containing the blank and standards, add 0.5 mL 0.1*M* HCl.

6.5 To the fleakers containing the samples, titrate with 0.1*M* HCl until the indicator shows a distinct red color and then add 0.5 mL excess (NOTE 2).

NOTE 2. If the water or water-suspended sediment samples have been acidified either at the time of collection or in the laboratory, titrate with 2*M* NaOH until the indicator shows a distinct yellow-orange color and then continue with paragraph 6.5. When the presence of interferences makes it impossible to adjust the pH with use of methyl orange, use a pH meter for this adjustment.

6.6 Add 3 drops $KMnO_4$ solution to each fleaker and heat to boiling on a hotplate, adding $KMnO_4$ as required to maintain a purple tint. If a precipitate of MnO_2 forms at this point, it will have no adverse effect.

6.7 After the volume has been reduced to approx 50 mL, add 2 mL 0.1*M* NaOH; evaporate to dryness, and allow the fleakers to cool. Avoid prolonged heating of the residue.

6.8 Add 5 mL concentrated HCl and 10 mL NH_4Cl solution. Heat in a boiling-water or steam bath for 20 + 0.5 min (NOTE 3).

NOTE 3. Samples can be heated on a hotplate at low temperature if boiling can be prevented.

6.9 Dilute each sample, blank, and standard to approx 100 mL with 6*M* HCl.

6.10 Attach one fleaker at a time to the rubber stopper containing the gas dispersion tube.

6.11 Fill the medicine dropper with 1 mL $SnCl_2$ solution and insert into hole in rubber stopper.

6.12 Add the $SnCl_2$ solution to the sample solution. After the absorbance has reached a maximum and has returned to the baseline, remove the fleaker. Rinse the gas dispersion tube in demineralized water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

7. Calculations

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

7.2 Determine the concentration of dissolved or total selenium in each sample as follows:

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

7.3 To determine the concentration of total suspended selenium, subtract dissolved-selenium concentration from total-selenium concentration.

7.4 Determine the concentration of selenium in air-dried bottom-material samples as follows:

$$\text{Se } (\mu g/g) = \frac{\mu g \text{ Se in sample}}{\text{wt of sample (g)}}$$

8. Report

8.1 Report selenium, dissolved (01145), total (01147), and suspended-total (01146), concentrations as follows: less than 100 μg/L, nearest microgram per liter; 100 μg/L and above, two significant figures.

8.2 Report selenium, total-in-bottom-material (01148), concentrations as follows: less than 100 μg/g, to the nearest microgram per gram; 100 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved selenium for 14 samples within the range of 2 to 42 μg/L may be expressed as follows:

$$S_T = 0.484X - 1.447$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of selenium, micrograms per liter.

The correlation coefficient is 0.9412.

9.2 Precision for dissolved selenium for five of the 14 samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
5	2.0	0
7	3.6	27
3	9.0	29
5	19	47
5	42	50

9.3 It is estimated that the percent relative standard deviation for total and suspended selenium and for total selenium in bottom material will be greater than that reported for dissolved selenium.

9.4 Precision for total selenium expressed in terms of the percent relative standard deviation for one water-suspended sediment mixture is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
8	6.5	34

References

Freeman, H. C., and Uthe, J. F., 1974, An improved hydride generation apparatus for determining arsenic and selenium by atomic absorption spectrometry: Atomic Absorption Newsletter, v. 13, p. 75-6.

Lansford, Myra, McPherson, E. M., and Fishman, M. J., 1974, Determination of selenium in water: Atomic Absorption Newsletter, v. 13, p. 103-5.

Selenium, atomic absorption spectrometric, hydride, automated

Parameters and Codes:
Selenium, dissolved, I-2667-85 (μg/L as Se): 01145
Selenium, total, I-4667-85 (μg/L as Se): 01147
Selenium, suspended total, I-7667-85 (μg/L as Se): 01146
Selenium, total-in-bottom-material, dry wt, I-6667-85 (μg/g as Se): 01148

1. Application

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

1.2 Suspended total selenium is calculated by subtracting dissolved selenium from total selenium.

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

1.4 This method may be used to analyze bottom material containing at least 1 μg/g of selenium. For samples containing more than 5.6 μg/g, use less sediment. The amount of sediment that can be used is limited to 40-mg dry weight because, if greater amounts are used, selenium will not be recovered completely from some organic selenium compounds such as diphenyl selenide.

1.5 Bottom material may be analyzed by this procedure after it has 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, with inorganic selenium originally present, is then reduced to the tetravalent state using a stannous chloride-potassium iodide mixture and is further converted 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) reported no significant interferences in the digestion, reduction, and selenium hydride-generation processes.

3.3 Pierce and Brown (1976) reported interferences from trace elements commonly found in water at concentrations greater than 300 μg/L when sodium borohydride was introduced in the sample stream before hydrochloric acid.

3.4 Nitric acid in excess of that usually added as a preservative in water and water-suspended sediment samples, is reported to cause erratic results.

4. Apparatus

4.1 *Atomic absorption spectrometer* and recorder.

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

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. 41). 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 IDX100-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 a 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*, 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 L.

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

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.

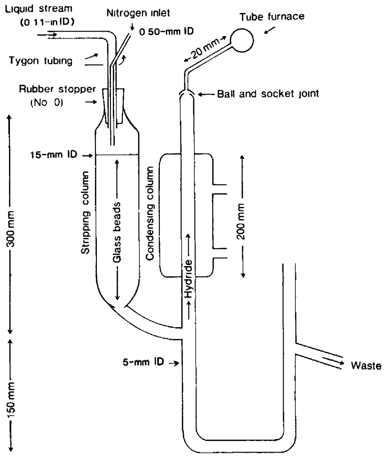


Figure 41.—Stripping-condensing column and quartz-tube furnace

5.6 *Selenium standard solution II*, 1.00 mL = 10.0 µg 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 µg 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 II (mL)	Selenium concentration (µg/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 L.

5.10 *Stannous chloride solution*, 1.3 g/L: Dissolve 1.6 g $SnCl_2 \cdot 2H_2O$ in 1 L concentrated HCl (sp gr 1.19). This solution is unstable. Prepare fresh daily.

6. Procedure

6.1 Follow instructions in paragraph 6.1.1 for waters or water-suspended sediment mixtures and in paragraph 6.1.2 for bottom materials.

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

6.1.2 Weigh 40 mg or less of bottom-material sample (0.225 μg Se max), 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 μg/L into 25-mL graduated test tubes.

6.3 To each tube, add 1.5 mL $K_2S_2O_8$ solution and 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 100 °C, and boil each tube for a minimum of 15 min but no longer than 20 min (NOTE 1). Cool the solution to room temperature, dilute to 17.0 mL with demineralized water, and mix (NOTE 2).

NOTE 1. Alternatively, the solutions may be digested in an autoclave. After addition of HCl and $K_2S_2O_8$, autoclave solutions for 20 min at 15 psi pressure. Cool the solutions and add 3.0 mL oxalic acid solution (dissolve 35 g oxalic acid dihydrate in demineralized water and dilute to 1 L). Autoclave solutions for an additional 20 min at 15 psi pressure. Cool solutions and dilute to 17.0 mL with demineralized water. Proceed to paragraph 6.5.

NOTE 2. A different volume may be used as long as the same volumes of standards and samples are used in each run.

6.5 Set up manifold (fig. 42) (NOTE 3).

NOTE 3. Change the acid flex tubing weekly.

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

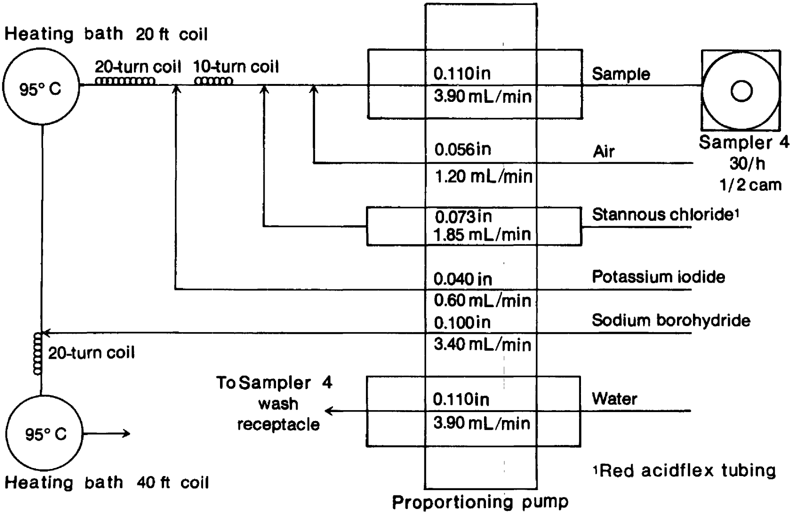


Figure 42.—Selenium, hydride manifold

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

Stripping column temperatures higher than 75 °C cause the peak to split. Monitor the tube-furnace temperature using a portable pyrometer with the thermocouple placed in the middle of the tube, and monitor the waste-stream temperature using a laboratory thermometer. Adjust voltages on the autotransformers as necessary 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 the 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 μg/L of selenium produces a peak approx 60 percent of full scale. If the sensitivity drops by 30 percent or more, replace or treat the tube furnace (cell) by one of the following methods:

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

6.10.2 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 Determine the concentration of dissolved or total 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 the concentration of suspended total selenium, subtract dissolved-selenium concentration from total-selenium concentration.

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

$$\text{Se in } \mu\text{g/g} = \frac{\mu\text{g/L Se} \times 0.015 \text{ L}}{\text{wt of sample (g)}}$$

8. Report

8.1 Report selenium, dissolved (01145), total (01147), and suspended-total (01146), concentrations as follows: less than 10 μg/L, nearest μg/L; 10 μg/L and above, two significant figures.

8.2 Report selenium, total-in-bottom-material (01148), concentrations as follows: less than 10 μg/g, nearest μg/g; 10 μg/g and above, two significant figures.

9. Precision

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

9.2 Precision for dissolved selenium also may be expressed in terms of percent relative standard deviation as follows:

Number of replicates	Mean (μg/L)	Relative standard deviation (percent)
5	3.3	3
5	4.2	10
5	6.4	3
5	8.5	1

9.3 Analysis of four samples for total selenium five times each by one operator resulted in mean values of 2.0, 8.6, 10.4, and 20.0 μg/L and standard deviations of 0.5, 0.2, 0.3, and 0.9 μg/L, respectively.

9.4 Precision for total selenium also may be expressed in terms of percent relative standard deviation as follows:

Number of replicates	Mean (μg/L)	Relative standard deviation (percent)
5	2.0	25
5	8.6	2
5	10.4	3
5	20.0	4

9.5 Analysis of four bottom-material samples for selenium five times each by one operator resulted in mean values of 1.4, 1.7, 2.4, and 3.4 μg/g and standard deviations of 0.3, 0.1, 0.2, and 0.1 μg/g, respectively.

9.6 Precision for selenium in bottom-material samples also may be expressed in terms of percent relative standard deviation as follows:

Number of replicates	Mean (μg/L)	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. 1431-6.

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. 693-5.

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

Selenium, total-in-sediment, atomic absorption spectrometric, hydride

Parameter and Code:

Selenium, total, I-5475-85 (mg/kg as Se): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200°C. Selenium is determined on the resulting solution by atomic absorption spectrometry. See method I-5475, metals, minor, total-in-sediment, atomic absorption spectrometric, hydride.

Silica, atomic absorption spectrometric, direct

Parameter and Code:

Silica, dissolved, I-1702-85 (mg/L as SiO_2): 00955

1. Application

This method may be used to analyze water containing at least 0.5 mg/L of silica. Samples containing more than 35 mg/L need either to be diluted or to be read on a less expanded scale. The sensitivity of the determination is dependent on the amount of acetylene remaining in the cylinder. When a full cylinder is used (290 psi), a sensitivity of about 0.40 mg SiO_2 per scale division may be expected. However, when a near-empty cylinder is used (for example, 50 psi), a sensitivity of only about 0.55 mg SiO_2 per scale division is observed. The significant amount of acetone vapor present in the last acetylene to be withdrawn from a cylinder decreases the sensitivity for silica in the nitrous oxide-acetylene flame.

2. Summary of method

Silica is determined by atomic absorption spectrometry by direct aspiration of the sample into a nitrous oxide-acetylene flame without preconcentration or pretreatment of the sample.

3. Interferences

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

4. Apparatus

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

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

Grating	Ultraviolet
Wavelength	251.6 nm
Source (hollow-cathode lamp)	Silica
Burner	Nitrous oxide
Oxidant	Nitrous oxide
Fuel	Acetylene
Type of flame	Fuel-rich

5. Reagents

5.1 *Silica standard solution*, 1.00 mL = 0.500 mg SiO_2: Dissolve 1.7655 g sodium metasilicate ($Na_2SiO_3 \cdot 5H_2O$) in demineralized water and dilute to 1,000 mL. Store in a plastic bottle.

5.2 *Silica working standards*: Prepare a series of at least six working standards containing from 0.5 to 35 mg/L of silica by appropriate dilution of silica standard solution. Store in plastic bottles.

6. Procedure

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

7. Calculations

Determine the milligrams per liter of dissolved silica (as SiO_2) in each sample from the digital display or printer output while aspirating each sample. Dilute those samples containing concentrations of silica that exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report silica, dissolved (00955), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved silica within the range of 1.10 to 16.5 mg/L for 20 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 1.49 mg/L ranged from 1.30 to 1.75 mg/L.

9.2 Precision for dissolved silica for four of the 20 samples expressed in terms of the percent relative standard deviations is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
3	3.83	21
8	10.4	12
7	16.4	8
4	16.5	4

Silica, atomic emission spectrometric, ICP

Parameter and Code:

Silica, dissolved, I-1472-85 (mg/L as SiO_2): 00955

2. Summary of method

Silica is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Silica, colorimetric, molybdate blue

Parameter and Code:

Silica, dissolved, I-1700-85 (mg/L as SiO_2): 00955

1. Application

This method may be used to analyze water containing from 0.1 to 100 mg/L of silica. Samples containing more than 100 mg/L need to be analyzed by standard gravimetric procedures (American Society for Testing and Materials, 1984; Kolthoff and others, 1969).

2. Summary of method

2.1 Silica in solution as silicic acid or silicate has the property of reacting with ammonium molybdate in an acid medium to form the yellow silicomolybdate complex. The silicomolybdate complex is then reduced by sodium sulfite to form the molybdate blue color. The silicomolybdate complex may form in water as alpha and beta polymorphs (Strickland, 1952), which have absorbance maxima at different wavelengths. In order to favor the development of the beta form, the pH of the reaction mixture is reduced below 2.5 (Govett, 1961).

2.2 The possibility of having unreactive silica is greater in water containing high concentrations of silica than in water containing low concentrations of silica. When significant amounts of unreactive silica are known or suspected to be present, a 1-h digestion of 50-mL sample with 5.0 mL of 1.0*M* NaOH is suggested to make all the silica available for reaction with the molybdate reagent.

3. Interferences

Phosphate produces a similar molybdate complex under certain pH conditions. In the following determination, tartaric acid is added to suppress phosphate interference. Hydrogen sulfide and ferric and ferrous iron apparently interfere with the determination. Hydrogen sulfide may be removed by boiling an acidified sample. The addition of disodium dihydrogen ethylenediamine tetraacetate (Na_2EDTA) eliminates the effect of high concentrations of iron, and also complexes calcium and prevents precipitation of calcium sulfite.

4. Apparatus

4.1 *Spectrometer* for use at 700 nm.

4.2 Refer to the manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Ammonium molybdate solution*: 49 g/L: Dissolve 52 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in water, adjust the pH to between 7 and 8 with 10*M* NaOH, and dilute to 1 L with demineralized water. Filter through 0.45-μm membrane filter if necessary.

5.2 *Hydrochloric acid*, 1.0*M*: Mix 88 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.3 *Silica standard solution I*, 1.00 mL = 0.500 mg SiO_2: Dissolve 1.7655 g sodium metasilicate ($Na_2SiO_3 \cdot 5H_2O$) in demineralized water. Store in a plastic bottle.

5.4 *Silica standard solution II*, 1.00 mL = 0.005 mg SiO_2: Dilute 10.0 mL silica standard solution I to 1,000 mL with demineralized water. Store in a plastic bottle.

5.5 *Na_2EDTA solution*, 10 g/L: Dissolve 10 g Na_2EDTA in demineralized water and dilute to 1 L.

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

5.7 *Sodium sulfite solution*, 170 g/L: Dissolve 170 g Na_2SO_3 in demineralized water and dilute to 1 L.

5.8 *Tartaric acid solution*, 100 g/L: Dissolve 100 g $H_2C_4H_4O_6$ in demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.5 mg SiO_2 (10.0 mL max) into a 50-mL beaker, and adjust the volume to 10.0 mL.

6.2 Pipet a demineralized water blank and sufficient standards into 50-mL beakers, and adjust the volume of each to 10.0 mL.

6.3 Add to each solution, with stirring, 5.0 mL 1.0*M* HCl, 5.0 mL Na_2EDTA solution, and 5.0 mL ammonium molybdate solution.

6.4 After 5 min add 5.0 mL tartaric acid solution and mix.

6.5 Add 10.0 mL Na_2SO_3 solution and mix.

6.6 Allow to stand approx 30 min. The color is stable for several hours.

6.7 Determine the absorbance of each test sample and standards against the blank.

7. Calculations

7.1 Determine milligrams of silica in each sample from a plot of absorbances of standards.

7.2 Determine the concentration of dissolved silica in milligrams per liter as follows:

$$SiO_2\ (\text{mg/L}) = \frac{1{,}000}{\text{mL sample}} \times \text{mg } SiO_2 \text{ in sample.}$$

8. Report

Report silica, dissolved (00955), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved silica for 35 samples within the range of 2.15 to 24.4 mg/L may be expressed as follows:

$$S_T = 0.065X + 0.10$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of silica, milligrams per liter.

The correlation coefficient is 0.8053.

9.2 Precision for dissolved silica for four of the 35 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
19	2.15	16
11	9.08	5
6	10.2	15
24	24.4	7

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 613–8.

Govett, G. J. S., 1961, Critical factors in the colorimetric determination of silica: Analytica Chimica Acta, v. 25, p. 69–80.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative chemical analysis, (4th ed.): New York, Macmillan, 1199 p.

Strickland, J. D. H., 1952, The preparation and properties of silicomolybdic acid; I. The properties of alpha silicomolybdic acid: American Chemical Society Journal, v. 74, p. 862–7.

Silica, colorimetric, molybdate blue, automated-segmented flow

Parameter and Code:

Silica, dissolved, I-2700-85 (mg/L as SiO_2): 00955

1. Application

This method may be used to determine concentrations of silica in surface, domestic, and industrial water in the range from 0.1 to 60 mg/L. Two analytical ranges are used: from 0.1 to 6.0 mg/L and from 1.0 to 60 mg/L.

2. Summary of method

2.1 Silica reacts with molybdate reagent in acid media to form a yellow silicomolybdate complex. This complex is reduced by ascorbic acid to form the molybdate blue color. The silicomolybdate complex may form either as an alpha or beta polymorph or as a mixture of both. Because the two polymorphic forms have absorbance maxima at different wavelengths, the pH of the mixture is kept below 2.5, a condition that favors formation of the beta polymorph (Govett, 1961; Mullen and Riley, 1955; Strickland, 1952).

2.2 The possibility of having "unreactive" silica is greater in water containing high concentrations of silica than in water containing low concentrations of silica. When significant amounts of unreactive silica are known or suspected to be present, a 1-h digestion of a 50-mL sample with 5.0 mL of 1.0*M* NaOH is suggested as a means of making all the silica available for reaction with the molybdate reagent.

3. Interferences

Interference from phosphate, which forms a phosphomolybdate complex, is suppressed by the addition of oxalic acid. Hydrogen sulfide must be removed by boiling the acidified sample prior to analysis. Large amounts of iron interfere.

4. Apparatus

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

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.1 to 60 mg/L:

Absorption cell ----------	15 mm
Wavelength -------------	660 nm
Cam -------------------	60/h (6/1)

5. Reagents

5.1 *Ammonium molybdate solution*, 9.4 g/L: Dissolve 5 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 0.05*M* H_2SO_4 and dilute to 500 mL with 0.05*M* H_2SO_4. Filter and store in an amber plastic container.

5.2 *Ascorbic acid solution*, 17.6 g/L: Dissolve 17.6 g ascorbic acid in 500 mL demineralized water containing 50 mL acetone. Dilute to 1 L with demineralized water. Add 0.5 mL Levor IV solution. The solution is stable for 1 week if stored at 4°C.

5.3 *Levor IV solution*: Technicon No. 21-0332 or equivalent.

5.4 *Oxalic acid solution*, 50 g/L: Dissolve 50 g oxalic acid in demineralized water and dilute to 1 L.

5.5 *Silica standard solution*, 1.00 mL = 0.500 mg SiO_2: Dissolve 1.7655 g sodium metasilicate ($Na_2SiO_3\cdot 5H_2O$) in demineralized water and dilute to 1,000 mL. Store in a plastic bottle.

5.6 *Silica working standards*: Prepare a blank and 1,000 mL each of a series of silica working standards by appropriate quantitative dilution of silica standard solution as follows:

Silica standard solution (mL)	Silica concentration (mg/L)
0.0	0.0
.5	0.25
1.0	.5
2.0	1.0
12.0	6.0
20.0	10
40.0	20
80.0	40
120.0	60

5.7 *Sulfuric acid,* 0.05*M*: *Cautiously* add 2.8 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Set up manifold (fig. 43).

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

6.3 Adjust 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 (6.0 or 60 mg/L) appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

7. Calculations

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

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

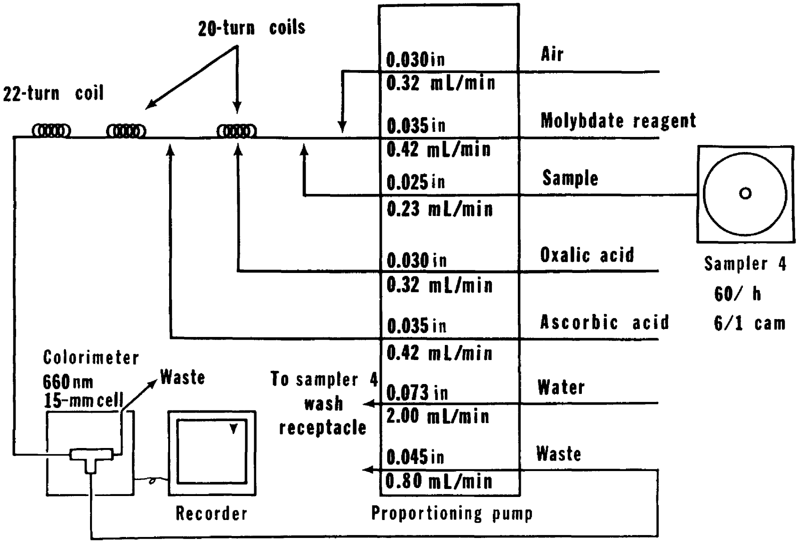


Figure 43.—Silica, molybdate manifold

8. Report

Report silica, dissolved (00955), concentrations as follows: less than 10 mg/L, nearest 0.1 mg/L; 10 mg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved silica within the range of 4.70 to 17.4 mg/L for 20 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 1.10 mg/L ranged from 0.97 to 1.26 mg/L.

9.2 Precision for dissolved silica for four of the 20 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
5	4.70	7
8	8.95	23
6	10.6	6
5	17.4	7

References

Govett, G. J. S., 1961, Critical factors in the colorimetric determination of silica: Analytica Chimica Acta, v. 25, p. 69–80.

Mullen, J. B., and Riley, J. P., 1955, The colorimetric determination of silicate with special reference to sea and natural waters: Analytica Chimica Acta, v. 12, p. 162–76.

Strickland, J. D. H., 1952, The preparation and properties of silicomolybdic acid: I. The properties of alpha silicomolybdic acid: American Chemical Society Journal, v. 74, p. 862–7.

Silica, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:

Silica, total, I-5473-85 (mg/kg as SiO_2): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1,000°C. The resulting bead is dissolved in acidified, boiling, demineralized water, and silica is determined by atomic absorption spectrometry. See method I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

Silver, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:

Silver, dissolved, I-1720-85 (μg/L as Ag): 01075
Silver, total recoverable, I-3720-85 (μg/L as Ag): 01077
Silver, suspended recoverable, I-7720-85 (μg/L as Ag): 01076

1. Application

1.1 This method may be used to analyze water, brines, and water-suspended sediment containing from 1 to 10 μg/L of silver. Samples containing more than 10 μg/L need to be diluted or to be read on a less expanded scale.

1.2 Suspended recoverable silver is calculated by subtracting dissolved silver from total recoverable silver.

1.3 Total recoverable silver in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

2. Summary of method

Silver is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer.

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the silver absorption.

4. Apparatus

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

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

Grating -------------	Ultraviolet
Wavelength --------	328.1 nm
Source (hollow-cathode lamp) ------------	Silver
Oxidant ------------	Air
Fuel ---------------	Acetylene
Type of flame -------	Oxidizing

4.3 Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate (APDC) solution*, 1 g/100 mL: Dissolve 1 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Citric acid-sodium citrate buffer solution*: Dissolve 126 g citric acid monohydrate and 44 g sodium citrate dihydrate in demineralized water and dilute to 1 L with demineralized water. See NOTE 3 before preparation.

5.3 *Methyl isobutyl ketone* (MIBK).

5.4 *Silver standard solution I*, 1.00 mL = 100 μg Ag: Crush approx 2 g of $AgNO_3$ crystals and dry to constant mass at 40°C. Dissolve 0.1575 g $AgNO_3$ in demineralized water and dilute to 1,000 mL. Store in amber bottle.

5.5 *Silver standard solution II*, 1.00 mL = 1.00 μg Ag: Dilute 10.0 mL silver standard solution I and 1.0 mL concentrated HNO_3 (sp gr 1.41) to 1,000 mL with demineralized water. This solution is used to prepare working standards at the time of analysis. Store in amber bottle.

5.6 *Potassium hydroxide*, 10*M*: Dissolve 56 g KOH in demineralized water, cool, and dilute to 100 mL.

5.7 *Potassium hydroxide*, 2.5*M*: Dissolve 14 g KOH in demineralized water and dilute to 100 mL (NOTE 1).

NOTE 1. Alternatively, a 2.5*M* NH_4OH solution may be used. Add 167 mL concentrated

NH_4OH (sp gr 0.90) to 600 mL demineralized water. Cool and dilute to 1 L.

5.8 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

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

6.2 Pipet a volume of sample solution containing less than 1.0 μg Ag (100 mL max) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.3 Prepare a blank of acidified water and sufficient standards, and adjust the volume of each to approx 100 mL with acidified water.

6.4 With a pH meter, adjust the pH of each solution to 2.4 with 2.5*M* KOH (NOTES 2 and 3).

NOTE 2. For water-suspended sediment samples that have been digested, add 1 to 2 mL 10*M* KOH or concentrated NH_4OH (sp gr 0.90) before pH adjustment.

NOTE 3. If an automated titration system is used to adjust the pH, add 2.5 mL citric acid-sodium citrate buffer solution prior to pH adjustment. This will prevent over-shooting the end point in poorly buffered samples.

