METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY--DETERMINATION OF INORGANIC AND ORGANIC CONSTITUENTS IN WATER AND FLUVIAL SEDIMENTS

By Marvin J. Fishman, Editor

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PREFACE

This manual supersedes those parts of "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments," edited by Fishman and Friedman (1989), and "Methods for the Determination of Organic Substances in Water and Fluvial Sediments," by Wershaw and others (1987) that are revised herein. It also includes additional methodology to that given in Fishman and Friedman (1989).

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CONVERSION FACTORS AND RELATED INFORMATION

Multiply	*By*	*To Obtain*
liter (L)	0.2642	gallon
milliliter (mL)	2.64×10^{-4}	gallon
microliter (µL)	2.64×10^{-7}	gallon
gram (g)	0.03527	ounce, avoirdupois
milligram (mg)	3.53×10^{-5}	ounce
meter (m)	3.281	foot
microgram (µg)	3.53×10^{-8}	ounce
centimeter (cm)	3.94×10^{-1}	inch
millimeter (mm)	3.94×10^{-2}	inch
micrometer (µm)	3.94×10^{-5}	inch
nanometer (nm)	0.001	micrometer

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = \frac{9}{5} (°C) + 32.$$

Abbreviated units of measurement used in report:

amu	atomic mass unit
cm/s	centimeter per second
eV	electronvolt
g/L	gram per liter
h	hour
kW	kilowatt
lb/in^2	pound per square inch
L/min	liter per minute
mM	millimolar
M	molar
mg/kg	milligram per kilogram
mg/L	milligram per liter
mL/min	milliliter per minute
MΩ-cm	megohm-centimeter
N	normal
ng/µL	nanogram per microliter
pg	picogram

rpm	revolution per minute
s	second
s/mL	second per milliliter
V	volt
W	watt
µg/g	microgram per gram
µg/L	microgram per liter
µg/mL	microgram per milliliter
µS/cm	microsiemens per centimeter at 25 degrees Celsius

Other abbreviations used in report:

ACS	American Chemical Society
APDC	ammonium pyrrolidine dithiocarbamate
ASTM	American Society for Testing and Materials
DFTPP	decafluorotriphenylphosphine
FEP	fluorinated ethylene propylene
GC	gas chromatograph
GC/MS	gas chromatograph/mass spectrometer
HPLC	high-performance liquid chromatography
ICP	inductively coupled plasma
ID	inside diameter
MIBK	methyl isobutyl ketone
NWQL	National Water Quality Laboratory
OD	outside diameter
PTFE	polytetrafluoroethylene
RFA	rapid flow analyzer
SLS	sodium lauryl sulfate
sp gr	specific gravity
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	volatile organic compounds
v/v	volume per volume
wt	weight
w/v	weight per volume
w/w	weight per weight

Notations used in report:

<	less than
≥	greater than or equal to

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METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY--DETERMINATION OF INORGANIC AND ORGANIC CONSTITUENTS IN WATER AND FLUVIAL SEDIMENTS

By Marvin J. Fishman

ABSTRACT

Book 5, chapter A1, entitled "Techniques of Water-Resources Investigations of the U.S. Geological Survey," contains methods used to analyze samples of water, suspended sediment, and bottom material for their content of inorganic and organic constituents. Technology continually changes, and so this laboratory manual includes new and revised methods for determining the concentration of dissolved constituents in water, whole water recoverable constituents in water-suspended sediment samples, and recoverable concentration of constituents in bottom material. Each method consists of the application, the principle of the method, interferences, the apparatus and reagents required, a detailed description of the analytical procedure, reporting results, units and significant figures, and analytical precision data. Included in this manual are 30 methods.

INTRODUCTION

The U.S. Department of the Interior has a basic responsibility for the appraisal, conservation, and efficient use of the Nation's natural resources. As one of several Interior agencies, the U.S. Geological Survey's (USGS) primary function in relation to water is to assess its availability and utility as a national resource for all uses.

The USGS 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 USGS is responsible for producing a large part of the water-quality data for rivers, lakes, and ground water that are used by planners, developers, water-quality managers, and pollution-control agencies. A high degree of reliability and standardization of these data is paramount.

Rapid changes in technology are constantly providing new and improved methods for the study of water-quality characteristics. Therefore, method manuals need to be updated frequently to gain the advantages of improved technology. This manual makes available recent (1993) revisions of procedures contained in publications entitled "Techniques of Water-Resources Investigations of the U.S. Geological Survey (Fishman and Friedman, 1989; Wershaw and others, 1987). Also included in this manual are some new methods which are in use in the USGS National Water Quality Laboratory (NWQL). Since the last inorganic and organic manuals were published, 30 methods have been approved for use in the NWQL. These methods are published herein.

This manual includes techniques and procedures suitable for the analysis of representative samples of water and fluvial sediment. 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. Each method, where applicable, applies to the determination of constituents in solution (dissolved), the determination of whole water recoverable constituents (substances in solution and adsorbed on or part of suspended sediment), and finally the determination of recoverable constituents from samples of bottom material.

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 spectroscopic 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 in 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 as new or revised methods are introduced.

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 as follows: dissolved, suspended recoverable, whole water recoverable, and recoverable from bottom material. These terms are defined by Fishman and Friedman (1989).

REFERENCES

Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments (3d ed.): U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.

Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., eds., 1987, Methods for the determination of organic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A3, 80 p.

ANALYTICAL METHODS

Acidity, low ionic-strength water, electrometric titration, automated

Parameter and Code:
Acidity, I-2022-90 (mg/L as H^+): 71825

1. Application

This method is used to determine acidity in samples of water with a specific conductance less than 100 µS/cm. The method was implemented in the National Water Quality Laboratory in January 1987.

2. Summary of method

2.1 Acidity is determined by titrating a water sample with a standard solution of strong base. The titration is stopped at pH 9.00, and the second derivative plot is used to calculate the acidity. For more information on the use of the second derivative, see Peters and others (1974, p. 376-381).

2.2 Acidity might be susceptible to change between time of collection and analysis, with changes occurring more rapidly after the sample is opened. The determination needs to be performed within 8 hours.

2.3 Water samples for the determination of acidity should not be filtered, diluted, concentrated, or altered physically or chemically.

3. Interferences

3.1 Exposure to carbon dioxide in air can cause variations in pH and acidity.

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

4. Apparatus

4.1 *Autoburet*, 1.0 mL capacity, Kyoto APB-118 or equivalent.

4.2 *Autosampler*, Kyoto CHG-310 with sample cover or equivalent.

4.3 *Potentiometric titrator*, Kyoto AT-310 automatic titrator or equivalent.

4.4 *pH meter,* capable of reading to the nearest 0.01 pH unit, Kyoto STD-310 preamplifier or equivalent.

4.5 *pH electrode,* Orion Ross 810300 semimicro or equivalent.

4.6 With this equipment and the manufacturer's manual, the following operating conditions have been found to be satisfactory:

Control parameters

Method (Intermit)	05
Titration form	EP stop
Number of endpoints	1
Gain	1
Cutoff time	20 seconds
Unit volume	0.005 mL
Piston speed	5 s/mL

Titration parameters

Buret	05
Reagent	0.01*N* HCl
Preamplifier	STD
PSU (preamplifier gain control)	1
Dimension	pH
Wait time	90 seconds
Maximum volume	3 mL

4.7 *Sample cover,* case to cover autosampler during operation. Cover contains inlet and outlet ports to purge autosampler of air with nitrogen gas.

5. Reagents

5.1 *Buffers,* pH 4.00 and 7.00 traceable to the National Institute for Standards and Technology.

5.2 *Sodium hydroxide solution,* 0.01*N*: Commercially available from J.T. Baker or equivalent.

6. Procedure

6.1 Purge autosampler with nitrogen (15-25 lb/in^2) for 15 minutes prior to calibration or analysis of samples. The nitrogen needs to flow through the autosampler during all operations.

6.2 Calibrate electrode daily according to manufacturer's instructions using pH 4.00 and 7.00 buffers.

6.3 Pipet 30 mL of sample into titration vessels. Place cups in autosampler and begin analysis. The titration stops at first endpoint detected electrometrically by the pH electrode or when maximum volume of 3 mL is exceeded.

7. Calculations

Acidity is calculated with the instrument's data reduction system and defined as follows:

$$\text{Acidity (mg/L as } H^+) = \frac{\text{mL titrant x } 0.01N \text{ NaOH x } 1.008 \text{ x } 1{,}000}{\text{mL sample}}$$

8. Report

Report acidity (71825) as hydrogen ion concentration to the nearest 0.01 mg/L.

9. Precision

Precision for acidity, measured in milligrams per liter as H^+, for three samples expressed in standard deviation and in percentage relative standard deviation, is as follows:

Mean (mg/L H^+)	Standard deviation (mg/L)	Relative standard deviation (percent)
7.79	0.16	2.1
.026	.0044	16.9
.021	.0037	17.6

Reference

Peters, D.G., Hayes, J.M., and Hieftje, G.M., 1974, Chemical separations and measurements--Theory and practice of analytical chemistry: Philadelphia, W.B. Saunders Co., p. 376-381.

Alkalinity, low ionic-strength water, electrometric titration, automated

Parameters and Codes:
Alkalinity, I-2034-86 (mg/L) as $CaCO_3$: 90410
Alkalinity, I-2034-86 (µeq/L): none

1. Application

This method is used to determine alkalinity in water samples containing more than 0.5 mg/L $CaCO_3$ and with a specific conductance less than 100 µS/cm. The method was implemented in the National Water Quality Laboratory in January 1986.

2. Summary of method

2.1 Alkalinity is determined by titrating a water sample with a standard solution of strong acid. The titration is stopped at pH 3.5, and the second derivative plot is used to calculate the alkalinity. This method approximates the results derived by Gran's titration calculations. For more information on the use of the second derivative, see Peters and others (1974, p. 376-381).

2.2 Alkalinity might be susceptible to change between time of collection and analysis, with changes occurring more rapidly after the sample bottle is opened. The determination needs to be performed within 8 hours.

2.3 Water samples for the determination of alkalinity should not be filtered, diluted, concentrated, or altered physically or chemically.

3. Interferences

3.1 Any ionized substance that reacts with a strong acid can contribute to alkalinity if the reaction occurs at a pH greater than that of the endpoint; examples are salts of weak organic and inorganic acid.

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

3.3 Exposure to carbon dioxide in air might cause variations in both the pH and alkalinity.

4. Apparatus

4.1 *Autoburet*, 1.0 mL capacity, Kyoto APB-118 or equivalent.

4.2 *Autosampler*, Kyoto CHG-310 or equivalent.

4.3 *Potentiometric titrator,* Kyoto AT-310 automatic titrator or equivalent.

4.4 *pH meter,* Kyoto STD-310 preamplifier or equivalent.

4.5 *pH electrode*, Orion Ross 810300 semimicro or equivalent.

4.6 With this equipment and the manufacturer's manual, the following operating conditions have been found to be satisfactory:

Control parameters

Method (Intermit)	05
Titration form	EP stop
Number of endpoints	1
Gain	1
Cutoff time	20 seconds
Unit volume	0.010 mL
Piston speed	5 s/mL

Titration parameters

Buret	05
Reagent	0.01*N* HCl
Preamplifier	STD
PSU (preamplifier gain control)	1
Dimension	pH
Wait time	90 seconds
Maximum volume	3 mL

4.7 *Sampler cover*, case to cover autosampler during operation. Cover contains inlet and outlet ports to purge autosampler of air with nitrogen gas.

5. Reagents

5.1 *Buffers,* pH 4.00 and 7.00 traceable to the National Institute for Standards and Technology.

5.2 *Hydrochloric acid standard solution (certified)* 0.01*N*: Commercially available from J.T. Baker or equivalent.

6. Procedure

6.1 Purge autosampler with nitrogen (15 to 25 lb/in^2) for 15 minutes prior to calibration or analysis of samples. The nitrogen needs to flow through the autosampler during all operations.

6.2 Calibrate electrode daily according to manufacturer's instructions using pH 4.00 and 7.00 buffers.

6.3 Pipet 30 mL of sample into titration vessels. Place cups in autosampler and begin analysis. The titration stops at first endpoint detected electrometrically by the pH electrode or when maximum volume of 3 mL is exceeded.

7. Calculations

Alkalinity is calculated with the instrument's data reduction system and defined as follows:

$$\text{Alkalinity (mg/L as } CaCO_3) = \frac{\text{mL titrant x } 0.01N \text{ HCl x } 50.05 \text{ x } 1{,}000}{\text{mL sample}}$$

8. Report

Report alkalinity (90410) as $CaCO_3$ concentration as follows: less than 0.5 mg/L as less than 0.5 mg/L; 0.5 mg/L and greater, nearest 0.1 mg/L.

9. Precision

9.1 Precision for total alkalinity, expressed in milligrams per liter as $CaCO_3$ in standard deviation and in percentage relative standard deviation, for three laboratories analyzing five samples in duplicate on three different days, is as follows:

Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
1.01	0.14	13.9
3.84	.12	3.1
5.16	.13	2.5
15.28	.40	2.6
31.71	.42	1.3

Reference

Peters, D.G., Hayes, J.M., and Hieftje, G.M., 1974, Chemical separations and measurements--Theory and practice of analytical chemistry: Philadelphia, W.B. Saunders Co., p. 376-381.

Aluminum, atomic emission spectrometry, dc plasma

Parameters and Codes:
Aluminum, dissolved, I-1054-86 (µg/L as Al): 01106
Aluminum, whole water recoverable, I-3054-86 (µg/L as Al): 01105
Aluminum, suspended recoverable, I-7054-86 (µg/L as Al): 01107
Aluminum, recoverable from bottom material, I-5054-86(µg/g as Al): 01108

1. Application

1.1 This method is used to analyze samples of finished water, natural water, industrial water, and water-suspended sediment containing from 10 to 10,000 µg/L of aluminum. Sample solutions containing more than 10,000 µg/L aluminum or with specific conductances greater than 10,000 µS/cm must be diluted. This modified method was implemented in the National Water Quality Laboratory in January 1986.

1.2 Suspended recoverable aluminum is calculated by subtracting dissolved aluminum from whole water recoverable aluminum.

1.3 This method is used to analyze bottom material containing at least 10 µg/g of aluminum.

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

2. Summary of method

Aluminum is determined by a direct-reading emission spectrometer that uses a dc argon plasma as an excitation source (Johnson and others, 1979a, 1979b). A solution 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 solution then is converted by a ceramic nebulizer into a fine aerosol and introduced into the plasma by means of a plastic spray chamber and Pyrex injection tube. Aluminum is determined on the average of two replicate exposures using a 10-second integrated intensity. A standard solution and a blank are used to calibrate the instrument.

3. Interferences

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

4. Apparatus

4.1 *Spectrometer*, Spectrametrics, DCP IV or Beckman, Spectrospan DCP VI with dc 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
Gas .....Argon
Sleeve pressure.....50 lb/in^2
Nebulizer pressure.....25 lb/in^2
Entrance slit.....25x300 µm
Exit slit .....50x300 µm
Voltage.....1,000 V
Wavelength.....308.215 nm
Signal amplification.....40-60 percent full-scale (1,000 µg/L)

5. Reagents

5.1 *Water*: All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

5.2 *Aluminum standard solution I,* 1 mL = 100 µg Al: Dissolve 0.100 g aluminum powder in a minimum 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 water. Store in plastic bottle.

5.3 *Aluminum working solution,* 1.00 mL = 10.0 µg Al: Dilute 100 mL aluminum standard solution I to 1,000 mL with 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 water and dilute to 1 L with water.

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

5.8 *Matrix modifier*: Dissolve 367 g LiCl in 1,000 mL water. Allow the solution to cool. Transfer to a 4-L polyethylene container, and while stirring

add 2,000 mL of glycerin. In a Teflon beaker slowly add with stirring 400 mL concentrated H_2SO_4 to 400 mL water. When the dilute acid has reached room temperature, add the acid slowly, with stirring, to the glycerin-LiCl solution. Dilute to 4,000 mL with 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 10.0 mL blank and working solution into plastic test tubes.

6.3 Add 2.0 mL matrix modifier to the samples, blank, and working solution.

6.4 Place plastic caps on the tubes and mix well.

6.5 Refer to manufacturer's manual for computer-operating and wavelength-optimization procedures. Use the prepared blank and aluminum working solution 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 solution after every eight samples for the DCP VI and after every three samples for the DCP IV. 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 4 percent.

7. Calculations

7.1 The computer system is designed so that the blank and the 10,000-µg/L aluminum working solution 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-solution instrument intensity readings, blank and standard concentrations, sample instrument intensity readings, sample concentrations, average of sample concentrations, and standard deviation.

7.2 Obtain the micrograms per liter of dissolved or whole water recoverable aluminum in each sample from the printer.

7.3 To determine micrograms per liter of suspended recoverable aluminum, subtract dissolved aluminum concentrations from whole water recoverable aluminum concentrations.

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

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

8. Report

8.1 Report concentrations of aluminum, dissolved (01106), whole water recoverable (01105), and suspended recoverable (01107), as follows: less than 100 µg/L, nearest 10 µg/L; 100 µg/L and greater, two significant figures.

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

9. Precision

9.1 Precision for dissolved aluminum, on the basis of 14 to 18 determinations by a single operator during a 47-day period, expressed in standard deviation and in percentage 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 percentage relative standard deviation for whole water recoverable and suspended recoverable aluminum, as well as for recoverable aluminum in bottom material, will be greater than that reported for dissolved aluminum.

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 45-47.

Johnson, G.W., Taylor, H.E., and Skogerboe, R.K., 1979a, Determination of trace elements in natural water 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.

(p 19 follows)

Anions, ion-exchange chromatography, automated

Parameters and Codes:
Anions, dissolved, I-2057-90 (see below)

Parameter	Code
Fluoride (mg/L as F)	**00950**
Chloride (mg/L as Cl)	**00940**
Sulfate (mg/L as SO_4)	**00945**

1. Application

1.1 This method is used to determine fluoride, chloride, and sulfate in natural-water samples. Approximate minimum and maximum concentration limits are listed in table 1. Samples containing anion concentrations greater than 300 mg/L for chloride and sulfate and 3 mg/L for fluoride must be diluted to fall within the analytical range. Dilutions will affect the detection limits for the three anions. This modified method was implemented in the National Water Quality Laboratory in March 1990.

Table 1.--*Analytical range for each anion by ion chromatography*
[Concentrations in milligrams per liter]

Constituent	Minimum concentration	Maximum concentration
Fluoride	0.1	3
Chloride	.2	300
Sulfate	.2	300

1.2 Filtered, unacidified samples need to be analyzed.

1.3 Bromide, nitrate, nitrite, and orthophosphate have been removed from the original method I-2057-85.

2. Summary of method

2.1 All three anions are separated chromatographically following a single sample injection on an ion exchange column. Ions are separated on the basis of their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical conductivity cell. Anions are identified on the basis of their retention times compared with known standards.

The peak height or area is measured and compared with an analytical curve generated from known standards to quantify the results.

2.2 For additional information on ion chromatography, see Small and others (1975), Fishman and Pyen (1979), Tater (1987), and Small (1989).

3. Interferences

3.1 A negative water-dip occurs immediately prior to the elution of fluoride, occasionally causing negative interference with the fluoride determination. It is eliminated by the introduction of a small stream of concentrated eluant to the sample (fig. 1).

3.2 Late eluting peaks might appear on subsequent chromatograms, and might give false values for the anions of interest. This problem can be prevented by careful review of each chromatogram produced.

4. Apparatus

4.1 *Ion chromatograph*, Dionex Model 4500 or equivalent, equipped with a Dionex AI450 data station or equivalent.

4.2 With this equipment the following operating conditions have been found optimal for the two analytical ranges being performed for sulfate, chloride, and fluoride (see 5.10 and 5.11):

Eluant flow rate ..... 2.0 mL/min
Sample loop ..... 5 to 30 µL
Eluant-head pressure ..... 5-7 lb/in^2
Regeneration pump stroke length ... 30-50 percent
Regeneration pump stroke rate ..... 80-90 percent

4.3 *Computer*, IBM AT or equivalent.

4.4 *Guard and separator columns*, Dionex OMNI-PAX 500 or equivalent. Approximate retention times: fluoride (1.2 minutes), chloride (1.5 minutes), and sulfate (2.5 minutes).

4.5 *Anion micro-membrane suppressor*, Dionex AMM-II or equivalent.

4.6 *Autosampler*, Gilson No. 212B or equivalent.

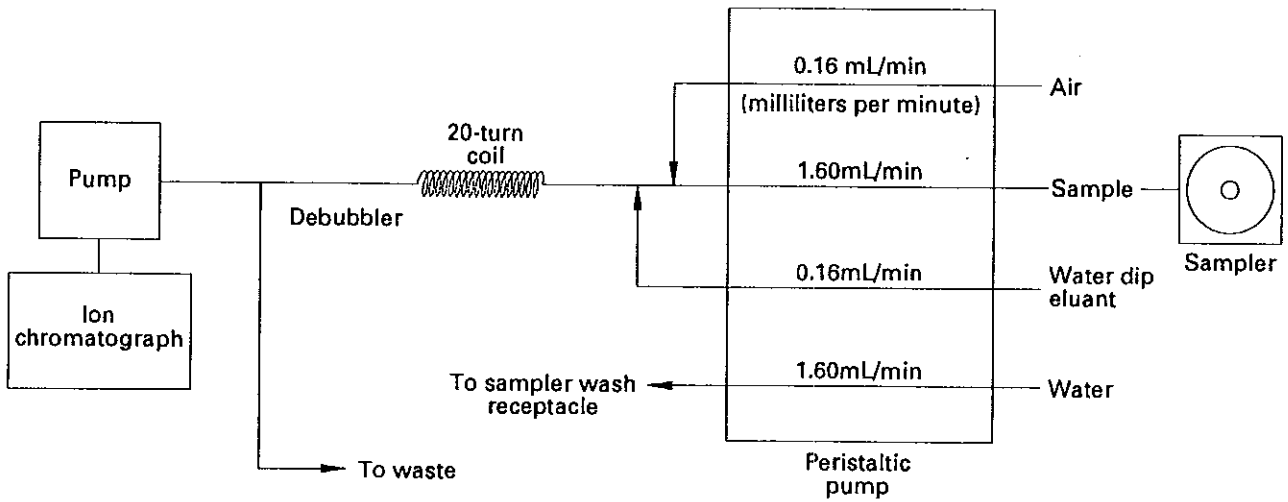

Figure 1.—Ion chromatography matrix matching manifold.

5. Reagents

5.1 *Eluant,* about 45 *mM* NaOH and 6 percent methanol: In a 4-L volumetric flask with about 2 L of water, pipet 9.0 mL of Baker Instra-Analyzed or equivalent, 50 percent NaOH solution, and 250 mL of helium-sparged HPLC grade methanol. Bring to volume with water.

5.2 *Water:* All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

5.3 *Water dip eluant:* Mix 45 mL 50 percent NaOH with water in a 2-L container, and bring to volume with water.

5.4 *Regenerant solution,* about 0.5 *mM* H_2SO_4. Add 5.00 mL concentrated H_2SO_4 (sp gr 1.84) to 4 L water.

5.5 *Fluoride stock solution I,* 1.00 mL = 1.0 mg F: Dissolve 2.2101 g NaF, dried at 105°C for 3 h in water, and dilute to 1,000 mL.

5.6 *Fluoride standard solution,* 1.00 mL = 0.02 mg F: Dilute 20.0 mL fluoride stock solution I to 1,000 mL.

5.7 *Chloride stock solution,* 1.00 mL = 10.0 mg Cl: Dissolve 16.4847 g NaCl, dried at 105°C for 3 h in water, and dilute to 1,000 mL.

5.8 *Sulfate stock solution,* 1.00 mL = 10.0 mg SO_4: Dissolve 14.7867 g Na_2SO_4, dried at 105°C for 3 h in water, and dilute to 1,000 mL.

5.9 *Mixed standard solution I* : Prepare by making appropriate dilutions of the anion stock solutions into a 1,000-mL volumetric flask:

Anion	Stock solution (mL)	Concentration (mg/L)
F	20.0	20
Cl	200.0	2,000
SO_4	200.0	2,000

5.10 *Mixed standard solution II*: Prepare a mixed-stock standard by making appropriate dilutions of the anion stock solutions into a 1,000-mL volumetric flask:

Anion	Stock solution (mL)	Concentration (mg/L)
Cl	10.0	100
SO_4	10.0	100

5.11 *Mixed working solutions,* high analytical range: Prepare a series of mixed working solutions as follows: Pipet appropriate volumes of mixed standard solution I into 1,000-mL volumetric flasks and bring to volume with water. For example:

Volume mixed standard solution I (mL)	Concentration SO_4 and Cl (mL)	Concentration F (mg/L)
150.0	300	3.00
100.0	200	2.00
50.0	100	1.00
25.0	50	.50
10.0	20	.20
5.0	10	.10

5.12 *Mixed working solutions,* low analytical range: Prepare a series of mixed working solutions as follows: Pipet appropriate volumes of mixed standard solution II and fluoride standard solution into 1,000-mL volumetric flasks and bring to volume with water. For example:

Volume mixed standard solution II (mL)	Volume fluoride standard solution (mL)	Concentration SO_4 and Cl (mg/L)	Concentration F (mg/L)
200.0	150.0	20	3.00
80.0	100.0	8	2.00
20.0	50.0	2	1.00
10.0	25.0	1	.50
2.0	10.0	.2	.20
1.0	5.0	.1	.10

6. Procedure

6.1 Load appropriate method software into system. Start eluant and regenerant pumps. Check to make sure appropriate head pressure is being maintained for the eluant being used (NOTE 1).

NOTE 1. It is best to sparge all eluants with ultrapure helium for 2 to 5 minutes prior to use. This aids in the removal of carbon dioxide from the eluants.

6.2 Allow 15 to 30 minutes for system equilibration. For the eluant being used, the conductivity meter must give a reading between 2.00 and 10.0 µS/cm; greater concentrations indicate contamination.

6.3 Analyze a blank through the system to check baseline and system characteristics.

6.4 Analyze working solutions from smallest to greatest concentration. The AI 450 software will determine curve fit and correlation coefficients. Six working solutions are to be used. An acceptable working curve needs to have a correlation coefficient of at least 0.992.

6.5 All samples with a specific conductance less than 250 µS/cm will be analyzed using the low analytical range. All other samples will be analyzed using the high analytical range.

6.6 Blanks and standard reference materials need to account for approximately 10 percent of the samples analyzed in any given run.

6.7 Because of the wide analytical range, samples with concentrations less than the minimum limit of the high analytical range need to be reanalyzed on the low analytical range. Likewise, samples whose concentrations exceed the maximum limit on the low analytical range need to be reanalyzed on the high analytical range.

7. Calculations

The AI 450 software automatically calculates analytical curves and computes the concentrations of each of the anions being determined.

8. Report

Report dissolved concentrations of fluoride (00950), chloride (00940), and sulfate (00945), as follows: less than 10 mg/L, to the nearest 0.1 mg/L; 10 mg/L and greater, two significant figures.

9. Precision

Single operator precision for each of the constituents (minimum of 10 replicates), as determined on standard reference water samples, is as follows:

Fluoride		Chloride		Sulfate	
Mean (mg/L)	Relative standard deviation (percent)	Mean (mg/L)	Relative standard deviation (percent)	Mean (mg/L)	Relative standard deviation (percent)
0.33	5.9	0.45	18	0.8	20
.34	7.4	1.02	24	28.2	2.8
2.28	1.7	.43	39	.35	20
2.46	3.2	12.3	6.7	41.4	2.0
2.53	1.7	36.3	2.1	220	1.8
		67.0	1.1	373	1.9
		269	1.2		

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 45-47.

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(p 27 follows)

Base/neutral and acid extractable compounds, gas chromatography/mass spectrometry

Parameters and Codes:
Base/neutral and acid extractables, whole water recoverable, O-3116-87

Parameter (µg/L)	Code	Parameter (µg/L)	Code
Acenaphthene	34205	2,4-Dinitrophenol	34616
Acenaphthylene	34200	2,4-Dinitrotoluene	34611
Anthracene	34220	2,6-Dinitrotoluene	34626
Benzo(a)anthracene	34526	Di-n-octyl phthalate	34596
Benzo(b)fluoranthene	34230	bis(2-Ethylhexyl) phthalate	39100
Benzo(k)fluoranthene	34242	Fluoranthene	34376
Benzo(g,h,i)perylene	34521	Fluorene	34381
Benzo(a)pyrene	34247	Hexachlorobenzene	39700
4-Bromophenyl phenyl ether	34636	Hexachlorobutadiene	39702
Butyl benzyl phthalate	34292	Hexachlorocyclopentadiene	34386
bis(2-Chloroethoxy)methane	34278	Hexachloroethane	34396
bis(2-Chloroethyl)ether	34273	Indeno(1,2,3-cd)pyrene	34403
bis(2-Chloroisopropyl)ether	34283	Isophorone	34408
4-Chloro-3-methylphenol	34452	2-Methyl-4,6-dinitrophenol	34657
2-Chloronaphthalene	34581	Naphthalene	34696
2-Chlorophenol	34586	Nitrobenzene	34447
4-Chlorophenyl phenyl ether	34641	2-Nitrophenol	34591
Chrysene	34320	4-Nitrophenol	34646
Dibenz(a,h)anthracene	34556	N-Nitrosodimethylamine	34438
1,2-Dichlorobenzene	34536	N-Nitrosodiphenylamine	34433
1,3-Dichlorobenzene	34566	N-Nitrosodi-n-propylamine	34428
1,4-Dichlorobenzene	34571	Pentachlorophenol	39032
2,4-Dichlorophenol	34601	Phenanthrene	34461
Diethyl phthalate	34336	Phenol	34694
2,4-Dimethylphenol	34606	Pyrene	34469
Dimethyl phthalate	34341	1,2,4-Trichlorobenzene	34551
Di-n-butyl phthalate	39110	2,4,6-Trichlorophenol	34621

1. Application

This method is suitable for the determination of methylene chloride extractable base/neutral and acid compounds in samples of water and water-

suspended sediment containing at least 5 to 30 µg/L of the analyte. Any compound amenable to methylene chloride extraction and gas chromatographic separation can be detected by the mass spectrometer, under the proper operating conditions. Thus this method is not necessarily limited to the determination of the target compounds listed. This method also can be used for broad spectrum screening and tentative identification of a wide variety of organic compounds when used in conjunction with computerized mass spectral reference library searches in the hands of a skilled mass spectrometrist. This modified method was implemented in the National Water Quality Laboratory in July 1986.

2. Summary

Base/neutral and acidic organic compounds are extracted from samples of water and water-suspended sediment with methylene chloride. The extract is concentrated and subjected to analysis by gas chromatography/mass spectrometry.

3. Interferences

Compounds having gas chromatography retention times and mass spectra similar to the compounds of interest may interfere with the analysis. Contamination of the sample and apparatus with the compounds to be determined also is a potential source of interference. Plastic materials particularly need to be avoided in the sampling and preparation process because of the presence of phthalate compounds (used as plasticizers), which might leach into the sample.

4. Instrumentation

4.1 *Gas chromatograph/mass spectrometer (GC/MS)*: Hewlett-Packard 5996, Finnigan 5100 or equivalent. Suggested gas chromatography configuration follows:

4.1.1 *Column*, fused silica capillary, 25-m x 0.20-mm inside diameter, 5 percent crosslinked phenylmethylsilicone, 0.33-µm film thickness, Hewlett-Packard Ultra-II or equivalent.

4.1.2 *Carrier gas*, helium, 30 cm/s linear flow velocity at 300°C.

4.1.3 *Injection mode*, splitless, injection port sweep flow 50 mL/min; turn off for 45 seconds at injection. Septum purge rate 1 mL/min.

4.1.4 *Injection port temperature*, 275°C.

4.1.5 *Transfer line temperature*, 300°C.

4.1.6 *Oven temperature program*, initial temperature 50°C, hold 5 minutes, program at 6°C per minute to 300°C. Hold at 300°C to allow sufficient time for all target compounds to elute.

4.2 *Suggested mass spectrometer configuration*:

4.2.1 *Ionization mode*, electron ionization, 70 eV ionization voltage.

4.2.2 *Scan range*, 45 to 450 amu.

4.2.3 *Scan rate*, at least two scans per second.

4.3 In addition, adjust instrument characteristics to meet the decafluorotriphenylphosphine (DFTPP) performance criteria described in section 9 and to achieve the reporting limits described in section 12.

5. Apparatus

5.1 *Concentrator, Kuderna-Danish (K-D)*, 500 mL, all glass, with ground-glass joints, a 10.0-mL receiver, and a three-ball Snyder column.

5.2 *Evaporative concentrator*, Organomation N-Evap or equivalent. Maintain water bath at room temperature.

5.3 *Separatory funnel*, 1-L capacity with Teflon stopcock, and ground-glass or Teflon stopper.

6. Reagents

6.1 *Methylene chloride*, distilled in glass, pesticide analysis grade, stabilized with cyclohexene, Burdick and Jackson or equivalent.

6.2 *Methanol*, distilled in glass, HPLC grade, Burdick and Jackson or equivalent.

6.3 *Sodium chloride*, granular, Baker analyzed or equivalent. Heat at 300°C overnight. Store in glass bottle at 110°C.

6.4 *Sodium sulfate*, anhydrous, Mallinckrodt 8024 or equivalent. Heat at 300°C overnight. Store in a glass bottle at 110°C.

6.5 *Sulfuric acid* (1+3): Prepare by *cautiously* adding one part concentrated sulfuric acid (Baker Ultrex or equivalent) to three parts organic-free water. Store in a refrigerator at 4°C.

6.6 *Potassium hydroxide solution*, 37 percent (w/v): *Cautiously* dissolve 185 g potassium hydroxide pellets (Baker analyzed or equivalent) in 500 mL organic-free water, and reflux for 8 h. Cool and store at 4°C.

6.7 *Water*, organic-free. All references to water shall be understood to mean ASTM Type II reagent water (American Society for Testing and Materials, 1991). Water needs to be tested for possible interfering peaks.

6.8 *Boiling chips*, 8 to 14 mesh, Hengar or equivalent. Heat at 300°C overnight, and store in a glass bottle at room temperature.

7. Calibration standards

7.1 *Internal standard solution*, perdeuteronaphthalene (naphthalene-d_8), Aldrich Chemical Company; perdeuterophenanthrene (phenanthrene-d_{10}), and perdeuterochrysene (chrysene-d_{12}), Kor Isotopes or equivalent. Weigh 25.0 mg of each compound, quantitatively transfer to a 25-mL volumetric flask, and dilute to volume with methylene chloride (1,000 ng/µL). Store in the dark at 4°C.

7.2 *Surrogate standard solution*, 1,4-dibromobenzene, 4,4'-dibromobiphenyl, 2,2'-difluorobiphenyl, phenol-d_5, 2,4-dibromophenol, and 2,4,6-tribromophenol, Aldrich Chemical Company. Weigh 5 mg of each of the six compounds to nearest hundredth of a milligram, quantitatively transfer to a 100-mL volumetric flask, and dilute to volume with methanol (50 ng/µL spiking solution). Prepare a similar solution in methylene chloride to use as a GC/MS calibration standard.

7.3 *Target compound calibration standards*, Supelco base/neutral solutions 1 through 4 and phenol mixture 604-M or equivalent. Using serial dilution or other appropriate technique, prepare target compound calibration standards in methylene chloride to cover the concentration range for the samples being analyzed. Add a volume of the internal standard solution (paragraph 7.1) to each standard solution sufficient to yield a concentration of 20 ng/µL of each internal standard. Store in the dark at 4°C.

7.4 *Target compound spiking solution.* Prepare a standard solution similar to that in paragraph 7.3, but bring to volume with methanol for use as a spiking solution. Do not add the internal standard solution to this solution.

7.5 *Decafluorotriphenylphosphine (DFTPP) mass spectrometer performance evaluation standard solution,* Aldrich. Weigh 1.25 mg of DFTPP, quantitatively transfer to a 25-mL volumetric flask, and dilute to volume with methylene chloride (50 ng/μL). Store in the dark at 4°C.

8. Sample extraction and concentration

All glassware is washed in warm detergent solution, rinsed with organic-free water, and heated at 300°C overnight. Immediately before use, the glassware is rinsed with methylene chloride. Stopcock grease is not to be used on ground-glass joints.

8.1 Weigh the sample bottle to the nearest gram and record the gross weight for subsequent calculations.

8.2 Add 100 g of sodium chloride to a separatory funnel.

8.3 Pour the sample into the separatory funnel and allow the sample bottle to drain completely.

8.4 Prepare a blank and spike sample with each set of samples by adding 800 mL of organic-free water to a 1-L separatory funnel containing 100 g of sodium chloride.

8.5 Stopper the separatory funnels and swirl to dissolve the salt completely.

8.6 Add to the spike sample a volume of target compound spiking solution (paragraph 7.4) sufficient to yield a concentration of 5 to 200 μg/L in the sample.

8.7 Add 0.2 mL of surrogate standard solution (paragraph 7.2) to each sample, blank, and spike.

8.8 Weigh the empty sample bottle to three significant figures, and record the tare weight. Calculate the net weight by subtracting the tare weight from the gross weight. Record the net sample weight.

8.9 *Base/neutral extraction*

8.9.1 Adjust the sample to pH 11 or greater, as indicated by pH paper, by the addition of potassium hydroxide solution.

8.9.2 Add 100 mL methylene chloride to the empty sample bottle, and swirl to wash the sides of the container with the solvent. The Teflon liner is not rinsed because of the potential of contamination from solvent that has contacted the cap threads and surface beneath the liner. Pour the contents of the bottle into the separatory funnel.

8.9.3 Stopper the separatory funnel and shake for at least 1 minute, venting often to relieve pressure. Allow the layers to separate.

8.9.4 Drain the organic layer into a 500-mL Erlenmeyer flask and stopper the flask.

8.9.5 Extract the sample two more times with 50 mL methylene chloride by repeating paragraphs 8.9.2 through 8.9.4. Collect the extracts in the same Erlenmeyer flask.

8.9.6 Add approximately 30 g sodium sulfate to the Erlenmeyer flask. Cover the flask with aluminum foil. Store in the dark at 4°C until ready for concentration.

8.10 *Acid extraction.* The acid extracts can be collected separately or combined with the base/neutral fraction.

8.10.1 Adjust the sample in the separatory funnel to pH 2 or lower with sulfuric acid (1+3).

8.10.2 Add 100 mL methylene chloride to the separatory funnel.

8.10.3 Stopper the separatory funnel and shake vigorously for at least 1 minute, venting often to release the pressure. Allow the layers to separate.

8.10.4 Drain the organic layer into a 500-mL Erlenmeyer flask and stopper the flask. The extracts can be combined with the base/neutral fraction at this step.

8.10.5 Extract the sample two more times with 50 mL methylene chloride by repeating paragraphs 8.10.2 through 8.10.4. Collect the extracts in the same Erlenmeyer flask.

8.10.6 Add approximately 30 g sodium sulfate to the Erlenmeyer flask. Cover the flask with aluminum foil. Store in the dark at 4°C until ready for concentration.

8.11 *Concentration of base/neutral and acid extractable compounds*

8.11.1 Swirl extract to loosen sodium sulfate. Pour dried extract into a K-D apparatus. Make sure that the sodium sulfate does not transfer into the K-D apparatus. Rinse the sodium sulfate with 15 mL methylene chloride and pour into the K-D apparatus. Rinse once more. Add one boiling chip and attach a three-ball Snyder column.

8.11.2 Concentrate in a fume hood to about 5 mL by heating in the water bath (65°C) so that the concentration is completed in 30 to 45 minutes.

8.11.3 Swirl the K-D flask to wash the inner surfaces and allow the K-D flask to cool to ambient temperature. Separate the Snyder column from the K-D flask, and rinse the walls of the K-D flask with approximately 2 mL of methylene chloride. Dry the receiver joint with a lint-free towel, and separate the receiver from the K-D flask.

8.11.4 Reduce the volume of the extract in the receiver to approximately 0.9 mL on the evaporative concentrator.

8.11.5 Stopper the receiver with a ground-glass stopper, and store the extract in the dark at 4°C or less until analysis can proceed.

8.11.6 Prior to analysis, add 20 µL of internal standard solution. Adjust the final volume of the sample extract in the receiver to 1.0 mL with methylene chloride.

9. Gas chromatography/mass spectrometry performance evaluation

9.1 *Mass spectrometer performance evaluation.* Check the instrument prior to analyzing any sample and every 24 h thereafter during a series of analyses to ensure mass spectrometer performance according to the DFTPP criteria listed in table 2. In addition, initially adjust the mass spectrometer to ensure that the established reporting level for each target compound can be achieved.

Table 2.--*Gas chromatography/mass spectrometry performance evaluation using decafluorotriphenylphosphine*

Mass	Ion abundance criteria
51	30-60 percent of mass 198
68	Less than 2 percent of mass 69
69	Reference only
70	Less than 2 percent of mass 69
127	40-60 percent of mass 198
197	Less than 1 percent of mass 198
198	Base peak, 100 percent relative abundance
199	5-9 percent of mass 198
275	10-30 percent of mass 198
365	Greater than 1 percent of mass 198
441	Less than mass 443
442	Greater than 40 percent of mass 198
443	17-23 percent of mass 442

9.1.1 Suggested gas chromatograph (GC) oven temperature programming conditions for the analysis of DFTPP are modified from those outlined in paragraph 4.1.6 to enable rapid analysis if repeated corrections need to be made to pass the DFTPP criteria. Program the GC oven temperature to ramp from 50°C (no hold time) to 300°C at 30°C per minute after injection of 1 µL of the DFTPP standard solution. Mass spectrometer conditions are the same as those outlined in paragraph 4.2.

9.1.2 Mass spectral peak abundance averaging and background correction can be used to obtain a DFTPP spectrum for evaluation.

9.1.3 If the mass spectrum for DFTPP fails to meet the criteria specified in table 2, retune the mass spectrometer and reanalyze the DFTPP until the criteria are passed.

9.2 *Gas chromatograph performance evaluation.* GC performance normally is reflected in the variation of the target compound response factors relative to response factors obtained using a new capillary column and freshly prepared standard solutions. In particular, the response for 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 4-nitrophenol, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, and benzo(g,h,i)perylene will deteriorate, indicating that the column needs to be maintained. A portion of the inlet end of the capillary column can be

removed to restore performance; however, the column needs to be replaced when N-nitrosodimethylamine becomes obscured by the methylene chloride solvent front.

10. Target compound calibration

Initial calibration data are acquired using a new GC column and freshly prepared standard solutions. These data are used in subsequent evaluation of system performance.

Prior to the analysis of each sample set and every 24 h thereafter during a series of analyses, analyze and evaluate a standard solution (or solutions) containing all of the target compounds and surrogates to ensure system performance is adequate.

10.1 Acquire data for each target compound and surrogate standard solution by injecting 1 to 3 μL of standard solution.

10.2 Calculate the relative retention time (RRT_c) for each compound as follows:

$$RRT_c = \frac{RT_c}{RT_i},$$

where RT_c = uncorrected retention time of the quantitation ion of the target compound or surrogate standard, and

RT_i = uncorrected retention time of the quantitation ion of the internal standard for the compound in question.

10.3 Most GC/MS data systems provide a linear least squares calibration curve fitting routine, which is usually suitable for calibration of the target compounds. The calibration routine should use the response of the target compound relative to that of the appropriate internal standard in relation to the target compound concentration. Take care to include enough data points (at least five suggested), with the smallest concentration standard within a factor of two of the minimum reporting limit. The respective quantitation ions and internal standard reference used in these calculations are listed in table 3.

10.4 System performance generally can be considered to be acceptable if back calculation of the standard compound concentrations agrees within ±20 percent of the expected values. However, given the wide range of functionalities represented by the target compounds, and the varied effects that different sample matrices might have on gas chromatography performance in particular, it may not be reasonable to expect all of the compounds to respond in a similar, predictable fashion.

Table 3.--*Quantitation information for base/neutral-acid compounds*

[µg/L, microgram per liter]

Compound name	Quantitation ion	Minimum reporting limit (µg/L)	Compound type	Internal standard reference
Perdeuteronaphthalene	136	Not used	Internal standard 1	
Perdeuterophenanthrene	188	Not used	Internal standard 2	
Perdeuterochrysene	240	Not used	Internal standard 3	
1,4-Dibromobenzene	236	Not used	Surrogate	1
4,4'-Dibromobiphenyl	152	Not used	Surrogate	2
2,4-Dibromophenol	252	Not used	Surrogate	1
2,2'-Difluorobiphenyl	190	Not used	Surrogate	1
Perdeuterophenol[1]	99	Not used	Surrogate	1
2,4,6-Tribromophenol	141	Not used	Surrogate	2
Acenaphthene	154	5	Target	2
Acenaphthylene	152	5	Target	1
Anthracene	178	5	Target	2
Benzo(a)anathracene	228	5	Target	3
Benzo(b)fluoranthene	252	10	Target	3
Benzo(k)fluoranthene	252	10	Target	3
Benzo(g,h,i)perylene	276	10	Target	3
Benzo(a)pyrene	252	10	Target	3
4-Bromophenyl phenyl ether	248	5	Target	2
Butyl benzyl phthalate	149	5	Target	3
bis(s-Chloroethoxy)methane	93	5	Target	1
bis(2-Chloroethyl)ether	93	5	Target	1
bis(2-Chloroisopropyl)ether	121	5	Target	1
4-Chloro-3-methylphenol	142	30	Target	1
2-Chloronaphthalene	162	5	Target	1
2-Chlorophenol	128	5	Target	1
4-Chlorophenyl phenyl ether	204	5	Target	2
Chrysene	228	10	Target	3
Dibenz(a,h)anthracene	278	10	Target	3
1,2-Dichlorobenzene	146	5	Target	1
1,3-Dichlorobenzene	146	5	Target	1
1,4-Dichlorobenzene	146	5	Target	1
2,4-Dichlorophenol	162	5	Target	1
Diethyl phthalate	149	5	Target	2
2,4-Dimethylphenol	122	5	Target	1
Dimethyl phthalate	163	5	Target	1
Di-n-butyl phthalate	149	5	Target	2
2,4-Dinitrophenol	184	20	Target	2

Table 3.--*Quantitation information for base/neutral-acid compounds*--Continued

Compound name	Quantitation ion	Minimum reporting limit (µg/L)	Compound type	Internal standard reference
2,4-Dinitrotoluene	165	5	Target	2
2,6-Dinitrotoluene	165	5	Target	2
Di-n-octyl phthalate	149	10	Target	3
bis(2-Ethylhexyl)phthalate	149	5	Target	3
Fluoranthene	202	5	Target	2
Fluorene	166	5	Target	2
Hexachlorobenzene	284	5	Target	2
Hexachlorobutadiene	225	5	Target	1
Hexachlorocyclo-pentadiene	237	5	Target	1
Hexachloroethane	201	5	Target	1
Indeno(1,2,3-cd)pyrene	276	10	Target	3
Isophorone	82	5	Target	1
2-Methyl-4,6-dinitrophenol	198	30	Target	2
Naphthalene	128	5	Target	1
Nitrobenzene	77	5	Target	1
2-Nitrophenol	139	5	Target	1
4-Nitrophenol	139	30	Target	2
N-Nitrosodimethylamine	74	5	Target	1
N-Nitrosodiphenylamine[2]	169	5	Target	2
N-Nitrosodi-n-propylamine	130	5	Target	1
Pentachlorophenol	266	30	Target	2
Phenanthrene	178	5	Target	2
Phenol	94	5	Target	1
Pyrene	202	5	Target	3
1,2,4-Trichlorobenzene	180	5	Target	1
2,4,6-Trichlorophenol	196	20	Target	1

[1]Perdeuterophenol reacts with atmospheric water, or water in the sample to yield phenol, d_5.

[2]N-Nitrosodiphenylamine degrades on the GC column, and is detected as diphenylamine.

10.5 If curve-fitting software is not available, the response factor RF_C for each target compound and surrogate standard is calculated as follows:

$$RF_C = \frac{C_i \times A_C}{C_C \times A_i}$$

where C_i = concentration of the internal standard, in micrograms per liter;

A_C = gas chromatograph peak area of the quantitation ion for the target compound or surrogate standard;

C_C = concentration of the target compound or surrogate standard, in micrograms per liter; and

A_i = gas chromatograph peak area of the quantitation ion for the internal standard.

The respective quantitation ions and internal standard reference used in these calculations are listed in table 3.

10.6 The average of the response factors calculated for each standard concentration needs to be used in subsequent target compound quantitation. Use of the average response factor is acceptable if the relative standard deviation over the calibration range is less than or equal to 35 percent.

10.7 After the initial calibration, at least one daily verification standard solution needs to be analyzed to ensure that the instrument is operating within the guidelines described in paragraphs 10.4 and 10.6.

11. Sample analysis and data evaluation

The GC/MS conditions for the determination of target compounds in sample extracts are the same as those used in the analysis of the standard solutions. Daily, prior to the analysis of any samples, the DFTPP mass spectral performance criteria need to be met, and the target compound calibration data need to be evaluated. In addition, the system needs to be tuned so that the reporting level for each compound can be achieved.

11.1 Inject 1 to 3 µL of the sample extract (paragraph 8.10.6) and acquire data.

11.2 *Qualitative identification*

11.2.1 Calculate the expected retention time as follows:

$$RT = RRT_C \times RT_i$$

where RT = expected retention time of the target compound or surrogate standard,

RRT_C = relative retention time of the target compound or surrogate standard (paragraph 10.2), and

RT_i = uncorrected retention time of the quantitation ion of the internal standard for the compound in question.

In general, the retention time of the GC peak for the quantitation ion of the compound in question needs to be within ±0.1 minute of that for the calibration standard. However, matrix effects can have a significant effect on GC retention times, and retention time reproducibility can be highly compound dependent.

11.2.2 Mass spectra for each target compound are verified by comparing the mass spectrum corresponding to the apex of the extracted ion profile of the quantitation ion with a reference spectrum obtained from a standard analyzed on the GC/MS system (see sections 9 and 10). It is difficult to define explicitly which features of a sample mass spectrum relative to that of a standard mass spectrum must be present to consider the identification to be positive. Experience and training are necessary for the analyst to recognize the relevant features of individual mass spectra as well as potential interferences. In general, the sample spectrum should have the same base peak, major fragmentation ions, significant isotope clusters, and molecular ion (where appropriate), as the standard spectrum. It is often beneficial to graphically plot extracted ion profiles of significant ions (or suspected interference ions) to determine whether they maximize at the expected retention time with intensities consistent with the reference mass spectrum. Computerized fit criteria or match factors might be valuable interpretation aids, but they are to be used only as a guide. A standard solution of the compound tentatively identified by the library search needs to be prepared and analyzed and the spectrum obtained. The retention time should be carefully compared with the spectra of the suspect compound.

11.3 *Quantitation*

If a compound has passed the qualitative identification criteria, calculate the concentration in the sample using the relevant software and calibration curve described in paragraph 10.3. If response factors were used for calibration (paragraph 10.5), then calculate the concentration as follows:

$$C = \frac{C_i \times A_c \times V \times 1{,}000}{RF_c \times A_i \times W}$$

where C = concentration of the compound in the sample, in micrograms per liter;

C_i = concentration of the corresponding internal standard, in micrograms per liter;

A_c = area of the quantitation ion for the compound identified;

V = extract volume, in milliliters;

RF_c = response factor (paragraph 10.5) for each target compound and surrogate standard;

A_i = area of the quantitation ion for the internal standard; and

W = weight of the sample extracted, in milliliters (1.0 g = 1.0 mL).

11.4 Percentage recovery of the surrogate standards is calculated as follows:

$$R = \frac{C_i \times A_c \times V}{RF_c \times A_i \times C_s \times V_s} \times 100$$

where R = percentage of recovery of the surrogate standard;

C_i = concentration of the corresponding internal standard, in micrograms per liter;

A_c = area of the quantitative ion for the compound identified;

V = extract volume, in milliliters;

RF_c = response factor (paragraph 10.5) for the surrogate standard;

A_i = area of the quantitation ion for the internal standard;

C_s = concentration of the surrogate standard in the spiking solution added to the sample, in micrograms per liter; and

V_s = volume of the surrogate spiking solution added to the sample, in milliliters.

12. Report

Report concentrations of base/neutral and acid extractable compounds as follows: if less than the reporting limit in table 3, report as "less than"; if greater than the reporting limit, two significant figures.

13. Precision and recovery

Precision and recovery data for target compounds from laboratory distilled water are presented in table 4:

Table 4.--*Precision and recovery data for target compounds*

[conc., concentration; µg/L, microgram per liter; No., number]

Compound name	Spike conc. (µg/L)	No. of replicates	Mean recovery (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Acenaphthene	50	8	44.2	2.92	6.61	88.4
	10	9	8.74	.57	6.52	87.4
	2.5	9	1.70	.11	6.47	68.0
Acenaphthylene	50	8	54	3.38	6.26	108
	10	9	10.8	.76	7.04	108
	2.5	9	2.56	.15	5.86	102
Anthracene	50	8	53	2.39	4.51	106
	10	9	11.1	.65	5.86	111
	2.5	9	2.16	.12	5.56	86.4
Benzo(a)anthracene	50	8	59.5	2.51	4.22	119
	10	9	11.7	.76	6.50	117
	2.5	9	2.64	.19	7.20	106
Benzo(b)fluoranthene	50	8	57.8	2.85	4.93	116
	10	9	6.02	.66	11.0	60.2
	2.5	9	1.11	.07	6.31	44.4
Benzo(k)fluoranthene	50	8	59.0	4.74	8.04	118
	10	9	5.93	.40	6.74	59.3
	2.5	9	1.02	.20	19.6	40.8
Benzo(g,h,i)perylene	50	8	54.3	4.77	8.78	109
	10	9	5.44	.78	14.3	54.4
Benzo(a)pyrene	50	8	55.6	4.32	7.77	111
	10	9	5.25	.67	12.8	52.5
	2.5	9	.65	.13	20.0	26.0

Table 4.--*Precision and recovery data for target compounds* --Continued

Compound name	Spike conc. (µg/L)	No. of replicates	Mean recovery (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
4-Bromophenyl phenyl ether	50	8	51.6	2.36	4.57	103
	10	9	8.28	.44	5.31	82.8
	2.5	9	1.83	.08	4.37	73.2
Butyl benzyl phthalate	50	8	58.6	4.64	7.92	117
	10	9	14.6	1.51	10.3	146
	2.5	9	2.80	.36	12.9	112
bis(2-Chloroethoxy) methane	50	8	56.0	2.50	4.46	112
	10	9	11.8	.66	5.59	118
	2.5	9	2.49	.11	4.42	99.6
bis(2-Chloroethyl) ether	50	8	51.0	1.90	3.73	102
	10	9	11.2	.73	6.52	112
	2.5	9	2.47	.08	3.24	98.8
bis(2-Chloroisopropyl) ether	50	8	49.2	1.46	2.97	98.4
	10	9	10.1	.61	6.04	101
	2.5	9	2.24	.39	17.4	89.6
4-Chloro-3-methylphenol	50	8	57.5	2.68	4.66	115
	10	9	11.5	.76	6.61	115
	2.5	9	2.12	.13	6.13	84.8
2-Chloronaphthalene	50	8	48.1	2.94	6.11	96.2
	10	9	9.58	.53	5.53	95.8
	2.5	9	2.41	.08	3.32	96.4
2-Chlorophenol	50	8	49.5	1.73	3.49	99.0
	10	9	10.3	.65	6.31	103
	2.5	9	2.22	.06	2.70	88.8
4-Chlorophenyl phenyl ether	50	8	45.1	2.44	5.41	90.2
	10	9	7.79	.47	6.03	77.9
	2.5	9	1.71	.60	35.1	68.4
Chrysene	50	8	58.0	1.92	3.31	116
	10	9	11.0	.62	5.64	110
	2.5	9	2.33	.14	6.01	93.2
Dibenz(a,h)anthracene	50	8	58.0	4.88	8.41	116
	10	9	5.39	.81	15.0	53.9
1,2-Dichlorobenzene	50	8	31.6	2.02	6.39	63.2
	10	9	7.13	.50	7.01	71.3
	2.5	9	1.64	.05	3.05	65.6

Table 4.--*Precision and recovery data for target compounds* --Continued

Compound name	Spike conc. (µg/L)	No. of replicates	Mean recovery (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
1,3-Dichlorobenzene	50	8	26.1	2.08	7.97	52.2
	10	9	5.74	.42	7.32	57.4
	2.5	9	1.38	.05	3.62	55.2
1,4-Dichlorobenzene	50	8	28.2	2.14	7.59	56.4
	10	9	6.16	.40	6.49	61.6
	2.5	9	1.47	.06	4.08	58.8
2,4-Dichlorophenol	50	8	55.0	1.86	3.38	110
	10	9	10.1	.57	5.64	101
	2.5	9	2.08	.10	4.82	83.8
Diethyl phthalate	50	8	55.0	2.58	4.69	110
	10	9	9.36	.59	6.30	93.6
	2.5	9	1.95	.15	7.69	78.0
2,4-Dimethylphenol	50	8	41.9	1.60	3.80	83.9
	10	9	8.68	.85	9.79	86.8
	2.5	9	1.41	.15	10.6	56.4
Dimethyl phthalate	50	8	47.6	1.97	4.14	95.2
	10	9	6.88	.92	13.4	68.8
	2.5	9	2.08	.31	14.9	83.2
Di-n-butyl phthalate	50	8	49.4	6.36	12.9	98.8
	10	9	16.5	1.10	6.67	165
	2.5	9	3.04	.21	6.91	122
2,4-Dinitrophenol	50	8	47.0	12.5	26.6	94.0
2,4-Dinitrotoluene	50	8	61.1	2.54	4.16	122
	10	9	10.5	.77	7.33	105
	2.5	9	1.14	.15	13.2	45.6
2,6-Dinitrotoluene	50	8	59.0	4.73	8.02	118
	10	9	9.49	.86	9.06	94.9
	2.5	9	.98	.10	9.90	39.3
Di-n-octyl phthalate	50	8	57.5	5.27	9.17	115
	10	9	7.97	.74	9.28	79.7
	2.5	9	.47	.06	12.8	18.8
Fluorene	50	8	50.0	2.70	5.40	100
	10	9	9.38	.56	5.97	93.8
	2.5	9	1.86	.08	4.30	74.4
Hexachlorobenzene	50	8	54.0	2.52	4.67	108
	10	9	9.25	.59	6.38	92.5
	2.5	9	1.77	.19	10.7	70.8

Table 4.--*Precision and recovery data for target compounds*--Continued

Compound name	Spike conc. (µg/L)	No. of replicates	Mean recovery (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Hexachlorobutadiene	50	8	10.4	1.78	17.1	20.8
	10	9	1.58	.25	15.8	15.8
	2.5	9	.89	.09	10.1	35.6
Hexachlorocyclo-pentadiene	50	8	7.06	1.41	20.0	14.1
	10	9	.61	.11	18.0	6.1
	2.5	9	.26	.04	15.4	10.4
Hexachloroethane	50	8	15.8	2.08	13.2	31.6
	10	9	2.70	.28	10.4	27.0
	2.5	9	.78	.07	8.97	31.2
Indeno(1,2,3-cd)pyrene	50	8	60.8	7.98	13.1	122
	10	8	5.68	.90	15.8	56.8
Isophorone	50	8	60.0	3.50	5.83	120
	10	9	11.3	.72	6.37	113
	2.5	9	2.16	.13	6.02	86.4
2-Methyl-4,6-dinitrophenol	50	8	64.0	9.81	15.3	128
Naphthalene	50	8	45.6	2.26	4.96	91.2
	10	9	10.1	.56	5.54	101
	2.5	9	2.29	.08	3.49	91.6
Nitrobenzene	50	8	59.0	3.44	5.83	118
	10	9	9.95	.69	6.93	99.5
	2.5	9	1.41	.08	5.67	56.4
2-Nitrophenol	50	8	56.5	2.15	3.81	113
	10	9	8.74	.74	8.47	87.4
	2.5	9	1.33	.15	11.3	53.2
4-Nitrophenol	50	8	36.7	2.55	6.95	73.4
	10	9	3.36	.63	18.8	33.6
N-Nitrosodimethylamine	50	8	39.4	4.27	10.8	78.8
	10	9	7.95	8.50	107	79.5
	2.5	9	1.57	.09	5.73	62.8
N-Nitrosodiphenylamine	50	8	61.5	3.07	4.99	123
	10	9	12.0	.61	5.08	120
	2.5	9	2.41	.12	4.98	96.4
N-Nitrosodi-n-propylamine	50	8	53.0	2.62	4.94	106
	10	9	10.4	.70	6.73	104
	2.5	9	1.80	.14	7.78	72.0
Pentachlorophenol	50	8	81.0	15.0	18.5	162

Table 4.--*Precision and recovery data for target compounds* --Continued

Compound name	Spike conc. (µg/L)	No. of replicates	Mean recovery (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Phenanthrene	50	8	53.5	2.54	4.75	107
	10	9	10.9	.57	5.23	109
	2.5	9	2.31	.11	4.76	92.4
Phenol	50	8	28.7	.81	2.82	57.4
	10	9	7.51	.49	6.52	75.1
	2.5	9	1.63	.07	4.29	65.2
Pyrene	50	8	28.1	3.53	12.6	56.2
	10	9	17.3	1.80	10.4	173
	2.5	9	3.08	.20	6.49	123
1.2.4-Trichlorobenzene	50	8	34.6	2.22	6.42	69.2
	10	9	6.72	.36	5.36	67.2
	2.5	9	1.69	.04	2.37	67.6
2,4,6-Trichlorophenol	50	8	57.0	3.22	5.65	114
	10	9	9.77	.75	7.68	97.7
	2.5	9	2.36	.18	7.63	94.4
			Surrogates			
1,4-Dibromobenzene	50	38	32.9	7.11	21.6	65.8
4,4'-Dibromobiphenyl	50	38	37.9	10.6	28.0	75.8
2,4-Dibromophenol	50	38	42.8	6.90	16.1	85.6
2,2'-Difluorobiphenyl	50	38	38.9	8.57	22.0	77.8
2,4,6-Tribromophenol	50	38	32.6	9.78	30.0	65.2
Phenol-d_5	50	38	24.6	5.80	23.6	49.2

Reference

American Society for Testing and Materials, 1991, Annual book of ASTM Standards, Section 11, Water: Philadelphia, v. 11.01, p. 45-47.