6.5 Add 2.5 mL APDC solution and shake for 3 min.

6.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.8 Aspirate the ketone layer of the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of the standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable silver in each sample from the digital display or printer. Dilute those samples containing concentrations of silver that exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

7.2 To determine micrograms per liter of suspended recoverable silver, subtract dissolved-silver concentration from total-recoverable-silver concentration.

8. Report

Report silver, dissolved (01075), total-recoverable (01077), and suspended-recoverable (01076), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved silver for 16 samples within the range of 1.5 to 13.6 μg/L may be expressed as follows:

$$S_T = 0.478X - 1.29$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of silver, micrograms per liter.

The correlation coefficient is 0.7681.

9.2 Precision for dissolved silver for five of the 16 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
4	1.5	40
5	2.0	0
5	5.4	20
6	10.4	14
5	13.4	26

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable silver will be greater than that reported for dissolved silver.

9.4 Precision for total recoverable silver expressed in terms of the percent relative standard deviation for one water-suspended sediment is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
8	8.1	30

Sodium, atomic absorption spectrometric, direct

Parameters and Codes:

Sodium, dissolved, I-1735-85 (mg/L as Na): 00930
Sodium, total recoverable, I-3735-85 (mg/L as Na): none assigned
Sodium, recoverable-from-bottom-material, dry wt, I-5735-85 (mg/kg as Na): 00934

1. Application

1.1 This method may be used to analyze atmospheric precipitation, water, brines, and water-suspended sediment.

1.2 Two analytical ranges for sodium are included: from 0.01 to 1.0 mg/L and from 0.10 to 80 mg/L. Sample solutions containing sodium concentrations greater than 80 mg/L need to be diluted.

1.3 This method may be used to analyze bottom material containing at least 10 mg/kg of sodium.

1.4 Total recoverable sodium in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable sodium in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

2.1 Sodium is determined by atomic absorption spectrometry by direct aspiration of the sample solution into an air-acetylene flame (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer.

3. Interferences

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

4. Apparatus

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

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

Grating	Visible
Wavelength	588.8 nm
Source (hollow-cathode lamp)	Sodium
Oxidant	Air
Fuel	Acetylene
Type of flame	Oxidizing

4.3 The 50-mm (2-in.), flathead, single-slot burner, rotated 90°, allows working ranges of 0.01 to 1.0 mg/L and 0.1 to 80 mg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Sodium standard solution*, 1.00 mL = 1.00 mg Na: Dissolve 2.542 g NaCl in demineralized water and dilute to 1,000 mL.

5.2 *Sodium working standards*: Prepare a series of at least six working standards containing either from 0.01 to 1.0 mg/L or from 0.10 to 80 mg/L sodium by appropriate dilutions of sodium standard solution. The preparation of an intermediate standard solution is desirable when preparing working solutions of extreme dilution.

6. Procedure

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

7. Calculations

7.1 Determine the milligrams per liter of dissolved or total recoverable sodium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing sodium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine milligrams per kilogram of sodium in bottom-material samples, first determine the milligrams per liter of sodium as in paragraph 7.1, then:

$$\text{Na (mg/kg)} = \frac{\text{mg/L Na} \times \dfrac{\text{mL original digest}}{1000}}{\text{wt of sample (kg)}}$$

8. Report

8.1 Report sodium, dissolved (00930), and total-recoverable (none assigned), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 to 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

8.2 Report sodium, recoverable-from-bottom-material (00934), concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

9.1 Precision for dissolved sodium for 33 samples within the range of 0.20 to 222 mg/L may be expressed as follows:

$$S_T = 0.046X + 0.186$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of sodium, milligrams per liter.

The correlation coefficient is 0.9461.

9.2 Precision for dissolved sodium for six of the 33 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
22	0.20	35
36	2.76	13
25	15.4	6
35	56.0	5
31	96.9	5
19	222	6

9.3 Precision for dissolved sodium within the range of 0.01 to 1.0 mg/L in terms of the percent relative standard deviation by a single operator is as follows:

Number of replicates	Mean (mg/L)	Relative standard deviation (percent)
8	0.009	26.5
8	.028	16.8
8	.136	3.8
8	.540	1.0

9.4 It is estimated that the percent relative standard deviation for total recoverable sodium and for recoverable sodium from bottom material will be greater than that reported for dissolved sodium.

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 38–41.

Sodium, atomic absorption spectrometric, direct-EPA

Parameter and Code:

Sodium, total recoverable, I-3736-85 (mg/L as Na): 00929

1. Application

1.1 This method may be used to analyze water-suspended sediment containing from 0.1 to 80 mg/L of sodium. If the sodium concentration exceeds 80 mg/L, the sample solution needs to be diluted. The method is very sensitive and can be extended to much lower sodium concentrations.

1.2 For ambient water, analysis may be made on an aliquot of the acidified water-suspended sediment sample.

1.3 For all other water, including domestic and industrial effluent, the atomic absorption procedure must be preceded by a digestion-solubilization as specified below. In cases where the analyst is uncertain of the type of sample, this procedure must be followed.

2. Summary of method

2.1 Sodium is determined by atomic absorption spectrometry by direct aspiration of the filtered or digested and filtered sample into an air-acetylene flame (Fishman and Downs, 1966).

2.2 Effluent samples must undergo a preliminary nitric acid digestion followed by a hydrochloric acid solubilization.

3. Interferences

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

4. Apparatus

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

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

Grating	Visible
Wavelength	588.8 nm
Source (hollow-cathode lamp)	Sodium
Oxidant	Air
Fuel	Acetylene
Type of flame	Oxidizing

4.3 The 50-mm (2-in.), flathead, single-slot burner, rotated 90°, allows a range of 0.1 to 80 mg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Hydrochloric acid* 6*M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.2 *Hydrochloric acid*, 0.3*M*: Dilute 25 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

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

5.4 *Sodium standard solution*, 1.00 mL = 1.00 mg Na: Dissolve 2.542 g NaCl in demineralized water and dilute to 1,000 mL.

5.5 *Sodium working standards*: Prepare a series of at least six working standards containing from 0.1 to 80 mg/L sodium by appropriate dilutions of sodium standard solution. The preparation of an intermediate standard solution is desirable when preparing working solutions of extreme dilution.

6. Procedure

6.1 When analyzing samples of ambient waters, begin the analysis at step 6.9.

6.2 Transfer the entire sample to a beaker.

6.3 Rinse the sample bottle with 3 mL concentrated HNO_3 for each 100 mL of sample and add to the beaker. Prepare a blank using 3 mL concentrated HNO_3 per 100 mL demineralized water.

6.4 Evaporate samples and blank to dryness on a hotplate, making sure the samples do not boil.

6.5 Cool and add an additional 3 mL concentrated HNO_3 to the beaker. Cover with a watchglass, return to the hotplate, and gently reflux the solution.

6.6 Continue heating, adding more acid as necessary until the digestion is complete (indicated by a light-colored residue). Evaporate just to dryness.

6.7 Add 6 mL 6*M* HCl solution per 100 mL original sample and warm the solution to dissolve the residue.

6.8 Filter (Whatman No. 41 or equivalent) the sample and wash the watchglass and beaker with demineralized water. Rinse the filter with hot 0.3*M* HCl. Dilute to the original volume with demineralized water.

6.9 While aspirating the blank use the automatic zero control to set the digital display to read zero concentration. While aspirating standards use the automatic concentration control to set the digital display to read concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

Determine the milligrams per liter of total recoverable sodium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing sodium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report sodium, total-recoverable (00929), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for total recoverable sodium is greater than 13 percent at 2.76 mg/L and greater than 5 percent at 96.9 mg/L.

References

Fishman, M. J., and Downs, S.C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 38-41.

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 273.1-1.

Sodium, atomic emission spectrometric, ICP

Parameter and Code:

Sodium, dissolved, I-1472-85 (mg/L as Na): 00930

2. Summary of method

Sodium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Sodium, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:

Sodium, total, I-5473-85 (mg/kg as Na): none assigned
Sodium, total, I-5474-85 (mg/kg as Na): none assigned

2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The sample is then treated and analyzed by one of the following techniques.

2.1.1 The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1,000 °C. The resulting bead is dissolved in acidified, boiling, demineralized water, and sodium is determined by atomic absorption spectrometry. See method I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

2.1.2 The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Sodium is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Sodium adsorption ratio, calculation

Parameter and Code:

Sodium adsorption ratio, I-1738-85: 00931

1. Application

This method may be applied to any sample for which measured values for sodium, calcium, and magnesium are available.

2. Summary of method

The sodium adsorption ratio (SAR) is computed from the individual determination of sodium, calcium, and magnesium after conversion of each to milliequivalents per liter (me/L).

7. Calculations

$$\mathrm{SAR} = \frac{\text{me/L Na}}{\sqrt{\dfrac{\text{me/L Ca} + \text{me/L Mg}}{2}}}$$

8. Report

Report sodium adsorption ratio, calculation (00931), as follows: less than 1.0, one decimal; 1.0 and above, whole numbers.

9. Precision

Precision data are not available for this method, but reproducibility should be comparable to that of the individual determinations.

Sodium, percent, calculation

Parameter and Code:

Sodium, percent, I-1740-85: 00932

1. Application

This method may be applied to any sample for which measured values for sodium, potassium, calcium, and magnesium are available.

2. Summary of method

Percent sodium is computed from the milliequivalent per liter (me/L) of sodium, potassium, calcium, and magnesium.

7. Calculations

Sodium (percent) =

$$\frac{\text{me/L Na}}{\Sigma\ \text{me/L}\ (\text{Na} + \text{K} + \text{Ca} + \text{Mg})} \times 100$$

8. Report

Report sodium, percent, calculation (00932), as whole numbers.

9. Precision

Precision data are not available for this method, but reproducibility should be comparable to that of the individual determinations.

Solids, residue on evaporation at 180°C, dissolved, gravimetric

Parameter and Code:

Solids, residue on evaporation at 180°C, dissolved I-1750-85 (mg/L): 70300

1. Application

The residue-on-evaporation method is applicable to all water regardless of concentration, provided that the residue layer in the evaporation dish is kept sufficiently thin.

2. Summary of method

2.1 A volume of filtered sample that will yield less than 200 mg residue is evaporated just to dryness on a steam bath. The residue is then dried at 180°C for exactly 2 hours, cooled in a desiccator, and immediately weighed.

2.2 The weight of the residue is limited to 200 mg to ensure subjection of all the residue to the full effects of drying at 180°C. Voluminous residues will often seal over during the evaporation process and entrap pockets of water that will not be completely vaporized during the drying process. Massive residues also release their water of crystallization more slowly than do thin films of residue. The chemical composition of the sample has a marked effect on the dissolved-solids value obtained, but the percentage of error incurred for any given chemical type of water is independent of the total concentration if the residue film is kept thin.

2.3 Biocarbonate is converted to carbonate in the evaporation and drying process. The following general observations have been reported by Howard (1933). The residues of carbonate-type water that contain considerable magnesium chloride can be expected to lose some weight (as much as 50 or 100 mg/L) during the drying process; however, such loss of weight is usually more than offset by the water of crystallization tightly held by the salts. Most of the water of crystallization is driven off from sulfates of sodium and magnesium when the residue is heated at 180°C, but this temperature is insufficient to dehydrate calcium sulfate completely. Residues of water with a high nitrate content may lose as much as 30 mg/L on heating.

2.4 Because many of the salts in the residue are hygroscopic, an efficient desiccant must be used. Silica gel (indicating), anhydrous $Mg(ClO_4)_2$ or $CaSO_4$, and $Mg(ClO_4)_2 \cdot 3H_2O$ are satisfactory and recommended. $CaCl_2$ is not suitable. Under no circumstances should the dried residues be allowed to stand for long periods of time before weighing.

3. Interferences

There are no known interferences to this method.

4. Apparatus

4.1 *Desiccator,* charged with indicating silica gel or other efficient desiccant.

4.2 *Oven,* 180°C, uniform temperature throughout.

4.3 *Platinum evaporating dishes,* 75- to 125-mL capacity, weighing less than 50 g, or zirconium dishes. Platinum or zirconium are recommended for precise work because the change in weight of glass or porcelain dishes may introduce appreciable error into the determination.

4.4 *Steam bath.*

5. Reagents

None required.

6. Procedure

6.1 Pipet a volume of filtered sample containing 10 to 200 mg dissolved solids (500 mL max) into a tared platinum dish.

6.2 Evaporate the sample just to dryness on a steam bath.

6.3 Dry in an oven at 180°C for 2.0 h.

6.4 Cool in a desiccator and immediately weigh. Record the weight to the nearest 0.1 mg.

7. Calculations

Dissolved solids (mg/L) =

$$\frac{1{,}000}{\text{mL sample}} \times \text{mg residue}$$

8. Report

Report solids, residue on evaporation at 180°C, dissolved (70300), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

9.1 Precision for dissolved solids for 22 samples within the range of 60 to 1760 mg/L may be expressed as follows:

$$S_T = 0.024X + 11.3$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of dissolved solids, milligrams per liter.

The correlation coefficient is 0.7633.

9.2 Precision for dissolved solids for six of the 22 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
27	59.2	8
28	267	4
39	524	11
28	558	2
29	1160	4
49	1760	3

Reference

Howard, C. S., 1933, Determination of total dissolved solids in water analysis: Industrial Engineering Chemistry, Analytical Edition, v. 5. p. 4.

Solids, residue on evaporation at 105°C, dissolved, gravimetric

Parameter and Code:

Solids, residue at 105°C, dissolved, I-1749-85 (mg/L): 00515

1. Application

The residue-on-evaporation method is applicable to all water regardless of concentration, provided that the residue layer in the evaporating dish is kept sufficiently thin.

2. Summary of method

2.1 A volume of filtered sample that will yield less than 200 mg residue is evaporated just to dryness on a steam bath. The residue is dried at 105°C for 2.0 h, cooled in a desiccator, and immediately weighed.

2.2 The weight of the residue is limited to 200 mg to ensure subjection of all the residue to the full effects of drying at 105°C. Voluminous residues will often seal over during the evaporation process and entrap pockets of water that will not be completely vaporized during the drying process. Massive residues also release their water of crystallization more slowly than do thin films of residue. The chemical composition of the sample has a marked effect on the dissolved-solids value obtained, but the percentage of error incurred for any given chemical type of water is independent of the total concentration if the residue film is kept thin.

2.3 Because many of the salts in the residue are hygroscopic, an efficient desiccant must be used. Silica gel (indicating), anyhydrous $Mg(ClO_4)_2$ or $CaSO_4$, and $Mg(ClO_4)_2 \cdot 3H_2O$ are satisfactory and recommended. $CaCl_2$ is not suitable. Under no circumstances should the dried residues be allowed to stand for long periods of time before weighing.

3. Interferences

There are no known interferences to this method.

4. Apparatus

4.1 *Desiccator*, charged with indicating silica gel or other efficient desiccant.

4.2 *Oven*, 105°C, uniform temperature throughout.

4.3 *Platinum evaporating dishes*, 75- to 125-mL capacity, weighing less than 50 g, or zirconium dishes. Platinum or zirconium is recommended for precise work because the change in weight of glass or porcelain dishes may introduce appreciable error into the determination.

4.4 *Steam bath.*

5. Reagents

None required.

6. Procedure

6.1 Pipet a volume of filtered sample containing 10 to 200 mg dissolved solids (500 mL max) into a tared platinum dish.

6.2 Evaporate the sample just to dryness on a steam bath.

6.3 Dry in an oven at 105°C for 2.0 h.

6.4 Cool in a desiccator and immediately weigh. Record the weight to the nearest 0.1 mg.

7. Calculations

$$\text{Dissolved solids (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times \text{mg residue}$$

8. Report

Report solids, residue on evaporation at 105°C, dissolved (00515), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

It is estimated that the percent relative standard deviation of this method is greater than 8 percent at 59 mg/L and greater than 3 percent at 1760 mg/L.

Reference

American Public Health Association and others, 1980, Standard methods for the examination of water and wastewater [15th ed]: Washington, D.C., p. 92–4.

Solids, residue on evaporation at 105°C, total, gravimetric

Parameter and Code:

Solids, residue on evaporation at 105°C, total, I-3750-85 (mg/L): 00500

1. Application

1.1 This method may be used to determine the total-solids concentration of any natural or treated water or industrial waste.

1.2 Total residue represents the sum of both dissolved and suspended (including colloidal) material in a sample. The determination is not exact, because of the compromise that must be made in selecting the temperature at which the evaporated residue is to be dried. At temperatures sufficient to release water of hydration of the hydrated salts that form on evaporation, there is risk of volatilization of the more volatile dissolved or suspended materials in the sample. On the other hand, drying at a sufficiently low temperature to conserve volatiles fails to remove much of the entrapped water and ordinary water of hydration. Because of these factors, the determination must be considered as providing only an approximation of the sum of dissolved and suspended matter.

1.3 The determination is not very useful; determination of dissolved solids (method I-1749) and suspended solids (method I-3765) provides more useful information.

2. Summary of method

A volume of well-mixed sample is evaporated to dryness. The residue is dried at 105 °C for 2.0 h, cooled in a desiccator, and immediately weighed.

3. Interferences

Care must be taken to ensure that a representative sample is provided. Usually, large, floating particles are excluded from the sample.

4. Apparatus

4.1 *Desiccator*, charged with indicating silica gel or other efficient desiccant.

4.2 *Oven*, 105 °C, uniform temperature throughout.

4.3 *Platinum evaporating dishes*, 75- to 125-mL capacity, weighing less than 50 g, or zirconium dishes. Platinum or zirconium is recommended because the change in weight of glass or porcelain dishes may introduce appreciable error into the determination.

6. Procedure

6.1 Shake the sample vigorously and rapidly pipet a suitable aliquot of unfiltered sample.

6.2 Transfer the sample to a tared platinum evaporating dish.

6.3 Rinse the pipet with demineralized water to ensure transfer of all particulate matter to the evaporating dish.

6.4 Evaporate the sample just to dryness on a steam bath.

6.5 Dry in an oven at 105 °C for 2.0 h.

6.6 Cool in a desiccator and immediately weigh. Record the weight to the nearest 0.1 mg.

7. Calculations

$$\text{Total solids (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times \text{mg residue}$$

8. Report

Report solids, residue on evaporation at 105 °C, total (00500), concentrations as follows:

less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

It is estimated that the percent relative standard deviation of this method is greater than 8 percent at 59 mg/L and greater than 3 percent at 1760 mg/L.

Reference

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 160.3.

Solids, residue at 105°C, suspended, gravimetric

Parameter and Code:

Solids, residue at 105°C, suspended, I-3765-85 (mg/L): 00530

1. Application

This method may be used to determine the suspended-solids concentration of any natural or treated water or industrial waste.

2. Summary of method

2.1 Suspended solids are those that are retained on a glass-fiber filter. The determined value is fairly representative of the sample but does not accurately represent the suspended-sediment concentration of a stream; suspended-solids values should not be confused with sediment concentration, which is the more accurate measure of material in suspension.

2.2 The unfiltered sample is mixed thoroughly and an appropriate volume is rapidly poured into a graduated cylinder. The suspended solids are collected on a glass-fiber filter, and the insoluble residue is dried and weighed.

3. Interferences

Precipitation in the sample during storage, such as iron, will produce erroneously high results.

4. Apparatus

4.1 *Desiccator*, charged with indicating silica gel or other efficient desiccant.

4.2 *Filtration apparatus*, consisting of suction flask, gooch crucible, glass-fiber filter disk, and suitable holder.

4.3 *Oven*, 105°C, uniform temperature throughout.

6. Procedure

6.1 Shake the sample bottle vigorously and rapidly pour a suitable volume into a graduated cylinder. Record the volume.

6.2 Quantitatively collect the suspended material from the sample on a tared glass-fiber filter disk. A blank should be determined with each set of samples.

6.3 Wash the suspended material on the filter sparingly with demineralized water.

6.4 Dry the residue and filter disk overnight at 105°C.

6.5 Cool in a desiccator and weigh the filter disk containing the dry residue to the nearest 0.1 mg. Record the weight.

7. Calculations

7.1 Apply a correction for any loss shown by the blank.

7.2 Determine suspended solids in milligrams per liter as follows:

Suspended solids, mg/L =

$$\frac{1000}{\text{mL sample}} \times \text{mg residue}$$

8. Report

Report solids, residue at 105°C, suspended (00530), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Reference

Guy, H. P., 1969, Laboratory theory and methods for sediment analysis: Techniques of Water-Resources Investigations of the U.S. Geological Survey, book 5, chapter C1, 58 p.

Solids, volatile-on-ignition, dissolved, gravimetric

Parameter and Code:

Solids, volatile-on-ignition, dissolved, I-1753-85 (mg/L): 00520

1. Application

This method may be used to analyze any natural, treated, or industrial water and other wastewater.

2. Summary of method

The residue obtained after determination of dissolved solids (method I-1750) is ignited at 550 °C. The loss in weight of residue represents a measure of dissolved volatile solids.

3. Interferences

3.1 None of the substances commonly occurring in natural waters interfere with this method.

3.2 Because of the great variability in the nature of the compounds that can be present in the sample, particularly in samples of industrial and other wastes, the determination can be considered only an approximation of the amount of volatile material present. Some of the volatile material may have been released during the determination of dissolved solids. Moreover, ignition at 550 °C volatilizes water of hydration from the hydrated salts present.

4. Apparatus

4.1 *Muffle furnace*, 550 °C.

4.2 For additional items of required apparatus, see solids, dissolved (method I-1750).

5. Reagents

None required.

6. Procedure

6.1 Determine dissolved solids as directed in method I-1750.

6.2 Place the weighed evaporating dish in a muffle furnace at 550 °C; heat for 1 h.

6.3 Remove and cool in a desiccator; weigh and record the weight to the nearest 0.1 mg.

7. Calculations

Solids, volatile on ignition, dissolved, mg/L =

$$\frac{1000}{\text{mL sample}} \times (ER-IR)$$

where

ER = weight of dissolved solids, milligrams,
IR = weight of ignited residue, milligrams.

8. Report

Report solids, volatile-on-ignition, dissolved (00520), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, volatile-on-ignition, total, gravimetric

Parameter and Code:

Solids, volatile-on-ignition, total, I-3753-85 (mg/L): 00505

1. Application

This method may be used to analyze any natural, treated, or industrial water and other waste.

2. Summary of method

A measured volume of well-mixed, unfiltered sample is evaporated to dryness. The residue is dried at 105 °C for 2.0 h, cooled in a desiccator, and immediately weighed. See solids, total (method I-3750). The residue is then ignited at 550 °C and weighed, the difference in weight representing total volatile solids.

3. Interferences

3.1 Care must be taken to ensure that a representative sample is provided. Usually, large, floating particles are excluded from the sample.

3.2 Because of the great variability in the nature of the compounds that can be present in the sample, particularly in samples of industrial and other wastes, the determination can be considered only an approximation of the amount of volatile material present. Much of the volatile material may have been released during the determination of total residue. Moreover, ignition at 550 °C certainly volatilizes water of hydration from the hydrated salts present.

4. Apparatus

4.1 *Muffle furnace*, 550 °C.

4.2 For additional items of required apparatus, see solids, dissolved (method I-3750).

5. Reagents

None required.

6. Procedure

6.1 Determine the total solids as directed in solids, total (method I-3750).

6.2 Place the weighed evaporating dish in a muffle furnace at 550 °C; heat for 1 h.

6.3 Remove and cool in a desiccator. Weigh and record the weight to the nearest 0.1 mg.

7. Calculations

Solids, volatile-on-ignition, total mg/L =

$$\frac{1000}{\text{mL sample}} \times (ER-IR)$$

where

ER = weight of evaporated total residue, milligrams,

IR = weight of ignited total residue, milligrams.

8. Report

Report solids, volatile-on-ignition, total (00505), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, volatile-on-ignition, suspended, gravimetric

Parameter and Code:

Solids, volatile-on-ignition, suspended, I-3767-85 (mg/L): 00535

1. Application

This method may be used to analyze any natural or treated water or industrial waste.

2. Summary of method

The dry residue obtained for the determination of suspended solids (method I-3765) is ignited at 550 °C for 1 h. The loss on ignition corresponds to the amount of volatile suspended solids.

3. Interferences

3.1 None of the substances commonly occurring in natural waters interfere with this method.

3.2 Because of the great variability in the nature of the compounds that can be present in the sample, particularly in samples of industrial waste, the determination can be considered only an approximation of the amount of volatile material present. Some of the volatile material may have been released during the determination of suspended solids. Moreover, ignition at 550 °C certainly volatilizes water of hydration from the hydrated salts present.

4. Apparatus

4.1 *Muffle furnace*, 550 °C.

4.2 For additional items of required apparatus, see solids, suspended (method I-3765).

5. Reagents

None required.

6. Procedure

6.1 Determine suspended solids as directed in method I-3765.

6.2 Place the weighed gooch crucible containing the dry suspended solids in a muffle furnace at 550 °C; heat for 1 h. A blank should be determined with each set of samples.

6.3 Remove and cool in a desiccator. Weigh and record the weight to the nearest 0.1 mg.

7. Calculations

Solids, volatile-on-ignition, suspended, mg/L =

$$\frac{1000}{\text{mL sample}} \times (ER\text{-}IR)$$

where

ER = weight of dry suspended solids, milligrams,

IR = weight of ignited suspended solids, milligrams.

8. Report

Report solids, volatile-on-ignition, suspended (00535), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, volatile-on-ignition, total-in-bottom-material, gravimetric

Parameter and Code:

Solids, volatile-on-ignition, total-in-bottom-material, dry wt, I-5753-85 (mg/kg): 00496

1. Application

This method may be used to analyze samples of bottom material. Usually, only the material that will pass a 2-mm sieve is taken for analysis.

2. Summary of method

A portion of well-mixed sample is dried at 105 °C. A portion of dry, well-mixed sample is carefully weighed and then ignited at 550 °C. The loss of weight on ignition represents the amount of volatile solids in the sample.

3. Interferences

None.

4. Apparatus

4.1 *Desiccator*, charged with indicating silica gel or other efficient desiccant.

4.2 *Muffle furnace*, 550 °C.

4.3 *Oven*, 105 °C, uniform temperature throughout.

4.4 *Platinum evaporating dishes*, 75- to 125-mL capacity, weighing less than 50 g. Platinum is recommended because the change in weight of glass or porcelain dishes may introduce appreciable error into the determination.

5. Reagents

None required.

6. Procedure

6.1 Spread approx 1 g of sample in the bottom of a platinum evaporating dish. Place in an oven at 105 °C and heat overnight.

6.2 Place the dish containing the dry sample in a desiccator, cool, and weigh to the nearest 0.1 mg.

6.3 Ignite the weighed dry residue at 550 °C for 1 h, cool in a desiccator, and weigh to the nearest 0.1 mg.

7. Calculations

Solids, volatile-on-ignition (mg/kg) =

$$\frac{(DR-IR) \times 10^6}{DR}$$

where

IR = weight of ignited residue, milligrams, and

DR = weight of dry residue, milligrams.

8. Report

Report solids, volatile-on-ignition, total-in-bottom-material (00496), concentrations as follows: less than 1,000 mg/kg, whole numbers; 1,000 mg/kg and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, nonvolatile-on-ignition, dissolved, calculation

Parameter and Code:

Solids, nonvolatile-on-ignition, dissolved, I-1752-85 (mg/L): 00525

1. Application

This method may be used to calculate nonvolatile dissolved solids on any sample for which the dissolved solids (method I-1750) and the volatile dissolved solids (method I-1753) have been determined.