(p 47 follows)

Boron, atomic emission spectrometry, dc plasma

Parameters and Codes:
Boron, dissolved, I-1114-86 (µg/L as B): 01020
Boron, whole water recoverable, I-3114-86 (µg/L as B): 01022
Boron, suspended recoverable, I-7114-86 (µg/L as B): 01021
Boron, recoverable from bottom material, I-5114-86 (µg/g as B): 01023

1. Application

1.1 This method is used to analyze samples of finished water, natural water, industrial water, and water-suspended sediment containing from 10 to 10,000 µg/L of boron. Sample solutions containing more than 10,000 µg/L boron or with specific conductances greater than 10,000 µS/cm must be diluted. This modified method was implemented in the National Water Quality Laboratory in January 1986.

1.2 Suspended recoverable boron is calculated by subtracting dissolved boron from whole water recoverable boron.

1.3 This method is used to analyze bottom material containing at least 10 µg/g of boron.

1.4 Recoverable boron in water-suspended sediment needs to undergo a 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.

2. Summary of method

Boron is determined by direct-reading emission spectrometer that uses a dc argon plasma as an excitation source (Johnson and others, 1979a, 1979b). A solution 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 solution then is converted by a ceramic nebulizer into a fine aerosol and introduced into the plasma by way of a plastic spray chamber and Pyrex injection tube. Boron is determined on the average of two replicate exposures using a 10-second integrated intensity. A standard solution and a blank are used to calibrate the instrument.

3. Interferences

Stray-light effects in a high-resolution, single-element dc argon plasma atomic emission spectrometer are found to be negligible.

4. Apparatus

4.1 *Spectrometer*, Spectrometrics, DCP IV or Beckman, Spectrospan DCP IV or VI with dc 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 0
Gas ..... Argon
Sleeve pressure ..... 50 lb/in^2
Nebulizer pressure ..... 25 lb/in^2
Entrance slit ..... 25x300 µm
Exit slit ..... 50x300 µm
Voltage ..... 1,000 V
Wavelength ..... 249.773 nm
Signal amplification ..... 40-60 percent full-scale (1,000 µg/L)

5. Reagents

5.1 *Water*: All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

5.2 *Boron standard solution I*, 1 mL = 100 µg B: Dissolve 0.5720 g ultrapure H_3BO_3, dried over desiccant for 24 h, in water, and dilute to 1,000 mL. Store in plastic bottle.

5.3 *Boron working solution,* 1.00 mL = 10.0 µg B: Dilute 100 mL boron standard solution I to 1,000 mL with 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 1,000 mL water. Transfer to a Teflon beaker and slowly add with stirring 10.0 mL concentrated H_2SO_4.

Heat the solution to 75 to 80°C on a padded hotplate and slowly add 25 mL methyl alcohol. The addition of methyl alcohol removes any boron contamination in the reagents. Stir rapidly for 1 h to volatilize excess methyl alcohol and any trimethyl borate that forms. Repeat the addition of methyl alcohol and heat two more times. Allow the solution to cool, transfer to a 4-L polyethylene container, and while stirring add 2,000 mL glycerin. In a Teflon beaker slowly add with stirring 400 mL concentrated H_2SO_4 to 400 mL 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 dilute acid has reached room temperature, add the acid slowly, with stirring, to the glycerin-LiCl solution. Dilute to 4,000 mL with 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 10.0 mL blank and working solution into plastic test tubes.

6.3 Add 2.0 mL matrix modifier to the sample, blank, and working solution.

6.4 Place plastic caps on the test tubes and mix well.

6.5 Refer to manufacturer's manual for computer-operating and wavelength-optimization procedures. Use the prepared blank and boron working solution 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 solution after every eight samples for the DCP VI and after every three samples for the DCP IV 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 4 percent.

7. Calculations

7.1 The computer system is designed so that the blank and the 10,000 µg/L of boron working solution 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-solution instrument intensity readings, sample concentrations, sample instrument intensity readings, average of sample concentrations, and standard deviation.

7.2 Obtain the micrograms per liter of dissolved or whole water recoverable boron in each sample from the printer.

7.3 To determine micrograms per liter of suspended recoverable boron, subtract dissolved boron concentrations from whole water recoverable boron concentrations.

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

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

8. Report

8.1 Report concentrations of boron, dissolved (01020), whole water recoverable (01022), and suspended recoverable (01021), as follows: less than 100 µg/L, nearest 10 µg/L; 100 µg/L and greater, two significant figures.

8.2 Report boron concentrations, recoverable from bottom material (01023), as follows: less than 1,000 µg/g, nearest 10 µg/g; 1,000 µg/g and greater, two significant figures.

9. Precision

9.1 Precision for dissolved boron, on the basis of 12 determinations by a single operator expressed in terms of standard deviation and percentage 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	.3

9.2 Precision for whole water recoverable boron, on the basis of 10 determinations by a single operator expressed in terms of standard deviation and percentage relative standard deviation is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
315	4.7	1.5
1,860	53	2.8
4,609	56	1.2
8,872	106	1.2

9.3 It is estimated that the percentage relative standard deviation for recoverable boron in bottom material will be greater than reported for dissolved boron.

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 45-47.

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.

Cadmium, atomic absorption spectrophotometry, graphite furnace

Parameters and Codes:
Cadmium, dissolved, I-2138-89 (µg/L as Cd): (01025)
Cadmium, whole water recoverable, I-4138-89 (µg/L as Cd): (01027)

1. Application

1.1 This method is used to determine cadmium in samples of water and water-suspended sediment with a specific conductance not greater than 10,000 µS/cm. With Zeeman background correction and a 20-µL sample, the method is applicable in the range from 1 to 5 µg/L. Sample solutions that contain cadmium concentrations greater than 5 µg/L must be diluted or be analyzed by an alternate method. This method was implemented in the National Water Quality Laboratory in May 1989.

1.2 The analytical range and detection limit can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings.

1.3 Whole water recoverable cadmium in samples of water-suspended sediment must undergo preliminary digestion by method I-3485 before being determined.

2. Summary of method

Cadmium is determined by atomic absorption spectrophotometry 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 then is evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal produced during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences for samples with specific conductances less than 10,000 µS/cm normally are small. In addition, the use of the graphite platform reduces the effects of many interferences.

3.2 Special precautionary measures to prevent contamination need to be used during sample collection and laboratory determination.

4. Apparatus

4.1 *Atomic absorption spectrophotometer*, for use at 228.8 nm and equipped with Zeeman background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer needs to have high-temperature ramping and controlled argonflow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize operations and instrumental performance. A 20-µL sample with a 5-µg/L concentration of cadmium should yield a signal of approximately 0.8 absorbance-second. If the absorbance-second exceeds 0.8, use a smaller sample injection. This absorbance signal is based on cadmium's characteristic mass of 0.5 pg for a signal of 0.0044 absorbance-second. A 20-µL sample generally requires 30 seconds at 130°C to dry. Samples that have a complex matrix might require a longer drying or charring time. Peak shapes may be used to detect insufficient drying, charring, or atomization times or temperatures.

4.1.2 *Graphite furnace*, capable of reaching 1,700°C, a temperature sufficient to atomize cadmium. Warning: dial settings frequently are inaccurate, and newly conditioned furnaces need to be temperature-calibrated.

4.1.3 *Graphite tubes and platform,* pyrolytically coated graphite tubes and platforms are suggested.

4.2 *Labware.* Many trace metals at small concentrations adsorb rapidly to glassware. To preclude this problem, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternatively, glassware, particularly flasks and pipets, can be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co.) according to the manufacturer's instructions. Check autosampler cups for contamination. Lancer polystyrene disposable cups are satisfactory after acid rinsing. Alternatively, reusable Teflon or FEP cups can be purchased.

4.3 *Argon,* standard, welder's grade, commercially available. Nitrogen also can be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Cadmium standard solution I*, 1.00 mL = 1,000 µg Cd: A commercially prepared and certified cadmium standard can be used. An alternate method is to dissolve 1.0000 g Cd wire in a minimum of dilute HNO_3. Heat to

increase rate of dissolution. Add 4 mL ultrapure concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with 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 1).

NOTE 1. Use acidified water (paragraph 5.7) to make dilutions. Store all standards in sealed Teflon or FEP containers. Rinse each container twice with a small volume of standard solution before filling the storage container. Standards stored for 6 months in FEP containers yielded values equal to freshly prepared standards.

5.3 *Cadmium standard solution III*, 1.00 mL = 1.00 µg Cd: Dilute 100 mL cadmium standard solution II to 1,000 mL with acidified water. Prepare fresh monthly.

5.4 *Cadmium working solution IV*, 1.00 mL = 0.0025 µg Cd: Dilute 2.5 mL cadmium standard solution III to 1,000 mL with acidified water. Prepare fresh monthly.

5.5 *Cadmium working solution V*, 1.00 mL = 0.005 µg Cd: Dilute 5.0 mL cadmium standard solution III to 1,000 mL with acidified water. Prepare fresh monthly.

5.6 *Nitric acid*, concentrated, ultrapure (sp gr 1.41): J.T. Baker Ultrex brand HNO_3 is adequately pure; however, check each lot for contamination. Analyze acidified water (paragraph 5.7) for cadmium. Add 1.5 mL of concentrated HNO_3 per liter of water, and repeat analysis. Integrated signal should not increase by more than 0.001 absorbance-second.

5.7 *Water, acidified:* Add 4-mL ultrapure concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water*: All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

5.9 *Matrix modifier solution*, 6.9 g/L $NH_4H_2PO_4$ and 1.005 g/L $Mg(NO_3)_2 \cdot 6H_2O$: Add 13.8 g $NH_4H_2PO_4$ to 950 mL water, mix, and dilute to 1,000 mL. Add 2.01 g $Mg(NO_3)_2 \cdot 6\ H_2O$ to 950 mL water, mix, and dilute to 1,000 mL. Mix the two solutions together 1 + 1. Analyze 20 µL of matrix modifier to determine if cadmium contamination is present. If the cadmium reading is more than 0.005 absorbance-second, purify the solution by chelation

with ammonium pyrrolidine dithiocarbamate (APDC) followed by extraction with methyl isobutyl ketone (MIBK) (NOTE 2). 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 2. To purify matrix modifier solution, pour the solution into a Teflon or FEP container. While stirring, adjust the solution to pH 2.9 by dropwise addition of concentrated HNO_3 (sp gr 1.41). Add 10.0 g APDC to 1 L of water and mix well. Add 5.0 mL of the APDC solution to each 100.0 mL of matrix modifier. Shake vigorously for 10 minutes. Add 10 mL MIBK/100 mL of solution and shake vigorously for at least 10 minutes. Separate MIBK by draining through separatory funnel. Repeat process at least once more. Since some MIBK will remain in the solution, boil for 10 minutes in a silicone-treated or acid-rinsed container covered with a watch glass.

6. Procedure

6.1 The autosampler and the graphite furnace need to be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1*N* HNO_3 solution.

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 a minimum of two standards (NOTE 3) in duplicate. Construct the analytical curve from the integrated peak areas (absorbance-seconds).

NOTE 3. The automatic sampler is programmed to inject 5.0 µL of matrix modifier along with blank, standards, and samples.

6.5 Similarly, inject and analyze the samples in duplicate. Every tenth sample cup needs to contain either a standard, blank, or a reference material.

6.6 Restandardize as required, although with the use of L'vov platforms, restandardization generally is not necessary. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, 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 factor.

8. Report

Report concentrations of cadmium, dissolved (01025), and whole water recoverable (01027), as follows: less than 10 µg/L, the nearest 1 µg/L; 10 µg/L and greater, two significant figures.

9. Precision

9.1 Analysis of five samples for dissolved cadmium by a single operator is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
5	1.1	0.04	3.6
36	5.1	.2	3.9
5	5.2	.38	7.3
34	17.7	1.88	10.6
10	19.9	.94	4.7

9.2 Analysis of four samples for whole water recoverable cadmium is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
5	1.1	0.04	3.6
11	5.2	.16	3.1
5	5.2	.38	7.3
10	17.6	.23	1.3

9.3 The precision and bias for dissolved cadmium was tested on several standard reference water samples. A known amount of cadmium was added to each sample, and single-operator precision and bias for the samples are as follows:

Amount present (µg/L)	Number of replicates	Amount added (µg/L)	Found (µg/L) (NOTE 4)	Standard deviation (percent)	Relative standard deviation (percent)	Percent recovery
4.4	4	16.0	18.0	0.5	2.6	112.5
4.7	6	15.0	14.8	.8	5.2	98.7
4.7	6	11.5	11.1	.4	3.6	96.5
4.7	6	5.0	6.1	.4	6.1	122.0
21.0	6	5.0	5.0	.7	13.7	100.0

NOTE 4. The amount originally present has been subtracted.

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 45-47.

Hinderberger, E.J., Kasser, 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.

Chromium, atomic emission spectrometry, dc plasma

Parameters and Codes:
Chromium, dissolved, I-1229-87 (µg/L as Cr): 01030
Chromium, whole water recoverable, I-3229-87 (µg/L as Cr): 01034
Chromium, suspended recoverable, I-7229-87 (µg/L as Cr): 01031

1. Application

1.1 This method is used to analyze samples of finished water, natural water, industrial water, and water-suspended sediment containing from 1 to 10,000 µg/L of chromium. Sample solutions containing more than 10,000 µg/L chromium or with specific conductances greater than 10,000 µS/cm must be diluted. This method was implemented in the National Water Quality Laboratory in December 1987.

1.2 Suspended recoverable chromium is calculated by substracting dissolved chromium from whole water recoverable chromium.

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

2. Summary of method

Chromium is determined by direct-reading emission spectrometer that uses a dc argon plasma as an excitation source (Johnson and others, 1979a, 1979b). A solution 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 solution then is converted by a ceramic nebulizer into a fine aerosol and introduced into the plasma by way of a plastic spray chamber and Pyrex injection tube. Chromium is determined on the average of three replicate exposures using a 5-second integrated intensity. A standard solution and a blank are used to calibrate the instrument.

3. Interferences

Stray-light from calcium emission from the 422.7-nm wavelength raises the background at the 425.4-nm chromium wavelength causing positive interference. This interference can be corrected by using a two-point background correction technique. Calcium concentrations as large as 1,500 mg/L can be tolerated. Samples exceeding this concentration need to be diluted.

4. Apparatus

4.1 *Spectrometer*, Beckman, Spectraspan VI with dc 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.....0
Gas .....Argon
Sleeve pressure.....50 lb/in^2
Nebulizer pressure.....25 lb/in^2
Entrance slit.....25x300 µm
Exit slit .....50x300 µm
Voltage.....800 V
Wavelength.....425.435 nm

5. Reagents

5.1 *Water*: All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

5.2 *Chromium standard solution I,* 1 mL = 1,000 µg Cr: Dissolve 1.000 g chromium 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 water. Store in plastic bottle.

5.3 *Chromium standard solution II*, 1.00 mL = 100 µg Cr: Dilute 100 mL chromium standard solution I to 1,000 mL with water. Store in plastic bottle.

5.4 *Chromium working solution*, 1.00 mL = 10.0 µg Cr: Dilute 100 mL chromium standard solution II to 1,000 mL with water. Store in plastic bottle.

5.5 *Glycerin,* USP.

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

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

5.8 *Lithium chloride*, LiCl, reagent grade.

5.9 *Matrix modifier*: Dissolve 367 g LiCl in 1,000 mL water. Allow the solution to cool. Transfer to a 4-L polyethylene container, and while stirring add 2,000 mL of glycerin. In a Teflon beaker slowly add with stirring 500 mL concentrated H_2SO_4 to 400 mL water. When the dilute acid has reached room temperature, add the acid slowly, with stirring, to the glycerin-LiCl solution. Dilute to 4,000 mL with water.

5.10 *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 10.0 mL blank and working solution into plastic test tubes.

6.3 Add 2.0 mL matrix modifier to the sample, blank, and working solution.

6.4 Place plastic caps on the tubes and mix well.

6.5 Refer to manufacturer's manual for computer-operating and wavelength-optimization procedures. Use the prepared blank and chromium working solution 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 solution after every eight samples. Begin analysis (NOTE 1).

NOTE 1. Because of thermal instability inherent with the high-resolution spectrometer, repeak the analytical line if the chromium standard drifts more than 4 percent.

7. Calculations

7.1 The computer system is designed so that the blank and the 10,000 µg/L of chromium standard solution 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 solution instrument intensity readings, sample concentrations, average of sample concentrations, and standard deviation.

7.2 Obtain the micrograms per liter of dissolved or whole water recoverable chromium in each sample from the printer.

7.3 To determine micrograms per liter of suspended recoverable chromium, subtract dissolved chromium concentrations from whole water rcoverable chromium concentrations.

8. Report

Report concentrations of chromium, dissolved (01030), whole water recoverable (01034), and suspended recoverable (01031), as follows: less than 100 µg/L, nearest microgram per liter; 100 µg/L and greater, two significant figures.

9. Precision

9.1 Precision for dissolved chromium, on the basis of five determinations by a single operator over a five-day period, expressed in standard deviation and in percentage relative standard deviation, is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
3.47	0.96	27.7
11.0	.45	4.1
18.5	.20	1.1
78.5	.90	1.1
158	2.0	1.3
205	2.6	1.3
410	8.3	2.0
505	5.2	1.0
616	9.6	1.6
743	14	1.9

9.2 Precision for whole water recoverable chromium, on the basis of 10 determinations by a single operator over a five-day period, expressed in standard deviation and in percentage relative standard deviation, is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
2.34	0.37	15.8
3.19	.38	11.9
5.83	.30	5.1
23.7	1.19	5.0

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 45-47.

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.

(p 65 follows)

Cobalt, atomic absorption spectrophotometry, graphite furnace

Parameters and Codes:
Cobalt, dissolved, I-2243-89 (µg/L as Co): 01035
Cobalt, whole water recoverable, I-4243-89 (µg/L as Co): 01037

1. Application

1.1 This method is used to determine cobalt in samples of water and water-suspended sediment with a specific conductance not greater than 10,000 µS/cm. With Zeeman background correction and a 20-µL sample, the method is applicable in the range from 1 to 25 µg/L. Sample solutions that contain cobalt concentrations greater than 25 µg/L must be diluted or be analyzed by an alternate method. This method was implemented in the National Water Quality Laboratory in May 1989.

1.2 The analytical range and detection limit can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings.

1.3 Whole water recoverable cobalt in samples of water-suspended sediment must undergo preliminary digestion by method I-3485 before being determined.

2. Summary of method

Cobalt is determined by atomic absorption spectrophotometry 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 then is evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal produced during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences for samples with specific conductances less than 10,000 µS/cm normally are small. In addition, the use of the graphite platform reduces the effects of many interferences.

3.2 Special precautionary measures to prevent contamination need to be used during sample collection and laboratory determination.

4. Apparatus

4.1 *Atomic absorption spectrophotometer*, for use at 242.5 nm and equipped with Zeeman background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer needs to have high-temperature ramping and controlled argon-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize operations and instrumental performance. A 20-µL sample with a 25-µg/L concentration of cobalt should yield a signal of approximately 0.31 absorbance-second. This absorbance signal is based on cobalt's characteristic mass of 7.0 pg for a signal of 0.0044 absorbance-second. A 20-µL sample generally requires 30 seconds at 130°C to dry. Samples that have a complex matrix might require a longer drying or charring time. Peak shapes may be used to detect insufficient drying, charring, atomization times or temperatures.

4.1.2 *Graphite furnace*, capable of reaching a temperature of 2,500°C sufficient to atomize cobalt. Warning: dial settings frequently are inaccurate, and newly conditioned furnaces need to be temperature-calibrated.

4.1.3 *Graphite tubes and platforms,* pyrolytically coated graphite tubes and platforms are suggested.

4.2 *Labware.* Many trace metals at small concentrations adsorb rapidly to glassware. To preclude this problem, fluorinated ethylene propylene (FEP) or Teflon labware can be used. Alternatively, glassware, particularly flasks and pipets, can be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co.) according to the manufacturer's instructions. Check autosampler cups for contamination. Lancer polystyrene disposable cups are satisfactory after acid rinsing. Alternatively, reusable Teflon or FEP cups can be purchased.

4.3 *Argon,* standard, welder's grade, commercially available. Nitrogen also can be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Cobalt standard solution I,* 1.00 mL = 1,000 µg Co: A commercially prepared and certified cobalt standard can be used. An alternate method is to dissolve 1.0000 g Co wire in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 4 mL ultrapure concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with 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 1).

NOTE 1. Use acidified water (paragraph 5.7) to make dilutions. Store all standards in sealed Teflon or FEP containers. Rinse each container twice with a small volume of standard solution before filling the storage container. Standards stored for 6 months in FEP containers yielded values equal to freshly prepared standards.

5.3 *Cobalt standard solution III,* 1.00 mL = 1.00 µg Co: Dilute 100 mL cobalt standard solution II to 1,000 mL with acidified water. Prepare fresh monthly.

5.4 *Cobalt working solution IV,* 1.00 mL = 0.025 µg Co: Dilute 25.0 mL cobalt standard solution III to 1,000 mL with acidified water. Prepare fresh monthly.

5.5 *Cobalt working solution V,* 1.00 mL = 0.010 µg Co: Dilute 10.0 mL cobalt standard solution III to 1,000 mL with acidified water. Prepare fresh monthly.

5.6 *Nitric acid,* concentrated, ultrapure (sp gr 1.41): J.T. Baker Ultrex brand HNO_3 is adequately pure; however, check each lot for contamination. Analyze acidified water (paragraph 5.7) for cobalt. Add 1.5 mL of concentrated HNO_3 per liter of water, and repeat analysis. Integrated signal should not increase by more than 0.001 absorbance-second.

5.7 *Water, acidified:* Add 4.0 mL ultrapure concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water:* All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

6. Procedure

6.1 The autosampler and the graphite furnace need to be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1*N* HNO_3 solution.

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 a minimum of two standards in duplicate. Construct the analytical curve from the integrated peak areas (absorbance-seconds).

6.5 Similarly, inject and analyze the samples in duplicate. Every tenth sample cup needs to contain either a standard, blank, or a reference material.

6.6 Restandardize as required, although with the use of L'vov platforms, restandardization generally is not necessary. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, 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 factor.

8. Report

Report concentrations of cobalt, dissolved (01035), and whole water recoverable (01037), as follows: less than 10 µg/L, the nearest 1 µg/L; 10 µg/L and greater, two significant figures.

9. Precision

9.1 Analysis of six samples for dissolved cobalt by a single operator is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
6	1.4	0.35	25.0
40	1.8	.60	33.3
7	4.9	.26	5.3
45	5.4	.57	10.6
41	5.5	.59	10.7
19	25.5	2.21	8.7

9.2 Analysis of three samples for whole water recoverable cobalt by a single operator is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
7	1.4	0.22	15.7
10	4.4	.27	6.1
11	4.8	.37	7.7

9.3 The precision and bias for dissolved cobalt was tested on several standard reference water samples. A known amount of cobalt was added to each sample, and single-operator precision and bias for the samples are as follows:

Amount present (µg/L)	Number of replicates	Amount added (µg/L)	Found (µg/L) (NOTE 2)	Standard deviation (percent)	Relative standard deviation (percent)	Percent recovery
2.3	6	49.4	44.8	1.6	3.6	90.7
2.4	6	22.7	22.7	1.7	7.4	100.0
2.5	6	9.7	9.0	.3	3.3	92.8
4.6	6	21.6	23.0	.3	1.3	106.5
5.0	6	8.4	8.1	.1	1.5	96.4
5.0	6	42.9	43.9	1.3	3.0	102.3
5.3	6	10.0	9.0	.2	2.6	90.0
5.5	5	42.5	44.0	1.1	2.5	103.5
5.5	6	22.2	21.9	.9	4.2	98.6

NOTE 2. The amount originally present has been subtracted.

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 45-47.

Hinderberger, E.J., Kasser, 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.

(p. 71 follows)

Copper, atomic absorption spectrophotometry, graphite furnace

Parameters and Codes:
Copper, dissolved, I-2274-89 (µg/L as Cu): 01040
Copper, whole water recoverable, I-4274-89 (µg/L as Cu): 01042

1. Application

1.1 This method is used to determine copper in samples of water and water-suspended sediment with a specific conductance not greater than 10,000 µS/cm. With Zeeman background correction and a 20-µL sample, the method is applicable in the range from 1 to 25 µg/L. Sample solutions that contain copper concentrations greater than 25 µg/L must be diluted or be analyzed by an alternate method. This method was implemented in the National Water Quality Laboratory in May 1989.

1.2 The analytical range and detection limit can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings.

1.3 Whole water recoverable copper in samples of water-suspended sediment must undergo preliminary digestion by method I-3485 before being determined.

2. Summary of method

Copper is determined by atomic absorption spectrophotometry 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 then is evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal produced during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences for samples with specific conductances less than 10,000 µS/cm normally are small. In addition, the use of the graphite platform reduces the effects of many interferences.

3.2 Special precautionary measures to prevent contamination need to be used during sample collection and laboratory determination.

4. Apparatus

4.1 *Atomic absorption spectrophotometer*, for use at 324.8 nm and equipped with Zeeman background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer needs to have high-temperature ramping and controlled argon-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize operations and instrumental performance. A 20-µL sample with a 25-µg/L concentration of copper should yield a signal of approximately 0.28 absorbance-second. This absorbance signal is based on copper's characteristic mass of 8.0 pg for a signal of 0.0044 absorbance-second. A 20-µL sample generally requires 30 seconds at 130°C to dry. Samples that have a complex matrix might require a longer drying or charring time. Peak shapes may be used to detect insufficient drying, charring, or atomization times or temperatures.

4.1.2 *Graphite furnace*, capable of reaching a temperature of 2,500°C sufficient to atomize copper. Warning: dial settings frequently are inaccurate, and newly conditioned furnaces need to be temperature-calibrated.

4.1.3 *Graphite tubes and platforms*, pyrolytically coated graphite tubes and platforms are suggested.

4.2 *Labware*. Many trace metals at small concentrations adsorb rapidly to glassware. To preclude this problem, fluorinated ethylene propylene (FEP) or Teflon labware is used. Alternatively, glassware, particularly flasks and pipets, can be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co.) according to the manufacturer's instructions. Check autosampler cups for contamination. Lancer polystyrene disposable cups are satisfactory after acid rinsing. Alternatively, reusable Teflon or FEP cups can be purchased.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen also is used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Copper standard solution I*, 1.00 mL = 1,000 µg Cu: A commercially prepared and certified copper standard is used. An alternate method is to dissolve 1.0000 g Cu wire in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 4 mL ultrapure concentrated HNO_3 (sp gr 1.41) Ultrex or equivalent, and dilute to 1,000 mL with 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 1).

NOTE 1. Use acidified water (paragraph 5.7) to make dilutions. Store all standards in sealed Teflon or FEP containers. Rinse each container twice with a small volume of standard before filling the storage container. Standards stored for 6 months in FEP containers yielded values equal to freshly prepared standards.

5.3 *Copper standard solution III*, 1.00 mL = 1.00 µg Cu: Dilute 100 mL copper standard solution II to 1,000 mL with acidified water. Prepare fresh monthly.

5.4 *Copper working solution IV*, 1.00 mL = 0.025 µg Cu: Dilute 25.0 mL copper standard solution III to 1,000 mL with acidified water. Prepare fresh monthly.

5.5 *Copper working solution V*, 1.00 mL = 0.010 µg Cu: Dilute 10.0 mL copper standard solution III to 1,000 mL with acidified water. Prepare fresh monthly.

5.6 *Nitric acid, concentrated*, ultrapure (sp gr 1.41): J.T. Baker Ultrex brand HNO_3 is adequately pure; however, check each lot for contamination. Analyze acidified water (paragraph 5.7) for copper. Add 1.5 mL of concentrated HNO_3 per liter of water, and repeat analysis. Integrated signal should not increase by more than 0.001 absorbance-second.

5.7 *Water, acidified:* Add 4.0 mL ultrapure concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water*: All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

6. Procedure

6.1 The autosampler and the graphite furnace need to be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1*N* HNO_3 solution.

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 a minimum of two standards in duplicate. Construct the analytical curve from the integrated peak areas (absorbance-seconds).

6.5 Similarly, inject and analyze the samples in duplicate. Every tenth sample cup needs to contain either a standard, blank, or a reference material.

6.6 Restandardize as required, although with the use of L'vov platforms, restandardization generally is not necessary. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, 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 concentrations of copper, dissolved (01040), and whole water recoverable (01042), as follows: less than 10 µg/L, the nearest 1 µg/L; 10 µg/L and greater, two significant figures.

9. Precision

9.1 Analysis of six samples for dissolved copper by a single operator is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
6	1.5	0.09	6.0
6	5.3	.20	3.8
114	15.7	.77	4.9
53	21.3	.75	3.5
97	25.7	2.08	8.1
107	33.4	1.57	4.7

9.2 Analysis of three samples for whole water recoverable copper by a single operator is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
10	14.4	2.32	16.1
7	21.7	.97	4.5
11	29.3	1.83	6.2

9.3 The precision and bias for dissolved copper was tested on several standard reference water samples. A known amount of copper was added to each sample, and single-operator precision and bias for the samples are as follows:

Amount present (µg/L)	Number of replicates	Amount added (µg/L)	Found (µg/L) (NOTE 2)	Standard deviation (percent)	Relative standard deviation (percent)	Percent recovery
14.7	6	24.8	23.5	0.6	2.6	94.8
15.9	6	46.4	47.1	2.0	4.3	101.5
21.1	6	50.4	49.2	1.9	3.9	97.6
21.2	6	25.1	24.6	.3	1.0	98.0
21.6	6	10.2	11.7	.8	4.9	114.7
24.4	6	23.8	24.5	.9	3.5	102.9
29.3	5	50.0	49.9	.9	1.9	99.8
37.5	6	51.1	47.4	4.5	9.4	92.7
37.0	6	28.0	25.8	2.0	7.7	92.1
38.0	6	11.3	11.5	.9	8.2	101.8

NOTE 2. The amount originally present has been subtracted.

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 45-47.

Hinderberger, E.J., Kasser, 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.

(p. 77 follows)

1,2-Dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP), gas chromatography, microextraction

Parameters and Codes:
EDB and DBCP, whole water recoverable, O-3120-90

Parameter (µg/L)	Code
1,2-Dibromoethane	82625
1,2-Dibromo-3-chloropropane	77651

1. Application

This method is suitable for the determination of 1,2-dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP) in samples of water and water-suspended sediment containing at least 0.04 µg/L of EDB and 0.03 µg/L of DBCP but not more than 10 µg/L. This method was implemented in the National Water Quality Laboratory in August 1990.

2. Summary of method

The method is an adaptation of USEPA Method 504 (U.S Environmental Protection Agency, 1988). The aqueous sample is extracted with hexane and the extract is analyzed by capillary column gas chromatography using an electron capture detector. The analytes are identified by using two dissimilar capillary columns. Aqueous calibration standards are extracted and analyzed in the same manner as the samples to compensate for possible extraction losses.

3. Interferences

3.1 Impurities in the extracting solvent, salt, or glassware might cause analytical problems. Analyze each new bottle of extracting solvent for contaminant interference before use. Analyze blanks daily to monitor the entire procedure. Whenever an interference is noted in the blank, identify and eliminate the source of interference.

3.2 Hexane-extractable compounds with retention times similar to EDB and DBCP can cause interference, or misidentification and improper quantitation.