2. Summary of method

The nonvolatile solids are determined by subtracting the volatile dissolved solids (method I-1753) from the dissolved solids (method I-1750).

7. Calculations

$$\text{Solids, nonvolatile-on-ignition, dissolved, mg/L} = DS - DV$$

where

DS = dissolved solids, milligrams per liter, and

DV = solids, volatile on ignition, dissolved, milligrams per liter.

8. Report

Report solids, nonvolatile-on-ignition, dissolved (00525), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, nonvolatile-on-ignition, total, calculation

Parameter and Code:

Solids, nonvolatile-on-ignition, total, I-3752-85 (mg/L): 00510

1. Application

This method may be used to calculate total nonvolatile solids on any sample for which the total solids (method I-3750) and the total volatile solids (method I-3753) have been determined.

2. Summary of method

Total nonvolatile solids are determined by subtracting the total volatile solids (method I-3753) from the total solids (method I-3750).

7. Calculations

Solids, nonvolatile-on-ignition, total, (mg/L) = $TS-TV$

where

TS = total solids, milligrams per liter,

and

TV = solids, volatile on ignition, total, milligrams per liter.

8. Report

Report solids, nonvolatile-on-ignition, total (00510), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, nonvolatile-on-ignition, suspended, calculation

Parameter and Code:

Solids, nonvolatile-on-ignition, suspended, I-3766-85 (mg/L): 00540

1. Application

This method may be used to calculate nonvolatile suspended solids on any sample for which the suspended solids (method I-3765) and volatile suspended solids (method I-3767) have been determined.

2. Summary of method

The nonvolatile suspended solids are determined by subtracting the volatile suspended solids (method I-3767) from the suspended solids (method I-3765).

7. Calculations

Solids, nonvolatile on ignition, suspended, mg/L = $SS-VS$

where

SS = suspended solids, milligrams per liter, and

VS = solids, volatile on ignition, suspended, milligrams per liter.

8. Report

Report solids, nonvolatile-on-ignition, suspended (00540), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, sum of constituents, calculation

Parameter and Code:

Solids, dissolved, I-1751-85 (mg/L): 70301

1. Application

The calculation method is applicable only to those analyses that include determinations of all major constituents. Such analyses are considered to be complete for all practical purposes. The chemist can never be certain of the completeness of the analysis, but for most alkaline waters other than brines, the determination of silica, calcium, magnesium, sodium, potassium, alkalinity, sulfate, chloride, and nitrate is sufficient. The wide range of metals possible in acid water precludes assumptions as to the completeness of the analysis.

2. Summary of method

2.1 The concentrations of all determined constituents are converted mathematically into the forms in which they would normally exist in an anhydrous residue. These quantities are then added. If the water is grossly polluted, it is usually necessary to determine the nitrogen components. Concentration of carbonaceous material can be estimated by redissolving the residue on evaporation and successively treating it with several amounts of hydrogen peroxide. The difference in weight between the nonoxidized residue and the oxidized residue is an indication of the carbonaceous solids. The estimated carbonaceous solids are not included in the calculated dissolved solids, but are one measure of the differences to be expected between dissolved solids determined by residue on evaporation and by calculation (Howard, 1933).

2.2 The conversion of the constituents in the analysis to the forms in which they would normally exist in an anhydrous residue involves many unknown variables. Consequently, summarizing the constituents requires the arbitrary assumption that all material present in the theoretical anhydrous residue be in the same form as reported in the analysis, with the exception of bicarbonate.

All bicarbonate in solution is assumed to exist as carbonate in the residue:

$$2HCO_3^{-1} \rightarrow CO_3^{-2} + CO_2 + H_2O$$

Therefore, the bicarbonate in solution is mathematically converted to its equivalent weight as carbonate in the residue.

2.3 The accuracy of the result is dependent on the completeness of the analysis and on the validity of each reported constituent concentration.

7. Calculations

7.1.1 If a field bicarbonate determination was made, convert bicarbonate concentration to carbonate concentration as follows:

$$\text{mg/L } CO_3^{-2} = \frac{\text{mg/L } HCO_3^{-1}}{2.03}$$

7.1.2 Alternatively, convert alkalinity concentration reported as mg/L $CaCO_3$ to carbonate concentration:

$$\text{mg/L } CO_3^{-2} = \text{mg/L } CaCO_3 \times 0.60$$

7.2 Add all determined dissolved constituents reported in the analytical statement. The following constituents must be included: calcium, magnesium, sodium, potassium, alkalinity, chloride, nitrate, sulfate, and silica.

8. Report

Report solids, dissolved, calculated (70301), concentrations as follows: less than 100 mg/L, whole numbers; 100 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method, but reproducibility should be comparable to that of the individual determinations.

Reference

Howard, C. S., 1933, Determination of total dissolved solids in water analysis: Industrial Engineering Chemistry, Analytical Edition, v. 5, p. 4.

Specific conductance, electrometric, Wheatstone bridge

Parameters and Codes:

Specific conductance, lab, I-1780-85 (µS/cm at 25°C): 90095
Specific conductance, lab, automated, I-2781-85 (µS/cm at 25°C): 90095

1. Application

This method may be applied to all natural, treated, and industrial water.

2. Summary of method

2.1 Specific conductance is determined by using a Wheatstone bridge in which a variable resistance is adjusted so that it is equal to the resistance of the unknown solution between platinized electrodes of a standardized conductivity cell. The ability of a solution to conduct an electric current is a function of the concentration and charge of the ions in the solution and also depends on the rate at which the ions can move under the influence of an electrical potential. As the number of ions per unit volume of solution increases, the rate at which individual ions can move decreases, because of interionic attraction and other effects. For this reason, a graph of total-ion concentration versus specific conductance, even for solutions of a single salt, is a simple straight line only for rather dilute solutions. As specific conductance increases beyond about 5,000 µS/cm at 25°C, the regression line curves, and beyond 50,000 µS/cm, the specific conductance is generally an unsatisfactory index of solute-ion concentration.

2.2 The temperature of the electrolyte affects the ionic velocities and, consequently, the conductance. Conductance increases about 2 percent per degree Celsius, which is about the same as the temperature coefficient of viscosity of water.

2.3 In the determination of the specific conductance, preparing a cell having electrodes exactly 1 cm^2 in area and exactly 1 cm apart would be difficult. Moreover, such an exact cell is unnecessary because a factor called the cell constant (C) can be determined. The cell constant is determined experimentally with a standard solution of known conductance. A 0.00702*N* potassium chloride solution has a specific conductance of 0.001000 S/cm at 25°C. The relation between resistance (*R*), cell constant (*C*), and specific conductance (*K*) is shown in the following equation, where *K* is known and *R* is determined:

$$RK = C$$

Thus, if the resistance of the cell, when filled with 0.00702*N* KCl, is, for example, 350 ohms, the cell constant would be 0.35 for the conductivity cell used. If the conductivity cell having a cell constant of 0.35 is filled with a sample at 25°C and the observed resistance is 865 ohms, the specific conductance of the sample could be derived from the cell-constant equation:

$$\frac{C}{R} = K$$

Substituting values from the example yields the following:

$$\frac{0.35}{865} = 0.00405 \text{ S at } 25\,^{\circ}\text{C}$$

2.4 Unless a constant-temperature room or bath is available, adjustment of sample temperature (T) to exactly 25°C is difficult. For most work, specific conductance is computed from the following equation: µS/cm = (*R* of 0.00702*N*

KCl at T of sample measurement × 1,000) × ($1/R$ of the sample).

2.5 New conductivity cells should be visually checked for cleanliness and platinum uniformity before use. Subsequently, they should be cleaned and replatinized whenever the readings become erratic or indistinct or inspection shows that any platinum black has flaked off. One platinization will usually suffice for a period of several months. To platinize the electrodes, clean them in chromic acid solution and rinse thoroughly in several changes of water. Place the electrodes in a solution of chloroplatinic acid and lead acetate (dissolve 3 g H_2PtCl_6 in 10 mL water to which 20 mg $Pb(C_2H_3O_2)_2$ is added; commercial platinizing solutions are also available). Connect the electrodes to two dry cells (1½-V each) in parallel and reverse the direction of the current once per minute for 6 min, or until the shiny platinum surface is covered. Avoid deposition of amorphous platinum on the electrodes.

Repeat the electrolytic process, using 10-percent sulfuric acid to remove chlorine. When not in use, the cell should be kept immersed in distilled water.

2.6 The accuracy and reproducibility of results obtainable depend largely on the type of bridge used, but can approach 2 percent with this equipment. Close attention to temperature is essential for reliable work.

2.7 Additional information on the theory and practice of specific conductance measurements can be found in Daniels and Alberty (1966), and in Scofield (1932).

2.8 This procedure may be automated by the addition of commercially available instrumentation.

3. Interferences

None.

4. Apparatus

4.1 *Conductivity cell*: Cells of at least two different cell constants should be available to measure a wide range of conductivities. The table below provides a general guide to the selection of an appropriate cell constant.

Specific conductance (µS/cm at 25°C)	Cell constant (cm⁻¹)
20-1,000	0.2
40-2,000	.5
100-4,000	1.0
200-10,000	2.0
400-20,000	5.0
1,000-40,000	10.0

4.2 *Conductivity meter*, Wheatstone-bridge type or equivalent direct-reading meter.

4.3 *Thermometer*, 0 to 50°C, graduated in 0.1°C. Some direct-reading conductivity meters have automatic temperature compensation built into the meter. Alternatively, a thermistor device as described by Hughes (1966) provides a convenient means of directly computing the necessary temperature correction.

5. Reagent

Potassium chloride solution, 0.00702*N*: Dissolve 0.5234 g KCl, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

6. Procedure

6.1 Meters measuring resistance: The manufacturer's instructions for operation of the bridge should be followed explicitly. A constant-temperature room or 25°C bath simplifies temperature consideration. Where such facilities are not available, the sample should be brought to approximately room temperature before the determination. However, samples in the laboratory are seldom at exactly the same temperature because of the influence of drafts, sunlight, radiators, ovens, and open flames. The temperature of each sample should be determined at the time of measurement.

6.1.1 Prepare a graph of resistance of 0.00702*N* KCl throughout the operating-temperature range.

6.1.2 Rinse the cell with sample.

6.1.3 Measure the resistance of the sample and record the temperature at the time of measurement. Record temperature to the nearest 0.1°C.

6.1.4 Determine the resistance of 0.00702*N* KCl at the temperature at which the sample resistance was measured from the graph prepared in step 6.1.1.

6.2 Direct-reading meters with built-in temperature compensators:

6.2.1 Prepare a table of conductance of 0.00702*N* KCl throughout the operating-temperature range. Calculate and enter in table the correction factors where measured conductance deviates from correct conductance.

6.2.2 Immerse probe-type cell in sample. (Cell will have been immersed in deionized water and blotted dry with tissue just before use.)

6.2.3 Measure conductance and temperature, and record both measurements.

6.2.4 Refer to table prepared in 6.2.1 and apply appropriate correction factors to conductance measurements as necessary.

7. Calculations

Specific conductance (μS/cm at 25 °C)

$$= \frac{R \text{ of } 0.00702N \text{ KCl}}{R \text{ of sample}} \times 1{,}000$$

where

R = resistance in ohms.

NOTE 1. Further calculations are unnecessary when measurements are made with a direct-reading meter with builtin temperature compensator.

8. Report

Report specific conductance, μS/cm at 25 °C (90095), as follows: less than 1,000 μS/cm, whole numbers; 1,000 μS/cm and above, three significant figures.

9. Precision

9.1 Precision for specific conductance for 36 samples within the range of 9.0 to 2080 μS/cm can be expressed as follows:

$$S_T = 0.054X - 3.80$$

where

S_T = overall precision, microsiemens per centimeter, at 25 °C,

and

X = specific conductance, microsiemens per centimeter, at 25 °C.

The correlation coefficient is 0.9005.

9.2 Precision for specific conductance for five of the 36 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μS/cm at 25 °C)	Relative standard deviation (percent)
32	9.0	19
31	112	4
28	557	3
36	1170	5
55	2080	47

9.3 Using automated instrumentation, analysis of two test samples by a single laboratory for 25 replicates of each resulted in mean values of 96.9 and 1,664 μS/cm and standard deviations of 0.8 and 11 μS/cm, respectively.

References

Daniels, Farrington, and Alberty, R. A., 1966, Physical chemistry (3rd ed.): New York, John Wiley and Sons, 671 p.

Hughes, L. S., 1966, Use of thermistor-thermometer in determination of specific conductance: U.S. Geological Survey Water-Supply Paper 1822, p. 66.

Scofield, C. S., 1932, Measuring the salinity of irrigation waters and of soil solutions with the Wheatstone bridge: U.S. Department of Agriculture Circular 232.

Strontium, atomic absorption spectrometric, direct

Parameters and Codes:

Strontium, dissolved, I-1800-85 (μg/L as Sr): 01080
Strontium, total recoverable, I-3800-85 (μg/L as Sr): 01082
Strontium, suspended recoverable, I-7800-85 (μg/L as Sr): 01081
Strontium, recoverable-from-bottom-material, dry wt, I-5800-85 (μg/g as Sr): 01083

1. Application

1.1 This method may be used to analyze water, brines, and water-suspended sediment containing from 10 to 5000 μg/L of strontium. Samples containing more than 5,000 μg/L need to be diluted.

1.2 Suspended recoverable strontium is calculated by subtracting dissolved strontium from total recoverable strontium.

1.3 This method may be used to analyze bottom material containing at least 1.0 μg/g of strontium. If the sample solution contains more than 5,000 μg/L of strontium, it must be diluted.

1.4 Total recoverable strontium in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable strontium from bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

1.5 Samples containing more than 2,500 mg/L of total solutes need first to be diluted. If the strontium concentration in the diluted sample is below detection, the undiluted sample needs to be analyzed by the standard-addition method.

2. Summary of method

2.1 Strontium is determined by atomic absorption spectrometry. Lanthanum chloride and excess potassium chloride are added to mask interferences and control ionization of strontium in the flame (Fishman and Downs, 1966).

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and a strip-chart recorder or a printer or both (fig. 44).

3. Interferences

3.1 Sodium and potassium decrease the strontium ionization in the flame. To control the ionization, 1,000 mg/L of potassium are added to both standards and samples.

3.2 Aluminum, phosphate, and silica interfere but are masked by the addition of lanthanum.

3.3 Nitrate interferes, but in the presence of lanthanum chloride-potassium chloride solution at least 2,000 mg/L can be tolerated. The addition of nitric acid in the field to preserve samples causes no problem.

3.4 Low strontium values result even in the presence of potassium and lanthanum if the dissolved-solids concentration exceeds 2,500 mg/L. For this reason, brines and highly mineralized waters must either be diluted or analyzed by the standard-addition method. For the standard-addition method, the dissolved solids content of the samples must be reduced to less than 20,000 mg/L.

4. Apparatus

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

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

Grating ------------	Visible
Wavelength --------	460.7 nm
Source (hollow-cathode lamp) ------------	Strontium
Oxidant ------------	Air
Fuel ---------------	Acetylene
Type of flame -------	Slightly reducing

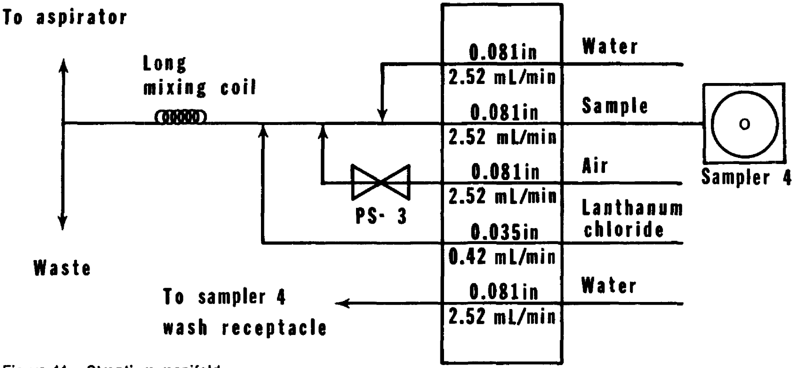


Figure 44.—Strontium manifold

4.3 The 100-mm (4-in.), single-slot burner allows a working range of 10 to 5,000 μg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Lanthanum chloride-potassium chloride solution*: Dissolve 117.3 g La_2O_3 in a minimum amount of dilute HCl. Add 19.1 g KCl, and dilute to 1,000 mL with demineralized water.

5.2 *Strontium standard solution*, 1.00 mL = 100 μg Sr: Dissolve 0.1684 g $SrCO_3$ in a minimum amount of dilute HCl, and dilute to 1,000 mL.

5.3 *Strontium working standards*: Prepare a blank and a series of at least six working standards containing from 10 to 5,000 μg/L of Sr by appropriate dilutions of strontium standard solution. Add 1.0 mL of $LaCl_3$-KCl solution to each 10 mL of working standards prepared. For example, to 500 mL of a working standard, add 50 mL $LaCl_3$-KCl solution.

6. Procedure

6.1 Add 1.0 mL $LaCl_3$-KCl solution to 10.0 mL of sample solution.

6.2 Aspirate the blank (10 mL demineralized water plus 1.0 mL $LaCl_3$-KCl solution) to set the automatic zero control. Use the automatic concentration control to set concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable strontium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing strontium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per liter of suspended recoverable strontium, subtract dissolved-strontium concentration from total-recoverable-strontium concentration.

7.3 To determine micrograms per gram of strontium in bottom-material samples, first determine the micrograms per liter of strontium as in paragraph 7.1; then

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

8. Report

8.1 Report strontium, dissolved (01080), total-recoverable (01082), and suspended-recoverable (01081), concentrations as follows:

less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

8.2 Report strontium, recoverable-from-bottom-material (01083), concentrations as follows: less than 10 μg/g, nearest microgram per gram; 10 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved strontium for 39 samples within the range of 55 to 2790 μg/L may be expressed as follows:

$$S_T = 0.119X + 12.886$$

where

S_T = overall precision, micrograms per liter, and

X = concentration strontium, micrograms per liter.

The correlation coefficient is 0.7322.

9.2 Precision for dissolved strontium for eight of the 39 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
8	55.0	22
12	99.2	30
12	583	32
10	592	14
19	818	12
13	1260	24
10	2150	25
9	2790	5

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable strontium and for recoverable strontium in bottom material will be greater than that reported for dissolved strontium.

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 41-3.

Strontium, atomic emission spectrometric, ICP

Parameter and Code:

Strontium, dissolved, I-1472-85 (μg/L as Sr): 01080

2. Summary of method

Strontium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Strontium, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:

Strontium, total, I-5474-85 (mg/kg as Sr): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Strontium is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Sulfate, dissolved, colorimetric, complexometric, methylthymol blue, automated-segmented flow

Parameter and Code:

Sulfate, dissolved, I-2822-85 (mg/L as SO_4): 00945

1. Application

This method can be used to determine concentrations of sulfate in surface, domestic, and industrial water in the range from 5 to 100 mg/L. The range can be extended to 300 mg/L by decreasing the sample-to-water ratio. Samples containing higher concentrations need to be diluted.

2. Summary of method

The sample stream is passed through a cation-exchange column before an acid solution is added containing equimolar quantities of barium chloride and methylthymol blue (MTB). Any sulfate ion is thereby precipitated as barium sulfate. When the mixture is then made basic, the remaining barium ions form a complex with MTB, and the absorbance of the uncomplexed MTB, which is gray, is directly proportional to the amount of sulfate originally present (Lazarus and others, 1968).

3. Interferences

Color is the only significant interference. Interfering cations are removed by a cation-exchange column, which is incorporated into the system.

4. Apparatus

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

4.2 With this equipment the following operating conditions have been found satisfactory for the ranges from 5 to 100 mg/L and from 100 to 300 mg/L:

Absorption cell -----	15 mm
Wavelength --------	460 nm
Cam ---------------	30/h (6/1)

5. Reagents

5.1 *Barium chloride stock solution*, 1.301 g/L: Dissolve 1.526 g $BaCl_2 \cdot 2H_2O$ (assay 99.0 percent min) in demineralized water and dilute to 1,000 mL.

5.2 *EDTA solution*: Dissolve 6.75 g NH_4Cl and 40 g disodium ethylenediaminetetra-acetic acid (EDTA) in 500 mL demineralized water and 57 mL concentrated NH_4OH (sp gr 0.90). Dilute to 1 L with demineralized water.

5.3 *Hydrochloric acid, 1M*: Add 83 mL concentrated hydrochloric acid (sp gr 1.19) to demineralized water and dilute to 1 L.

5.4 *Methylthymol blue (MTB) solution*, 0.5417 g/100 mL: Dissolve 0.5417 g MTB (Eastman Kodak No. 8068, M.W. = 866.73) in demineralized water and dilute to 100 mL.

5.5 *MTB-barium chloride reagent*: The purity of MTB may vary from one lot to another; this variation affects the linearity of the analytical curve (Colovos and others, 1976). It is, therefore, necessary to adjust the Ba-MTB ratio by the following calibration procedure in order to achieve a linear relationship between absorbance and sulfate concentration. Add 25.0 mL $BaCl_2$ stock solution to each of several 500-mL volumetric flasks. Then add volumes of MTB solution ranging from 26.0 to 36.0 mL (0.96 to 0.69 Ba-MTB molar ratio), in 2.0-mL increments, to each flask. Add 4.0 mL 1*M* HCl and an appropriate volume of demineralized water to bring the total volume to 100 mL. Dilute to 500 mL with 95-percent ethanol and add 1 mL Brij-35 solution. Analyze eight sulfate standards covering the 5- to 100-mg/L operating range (5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 75.0, and 100.0 mg/L) with reagent solutions of varying Ba-MTB molar ratios. Do not vary the instrumental parameters, but adjust the baseline as necessary. Plot an analytical curve of peak height versus known sulfate concentration for each Ba-MTB ratio. Determine least-squares equation and a coefficient of correlation on a programmable calculator or computer. From the coefficient of correlation, determine the optimum Ba-MTB ratio for a particular lot of MTB. Use this ratio when preparing subsequent solutions of MTB-barium chloride reagent. Repeat this calibration procedure only when a different lot of MTB is used.

5.6 *Sodium hydroxide*, 0.18*M*: *Cautiously* dissolve 7.2 g NaOH in demineralized water and dilute to 1 L.

5.7 *Sulfate standard solution I*, 1.00 mL = 1.00 mg SO_4: Dissolve 1.4787 g Na_2SO_4, dried for 2 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.8 *Sulfate working standards*: Prepare a blank and 1,000 mL each of a series of sulfate

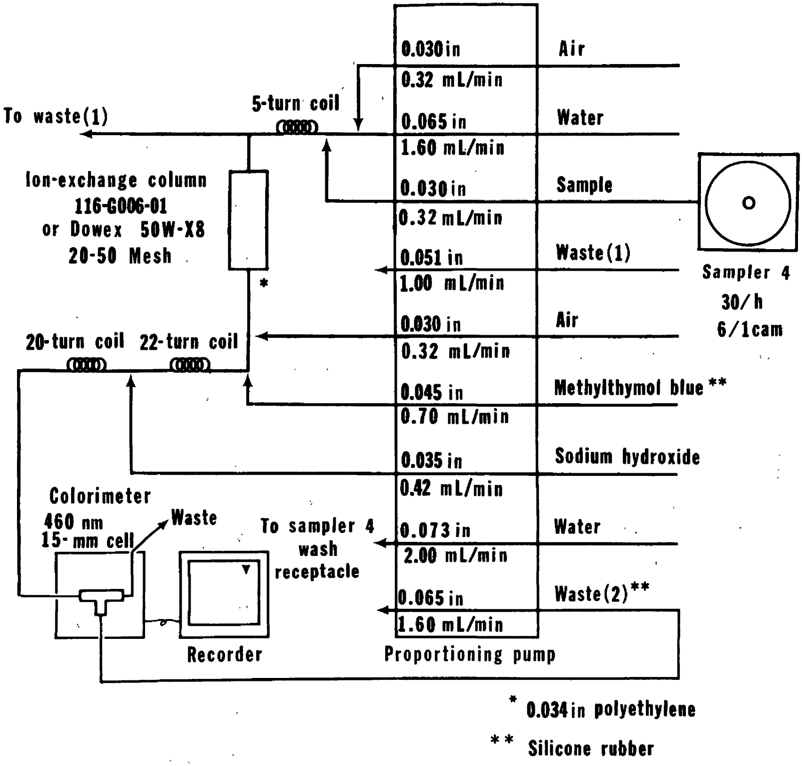


Figure 45.—Sulfate, methylthymol blue manifold, low range, 5 to 100 mg/L SO_4

working standards by appropriate quantitative dilution of sulfate standard solution I as follows:

Sulfate standard solution I (mL)	Sulfate concentration (mg/L)
0.0	0.0
5.0	5.0
10.0	10.0
20.0	20
30.0	30
40.0	40
50.0	50
75.0	75
100.0	100
150.0	150
200.0	200
300.0	300

6. Procedure

6.1 Set up manifold (fig. 45 or 46, NOTES 1 and 2).

NOTE 1. The manifold includes a cation-exchange column consisting of a 2.0-mm ID Pyrex tube approx 19-cm (7.5-in.) long filled with Dowex 50W-X8 (20 to 50 mesh), or equivalent, cation-exchange resin. The resin is held in place by a loose plug of glass wool on the exit end. Regenerate the resin daily with 1*M* HCl. Tygon transmission tubing may be used in place of the Pyrex tube. The column must be replaced if air bubbles are introduced.

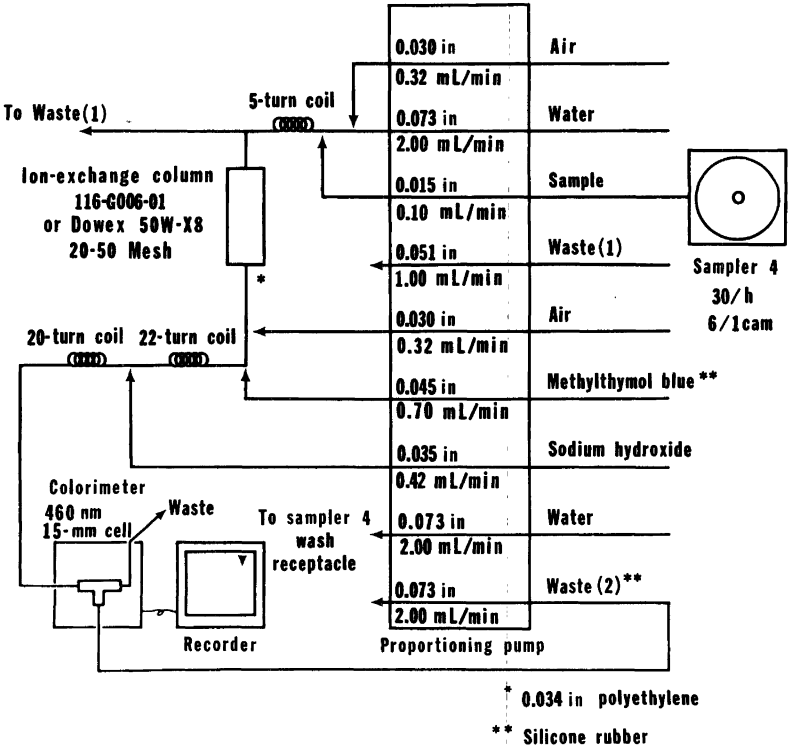


Figure 46.—Sulfate, methylthymol blue manifold, high range, 100 to 300 mg/L SO_4

NOTE 2. At the end of each day wash the system with a solution of EDTA: Place the MTB line and the NaOH line in water for a few minutes and then into the EDTA solution for 10 min. Wash the system with water for 15 min before shutting down.

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

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 approx every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample 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 sulfate concentration.

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

8. Report

Report sulfate, dissolved (00945), concentrations as follows: 5-9 mg/L, nearest 1 mg/L; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved sulfate for 16 samples within the range of 14 to 943 mg/L may be expressed as follows:

$$S_T = 0.029X + 3.42$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of sulfate, milligrams per liter.

The correlation coefficient is 0.8863.

9.2 Precision for dissolved sulfate for five of the 16 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
7	13.9	12
10	59.2	9
12	143	5
6	526	2
15	943	3

References

Colovos, G., Panesar, M. R., and Parry, E. P., 1976, Linearizing the calibration curve in determination of sulfate by the methylthymol blue method: Analytical Chemistry, v. 48, p. 1693-6.

Lazarus, A., Lorange, E., and Lodge, J. P., Jr., 1968, New automated microanalyses for total inorganic fixed nitrogen and for sulfate ion in water, *in* Trace inorganics in water: American Chemical Society, Advances in Chemistry Series, No. 73, p. 164-71.

Sulfate, turbidimetric, barium sulfate, automated-discrete

Parameter and Code:

Sulfate, dissolved, I-2823-85 (mg/L as SO_4): 00945

1. Application

This method may be used to determine concentrations of sulfate in surface, domestic, and industrial water in the ranges of 0.2 to 1000 mg/L. Samples containing greater concentrations must first be diluted. Three working ranges are provided: from 0.2 to 10.0 mg/L, from 10 to 200 mg/L, and from 200 to 1000 mg/L.

2. Summary of method

Sulfate ion is reacted with barium chloride under acidic conditions to form barium sulfate. The absorbance of the resulting suspension is measured photometrically and is proportional to the sulfate concentration present in the original sample (Santiago and others, 1975).

3. Interferences

Suspended matter in large amounts will interfere. Natural color exceeding 50 platinum cobalt units may interfere. Silica, at concentrations less than 200 mg/L, does not interfere.

4. Apparatus

4.1 *Discrete analyzer system*, American Monitor IQAS or equivalent.

4.2 With this equipment the following operating conditions have been found satisfactory for the ranges: from 0.2 to 10.0 mg/L, from 10 to 200 mg/L, and from 200 to 1000 mg/L.

Wavelength	340 nm for 0.2 to 10.0 mg/L 410 nm for 10 to 200 mg/L 458 nm for 200 to 1000 mg/L
Absorption cell -----	1 cm square, temperature-controlled, flow-through quartz cuvette
Reaction temperature -	ambient
Sample volumes	0.450 mL with 0.050 mL of diluent for 0.2 to 10.0 mg/L 0.200 mL with 0.050 mL of diluent for 10 to 200 mg/L 0.140 mL with 0.075 mL of diluent for 200-1000 mg/L (NOTE 1)
Reagent volumes	0.25 mL $BaCl_2$-NaCl-HCl-gelatin solution and 0.25 mL sulfate standard solution IV for 0.2 to 10 mg/L 1.0 mL $BaCl_2$-NaCl-HCl-gelatin solution for 10 to 200 mg/L 2.0 mL $BaCl_2$-NaCl-HCl-gelatin solution for 200 to 1000 mg/L (NOTE 1)

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each individual instrument according to manufacturer's specifications.

5. Reagents

5.1 *Barium chloride-sodium chloride-hydrochloric acid-gelatin solution.*

5.1.1. *Sulfate ranges 0.2 to 10.0 mg/L and 10 to 200 mg/L*: Dissolve 20 g $BaCl_2 \cdot 2H_2O$ in 500 mL demineralized water, and add 10 mL concentrated HCl (sp gr 1.19), 0.5 g gelatin (USP) and 20 g NaCl. Mix well, dilute to 1,000 mL with demineralized water, and filter. Prepare fresh weekly.

5.1.2. *Sulfate range, 200 to 1000 mg/L*: Dissolve 10 g $BaCl_2 \cdot 2H_2O$ in 500 mL demineralized water, and add 10 mL concentrated HCl (sp gr 1.19), 0.125 g gelatin (USP) and 20 g NaCl. Mix well, dilute to 1,000 mL with demineralized water, and filter. Prepare fresh weekly.

5.2 *Sulfate standard solution I*, 1.00 mL = 10.0 mg SO_4: Dissolve 14.787 g Na_2SO_4, dried for 2 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.3 *Sulfate standard solution II*, 1.00 mL = 1.00 mg SO_4: Dilute 100 mL standard solution I to 1,000 mL with demineralized water.

5.4 *Sulfate standard solution III*, 1.00 mL = 0.100 mg SO_4: Dilute 100 mL standard solution II to 1,000 mL with demineralized water.

5.5 *Sulfate standard solution IV*, 1.00 mL = 0.010 mg SO_4: Dilute 10.0 mL sulfate standard solution II to 1,000 mL with demineralized water.

5.6 *Sulfate working standards*: Prepare a blank and 1,000 mL each of a series of sulfate working standards by the appropriate dilution of sulfate standard solution I, II, or III as follows:

Standard solution I (mL)	Standard solution II (mL)	Standard solution III (mL)	Sulfate concentration (mg/L)
		5.0	0.5
		10.0	1.0
		50.0	5.0
		100.0	10.0
	20.0		20
	50.0		50
	125.0		125
20.0			200
30.0			300
50.0			500
80.0			800
100.0			1000

6. Procedure

6.1 Set up analyzer and computer-card assignments according to the manufacturer's instructions.

6.2 Place standards, beginning with the lowest concentration, in ascending order (computer-calibration curve) in the first five positions on the sample turntable. For the low range use 0.0, 0.5, 1.0, 5.0, and 10.0 mg/L SO_4; for the mid-range use 10, 20, 50, 125, and 200 mg/L; and for the high range use 200, 300, 500, 800, and 1,000 mg/L. Place samples and quality-control reference samples in the remainder of the sample turntable.

6.3 Begin analysis (NOTE 2).

NOTE 2. The cathode-ray tube (CRT) will acknowledge parameter and concentration range selected, listing each sample-cup number and corresponding concentrations calculated from the working curve. During each run, the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from the printer.

7. Calculations

Determine the milligrams per liter of sulfate in each sample from either the CRT display or the computer printout.

8. Report

Report sulfate, dissolved (00945), concentrations as follows: 0.2 to 10.0 mg/L, one decimal, 10 mg/L and above, two significant figures.

9. Precision

Precision expressed in terms of the standard deviation the and percent relative standard deviation for replicates analysis by a single operator is as follows (NOTE 3):

Mean (mg/L)	Number of replicates	Standard deviation (mg/L)	Relative standard deviation (percent)
0.7	22	0.08	11.0
1.3	22	.14	7.6
2.7	22	.14	5.0
4.4	22	.12	2.7
6.2	22	.12	1.9
14.3	21	.11	.5
272	22	1.14	4.2
112	21	.68	3.2
387	10	5.5	1.4
612	10	5.0	.8

NOTE 3. Some imprecision has been observed in the range from 8 to 12 mg/L. More precise data can be obtained by diluting samples within this range and determining sulfate in the 0.2 to 10 mg/L range.

Sulfate, ion-exchange chromatographic, automated

Parameters and Codes:

Sulfate, dissolved, I-2057-85 (mg/L as SO_4): 00945
Sulfate, dissolved, I-2058-85 (mg/L as SO_4): 00945

2. Summary of method

Sulfate is determined sequentially with six other anions by ion-exchange chromatography. Ions are separated based on their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical-conductivity cell. See method I-2057, anions, ion-exchange chromatographic, automated and method I-2058, anions, ion-exchange chromatographic, precipitation, automated.

Sulfate, titrimetric, thorin

Parameter and Code:

Sulfate, dissolved, I-1820-85 (mg/L as SO_4): 00945

1. Application

This method may used to analyze water containing from 0.5 to 200 mg/L of sulfate. Samples with greater concentrations need to be diluted or analyzed by an alternate method.

2. Summary of method

2.1 Thorin and barium react to form a complex that is deep red. The intensity of the color is dependent on pH, indicator concentration, and nature of the solvent. The color is more intense in organic than in aqueous solutions and also varies in intensity with different organic solvents. The color reaction can be utilized to titrate sulfate directly with barium chloride by adding a large volume of organic solvent to the sample and titrating in this mixed medium. When the end point is detected spectrometrically, the preferred titration medium is 80-percent alcohol maintained at pH 5 with a sodium acetate buffer.

2.2 The end point may also be detected by viewing the solution through a didymium glass filter. When visual detection is made, the titration medium should be 66-percent dioxane, adjusted to a pH between 2.2 and 5. The initial yellow color of thorin in the dioxane-water medium changes to pink at the end point.

3. Interferences

Thorin reacts with many metals, including calcium; therefore, all metal ions must be removed by cation exchange prior to titration. Phosphate interferes somewhat by coprecipitation; with 100 mg/L of sulfate, 10 and 20 mg/L of phosphate result in a positive error of about 2 and 3 percent, respectively. Color may interfere with the spectrometric reading and require correction.

4. Apparatus

4.1 *Absorption cells*, 50-mm. The cement in some cells reacts with thorin to produce a red color. Cells should be tested for thorin reaction, and those that produce a red color in 10 to 15 min should be rejected. Alternatively, 100-mL beakers may be used, providing the titration assembly is designed to accept such beakers.

4.2 *Buret*, 10-mL.

4.3 *Cation-exchange column* (fig. 47). The column should be filled to within 5 to 8 cm of the top with Amberlite IR-120 or equivalent,

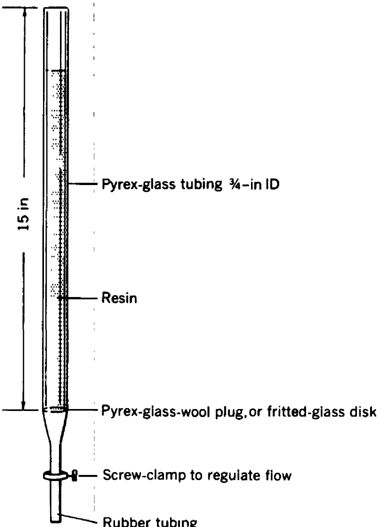


Figure 47.—Cation-exchange column for sulfate

operating on the hydrogen cycle. The resin is regenerated with 30-percent (volume-to-volume) HCl solution. The frequency of regeneration depends on the mineral content of the samples. The need for regeneration may be determined by checking a small portion of column effluent for the presence of calcium.

4.4 *Spectrophotometer* with titration assembly for use at 520 nm. Commercial instrumentation is available. Follow manufacturer's instruction for optimizing instrument conditions.

5. Reagents

5.1 *Barium standard solution*, 1.00 mL ≎ 0.20 mg SO_4^{-2}: Dissolve 0.5086 g $BaCl_2 \cdot 2H_2O$ (assay 99.0 percent minimum) in demineralized water and dilute to 1,000 mL. The exact concentration of this standard solution may be verified by titrating a known volume of sulfate standard solution as in the analytical procedure.

5.2 *Solvent indicator solution*: Dissolve 0.025 g thorin and 0.5 g anhydrous sodium acetate in 10 mL water, warming gently if necessary to ensure complete dissolution. Filter the solution through Whatman No. 1 filter paper into 1 L of 95-percent ethanol and discard the filter paper without washing or rinsing. Add 12 mL glacial CH_3COOH (sp gr 1.06) and mix. Difficulty in preparing a clear solution of the indicator is probably due to poor-quality thorin reagent.

5.3 *Sulfate standard solution*, 1.00 mL = 1.00 mg SO_4^{-2}: Dissolve 1.4787 g Na_2SO_4, dried for 2 h at 180°C, in demineralized water and dilute to 1,000 mL.

6. Procedure

6.1 Rinse the cation-exchange columns with 20 to 30 mL of sample and discard the rinse. (Check a portion for the presence of calcium.)

6.2 Pass sufficient sample through the exchanger to provide at least 10 mL of effluent for the determination.

6.3 Pipet a volume of sample containing less than 2 mg SO_4^{-2} and 10 mg dissolved solids (10.0 mL max) into a 50-mm absorption cell and adjust the volume to 10.0 mL.

6.4 Add 40 mL solvent indicator solution.

6.5 Insert cell in titration assembly and begin analysis.

6.6 Titrate with $BaCl_2$ (1.00 mL ≎ 0.20 mg SO_4^{-2}).

6.7 Determine a blank correction by titrating demineralized water. The blank is constant throughout the concentration range of the method. A blank of 0.05 mL has been found. Correct for water color when necessary.

7. Calculations

$$SO_4 \text{ in mg/L} = \frac{1{,}000}{\text{mL sample}} \times 0.2 \times (\text{mL titrant} - \text{mL blank})$$

8. Report

Report sulfate, dissolved (00945), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved sulfate for 11 samples within the range of 9.8 to 394 mg/L may be expressed as follows:

$$S_T = 0.026X + 0.686$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of sulfate, milligrams per liter.

The correlation coefficient is 0.9010.

9.2 Precision for dissolved sulfate for four of the 11 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
13	9.8	6
18	50.8	4
18	141	2
16	394	3

Sulfide, titrimetric, iodometric

Parameter and Code:

Sulfide, total, I-3840-85 (mg/L as S): 00745

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing more than 0.5 mg/L of sulfide.

1.2 Water-suspended sediment may be analyzed by this method if sample is shaken vigorously and a suitable aliquot of well-mixed sample is rapidly withdrawn.

1.3 Water containing dissolved sulfides readily loses hydrogen sulfide, particularly if the pH of the sample is low. Oxygen destroys sulfides by oxidation, particularly if the pH of the sample is high. Aeration and agitation of the sample should, therefore, be avoided. The addition of 2 g of zinc acetate per liter of water will fix the sample for several days. Acidic water must be neutralized before addition of zinc acetate.

2. Summary of method

2.1 This iodometric method does not differentiate the forms of the sulfide ion in solution.

2.2 Sulfide is reacted with an excess of iodine in acid solution, and the remaining iodine is then determined by titration with sodium thiosulfate, using starch as an indicator (Kolthoff and others, 1969).

$$S^{-2} + I_2 \xrightarrow{H^{+1}} S + 2I^{-1}$$

$$I_2 + 2S_2O_3^{-2} \xrightarrow{H^{+1}} S_4O_6^{-2} + 2I^{-1}$$

A blank is treated exactly the same as the samples. The sulfide concentration is calculated from the difference between the volume of thiosulfate required for the blank and the volume used for the sample.

2.3 This method is similar to that in an article published by the American Public Health Association (1980).

3. Interferences

Reducing substances such as sulfites and heavy-metal ions react with iodine, which contributes to positive errors. Oxygen and other oxidants may react with hydriodic acid to liberate iodine, which contributes to negative errors.

4. Apparatus

4.1 *Buret*, 10-mL capacity.

4.2 *Flasks*, Erlenmeyer, 250-mL capacity.

5. Reagents

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

5.2 *Iodine standard solution*, 0.010*N*: Dissolve 6 g iodate-free KI in approx 25 mL water. Add 1.2690 g resublimed I_2. When solution is complete, dilute to 1 L. Standardize with 0.010*N* $Na_2S_2O_3$, using starch as an indicator.

$$\text{Normality of } I_2 = \frac{0.010 \times \text{mL } Na_2S_2O_3}{\text{mL } I_2}$$

Adjust the normality of the iodine standard solution, if necessary, to 0.010 by addition of small quantities of demineralized water or iodine as indicated by the first titration. Confirm the normality by restandardization.

5.3 *Potassium iodide*, crystals, iodate-free: The KI can be tested for IO_3^{-1} by dissolving about 0.1 g in 5 mL water, acidifying with 1 or

2 drops concentrated H_2SO_4 (sp gr 1.84) and adding 2 to 3 mL starch indicator solution. Immediate appearance of blue color indicates the presence of IO_3^{-1}; slow color formation is caused by atmospheric oxidation.

5.4 *Sodium thiosulfate standard solution,* 0.010*N*: Dissolve 2.482 g $Na_2S_2O_3 \cdot 5H_2O$ in carbon dioxide-free water and dilute 1 L with carbon dioxide-free water. Standardize against KIO_3 as follows: Dry approx 0.5 g KIO_3 for 2 h at 180°C. Dissolve 0.3567 g in water and dilute to 1,000 mL. Pipet 25.0 mL KIO_3 solution into a 250-mL Erlenmeyer flask, then add successively 75 mL deionized water and 0.5 g iodate-free KI. After solution is complete, add 10 mL HCl (sp gr 1.19). Allow the stoppered flask to stand 5 min in the dark and titrate with $Na_2S_2O_3$ solution, adding starch indicator solution as the end point is approached (light-straw color):

$$\text{Normality of } Na_2S_2O_3 = \frac{0.25}{\text{mL } Na_2S_2O_3}$$

Adjust the normality of the thiosulfate standard solution, if necessary, to 0.010 by addition of small quantities of demineralized water or sodium thiosulfate as indicated by the first titration. Confirm the normality by restandardization.

5.5 *Starch indicator solution,* stable (NOTE 1).

NOTE 1. A convenient substitute for starch indicator solution is the product thyodene, sold by Fisher Scientific Co. It can be used in its dry form and produces an end point similar to that of starch.

6. Procedure

6.1 Shake the sample vigorously and immediately pipet a volume of sample with ZnS in suspension containing less than 1.5 mg S^{-2} (100.0 mL max) into a 250-mL Erlenmeyer flask, and adjust the volume to approx 100 mL.

6.2 Prepare a blank of approx 100 mL demineralized water, and carry it through the procedure with the sample.

6.3 Add 10.0 mL 0.010*N* I_2 and mix.

6.4 Without delay add 10 mL concentrated HCl.

6.5 Immediately titrate the excess I_2 with 0.010*N* $Na_2S_2O_3$, adding 2 to 3 mL starch indicator solution as the end point is approached (light-straw color).

7. Calculations

$$S^{-2} \text{ (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times 0.1603$$

$$\times \text{ (mL blank titrant} - \text{mL sample titrant)}$$

8. Report

Report sulfide, total (00745), concentrations as follows: 0.5 to 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

American Public Health Association, 1980, Standard methods for the examination of water and wastewater (15th ed.): Washington, D.C., p. 448.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative Chemical Analysis (4th ed.): New York, Macmillan, p. 857.

Thallium, atomic absorption spectrometric, graphite furnace

Parameter and Code:

Thallium, dissolved, I-1866-85 (μg/L as Tl): 01057

1. Application

This method may be used to analyze water containing at least 1 μg/L of thallium. Samples containing more than 9 μg/L need either to be diluted or a smaller volume needs to be used for analysis.

2. Summary of method

2.1 Thallium is determined by atomic absorption spectrometry in conjunction with a graphite furnace and the method of standard additions. The sample is placed in the graphite tube and is then evaporated to dryness, charred, and atomized. The absorbance signal generated during atomization is recorded. Known concentrations of thallium are added to aliquots of the sample in the tube and the technique is repeated. The absorbances are then plotted and the concentration of thallium is determined by extrapolation.

2.2 Pretreatment of the graphite tube with ammonium molybdate and addition of ammonium nitrate to the sample in the graphite tube are employed to reduce background scattering.

2.3 For discussion of standard additions, see this chapter, Analytical techniques, atomic absorption spectrometry.

3. Interferences

False peaks or recorder deflections below the baseline often occur during the atomization cycle because of heavy background scattering in this wavelength region (276.8 nm) and because of the requirement for very close alignment of the deuterium background corrector and source (electrodeless-discharge lamp).

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 276.8 nm, equipped with deuterium background correction, graphite furnace, and recorder with 2.5-mv or 5.0-mv range.

4.2 Refer to the manufacturer's manual to optimize instrumental performance.

4.3 *Graphite furnace*, capable of reaching temperatures sufficient to atomize thallium. *CAUTION*: Dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration. Use the following operating conditions:

Drying temperature ------	100°C
Charring temperature -----	400°C
Atomizing temperature ---	2400°C
Drying time -------------	(NOTE 1)
Charring time -----------	15 s
Atomizing time ----------	10 s
Purge gas ---------------	Argon, 25 cm^3/min normal flow

NOTE 1. Set drying time for as many seconds as the total microliters of sample plus standard injected.

4.4 *Graphite tubes*, compatible with furnace. Standard graphite tubes are preferred.

4.5 *Pipets*, microliter with disposable tips, 1- to 50-μL capacity.

4.6 *Thallium light source*, thallium electrodeless-discharge lamp.

4.7 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Ammonium hydroxide solution*, 3*M*: Dilute 20 mL concentrated NH_4OH (sp gr 0.90) to 100 mL with demineralized water.

5.2 *Ammonium molybdate solution*, 8.7 g/50 mL: Dissolve 9.2 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 40 mL 3*M* ammonium hydroxide solution and dilute to 50 mL with demineralized water.

5.3 *Ammonium nitrate solution*, 25 g/50 mL: Dissolve 25 g NH_4NO_3 in 50 mL demineralized water.

5.4 *Nitric acid*, concentrated (sp gr 1.41): High-purity, Ultrex or equivalent.

5.5 *Nitric acid solution*, (1 + 499): Mix 1 part concentrated HNO_3 (sp gr 1.41) with 499 parts demineralized water.

5.6 *Thallium standard solution I*, 1.00 mL = 1000 μg Tl: Dissolve 1.303 g $TlNO_3$ in demineralized water. Add 2 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1000 mL with demineralized water.

5.7 *Thallium standard solution II*, 1.00 mL = 20.0 μg Tl: Dilute 20.0 mL thallium standard solution I to 1,000 mL with nitric acid solution (1 + 499).

5.8 *Thallium working standards*: Dilute 50, 100, and 150 μL each of thallium standard solution II to 250 mL with nitric acid solution. These working standards represent concentrations of 4, 8, and 12 pg/μL of thallium. Prepare fresh daily (NOTE 2).

NOTE 2. Clean the 250-mL volumetric flasks with dilute nitric acid (1 + 50) and rinse with demineralized water immediately before use. Rinse the 50-μL micropipet disposable plastic tip twice in a solution of nitric acid (1 + 2), twice in demineralized water, and twice in thallium standard solution II before preparing the working standards.

6. Procedure

6.1 Prior to use, rinse pipet tips twice with a solution of nitric acid (1 + 2) and then twice in demineralized water.

6.2 Pretreat the graphite tube. Inject 25 μL ammonium molybdate solution and cycle as follows: dry for 20 s at 110 °C, char for 15 s at 550 °C, and atomize for 10 s at 2500 °C. Use an argon flow of 12 mL/min in the interrupt mode. Repeat injection and cycle three times.

6.3 Inject 30 μL of sample into the graphite tube and dry, char, and atomize as given in step 4.3.

6.4 From the signal's peak height obtained in paragraph 6.3, choose a sample volume which will give a signal less than 40 percent of full scale on the recorder.

6.5 Choose a volume of thallium working standards that, when added to the sample aliquot, will produce a 50-, 100-, and 150-percent increase in signal peak height (NOTE 3). Inject the same volume of demineralized water to the sample for the blank spike.

NOTE 3. To determine the approx signal (absorbances or peak heights) of the thallium working standards, inject 30 μL of the low working standard, cycle, and record signal. From this information, the volume of standard can be determined.

6.6 Inject in the graphite tube the aliquot of sample and blank as determined in steps 6.4 and 6.5. Cycle as given in paragraph 4.3 and record absorbance or peak height. Repeat process with sample and the standard additions of thallium working standards as determined in steps 6.4 and 6.5. Analyze the sample plus standards twice (NOTE 4).

NOTE 4. If background interferences occur as mentioned in paragraph 2.2, inject 20 μL ammonium nitrate solution to each sample, standard, and blank.

7. Calculations

7.1 Plot absorbances (or peak heights) of sample plus standards on the vertical axis of a graph and the mass, in pg, added on the horizontal axis.

7.2 Fit the points to a straight line by the least-squares method and extrapolate the line to the horizontal axis. The mass of thallium present in the sample is the reading at the horizontal intercept.

7.3 Determine the micrograms per liter of dissolved thallium in each sample as follows:

$$\text{Tl}(\mu g/L) = \frac{\text{mass Tl in sample (pg)}}{\text{volume of sample } (\mu L)}$$

8. Report

Report thallium, dissolved (01057), concentrations to the nearest microgram per liter.

9. Precision

9.1 Precision for dissolved thallium for four samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
4	3.2	75
5	3.4	38
6	3.8	39
3	5.0	20

9.2 Analyses of two samples six times each by a single operator resulted in mean values of 5.6 and 10.9 µg/L and relative standard deviations of 10 and 3 percent, respectively.

Tin, atomic absorption spectrometric, hydride, automated

Parameters and Codes:

Tin, dissolved, I-2851-85 (μg/L as Sn): 01100
Tin, total recoverable, I-4851-85 (μg/L as Sn): 01102
Tin, suspended recoverable, I-7851-85 (μg/L as Sn): 01101
Tin, recoverable-from-bottom-material, dry wt, I-6851-85 (μg/g as Sn): 01103

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 1 to 10 μg/L of tin. Samples containing more than 10 μg/L need to be diluted.

1.2 Suspended recoverable tin is calculated by subtracting dissolved tin from total recoverable tin.

1.3 This method may used to analyze bottom material containing at least 0.1 μg/g of inorganic tin. Sample solutions containing more than 10 μg/L must be diluted.

1.4 Total recoverable tin in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable tin from bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

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 to 1 mg/L each, or from calcium, potassium, and sodium at concentrations up to 1,000 mg/L each.

3.2 Antimony, arsenic, copper, and silver concentrations greater than 200 μg/L, 100 μg/L, 300 μg/L and 100 μg/L, respectively, depress the tin absorption. At 300 μg/L of antimony, 200 μg/L of arsenic, 400 μg/L of copper, and 200 μg/L of silver, the depression is approx 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 instrument for the following:

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 to 1200 °C. Thermolyne Model PM-20700 or equivalent.

4.4 *Stripping-condensing column*, Pyrex, packed with 3- to 5-mm Pyrex beads (fig. 48). The condensing column need not be cooled. The nitrogen gas flow rate is adjusted for maximum sensitivity by analyzing a series of identical standards. A flow rate of approx 225 mL/min has been found satisfactory.

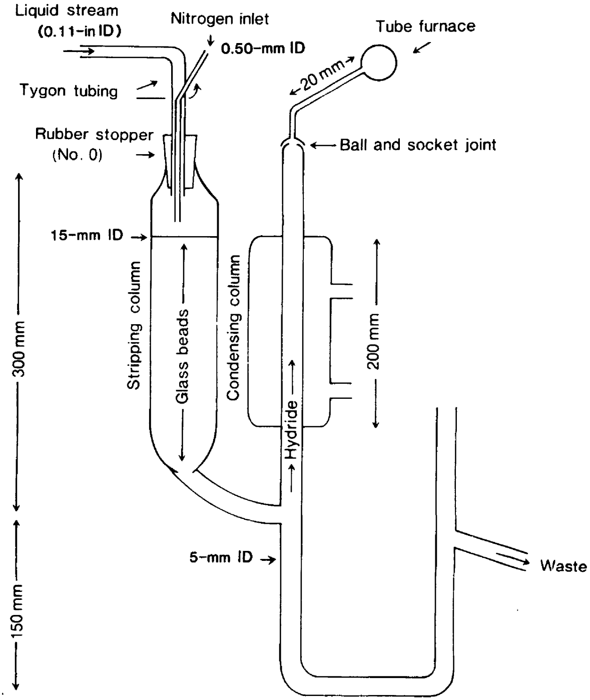


Figure 48.—Stripping-condensing column and quartz tube furnace

4.5 *Tube furnace,* quartz, 10-mm ID×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, proportioning pump, and recorder.