3.3 Dibromochloromethane interferes with the detection and quantitation of EDB on column B. Therefore, the quantitative results are reported only from column A.

4. Instrumentation

4.1 *Gas chromatograph,* Hewlett-Packard 5890 with integrator 3396 and automated sample injector 7673A or equivalent.

4.2 Suggested gas chromatographic configuration:

4.2.1 *Column A (primary),* fused silica capillary, 30-m by 0.32-mm inside diameter (ID), with dimethyl silicone mixed phase (Restek-RTX5, Restek or equivalent).

4.2.2 *Column B (confirmation),* fused silica capillary, 30-m by 0.32-mm ID, with methyl polysiloxane phase (Restek-1701, Restek or equivalent).

4.2.3 *Detector,* electron capture, operated at 350°C.

4.2.4 *Injection port temperature,* 200°C.

4.2.5 *Oven temperature program,* initial temperature 40°C, hold for 10 minutes, program at 5°C per minute to 130°C, then program at 10°C per minute to 160°C. Hold at 160°C for 3 minutes or until all expected compounds have eluted. Bake column at 50°C per minute to 280°C and hold for 1 minute.

4.2.6 *Carrier gas,* helium, grade 5 or research grade, 25 cm/s linear flow velocity at 140°C.

4.2.7 *Make-up gas,* 5-percent methane in argon, flow rate at 30 mL/min.

5. Apparatus

5.1 *Screw-cap amber-glass vials,* 1.8-mL capacity, caps lined with Teflon-faced Neoprene septa.

5.2 *VOC amber-glass vials,* 40-mL capacity, with open-top screw cap lined with PTFE-faced silicone septa.

5.3 *Autosampler crimp-seal glass vials,* 1.8-mL capacity, with crimp-on seals and Teflon-faced silicone liners.

6. Reagents

6.1 *Hexane,* trihalomethane analysis grade, Burdick and Jackson or equivalent.

6.2 *Methanol,* HPLC grade, Burdick and Jackson or equivalent, demonstrated to be free of analytes.

6.3 *Sodium chloride,* ACS reagent grade, granular. Heat at 400°C for 30 minutes and store in a glass bottle.

6.4 *Water,* organic free. All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991). Water needs to be tested for possible interfering peaks.

7. Standards

7.1 *Reference standards.* EDB and DBCP at a concentration of 5,000 µg/mL ± 500 µg/mL. Obtain from the Materials Data Bank of the U.S. Environmental Protection Agency.

7.2 *EDB and DBCP standard solution I,* 50 µg/mL each. Dilute 50.0 µL of each reference standard solution to 5.0 mL with methanol. Store standard solution I in a 1.8-mL amber-glass vial at <-10°C. Discard after 6 months.

7.3 *EDB and DBCP standard solution II,* 0.50 µg/mL. Dilute 50.0 µL of standard solution I to 5.0 mL with methanol. Store standard solution II in a 1.8- mL amber-glass vial at <-10°C. Discard after 6 months.

7.4 *EDB and DBCP quality control (QC) check solution,* 0.25 µg/L. Add 17.5 µL of standard solution II to 35.0 mL of water in a 40-mL VOC vial. Extract QC check solution according to instructions in paragraphs 8.4 through 8.6.

7.5 *EDB and DBCP method-detection-limit (MDL) check solution,* 0.05 µg/L. Add 3.5 µL of standard solution II to 35.0 mL of water in a 40-mL VOC vial. Extract MDL check solution according to instructions in paragraphs 8.4 through 8.6.

8. Sample extraction

8.1 Remove the samples and field blanks from cold storage and allow to reach room temperature.

8.2 Uncap the VOC 40-mL vials containing the samples and field blanks. Discard 5 mL using a 5-mL volumetric pipet. Recap the vials.

8.3 Weigh each vial with contents to the nearest 0.1 g, and record the gross weight for subsequent calculations (see paragraph 13.3).

8.4 Add 7 g of sodium chloride to each vial, and shake to dissolve the salt completely.

8.5 Add 2 mL of hexane to each vial, cap, and shake vigorously by hand for 1 minute. The hexane and water phases will separate.

8.6 Transfer two 0.5-mL aliquots of the hexane layer into two autosampler vials and seal. The samples and blank extracts are ready for analysis as described in Section 10. Store vials at <-10°C. Analyze samples and field blanks within 14 days.

8.7 The remaining water/hexane solution is discarded. Each vial is weighed to the nearest 0.1 g. Use this weight to calculate the gravimetric volume of water extracted in milliliters (see paragraph 13.3).

9. Calibration

Add 35 mL of water to six 40-mL vials. To prepare a blank and a series of working standard solutions, add to each vial an appropriate volume of either standard solution I or II as follows:

Working standard solutions (µg/L)	Solution added (µL)	Solution used
0.05	3.5	Standard solution II
.2	14	Standard solution II
.5	35	Standard solution II
2.0	140	Standard solution II
9.0	6.3	Standard solution I

10. Sample analysis

10.1 Allow the samples and blank extracts to reach room temperature.

10.2 Transfer the vials to the gas chromatograph for analysis on column A. Reanalyze the samples on column B for confirmation.

10.3 Run a duplicate on a field sample to check the precision of replicate analyses. A properly operating method will produce less than 10-percent difference in concentration.

11. Quality control

11.1 On a frequency equivalent to 10 percent of the sample load, demonstrate that the measurement system is in control by analyzing the QC check solution.

11.2 Extract the QC check solution as described in paragraphs 8.4 through 8.6, and analyze as described in Section 10.

11.3 The recovery needs to be between 60 and 140 percent of the expected value for each analyte. If the recovery for either analyte falls outside the designated range, a second QC check standard needs to be analyzed for those analytes that failed. Repeated failure will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem, and reanalyze samples and standards.

12. Method detection limit

12.1 Analyze daily the method detection limit (MDL) check solution to prove that the method can be used to analyze low-level samples at the 0.05-µg/L concentration.

12.2 Extract the MDL check solution described in paragraphs 8.4 through 8.6, and analyze as described in Section 10.

12.3 The MDL response needs to be distinguished from instrument background signal for each analyte (see paragraph 15.2). The signal-to-noise ratio needs to be determined for each analytical system because a particular system might have a different MDL. The recovery needs to be between 60 and 140 percent of the expected value for each analyte. If the recovery for either analyte falls outside the designated range, a second MDL check sample needs to be analyzed for those analytes that failed. Repeated failure will confirm a general problem with the instrument system, faulty MDL check solution, or calibration standards. In the event of repeated failure, locate and correct the source of the problem(s), and reanalyze samples and standards.

13. Calculations

13.1 Identify EDB and DBCP in the sample chromatogram by comparing the retention time of the suspect peak to retention times produced by the calibration standards.

13.2 Use the calibration curve to directly calculate the uncorrected concentration Ci of each analyte in the sample.

13.3 Calculate the gravimetric sample volume Vs as equal to the net sample weight:

Vs = gross weight (see paragraph 8.3) – vial tare (see paragraph 8.7).

13.4 Calculate the corrected concentration as follows:

$$\text{Concentration EDB or DBCP } (\mu g/L) = Ci\ (\mu g/L) \times \frac{35\ mL^{1}}{Vs\ (mL)}$$

14. Report

14.1 Report the results from column A for the unknown samples in micrograms per liter when the results are confirmed by column B both qualitatively and quantitatively.

14.2 Report concentrations of EDB and DBCP as follows: less than 0.1 µg/L, one significant figure; 0.1 µg/L and greater, two significant figures.

15. Accuracy and precision

15.1 Accuracy and precision data for EDB and DBCP at several concentrations in three water matrices are listed in tables 5 and 6.

15.2 The method detection limit (MDL) for each analyte was determined with reference to the U.S. Federal Register (1984).

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[1]Standards are extracted from 35 mL of water (see Section 9).

15.2.1 The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing the analyte.

Table 5.--*Accuracy and precision data for 1,2-dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP) on column A (DX-3)*

[µg/L, microgram per liter; <, less than]

Analyte	Source	Number of replicates	Concentration added (µg/L)	Mean recovery (µg/L)	Recovery (percent)	Relative standard deviation (percent)
EDB						
	Deionized water	8	0.040	0.033	82	4.2
		8	.15	.14	93	2.5
		8	.30	.28	94	1.5
		10	1.7	1.6	94	4.4
	Natural water A	10	.030	<.04	<.04	<.04
		10	.70	.63	90	5.0
		8	1.7	1.60	90	4.4
	Natural water B	10	.050	.042	84	6.6
	Drinking water	11	.030	.033	110	5.2
DBCP						
	Deionized water	8	.040	.040	100	3.6
		8	.15	.14	93	2.5
		8	.30	.28	93	1.1
		10	1.7	1.7	100	2.0
	Natural water A	9	.030	.034	110	3.8
		10	.70	.68	97	3.4
		8	1.7	1.7	100	3.4
	Natural water B	10	.050	.046	91	5.4
	Drinking water	11	.030	.031	100	6.5

Table 6.--*Accuracy and precision data for 1,2-dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP) on column B (DB-1)*

[µg/L, microgram per liter; <, less than]

Analyte	Source	Number of replicates	Concentration added (µg/L)	Mean recovery (µg/L)	Recovery (percent)	Relative standard deviation (percent)
EDB						
	Deionized water	8	0.040	0.030	75	4.1
		8	.15	.12	80	6.8
		8	.30	.24	80	1.5
		10	1.7	1.8	110	2.1
	Natural water A	9	.030	.022	72	5.2
		10	.70	.60	86	2.6
		8	1.7	1.8	110	2.9
	Natural water B	7	.050	.054	110	10
	Drinking water	11	.030	<.04	<.04	<.04
DBCP						
	Deionized water	8	.040	.04	100	4.0
		8	.15	.13	87	3.9
		7	.30	.26	87	1.9
		10	1.7	1.8	110	2.5
	Natural water A	9	.030	.055	180	66
		10	.70	.69	98	6.0
		8	1.7	1.8	100	3.6
	Natural water B	7	.050	.045	90	2.4
	Drinking water	11	.030	.034	110	5.6

15.2.2 The experimentally determined MDLs for EDB and DBCP were calculated to be 0.01 µg/L and are listed in table 7. The method has been shown to be useful for these analytes over a concentration range from approximately 0.04 to 10 µg/L for EDB and from 0.03 to 10 µg/L for DBCP. Actual detection limits are dependent on the characteristics of the gas chromatographic system used.

Table 7.--*Method detection limits for 1,2-dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP)*

[µg/L, microgram per liter; MDL, method detection limit]

Column	Analyte	Number of replicates	Concentration added - (µg/L)	Standard deviation (µg/L)	MDL (µg/L)
A(DX-3)	EDB	8	0.30	0.0045	0.014
		8	.15	.0037	.011
		8	.040	.0017	.005
A(DX-3)	DBCP	8	.30	.0034	.010
		8	.15	.0037	.011
		8	.040	.0014	.004
B(DB-1)	EDB	8	.30	.0037	.011
		8	.15	.0080	.024
		8	.040	.0012	.004
B(DB-1)	DBCP	7	.30	.0048	.014
		8	.15	.0050	.015
		8	.040	.0016	.005

References

U.S. Environmental Protection Agency, 1988, Methods for the determination of organic compounds in drinking water: Washington, D.C., U.S. Government Printing Office, EPA/600/4-88/039.

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 45-47.

U.S. Federal Register, 1984, Definition and procedure for the determination of the method detection limit, Appendix B to Part 136: v. 49, no. 209, p. 198.

(p. 87 follows)

Lead, atomic absorption spectrophotometry, graphite furnace

Parameters and Codes:
Lead, dissolved, I-2403-89 (µg/L as Pb): (01049)
Lead, whole water recoverable, I-4403-89 (µg/L as Pb): (01051)

1. Application

1.1 This method is used to determine lead in samples of water and water-suspended sediment with a specific conductance not greater than 10,000 µS/cm. With Zeeman background correction and a 20-µL sample, the method is applicable in the range from 1 to 25 µg/L. Sample solutions that contain lead concentrations greater than 25 µg/L must be diluted or be analyzed by an alternate method. This method was implemented in the National Water Quality Laboratory in May 1989.

1.2 The analytical range and detection limit can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings.

1.3 Whole water recoverable lead in samples of water-suspended sediment must undergo preliminary digestion by method I-3485 before being determined.

2. Summary of method

Lead is determined by atomic absorption spectrophotometry 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 then is evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal produced during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences for samples with specific conductances less than 10,000 µS/cm normally are small. In addition, the use of the graphite platform reduces the effects of many interferences.

3.2 Special precautionary measures to prevent contamination need to be used during sample collection and laboratory determination.

4. Apparatus

4.1 *Atomic absorption spectrophotometer,* for use at 283.3 nm and equipped with Zeeman background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer needs to have high-temperature ramping and controlled argon-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize operations and instrumental performance. A 20-µL sample with a 25-µg/L concentration of lead should yield a signal of approximately 0.18 absorbance-second. This absorbance signal is based on lead's characteristic mass of 12.0 pg for a signal of 0.0044 absorbance-second. A 20-µL sample generally requires 30 seconds at 130°C to dry. Samples that have a complex matrix might require a longer drying or charring time. Peak shapes may be used to detect insufficient drying, charring, or atomization times or temperatures.

4.1.2 *Graphite furnace,* capable of reaching a temperature of 1,800°C sufficient to atomize the lead. Warning: dial settings frequently are inaccurate, and newly conditioned furnaces need to be temperature-calibrated.

4.1.3 *Graphite tubes and platforms,* pyrolytically coated graphite tubes and platforms are suggested.

4.2 *Labware.* Many trace metals at small concentrations adsorb rapidly to glassware. To preclude this problem, fluorinated ethylene propylene (FEP) or Teflon labware is used. Alternatively, glassware, particularly flasks and pipets, can be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co.) according to the manufacturer's instructions. Check autosampler cups for contamination. Lancer polystyrene disposable cups are satisfactory after acid rinsing. Alternatively, reusable Teflon or FEP cups can be purchased.

4.3 *Argon,* standard, welder's grade, commercially available. Nitrogen also is used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Lead standard solution I,* 1.00 mL = 1,000 µg Pb: A commercially prepared and certified lead standard is used. An alternate method is to dissolve 1.0000 g lead wire in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 4.0 mL ultrapure concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with 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 1).

NOTE 1. Use acidified water (paragraph 5.7) to make dilutions. Store all standards in sealed Teflon or FEP containers. Rinse each container twice with a small volume of standard before filling the storage container. Standards stored for 6 months in FEP containers yielded values equal to freshly prepared standards.

5.3 *Lead standard solution III,* 1.00 mL = 1.00 µg Pb: Dilute 100 mL lead standard solution II to 1,000 mL with acidified water. Prepare fresh monthly.

5.4 *Lead working solution IV,* 1.00 mL = 0.025 µg Pb: Dilute 25.0 mL lead standard solution III to 1,000 mL with acidifed water. Prepare fresh monthly.

5.5 *Lead working solution V,* 1.00 mL = 0.010 µg Pb: Dilute 10.0 mL lead standard solution III to 1,000 mL with acidifed water. Prepare fresh monthly.

5.6 *Nitric acid, concentrated,* ultrapure (sp gr 1.41): J.T. Baker Ultrex brand HNO_3 is adequately pure; however, check each lot for contamination. Analyze acidified water (paragraph 5.7) for lead. Add 1.5 mL of concentrated HNO_3 per liter of water, and repeat analysis. Integrated signal should not increase by more than 0.001 absorbance-second.

5.7 *Water, acidified:* Add 4.0 mL ultrapure concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water:* All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

5.9 *Matrix modifier solution,* 6.9 g/L $NH_4H_2PO_4$ and 1.005 g/L $Mg(NO_3)_2 \cdot 6H_2O$: Add 13.8 g $NH_4H_2PO_4$ to 950 mL water, mix, and dilute to 1,000 mL. Add 2.01 g $Mg(NO_3)_2 \cdot 6H_2O$ to 950 mL water, mix, and dilute to 1,000 mL. Mix the two solutions together 1 + 1. Analyze 20 µL of matrix modifier to determine if lead contamination is present. If the lead reading is more than 0.005 absorbance-second, purify the solution by chelation with ammonium pyrrolidine dithiocarbamate (APDC) followed by extraction with methyl isobutyl ketone (MIBK) (NOTE 2). 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 2. To purify matrix modifier solution, pour the solution into a Teflon or FEP container. While stirring, adjust the solution to pH 2.9 by dropwise addition of concentrated HNO_3 (sp gr 1.41). Add 10.0 g APDC to 1 L of water and mix well. Add 5.0 mL of the APDC solution to each 100.0 mL of matrix modifier. Shake vigorously for 10 minutes. Add 10 mL MIBK/100 mL of solution and shake vigorously for at least 10 minutes. Separate MIBK by draining through separatory funnel. Repeat process. Since some MIBK will remain in the solution, boil for 10 minutes in a silicone-treated or acid-rinsed container covered with a watch glass.

6. Procedure

6.1 The autosampler and the graphite furnace need to be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1*N* HNO_3 solution.

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 a minimum of two standards (NOTE 3) in duplicate. Construct the analytical curve from the integrated peak areas (absorbance-seconds).

NOTE 3. The automatic sampler is programmed to inject 5.0 µL of matrix modifier along with blank, standards, and samples.

6.5 Similarly, inject and analyze the samples in duplicate. Every tenth sample cup needs to contain either a standard, blank, or a reference material.

6.6 Restandardize as required, although with the use of L'vov platforms, restandardization generally is not necessary. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, 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 factor.

8. Report

Report concentrations of lead, dissolved (01049), and whole water recoverable (01051), as follows: less than 10 µg/L, the nearest 1 µg/L; 10 µg/L and greater, two significant figures.

9. Precision

9.1 Analysis of five samples for dissolved lead by a single operator is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
7	1.7	0.03	1.8
108	11.8	.79	6.7
111	15.2	1.04	6.8
41	24.0	.94	3.9

9.2 Analysis of three samples for whole water recoverable lead by a single operator is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
7	0.6	0.47	78.3
11	11.3	1.51	13.4
10	16.6	.66	4.0

9.3 The precision and bias for dissolved lead was tested on several standard reference water samples. A known amount of lead was added to each sample, and single-operator precision and bias for the samples are as follows:

Amount present (µg/L)	Number of replicates	Amount added (µg/L)	Found (µg/L) (NOTE 4)	Standard deviation (percent)	Relative standard deviation (percent)	Percent recovery
11.2	6	44.9	40.8	2.1	5.1	90.9
11.4	6	21.5	21.4	4.3	19.9	99.5
11.7	6	9.3	8.9	.6	6.6	95.7
17.5	6	15.8	18.3	1.1	6.1	115.8
23.0	6	4.9	5.4	1.6	29.6	110.2
23.7	6	13.8	12.9	.8	6.2	93.5
23.9	6	10.0	10.8	1.0	9.7	108.0

NOTE 4. The amount originally present has been subtracted.

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 45-47.

Hinderberger, E.J., Kasser, 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.

Mercury, total-in-sediment, atomic absorption spectrophotometry, flameless, direct

Parameter and Code:
Mercury, total, I-6463-86 (µg/g as Hg): none assigned

1. Application

1.1 This method is used to analyze samples of suspended sediment and bottom material for the determination of total concentrations of mercury in samples containing at least 0.01 µg/g and not more than 5.0 µg/g. Samples containing mercury concentrations greater than 5.0 µg/g can be analyzed after appropriate dilution; either use less sediment or dilute the sample solution. This method was implemented in April 1986.

1.2 Analyze dried and ground samples that have been digested with a combination of concentrated nitric and hydrochloric acids (Lefort aqua regia) and heat. These solutions then are analyzed by atomic absorption spectrophotometry.

2. Summary of method

A sample is dried, ground, and homogenized and then is digested by a hot Lefort aqua regia solution (3:1 nitric acid to hydrochloric acid). The solution is preserved by the addition of potassium dichromate, and diluted to a known volume with demineralized water. The solution then is made basic and the mercury is reduced to the metal with stannous chloride, purged from the solution with nitrogen, and quantified by flameless-cold vapor atomic absorption spectrophotometry.

3. Interferences

3.1 Volatile organic constituents interfere; however, digestion of samples with hot Lefort aqua regia will decompose organic material if present. In an alkaline media, interferences from gold, platinum, silver, copper, selenium, and tellurium are eliminated.

3.2 Further information can be found in Band and Wilkinson (1972), Koirtyohann and Khalil (1976), Bartha and Ikre'nyi (1981), and Suddendorf (1981).

4. Apparatus

4.1 *Atomic absorption spectrophotometer,* equipped with electronic digital readout, automatic zero and automatic concentration controls, and a deuterium source background corrector. A printer or chart recorder allows automation of the analytical process. A personal computer with a suitable program is used for automatic data reduction and data transfer.

4.2 *Autosample,* Varian PSC 55 or equivalent (optional).

4.3 Refer to manufacturer's manuals to optimize the instruments for the following:

4.3.1 *Atomic absorption spectrophotometer*

Grating	Ultraviolet
Wavelength	253.7 nm
Source	Hollow cathode or electrodeless discharge lamp
Background	On
Slit width	0.5 nm

4.3.2 *Autosampler*

Rinse rate	1
Rinse time	40 seconds
Delay time	70 seconds

4.4 *Vapor generation accessory,* Varian VGA 76 or equivalent. This system consists of a three-channel peristaltic pump, reaction coil, gas-liquid separator, flow-through absorption cell, and bracket for holding the cell in the light path of the spectrophotometer (fig. 2).

4.5 *Erlenmeyer flasks,* pyrex or equivalent, 125-mL capacity.

4.6 *Hot plate,* gas or electric, with surface temperature of 150°C.

4.7 *Centrifuge tubes,* with caps, 50-mL capacity.

4.8 *Centrifuge (optional).*

4.9 *Drying tube.*

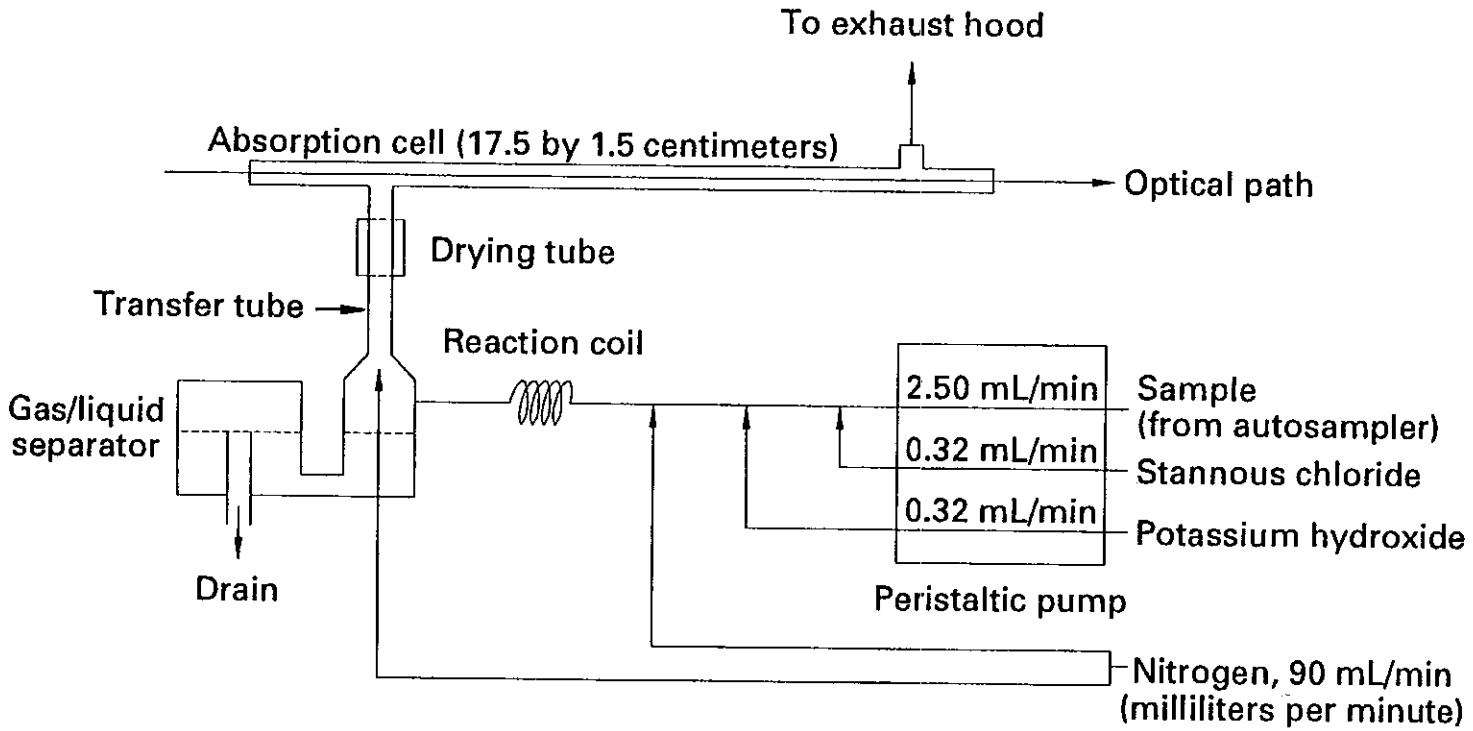


Figure 2.—Mercury vapor generation accessory.

5. Reagents

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

5.2 *Magnesium perchlorate*, for drying tube (NOTE 1).

NOTE 1. The drying tube is used to prevent moisture carryover into the absorption cell where it can condense and cause erratic readings. The magnesium perchlorate needs to be replaced daily, or sooner if it begins to cake (two-thirds of the drying tube) or if blockage occurs.

5.3 *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 10 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL with demineralized water. Alternatively, a commercially prepared stock solution can be diluted and used.

5.4 *Mercury standard solution II*, 1.00 mL = 10.0 µg Hg: Dilute 10.0 mL mercury standard solution I, 10 mL concentrated HNO_3 (sp gr 1.41), and 10 mL $K_2Cr_2O_7$ solution to 100 mL with demineralized water.

5.5 *Mercury working solutions I, II, III*: Pipet 40 µL (working solution I), 500 µL (working solution II), and 1,000 µL (working solution III) of mercury standard solution II into 200-mL volumetric flasks. Add 20 mL concentrated HNO_3 (sp gr 1.41) and 20 mL $K_2Cr_2O_7$ solution to each flask, and dilute each to 200 mL with demineralized water. Prepare fresh daily. Concentrations are as follows: Working solution I (2 µg/L), working solution II (25 µg/L), and working solution III (50 µg/L).

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

5.7 *Potassium hydroxide solution*, 45 percent w/v: Dissolve 45 g KOH in 100 mL demineralized water.

5.8 *Potassium dichromate solution*, 50 g/L: Dissolve 50 g $K_2Cr_2O_7$ in demineralized water and dilute to 1,000 mL with demineralized water.

5.9 *Stannous chloride solution*, 125 g/L: Dissolve 125 g $SnCl_2 \cdot H_2O$ in 150 mL concentrated HCl (sp gr 1.19) and dilute to 250 mL with concentrated HCl. Do not heat this solution to dissolve the $SnCl_2 \cdot H_2O$ because heat will cause

the solution to rapidly lose its reductive capacity. Dilute this solution to 1 L with demineralized water.

5.10 *Rinse solution*: Dilute 100 mL concentrated HNO_3 (sp gr 1.41) to 1 L with demineralized water.

6. Procedure

6.1 Dry the sediment by freeze-drying, oven-drying at either 105°C or 40°C, or air-drying at room temperature (NOTE 2).

NOTE 2. A search of the literature has indicated that sample drying procedures can have a significant effect on mercury quantitation. Various procedures for drying samples prior to digestion and analysis have been used; these include air-drying, freeze-drying, or oven-drying at either 105°C or 40°C. Some investigators recommend that a wet sample be digested and analyzed and that moisture be determined on a separate sample aliquot. Analytical results are corrected for moisture content. Various drying procedures were investigated on several sediment samples from various locations to determine the best procedure for drying the sediments. Data show no significant losses of mercury because of the drying procedures; the variations encountered fall within the variability of the original samples and seem to be caused by inhomogeneity of the samples. Data need to be compared to determine which procedure is most suitable.

6.2 If the sediment sample is greater than 100 g, split to less than 100 g by the use of a nonmetallic sample splitter (riffle splitter), 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 125-mL Erlenmeyer flask; weigh appropriate reference standard materials (for example, National Institute of Standards and Technology sediment or U.S. Geological Survey Rock Standards (NOTE 3) and analyze with environmental samples.

NOTE 3. This procedure is used with sample weights between 0.2500 and 1.0000 g. Sample weights greater than 1 g might cause erroneous readings because of unoxidized organic matter.

6.5 Carry several blanks (reagents only) through the digestion steps.

6.6 Add 9 mL concentrated HNO_3 (sp gr 1.41) and 3 mL concentrated HCl (sp gr 1.19) to each flask, and mix. Allow to stand in the hood for 15 to 20 minutes, or until foaming stops.

6.7 Place hotplate in hood and adjust to produce a surface temperature of 150°C.

6.8 Place flasks on hotplate for 15 to 30 minutes, or until reagent blanks become colorless.

6.9 Remove flasks from hotplate and allow to cool for 10 to 15 minutes.

6.10 Add 5 mL $K_2Cr_2O_7$ solution to each flask (NOTE 4).

NOTE 4. If there is an excess of unoxidized material remaining in the sample, it might be necessary to add a 5-mL aliquot of the $K_2Cr_2O_7$ solution if the orange color of dichromate changes to green.

6.11 Quantitatively transfer the solutions from the 125-mL Erlenmeyer flasks to 50-mL centrifuge tubes, dilute to the 50-mL mark with demineralized water, and shake to ensure thorough mixing.

6.12 Centrifuge the samples at 2,000 rpm for 20 minutes to settle the undissolved sediment. Alternatively, allow the samples to stand overnight.

6.13 Set up atomic absorption spectrophotometer, vapor generation accessory, and autosampler according to conditions outlined in Section 4. Allow instruments to warm for 10 minutes or longer using rinse solution in the sample line.

6.14 Analyze the working solution III and the blank alternatively until stable readings are obtained for each.

6.15 Analyze the samples and any standard reference solution for Hg using working solutions I, II, and III. Dilute the sample solutions if they have a concentration greater than working solution III.

7. Calculations

7.1 Determine the concentration of Hg in micrograms per liter from the digital display, printer, or chart recorder, and record the results.

7.2 To convert results from micrograms per liter to micrograms per gram, use the following equation:

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

8. Report

Report mercury, total concentration, as follows: less than 1.0 µg/g, nearest 0.01 µg/g; between 1.0 and 10.0 µg/g, nearest 0.1 µg/g; 10 µg/g and greater, two significant figures.

9. Precision

Precision for 10 replicates expressed in standard deviation and percentage relative standard deviation is as follows:

Mean (µg/g)	Standard deviation (µg/g)	Relative standard deviation (percent)
0.04	0.006	15.0
.92	.09	9.8
3.3	.06	1.8
4.3	.08	1.9

References

Band, R.B., and Wilkinson, N.M., 1972, Interferences in the determination of mercury in mineralized samples by the wet reduction-flameless atomic absorption method: Journal of Geochemical Exploration, v. 1, p. 195-198.

Bartha, A., and Ikre'nyi, K., 1981, Interfering effects on the determination of low concentrations of mercury in geological materials by cold-vapor atomic absorption spectrometry: Analytica Chimica Acta, v. 139, p. 329-332.

Koirtyohann, S.R., and Khalil, Moheb, 1976, Variables in the determination of mercury by cold vapor atomic absorption: Analytical Chemistry, v. 48, p. 136-139.

Suddendorf, R.F., 1981, Interference by selenium or tellurium in the determination of mercury by cold-vapor-generation atomic absorption spectroscopy: Analytical Chemistry, v. 53, p. 22-36.

Metals, atomic emission spectrometry, inductively coupled plasma (ICP)

Parameters and Codes:
Metals, dissolved, I-1472-87 (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	Nickel	(µg/L as Ni)	01065
Chromium (µg/L as Cr)	01030	Silica	(mg/L as SiO_2)	00955
Cobalt (µg/L as Co)	01035	Silver	(µg/L as Ag)	01075
Copper (µg/L as Cu)	01040	Sodium	(mg/L as Na)	00930
Iron (µg/L as Fe)	01046	Strontium	(µg/L as Sr)	01080
Lead (µg/L as Pb)	01049	Vanadium	(µg/L as V)	01085
Lithium (µg/L as Li)	01130	Zinc	(µg/L as Zn)	01090

1. Application

1.1 This method is used only for the determination of dissolved metals in water samples that have a measured specific conductance of less than 2,000 µS/cm at 25°C. The concentration limits are listed in table 8. Samples containing analyte concentrations greater than the maximum concentration limit can be analyzed for calcium, magnesium, silica, and sodium if the sample is diluted and if, after dilution, the specific conductance is less than 2,000 µS/cm. Trace metals also can be determined after appropriate dilution in samples that have a measured specific conductance greater than 2,000 µS/cm; however, detection levels and sensitivity will change proportionally. This modified method was implemented in the National Water Quality Laboratory in August 1987.

Table 8.--*Concentration limits of metals for inductively coupled plasma*

[µg/L, microgram per liter; mg/L, milligram per liter]

Metals	Minimum limit (µg/L, except where noted)	Maximum limit (µg/L, except where noted)	Wavelength
Barium	1	10,000	455.5
Beryllium	.5	10,000	313.0
Cadmium	1	10,000	214.4
Calcium (1)	.02 mg/L	25 mg/L	396.8
Calcium (2)	25 mg/L	400 mg/L	315.8
Chromium	5	10,000	267.7
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	10,000	670.7
Magnesium (1)	.01 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
Nickel	10	10,000	[1]231.6
Silica (SiO_2)	.01 mg/L	100 mg/L	288.1
Silver	1	10,000	328.1
Sodium (1)	.2 mg/L	50 mg/L	589.0
Sodium (2)	50 mg/L	400 mg/L	330.2
Strontium	.5	10,000	421.5
Vanadium	6	10,000	292.4
Zinc	3	10,000	[1]206.0

[1]Second order.

1.2 Analyze filtered and acidified samples. Water-suspended sediment or bottom material samples cannot be analyzed.

1.3 The inductively coupled plasma (ICP) methods approved for U.S. Geological Survey use are linked to a specific instrument and associated software. This does not imply endorsement of one product over another.

2. Summary of method

All metals are determined simultaneously on a single sample by a direct-reading emission spectrometric method using an inductively coupled argon plasma as an excitation source. Samples are pumped into a crossflow pneumatic nebulizer, and introduced into the plasma through a spray chamber and torch assembly. Each analysis is determined on the basis of the average of three replicate integrations, each of which is background corrected by a spectrum-shifting technique except for lithium (670.7 nm) and sodium (589.0 nm). A series of five mixed-element standards and a blank are used for calibration.

3. Interferences

3.1 Several interelement interference effects have been evaluated. Interelement correction factors are programmed into the Thermo Jarrell-Ash system software, and corrections are automatically applied internally to the data before they are printed.

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

4. Apparatus

4.1 *Emission spectrometry system* consisting of the following:

4.1.1 *Autosampler.*

4.1.2 *Computer,* IBM PS/2 or equivalent.

4.1.3 *Peristaltic pump.*

4.1.4 *Quartz torch assembly.*

4.1.5 *Spectrometer,* Jarrell-Ash Plasma Spectrometer, 0.75-m focal curve with spectrum shifter background correction, crossflow pneumatic nebulizer, and radio frequency generator. (See table 8 for element wavelengths.)

4.2 Refer to the Jarrell-Ash instruction manual (ICAP61E) for operating techniques. Operating conditions (see NOTE 1):

NOTE 1. Operating conditions are approximate and will vary from instrument to instrument.

Incident radio frequency power	1.25 kW
Reflected radio frequency 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 flow rate for crossflow nebulizer	0.9 L/min
Coolant argon flow rate	18 L/min
Sample pumping rate for crossflow nebulizer	10 percent above aspiration
Refractor plate position	Optimized for Hg profile
Spectrum shifter	0.03 nm on high side of wavelength

5. Reagents

5.1 Use Ultrex grade acids or equivalent to prepare standards.

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

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

5.2 *Water:* All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

5.3 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.

5.3.1 *Barium standard solution I,* 1.00 mL = 1,000 µg Ba: Dissolve 1.512 g $BaCl_2$ dried at 180°C for 1 h and cooled in a desiccator, in a 1,000-mL volumetric flask containing 100 mL water. In a well-ventilated hood, slowly add 100 mL concentrated HNO_3 (sp gr 1.41) while stirring. After the $BaCl_2$ has dissolved, dilute to 1,000 mL with water.

5.3.2 *Beryllium standard solution I,* 1.00 mL = 1,000 µg Be: Transfer 1.000 g Be flakes into a 1,000-mL volumetric flask with minimum water. Use a well-ventilated hood (Caution, see Note 2). Add 90 mL concentrated HNO_3 (sp gr 1.41) and 10 mL concentrated HCl (sp gr 1.19). Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water.

NOTE 2. Beryllium is extremely toxic. May be fatal if swallowed or inhaled.

5.3.3 *Cadmium standard solution I,* 1.00 mL = 1,000 µg Cd: Transfer 1.000 g Cd splatters into a 1,000-mL volumetric flask containing 100 mL water. Add 100 mL concentrated HNO_3 (sp gr 1.41). Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water.

5.3.4 *Calcium (1) standard solution I,* 1.00 mL = 1,000 µg Ca: Weigh 2.4973 g $CaCO_3$ dried at 180°C for 1 h and quickly transfer into a 1,000-mL volumetric flask containing 100 mL water. Dissolve cautiously with 10 mL concentrated HNO_3 (sp gr 1.41). Cool and dilute the solution to 1,000 mL with water.

5.3.5 *Calcium (2) standard solution I,* 1.00 mL = 5,000 µg Ca: Dry 12.4865 g $CaCO_3$ at 180°C for 1 h and cool in a desiccator. Weigh quickly, transfer into a 1,000-mL volumetric flask containing 100 mL water, and dissolve cautiously with 10 mL concentrated HNO_3 (sp gr 1.41). Dilute to 1,000 mL with water. After cooling, adjust volume to 1,000 mL.

5.3.6 *Chromium standard solution I,* 1.00 mL = 1,000 µg Cr: Transfer 1.000 g Cr metal into a 1,000-mL volumetric flask with minimum water. Add 50 mL concentrated HCl (sp gr 1.19) and stir. Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water.

5.3.7 *Cobalt standard solution I,* 1.00 mL = 1,000 µg Co: Transfer 1.000 g Co powder into a 1,000-mL volumetric flask with minimum water. Add 100 mL concentrated HNO_3 (sp gr 1.41). Place in an ultrasonic bath to increase rate of dissolution. Dilute to 1,000 mL with water.

5.3.8 *Copper standard solution I,* 1.00 mL = 1,000 µg Cu: Transfer 1.000 g Cu powder into a 1,000-mL volumetric flask with minimum water. Slowly add 100 mL concentrated HNO_3 (sp gr 1.41) while stirring. If necessary, heat to increase rate of dissolution. Dilute to 1,000 mL with water.

5.3.9 *Iron standard solution I,* 1.00 mL = 1,000 µg Fe: Transfer 1.000 g Fe powder into a 1,000-mL volumetric flask with minimum water. Place flask in hood and, while stirring, add 15 mL concentrated HCl (sp gr 1.19). Heat to increase rate of dissolution. After dissolution, slowly add 85 mL concentrated HNO_3 (sp gr 1.41). Cool and dilute to 1,000 mL with water.

5.3.10 *Lead standard solution I,* 1.00 mL = 1,000 µg Pb: Transfer 1.000 g Pb powder into a 1,000-mL Teflon volumetric flask with minimum water. Place flask into an ultrasonic bath in a well-ventilated hood and add 15 mL concentrated HCl (sp gr 1.19). Slowly add 85 mL concentrated HNO_3 (sp gr 1.41) while stirring. Dilute to 1,000 mL with water.

5.3.11 *Lithium standard solution I,* 1.00 mL = 1,000 µg Li: Dry $LiCO_3$ in oven at 180°C for 2 h, cool, and transfer 5.3235 g into a 1,000-mL volumetric flask containing 100 mL water. Slowly add 10 mL concentrated HNO_3 (sp gr 1.41). Dilute to 1,000 mL with water.

5.3.12 *Magnesium standard solution I,* 1.00 mL = 1,000 µg Mg: Transfer 1.000 g Mg granules into a 1,000-mL volumetric flask containing 100 mL water. In a well-ventilated hood, slowly add 100 mL concentrated HNO_3 (sp gr 1.41). Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water.

5.3.13 *Manganese standard solution I,* 1.00 mL = 1,000 µg Mn: Transfer 1.000 g Mn flakes into a 1,000-mL volumetric flask with minimum water. In a well-ventilated hood, slowly add 100 mL concentrated HNO_3 (sp gr 1.41). Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water.

5.3.14 *Molybdenum standard solution I,* 1.00 mL = 1,000 µg Mo: Transfer 1.000 g Mo powder into a 1,000-mL volumetric flask with minimum water. In a well-ventilated hood while stirring, slowly add 10 mL concentrated HNO_3 (sp gr 1.41). After fumes dissipate, add 90 mL concentrated HNO_3 (sp gr 1.41) and 20 mL water. Heat to increase rate of dissolution. If solution turns cloudy and a precipitate appears, turn heat up on hot plate and stir for an additional 15 to 30 minutes until precipitate disappears. Cool and dilute to 1,000 mL with water.

5.3.15 *Nickel standard solution I,* 1.00 mL = 1,000 µg Ni: Transfer 1.000 g Ni powder into a 1,000-mL volumetric flask containing 100 mL water. In a well-ventilated hood while stirring, slowly add 100 mL concentrated HNO_3 (sp gr 1.41). Heat and stir for 30 minutes or until dissolution is complete. Cool and dilute to 1,000 mL with water.

5.3.16 *Silica standard solution I,* 1.00 mL = 1,000 µg SiO_2: Transfer 1.7654 g $Na_2SiO_3 \cdot 5H_2O$ into a 500-mL polypropylene or Teflon volumetric flask and dissolve with small amount of water. Add 50 mL concentrated HNO_3 (sp gr 1.41) and dilute to 500 mL with water.

5.3.17 *Silver standard solution I,* 1.00 mL = 1,000 µg Ag: Transfer 1.000 g Ag powder into a 1,000-mL volumetric flask containing 100 mL water. In a well-ventilated hood while stirring, slowly add 100 mL concentrated HNO_3 (sp gr 1.41). Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water. Store in an opaque bottle.

5.3.18 *Sodium standard solution I,* 1.00 mL = 5,000 µg Na: Dissolve 12.7107 g NaCl in a 1,000-mL volumetric flask containing 100 mL water. Slowly add 100 mL concentrated HNO_3 (sp gr 1.41) while stirring. Cool and dilute to 1,000 mL with water.

5.3.19 *Strontium standard solution I,* 1.00 mL = 1,000 µg Sr: Dissolve 2.4153 g $Sr(NO_3)_2$ dried for 1 h at 180°C in a 1,000-mL volumetric flask containing 100 mL water. While stirring, add 100 mL concentrated HNO_3 (sp gr 1.41). Dilute to 1,000 mL with water.

5.3.20 *Vanadium standard solution I,* 1.00 mL = 1,000 µg V: Transfer 2.2963 g NH_4VO_3 into a 1,000-mL volumetric flask containing 20 mL concentrated HNO_3 (sp gr 1.41). Heat to increase rate of dissolution and continue to heat while stirring for 1 h. Cool and dilute to 1,000 mL with water.

5.3.21 *Zinc standard solution I,* 1.00 mL = 1,000 µg Zn: Transfer 1.0000 g Zn powder into a 1,000-mL volumetric flask containing 200 mL water. While stirring, slowly add 100 mL concentrated HNO_3 (sp gr 1.41). Dilute to 1,000 mL with water.

5.4 *Standard solution II,* 1.00 mL = 100 µg metal [except calcium (2) and sodium, 1.00 mL = 500 µg]: Dilute 100 mL of each individual metal standard solution I to 1,000 mL with water.

5.5 Mixed working standard solutions.

5.5.1 Prepare five mixed working standard solutions as follows: Pipet 25.0 mL of each appropriate standard solution II into a 250-mL volumetric flask. Dilute to 250 mL with water. Transfer to acid-rinsed PTFE bottle for storage. Fresh mixed standards need to be prepared weekly. Final concentration will be 1.00 mL = 10.0 µg for all metals with the exception of sodium and calcium (2), which will be 1.00 mL = 50.0 µg. Composition for mixed standard solutions will be as follows:

5.5.2 *Mixed standard solution I*--Iron, cadmium, chromium, lead, and zinc.

5.5.3 *Mixed standard solution II*--Barium, beryllium, copper, nickel, strontium, vanadium, and cobalt.

5.5.4 *Mixed standard solution III*--Molybdenum, lithium, silica, silver, and calcium (2).

5.5.5 *Mixed standard solution IV*--Calcium (1), manganese, and sodium.

5.5.6 *Standard solution V*--Magnesium.

5.5.7 *Rinse solution* is prepared by diluting 20 mL concentrated HNO_3 (sp gr 1.41) with 2,000 mL water.

5.6 *Check standard solution*: Pipet 25 mL of each standard solution II into a 500-mL volumetric flask. Dilute to 500 mL with water. Transfer to PTFE bottle for storage. Fresh check standard solution is to be prepared as needed. Final concentration will be 1.00 mL = 5.00 µg for all metals, with the exception of Na, which will be 1.00 mL = 28.83 µg (because of Na in the Si standard solution).

6. Procedure

6.1 Set up instrument with proper operating conditions (paragraph 4.2) and ignite plasma. Warm the instrument for 30 minutes prior to standardization.

6.2 Initiate the *operation* sequence in the software.

6.3 Aspirate a profiling solution or 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 profiling spectral line. Position the micrometer to the average setting.

6.4 Standardize the data system by running a blank and the series of five mixed standard solutions. Pump rinse solution for 30 seconds between standards. Allow 30 seconds for equilibration each time a new solution is introduced.

6.5 Analyze check standard solution described in paragraph 5.6. Concentration values are not to deviate from the actual values by more than 2 percent. If values do deviate more than 2 percent, recalibrate.

6.6 Check standardization by running certified reference samples in natural matrix materials. The determined concentrations need to be within one standard deviation unit of the concentration given for each constituent in the reference material.

6.7 Analyze samples, allowing 30 seconds for equilibration. Pump rinse solution for 30 seconds between samples. Check calibration after analyzing 10 samples by rerunning a reference sample and the check standard solution. The results for the reference sample and check standard solution need to be within one standard deviation unit of the concentration given for each metal in the reference material and less than ± 2 percent for each element. If not, the data system has to 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 µm units, the instrument will need to be restandardized (starting with paragraph 6.2).

7. Calculations

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

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

8. Report

8.1 All results are printed out directly in the appropriate reporting units.

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 greater, two significant figures.

8.2.2 Beryllium (01010), cadmium (01025), manganese (01056), silver (01075), and strontium (01080): less than 10 µg/L, nearest microgram per liter; 10 µg/L and greater, two significant figures.

8.2.3 Barium (01005), chromium (01030), cobalt (01035), iron (01046), lithium (01130), vanadium (01085), and zinc (01090): less than 10 µg/L, nearest microgram per liter to the lower limit of detection as specified in table 8; 10 µg/L and greater, two significant figures.

8.2.4 Copper (01040), lead (01049), molybdenum (01060), and nickel (01065): less than 100 µg/L, nearest 10 µg/L; 100 µg/L and greater, two significant figures.

9. Precision

Within its designated range, single-operator precision of the method for each metal can be expressed as listed in table 9. A minimum of 10 replicates was analyzed to obtain each regression equation shown.

Table 9.--*Single-operator precision data for inductively coupled plasma*

[µg/L, microgram per liter; mg/L, milligram per liter]

Metal	Slope[1]	Intercept
Barium (µg/L)	0.0061	0.83
Beryllium (µg/L)	.0061	.06
Cadmium (µg/L)	.0203	.30
Calcium (mg/L)	.0044	.30
Cobalt (µg/L)	.0650	.40
Copper (µg/L)	.0039	1.32
Iron (µg/L)	.0071	.059
Lead (µg/L)	.1210	5.0
Lithium (µg/L)	.0240	.076
Magnesium (mg/L)	.0060	.018
Manganese (µg/L)	.0042	.30
Molybdenum (µg/L)	.1220	.18
Silica (mg/L)	.0040	.019
Sodium (mg/L)	.0077	.26
Strontium (µg/L)	.0089	.076
Vanadium (µg/L)	.1000	1.80
Zinc (µg/L)	.0059	1.24

[1]The standard deviation S_0 is calculated by $S_0=mx+b$, where m is slope of line, x is concentration of constituent in units specified, and b is intercept.

9.3 Single-operator precision for dissolved chromium, nickel, and silver for five samples, expressed as the standard deviation and percentage relative standard deviation, is as follows:

9.3.1 Chromium

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
11	1.1	1.2	109
12	10.9	.76	7
18	16.6	1.0	6
11	19.7	1.4	7
12	24.6	.98	4

9.3.2 Nickel

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
12	10.6	7.0	66
12	12.7	4.1	32
9	19.8	5.3	27
12	25.2	3.3	13
18	46.8	4.2	9

9.3.3 Silver

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
9	0.37	0.38	102
12	2.48	.52	21
12	3.87	.66	17
12	4.95	1.5	30
18	10.4	1.8	17

Reference

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 45-47.

Nickel, atomic absorption spectrophotometry, graphite furnace

Parameters and Codes:
Nickel, dissolved, I-2503-89 (µg/L as Ni): (01065)
Nickel, whole water recoverable, I-4503-89 (µg/L as Ni): 01067

1. Application

1.1 This method is used to determine nickel in samples of water and water-suspended sediment with a specific conductance not greater than 10,000 µS/cm. With Zeeman background correction and a 20-µL sample, the method is applicable in the range from 1 to 25 µg/L. Sample solutions that contain nickel concentrations greater than 25 µg/L must be diluted or be analyzed by an alternate method. This method was implemented in the National Water Quality Laboratory in May 1989.

1.2 The analytical range and detection limit can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings.

1.3 Whole water recoverable nickel in samples of water-suspended sediment must undergo preliminary digestion by method I-3485 before being determined.

2. Summary of method

Nickel is determined by atomic absorption spectrophotometry 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 then is evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal produced during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences for samples with specific conductances less than 10,000 µS/cm normally are small. In addition, the use of the graphite platform reduces the effects of many interferences.

3.2 Special precautionary measures to prevent contamination need to be used during sample collection and laboratory determination.

4. Apparatus

4.1 *Atomic absorption spectrophotometer*, for use at 232.0 nm and equipped with Zeeman background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer needs to have high-temperature ramping and controlled argon-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize operations and instrumental performance. A 20-µL sample with a 25-µg/L concentration of nickel should yield a signal of approximately 0.17 absorbance-second. This absorbance signal is based on nickel's characteristic mass of 13.0 pg for a signal of 0.0044 absorbance-second. A 20-µL sample generally requires 30 seconds at 130°C to dry. Samples that have a complex matrix might require a longer drying or charring time. Peak shapes may be used to detect insufficient drying, charring, or atomization times or temperatures.

4.1.2 *Graphite furnace*, capable of reaching a temperature of 2,600°C sufficient to atomize the nickel. Warning: dial settings frequently are inaccurate, and newly conditioned furnaces need to be temperature-calibrated.

4.1.3 *Graphite tubes and platforms*, pyrolytically coated graphite tubes and platforms are suggested.

4.2 *Labware*. Many trace metals at small concentrations adsorb rapidly to glassware. To preclude this problem, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternatively, glassware, particularly flasks and pipets, can be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co.) according to the manufacturer's instructions. Check autosampler cups for contamination. Lancer polystyrene disposable cups are satisfactory after acid rinsing. Alternatively, reusable Teflon or FEP cups can be purchased.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen also can be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Nickel standard solution I*, 1.00 mL = 1,000 µg Ni: A commercially prepared and certified nickel standard can be used. An alternate method is to dissolve 1.0000 g nickel wire in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 4 mL ultrapure concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with 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 1).

NOTE 1. Use acidified water (paragraph 5.7) to make dilutions. Store all standards in sealed Teflon or FEP containers. Rinse each container twice with a small volume of standard solution before filling the storage container. Standards stored for 6 months in FEP containers yielded values equal to freshly prepared standards.

5.3 *Nickel standard solution III,* 1.00 mL = 1.00 µg Ni: Dilute 100 mL nickel standard solution II to 1,000 mL with acidified water. Prepare fresh monthly.

5.4 *Nickel working solution IV,* 1.00 mL = 0.025 µg Ni: Dilute 25.0 mL nickel standard solution III to 1,000 mL with acidified water. Prepare fresh monthly.

5.5 *Nickel working solution V,* 1.00 mL = 0.010 µg Ni: Dilute 10.0 mL nickel standard solution III to 1,000 mL with acidified water. Prepare fresh monthly.

5.6 *Nitric acid,* concentrated, ultrapure (sp gr 1.41): J.T. Baker Ultrex brand HNO_3 is adequately pure; however, check each lot for contamination. Analyze acidified water (paragraph 5.7) for nickel. Add 1.5 mL concentrated HNO_3 per liter of water, and repeat analysis. Integrated signal should not increase by more than 0.001 absorbance-second.

5.7 *Water, acidified:* Add 4.0 mL ultrapure concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water:* All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

6. Procedure

6.1 The autosampler and the graphite furnace need to be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1*N* HNO_3 solution.

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 a minimum of two standards in duplicate. Construct the analytical curve from the integrated peak areas (absorbance-seconds).

6.5 Similarly, inject and analyze the samples in duplicate. Every tenth sample cup needs to contain either a standard, blank, or a reference material.

6.6 Restandardize as required, although with the use of L'vov platforms, restandardization generally is not necessary. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, or platform. A major variation usually indicates either auto-sampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculation

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 factor.

8. Report

Report concentrations of nickel, dissolved (01065), and whole water recoverable (01067), as follows: less than 10 µg/L, the nearest 1 µg/L; 10 µg/L and greater, two significant figures.

9. Precision

9.1 Analysis of six samples for dissolved nickel by a single operator is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
5	1.6	0.12	7.5
15	4.2	.75	17.9
5	5.3	.52	9.8
18	11.4	.83	7.3
15	12.1	1.88	15.5
22	48.1	2.82	5.9

9.2 Analysis of three samples for whole water recoverable nickel by a single operator is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
7	5.9	0.67	11.4
11	13.9	1.51	10.9
10	17.6	.23	1.3

9.3 The precision and bias for dissolved nickel was tested on several standard reference water samples. A known amount of nickel was added to each sample, and single-operator precision and bias for the samples are as follows:

Amount present (µg/L)	Number of replicates	Amount added (µg/L)	Found (µg/L) (NOTE 2)	Standard deviation (µg/L)	Relative standard deviation (percent)	Percent recovery
4.7	6	22.2	22.2	2.1	9.2	100.0
4.8	6	46.2	46.0	2.4	5.1	99.6
5.1	6	9.2	9.1	.5	5.0	98.9
10.0	6	23.7	22.9	1.3	5.8	96.6
10.1	6	45.2	43.6	2.9	6.7	96.5

NOTE 2. The amount originally present has been subtracted.

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 45-47.

Hinderberger, E.J., Kasser, 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.

Nitrogen, ammonia, low ionic-strength water, colorimetry, salicylate-hypochlorite, automated-segmented flow

Parameter and Code:
Nitrogen, ammonia, dissolved, I-2525-89 (mg/L as N): 00608

1. Application

This method is used to analyze samples of precipitation and natural water containing from 0.002 to 0.30 mg/L of ammonia-nitrogen. Concentrations greater than 0.30 mg/L must be diluted. This method was implemented in the National Water Quality Laboratory in March 1986 and modified in May 1989.

2. Summary of method

Ammonia reacts with hypochlorite and salicylate ions in the presence of ferricyanide ions to form the salicylic acid analog of indophenol (Reardon and others, 1966; Patton and Crouch, 1977; Harfmann and Crouch, 1989).

3. Interferences

3.1 No substance found in natural water seems to interfere with this method.

3.2 The samples are easily contaminated by ammonia in the laboratory atmosphere; therefore, sample handling and analysis need to be performed where there is no possibility of ammonia contamination.

4. Apparatus

4.1 *Alpkem rapid flow analyzer (RFA)*, consisting of sampler, peristaltic pump, analytical cartridge, heating bath, colorimeter, data station, and printer.

4.2 With this equipment, the following operating conditions are satisfactory for the range from 0.002 to 0.30 mg/L of ammonia-nitrogen:

Flow cell .....20 mm
Wavelength.....660 nm
Sample time.....24 seconds
Wash time.....32 seconds
Sampling rate.....64 per hour
Heating bath (4 mL).....37°C
Pecking .....OFF
Damp (RC).....1 second

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 1,000 mL. Refrigerate.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.0015 mg NH_3-N: Dilute 3.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh weekly and refrigerate.

5.3 *Ammonia working solutions*: Prepare an ammonia-free blank, 200 mL each of a series of ammonia working solutions by dilution of ammonia standard solution II or ammonia working solution No. 3 with ammonia-free water as listed in the following table. If the samples to be analyzed are preserved, the ammonia working solutions need to contain an equivalent concentration of the same preservative.

Working solution No.	Solution added (mL)	Solution used	Ammonia concentration (mg/L)
1	40	Standard solution II	0.3000
2	20	Standard solution II	.1500
3	10	Standard solution II	.0750
4	2	Standard solution II	.0150
5	20	Working solution No. 3	.0075
6	8	Working solution No. 3	.0030
7	4	Working solution No. 3	.0015

Prepare fresh weekly and refrigerate.

5.4 *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.

5.5 *Buffer working solution*: Add, with stirring, 250 mL stock potassium sodium tartrate solution to 200 mL buffer stock 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. Filter and degas for at least 30 minutes.

5.6 *Potassium sodium tartrate solution*, 149 g/L: Dissolve 200 g $NaKC_4H_4O_6 \cdot 4H_2O$ in about 600 mL ammonia-free water. Dilute to 1 L.

5.7 *Sodium hydroxide solution, 5M*: CAUTION: Add, with cooling and stirring, 200 g NaOH to about 800 mL ammonia-free water. Cool and dilute to 1 L.

5.8 *Sodium hypochlorite solution*: Dilute 25 mL sodium hypochlorite solution (a commercial bleach solution containing 5.25-percent available chlorine is satisfactory) to 100 mL with ammonia-free water. Prepare fresh daily.

5.9 *Sodium salicylate–sodium nitroferricyanide solution*: Dissolve 83 g sodium salicylate and 0.17 g sodium nitroferricyanide $[Na_2Fe(CN)_2NO \cdot 2H_2O]$ in about 300 mL ammonia-free water. Filter through Whatman 41 filter paper or equivalent, and dilute to 1 L. Add 2.0 mL Brij-35 solution, degas for at least 30 minutes, and store in a light-resistant container.

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

5.11 *Sulfuric acid, 2.5M*: Cautiously add 138 mL concentrated H_2SO_4 (sp gr 1.84) to about 700 mL ammonia-free water. Cool and dilute to 1 L with ammonia-free water.

6. Procedure

6.1 Set up manifold (fig. 3). If the laboratory air is contaminated with ammonia, it needs to be passed through a scrubber containing 2.5*M* H_2SO_4 before it enters the air-manifold tube.

6.2 Allow the colorimeter, recorder, and heating bath to warm for at least 10 minutes or until the temperature of the heating bath reaches 37°C.

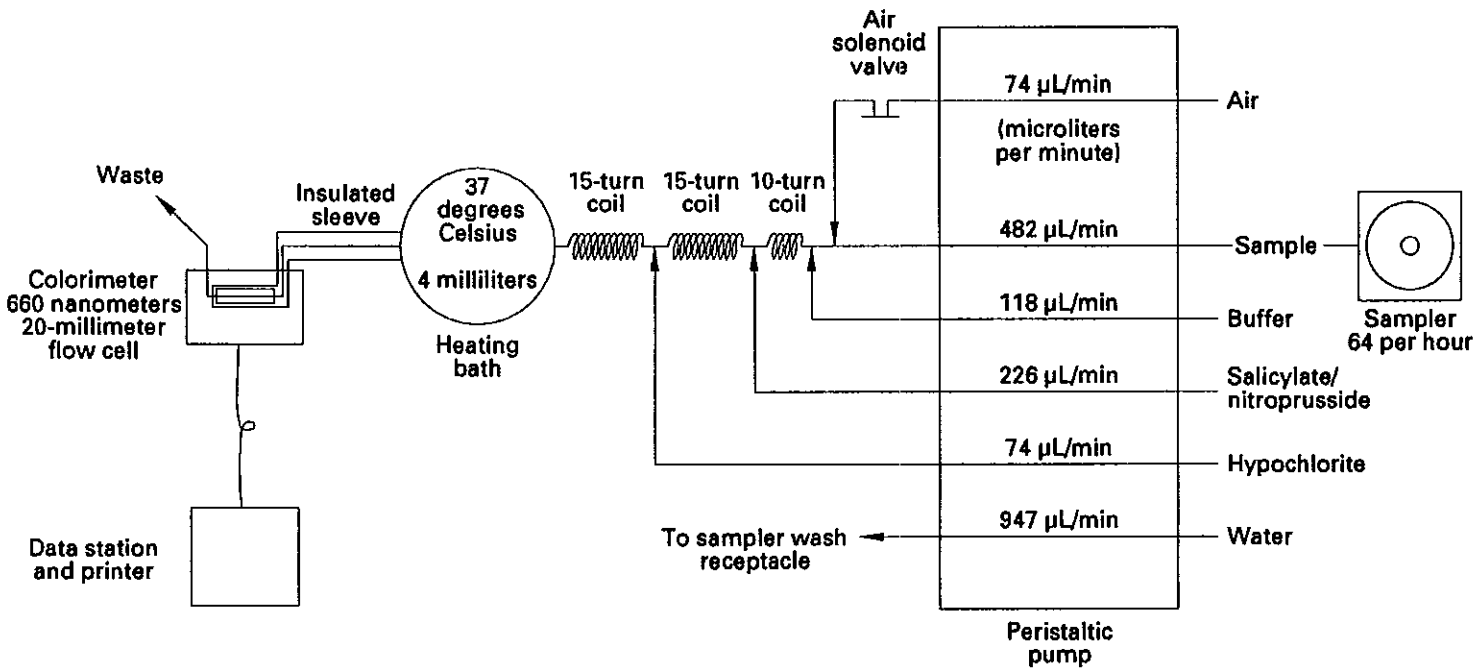


Figure 3.—Nitrogen, ammonia, low ionic-strength water, salicylate-hypochlorite manifold.