Cam ---------------- 20 (2/1)

5. Reagents (NOTE 1)

NOTE 1. Because 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_4EDTA 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 each month.

5.6 *Tin standard solution II*, 1.00 mL = 10.0 μg 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 daily.

5.7 *Tin standard solution III*, 1.00 mL = 0.10 μg 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 daily.

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 (μg/L)
0.0	2.0	0
2.0	1.8	1
4.0	1.6	2
10.0	1.0	5
20.0	.0	10

6. Procedure

6.1 Set up manifold (fig. 49).

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 the blank in decreasing concentrations; (2) place individual standards of differing concentrations in

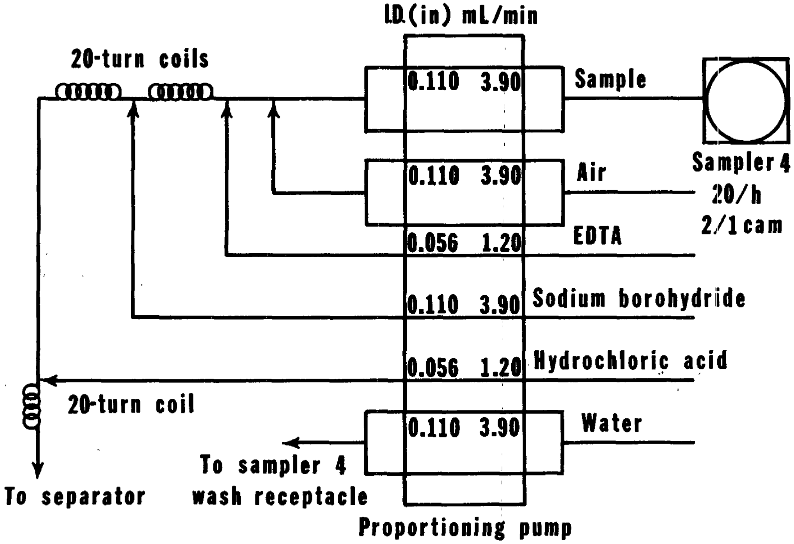


Figure 49.—Tin, hydride manifold

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 μg/L of tin will give a peak approx 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:

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

6.6.2 Grind the cell with silicon carbide as follows: Mount cell with suitable cushioning in a ¾-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 Determine the concentration of dissolved or total recoverable 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 liter of suspended recoverable tin, subtract dissolved-tin concentration from total-recoverable-tin concentration.

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

$$\mathrm{Sn}\ (\mu g/g) = \frac{\mu g/L\ \mathrm{Sn} \times mL\ \text{of digest}/1000}{\text{wt of sample (g)}}$$

8. Report

8.1 Report tin, dissolved (01100), total-recoverable (01102), and suspended-recoverable (01101), concentrations as follows: less than 10 μg/L, nearest μg/L; 10 μg/L and above, two significant figures.

8.2 Report tin, recoverable-from-bottom-material (01103), concentrations as follows: less than 1.0 μg/g, nearest 0.1 μg/g; 1.0 μg/g and above, two significant figures.

9. Precision

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

9.2 Precision for dissolved tin also may be expressed in terms of the percent relative standard deviation as follows:

Number of replicates	Mean (μg/L)	Relative standard deviation (percent)
10	5.1	6
10	9.2	3
10	9.7	4
10	10.0	1

9.3 Determination of total recoverable tin in 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 μg/L and standard deviations of 0.2, 0.4, 0.2, 0.3, and 0.5, respectively.

9.4 Precision for total recoverable tin also may be expressed in terms of the percent relative standard deviation as follows:

Number of replicates	Mean (μg/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

9.5 Determination of tin in bottom material in four test samples 10 times each by one operator resulted in mean values of 0.36, 0.56, 0.68, and 0.94 μg/g and standard deviations of 0.04, 0.03, 0.03, and 0.02, respectively.

9.6 Precision for tin in bottom material also may be expressed in terms of percent relative standard deviation as follows:

Number of replicates	Mean (µg/L)	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. 34-26.

Vijan, P. N., and Chan, C. Y., 1976, Determination of tin by gas phase atomization atomic absorption spectrometry: Analytical Chemistry, v. 48, p. 1788-92.

Titanium, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:

Titanium, total, I-5474-85 (mg/kg as Ti): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hot plate at 200 °C. Titanium is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Turbidity, nephelometric

Parameter and Code:

Turbidity, I-3860-85 (nephelometric turbidity unit): 00076

1. Application

This method is generally applicable to any water that does not contain coarse material that settles rapidly. Samples having greater than 100 nephelometric turbidity units (NTU) must be diluted prior to analysis.

2. Summary of method

2.1 The method presented below is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension under the same conditions. The greater the intensity of scattered light, the greater the turbidity. Formazin polymer, which has gained acceptance as the turbidity standard reference suspension in the brewing industry, is also used as the turbidity standard reference suspension for water. It is easy to prepare and is more reproducible in its light-scattering properties than is clay or turbid, natural-water standards. The turbidity of a particular concentration of Formazin suspension is defined as 40 NTU. This same suspension of Formazin has a turbidity of approximately 40 units when measured on the Jackson candle turbidimeter; therefore, turbidity units based on the Formazin preparation will closely approximate those derived from the Jackson candle turbidimeter but may not always be identical to them.

2.2 For additional information on the turbidity measurement and its significance, see American Public Health Association and others (1980), California State Water Quality Control Board (1963), and U.S. Public Health Service (1962).

3. Interferences

The presence of colored solutes causes measured turbidity values to be low. Precipitation of dissolved constituents (for example, Fe) causes measured turbidity values to be high.

4. Apparatus

Hach turbidimeter, Model No. 2100 or 2100A.

5. Reagents

5.1 *Hexamethylenetetramine solution*, 10 g/100 mL: Dissolve 10.0 g hexamethylenetetramine in demineralized water and dilute to 100.0 mL.

5.2 *Hydrazine sulfate solution*, 1 g/100 mL: Dissolve 1.000 g $(NH_2)_2 \cdot H_2SO_4$ in demineralized water and dilute to 100.0 mL.

5.3 *Turbidity standard suspension I* (Formazin): In a 100-mL volumetric flask mix 5.0 mL hydrazine sulfate solution with 5.0 mL hexamethylenetetramine solution. After 24 h standing at 25 ± 3°C, dilute to 100.0 mL with demineralized water and mix well. Prepare fresh monthly (NOTE 1).

NOTE 1. Prepared standards of several ranges are available from the instrument manufacturer. These have a reliable shelf life of 4 to 6 months, thereby making more frequent preparation unnecessary.

5.4 *Turbidity standard suspension II*: Dilute 10.0 mL turbidity standard suspension I to 100.0 mL with demineralized water. The turbidity of this suspension is defined as 40 nephelometric turbidity units (NTU). Prepare fresh weekly. This suspension may be diluted as required to prepare more dilute turbidity standards.

6. Procedure

6.1 *Turbidimeter calibration*: The manufacturer's operating instructions should be followed. Measure the standards on the turbidimeter covering the range of 0 to 100 NTU. If the instrument is already calibrated in standard turbidity units, this procedure will check the accuracy of the calibration. At least one standard should be included for each instrument range to be used. Some instruments permit adjustment of sensitivity so that scale values will correspond to turbidities. *Reliance on a manufacturer's solid-scattering standard for setting overall instrument sensitivity for all ranges is not an acceptable practice unless the turbidimeter has been shown to be free of drift on all ranges.* If a pre-calibrated scale is not supplied, then a calibration graph should be prepared for each range of the instrument.

6.2 *Turbidity less than 100 NTU*: Shake the sample to disperse the solids thoroughly. Wait until air bubbles disappear; then pour the sample into the turbidimeter tube. Read the turbidity directly from the instrument scale or from the appropriate calibration curve.

6.3 *Turbidity exceeding 100 NTU*: Dilute the sample with one or more volumes of nonturbid water until the turbidity falls below 100 NTU.

7. Calculations

$$\text{Turbidity (NTU)} = \text{observed turbidity} \times \frac{\text{final dilution volume}}{\text{original sample volume}}$$

8. Report

Report turbidity (00076) as follows: less than 10 NTU, one decimal; 10 NTU and above, two significant figures.

9. Precision

According to data reported by the U.S. Environmental Protection Agency, the precision of data from a single laboratory expressed in terms of the percent relative standard deviation is as follows:

Mean (NTU)	Relative standard deviation (percent)
0.26	2

References

American Public Health Association and others, 1980, Standard methods for the examination of water and wastewater 15th ed. : Washington, D.C., p. 132-4.

California State Water Quality Control Board, 1963, Water quality criteria: Publication 3-A, p. 290.

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 180.1-1.

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

Vanadium, colorimetric, catalytic oxidation

Parameter and Code:

Vanadium, dissolved, I-1880-85 (µg/L as V): 01085

1. Application

This method may be used to analyze most waters containing from 0.5 to 5.0 µg/L of vanadium, provided that the interferences identified below are not exceeded. By reducing the reaction time, concentrations up to 100 µg/L may be determined.

2. Summary of method

2.1 The oxidation of gallic acid by acid-persulfate is catalyzed by the presence of small amounts of vanadium (Jarabin and Szarvas, 1961). Depending on the amount of vanadium present, the reaction produces a yellow-to-red color, the absorbance of which is measured spectrometrically at 415 nm. Under given conditions of reactant concentration, temperature, and reaction time, the extent of oxidation of gallic acid is proportional to the concentration of vanadium present (Fishman and Skougstad, 1964).

2.2 This method is essentially the same as that reported by the American Society for Testing and Materials (1984).

3. Interferences

3.1 Several substances interfere, including chloride above 100 mg/L and bromide and iodide at lower concentrations. Their interference is eliminated or minimized by the addition of mercuric nitrate solution. In the presence of mercuric nitrate, concentrations of 100 mg/L Cl^{-1}, 0.25 mg/L Br^{-1}, and 0.25 mg/L I^{-1} can be tolerated. The following ions interfere when the indicated concentrations are exceeded: silver, 2,000 µg/L; cobalt, 1,000 µg/L; nickel, 3,000 µg/L; copper, 50 µg/L; chromium, 1,000 µg/L; and ferrous iron, 300 µg/L.

3.2 Nitric acid causes erratic and uncertain results.

4. Apparatus

4.1 *Water bath*, regulated to 25 + 0.5°C.

4.2 *Spectrometer*, for use at 415 nm. Refer to manufacturer's manual for optimizing instrumental parameters.

5. Reagents

5.1 *Ammonium persulfate-phosphoric acid reagent*: Dissolve 2.5 g $(NH_4)_2S_2O_8$ in 25 mL demineralized water. Heat solution to just below boiling, remove from heat, and add an equal volume of concentrated H_3PO_4 (sp gr 1.69). Let stand for approx 24 h before using. Discard after 2 days.

5.2 *Gallic acid solution*, 1 g/100 mL: Dissolve 0.5 g gallic acid in 50 mL hot demineralized water and filter through Whatman No. 42 filter paper. Prepare fresh daily.

5.3 *Mercuric nitrate solution*, 332 mg/L: Dissolve 0.350 g $Hg(NO_3)_2 \cdot H_2O$ in demineralized water and dilute to 1 L.

5.4 *Vanadium standard solution I*, 1.00 mL = 100 µg V: Dissolve 0.2309 g ammonium metavanadate (NH_4VO_3) in demineralized water and dilute to 1,000 mL.

5.5 *Vanadium standard solution II*, 1.00 mL = 1.0 µg V: Dilute 10.0 mL vanadium standard solution I to 1,000 mL with demineralized water.

5.6 *Vanadium standard solution III*, 1.00 mL = 0.01 µg V: Immediately before use, dilute 10.0 mL vanadium standard solution II to 1,000 mL with demineralized water. This standard is used to prepare working standards at time of analysis.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.05 µg V (10.0 mL max) into a 23-mm absorbance cell or a 25-mL test tube, and adjust the volume to 10.0 mL.

6.2 Prepare a blank and sufficient standards containing from 0.01 to 0.05 μg V in 23-mm absorbance cells or 25-mL test tubes, and adjust the volume of each to 10.0 mL with demineralized water. (Standards must be included with each set of samples.)

6.3 Add 1.0 mL mercuric nitrate solution to samples, standards, and blank, and place all cells or test tubes in a water bath (25 °C). Allow 30 to 45 min for samples to reach temperature equilibrium.

6.4 Add 1.0 mL ammonium persulfate-phosphoric acid reagent (temperature equilibrated). Mix and return to water bath.

6.5 Add 1.0 mL gallic acid (temperature equilibrated). Mix and return to water bath (NOTE 1).

NOTE 1. Because time and temperature are critical factors, the absorbance of each sample must be measured exactly 60 min after the gallic acid is added. Time the analyses of several samples most easily by starting a stopwatch with the addition of gallic acid to the first sample and by adding the gallic acid to subsequent samples at appropriate intervals.

6.6 After about 58 min, remove all cells or test tubes from the water bath; and at exactly 60 min, measure the absorbance at 415 nm, using demineralized water as a reference (NOTE 2).

NOTE 2. All samples may be removed from the water bath 1 or 2 min before the end of the 60-min period. The samples are then prepared for measurement, and the absorbance of each sample is measured exactly 60 min after the addition of the gallic acid.

7. Calculations

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

7.2 Determine the concentration of vanadium in micrograms per liter as follows:

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

8. Report

Report vanadium, dissolved (01085), concentrations as follows: less than 10 μg/L, 1 μg/L; 10 μg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved vanadium within its designated range may be expressed as follows (American Society for Testing and Materials, 1984):

$$S_T = 0.069X + 0.422$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of vanadium, micrograms per liter.

9.2 Precision for dissolved vanadium for four samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
3	1.3	46
3	2.3	65
3	6.7	31
3	12.6	57

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 31, water: Philadelphia, v. 1101, p. 676–81.

Fishman, M. J., and Skougstad, M. W., 1964, Catalytic determination of vanadium in water: Analytical Chemistry, v. 36, p. 1643–6.

Jarabin, Z., and Szarvas, P., 1961, Detection of small amounts of vanadium by catalytic reaction with the addition of gallic acid: Acta University Debrecen, v. 7, p. 131; Chemical Abstracts, 1962, v. 57, 9192c.

Vanadium, colorimetric, catalytic oxidation, automated-segmented flow

Parameter and Code:

Vanadium, dissolved, I-2880-85 (µg/L as V): 01085

1. Application

This method may be used to analyze most waters containing from 1 to 10 µg/L vanadium, provided that the interferences identified below are not exceeded.

2. Summary of method

Low concentrations of vanadium catalyze the acid-persulfate oxidation of gallic acid. This reaction proceeds rapidly in the presence of vanadium but only very slowly in its absence. The amount of colored oxidation product formed by this reaction is directly proportional to the concentration of vanadium when temperature, reaction time, and concentration of reactants are carefully controlled (Fishman and Skougstad, 1964; Jarabin and Szarvas, 1961).

3. Interferences

3.1 Chloride, bromide, and iodide interfere when their concentrations exceed 100 mg/L, 10 µg/L, and 1 µg/L, respectively. Iron(II), iron(III), and copper(II) interfere when their concentrations exceed 300 µg/L, 500 µg/L, and 50 µg/L, respectively. The concentrations of other ions are rarely high enough to interfere.

3.2 Nitric acid causes erratic and uncertain results.

4. Apparatus

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

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 1 to 10 µg/L vanadium.

Absorption cell ---------- 15 mm
Wavelength ------------- 410 nm
Cam ------------------- 20/h (1/1)
Water-bath temperature -- 60°C

5. Reagents

5.1 *Ammonium persulfate-phosphoric acid reagent*: Dissolve 2.5 g $(NH_4)_2S_2O_8$ in 25 mL demineralized water. Heat solution to just below boiling, remove from heat, and add an equal volume of concentrated H_3PO_4 (sp gr 1.69). Let stand for approx 24 h before use. Before use, dilute with 50 mL demineralized water. Discard after 2 days.

5.2 *Gallic acid solution*, 20 g/L: Dissolve 5 g gallic acid in 250 mL hot, demineralized water and filter through paper (Whatman No. 42 or equivalent). Prepare fresh daily. Keep the solution warm during analysis to prevent the gallic acid from precipitating.

5.3 *Mercuric nitrate solution*, 332 mg/L: Dissolve 350 mg $Hg(NO_3)_2 \cdot H_2O$ in demineralized water and dilute to 1 L.

5.4 *Vanadium standard solution I*, 1.00 mL = 100 µg V: Dissolve 0.2309 g ammonium metavanadate (NH_4VO_3) in demineralized water and dilute to 1,000 mL.

5.5 *Vanadium standard solution II*, 1.00 mL = 1.0 µg V: Dilute 10.0 mL vanadium standard solution I to 1,000 mL with demineralized water.

5.6 *Vanadium standard solution III*, 1.00 mL = 0.05 µg V: Dilute 50.0 mL vanadium standard solution II to 1,000 mL with demineralized water.

5.7 *Vanadium working standards*: Prepare a blank and 250 mL each of a series of vanadium working standards by appropriate quantitative dilution of vanadium standard solution III as follows:

Vanadium standard solution III (mL)	Vanadium concentration (µg/L)
0.0	0.0
5.0	1.0
10.0	2.0
20.0	4.0
30.0	6.0
40.0	8.0
50.0	10.0

6. Procedure

6.1 Set up manifold (fig. 50).

6.2 Allow colorimeter, recorder, and water bath to warm for at least 30 min or until the temperature of the water bath reaches 60°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 approx 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 standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

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

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

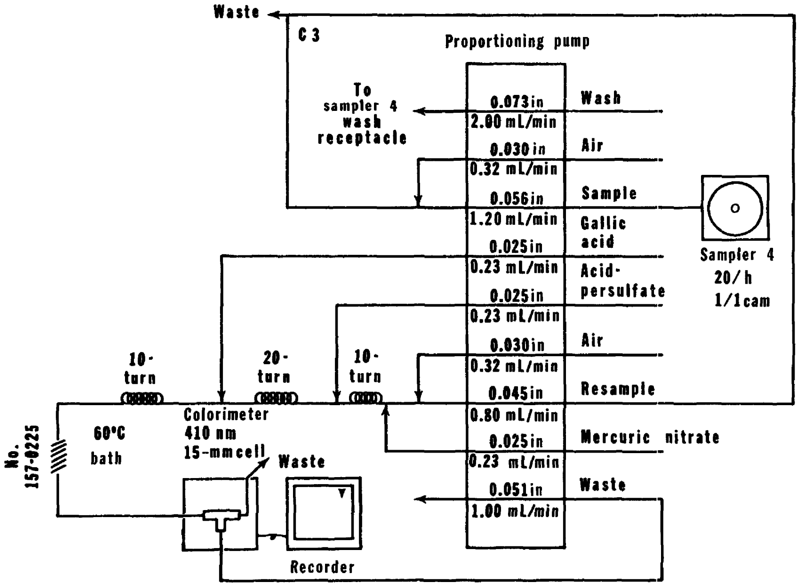


Figure 50.—Vanadium, catalytic oxidation manifold

8. Report

Report vanadium, dissolved (01085), concentrations as follows: less than 10 µg/L, nearest 1 µg/L; 10 µg/L and above, two significant figures.

9. Precision

Single-operator precision for dissolved vanadium for three samples expressed in terms of percent relative standard deviation is as follows:

Number of replicates	Mean (µg/L)	Relative standard deviation (percent)
4	3.5	3
8	8.1	1
8	53.9	1

References

Fishman, M. J., and Skougstad, M. W., 1964, Catalytic determination of vanadium in water: Analytical Chemistry, v. 36, p. 1643–6.

Jarabin, Z., and Szarvas, P., 1961, Detection of small amounts of vanadium by catalytic reaction with the addition of gallic acid: Acta University Debrecen, v. 7, p. 131; Chemical Abstracts, 1962, v. 57, 9192c.

Vanadium, atomic emission spectrometric, ICP

Parameter and Code:

Vanadium, dissolved, I-1472-85 (μg/L as V): 01085

2. Summary of method

Vanadium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Zinc, atomic absorption spectrometric, direct

Parameters and Codes:

Zinc, dissolved, I-1900-85 (μg/L as Zn): 01090
Zinc, total recoverable, I-3900-85 (μg/L as Zn): 01092
Zinc, suspended recoverable, I-7900-85 (μg/L as Zn): 01091
Zinc, recoverable-from-bottom-material, dry wt, I-5900-85 (μg/g as Zn): 01093

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 10 to 500 μg/L of zinc. Sample solutions containing more than 500 μg/L need to be diluted or to be read on a less expanded scale.

1.2 Suspended-recoverable zinc is calculated by subtracting dissolved zinc from total recoverable zinc.

1.3 This method may be used to analyze bottom material containing at least 1.0 μg/g of zinc. Sample solutions containing more than 500 μg/L of zinc need to be diluted or less scale expansion used.

1.4 Total recoverable zinc in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable zinc in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

2.1 Zinc is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame.

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer or both.

3. Interferences

3.1 Magnesium at concentrations greater than 100 mg/L interferes unless other cations, such as sodium, are present in the sample.

3.2 Individual concentrations of sodium, potassium, sulfate, chloride (9,000 mg/L of each), calcium (4,500 mg/L), nitrate (2,000 mg/L), iron (4×10^6 μg/L), and cadmium, nickel, copper, lead, cobalt, and chromium (10,000 μg/L each) do not interfere. Greater concentrations of each constituent were not investigated.

3.3 Samples containing 100 mg/L of silica cause no interference; however, zinc recovery is approx 10 percent low in samples containing 200 mg/L of silica.

4. Apparatus

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

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

Grating ------------	Ultraviolet
Wavelength --------	213.8 nm
Source (hollow-cathode lamp) ------------	Zinc
Oxidant ------------	Air
Fuel ---------------	Acetylene
Type of flame -------	Oxidizing

4.3 The 50-mm (2-in.) and 100-mm (4-in.) flathead, single-slot burners allow a working range from 10 to 500 μg/L of zinc. Different burners may be used according to manufacturer's instructions.

5. Reagents

5.1 *Zinc standard solution I*, 1.00 mL = 100 μg Zn: Dissolve 0.100 g reagent grade zinc (30-mesh) in a slight excess of concentrated HCl (sp gr 1.19), and dilute to 1,000 mL with demineralized water.

5.2 *Zinc standard solution II*, 1.00 mL = 1.0 μg Zn: Dilute 10.0 mL zinc standard solution I to 1,000 mL with demineralized water containing 1 mL concentrated HNO_3 (sp gr 1.41).

5.3 *Zinc working standards*: Prepare a series of at least six working standards containing from 10 to 500 μg/L of zinc by appropriate dilutions of zinc standard solution II with acidified water.

5.4 *Water, acidified.* Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

Aspirate the blank (acidified water) to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

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

7.2 To determine micrograms per liter of suspended recoverable zinc, subtract dissolved-zinc concentration from total-recoverable-zinc concentration.

7.3 To determine micrograms per gram of zinc in bottom-material samples, first determine the micrograms per liter of zinc as in paragraph 7.1, then

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

8. Report

8.1 Report zinc, dissolved (01090), total-recoverable (01092), and suspended- recoverable (01091), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

8.2 Report zinc, recoverable-from-bottom-material (01093), concentrations as follows: less than 10 μg/g, nearest microgram per gram; 10 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved zinc for 30 samples within the range of 14 to 1110 μg/L may be expressed as follows:

$$S_T = 0.070X + 6.51$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of zinc, micrograms per liter.

The correlation coefficient is 0.7967.

9.2 Precision for dissolved zinc for six of the 30 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
33	14	43
47	104	10
19	116	22
41	236	7
22	520	5
17	1110	9

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable zinc and recoverable zinc in bottom material will be greater than that reported for dissolved zinc.

9.4 Precision for total recoverable zinc expressed in terms of the percent relative standard deviation for two water-suspended sediment mixtures is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
23	78.4	27
26	172	31

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: United States Geological Survey Water-Supply Paper 1540-C., p. 43-5.

Zinc, atomic absorption spectrometric, graphite furnace

Parameter and Code:

Zinc, dissolved, I-1901-85 (μg/L as Zn): 01090

1. Application

1.1 This method may be used to determine zinc in low ionic-strength water and precipitation. With Zeeman background correction and a 20-μL sample, the method is applicable in the range from 0.5 to 40 μg/L. Sample solutions that contain zinc concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric method, or by the atomic emission spectrometry ICP method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Zinc is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform and a matrix modifier is added. The sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (25 mg/L), magnesium (8 mg/L), sodium (20 mg/L), sulfate (34 mg/L), and chloride (25 mg/L) do not interfere. Greater concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of zinc. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 213.8 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high-temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-μL sample with 5 μL of matrix modifier (NOTE 1).

NOTE 1. A 20-μL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms*. Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware*. Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Matrix modifier solution*, 40g $NH_4H_2PO_4$/L: Add 40.0 g $NH_4H_2PO_4$ to 950 mL Type 1 water, mix, and dilute to 1,000 mL. Analyze 20 μL of matrix modifier for zinc contamination. If the zinc reading is more than 0.005 absorbance-seconds, purify the solution by chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK, NOTE 2). Analyze 20 μL of the purified solution. Repeat extractions until the zinc level is reduced to the acceptable level. **DO NOT ADD ACID TO THE PURIFIED MATRIX MODIFIER SOLUTION.**

NOTE 2. To purify matrix modifier solution, pour the solution into a Teflon or FEP container. Add 0.25 g APDC for each liter of solution. While stirring, adjust the solution to pH 2.9 by dropwise addition of concentrated HNO_3 (sp gr 1.41). Transfer portions of the solution to a separatory funnel, add 100 mL MIBK/liter of solution, and shake vigorously for at least 5 min. Frequently, vent the funnel in a hood. Collect the extracted solution in the FEP container. Repeat the extraction with 50 mL MIBK/liter of solution. Because MIBK can dissolve some plastic autosampler cups, boil the solution for at least 10 min in a silicone-treated or acid-rinsed container covered with a watchglass to remove MIBK.

5.2 *Nitric acid, concentrated*, high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HN_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for zinc. Add an additional 1.5 mL of concentrated HNO_3/liter of water, and repeat analysis. The integrated signal should not increase by more than 0.001 absorbance-seconds.

5.3 *Water, acidified*, Type 1: Add 1.5 mL high-purity, concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.4 *Water, Type 1.*

5.5 *Zinc standard solution I*, 1.00 mL = 1,000 μg Zn: Dissolve 1.0000 g Zn powder in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41) Ultrex or equivalent and dilute to 1,000 mL with Type 1 water. Alternatively, a certified standard solution at this concentration may be purchased.

5.6 *Zinc standard solution II*, 1.00 mL = 10.0 μg Zn: Dilute 10.0 mL zinc standard solution I to 1,000 mL (NOTE 3).

NOTE 3. Use acidified, Type 1 water (paragraph 5.3) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.7 *Zinc standard solution III*, 1.00 mL = 1.00 μg Zn: Dilute 100.0 mL zinc standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.8 *Zinc standard solution IV*, 1.00 mL = 0.010 μg Zn: Dilute 10.0 mL zinc standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1 + 1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-μL aliquots of blank and working standards plus 5 μL of modifier each and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear up to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and/or platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of zinc in each sample from the digital display or printer output. Dilute those samples containing concentrations of zinc that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report zinc, dissolved (01090), concentrations as follows: less than 10.0 μg/L, nearest 0.1 μg/L; 10 μg/L and above, two significant figures.

9. Precision

9.1 Analysis of four samples by a single operator using Zeeman background correction is as follows:

Number of replicates	Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
6	5.92	0.24	4.1
4	16.02	.26	1.6
6	19.70	1.29	6.5
12	40.21	3.18	7.9

9.2 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 μS/cm). A known amount of zinc was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (μg/L)	Amount found (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
3.05	4.20	1.16	27.6	138
5.5	5.53	.86	15.6	101
6.1	6.13	.63	10.3	100
11	11.30	.62	5.5	103
36	39.95	4.51	11.3	111
Tap water (NOTE 4)				
3.05	2.17	.73	7.2	71
5.5	4.27	.65	5.3	78
6.1	6.38	1.44	10.1	105
11	8.85	.92	5.5	80
36	42.93	4.67	10.0	119

NOTE 4. The tap water contained 8 μg/L of zinc, and the standard deviation and percent relative standard deviation were calculated prior to subtraction of zinc originally present.

References

American Society for Testing and Materials, 1984, Annual book of ASTM Standards, section 11, water: Philadelphia, v. 11.01, p. 39-42.

Cooksey, M., and Barnett, W. B., 1979, Matrix modification and the method of additions in flameless atomic absorption: Atomic Absorption Newsletter, v. 18, p. 101-5.

Fernandez, F. J., Beatty, M. M., and Barnett, W. B., 1981, Use of the L'vov platform for furnace atomic absorption applications: Atomic Spectroscopy, v. 2, p. 16-21.

Hinderberger, E. J., Kaiser, M. L., and Koirtyohann, S. R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1-11.

Manning, D. C., and Slavin, W., 1983, The determination of trace elements in natural waters using the stabilized temperature platform furnace: Applied Spectroscopy, v. 37, p. 1-11.

Ottaway, J. M., 1982, A revolutionary development in graphite furnace atomic absorption: Atomic Spectroscopy, v. 3, p. 89-92.

Slavin, W., Carnrick, G. R., and Manning, D. C., 1982, Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace: Analytical Chemistry, v. 54, p. 621-4.

Zinc, atomic emission spectrometric, ICP

Parameter and Code:

Zinc, dissolved, I-1472-85 (μg/L as Zn): 01090

2. Summary of method

Zinc is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Zinc, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:

Zinc, total, I-5474-85 (mg/kg as Zn): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200°C. Zinc is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Metals, atomic emission spectrometric, ICP

Parameters and Codes: Metals, dissolved, I-1472-85 (see below)

Parameter	Code	Parameter	Code
Barium (μg/L as Ba)	01005	Magnesium (mg/L as Mg)	00925
Beryllium (μg/L as Be)	01010	Manganese (μg/L as Mn)	01056
Cadmium (μg/L as Cd)	01025	Molybdenum (μg/L as Mo)	01060
Calcium (mg/L as Ca)	00915	Silica (mg/L as SiO_2)	00955
Cobalt (μg/L as Co)	01035	Sodium (mg/L as Na)	00930
Copper (μg/L as Cu)	01040	Strontium (μg/L as Sr)	01080
Iron (μg/L as Fe)	01046	Vanadium (μg/L as V)	01085
Lead (μg/L as Pb)	01049	Zinc (μg/L as Zn)	01090
Lithium (μg/L as Li)	01130		

1. Application

1.1 This method may be used only for the determination of dissolved constituents in water that have a measured specific conductance of less than 2,000 μS/cm at 25 °C. Table 8 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 μS/cm. Trace metals can also be determined in samples that have a measured specific conductance greater than 2,000 μS/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 and bottom material cannot be analyzed.

1.3 The induction-coupled argon plasma (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. Until operating conditions of various manufacturers' instruments become more comparable and the equivalency of methods using those instruments are established by extensive testing, the ICP methods approved for U.S. Geological Survey use will specify instrument and associated software brands. This does not imply endorsement of one product over another, but rather, acknowledges that 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, atomized, and introduced into the plasma via a spray chamber and torch assembly. 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.

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 they are printed as output.

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 μS/cm or less.

Table 8.—Working ranges of constituents for ICP

Constituent	Lower limit (µg/L except where noted)	Upper limit (µg/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 mg/L	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 (1)	.001 mg/L	5 mg/L	279.5
Magnesium (2)	5 mg/L	100 mg/L	382.9
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 mg/L	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.

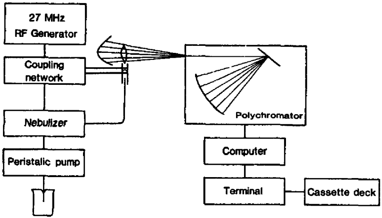


Figure 51.—Block diagram of spectrometer system

4. **Apparatus** (do not substitute)

4.1 *Emission Spectrometry System* (fig. 51) 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 8 for element wavelengths.)

4.1.2 *Computer*, Digital Equipment Co., PDP8e.

4.1.3 *Quartz Torch* (fig. 52).

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

4.1.5 *Peristaltic Pump*, Gilson, Model HP4 (fig. 53).

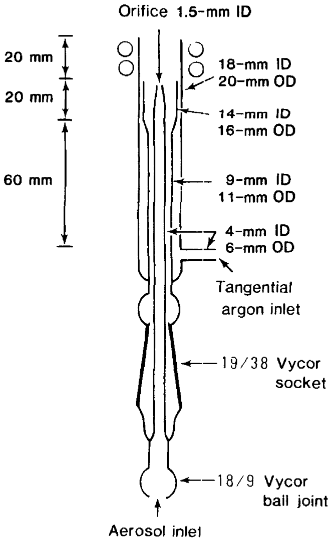
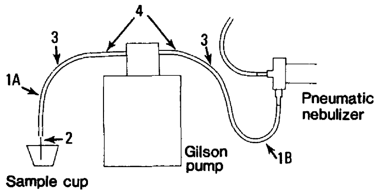


Figure 52.—Quartz torch

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



1 Technicon tubing SMA_{TM}, flow rate 0.42 mL/min part 116–0549P08, 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 53.—Pump system

4.2.1

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 (approx) -----------	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 to 5 mL/min
Refractor plate position	Optimized for Hg profile
Spectrum shifter ------	Full shift

4.2.2 The software matrix containing all the required parameters for data acquisition is shown in table 9. 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 setting them equal to 1.000, except for Li-channel 24 and Na-channel 23, by aspirating the blank solution, and then by 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 setting them equal to zero, standardizing the instrument, analyzing each interfering-element standard stock solution, and printing 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_i = 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*, 6*M*: 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*, 1.00 mL = 100 µg Ba: Dissolve 0.1516 g $BaCl_2$ dried at 180°C for 1 h in 10 mL demineralized water with 1 mL 6*M* HCl. Add 10.0 mL 6*M* HCl and dilute to 1,000 mL with demineralized water.

5.2.2 *Beryllium standard solution I*, 1.00 mL = 100 µg Be: Dissolve 0.1000 g beryllium flakes—**CAUTION: deadly poison**—in a minimum of aqua regia. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water (NOTE 1).

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

5.2.3 *Calcium standard solution I*, 1.00 mL = 100 µg 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*, 1.00 mL = 100 µg Cd: Dissolve 0.1000 g cadmium splatters in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.5 *Cobalt standard solution I*, 1.00 mL = 100 µg Co: Dissolve 0.4939 g cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$, in demineralized water. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.6 *Copper standard solution I*, 1.00 mL = 100 µg Cu: Dissolve 0.1000 g copper shot in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.7 *Iron standard solution I*, 1.00 mL = 100 µg Fe: Dissolve 0.1000 g iron wire in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.8 *Lead standard solution I*, 1.00 mL = 100 µg Pb: Dissolve 0.1000 g lead shot in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.9 *Lithium standard solution I*, 1.00 mL = 100 µg 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*, 1.00 mL = 100 µg Mg: Dissolve 0.1000 g magnesium rod in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.11 *Manganese standard solution I*, 1.00 mL = 100 µg Mn: Dissolve 0.1000 g manganese flakes in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2.12 *Molybdenum standard solution I*, 1.00 mL = 100 µg 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*, 1.00 mL = 100 µg SiO_2: Dissolve 0.3531 g $Na_2SiO_3 \cdot 5H_2O$ 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*, 1.00 mL = 500 µg Na: Dissolve 1.271 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*, 1.00 mL = 100 µg 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*, 1.00 mL = 100 µg 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*, 1.00 mL = 100 μg Zn: Dissolve 0.1000 g 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. Freshly mixed standards should be prepared weekly. Final concentration will be 1.00 mL = 10.0 μg for all parameters exception sodium, which will be 1.00 mL = 50.0 μg. Composition for mixed standards should be as follows:

5.3.2 *Mixed standard solution I*: Iron, 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, manganese, and sodium.

5.3.6 *Reagent blank*: Dilute 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 1.00 mL = 5.00 μg for all parameters except Na, which will be 1.00 mL = 28.83 μg (due to the Na in the SiO_2 standard).

6. Procedure

6.1 Set up instrument with proper operating parameters (paragraph 4.2) and ignite plasma. Instrument must warm for 30 min prior to standardization.

6.2 Retrieve the appropriate proprietary software matrix from 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 of 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 paragraph 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 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 of the elemental mean given for the reference material and less than ± 2 percent for each element respectively. If not, the data system *must* be restandardized as described starting at paragraph 6.3.

6.8 Reprofile instrument (paragraph 6.3) as necessary. If profile position changes by more than 4 micrometer units, the 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 directly in milligrams per liter (NOTE 2).

Table 9.—Single-operator precision data for ICP

Constituent	Slope	Intercept	Units
Barium	0.0061	0.83	μg/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 (SiO_2)	.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.

NOTE 2. If either the reported calcium or sodium concentration is greater than 100 mg/L or the magnesium concentration is greater than 5.0 mg/L, report the second value given, otherwise report only the first value. 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 μg/L, nearest μg/L; 10 μg/L and above, two significant figures.

8.2.3 Barium (01005), cobalt (01035), iron (01046), lithium (01130), and zinc (01090): less than 10 μg/L, nearest μg/L to the lower limit of detection as specified in table 8; 10 μg/L and above, two significant figures.

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

9. Precision

9.1 Within its designated range, single-operator precision of the method for each metal may be expressed as described in table 9. A minimum of 10 replicate analyses were performed to obtain each regression equation shown.

9.2 Interlaboratory precision data obtained on standard reference water samples are shown in table 10. The specific instrument described in this method may not have been used. Laboratories were not asked to provide this information.

Reference

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. 584–90.

Table 10.—Interlaboratory precision data for ICP

[S_T = overall precision, in units specified and X = concentration of constituent, in units specified; SD_p = average standard deviation, in units specified and CI = 95 percent confidence intervals for the average standard deviation, in units specified.]

Constituent	Number of samples	Range (μg/L except where noted)	Precision	Correlation coefficient
Barium	6	18 to 240	$S_T = 0.055X + 1.68$	0.9448
Beryllium	6	4.0 to 47	$S_T = 0.056X + 0.836$	.8442
Cadmium	6	4.0 to 15	$S_T = 0.396X - 1.50$	.8992
Calcium	7	.77 to 186 mg/L	$S_T = 0.067X - 0.433$	.9907
Cobalt	6	3.5 to 14	$SDp = 3.3$ $CI = 2.6$ to 4.6	--
Copper	6	22 to 470	$S_T = 0.065X + 2.97$	.9915
Iron	7	100 to 770	$SDp = 24.1$ $CI = 20.1$ to 29.8	
Lithium	6	43 to 650	$S_T = 0.092X + 3.59$	.8337
Magnesium	7	.10 to 120 mg/L	$S_T = 0.044X + 0.072$	.9985
Manganese	6	38 to 570	$SDp = 23.1$ $CI = 18.8$ to 28.5	--
Molybdenum	5	12 to 36	$SDp = 5.7$ $CI = 4.5$ to 8.1	--
Silica (SiO_2)	5	5.2 to 11 mg/L	$SDp = 0.78$ $CI = 0.62$ to 1.06	--
Sodium	7	.33 to 160 mg/L	$S_T = 0.027X + 0.763$	.9215
Strontium	12	57 to 2700	$S_T = 0.042X + 3.73$	.9345
Vanadium	5	6.0 to 10	$S_T = 0.879X - 4.72$	.9557
Zinc	6	15 to 570	$SDp = 14.0$ $CI = 11.6$ to 17.8	--

Anions, ion-exchange chromatographic, automated

Parameters and Codes:

Anions, dissolved, I-2057-85 (see below)

Parameter	Code	Parameter	Code
Bromide (mg/L as Br)	71870	Nitrite (mg/L as N)	00613
Chloride (mg/L as Cl)	00940	Orthophosphate (mg/L as P)	00671
Fluoride (mg/L as F)	00950	Sulfate (mg/L as SO_4)	00945
Nitrate (mg/L as N)	00618		

1. Application

1.1 This method may be used only for the determination of dissolved bromide, chloride, fluoride, nitrate, nitrite, orthophosphate, and sulfate in natural water. Table 11 shows approximate lower and upper concentration limits. Actual limits depend on many factors including the column age, which affects column resolution, the relative concentrations of closely eluting species, and the volume of the sample injected. Samples containing anion concentrations high enough to overload the column resins or interfere with closely eluting species need to be diluted or a sample loop smaller than the 200-μL sample loop specified in this method needs to be used. Sample dilution or use of smaller volumes will change the detection limits for all anions.

1.2 Analyses must be performed on filtered and unacidified samples.

1.3 The ion chromatographic (IC) 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 operating conditions of various manufacturers' instruments become more comparable and the equivalency of methods using those instruments is established by extensive testing, the IC method approved for U.S. Geological Survey use will specify instrument and associated software brands. This does not imply endorsement of one product over another, but rather, acknowledges that IC technology is rapidly changing and developing.

Table 11.—Working ranges of anions by ion chromatography

Constituent	Minimum concentration[1] (mg/L)	Maximum concentration (mg/L)
Fluoride	0.01	50
Chloride	.20	50
Nitrite-nitrogen	.02	70
Orthophosphate-phosphorus	.06	40
Bromide	.10	150
Nitrate-Nitrogen	.05	150
Sulfate	.20	100

[1] With a larger sample loop (for example, 600 μL), minimum concentration levels can be lowered.

2. Summary of method

2.1 A sample is injected into an ion chromatograph and is pumped through three different ion-exchange columns into a specific-conductivity detector. The first two columns, a precolumn and separator column, are packed with low-capacity anion exchanger. Ions are separated based on their affinity for the exchange sites of the resin. The last column is a suppressor column that contains cation-exchange resin in the hydrogen form. The suppressor column reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample into their corresponding acids. The separated anions in their acid form are measured using an electrical-conductivity cell. Anions are identified based on their retention times compared with known standards. Quantitation is accomplished by measuring the peak height or area and by comparing it with an analytical curve generated from known standards.

2.2 During analysis, the suppressor column will slowly be exhausted and, therefore, will need to be regenerated. Other suppressors, such as the hollow-fiber suppressor, which is continuously regenerated, may be used.

2.3 For additional information on ion chromatography, see Small and others (1975) and Fishman and Pyen (1979).

3. Interferences

3.1 Because bromide and nitrate elute very closely together, they potentially interfere with each other. Bromide-to-nitrate ratios should not exceed 1:10 or 10:1 if both ions are to be quantitated.

3.2 High levels of organic acids may be present in industrial and domestic wastes which may interfere with inorganic-anion analysis. Two common species, formate and acetate, elute between fluoride and chloride.

3.3 Water from the sample injection will cause a negative peak or dip in the chromatogram when it elutes, because its conductivity is less than that of the suppressed eluent. This dip usually occurs between F^{-1} and Cl^{-1}. Any peak of interest eluting near the water dip must be sufficiently resolved from the dip to be accurately quantitated. A method of eliminating the conductivity drop due to bicarbonate and carbonate is to introduce into the sample concentrations of bicarbonate and carbonate that closely approximate those of the eluent used for analysis. Adjustment of the sample background may be accomplished in two ways.

3.3.1 Dilute the sample with eluent if sample dilution is required prior to analysis.

3.3.2 A volume of 1.0 mL of a prepared eluent concentrate (a solution that is 100 times more concentrated than the eluent with respect to bicarbonate and carbonate ions) can be added per 100.0 mL of sample. CAUTION: Samples prepared in this manner have a pH of about 10 and will readily absorb carbon dioxide if left exposed to the atmosphere. The result will cause a positive-peak interference.

3.3.3 Standard solutions need to be prepared in the same manner as the samples. It is important to prepare a blank using demineralized water at eluent strength in bicarbonate and carbonate to indicate any interferences that may have been introduced by the sample-preparation technique.

3.4 Samples containing high concentrations of chloride or other anions may prevent resolution of closely eluting peaks. For example, the peak for 0.1 mg of bromide per liter in the presence of greater than 1,000 mg of chloride per liter is swamped by the chloride peak. Bromide begins to elute before the chloride peak completely returns to the baseline.

3.5 Unexpected, late-eluting peaks are a potential source of interference. A peak eluting about two minutes after sulfate, believed to be oxalate, has been observed in some precipitation samples.

4. Apparatus

4.1 *Ion Chromatograph, Dionex Model 12; auto-sampler, Gilson; integrator (NOTE 1), Spectra Physics* using the following operating conditions:

Sample loop --------	200 µL
Eluent flow rate -----	138 mL/h (30 percent of full capacity)
Sample pump flow rate	50 percent of full capacity
Specific conductance meter settings ----	10, 30, or 100 µS

NOTE 1. A dual pen recorder (1 V and 100 mV) may replace an integrator. The recorder should be capable of full-scale response in two seconds or less. A typical chart speed is 0.5 cm/min.

4.1.1 *Precolumn*, 4 × 50-mm, fast-run, anion-resin column (Dionex P/N 030831 or equivalent) placed before the separator column to protect the separator column from contamination by particulates or species strongly retained by the ion-exchange resin.

4.1.2 *Separator column*, 4 × 250-mm, fast-run, anion-separator column packed with low-capacity, pellicular, anion-exchange resin (Dionex P/N 030830 or equivalent) that is styrene divinylbenzene-based. This is suitable for resolving fluoride, chloride, nitrite, orthophosphate, bromide, nitrate, and sulfate.

4.1.3 *Suppressor column*, 6 × 250-mm, column-packed, with a high-capacity, column- exchange resin (Dowex 50W-X 16-H form resin or equivalent) that is capable of converting the eluent and separated anions to their respective acid forms.

4.2 For additional information, refer to the different manufacturers' instruction manuals.

5. Reagents

5.1 *Eluent*, 0.003 *M* sodium bicarbonate-0.0024 *M* sodium carbonate: Dissolve 0.2520 g $NaHCO_3$ and 0.2544 g Na_2CO_3 in demineralized water and dilute to 1 L (NOTE 2).

NOTE 2: Eluent concentration may be varied slightly to obtain the same retention times for each anion when a new separator column is used. The $NaHCO_3$ is subject to thermal decomposition and must be weighed without prior drying.

5.2 *Suppressor regeneration solution*, 1*N* H_2SO_4: *Cautiously* add 111 mL concentrated H_2SO_4 (sp gr 1.84) to approx 600 mL demineralized water. Cool and dilute to 4 L with demineralized water.

5.3 *Standard anion solutions*: Dry all salts for 1 h at 105°C unless otherwise specified. Store each standard solution in TFE-fluorocarbon bottles.

5.3.1 *Bromide standard solution*, 1.00 mL = 1.00 mg Br: Dissolve 1.2877 g NaBr in demineralized water and dilute to 1,000 mL.

5.3.2 *Chloride standard solution*, 1.00 mL = 1.00 mg Cl: Dissolve 1.6484 g NaCl in demineralized water and dilute to 1,000 mL.

5.3.3 *Fluoride standard solution*, 1.00 mL = 1.00 mg F: Dissolve 2.2101 g NaF in demineralized water and dilute to 1,000 mL.

5.3.4 *Nitrate-nitrogen standard solution*, 1.00 mL = 1.00 mg NO_3-N: Dissolve 6.0681 g $NaNO_3$ in demineralized water and dilute to 1,000 mL.

5.3.5 *Nitrite-nitrogen standard solution*, 1.00 mL = 1.00 mg NO_2-N: Dissolve 4.9259 g $NaNO_2$ in demineralized water and dilute to 1,000 mL.

5.3.6 *Phosphorus standard solution*, 1.00 mL = 1.00 mg P: Dissolve 4.3936 g anhydrous KH_2PO_4 in demineralized water and dilute to 1,000 mL.

5.3.7 *Sulfate standard solution*, 1.00 mL = 1.00 mg SO_4: Dissolve 1.8140 g K_2SO_4 in demineralized water and dilute to 1,000 mL.

5.4 *Mixed stock solution*: Prepare 1,000 mL mixed stock solution by appropriate quantitative dilution of each standard solution (NOTES 3 and 4).

Anion	Concentration (mg/L)	Volume (mL)
F	5.00	5
Cl	50.0	50
NO_2-N	5.0	5
PO_4-P	5.0	55
Br	5.0	5
NO_3-N	50.0	50
SO_4	50.0	50

NOTE 3. If nitrite is omitted from the mixed stock solution, the solution is stable for at least 1 month when stored and refrigerated in a clean TFE-fluorocarbon bottle. If nitrite is included in the mixed-stock solution, the solution needs to be prepared fresh daily.

NOTE 4. The above is only an example of a mixed-stock solution. Other appropriate concentrations can be prepared.

5.5 *Mixed standard solutions*: Prepare at least three mixed standard solutions by appropriate dilution of the mixed stock solution. The solutions should bracket the concentration range of interest.

6. Procedure

6.1 Set up the ion chromatograph according to the operating parameters described in 4.1. Equilibrate the columns with eluent until a stable baseline is obtained. Allow approximately 30 min for equilibration.

6.2 Set the full-scale conductivity to 10, 30, or 100 μS as is appropriate for the expected sample-anion concentrations. The higher settings are required for higher sample-anion concentrations.

6.3 Level the integrator at 10 mV (a display of 1000 with no signal). Adjust the ion chromatograph's offset to approximately 11 mV (a display of 1100). This ensures that the ion chromatograph's signal will not fall below 10 mV during the course of the analyses. The baseline signal tends to drift in a negative direction over a long period of time. Each chromatogram can be started at a signal level of 10 mV using the integrator's automatic-zero control.

6.4 Enter an appropriate program into the main program controller of the ion chromatograph according to the manufacturer's instruction manual. The system is configured so that the ion chromatograph controls the autosampler and starts the integrator at the beginning of each sample injection (NOTE 5).

NOTE 5. For additional information on computerized data reduction, see Hedley and Fishman (1982).

6.5 Place the mixed standard solutions in the first positions of the sample tray followed by a standard reference material and then the samples. Place a standard reference material in every twentieth position of the remainder of the sample tray.

6.6 Create an information file in the integrator by pressing the DIALOG key. Through this information file, various integrator functions can be enabled or disabled during the recording of a chromatogram. The only necessary function is ER (end run). It terminates the chromatogram at the appropriate time as determined by the operator's setting of the ion chromatograph's controller, which actuates the sampler and causes the injection of a new sample.

6.7 Press the integrator's PT EVAL key before starting a series of analyses. The integrator will take about 50 s to store the baseline signal so that a peak can be distinguished from baseline noise. The baseline noise can be evaluated before each chromatogram, using the integrator's ET function.

6.8 Set the ion chromatograph's PGM/AUTO/MANUAL switch from MANUAL to AUTO and press Start/Step to begin the analyses.

7. Calculation

7.1 The integrator automatically computes the concentration of each anion in each sample by comparing its peak height or area to the analytical curve. Retention times for the seven anions are given in table 12.

8. Report

8.1 Report bromide (71870), chloride (00940), fluoride (00950), nitrate-nitrogen (00618), nitrite-nitrogen (00613), orthophosphate-phosphorus (00660), and sulfate (00945), dissolved, concentrations as follows: less than 1 mg/L, nearest 0.01 mg/L; 1 mg/L and above, two significant figures.

9. Precision

9.1 Analysis of a number of test samples 10 times each by one operator resulted in mean values, standard deviations, and percent relative standard deviations as shown in table 13.

Table 12.—Approximate retention times of anions by ion chromatography

Constituent	Time (min)
Fluoride	2.2
Chloride	3.3
Nitrate-nitrogen	4.0
Orthophosphate-phosphorus	4.9
Bromide	6.5
Nitrate-nitrogen	7.5
Sulfate	8.6

Table 13.—Precision for ion chromatographic determination of anions

Constituent	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
Bromide	0.295	0.020	6.8
Chloride	.72	.04	5.6
Do.	1.71	.06	3.5
Do.	2.72	.24	8.8
Do.	5.84	.19	3.2
Do.	9.90	.39	3.9
Do.	58.6	.7	1.2
Do.	119	1.2	1.0
Fluoride	.018	.004	22.2
Do	.080	.010	12.5
Do	.79	.02	2.5
Do	.92	.01	1.1
Do.	2.02	.15	7.4
Nitrate-nitrogen	.12	.01	8.3
Do	.42	.051	1.9
Do	.70	.081	1.4
Do.	1.27	.05	3.9
Do.	5.26	.14	2.7
Nitrite-nitrogen	.03	.01	33.3
Orthophosphate-phosphorus	.273	.010	3.7
Sulfate	1.68	.05	3.0
Do.	3.88	.10	2.6
Do.	15.1	.80	5.3
Do.	62.1	.9	1.4
Do.	100	1.4	1.4
Do.	146	3	2.0

References

Fishman, M. J., and Pyen, G. S., 1979, Determination of selected anions in water by ion chromatography: U.S. Geological Survey Water-Resources Investigations, 79-101, 30 p.

Hedley, A. G., and Fishman, M. J., 1982, Automation of an ion chromatograph for precipitation analysis with computerized data reduction: U.S. Geological Survey Water-Resources Investigations, 81-78, 33 p.

Small, H., Stevens, T. S., Bauman, W. C., 1975, Novel ion exchange chromatographic method using conductimetric detection: Analytical Chemistry, v. 47, p. 1801-9.

Anions, ion-exchange chromatographic, low ionic-strength water, automated

Parameters and Codes:

Anions, dissolved, I-2058-85 (see below)

Parameter	Code	Parameter	Code
Bromide (mg/L as Br)	71870	Nitrate (mg/L as N)	00618
Chloride (mg/L as Cl)	00940	Orthophosphate (mg/L as P)	00671
Fluoride (mg/L as F)	00950	Sulfate (mg/L as SO_4)	00945

1. Application

1.1 This method may be used only for the determination of dissolved bromide, chloride, fluoride, nitrate, orthophosphate, and sulfate in water with a specific conductance of approx 100 μS/cm or less. Table 14 specifies the lower and upper concentration limits using a 200-μL sample loop. Samples containing anion concentrations greater than the upper concentration limits must be diluted or the conductivity meter must be changed to a less sensitive setting before analysis.