6.3 After all reagents are on line (NOTE 1), adjust the sample output of the photometer to 5 V. Then switch the photometer to "absorbance" mode and use the reference detector "fine gain" control to adjust the baseline absorbance to about 0.2 V. See operation manuals for complete details (Alpkem Corp., 1986). The solution remaining in the wash reservoir from previous determinations might be contaminated; therefore, this reservoir needs to 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 minutes 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 or remake them, and start again using the aforementioned procedure.

6.4 Place the most concentrated working solution in two cups before analysis. As the peaks appear on the recorder, adjust the STD CAL control until the peak obtains 95 percent of full scale.

6.5 When the system is clear of all working solutions, determine a dwell time using the most concentrated working solution.

6.6 Place a complete set of working solutions and a blank in the first positions of the sample tray beginning with the most concentrated working solution (NOTE 2). Place individual working solutions of differing concentrations in approximately every eighth position on the tray following the accepted protocol. Fill the remainder of each tray with unknown samples.

NOTE 2. To avoid possible contamination of the sample cups, they need to remain sealed in their packages until just prior to use. Rinse each sample cup with sample prior to filling.

6.7 Begin analysis.

7. Calculations

7.1 Prepare an analytical curve by plotting the voltage of each working solution peak in relation to its respective ammonia-nitrogen concentration, or by using the RFA Softpac data reduction package. See operation manuals for complete details (Alpkem Corp., 1986).

7.2 Compute the concentration of dissolved ammonia-nitrogen in each sample by comparing its voltage to the analytical curve or by using the software. Any baseline drift needs to be accounted for when computing the voltage of a sample or working solution peak; the RFA software automatically corrects for baseline drift.

8. Report

Report concentrations of ammonia-nitrogen, dissolved (00608), as follows: less than 0.10 mg/L, three decimals; 0.10 mg/L and greater, two significant figures.

9. Precision

Single operator precision for ammonia-nitrogen, as determined for natural-water samples, expressed as standard deviation and percentage relative standard deviation, is as follows:

Number of determinations	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
22	0.030	0.004	14.0
22	.168	.004	2.3
34	.197	.005	2.4

References

Alpkem Corp., 1986, Rapid flow analyzer operator's manual: ALPKEM, methodology section.

Harfmann, R.G., and Crouch, S.R., 1989, Kinetic study of Berthelot reaction steps in the absence and presence of coupling reagents: Talanta, v. 36, p. 261-269.

Patton, C.J., and Crouch, S.R., 1977, Spectrophotometric and kinetics investigation of the Berthelot reaction for the determination of ammonia: Analytical Chemistry, v. 49, p. 464-469.

Reardon, J., Foreman, J.A., and Searcy, R.L., 1966, New reactants for the colorimetric determination of ammonia: Clinical Chimica Acta, v. 14, p. 403-405.

Nitrogen, ammonia, colorimetry, salicylate-hypochlorite, automated-segmented flow

Parameters and Codes:
Nitrogen, ammonia, dissolved, I-2522-90 (mg/L as N): 00608
Nitrogen, ammonia, total-in-bottom-material, I-6522-90 (mg/L as N): 00611

1. Application

1.1 This method is used to analyze samples of surface, domestic, and industrial water, and brines containing from 0.01 to 1.5 mg/L of ammonia-nitrogen. Concentrations greater than 1.50 mg/L must be diluted. This modified method was implemented in the National Water Quality Laboratory in March 1988.

1.2 This method also is used to determine concentrations of ammonia-nitrogen in samples of 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 need to be diluted.

1.3 Sodium ion is a good replacement for ammonium ion in the slow-exchange positions of soil minerals (Jackson, 1958). Bottom material is treated with an acidified sodium chloride solution, and the resulting mixture is allowed to settle and then decanted to obtain a clear supernatant solution for analysis.

2. Summary of method

Ammonia reacts with salicylate and hypochlorite ions in the presence of ferricyanide ions to form the salicylic acid analog of indophenol blue (Reardon and others, 1966; Patton and Crouch, 1977; Harfmann and Crouch, 1989). The resulting color is directly proportional to the concentration of ammonia present.

3. Interferences

3.1 Sulfide interferes. Bromide and nitrite can interfere. Calcium and magnesium in highly alkaline waters (pH greater than 13.6) can exceed the ability of the tartrate to complex both ions.

3.2 The samples are easily contaminated by ammonia in the laboratory atmosphere; therefore, sample handling and analysis need to be performed where there is no possibility of ammonia contamination.

4. Apparatus

4.1 *Shaker,* wrist action.

4.2 *Alpkem rapid flow analyzer (RFA),* consisting of sampler, peristaltic pump, analytical cartridge, heating bath, colorimeter, data station, and printer.

4.3. With this equipment, the following operating conditions are satisfactory for the range from 0.01 to 1.50 mg/L of ammonia-nitrogen:

Flow cell .....15 mm
Wavelength.....660 nm
Sample time .....24 seconds
Wash time.....16 seconds
Sampling rate.....90 per hour
Heating bath (2 mL).....37°C
Pecking .....ON
Damp (RC).....1 second

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 1,000 mL. Refrigerate.

5.2 *Ammonia standard solution II,* 1.00 mL = 0.0015 mg NH_3-N: Dilute 3.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh weekly and refrigerate.

5.2.1 *Ammonia working solutions,* bottom materials: Prepare an ammonia-free blank and 250 mL each of a series of ammonia working solutions by appropriate quantitative dilution of ammonia standard solution II or working solutions with acidified sodium chloride solution (paragraph 5.7), as follows:

Working solution No.	Solution added (mL)	Solution used	Ammonia concentration (mg/L)
1	250	Standard solution II	1.50
2	125	Standard solution II	.75
3	50	Standard solution II	.30
4	25	Standard solution II	.15
5	25	Working solution No. 2	.075
6	25	Working solution No. 4	.015

5.2.2 *Ammonia working solutions,* water: Prepare an ammonia-free blank and 250 mL each of a series of ammonia working solutions by dilution of ammonia standard solution II or working solutions with ammonia-free water as listed in the following table. If the samples to be analyzed are preserved, the ammonia working solutions need to contain an equivalent concentration of the same preservative.

Working solution No.	Solution added (mL)	Solution used	Ammonia concentration (mg/L)
1	250	Standard solution II	1.50
2	125	Standard solution II	.75
3	50	Standard solution II	.30
4	25	Standard solution II	.15
5	25	Working solution No. 2	.075
6	25	Working solution No. 4	.015

Prepare weekly and refrigerate.

5.3 *Buffer stock solution,* 71 g/L: Dissolve 134 g $Na_2HPO_4 \cdot 7H_2O$ in 800 mL of 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, while stirring, 250 mL stock potassium sodium tartrate solution to 200 mL buffer stock solution. Slowly, while stirring, add 120 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water, add 1 mL of Brij-35 solution, and mix thoroughly.

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

5.6 *Potassium sodium tartrate solution*, 149 g/L: Dissolve 200 g $NaKC_4H_4O_6 \cdot 4H_2O$ in about 600 mL ammonia-free water. Dilute to 1 L.

5.7 *Sodium chloride solution*, 100 g/L: Dissolve 100 g NaCl in 800 mL ammonia-free water, mix thoroughly, adjust the pH to 2.5 using concentrated HCl (sp gr 1.19), and dilute to 1 L.

5.8 *Sodium hydroxide solution*, 5*M*: CAUTION: Add, while cooling and stirring, 200 g NaOH to about 800 mL ammonia-free water. Cool and dilute to 1 L.

5.9 *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. Prepare fresh daily.

5.10 *Sodium salicylate–sodium nitroferricyanide solution*: Dissolve 150 g sodium salicylate and 0.30 g sodium nitroferricyanide $[Na_2Fe(CN)_5NO \cdot 2H_2O]$ in about 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.

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

5.12 *Sulfuric acid*, 2.5*M*: Cautiously add 138 mL concentrated H_2SO_4 (sp gr 1.84) to about 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 water. For bottom materials, begin with paragraph 6.1.1.

6.1.1 Weigh, to the nearest milligram, about 5 g of sample prepared as directed in method P-0520, and transfer to a 250-mL Erlenmeyer flask.

6.1.2 Add 50 mL of the acidic sodium chloride solution (paragraph 5.7), shake on the wrist-action shaker for 30 minutes, and allow to settle.

6.1.3 Transfer the supernatant solution to a 200-mL volumetric flask, taking care not to disturb the residue in the bottom of the Erlenmeyer flask.

6.1.4 Wash the sediment in the Erlenmeyer flask with 20 mL acidic sodium chloride solution (paragraph 5.7), let settle, and transfer the clear wash solution to the volumetric flask. Adjust to volume with acidic sodium chloride solution (paragraph 5.7). Proceed to paragraph 6.2.

6.2 Set up manifold (fig. 4). If the laboratory air is contaminated with ammonia, the air needs to be passed through a scrubber containing 2.5*M* H_2SO_4 before it enters the air manifold tube.

6.3 Allow the colorimeter, recorder, and heating bath to warm for at least 10 minutes or until the temperature of the heating bath reaches 37°C.

6.4 After all reagents are on line (NOTE 1), adjust the sample output of the photometer to 5 V. Then switch the photometer to "absorbance" mode and use the reference detector "fine gain" control to adjust the baseline absorbance to about 0.2 V. See operation manuals for complete details (Alpkem Corp., 1986). The solution remaining in the wash reservoir from previous determinations might be contaminated; therefore, this reservoir needs to 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 minutes 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 remake them, and start again using the aforementioned procedure.

6.5 Place the most concentrated working solution in two cups before analysis. As the peaks appear on the recorder, adjust the STD CAL control until the peak obtains 95 percent of full scale.

6.6 When the system is clear of all working solutions, determine a dwell time using the most concentrated working solution.

6.7 Place a complete set of working solutions and a blank in the first positions of the sample tray beginning with the most concentrated working solution (NOTES 2 and 3). Place individual working solutions of differing concentrations in approximately every tenth position on the tray following the accepted protocol. Fill the remainder of each tray with unknown samples.

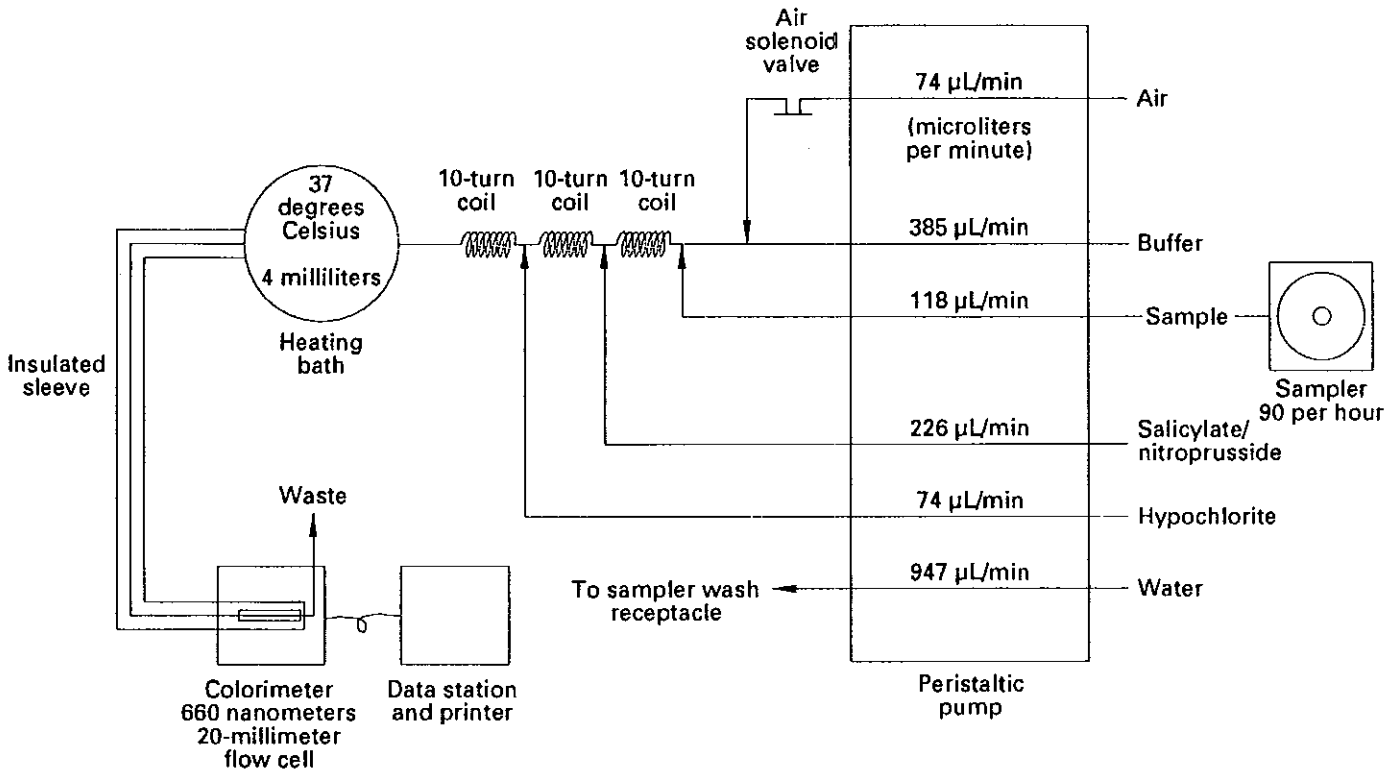


Figure 4.—Nitrogen, ammonia, salicylate-hypochlorite manifold.

NOTE 2. For analysis of bottom materials, use blank and working solutions as prepared in paragraph 5.2.1. For analysis of water, use blank and working solutions as prepared in paragraph 5.2.2.

NOTE 3. To avoid possible contamination of the sample cups, they need to remain sealed in their packages until just prior to use. Rinse each sample cup with sample prior to filling.

6.8 Begin analysis.

7. Calculations

7.1 Prepare an analytical curve by plotting the voltage of each working solution peak in relation to its respective ammonia-nitrogen concentration, or by using the RFA Softpak data reduction package. See operation manuals for complete details (Alpkem Corp., 1986).

7.2 Compute the concentration of dissolved ammonia-nitrogen in each sample by comparing its voltage to the analytical curve or by using the software. Any baseline drift needs to be accounted for when computing the voltage of a sample or standard peak; the RFA software automatically corrects for baseline drift.

7.3 Compute the concentration of ammonia-nitrogen in each sample of bottom material, as follows:

$$NH_3\text{-N (mg/kg)} = \frac{C_N \times 200 \text{ (NOTE 4)}}{\text{wt of sample, in g}}$$

where $C_N = NH_3$-N concentration in sample, in milligrams per liter.

NOTE 4. The factor 200 is used in converting to milligrams per kilogram.

8. Report

8.1 Report concentrations of ammonia-nitrogen, dissolved (00608), as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and greater, two significant figures.

8.2 Report ammonia-nitrogen, total-in-bottom-material (00611), as follows: less than 10 mg/kg, one decimal; 10 mg/kg and greater, two significant figures.

9. Precision

Single operator precision for ammonia-nitrogen, as determined for natural-water samples, expressed as standard deviation and percentage relative standard deviation, is as follows:

Number of determinations	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
180	1.23	0.011	0.89
193	.17	.001	.59
147	.28	.004	1.4
252	.71	.005	.70
240	.54	.006	1.1
209	.06	.001	1.7
240	.12	.002	1.7

References

Alpkem Corp., 1986, Rapid flow analyzer operator's manual, ALPKEM, methodology section.

Harfmann, R.G., and Crouch, S.R., 1989, Kinetic study of Berthelot reaction steps in the absence and presence of coupling reagents: Talanta, v. 36, p. 261-269.

Jackson, M.L., 1958, Soil chemical analysis: Englewood Cliffs, N.J., Prentice-Hall, p. 193.

Patton, C.J., and Crouch, S.R., 1977, Spectrophotometric and kinetics investigation of the Berthelot reaction for the determination of ammonia: Analytical Chemistry, v. 49, p. 464-469.

Reardon, J., Foreman, J.A., and Searcy, R.L., 1966, New reactants for the colorimetric determination of ammonia: Clinical Chimica Acta, v. 14, p. 403-405.

Nitrogen, ammonia plus organic, titrimetry, digestion-distillation

Parameter and Code:
Nitrogen, ammonia plus organic, total-in-bottom-material, dry weight, I-5553-91 (mg/kg as N): 00626

1. Application

This method is used to analyze samples 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). This modified method was implemented in the National Water Quality Laboratory in October 1990.

2. Summary of method

The sample is digested so that all organic nitrogen-containing compounds are converted to ammonium salts. The resulting solution then is made strongly alkaline, and the ammonia so formed is distilled 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

4.1 *Kjeldahl auto analyzer,* Tecator, Kjeltec Auto 1030 Analyzer or equivalent. Refer to manufacturer's manual for operation of instrument.

4.2 *Block digestor,* Tecator Model 40 with 250-mL digestion tubes or equivalent.

4.3 With this equipment, the following operating conditions are satisfactory:

Low temperature..... 150°C (3 to 4 hours)
High temperature..... 370°C (1 hour)

5. Reagents

5.1 *Ammonium chloride crystals.*

5.2 *Boric acid indicator solution, Kjel-Sorb*™ (Fisher Scientific, Catalog No. SK-15-4) saturated boric acid solution (about 4 percent), with indicator.

5.3 *Digestion catalyst*: Tablets containing 3.5 g K_2SO_4 and 0.175 g HgO (Fisher Scientific No. 13159A or equivalent).

5.4 *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.

5.5 *Sodium hydroxide-sodium thiosulfate solution*: Add 80 g $Na_2S_2O_3 \cdot 5H_2O$ to each liter of 40 percent (w/w) sodium hydroxide (Fisher Scientific, Catalog No. SS411-4 or equivalent).

5.6 *Sodium thiosulfate,* crystals: $Na_2S_2O_3 \cdot 5H_2O$.

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

5.8 *Sulfuric acid standard solution,* approximately 0.01639*N*: Cautiously, add 1.0 mL concentrated H_2SO_4 (sp gr 1.84) to 800 mL ammonia-free water and dilute to 2 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 Weigh to the nearest milligram, 2 g of bottom-material sample, prepared as directed in method P-0810, and transfer to the digestion tube.

6.2 Cautiously, add 15 mL concentrated H_2SO_4 (sp gr 1.84) in a well-ventilated hood, and swirl the contents of the tube until thoroughly mixed.

6.3 Add two digestion-catalyst tablets and mix well. Add a few glass beads. Digest at 150°C until a clear solution is obtained (3 to 4 h), and then continue digesting at 370°C for 1 hour.

6.4 Cool the flask until crystals appear (do not cool completely). Add 90 mL ammonia-free water; mix and allow to cool.

6.5 Carry a blank through all steps of the procedure with each group of samples.

6.6 Insert cooled flask into Kjeltec Auto 1030 Analyzer that has been set up as described in the manufacturer's manual. Add a predetermined volume (60 mL) of sodium hydroxide-sodium thiosulfate solution to the flask and start distillation. Ammonia is collected in boric acid indicator solution and the buret automatically dispenses sulfuric acid standard solution until the end point is determined.

7. Calculations

$$\text{Nitrogen, ammonia plus organic (mg/kg)} = \frac{V_a \times N_a \times 14{,}000}{Wt_s}$$

where V_a = volume of H_2SO_4 standard solution used to titrate sample, in milliliters, minus volume used to titrate blank, in milliliters;

N_a = normality of H_2SO_4 standard solution; and

Wt_s = weight of sample, in grams.

The Kjeltec 1030 allows for the value of the blank to be determined and entered into the microprocessor along with the acid strength. The total nitrogen for the sample then is displayed at the end of the distillation.

8. Report

Report concentrations of nitrogen, ammonia plus organic, total-in-bottom-material (00626), as follows: 10 to 100 mg/kg, nearest 1 mg/kg; 100 mg/kg and greater, two significant figures.

9. Precision

For ammonium chloride standards, the precision by a single operator within the range of 100 to 2,500 mg/kg, expressed in standard deviation and percentage relative standard deviation, is as follows:

Number of determinations	Mean (mg/kg)	Standard deviation (mg/kg)	Relative standard deviation (percent)
13	97.3	11.5	11.8
13	496	21.3	4.3
12	2,511	35.2	1.4

Nitrogen, nitrite, low ionic-strength water, colorimetry, diazotization, automated-segmented flow

Parameter and Code:
Nitrogen, nitrite, dissolved, I-2542-89 (mg/L as N): 00613

1. Application

This method is used to analyze samples of precipitation or natural water containing from 0.001 to 0.20 mg/L of nitrite-nitrogen. Concentrations greater than 0.20 mg/L must be diluted. This method was implemented in the National Water Quality Laboratory in March 1986 and modified in May 1989.

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 (Shinn, 1941; Bendschneider and Robinson, 1952; Fox, 1979, 1985; Pai and others, 1990).

3. Interferences

Concentrations of potentially interfering substances generally are negligible. For specific details of inorganic and organic compounds that interfere with the reaction, see Norwitz and Keliher (1985, 1986) as well as more general information from the American Society for Testing and Materials (1991).

4. Apparatus

4.1 *Alpkem rapid flow analyzer (RFA)*, consisting of sampler, peristaltic pump, analytical cartridge, colorimeter, data station, and printer.

4.2 With this equipment, the following operating conditions are satisfactory for the range from 0.001 to 0.20 mg/L N:

Flow cell.....10 mm
Wavelength.....540 nm
Sampling rate.....64 per hour
Sample time.....24 seconds
Wash time.....32 seconds
Pecking.....OFF
Damp (RC).....1 second

5. Reagents

5.1 *Color reagent*: Add 200 mL of concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to about 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 mL Brij-35 solution. Store in an amber bottle and refrigerate. The reagent is stable for about 1 month.

5.2 *Nitrite-nitrogen standard solution I*, 1.00 mL = 0.100 mg NO_2-N: Dissolve 0.6706 g KNO_2, dried overnight over sulfuric acid, in demineralized water and dilute to 1,000 mL. This solution and the following nitrite standard solutions (paragraphs 5.3 and 5.4) are not stable indefinitely; their concentrations need to be checked frequently.

5.3 *Nitrite-nitrogen standard solution II*, 1.00 mL = 0.001 mg NO_2-N: Dilute 10.0 mL nitrite-nitrogen standard solution I to 1,000 mL with demineralized water.

5.4 *Nitrite-nitrogen working solutions*: Prepare a blank and 200 mL of a series of working solutions by appropriate dilution of nitrite-nitrogen standard solution II or working solution No. 3, as listed in the following table. If the samples to be analyzed are preserved, the nitrite-nitrogen working solutions need to contain an equivalent concentration of the same preservative.

Working solution No.	Solution added (mL)	Solution used	Nitrite-nitrogen concentration (mg/L)
1	40	Standard solution II	0.200
2	20	Standard solution II	.100
3	10	Standard solution II	.050
4	2	Standard solution II	.010
5	20	Working solution No. 3	.005
6	8	Working solution No. 3	.002
7	4	Working solution No. 3	.001

6. Procedure

6.1 Set up manifold (fig. 5).

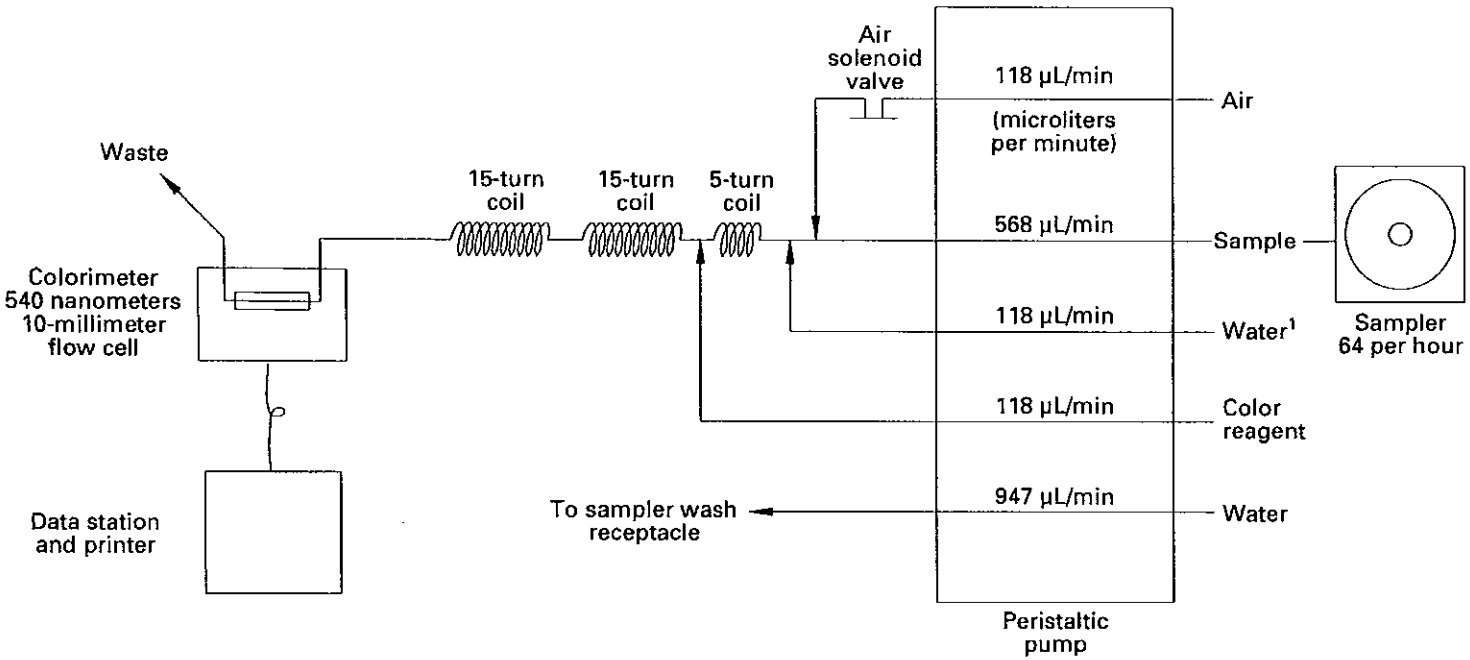


Figure 5.—Nitrogen, nitrite, low ionic-strength water, diazotization manifold.

6.2 Allow colorimeter recorder to warm for at least 10 minutes.

6.3 After all reagents are on line, adjust the sample output of the photometer to 5 V. Then switch the photometer to "absorbance" mode and use the reference detector "fine gain" control to adjust the baseline absorbance to about 0.2 V. See operation manuals for complete details (Alpkem Corp., 1986).

6.4 Place the most concentrated working solution in two cups before analysis. As the peaks appear on the recorder, adjust the STD CAL control until the peak obtains 95 percent of full scale.

6.5 When the system is clear of all working solutions, determine a dwell time using the most concentrated working solution.

6.6 Place a complete set of working solutions and a blank in the first positions of the sample tray beginning with the most concentrated working solution. Place individual working solutions of differing concentrations in approximately every eighth position on the tray following the accepted protocol. Fill the remainder of each tray with unknown samples.

6.7 Begin analysis.

7. Calculations

7.1 Prepare an analytical curve by plotting the voltage of each working solution peak in relation to its respective nitrite-nitrogen concentration, or by using the RFA Softpac data reduction package. See operation manuals for complete details (Alpkem Corp., 1986).

7.2 Compute the concentration of dissolved nitrogen in each sample either by comparing its voltage to the analytical curve or by using the software. Any baseline drift needs to be accounted for when computing the voltage of a sample or working solution peak; the RFA software automatically corrects for baseline drift.

8. Report

Report concentrations of nitrite-nitrogen, dissolved (00613), as follows: less than 0.10 mg/L, three decimals; 0.10 mg/L and greater, two significant figures.

9. Precision

Single operator precision for nitrite-nitrogen, as determined for natural-water samples, expressed as standard deviation and percentage relative standard deviation, is as follows:

Number of determinations	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
22	0.011	0.001	9.1
22	.063	.002	3.2
20	.144	.003	2.1

References

Alpkem Corp., 1986, Rapid flow analyzer operator's manual: ALPKEM, methodology section.

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 508-515.

Bendschneider, Kenneth, and Robinson, R.J., 1952, A new spectrophotometric method for the determination of nitrite in sea water: Journal of Marine Research, v. 11, p. 87-96.

Fox, J.B., 1979, Kinetics and mechanism of the Greiss reaction: Analytical Chemistry, v. 51, p. 1493-1502.

_____ 1985, The determination of nitrite, a critical review: CRC Critical Reviews in Analytical Chemistry, v. 15, p. 283-313.

Norwitz, George, and Keliher, P.N., 1985, Study of interferences in the spectrophotometric determination of nitrite using composite diazotization - coupling reagents: Analyst, v. 110, p. 689-694.

_____ 1986, Study of organic interferences in the spectrophotometric determination of nitrite using composite diazotization - coupling reagents: Analyst, v. 111, p. 1033-1037.

Pai, S.C., Yang, C.C., and Riley, J.P., 1990, Formation kinetics of the pink azo dye in the determination of nitrite in natural waters: Analytica Chimica Acta, v. 232, p. 345-349.

Shinn, M.B., 1941, A colorimetric method for the determination of nitrite (ann. ed.): Industrial Engineering Chemistry, v. 13, p. 33-35.

Nitrogen, nitrite, colorimetry, diazotization, automated-segmented flow

Parameter and Code:
Nitrogen, nitrite, dissolved, I-2540-90 (mg/L as N): 00613

1. Application

This method is used to analyze samples of surface, domestic, and industrial water and brines containing from 0.01 to 1.0 mg/L of nitrite-nitrogen. Concentrations greater than 1.0 mg/L must be diluted. This modified method was implemented in the National Water Quality Laboratory in March 1988.

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 (Shinn, 1941; Bendschneider and Robinson, 1952; Fox, 1979, 1985; Pai and others, 1990).

3. Interferences

Concentrations of potentially interfering substances generally are negligible. For specific details of inorganic and organic compounds that interfere with the reaction, see Norwitz and Keliher (1985, 1986) as well as more general information from the American Society for Testing and Materials (1991).

4. Apparatus

4.1 *Alpkem rapid flow analyzer (RFA)*, consisting of sampler, peristaltic pump, analytical cartridge, colorimeter, data station, and printer.

4.2 With this equipment, the following operating conditions are satisfactory for the range from 0.01 to 1.0 mg/L N:

Flow cell .....10 mm
Wavelength.....540 nm (or 520 nm)
Sampling rate.....90 per hour
Sample time.....24 seconds
Wash time.....16 seconds
Pecking .....ON
Damp (RC).....1 second

5. Reagents

5.1 *Color reagent*: Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to about 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 mL Brij-35 solution. Store in an amber bottle and refrigerate. The reagent is stable for about 1 month.

5.2 *Nitrite-nitrogen standard solution I*, 1.00 mL = 0.100 mg NO_2-N: Dissolve 0.6706 g KNO_2, dried overnight over sulfuric acid, in demineralized water and dilute to 1,000 mL. This solution and the following nitrite standard solutions (paragraphs 5.3 and 5.4) are not stable indefinitely; their concentrations need to be checked frequently.