1.2 Analyses must be performed on a filtered (rinsed 0.45-μm membrane filter) or particulate-free, unacidified sample.

2. Summary of method

2.1 All six anions are determined on a single filtered or particulate-free, unacidified sample with an ion chromatograph.

2.2 In anion analysis, the ions of interest elute through an anion-ion exchange separator column at different rates, depending upon the affinity of each anion for the ion- exchange resin. Then the ions elute through a fiber suppressor, which consists of a semi-permeable membrane in the interior of the suppressor's outer shell. The membrane is wrapped around the interior of the fiber, which is packed with inert beads. A suppressor regenerant solution flows countercurrent to the eluent intrained samples and surrounds the outside of the semi-permeable fiber. The regenerant is continuously fed by gravity through the suppressor's interior. This latter process operates continuously.

Table 14.—Analytical ranges used in the determination of the six anions

Constituent	Minimum concenration (mg/L)	Maximum concentration (mg/L)
Fluoride	0.01	0.5
Chloride	.01	3.0
Orthophosphate-phosphorus	.01	.6
Bromide	.01	.6
Nitrate-nitrogen	.01	.6
Sulfate	.01	10.0

2.3 For additional information on ion chromatography, see Small and others (1975).

3. Interferences

3.1 A negative peak or dip, which is caused by a combination of water and carbonate, is seen in the chromatogram using a fiber suppressor. This interference is eliminated by adding concentrated eluent to the sample.

3.2 Because low ionic-strength samples contain low concentrations of these six anions, there will be no unresolved peaks and, therefore, no interferences.

3.3 Oxalate, acetate, or formate may interfere if present.

4. Apparatus

4.1 *Ion Chromatograph, Dionex Model 2120i* (NOTE 1) or equivalent, using the following operating conditions:

Eluent-pump flow rate	2.0 mL/min
Sample loop --------	200 μL
Specific-conductance meter settings ----	1,3,10,30 μS

NOTE 1. Concentration limits and operating conditions may vary according to model of instrument.

4.2 *Pump, LDC/Milton Roy miniMetric I* (NOTE 2) or equivalent that gives pulse-free flow of liquid. These pumps are used to eliminate "water and carbonate dip" by adding a volume of concentrated eluent (10x) to each sample.

Sample pump flow rate	2.4 mL/min
Concentrated eluent pump flow rate ---	0.23 mL/min (NOTE 3)

NOTE 2. Deactivate the Reset switch to bypass the low-pressure-limit adjustment.

NOTE 3. These flow rates will vary slightly depending on the eluent concentration. Adjust flow rates of pumps by injecting a blank until "water and carbonate dip" disappears.

4.2.1 Sample and concentrated eluent pumps are connected to the ion chromatographic Relays 3 and 4, respectively, and are controlled by Auto Ion 100 Controller program.

4.3 *Integrator, Spectra Physics; auto sampler, Gilson* or their equivalents, connected to the ion chromatograph's Relays 1 and 2, respectively.

4.4 *Proportioning pump, Technicon*, or equivalent, provides demineralized water into the wash receptacle of the sampler.

4.5 *Precolumn*, HPIC AS-4 Dionex pellicular anion-resin or equivalent.

4.6 *Separator column*, HPIC AS-4 Dionex pellicular anion-resin or equivalent.

4.7 *Suppressor*, Dionex anion fiber suppressor, No. 35350.

4.8 For additional information, refer to the manufacturers' instruction manuals.

5. Reagents

5.1 *Anion stock solutions I*, 1.00 mL = 1.00 mg: Prepare six individual anion stock solutions I by dissolving indicated amount of reagent-grade chemicals, dried to a constant weight at 105°C, in demineralized water and dilute to 1,000 mL and store in Teflon bottles.

Anion	Salt	g/L
Br	NaBr	1.2877
Cl	NaCl	1.6484
F	NaF	2.2101
NO_3-N	$NaNO_3$	6.0681
PO_4-P	KH_2PO_4	4.3936
SO_4	K_2SO_4	1.8140

5.2 *Anion Stock Solutions II*, 1.00 mL = 0.10 mg: Prepare chloride and sulfate stock solutions by diluting 100 mL each of chloride and sulfate stock solutions I to 1,000 mL with demineralized water and store in Teflon bottles.

5.3 *Concentrated eluent*, 0.0280*M* sodium bicarbonate-0.0225*M* sodium carbonate: Dissolve 9.408 g $NaHCO_3$ and 9.540 g Na_2CO_3 in demineralized water and dilute to 4 L.

5.4 *Demineralized water*: Pass water through a post column (millipore or equivalent) with 0.2-μm pore size filter which is placed after laboratory demineralized water system.

5.5 *Eluent*, 0.00280*M* sodium bicarbonate-0.00225*M* sodium carbonate (NOTE 4): Dissolve 5.410 g $NaHCO_3$ and 5.486 g Na_2CO_3 in demineralized water and diulute to 23 L.

NOTE 4. Eluent concentration may be varied slightly to obtain the same retention times for each anion when a new separator column is used.

5.6 *Mixed-anion standard solution I*: Prepare 1,000 mL by appropriate quantitative dilution of anion stock solutions I with demineralized water.

Anion	Concentration (mg/L)	Volume (m/L)
Br	10	10.0
Cl	250	250
F	10	10.0
NO_3-N	30	30.0
PO_4-P	10	10.0
SO_4	300	300

5.7 *Mixed-anion standard solution II*: Dilute 10.0 mL mixed anion standard solution I to 1,000 mL with demineralized water.

Anion	Concentration (mg/L)
Br	0.1
Cl	2.5
F	.1
NO_3-N	.3
PO_4-P	.1
SO_4	3.0

5.8 *Mixed-anion standard solution III*: Prepare 1,000 mL by appropriate dilution of anion stock solutions II.

Anion	Concentration (mg/L)	Volume (mL)
Cl	0.2	2.0
SO_4	0.2	2.0

5.9 *Suppressor-regeneration solution*, $0.025N$ H_2SO_4: *Cautiously* add 2.8 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water, cool, and dilute to 4L with demineralized water.

6. Procedure

6.1 Operate instrument according to parameters described in paragraph 4.1. Supply continuously by gravity-feeding suppressor-regeneration solution for fiber supressor ($0.025N$ H_2SO_4) at a flow rate of 2.4 mL/min. Equilibrate the columns with $0.00280M$ $NaHCO_3$-$0.00225M$ Na_2CO_3 eluent until baseline stabilizes. Allow approximately 30 min for equilibration.

6.2 Enter appropriate program into the Auto Ion 100 Controller of ion chromatograph according to manufacturer's instructions. This controls autosampler, integrator, sample pump, and concentrated-eluent pump. This program is best suited for most of the precipitation samples. Set the OutPut Range of the conductivity meter similar to the expected concentration of samples.

6.3 Press the PT EVAL (peak threshold evaluation) key for integrator to evaluate the detector signal for noise and drift.

6.4 Create the information file through a "dialog" with the integrator.

Select calculation of the best straight-line fit using method 5 (external standard method) (NOTE 5).

NOTE 5. For additional information on computerized data reduction, see Hedley and Fishman (1982).

6.5 Run a demineralized water blank through the system to ensure that flow rates of sample and concentrated-eluent pumps are in correct proportion to eliminate the "water and carbonate dip."

6.6 Place mixed-anion standard solutions III and II at the beginning of the sample holder followed by standard reference materials and samples. Place a standard reference material in every tenth position of the remainder of this sample holder.

6.7 Turn on the proportioning pump to deliver demineralized water into the wash receptacle of the sampler.

6.8 Press START on the OPERATION-SELECT of AutoIon 100 Controller to begin the analysis.

7. Calculations

7.1 The integrator automatically computes the concentrations of six anions in each sample by comparing their peak heights to the analytical curve. Approximate retention times for the six anions are given in table 15.

8. Report

8.1 Report bromide (71870), chloride (00940), fluoride (00950), nitrate-nitrogen (00618), orthophosphate-phosphorus (00660), and sulfate (00945), dissolved, concentrations as follows: less than 1 mg/L, nearest 0.01 mg/L; 1.0 mg/L and above, nearest 0.1 mg/L.

9. Precision and Bias

9.1 Analysis of a number of test samples 10 times each by one operator resulted in mean values, standard deviations, and percent relative standard deviations as shown in table 16.

Table 15.—Approximate retention times of anions

Constituent	Time (min)
Fluoride	1.4
Chloride	2.2
Orthophosphate-phosphorus	3.4
Bromide	4.8
Nitrate-nitrogen	5.6
Sulfate	7.6

Table 16.—Precision and bias for ion chromatography on simulated precipitation samples

Standard reference water sample number	Constituent	Ion chromatography data[1]			Interlaboratory standard reference water sample data	
		Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)	Mean (mg/L)	Standard deviation[2] (mg/L)
70 (1:10)	F	0.09	0.01	8.1	0.089	0.06
	Cl	.23	.01	4.3	.271	.84
	NO_3-N	.06	.005	7.7	.069	.065
	SO_4	2.60	.07	2.6	2.62	1.4
72 (1:10)	F	.10	.01	9.3	.09	0.06
	Cl	4.89	.14	2.8	4.50	1.4
	PO_4-P	.05	.004	8.8	.059	.048
	NO_3-N	.30	.01	4.4	.302	.29
	SO_4	10.6	.34	3.2	11.1	10
P-1	Cl	.40	.01	2.3	.44	.045
	NO_3-N	.13	.003	2.3	.12	.016
	SO_4	1.14	.03	2.5	1.18	.09
P-2	F	.10	.01	7.8	.10	.00
	Cl	.47	.01	1.8	.60	.33
	NO_3-N	.04	.002	6.0	.074	.068
	SO_4	2.96	.06	1.9	3.24	1.43
80 (1:10)	F	.11	.01	9.4	.114	.07
	Cl	3.20	.09	3.0	3.15	1.5
	PO_4-P	.06	.005	9.6	.073	.063
	NO_3-N	.06	.004	7.3	.055	.070
	SO_4	7.08	.16	2.3	7.24	5.15

[1] Values based on 10 replicate determinations of SRWS.
[2] Standard deviations for undiluted SRWS.

References

Fishman, M. J., and Pyen, G. S., 1979, Determination of selected anions in water by ion chromatography: U.S. Geological Survey Water-Resources Investigations, 79-101, 30 p.

Hedley, A. G., and Fishman, M. J., 1982, Automation of an ion chromatograph for precipitation analysis with computerized data reduction: U.S. Geological Survey Water-Resources Investigations, 81-78, 33 p.

Small, H., Stevens, T. S., Bauman, W. C., 1975, Novel ion exchange chromatographic method using conductimetric detection: Analytical Chemistry, v. 47, p. 1801-9.

Stevens, T. S., Davis J. C., and Small, H., 1981, Hollow fiber ion-exchange suppressor for ion chromatography: Analytical Chemistry, v. 53, p. 1488-92.

Metals, major, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:

Metals, total, (I-5473-85): none assigned
Aluminum (mg/kg as Al)
Calcium (mg/kg as Ca)
Iron (mg/kg as Fe)
Magnesium (mg/kg as Mg)
Manganese (mg/kg as Mn)
Potassium (mg/kg as K)
Silica (mg/kg as Si)
Sodium (mg/kg as Na)

1. Application

1.1 This method may be used to analyze suspended and bottom sediment for the determination of total concentrations of the constituents. The upper- and lower-concentration-reporting limits are specified below. Samples containing analyte concentrations greater than the upper limit may be analyzed after appropriate dilution.

Constituent	Lower limit (mg/kg)	Upper limit (mg/kg)
Aluminum	20,000	150,000
Calcium	1,000	50,000
Iron	5,000	100,000
Magnesium	1,000	20,000
Manganese	100	4,000
Potassium	1,000	35,000
Silica	40,000	150,000
Sodium	1,000	25,000

1.2 Analyses must be performed on dried and ground samples that have been fused with a lithium metaborate-lithium tetraborate flux, with the resulting bead dissolved in acidified, deionized water. These solutions are then analyzed by atomic absorption spectrometry.

2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The dried, ground, and homogenized sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1,000 °C. The resulting bead is dissolved in acidified, boiling, demineralized water. The resulting solutions are analyzed by atomic absorption spectrometry after the addition of appropriate matrix modifiers. Additional interferences are removed or compensated for by the use of mixed-salt standards.

2.2 Additional information on the principles of the method may be found in Shapiro (1975), Johnson and Maxwell (1981), and Pinta (1982).

3. Interferences

3.1 Both positive and negative, interelement interferences occur and have been documented (Johnson and Maxwell, 1981; Pinta, 1982).

3.2 Interferences are eliminated and (or) compensated for by use of cesium chloride (CsCl), orthoboric acid (H_3BO_3), lithium metaborate ($LiBO_2$), lithium tetraborate ($Li_2B_4O_7$), and by the use of mixed-salt standards.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero and concentration controls, and an autosampler (optional).

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

Constituent	Grating: ultraviolet (uv) or visible (vis)	Wavelength (nm)	Burner: nitrous oxide (N_2O) or air	Oxidant: nitrous oxide (N_2O) or air	Flame type
Al	uv	309.3	N_2O	N_2O	fuel-rich
Ca	vis	422.7	N_2O	N_2O	oxidizing
Fe	uv	372.0	N_2O	N_2O	oxidizing
Mg	uv	202.6	N_2O	N_2O	oxidizing
Mn	uv	279.5	N_2O	N_2O	oxidizing
K	vis	766.5	air	air	oxidizing
Si	uv	251.6	N_2O	N_2O	reducing
Na	vis	589.0	air	air	oxidizing

4.3 *Fuel*, acetylene.

4.4 *Graphite crucibles*, drill-point, 7.5-mL capacity, 1-in. OD, ¾-in. ID, and 1 5/8-in. total depth.

4.5 *Hollow-cathode lamps*, single-element lamps.

4.6 *Magnetic stirrer.*

4.7 *Muffle furnace*, capable of reaching a temperature of at least 1000 °C.

5. Reagents

5.1 *Cesium chloride solution*, 4 g/L: Dissolve 4 g CsCl of at least 5/9ths (<10 ppm impurities) purity in demineralized water and dilute to 1L.

5.2 *Flux mixture*: Thoroughly mix 1 part reagent-grade powdered anhydrous lithium metaborate, $LiBO_2$, and 2 parts anhydrous lithium tetraborate, $Li_2B_4O_7$. Store in a tightly closed bottle (NOTE 1).

5.3 *Lithium metaborate*, $LiBO_2$, at least 5/9ths purity (<10 ppm impurities) (NOTE 1).

5.4 *Lithium tetraborate*, $Li_2B_4O_7$ at least 5/9ths purity (<10 ppm impurities) (NOTE 1). NOTE 1. Pre-mixed fusion fluxes are available from several suppliers and, if sufficiently pure, are satisfactory.

5.5 *Mixed-salt standard solution*: Dissolve, by appropriate means, the following compounds or elements: Al powder (1.500 g), $CaCO_3$ (1.249 g), Fe wire (1.000 g), Mg rod (0.200 g), Mn flakes (0.040 g), KCl (0.668 g), $(NH_4)_2SiF_6$ (18.987 g), NaCl (0.636 g), and $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ (1.227 g), and dilute to 1000 mL with standard diluent solution. This solution will contain the following concentrations: Al (1500 mg/L), Ca (500 mg/L), Fe (1000 mg/L), Mg (200 mg/L), Mn (40 mg/L), K (350 mg/L), Si (3000 mg/L), Na (250 mg/L), and Ti (200 mg/L). Store in a plastic or Teflon bottle.

5.6 *Working standard solutions 1, 2, and 3*: Pipet 10 mL (standard 1), 6 mL (standard 2), and 2 mL (standard 3) mixed-salt standard solutions (5.5) into 100 mL volumetric flasks, and dilute each to 100 mL with standard diluent solution (5.10). Concentrations are as follows:

Constituent	Standard 1 (mg/L)	Standard 2 (mg/L)	Standard 3 (mg/L)
Fe	100	60	20
Mg	20	12	4
Si	300	180	60
Al	150	90	30
Ti	20	12	4
Ca	50	30	10
Na	25	15	5
K	35	21	7
Mn	4	2	1

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

5.8 *Nitric acid*, dilute (1+1): Add 250 mL concentrated HNO_3 (sp. gr. 1.41) to 250 mL demineralized water. Store in a plastic bottle.

5.9 *Orthoboric acid solution*, 50 g/L: Dissolve 50 g H_3BO_3 of at least 5/9ths (10 ppm impurities) purity in demineralized water and dilute to 1 L. Heat may be required to complete dissolution. Prepare fresh daily, because orthoboric acid will precipitate within 12 to 18 hours.

5.10 *Standard diluent solution*: Dissolve 6 g of flux mixture in 500 mL demineralized water. Add 12.5 mL concentrated HNO_3 (sp. gr. 1.41), and dilute to 1 L with demineralized water.

6. Procedure

Immediately before each use, clean all glassware by rinsing, first with dilute nitric acid (1 + 1) and then with demineralized water.

6.1 Dry the sediment sample by an appropriate procedure such as freeze-drying or oven-drying at 105 °C.

6.2 If the sediment sample is greater than 100 g, split to less than 100 g by the use of a non-metallic sample splitter (riffle sampler) or by coning and quartering.

6.3 Grind the sample with a mixer mill or with an agate mortar and pestle until all material is finer than 100 mesh.

6.4 Transfer approximately 1.2 g of flux mixture to a waxed or plastic-coated weighing paper (6 in. × 6 in). Weigh and transfer 0.2000 g of finely ground sample to the flux mixture and mix by rolling successive corners of the paper about 30 times. Carefully transfer the combined sample-flux to a graphite crucible, and tamp.

6.5 Weigh appropriate standard reference materials and treat as in paragraph 6.4.

6.6 Carry several blanks through the procedure by using only flux and treat as in paragraph 6.4.

6.7 Fuse the mixtures in a muffle furnace, pre-heated to 1,000 °C, for 30 min (NOTE 2).

NOTE 2. When the crucibles, samples, and crucible racks are placed in the muffle furnace, the temperature may drop as much as 200 °C. Time is measured from the time of insertion in the furnace.

6.8 Remove the crucibles from the furnace and allow to cool; dislodge the beads by gentle tapping or with a spatula (NOTE 3).

NOTE 3. The beads can be dissolved immediately after cooling or can be stored in plastic vials for dissolution at a later time.

6.9 Place the beads in an acid-washed, 250-mL, plastic bottle and add a ¾- to 1-in. stirring bar. Add approx 50 mL boiling demineralized water using a plastic graduate, place the bottle on a magnetic stirrer, and mix. Add 5 mL dilute nitric acid (1 + 1) to each bottle and stir rapidly for about 60 min. Cap the bottle lightly to prevent contamination and possible spattering.

6.10 Immediately after 60 min, remove the bottles from the magnetic stirrers, and add about 100 mL demineralized water to prevent the polymerization of silica (NOTE 4).

NOTE 4. The solutions may contain small amounts of graphite from the crucibles, which can be ignored. However, if the solution is cloudy, this indicates that the original sample contained a very high concentration of silica that has polymerized. Discard the solution and perform a new fusion using a smaller quantity of sample.

6.11 Pour each solution into a 200-mL volumetric flask, using a funnel, in order to retain the stirring bar. Rinse the bottle and cap, and dilute to volume with demineralized water. Pour the solution back into the plastic bottle for storage.

6.12 Add 10 mL CsCl solution and 20 mL H_3BO_3 solution to each bottle (NOTE 5).

6.13 Prepare the mixed-salt working standards (see paragraph 5.6), and to each 100 mL, add 5 mL CsCl solution and 10 mL H_3BO_3 solution (NOTE 5).

NOTE 5. The CsCl acts as an ionization suppressant and the H_3BO_3 stabilizes the silica.

6.14 Set up the atomic absorption spectrometer as outlined in paragraph 4.2, and analyze the solutions for Fe, Mn, Mg, Si, and Al. Dilute samples if required (NOTE 6).

NOTE 6. Although the mixed-salt standard contains as much as 300 mg/L Si, samples containing more than 150 mg/L Si should be diluted prior to quantitation. There is a significant suppression of Si above 150 mg/L. The high Si level in the mixed salt is necessary for matrix-matching requirements.

6.15 Transfer 10.0-mL aliquots of each sample and working standard solution to 100-mL volumetric flasks and dilute to 100 mL. Transfer solutions to plastic bottles and add 5 mL CsCl and 10 mL H_3BO_3 solutions.

6.16 Set up the atomic absorption spectrometer as outlined in paragraph 4.2, and analyze the solutions for Ca, K, and Na. Dilute samples if required.

7. Calculations

7.1 Determine the concentration of each constituent (Fe, Mn, Mg, Si, and Al) in each sample solution from the digital display or printer output while aspirating each sample, and record the results. The concentration of each constituent (in mg/kg) is obtained by multiplying the concentration in each sample solution by 1000, if no dilutions are made.

7.2 Determine the concentration of each constituent (Ca, K, and Na) in each sample solution from the digital display or printer output while aspirating each sample and record the results.

The concentration of each constituent (in mg/kg) is obtained by multiplying the concentration in each sample solution by 10,000, if no dilutions are made.

8. Report

Report aluminum, calcium, iron, magnesium, potassium, silica, and sodium, total, concentrations to the nearest 1000 mg/kg (0.1 percent). Report manganese, total, concentration to the nearest 100 mg/kg (0.01 percent).

9. Precision

The precision on the two samples expressed in terms of the relative standard deviation is as follows:

	Sample 1			Sample 2		
Constituent	Number of replicates	Mean (percent)	Relative standard deviation (percent)	Number of replicates	Mean (percent)	Relative standard deviation (percent)
Aluminum	5	3.5	3	10	8.5	1
Calcium	5	.7	11	10	7.8	3
Iron	5	1.2	3	10	9.3	1
Magnesium	10	.5	2	5	4.3	3
Manganese	10	.02	20	5	.16	12
Potassium	10	.5	10	10	3.7	3
Silica	5	13.2	2	10	32.4	1
Sodium	5	.7	9	10	3.1	3

References

Johnson, W. M., and Maxwell, J. A., 1981, Rock and mineral analysis, 2d ed. : New York, John Wiley & Sons, 489 p.

Pinta, M., 1982, Modern methods for trace element analysis, translated by STS Inc., Ann Arbor, Ann Arbor Science Publishers, 492 p.

Shapiro, L., 1975, Rapid analysis of silicate, carbonate, and phosphate rocks: U.S. Geological Survey Bulletin 1401, 76 p.

Metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:

Metals, total, (I-5474-85): none assigned
Aluminum (mg/kg as Al)
Cadmium (mg/kg as Cd)
Calcium (mg/kg as Ca)
Chromium (mg/kg as Cr)
Cobalt (mg/kg as Co)
Copper (mg/kg as Cu)
Iron (mg/kg as Fe)
Lead (mg/kg as Pb)
Lithium (mg/kg as Li)
Magnesium (mg/kg as Mg)
Manganese (mg/kg as Mn)
Nickel (mg/kg as Ni)
Potassium (mg/kg as K)
Sodium (mg/kg as Na)
Strontium (mg/kg as Sr)
Titanium (mg/kg as Ti)
Zinc (mg/kg as Zn)

1. Application

1.1 This method may be used to analyze suspended and bottom sediment for the determination of total concentration of the constituents. The upper- and lower-concentration reporting limits are specified below. Samples containing analyte concentrations greater than the upper limit may be analyzed after appropriate dilution.

Constituent	Lower limit (mg/kg)	Upper limit (mg/kg)
Aluminum	20,000	150,000
Cadmium	.5	100
Calcium	1,000	50,000
Chromium	3	400
Cobalt	3	600
Copper	1	400
Iron	5,000	100,000
Lead	3	1,000
Lithium	2	200
Magnesium	1,000	20,000
Manganese	100	4,000
Nickel	3	600
Potassium	1,000	35,000
Sodium	1,000	25,000
Strontium	2.5	500
Titanium	1,000	20,000
Zinc	1	160

1.2 Analyses must be performed on dried and ground samples that have been solubilized with a combination of nitric, hydrofluoric, and perchloric acids heated in open Teflon beakers. These solutions are then analyzed by atomic absorption spectrometry.

2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The dried, ground, and homogenized sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. The resulting salts are dissolved in hydrochloric acid and demineralized water. The resulting solutions are analyzed by atomic absorption spectrometry after the addition, in certain cases, of appropriate matrix modifiers. Additional interferences are removed or compensated for through the use of mixed-salt standards and background correction.

2.2 Additional information on the principles of the method may be found in Walsh (1977), Johnson and Maxwell (1981), and Pinta (1982).

3. Interferences

3.1 Both positive and negative interelement interferences occur and have been documented (Walsh, 1977; Johnson and Maxwell, 1981; Pinta, 1982).

3.2 Interferences are eliminated or compensated for by the use of cesium chloride (CsCl), the use of mixed-salt standards, and the use of a deuterium-source background corrector.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero and concentration controls, a deuterium-source background corrector, and an autosampler (optional).

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

Constituent	Grating: ultraviolet (uv) or visible (vis)	Wavelength (nm)	Burner: nitrous oxide(N_2O) or air	Oxidant: nitrous oxide (N_2O) or air	Flame type	Background corrector
Al	uv	309.3	N_2O	N_2O	fuel-rich	no
Cd	uv	228.8	air	air	oxidizing	yes
Ca	vis	422.7	N_2O	N_2O	oxidizing	no
Cr	uv	357.9	N_2O	N_2O	oxidizing	no
Co	uv	240.7	air	air	oxidizing	yes
Cu	uv	324.7	air	air	oxidizing	yes
Fe	uv	372.0	air	air	oxidizing	no
Pb	uv	217.0	air	air	oxidizing	yes
Li	vis	670.8	air	air	oxidizing	no
Mg	uv	202.6	N_2O	N_2O	oxidizing	no
Mn	uv	279.5	air	air	oxidizing	no
Ni	uv	232.0	air	air	oxidizing	yes
K	vis	766.5	air	air	oxidizing	no
Na	vis	589.0	air	air	oxidizing	no
Sr	vis	460.7	N_2O	N_2O	oxidizing	no
Ti	uv	364.3	N_2O	N_2O	fuel-rich	no
Zn	uv	213.9	air	air	oxidizing	yes

4.3 *Beakers*, Teflon, 100-mL capacity, thick-wall, capable of withstanding temperatures up to 260 °C.

4.4 *Fuel*, acetylene.

4.5 *Hollow-cathode lamps*, single-element lamps.

4.6 *Hot plate*, electric or gas, capable of reaching at least 250 °C.

4.7 *Perchloric acid hood*, with appropriate washdown facility and gas or electric outlets.

5. Reagents

5.1 *Aluminum standard solution*, 1.00 mL = 1.00 mg Al: Dissolve 1.000 g Al powder in a minimum of HCl (1 + 1). Heat to increase rate of dissolution. Add 10.0 mL HCl (1 + 1) and dilute to 1000 mL with demineralized water.

5.2 *Cesium chloride solution*, 4 g/L: Dissolve 4 g CsCl of at least 5/9ths purity (<10 ppm impurities) in demineralized water and dilute to 1 L.

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

5.4 *Hydrochloric acid*, dilute (1 + 1): Add 250 mL concentrated HCl (sp gr 1.19) to 250 mL demineralized water. Store in a plastic bottle.

5.5 *Hydrochloric acid*, dilute (1 + 49): Add 10 mL concentrated HCl (sp gr 1.19) to 490 mL demineralized water. Store in a plastic bottle.