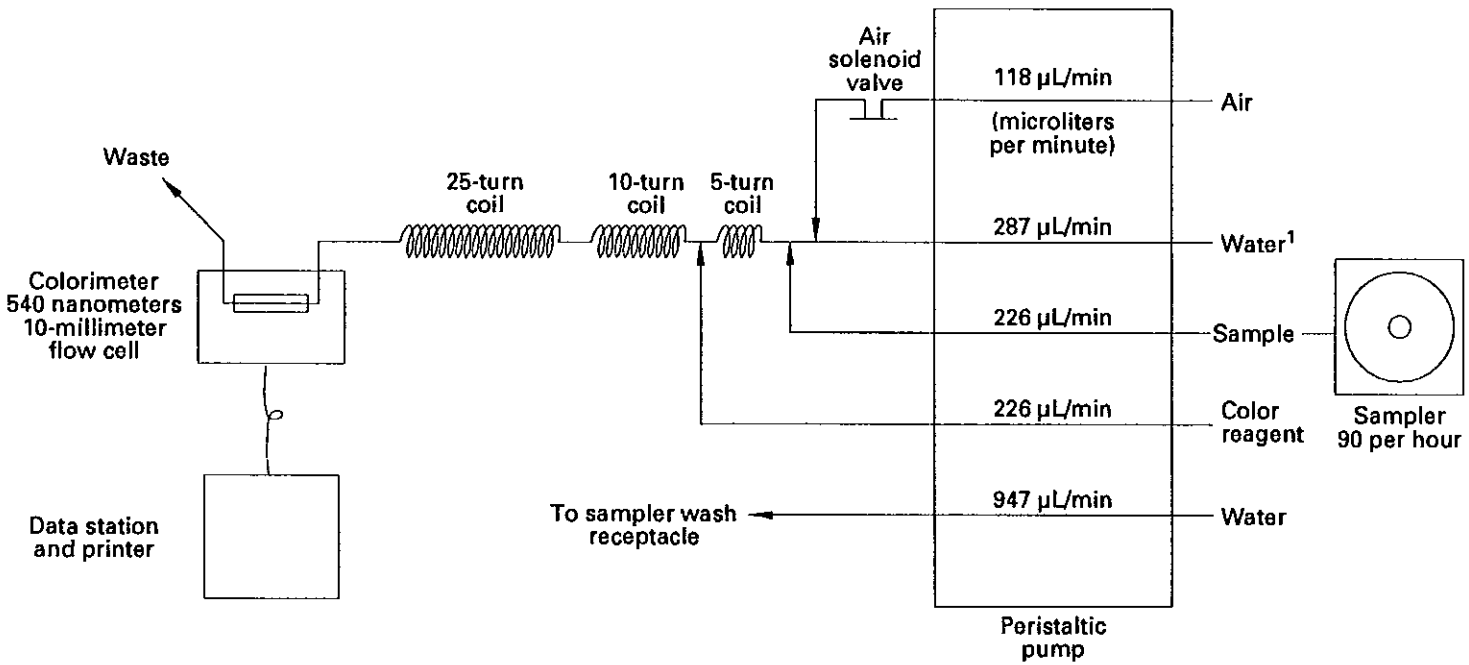
5.3 *Nitrite-nitrogen standard solution II*, 1.00 mL = 0.001 mg NO_2-N: Dilute 10.0 mL nitrite-nitrogen standard solution I to 1,000 mL with demineralized water.

5.4 *Nitrite-nitrogen working solutions*: Prepare a blank and 250 mL of a series of working solutions by appropriate dilution of nitrite-nitrogen standard solution II and appropriate working solutions, as listed in the following table. If the samples to be analyzed are preserved, the nitrite-nitrogen working solutions need to contain an equivalent concentration of the same preservative.

Working solution No.	Solution added (mL)	Solution used	Nitrite-nitrogen concentration (mg/L)
1	250	Standard solution II	1.00
2	125	Standard solution II	.50
3	50	Standard solution II	.20
4	25	Standard solution II	.10
5	25	Working solution No. 2	.05
6	25	Working solution No. 4	.01

6. Procedure

6.1 Set up manifold (fig. 6).



[1] Contains 0.5-milliliter Brij solution per liter.

Figure 6.—Nitrogen, nitrite, diazotization manifold.

6.2 Allow colorimeter recorder to warm for at least 10 minutes.

6.3 After all reagents are on line, adjust the sample output of the photometer to 5 V. Then switch the photometer to "absorbance" mode and use the reference detector "fine gain" control to adjust the baseline absorbance to about 0.2 V. See operation manuals for complete details (Alpkem Corp., 1986).

6.4 Place the most concentrated working solution in two cups before analysis. As the peaks appear on the recorder, adjust the STD CAL control until the peak obtains 95 percent of full scale.

6.5 When the system is clear of all working solutions, determine a dwell time using the most concentrated working solution.

6.6 Place a complete set of working solutions and a blank in the first positions of the sample tray beginning with the most concentrated working solution. Place individual working solutions of differing concentrations in approximately every tenth position on the tray following the accepted protocol. Fill the remainder of each tray with samples.

6.7 Begin analysis.

7. Calculations

7.1 Prepare an analytical curve by plotting the voltage of each working solution peak in relation to its respective nitrite-nitrogen concentration, or by using the RFA Softpac data reduction package. See operation manuals for complete details (Alpkem Corp., 1986).

7.2 Compute the concentration of dissolved nitrite-nitrogen in each sample either by comparing its voltage to the analytical curve or by using the software. Any baseline drift needs to be accounted for when computing the voltage of a sample or working solution peak; the RFA software automatically corrects for baseline drift.

8. Report

Report concentrations of nitrite-nitrogen, dissolved (00613), as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and greater, two significant figures.

9. Precision

Single operator precision for nitrite-nitrogen, as determined for natural-water samples, expressed as standard deviation and percentage relative standard deviation, is as follows:

Number of determinations	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
240	0.05	0.001	2.0
209	.03	.001	3.3
240	.26	.001	.38

References

Alpkem Corp., 1986, Rapid flow analyzer operator's manual: ALPKEM, methodology section.

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 508-515.

Bendschneider, Kenneth, and Robinson, R.J., 1952, A new spectrophotometric method for the determination of nitrite in sea water: Journal of Marine Research, v. 11, p. 87-96.

Fox, J.B., 1979, Kinetics and mechanism of the Greiss reaction: Analytical Chemistry, v. 51, p. 1493-1502.

_____ 1985, The determination of nitrite, a critical review: CRC Critical Reviews in Analytical Chemistry, v. 15, p. 283-313.

Norwitz, George, and Keliher, P.N., 1985, Study of interferences in the spectrophotometric determination of nitrite using composite diazotization - coupling reagents: Analyst, v. 110, p. 689-694.

_____ 1986, Study of organic interferences in the spectrophotometric determination of nitrite using composite diazotization - coupling reagents: Analyst, v. 111, p. 1033-1037.

Pai, S.C., Yang, C.C., and Riley, J.P., 1990, Formation kinetics of the pink azo dye in the determination of nitrite in natural waters: Analytica Chimica Acta, v. 232, p. 345-349.

Shinn, M.B., 1941, A colorimetric method for the determination of nitrite (ann. ed.): Industrial Engineering Chemistry, v. 13, p. 33-35.

Nitrogen, nitrite plus nitrate, low ionic-strength water, colorimetry, cadmium reduction-diazotization, automated-segmented flow

Parameter and Code:
Nitrogen, nitrite plus nitrate, dissolved, I-2546-91 (mg/L as N): 00631

1. Application

This method is used to analyze samples of precipitation or natural water, containing from 0.005 to 1.0 mg/L of nitrite- plus nitrate-nitrogen. Concentrations greater than 1.0 mg/L must be diluted. This method was implemented in the National Water Quality Laboratory in March 1986 and modified in May 1989.

2. Summary of method

Nitrate is reduced to nitrite by cadmium metal. The sample stream then is treated with sulfanilamide under acidic conditions to yield a diazo compound, which couples with N-1-naphthylethylenediamine dihydrochloride to form an azo dye, the absorbance of which is measured colorimetrically. The result is the sum of the nitrite originally present plus that formed by the reduction of the nitrate (Morris and Riley, 1963; Brewer and Riley, 1965; Wood and others, 1967; Strickland and Parsons, 1972; Nydahl, 1976; Sherwood and Johnson, 1981; Patton, 1982; U.S. Environmental Protection Agency, 1983).

3. Interferences

3.1 Concentrations of potentially interfering substances generally are negligible in unpolluted surface and ground water. For specific details of inorganic and organic compounds that interfere, see Norwitz and Keliher (1985, 1986) as well as more general information from the American Society for Testing and Materials (1991).

3.2 Sulfides, often present in anoxic water, rapidly deactivate cadmium reactors by forming an insoluble layer of cadmium sulfide on the active metal surface (Strickland and Parsons, 1972).

3.3 The buffer capacity of the imidazole solution and the approximate 10:1 volume ratio of buffer to sample eliminate the possibility of erroneous results for moderately acidic ($pH \geq 1$) samples.

4. Apparatus

4.1 *Alpkem rapid flow analyzer (RFA),* consisting of sampler, peristaltic pump, analytical cartridge (including copper-cadmium reduction column), colorimeter, data station, and printer.

4.2 With this equipment, the following operating conditions are satisfactory for the range from 0.005 to 1.0 mg/L ($NO_2 + NO_3$) as N:

Flow cell .....10 mm
Wavelength.....540 nm
Sample time.....24 seconds
Sampling rate.....64 per hour
Wash time.....32 seconds
Pecking .....OFF
Damp (RC).....1 second

5. Reagents

5.1 *Brij-35 solution,* 30-percent aqueous solution.

5.2 *Cadmium powder,* 100 mesh: Weigh 10 g cadmium powder into a 50-mL Griffin beaker and wash with 1*M* HCl. Stir vigorously to break clumps of cadmium formed by the addition of HCl. Rinse with copper sulfate solution (20 g/L). Wash thoroughly with imidazole solution to remove colloidal copper which is visible as a blue color in the wash solution. A minimum of five washings usually is required to eliminate perceptible blue color. Store in imidazole solution.

5.3 *Cadmium reduction column:* The reduction column is 4 cm long, 1/8-in. OD standard Teflon tubing (about 3.0-mm OD x 1.5-mm ID). Plugs to retain the cadmium in the column are cut from a sheet of hydrophilic, porous plastic with an average pore size of 40 µm. The cadmium column is plugged at the bottom with a plastic frit and attached to a syringe filled with imidazole solution. A custom-made funnel is attached to the top of the cadmium column, and the column and part of the funnel are filled with imidazole solution. The cadmium is added slowly to prevent air bubbles and pockets. Decant the solution in the funnel to facilitate the insertion of the top frit without introducing air to the column. The reduction efficiency of the column needs to 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 to less than 90 percent.

5.4 *Color reagent*: Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to about 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 mL Brij-35 solution. Store in an amber bottle and refrigerate. This reagent is stable for about 1 month.

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

5.6 *Hydrochloric acid, 1M*: Add 83 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.7 *Imidazole solution:* Dissolve 6.8 g of imidazole in demineralized water. Stir and dilute to about 950 mL. Adjust pH to 7.5 $\pm$ 0.1 with concentrated HCl (about 4 mL). Add 0.5 mL copper sulfate solution and dilute to 1 L. Add 1 mL Brij-35 solution.

5.8 *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 L.

5.9 *Nitrate-nitrogen standard solution II*, 1.00 mL = 0.005 mg NO_3-N: Dilute 10.0 mL nitrate-nitrogen standard solution I to 1,000 mL with demineralized water.

5.10 *Nitrate-nitrogen working solutions:* Prepare a blank and 200 mL of a series of working solutions by appropriate dilution of nitrate-nitrogen standard solution II or working solution No. 3 as listed in the following table. If the samples to be analyzed are preserved, the nitrate-nitrogen working solutions need to contain an equivalent concentration of the same preservative.

Working solution No.	Solution added (mL)	Solution used	Nitrate-nitrogen concentration (mg/L)
1	40	Standard solution II	1.000
2	20	Standard solution II	.500
3	10	Standard solution II	.250
4	2	Standard solution II	.050
5	20	Working solution No. 3	.025
6	8	Working solution No. 3	.010
7	4	Working solution No. 3	.005

6. Procedure

6.1 Set up manifold (fig. 7).

6.2 Allow colorimeter recorder to warm for at least 10 minutes.

6.3 Allow the color reagent to come to room temperature.

6.4 Begin pumping reagents but do not connect the reduction column to the analytical cartridge until all air has been removed from the reagent and sample tubes (NOTE 1).

NOTE 1. 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 needs to be replaced if air bubbles are introduced.

6.5 After all reagents are on line, adjust the sample output of the photometer to 5 V. Then switch the photometer to "absorbance" mode and use the reference detector "fine gain" control to adjust the baseline absorbance to about 0.2 V. See operation manuals for complete details (Alpkem Corp., 1986).

6.6 Place the most concentrated working solution in two cups before analysis. As the peaks appear on the recorder, adjust the STD CAL control until the peak obtains 95 percent of full scale.

6.7 When the system is clear of all working solutions, determine a dwell time using the most concentrated working solution.

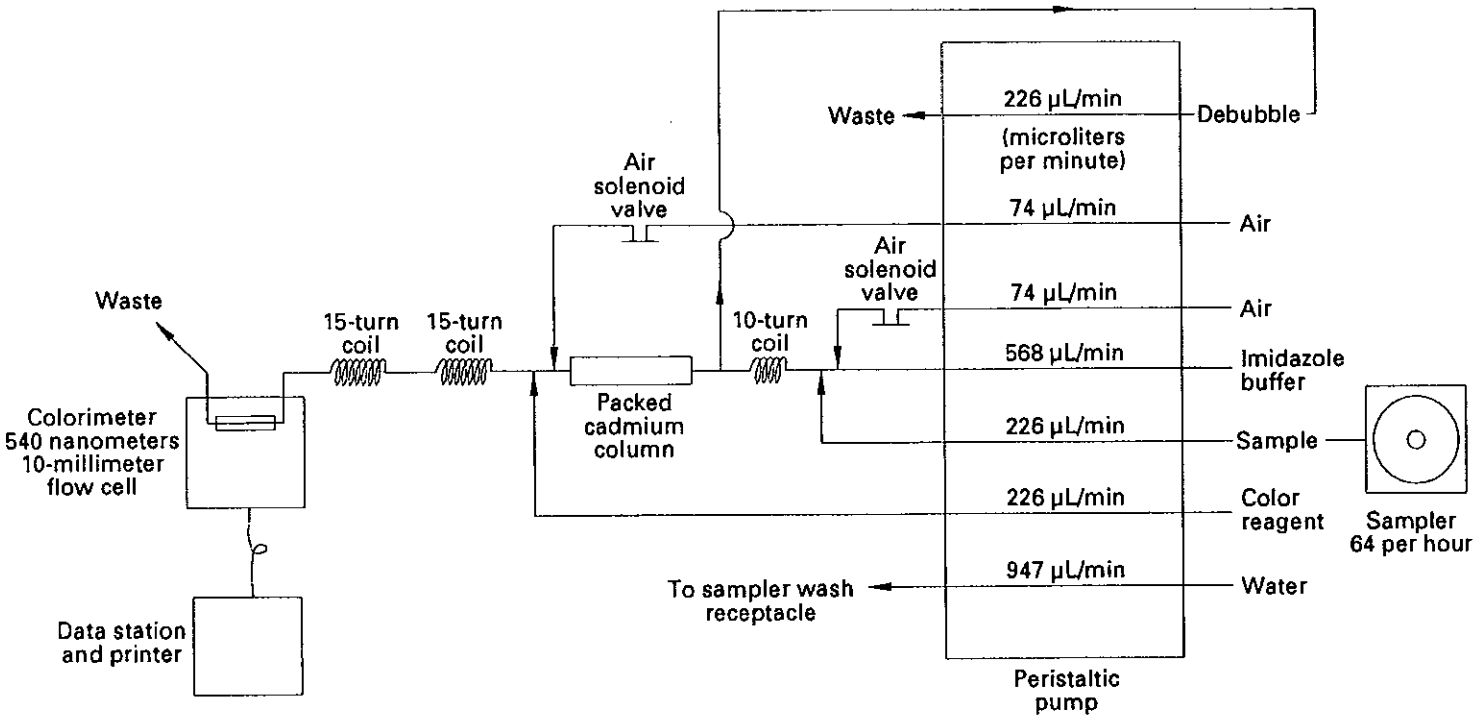


Figure 7.—Nitrogen, nitrite plus nitrate, low ionic-strength water, cadmium reduction-diazotization manifold.

6.8 Place a complete set of working solutions and a blank in the first positions of the sample tray beginning with the most concentrated working solution. Place individual working solutions of differing concentrations in about every eighth position on the tray following the accepted protocol. Fill the remainder of each tray with unknown samples.

6.9 Begin analysis.

7. Calculations

7.1 Prepare an analytical curve by plotting the voltage of each working solution peak in relation to its respective nitrite- plus nitrate-nitrogen concentration, or by using the RFA Softpac data reduction package. See operation manuals for complete details (Alpkem Corp., 1986).

7.2 Compute the concentration of dissolved nitrite- plus nitrate-nitrogen in milligrams per liter in each sample either by comparing its voltage to the analytical curve or by using the software. Any baseline drift needs to be accounted for when computing the voltage of a sample or working solution peak; the RFA software automatically corrects for baseline drift.

8. Report

Report concentrations of nitrogen, nitrite plus nitrate, dissolved (00631), as follows: 0.005 to 0.10 mg/L, three decimals; 0.10 mg/L and greater, two significant figures.

9. Precision

Single operator precision for nitrite- plus nitrate-nitrogen, as determined for natural-water samples, expressed as standard deviation and percentage relative standard deviation, is as follows:

Number of determinations	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
11	0.009	0.001	11.1
21	.105	.006	5.7
22	.465	.015	3.2
22	.717	.011	1.5

References

Alpkem Corp., 1986, Rapid flow analyzer operator's manual: ALPKEM, methodology section.

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 508-515.

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

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Norwitz, George, and Keliher, P.N., 1985, Study of interferences in the spectrophotometric determination of nitrite using composite diazotization-coupling reagents: Analyst, v. 110, p. 689-694.

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U.S. Environmental Protection Agency, 1983, Methods for the chemical analysis of water and wastes: Washington, D.C., U.S. Government Printing Office, p. 353.2-1.

Wood, E.D., Armstrong, F.A.J., and Richards, F.A., 1967, Determination of nitrate in sea water by cadmium-copper reduction to nitrite: Journal of Marine Biology Association, U.K., v. 47, p. 23-31.

Nitrogen, nitrite plus nitrate, colorimetry, cadmium reduction-diazotization, automated-segmented flow

Parameters and Codes:
Nitrogen, nitrite plus nitrate, dissolved, I-2545-90 (mg/L as N): 00631
Nitrogen, nitrite plus nitrate, total-in-bottom-material, dry weight, I-6545-90 (mg/kg as N): 00633

1. Application

1.1 This method is used to analyze samples of surface, domestic, and industrial water and brines containing from 0.1 to 5.0 mg/L of nitrite- plus nitrate-nitrogen. Samples containing greater concentrations must be diluted. This modified method was implemented in the National Water Quality Laboratory in March 1988.

1.2 This method is used to determine the sum of nitrite- plus nitrate-nitrogen concentrations in samples of 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 samples of bottom material for this determination (Jackson, 1958).

2.2 Nitrate is reduced to nitrite by cadmium metal. Imidazole is used to buffer the analytical stream. The sample stream then is treated with sulfanilamide to yield a diazo compound, which couples with N-1-naphthylethylenediamine dihydrochloride to form an azo dye, the absorbance of which is measured colorimetrically. The result is the sum of the nitrite originally present plus that formed by the reduction of the nitrate (Morris and Riley, 1963; Brewer and Riley, 1965; Wood and others, 1967; Strickland and Parsons, 1972; Nydahl, 1976; Sherwood and Johnson, 1981; Patton, 1982; U.S. Environmental Protection Agency, 1983).

3. Interferences

3.1 Concentrations of potentially interfering substances generally are negligible in unpolluted surface and ground water. For specific details of inorganic and organic compounds that interfere, see Norwitz and Keliher (1985, 1986) as well as more general information from the American Society for Testing and Materials (1991).

3.2 Sulfides, often present in anoxic water, rapidly deactivate cadmium reactors by forming an insoluble layer of cadmium sulfide on the active metal surface (Strickland and Parsons, 1972).

3.3 The buffer capacity of the imidazole solution and the approximate 10:1 volume ratio of buffer to sample eliminate the possibility of erroneous results for moderately acidic ($pH \geq 1$) samples.

3.4 Mercury (II) does not interfere. It rapidly forms an amalgam on the inlet end of the cadmium reactor without detriment to the reduction reaction.

4. Apparatus

4.1 *Centrifuge.*

4.2 *Shaker,* wrist-action.

4.3 *Alpkem rapid flow analyzer (RFA),* consisting of sampler, peristaltic pump, analytical cartridge (including copper-cadmium reduction column), colorimeter, data station, and printer.

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

Flow cell.....10 mm
Wavelength.....520 nm
Sample time.....24 seconds
Sampling rate.....90 per hour
Wash time.....16 seconds
Pecking .....ON
Damp (RC).....1 second

5. Reagents

5.1 *Brij-35 solution,* 30-percent aqueous solution.

5.2 *Cadmium powder,* 100 mesh: Weigh 10 g cadmium powder into a 50-mL Griffin beaker and wash with 1*M* HCl. Stir vigorously to break clumps of cadmium formed by the addition of HCl. Rinse with copper sulfate solution (20 g/L). Wash thoroughly with imidazole solution to remove colloidal copper which is visible as a blue color in the wash solution. A minimum of five washings usually is required to eliminate perceptible blue color. Store in imidazole solution.

5.3 *Cadmium reduction column:* The reduction column is 4 cm long, 1/8-in. OD standard Teflon tubing (about 3.0 mm OD x 1.5 mm ID). Plugs to retain the cadmium in the column are cut from a sheet of hydrophilic, porous plastic with an average pore size of 40 µm. The cadmium column is plugged at the bottom with a plastic frit and attached to a syringe filled with imidazole solution. A custom-made funnel is attached to the top of the cadmium column, and the column and part of the funnel are filled with imidazole solution. The cadmium is added slowly to prevent air bubbles and pockets. Decant the solution in the funnel to facilitate the insertion of the top frit without introducing air to the column. The reduction efficiency of the column needs to be checked regularly by comparing the peak heights of nitrite and nitrate standards. Equal concentration standards give equal heights. Replace the column if the efficiency falls to less than 90 percent.

5.4 *Color reagent:* Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to about 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 mL Brij-35 solution. Store in an amber bottle and refrigerate. This reagent is stable for about 1 month.

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

5.6 *Hydrochloric acid, 1M:* Add 83 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.7 *Imidazole solution*: Dissolve 6.8 g of imidazole in demineralized water. Stir and dilute to about 950 mL. Adjust pH to 7.5 $\pm$ 0.1 with concentrated HCl (about 4 mL). Add 0.5 mL copper sulfate solution and dilute to 1 L. Add 1 mL Brij-35 solution.

5.8 *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 L.

5.9 *Nitrate-nitrogen standard solution II,* 1.00 mL = 0.005 mg NO_3-N: Dilute 10.0 mL nitrate-nitrogen standard solution I to 1,000 mL with demineralized water.

5.10 *Nitrate-nitrogen working solutions:* Prepare a blank and 200 mL of a series of working solutions by appropriate dilution of nitrate-nitrogen standard solutions I and II, as listed in the following table. If the samples to be analyzed are preserved, the nitrate-nitrogen working solutions need to contain an equivalent concentration of the same preservative.

Working solution No.	Solution added (mL)	Solution used	Nitrate-nitrogen concentration (mg/L)
1	2	Standard solution II	5.00
2	1	Standard solution I	2.50
3	40	Standard solution II	1.00
4	20	Standard solution II	.50
5	10	Working solution II	.25
6	4	Working solution II	.10

5.11 *Sodium chloride solution,* 100 g/L, acidified: Dissolve 100 g NaCl in 950 mL demineralized 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 processing samples of water. For bottom material, begin with paragraph 6.1.1.

6.1.1 Weigh about 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 (paragraph 5.11) and shake on the wrist-action shaker for 30 minutes.

6.1.3 Carefully transfer the entire sample, including all sediment particles, to a centrifuge tube. Centrifuge for 5 minutes; 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 a

volumetric flask. Adjust to volume with sodium chloride solution (5.11). Proceed to paragraph 6.2.

6.2 Set up manifold (fig. 8).

6.3 Allow the color reagent to come to room temperature.

6.4 Allow colorimeter and recorder to warm for at least 10 minutes.

6.5 Begin pumping reagents but do not connect the reduction column to the analytical cartridge until all air has been removed from the reagent and sample tubes (NOTE 1).

NOTE 1. It is important to avoid introduction of air bubbles to the reduction column because they adversely affect sample contact with the cadmium powder and decrease the reduction efficiency. Column needs to be replaced if air bubbles are introduced.

6.6 After all reagents are on line, adjust the sample output of the photometer to 5 V. Then switch the photometer to "absorbance" mode and use the reference detector "fine gain" control to adjust the baseline absorbance to about 0.2 V. See operation manuals for complete details (Alpkem Corp., 1986).

6.7 Place the most concentrated working solution in two cups before analysis. As the peaks appear on the recorder, adjust the STD CAL control until the peak obtains 95 percent of full scale.

6.8 When the system is clear of all working solutions, determine a dwell time using the most concentrated working solution.

6.9 Place a complete set of working solutions and a blank in the first positions of the sample tray, beginning with the most concentrated working solution. Place individual working solutions of differing concentrations in about every eighth position on the tray following the accepted protocol. Fill remainder of each tray with unknown samples.

6.10 Begin analysis.

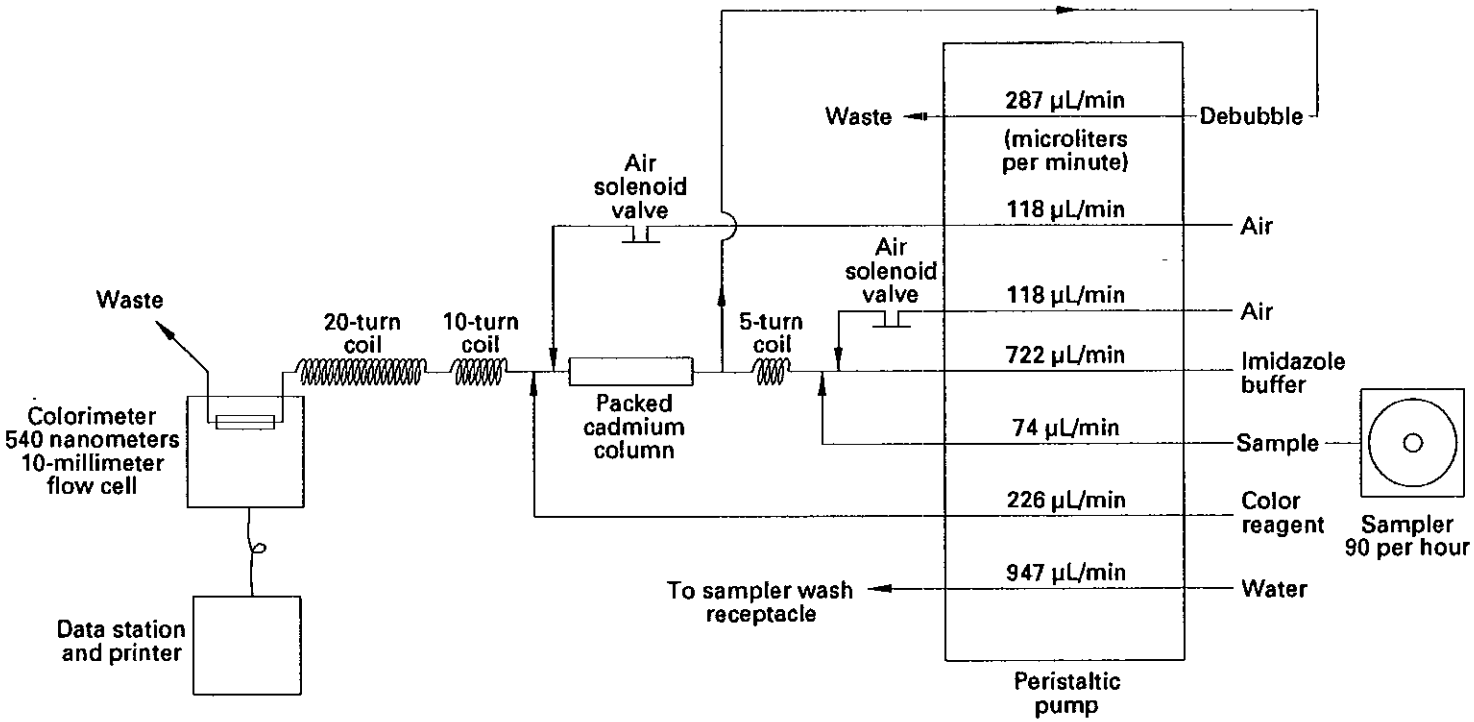

Figure 8.—Nitrogen, nitrite plus nitrate, cadmium reduction-diazotization manifold.

7. Calculations

7.1 Prepare an analytical curve by plotting the voltage of each working solution peak in relation to its respective nitrite- plus nitrate-nitrogen concentration, or by using the RFA Softpac data reduction package. See operation manuals for complete details (Alpkem Corp., 1986).

7.2 Compute the concentration of dissolved nitrite- plus nitrate-nitrogen in milligrams per liter in each sample either by comparing its voltage to the analytical curve or by using the software. Any baseline drift needs to be accounted for when computing the voltage of a sample or working solution peak; the RFA software automatically corrects for baseline drift.

7.3 Compute the concentration of nitrite- plus nitrate-nitrogen in each bottom material sample in milligrams per liter either by comparing its voltage to the analytical curve or by using the software. Any baseline drift needs to be accounted for when computing the voltage 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 $C_N = NO_3\text{-}N + NO_2\text{-}N$ concentration in sample, in milligrams per liter.

8. Report

8.1 Report concentrations of nitrogen, nitrite plus nitrate, dissolved (00631), as follows: 0.1 to 1.0 mg/L, two decimals; 1.0 mg/L and greater, two significant figures.

8.2 Report concentrations of nitrogen, nitrite plus nitrate, total-in-bottom-material (00633), as follows: less than 10 mg/kg, one decimal; 10 mg/kg and greater, two significant figures.

9. Precision and accuracy

9.1 Within-analytical run precision (repeatability) data for natural-water samples with "large", "medium", and "small" concentrations of dissolved nitrite-plus nitrate-nitrogen are shown in the following table. In each case, the mean, standard deviation, and percentage of relative deviation result from five replicate determinations of each sample, which were performed at an analysis rate of 90

samples per hour. Sample interaction was 1 percent. During this analytical run, four different samples in the medium concentration range were spiked at a level of 1 mg/L. The average recovery was 96.2 percent.