5.6 *Hydrofluoric acid*, concentrated, 48- to 51-percent, (sp gr 1.17).

5.7 *Iron standard solution*, 1.00 mL = 1.00 mg Fe: Dissolve 1.000 g Fe wire in 20 mL HCl (1 + 1) and dilute to 1000 mL with demineralized water.

5.8 *Mixed-salt standard stock solution I*: Dissolve, by appropriate means, the following compounds or elements: Cd splatters (0.200 g), Cr metal (0.800 g), Co metal (1.200 g), Cu shot (0.800 g), Pb shot (2.000 g), Li_2CO_3 (2.130 g), Mn flakes (2.000 g), Ni powder (1.200 g), $SrCO_3$ (1.685 g), and Zn powder (0.320 g). Add 20 mL concentrated HCl (sp gr 1.19), and dilute to 1,000 mL with demineralized water. This solution will contain the following concentrations: Cd (200 mg/L), Cr (800 mg/L), Co (1200 mg/L), Cu (800 mg/L), Pb (2000 mg/L), Li (400 mg/L), Mn (2000 mg/L), Ni (1200 mg/L), Sr (1000 mg/L), and Zn (320 mg/L). Store in a plastic or Teflon bottle.

5.9 *Mixed-salt standard stock solution II*: Dilute 100 mL of mixed salt standard stock solution I (5.8) and 20 mL concentrated HCl (sp gr 1.19) to 1,000 mL with demineralized water. This solution will contain the following concentrations: Cd (20 mg/L), Cr (80 mg/L), Co (120 mg/L), Cu (80 mg/L), Pb (200 mg/L), Li (40 mg/L), Mn (200 mg/L), Ni (120 mg/L), Sr (100 mg/L), and Zn (32 mg/L). Alternatively, certified standard solutions for each constituent may be purchased and the mixed standard solution prepared. Store in a plastic or Teflon bottle. This solution is stable for 3 months.

5.10 *Mixed-salt standard stock solution III*: Dissolve, by appropriate means, the following compounds or elements: Al powder (1.500 g), $CaCO_3$ (1.249 g), Fe wire (1.000 g), Mg rod (0.200 g), Mn flakes (0.040 g), KCl (0.668 g), NaCl (0.636 g), and $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ (1.227 g). Add 20 mL concentrated HCl (sp gr 1.19), and dilute to 1,000 mL with demineralized water. This solution will contain the following concentrations: Al (1,500 mg/L), Ca (500 mg/L), Fe (1,000 mg/L), Mg (200 mg/L), Mn (40 mg/L), K (350 mg/L), Na (250 mg/L), and Ti (200 mg/L). Store in a plastic or Teflon bottle.

5.11 *Working standard solutions 1, 2, and 3*: Pipet 10 mL (standard 1), 5 mL (standard 2), and 1 mL (standard 3) mixed-salt standard stock solution II into 200-mL volumetric flasks. Add 4 mL concentrated HCl (sp gr 1.19) and 20 mL mixed-salt standard stock solution III (5.10) to each flask, and dilute to 200 mL with demineralized water. Store in plastic or Teflon bottles and prepare fresh daily. Concentrations are as follows:

Constituent	Standard 1 (mg/L)	Standard 2 (mg/L)	Standard 3 (mg/L)
Cd	1	0.5	0.10
Cr	4	2	.40
Co	6	3	.60
Cu	4	2	.40
Pb	10	5	1.00
Li	2	1	.20
Ni	6	3	.60
Sr	5	2.5	.5
Zn	1.6	0.8	.16

5.12 *Working standard solutions 4, 5, and 6*: Pipet 10 mL (standard 4), 6 mL (standard 5), and 2 mL (standard 6) mixed-salt standard stock solution III into 100-mL volumetric flasks. Add 2 mL concentrated HCl (sp gr 1.19) and 10 mL CsCl solution (5.2) to each flask, and dilute to 100 mL with demineralized water. Store in plastic or Teflon bottles and prepare fresh daily. Concentrations are as follows:

Constituent	Standard 4 (mg/L)	Standard 5 (mg/L)	Standard 6 (mg/L)
Al	150	90	30
Fe	100	60	20
Mg	20	12	4
Mn	4	2	1

5.13 *Working standard solutions 7, 8, and 9*: Pipet 10 mL of standards 4, 5, and 6 (5.12) into 100-mL volumetric flasks. Add 2 mL concentrated HCl (sp gr 1.19) and 10 mL CsCl solution (5.2) to each flask, and dilute to 100 mL with demineralized water. Store in plastic or Teflon bottles and prepare fresh daily. Concentrations are as follows:

Constituent	Standard 7 (mg/L)	Standard 8 (mg/L)	Standard 9 (mg/L)
Ca	5.0	3	1
K	3.5	2.1	.7
Na	2.5	1.5	.5

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

5.15 *Perchloric acid*, concentrated, 70- to 72-percent (sp gr 1.67).

5.16 *Sodium standard solution*, 1.00 mL = 1.00 mg Na: Dissolve 2.542 g NaCl in demineralized water, add 20 mL HCl (sp gr 1.19), and dilute to 1,000 mL with demineralized water.

5.17 *Titanium standard solution*, 1.00 mL = 1.00 mg Ti: Dissolve 6.135 g $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ in demineralized water, and dilute to 1,000 mL with demineralized water.

5.18 *Titanium working standard solutions*: Pipet 2 mL, 1 mL, and 0.5 mL of titanium standard solution (5.17) into 100-mL volumetric flasks. Add 10 mL aluminum standard solution (5.1), 5 mL iron standard solution (5.7), 3.5 mL sodium standard solution (5.16), 10 mL CsCl solution (5.2), and 2 mL concentrated HCl (sp gr 1.19) to each flask, and dilute to 100 mL with demineralized water. The standards contain 20, 10, and 5 mg/L titanium, respectively.

6. Procedure

Immediately before each use, clean all glassware by rinsing, first with dilute HCl (1 + 1), and then with demineralized water.

6.1 Dry the sediment sample by an appropriate procedure such as freeze-drying or oven drying at 105°C.

6.2 If the sediment sample is greater than 100 g, split to less than 100 g by the use of a non-metallic sample splitter (riffle sampler) or by coning and quartering.

6.3 Grind the sample with a mixer mill or with an agate mortar and pestle until all material is finer than 100 mesh.

6.4 Weigh and transfer 0.5000 g of finely ground sample to a 100 mL Teflon beaker; weigh appropriate reference standard materials as well (NOTE 1).

NOTE 1. The procedure can be used with sample weights between 0.2500 and 1.000 g, with appropriate adjustments to the final-solution volumes and acid strengths (paragraphs 6.4 through 6.12). Weights greater than 1.000 g may be used, but may require an extra digestion with HF and $HClO_4$ (see steps 6.8 and 6.9).

6.5 Carry several blanks through the procedure.

6.6 Place hotplate in a perchloric acid hood, and adjust the hotplate to produce a surface temperature of 200°C.

6.7 Add 6 mL concentrated HNO_3 (sp gr 1.41) to each beaker and place the beakers on the hotplate for approx 30 min (NOTE 2).

NOTE 2. CAUTION: This step is designed to oxidize organic matter in the sample. This step must be carried out prior to the addition of perchloric acid; otherwise, a violent explosion could occur.

6.8 Remove the beakers from the hotplate and wait 5 min. Add 6 mL HF (sp gr 1.17 and 2 mL $HClO_4$ (sp gr 1.67), and return the beakers to the hotplate. Continue heating the beakers until white perchloric fumes are produced and the solution has reached incipient dryness; however, do not bake the residues.

6.9 Remove the beakers from the hotplate and wait 5 min. Repeat paragraph 6.8.

6.10 Remove the beakers from the hotplate and wait 5 min. Add 2 mL $HClO_4$ (sp gr 1.67) and return the beakers to the hotplate. Continue heating until the solution has reached incipient dryness; however, do not bake the residues.

6.11 Remove the beakers from the hotplate, and lower the temperature of the hotplate to 100°C. Add 2 mL dilute HCl (1 + 1) to each beaker and swirl; add 10 mL demineralized water to each beaker, mix, and return to the hotplate to dissolve the residue.

6.12 Cool the solutions, and pour each into a 50-mL volumetric flask. Rinse the beaker several times with demineralized water and bring to volume with demineralized water (NOTE 3). Pour the solutions into acid-rinsed plastic bottles for storage. These solutions represent a dilution factor of 100 × .

NOTE 3. If a sample contained a large amount of organic matter, the final solution will commonly contain black "flecks." These can be ignored if they are allowed to settle before aspiration of the solutions into an atomic absorption spectrometer.

6.13 Pipet 5 mL from the 100 × solutions (paragraph 6.12) into 50-mL volumetric flasks. Add 1 mL concentrated HCl (sp gr 1.19) and 5 mL CsCl solution (paragraph 5.2) (NOTE 4) to each flask, and bring to volume with demineralized water. Pour the solutions into acid-rinsed plastic bottles for storage. These solutions represent a dilution factor of 1000 × .

NOTE 4. The cesium chloride acts as an ionization suppressant.

6.14 Pipet 5 mL from the 1000 × solutions (paragraph 6.13) into 50-mL volumetric flasks. Add 1 mL concentrated HCl (sp gr 1.19) and 5 mL CsCl solution (paragraph 5.2) to each, and bring to volume with demineralized water. Pour the solutions into acid-rinsed plastic bottles for storage. These solutions represent a dilution factor of 10,000 × .

6.15 Set up the atomic absorption spectrometer as outlined in paragraph 4.2, and analyze the 100 × solutions (paragraph 6.12) for Cd, Cr, Co, Cu, Pb, Ni, and Zn using standards 1, 2, and 3 (paragraph 5.11). Dilute samples if required.

6.16 Pipet 5.0 mL of each sample (paragraph 6.12) and working standard solution (paragraph 5.11) to an appropriate container. Add 5.0 mL dilute HCl (1+49) (paragraph 5.5) and 1.0 mL CsCl solution (paragraph 5.2). Analyze the solutions for Li and Sr using the atomic-absorption spectrometer conditions outlined in paragraph 4.1 (NOTE 5).

NOTE 5. The added dilution is required to eliminate interferences due to density differences (Abbey, 1967).

6.17 Set up the atomic-absorption spectrometer as outlined in paragraph 4.2, and analyze the 1000 × solutions (paragraph 6.13) for Fe, Mn, Mg, and Al using standards 4, 5, and 6 (paragraph 5.12). Dilute samples if required.

6.18 Set up the atomic-absorption spectrometer as outlined in paragraph 4.2, and analyze 1000 × solutions (paragraph 6.13) for Ti, using the titanium working standards (paragraph 5.18) (NOTE 6).

NOTE 6. Titanium determinations by atomic absorption are subject to severe interferences and sensitivity is heavily dependent on flame stoichiometry (Walsh, 1977). Adjust the nitrous oxide flame until it is nearly luminous (increase the fuel flow until the reducing red cone turns orange-yellow, then reduce the fuel flow until the flame just becomes red again).

6.19 Set up the atomic absorption spectrometer as outlined in paragraph 4.2, and analyze the 10,000 × solutions (paragraph 6.14) for Ca, K, and Na using standards 7, 8, and 9 (paragraph 5.13). Dilute samples if required.

7. Calculations

7.1 Determine the concentration of each constituent (Cd, Cr, Co, Cu, Pb, Ni, and Zn) from the digital display or printer output while aspirating each sample, and record the results. The concentration of each constituent (in mg/kg) is obtained by multiplying the concentration in each sample solution by 100, if no dilutions are made.

7.2 Determine the concentration of each constituent (Li and Sr) from the digital display or printer output while aspirating each sample, and record the results. The concentration of each constituent (in mg/kg) is obtained by multiplying the concentration in each sample solution by 200, if no dilutions are made.

7.3 Determine the concentration of each constituent (Fe, Mn, Al, Mg, and Ti) from the digital display or printer output while aspirating each sample, and record the results. The concentration of each constituent (in mg/kg) is obtained by multiplying the concentration in each sample solution by 1000, if no dilutions are made.

7.4 Determine the concentration of each constituent (Ca, K, and Na) from the digital display or printer output while aspirating each sample, and record the results. The concentration of each constituent (in mg/kg) is obtained by multiplying the concentration in each sample solution by 10,000, if no dilutions are made.

8. Report

Report aluminum, calcium, iron, magnesium, potassium, sodium, and titanium, total, concentrations to the nearest 1000 mg/kg (0.1 percent). Report manganese, total, concentration to the nearest 100 mg/kg (0.01 percent). Report cadmium, total, concentrations to the nearest 0.1 mg/kg. Report chromium, cobalt, copper, lead, lithium, nickel, strontium, zinc, total, concentrations to the nearest 1 mg/kg.

9. Precision

9.1 The precision for five replicates expressed in terms of relative standard deviation is as follows:

Constituent	Sample mean (percent)	Relative standard deviation (percent)	Sample mean (percent)	Relative standard deviation (percent)
Aluminum	2.4	2	8.7	3
Calcium	.7	7	7.7	3
Iron	1.8	0	10.8	2
Magnesium	.44	2	3.8	4
Manganese	.02	25	.14	0
Potassium	.6	8	3.7	2
Sodium	.6	15	2.9	3
Titanium	.2	5	1.4	4

9.2 The precision for six replicates expressed in terms of relative standard deviation is as follows:

Constituent	Sample mean (mg/kg)	Relative standard deviation (percent)	Sample mean (mg/kg)	Relative standard deviation (percent)
Cadmium	0.4	20	10.0	4
Chromium	8	13	102	3
Cobalt	6	17	44	5
Copper	10	20	106	2
Lead	13	7	708	1
Lithium	8	13	132	4
Nickel	3	33	51	2
Strontium	163	4	475	3
Zinc	80	4	134	2

References

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Metals, minor, total-in-sediment, atomic absorption spectrometric, hydride

Parameters and Codes:
Metals, total (I-5475-85): none assigned
Arsenic (mg/kg as As)
Antimony (mg/kg as Sb)
Selenium (mg/kg as Se)

1. Application

1.1 This method may be used to analyze suspended and bottom sediment for the determination of total concentrations of arsenic, antimony, and selenium. The upper and lower concentration reporting limits are specified below. Samples containing analyte concentrations greater than the upper limit may be analyzed after appropriate dilution.

Constituent	Lower limit (mg/kg)	Upper limit (mg/kg)
Arsenic	0.05	5.0
Antimony	0.05	5.0
Selenium	0.05	5.0

1.2 Analyses must be performed on dried and ground samples that have been solubilized with a combination of nitric, hydrofluoric, and perchloric acids heated in open Teflon beakers. These solutions are then analyzed by atomic absorption spectrometry, coupled with hydride generation.

2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized, and then is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200°C. The resulting salts are dissolved in concentrated hydrochloric acid and demineralized water. This serves to reduce the selenium to the +4 valence state for subsequent quantitation. Separate aliquots are then heated with a reductant; a stabilizer is added, and arsenic and antimony are determined. All determinations are made by hydride generation, coupled with atomic absorption spectrometry.

2.2 Additional information on the principles of the method can be found in Thompson and Thomerson (1974), Aslin (1976), Chapman and Dale (1979), Johnson and Maxwell (1981), Crock and Lichte (1982), and Narasaki and Ikeda (1984).

3. Interferences

3.1 Total digestion, dilution, and hydride generation frees the arsenic, antimony and selenium from the original matrix, and minimizes interferences. Mixed-salt standards for antimony and selenium, and background correction for selenium, further compensate for any interferences.

3.2 Interferences, primarily negative, do occur and are documented by Johnson and Maxwell (1981), and Narasaki and Ikeda (1984).

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout, automatic zero and concentration controls, and a deuterium-source background corrector; an autosampler and printer or chart recorder permits automation of the analytical process.

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

Constituent	Grating: ultra-violet(uv)	Wavelength (nm)	Burner	Fuel	Oxidant	Background Flame type	correction
As	uv	193.7	N_2O	C_2H_2	air	lean	off
Sb	uv	217.6	N_2O	C_2H_2	air	lean	off
Se	uv	196.0	N_2O	C_2H_2	air	lean	on

The N_2O burner head is used because of its shorter flame width. This burner produces very good analytical results while considerably extending the life of the quartz cell. The effect of the N_2O burner may vary with different instrumentation.

4.3 *Hydride generator*, Varian VGA 76 or equivalent. This system consists of a peristaltic pump, reaction coil, gas-liquid separator, and a flame-heated quartz cell.

4.4 *Beakers*, Teflon, 100-mL capacity, thick-walled, capable of withstanding temperatures as high as 260 °C.

4.5 *Hotplate*, gas or electric, capable of reaching at least 250 °C.

4.6 Perchloric acid hood, with appropriate washdown facility and gas or electrical outlets.

5. Reagents

5.1 *Antimony standard solution*, 1.00 mL = 1000 µg Sb: Dissolve 1.0000 g Sb metal in 10 mL concentrated HNO_3 (sp gr 1.41) plus 5 mL concentrated HCl (sp gr 1.19). Dilute to 1000 mL with dilute HCl (1+1).

5.2 *Arsenic standard solution*, 1.00 mL = 1000 µg As: Dissolve 1.3203 g As_2O_3 in a minimum of concentrated HCl (sp gr 1.19). Dilute to 1000 mL with dilute HCl (1+1).

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

5.4 *Hydrochloric acid*, dilute (1 + 1): Add 500 mL concentrated HCl (sp gr 1.19) to 500 mL demineralized water. Store in glass or plastic bottle.

5.5 *Hydroxylamine hydrochloride solution*, in a saturated solution of oxalic acid: Dissolve 200 g $NH_2OH{\cdot}HCl$ in 800 g of saturated solution of oxalic acid.

5.6 Hydrofluoric acid, concentrated, 48- to 51-percent (sp gr 1.17).

5.7 *Mixed-element standard solution*, 1.00 mL = 50.0 µg Sb, As, and Se: Pipet 10.0 mL of each element standard solution (As, Sb, Se) into a 200-mL volumetric flask. Add 100 mL concentrated HCl (sp gr 1.19), and dilute to volume with demineralized water. Store in plastic bottle. Solution should be remade weekly.

5.8 *Mixed-salt standard solution I*: Dissolve, by appropriate means, the following compounds or elements: Cd splatters (0.200 g), Cr metal (0.800 g), Co metal (1.200 g), Cu shot (0.800 g), Pb shot (2.000 g), Li_2CO_3 (2.130 g), Mn flakes (2.000 g), Ni powder (1.200 g), $SrCO_3$ (1.685 g), and Zn powder (0.320 g). Add 20 mL concentrated HCl (sp gr 1.19), and dilute to 1000 mL with demineralized water. This solution will contain the following concentrations: Cd (200 mg/L), Cr (800 mg/L), Co (1200 mg/L), Cu (800 mg/L), Pb (2000 mg/L), Li (400 mg/L), Mn (2000 mg/L), Ni (1200 mg/L), Sr (1000 mg/L), and Zn (320 mg/L). Store in plastic or Teflon bottle.

5.9 *Mixed-salt standard solution II*: Dissolve, by appropriate means, the following compounds or elements: Al powder (1.500 g), $CaCO_3$ (1.249 g), Fe wire (1.000 g), Mg rod (0.200 g), Mn flakes (0.040 g), KCl (0.688 g), NaCl (0.636 g), and $(NH_4)_2TiO(C_2O_4)_2{\cdot}H_2O$ (1.227 g). Add 20 mL concentrated HCl (sp gr 1.19), and dilute to 1000 mL with demineralized water. This solution will contain the following concentrations: Al (1500 mg/L), Ca (500 mg/L), Fe (1000 mg/L), Mg (200 mg/L), Mn (40 mg/L), K (350 mg/L), Na (250 mg/L), and Ti (200 mg/L). Store in plastic or Teflon bottle.

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

5.11 *Oxalic acid solution*, saturated: Dissolve approximately 150 g oxalic acid in demineralized water using mild heating. Cool until crystallization stops.

5.12 *Perchloric acid*, concentrated, 70- to 72-percent (sp gr 1.67).

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

5.14 *Selenium standard solution*, 1.00 mL = 1000 µg Se: Dissolve 1.0000 g Se metal in 5 mL concentrated HNO_3 (sp gr 1.41). Dilute to 1000 mL with dilute HCl (1 + 1).

5.15 *Sodium borohydrate solution*, 0.6 g/100 mL: Dissolve 3.0 g $NaBH_4$ and 2.5 g NaOH in demineralized water and dilute to 500 mL.

5.16 *Working standard solutions 1, 2, 3*: Pipet 200 μL (standard 1), 100 μL (standard 2), and 8 μL (standard 3) of the mixed-element standard solution into 200-mL volumetric flasks. Add 100 mL concentrated HCl (sp gr 1.19), 1 mL mixed-salt standard stock solution I, and 20 mL mixed-salt standard stock solution II to each flask and dilute to 200 mL with demineralized water. Store in plastic or Teflon bottles and prepare fresh daily. Concentrations are as follows:

Constituent	Standard 1 (μg/L)	Standard 2 (μg/L)	Standard 3 (μg/L)
Sb	50	25	2
Se	50	25	2

5.17 *Working standard solutions 4, 5, 6*: Pipet 200 μL (standard 4), 100 μL (standard 5), and 8 μL (standard 6) mixed-element standard solution into 200-mL volumetric flasks. Add 100 mL concentrated HCl (sp gr 1.19) to each flask, and dilute to 200 mL with demineralized water. Store in plastic or Teflon bottles. Concentrations are as follows:

Constituent	Standard 4 (μg/L)	Standard 5 (μg/L)	Standard 6 (μg/L)
As	50	25	2

6. Procedure

Immediately before each use, clean all glassware by rinsing first with dilute HCl (1 + 1) and then with demineralized water.

6.1 Dry the sediment by freeze-drying or air-drying at room temperature.

6.2 If the sediment sample is greater than 100 g, split to less than 100 g by the use of a nonmetalic sample splitter (riffle sampler) or by coning and quartering.

6.3 Grind the sample with a mixer mill or an agate mortar and pestle until all material is finer than 100 mesh.

6.4 Weigh and transfer 0.5000 g of finely ground sample to a 100-mL Teflon beaker; weigh appropriate reference standard materials (NOTE 1).

NOTE 1. The procedure can be used with sample weights between 0.2500 and 1.000 g, with appropriate adjustment to the final solution volumes and acid strengths (paragraphs 6.4 through 6.12). Weights greater than 1.000 g may be used, but will require an extra digestion with HF and $HClO_4$ (see paragraphs 6.8 and 6.9).

6.5 Carry several blanks (reagents only) through the procedure.

6.6 Place hotplate in a perchloric acid hood and adjust to produce a surface temperature of 200 °C.

6.7 Add 6 mL concentrated HNO_3 (sp gr 1.41)—CAUTION: Explosive with perchloric acid—to each beaker and place the beakers on the hotplate. Continue heating until the residue is nearly dry, approx 30 min. If sample is still evolving brown fumes of NO_X at this point, repeat this step (NOTE 2).

NOTE 2. **CAUTION: This step is designed to oxidize organic matter in the sample. This step must be carried out prior to the addition of perchloric acid; otherwise, a violent explosion could occur.**

6.8 Remove the beakers from the hotplate and cool for 5 min. Add 6 mL HF (sp gr 1.17) and 2 mL $HClO_4$ (sp gr 1.67), and return the beakers to the hotplate. Continue heating the beakers until dense, white perchloric fumes have been produced and the solution has reached incipient dryness; however, do not bake the residues.

6.9 Remove beakers from the hotplate and cool for 5 min; repeat paragraph 6.8.

6.10 Remove beakers from the hotplate and cool for 5 min. Add 2 mL $HClO_4$ (sp gr 1.67) and return the beakers to the hotplate. Continue heating until the solution has reached incipient dryness; however, do not bake the residues.

6.11 Remove the beakers from the hotplate, and lower the temperature of the hotplate to 100 °C. Add 25 mL concentrated HCl (sp gr 1.19) to each beaker and swirl; return to hotplate to dissolve the residue.

6.12 Cool the solutions, and pour each into a 50-mL volumetric flask. Rinse the beaker several times with demineralized water and dilute to the mark with demineralized water

(NOTE 3). Pour the solutions into acid-rinsed plastic bottles for storage.

NOTE 3. If a sample contained a large amount of organic matter, the final solution will commonly contain black "flecks." Allow the flecks to settle before pumping the solutions into the hydride generator.

6.13 Determination of selenium:

6.13.1 Feed the concentrated HCl (sp gr 1.19) and $NaBH_4$ solution into the hydride generator using demineralized water in the sample line.

6.13.2 Set up the atomic absorption spectrometer as outlined in paragraph 4.2. Allow the quartz cell to come to thermal equilibrium (approx 5 min). Analyze the 50 µg/L of Se and blank alternately until stable readings are attained for each. Analyze the solutions (paragraph 6.12) for selenium, using working standards 1, 2, and 3. Dilute the samples if required.

6.14 Determination of antimony and arsenic:

6.14.1 Pipet 20 mL of each sample (paragraph 6.12), working standard solutions 1, 2, and 3 (Sb), and working standard solutions 4, 5, and 6 (As) into 18 × 150-mm (or larger) test tubes. Add 2 mL KI solution and heat in a dry bath at 90°C for 1 h. Allow to cool, add 2 mL $NH_2OH \cdot HCl$/oxalic acid solution, and mix thoroughly with a vortex mixer (NOTE 4).

NOTE 4. The addition of KI reduces the As and Sb to valence states most favorable to hydride generation (+3). The addition of the $NH_2OH \cdot HCl$-oxalic acid solution was found to stabilize the solutions and to give more consistent results. The oxalic acid also appears to minimize interference from Fe (Crock and Lichte, 1982).

6.14.2 Set up the atomic absorption spectrometer as outlined paragraph section 4.2. Allow the quartz cell to come to thermal equilibrium (approx 5 min). Analyze the 50 µg/L As and Sb standards and blanks alternately until stable readings are attained for each. Analyze the solutions for As and Sb using working standards 1, 2, and 3 for Sb, and working standards 4, 5, and 6 for As. Dilute the samples if required. (NOTE 5)

NOTE 5. With use, the quartz cell may become coated with a white layer of oxides. If left on the cell, these oxides can cause the cell to crack when heated. To remove the oxides, soak the cell for a short time (10 to 15 min is usually sufficient) in concentrated HF (sp gr 1.17); then rinse the cell thoroughly to remove any traces of HF. A strong (45-percent) solution of NaOH or KOH may be used in place of HF.

7. Calculations

7.1 Determine the concentration of As, Sb, and Se (in µg/L) from the digital display, printer, or chart recorder, and record the results.

7.2 To convert the results from µg/L to mg/kg, use the following equation:

$$\text{As, Sb, or Se (mg/kg)} = \frac{\mu\text{g/L (As, Sb, or Se)} \times \dfrac{\text{mL digest}}{1000}}{\text{wt of sample (g)}}$$

8. Report

Report the concentration of each determined constituent to the nearest 0.1 mg/kg.

9. Precision

The precision for ten replicates on U.S. Geological Survey and National Bureau of Standards reference materials expressed in terms of relative standard deviation is as follows:

Constituent	Mean sample 1 mean (mg/kg)	Relative standard deviation (percent)	Mean sample 2 mean (mg/kg)	Relative standard deviation (percent)
Arsenic	0.4	25	12.4	9
Antimony	.4	13	3.3	6
Selenium	.5	13	3.4	4

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