Sample No.	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
1	0.55	0.004	0.7
2	2.66	.016	.6
3	4.82	.014	.3

9.2 Between-day precision was estimated from dissolved nitrite- plus nitrate-nitrogen concentrations determined for standard reference water samples submitted as blind samples from March 1990 to March 1992. Data listed in the following table indicate long-term accuracy of the method with typical between-day precision in the range from 3 to 6 percent:

Standard reference water sample	Number of replicates	Concentration found (mg/L)	Most probable concentration (mg/L)
N-21	24	0.56 ± 0.03	0.58 ± 0.02
N-22	8	1.47 ± 0.04	1.54 ± 0.03
N-23	15	0.92 ± 0.08	0.97 ± 0.03
N-24	8	2.05 ± 0.70	1.82 ± 0.05
N-26	9	0.27 ± 0.06	0.29 ± 0.02
N-27	15	1.51 ± 0.16	1.66 ± 0.04
N-28	30	0.34 ± 0.02	0.36 ± 0.01
N-29	41	1.15 ± 0.04	1.23 ± 0.02
N-30	33	0.39 ± 0.02	0.41 ± 0.05
N-31	32	1.41 ± 0.04	1.42 ± 0.10
N-32	5	0.13 ± 0.00	0.14 ± 0.04
N-33	10	0.59 ± 0.02	0.59 ± 0.06

9.3 It is estimated that the percentage relative standard deviation for total nitrite- plus nitrate-nitrogen in bottom material will be greater than that reported for dissolved nitrite- plus nitrate-nitrogen.

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Nitrogen, total, pyrochemiluminescence

Parameter and Code:
Nitrogen, total, dissolved, I-2511-90 (mg/L as N): 00600

1. Application

This method is used to determine total nitrogen concentrations up to 5.00 mg/L in samples of natural water. Samples containing concentrations greater than 5.00 mg/L must be diluted. This method currently is valid only for water samples which have been filtered through a 0.45-µm filter. The method was implemented in the National Water Quality Laboratory in November 1989.

2. Summary of method

All forms of nitrogen are converted to nitrous oxide gas in a 1,100°C oven under an oxygen-rich atmosphere. Nitrous oxide is reacted with ozone to create nitrogen dioxide in an excited state. A photon then is emitted and subsequently detected using a photodetector. Emission is proportional to the concentration of total nitrogen in the sample (Van Hall and others, 1963; Winer and others, 1974; Jones and Daughton, 1985).

3. Interferences

Compounds containing N-N or N=N azo-linkages will yield less than 100-percent recoveries because of their difficulty to form the nitrous oxide gas.

4. Apparatus

4.1 *Total nitrogen analyzer*, Antek No. 720C consisting of furnace, detector, autosampler PC with Delta software package or equivalent.

4.2 With this equipment, the following operating conditions are satisfactory for the range from 0.1 to 5.00 mg/L nitrogen:

Furnace temperature.....1,100°C
Atmosphere.....100-percent oxygen
Rinse pressure.....2 lb/in^2
Sample size.....5 µL

5. Reagents

5.1 *Oxygen*, reagent grade oxygen gas.

5.2 *Nitrite-nitrogen stock solution,* 1.00 mL = 0.100 mg NO_2-N: Dissolve 0.6076 g potassium nitrite (KNO_2) in demineralized water and dilute to 1,000 mL. This standard solution is not stable indefinitely. Refrigerate and check periodically.

5.3 *Nitrate-nitrogen stock solution,* 1.00 mL = 0.50 mg NO_3-N: Dissolve 3.609 g potassium nitrate (KNO_3), dried overnight over concentrated sulfuric acid (sp gr 1.84), in demineralized water, and dilute to 1,000 mL. Refrigerate.

5.4 *Ammonia-nitrogen stock solution,* 1.00 mL = 0.50 mg NH_3-N: Dissolve 1.909 g ammonium chloride (NH_4Cl), dried overnight over concentrated sulfuric acid (sp gr 1.84), in demineralized water, and dilute to 1,000 mL. Refrigerate.

5.5 *Combined nitrogen standard solution,* 1.00 mL = 0.05 mg N. Add to a 1,000-mL volumetric flask the following: 150 mL nitrite-nitrogen stock solution, 30 mL nitrate-nitrogen stock solution, and 40 mL ammonia-nitrogen stock solution. Dilute to 1,000 mL and refrigerate.

5.6 *Nitrogen working solutions*: Prepare a nitrogen-free blank and 250 mL each of a series of total nitrogen working solutions by dilution of the combined nitrogen standard solution as listed in the following table. If the samples to be analyzed are preserved, the nitrogen working solutions need to contain an equivalent concentration of the same preservative.

Working solution No.	Combined nitrogen standard solution (mL)	Nitrogen concentration (mg/L)
1	0.50	0.10
2	1.00	.20
3	3.00	.60
4	5.00	1.00
5	10.0	2.00
6	20.0	5.00

6. Procedure

6.1 Allow the furnace to stabilize to a temperature of about 1,100°C.

6.2 Optimize the oxygen flow by running check standards made of the individual nitrogen species (NO_2-N, NO_3-N, and NH_3-N). Oxygen flow is correct when full nitrogen recovery is attained for each of the nitrogen species being tested.

6.3 Program the software for the correct number of standards and samples.

6.4 Analyze working solutions from largest to smallest concentration. Monitor analytical curve for linearity.

6.5 During each run, analyze at least one set of individual check standards prior to analysis of samples to ensure full recovery of each of the nitrogen species present.

6.6 A blank and a standard reference material need to be analyzed at least once every 10 samples. System needs to be re-calibrated at least once every 6 h to ensure reliable accuracy.

7. Calculations

7.1 Prepare an analytical curve by plotting the voltage for each working solution against its respective concentration, or use the system software to perform the function if available.

7.2 Compute the concentration of dissolved nitrogen in each sample by comparing its voltage to the analytical curve or by using the software functions.

8. Report

Report concentrations of total nitrogen, dissolved (00600), as follows: less than 10.0 mg/L, one decimal; 10 mg/L and greater, two significant figures.

9. Precision

Single operator precision for total nitrogen as determined for natural-water samples, expressed as standard deviation and percentage relative standard deviation, is as follows:

Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
0.110	0.037	33.6
.430	.037	8.6
.900	.048	5.3
1.35	.065	4.8
1.43	.091	6.4
1.83	.059	3.2
1.90	.059	3.1
2.89	.092	3.2

References

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pH, low ionic-strength water, electrometry, automated

Parameter and code:
pH, I-2588-90: (units): 00403

1. Application

This method is used to determine the pH of samples of low ionic-strength natural water, specifically snow melt or precipitation. Samples analyzed by this method need to have a specific conductance of less than 100 µS/cm. The method was implemented in the National Water Quality Laboratory in January 1987.

2. Summary of method

See the introduction to electrometry for the principles of pH meter operation (Fishman and Friedman, 1989). See also Barnes (1964), Bates (1973), and Willard and others (1974).

3. Interferences

3.1 The low-hydrogen ion activity of low ionic-strength samples can make this a difficult determination because of slow reaction by the electrode.

3.2 The pH measurement is temperature dependent, and a significant error results if the temperatures of the buffers and samples differ appreciably. A variation of 3°C or less usually is not significant.

4. Apparatus

4.1 *pH meter*, Radiometer PHM 84 with temperature compensator or equivalent.

4.2 *Autosampler*, Radiometer SAC 80 or equivalent.

4.3 *Microcomputer*, Hewlett-Packard 85B or equivalent.

4.4 *pH electrode*, Orion 810300 semi-micro or equivalent (NOTES 1 and 2).

NOTE 1. The pH electrode and sample(s) are enclosed in a nitrogen atmosphere.

NOTE 2. New glass electrodes are soaked in pH 7.00 buffer solution for at least one day before the electrodes are installed on line. The electrode is stored in pH 7.00 buffer when it is not in use.

5. Reagents

Standard buffer solutions, pH 4.00 and 7.00. These buffers need to cover the range of pH of the samples to be measured. For low ionic-strength samples, the pH will seldom be greater than 7.00 or less than 4.00. Commercially made buffer solutions are satisfactory.

6. Procedure

6.1 After an appropriate warm-up period, standardize the instrument using the pH 4.00 and 7.00 buffer solutions. Samples and buffers need to be at the same temperature, and standardization needs to be carried out under a nitrogen blanket.

6.2 With constant stirring, the computer directs the arm of the autosampler to immerse the electrode in the sample for 5 minutes.

6.3 After 5 minutes, the microcomputer instructs the autosampler to remove the electrode from the sample, rotate to the next cup, and immerse the arm in a duplicate aliquot of sample. The computer turns off the stir motor and begins monitoring the pH for about 5 minutes or until the electrode has stabilized enough to produce values with a deviation less than 0.03 pH per 30 seconds.

6.4 The system soaks the electrode thoroughly with deionized water for 2 minutes between each sample.

7. Calculations

The pH value is read directly from the pH meter and sent through an analog to digital converter to the microcomputer where it is processed and printed.

8. Report

Report pH (00403) to the nearest 0.1.

9. Precision

Single operator precision for pH for three samples is as follows:

Mean (pH)	Standard deviation (pH)
6.08	0.069
5.52	.098
6.97	.088

References

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(p. 175 follows)

Phosphorus, low ionic-strength water, colorimetry, phosphomolybdate, automated-segmented flow

Parameters and Codes:
Phosphorus, dissolved, I-2607-90 (mg/L as P): 00666
Phosphorus, total, I-4607-90 (mg/L as P): 00665

1. Application

This method is used to analyze samples of precipitation or natural water with a specific conductance of less than 100 µS/cm containing from 0.001 to 0.20 mg/L of phosphorus. Concentrations greater than 0.20 mg/L must be diluted. This method was implemented in the National Water Quality Laboratory in March 1990.

2. Summary of method

2.1 All forms of phosphorus, including organic phosphorus compounds, 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 reaction with ascorbic acid produces an intensely blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales and others, 1966; Pai and others, 1990).

3. Interferences

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

3.2 Arsenic as arsenate (AsO_4^{-3}) produces a similar color as phosphate (Murphy and Riley, 1962) and might cause a positive interference. Arsenic concentrations as much as 100 µg/L do not interfere.

4. Apparatus

4.1 *Autoclave.*

4.2 *Alpkem rapid flow analyzer (RFA),* consisting of sampler, analytical cartridge, peristaltic pump, heating bath, colorimeter, data station, and printer.

4.3 With this equipment, the following operating conditions are satisfactory for the range from 0.001 to 0.200 mg/L P:

Flow cell	30 mm
Wavelength	880 nm
Sample time	38 seconds
Sampling rate	60 per hour
Wash time	22 seconds
Heating bath (2 mL)	37°C
Pecking	OFF
Damp (RC)	4 seconds

4.4 *Glass tubes with plastic caps,* disposable, 16 x 150 mm.

5. Reagents

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

5.2 *Ascorbic acid solution,* 18 g/L: Dissolve 18 g ascorbic acid ($C_6H_8O_6$) in 800 mL demineralized water and dilute to 1 L. Keep in 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 $K(SbO)C_4H_4O_6{\cdot}1/2H_2O$ in 800 mL demineralized water and dilute to 1 L.

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

Sulfuric acid, 2.45*M*	100 mL
Ammonium molybdate solution	30 mL
Ascorbic acid solution	60 mL
Antimony potassium tartrate solution	10 mL

5.5 *Sodium lauryl sulfate (SLS) solution*, 15 percent w/w: Dissolve 30 g SLS in 170 mL demineralized water. CAUTION: Solid sodium lauryl sulfate is a nasal irritant; work in a well-ventilated hood. Place flask in an ultrasonic bath to aid in dissolving SLS.

5.6 *Phosphorus standard solution I*, 1.00 mL = 0.100 mg P: Dissolve 0.4394 g KH_2PO_4, dried overnight over concentrated sulfuric acid (sp gr 1.84), in demineralized water and dilute to 1,000 mL.

5.7 *Phosphorus standard solution II*, 1.00 mL = 0.001 mg P: Dilute 10 mL phosphorus standard solution I to 1,000 mL with demineralized water.

5.8 *Phosphorus working solutions*: Prepare a blank and 1,000 mL each of a series of working solutions by appropriate dilution of phosphorus standard solutions I and II, as listed in the following table. If the samples to be analyzed are preserved, the phosphorus working solutions need to contain an equivalent concentration of the same preservative.

Working solution No.	Solution added (mL)	Solution used	Phosphorus concentration (mg/L)
1	2	Standard solution I	0.200
2	1	Standard solution I	.100
3	50	Standard solution II	.050
4	10	Standard solution II	.010
5	5	Standard solution II	.005
6	1	Standard solution II	.001

5.9 *Sulfuric acid solution, 2.45M:* Cautiously, add slowly, with constant stirring, 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL demineralized water. Cool, and dilute to 1,000 mL with demineralized water.

5.10 *Phosphorus catalyst*: Add slowly 25 mL concentrated sulfuric acid and 4.0 g potassium persulfate ($K_2S_2O_8$) to 1,800 mL demineralized water and dilute to 2 L.

5.11 *Water diluent:* Add 5 mL sodium lauryl sulfate solution to 250 mL demineralized water.

6. Procedure

6.1 Pipet a volume of well-mixed sample containing less than 0.002 mg total phosphorus (10.0 mL maximum) into a disposable glass tube, and adjust volume to 10 mL.

6.2 Pipet 10 mL of blank and each of the working solutions into disposable glass tubes.

6.3 Add 4.0 mL phosphorus catalyst to each sample, working solution, and blank.

6.4 Place plastic caps on top of tubes. Autoclave for 30 minutes at 15 lb/in^2 pressure.

6.5 Set up manifold (fig. 9).

6.6 Allow colorimeter, recorder, and heating bath to warm up for at least 10 minutes or until the heating bath temperature reads 37°C.

6.7 After all reagents are on line, adjust the sample output of the photometer to 5 V. Then switch the photometer to "absorbance" mode and use the reference detector "fine gain" control to adjust the baseline absorbance to about 0.2 V. See operation manuals for complete details (Alpkem Corp., 1986).

6.8 Place the most concentrated working solution in two cups before analysis. As the peaks appear on the recorder, adjust the STD CAL control until the peak obtains 95 percent of full scale.

6.9 When the system has cleared of all working solutions, determine a dwell time using the most concentrated working solution.

6.10 Place a complete set of working solutions and a blank in the first positions of the first sample tray, beginning with the most concentrated working solution. Place individual working solutions of differing concentrations in approximately every eighth position on the tray following the accepted protocol. Fill the remainder of each tray with unknown samples.

6.11 Begin analysis.

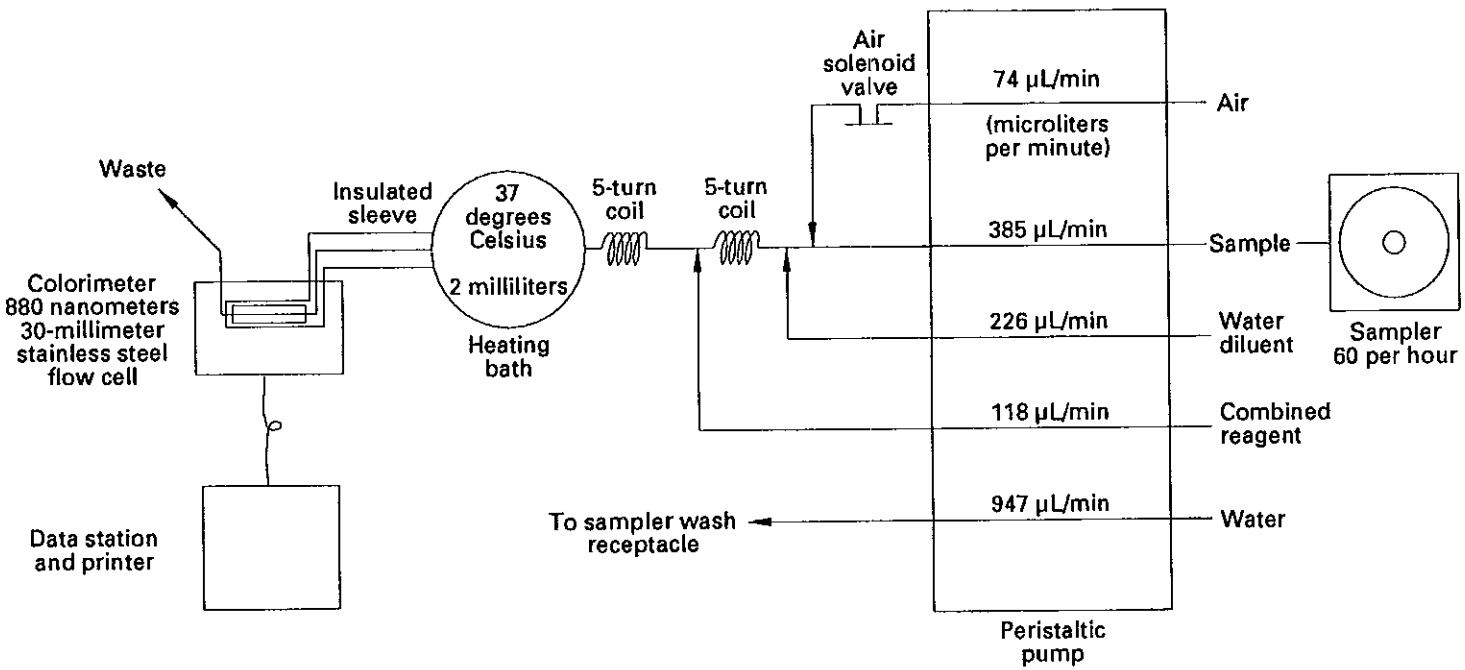

Figure 9.—Phosphorus, low ionic-strength water, phosphomolybdate manifold.

7. Calculations

7.1 Prepare an analytical curve by plotting the voltage of each working solution peak in relation to its respective phosphorus concentration, or by using the RFA Softpac data reduction package. See operation manual for complete details (Alpkem Corp., 1986).

7.2 Compute the concentration of dissolved or total phosphorus in each sample either by comparing its voltage to the analytical curve or by using the software. Any baseline drift needs to be accounted for when computing the voltage of a sample or working solution peak; the RFA software automatically corrects for baseline drift.

8. Report

Report concentrations of phosphorus, dissolved (00666), or phosphorus, total (00665), as follows: less than 0.10 mg/L, three decimals; 0.10 mg/L and greater, two significant figures.

9. Precision

Single operator precision for dissolved and total phosphorus, as determined for natural-water samples, expressed as standard deviation and percentage relative standard deviation, is as follows:

Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
0.177	0.005	2.69
.176	.004	2.17
.092	.006	6.89
.038	.002	6.64
.004	.001	31.43

References

Alpkem Corp., 1986, Rapid flow analyzer operator's manual: ALPKEM, methodology section.

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 -1368.

Murphy, J., and Riley, J.P., 1962, A modified single-solution method for the determination of phosphorus in natural water: Analytica Chimica Acta, v. 27, p. 31-36.

Pai, Su-Cheng, Yang, Chung-Cheng, and Riley, J.P., 1990, Effects of acidity and molybdate concentration on the kinetics of the formation of the phosphoantimonylmolybdenum blue complex: Analytica Chimica Acta, v. 229, p. 115-120.

(p. 183 follows)

Phosphorus, colorimetry, phosphomolybdate, automated-segmented flow

Parameter and code:
Phosphorus, total-in-bottom-material, dry weight, I-6600-88 (mg/kg as P): 00668

1. Application

This method is used to analyze samples of bottom material containing from 40 to 4,000 mg/kg of phosphorus. This modified method was implemented in the National Water Quality Laboratory in March 1988.

2. Summary of method

2.1 All forms of phosphorus, including organic phosphorus compounds, 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 blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales and others, 1966; Pai and others, 1990).

3. Interferences

3.1 The color of the molybdate blue complex is strongly affected by pH.

3.2 Barium, lead, and silver interfere by forming a phosphorus precipitate but the effect is negligible. The interference from silica, which forms a pale-blue complex, is negligible. Residual chlorine needs to be removed by boiling the sample.

3.3 Arsenic as arsenate AsO_4^{-3} produces a similar color as phosphate (Murphy and Riley, 1962) and might 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 *Glass tubes with plastic caps,* disposable: 18x150 mm.

4.3 *Technicon AutoAnalyzer II,* consisting of sampler, analytical cartridge, peristaltic pump, colorimeter, voltage stabilizer, data station, and printer.

4.4 With this equipment, the following operating conditions are satisfactory for the range from 0.01 to 1.0 mg/L phosphorus:

Absorption cell.....50 mm
Wavelength.....880 or 660 nm
Cam.....40/h (5/1)
Heating-bath temperature .....37°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 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 $K(SbO)C_4H_4O_6{\cdot}1/2H_2O$ in 800 mL demineralized water and dilute to 1 L.

5.4 *Combined working reagent*: Combine reagents in following order (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 *Phosphorus 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.

5.6 *Phosphorus standard solution II,* 1.00 mL = 0.010 mg P: Dilute 100.0 mL phosphorus standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphorus working solutions*: Prepare a blank and 200 mL each of a series of working solutions by appropriate quantitative dilution of phosphorus standard solution II as listed in the following table.

Working solution No.	Phosphorus standard solution II (mL)	Phosphorus concentration (mg/L)
1	1	0.05
2	2	.10
3	5	.25
4	10	.50
5	20	1.00

5.8 *Potassium persulfate,* crystals.

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 *Sodium lauryl sulfate (SLS) solution,* 15 percent w/w: Dissolve 30 g SLS in 170 mL demineralized water. Place flask in an ultrasonic bath to aid in dissolving SLS. CAUTION: Sodium lauryl sulfate is a nasal irritant; work in a well-ventilated hood.

5.11 *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.

5.12 *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.

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

5.14 *Water diluent*: Dissolve 20 g NaCl in 800 mL demineralized water. Add 5.0 mL sodium lauryl sulfate solution and dilute to 1 L with demineralized water.

6. Procedure

6.1 Air dry an aliquot of thoroughly mixed bottom material at room temperature. (The sample needs to be sieved through a 2-mm plastic mesh sieve before air drying.)

6.2 Grind and sieve the air-dried sample through a 500-µm mesh sieve. Discard the portion retained on the sieve, and use for analysis only the portion that passed through the sieve. Run samples in duplicate. Samples need to agree within a relative percent difference of 20 percent (NOTE 1).

NOTE 1. Relative percentage difference = $\frac{\text{Absolute difference between duplicates}}{\text{Average of duplicates}} \times 100$

6.3 Weigh, to the nearest 0.0001 g, about 0.1 g of sample.

6.4 Transfer the samples to a 200-mL round bottom volumetric flask.

6.5 Add about 150 mL of demineralized water to each flask and place in an ultrasonic bath for 10 minutes.

6.6 Bring the flask to volume with demineralized water.

6.7 While stirring, pipet 5.0 mL of each sample into disposable glass tubes. Add 5.0 mL demineralized water. Prepare each sample in duplicate.

6.8 Pipet 10.0 mL of each working solution and a blank into disposable glass tubes.

6.9 Add 4.0 mL of sulfuric acid persulfate reagent.

6.10 Mix the sample and reagent thoroughly, using a vortex mixer.

6.11 Autoclave the samples for 30 minutes at 15 lb/in^2.

6.12 Allow the samples to cool.

6.13 Set up manifold (fig. 10).

6.14 Allow colorimeter, recorder, and heating bath to warm for at least 10 minutes or until the temperature of the heating bath is 37°C.

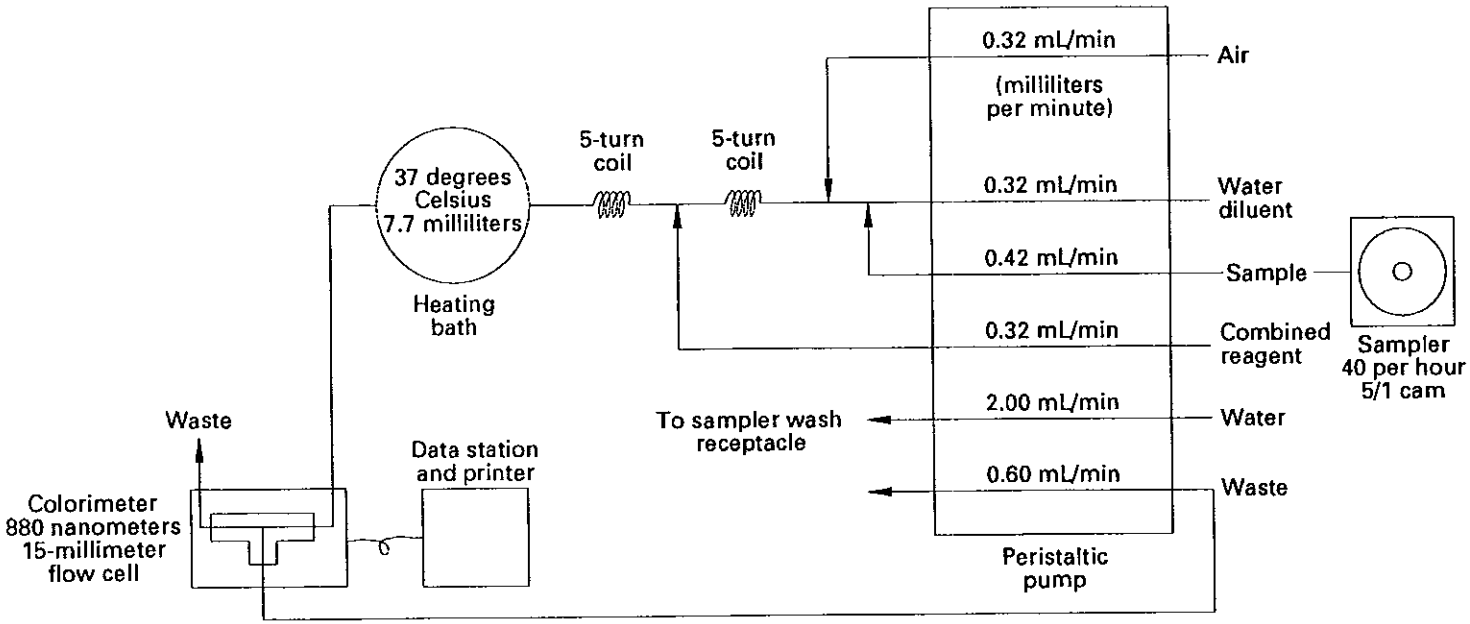

Figure 10.—Phosphorus, phosphomolybdate manifold.

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

6.16 Place a complete set of working solutions and a blank in the first positions of the sample tray beginning with the most concentrated working solution. Place individual working solutions of differing concentrations in about every eighth position of the remainder of this and subsequent sample trays. Fill the remainder of each tray with unknown samples.

6.17 Begin analysis. When the peak from the most concentrated working solution 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 working solution peak in relation to its respective phosphorus concentration or use a data reduction package. See operation manuals for complete details.

7.2 Compute total phosphorus concentrations in each bottom-material sample as follows:

$$\text{Total phosphorus (mg/kg)} = \frac{P \times 0.01 \times 1{,}000 \times 40 \text{ (dilution factor)}}{W}$$

where P = concentration of phosphorus, in the sample, in milligrams per liter; and

W = dry weight of sample, in grams.

8. Report

Report concentrations of phosphorus, total-in-bottom-material (00668), in milligrams per kilogram, to two significant figures.

9. Precision

Typical precision for total phosphorus, expressed in standard deviation and percentage relative standard deviation, is as follows:

Number of laboratories	Mean (mg/kg)	Standard deviation (mg/kg)	Relative standard deviation (percent)
3	0.183	0.022	12
13	.572	.046	8
18	1.411	.127	9
15	3.59	.682	19

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. 1363-1368.

Murphy, J., and Riley, J.P., 1962, A modified single-solution method for the determination of phosphorus in natural waters: Analytica Chimica Acta, v. 27, p. 31-36.

Pai, Su-Cheng, Yang, Chung-Cheng, and Riley, J.P., 1990, Effects of acidity and molybdate concentration on the kinetics of the formation of the phosphoantimonylmolybdenum blue complex: Analytica Chimica Acta, v. 229, p. 115-120.

(p. 191 follows)

Phosphorus, orthophosphate, low ionic-strength water, colorimetry, phosphomolybdate, automated-segmented flow

Parameter and code:
Phosphorus, orthophosphate, dissolved, I-2606-89 (mg/L as P): 00671

1. Application

This method is used to analyze samples of precipitation or natural water with a specific conductance of less than 100 µS/cm containing from 0.001 to 0.20 mg/L of orthophosphate-phosphorus. Concentrations greater than 0.20 mg/L must be diluted. The method was implemented in the National Water Quality Laboratory in March 1986 and modified in May 1989.

2. Summary of method

Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales and others, 1966; Pai and others, 1990).

3. Interferences

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

3.2 Arsenic as arsenate (AsO_4^{-3}) produces a color similar to phosphate (Murphy and Riley, 1962) and might cause a positive interference. Arsenic concentrations as much as 100 µg/L do not interfere.

4. Apparatus

4.1 *Alpkem rapid flow analyzer (RFA),* consisting of sampler, peristaltic pump, analytical cartridge, heating bath, colorimeter, data station, and printer.

4.2 With this equipment, the following operating conditions are satisfactory for the range from 0.001 to 0.20 mg/L phosphorus:

Flow cell .....30 mm
Wavelength.....880 nm
Sample time.....24 seconds
Sampling rate.....64 per hour
Wash time.....32 seconds
Heating bath (2 mL).....37°C
Pecking .....OFF
Damp (RC).....1 second

5. Reagents

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

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

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

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

Sulfuric acid, 2.45*M*..... 100 mL
Ammonium molybdate solution..... 30 mL
Ascorbic acid solution..... 60 mL
Antimony potassium tartrate solution..... 10 mL

5.5 *Phosphorus 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.

5.6 *Phosphorus standard solution II*, 1.00 mL = 0.001 mg P: Dilute 10.0 mL phosphorus standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphorus working solutions*: Prepare a blank and 200 mL each of a series of working solutions by appropriate dilution of phosphorus standard solution II or working solution No. 3, as shown in the following table. If the samples to be analyzed are preserved, the phosphorus working solutions need to contain an equivalent concentration of the same preservative.

Working solution No.	Solution added (mL)	Solution used	Phosphorus concentration (mg/L)
1	40	Standard solution II	0.200
2	20	Standard solution II	.100
3	10	Standard solution II	.050
4	2	Standard solution II	.010
5	20	Working solution No. 3	.005
6	8	Working solution No. 3	.002
7	4	Working solution No. 3	.001

Prepare fresh weekly and refrigerate.

5.8 *Sodium lauryl sulfate solution*, 15 percent w/w: Dissolve 30 g sodium lauryl sulfate in 170 mL of demineralized water. Place flask in an ultrasonic bath to aid in dissolving sodium lauryl sulfate. CAUTION: Solid sodium lauryl sulfate is a nasal irritant; work in a well-ventilated hood.

5.9 *Sulfuric acid, 2.45M*: 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 1,000 mL with demineralized water.

5.10 *Water diluent*: Dissolve 2.5 g NaCl in 400 mL demineralized water. Add 10 mL of sodium lauryl sulfate solution (paragraph 5.8) and dilute to 500 mL with demineralized water.

6. Procedure

6.1 Set up manifold (fig. 11).

6.2 Allow colorimeter, recorder, and heating bath to warm for at least 10 minutes or until the temperature of the heating bath is 37°C.

6.3 After all reagents are on line, adjust the sample output of the photometer to 5 V. Then switch the photometer to "absorbance" mode and use the reference detector "fine gain" control to adjust the baseline absorbance to about 0.2 V. See operation manuals for complete details (Alpkem Corp., 1986).

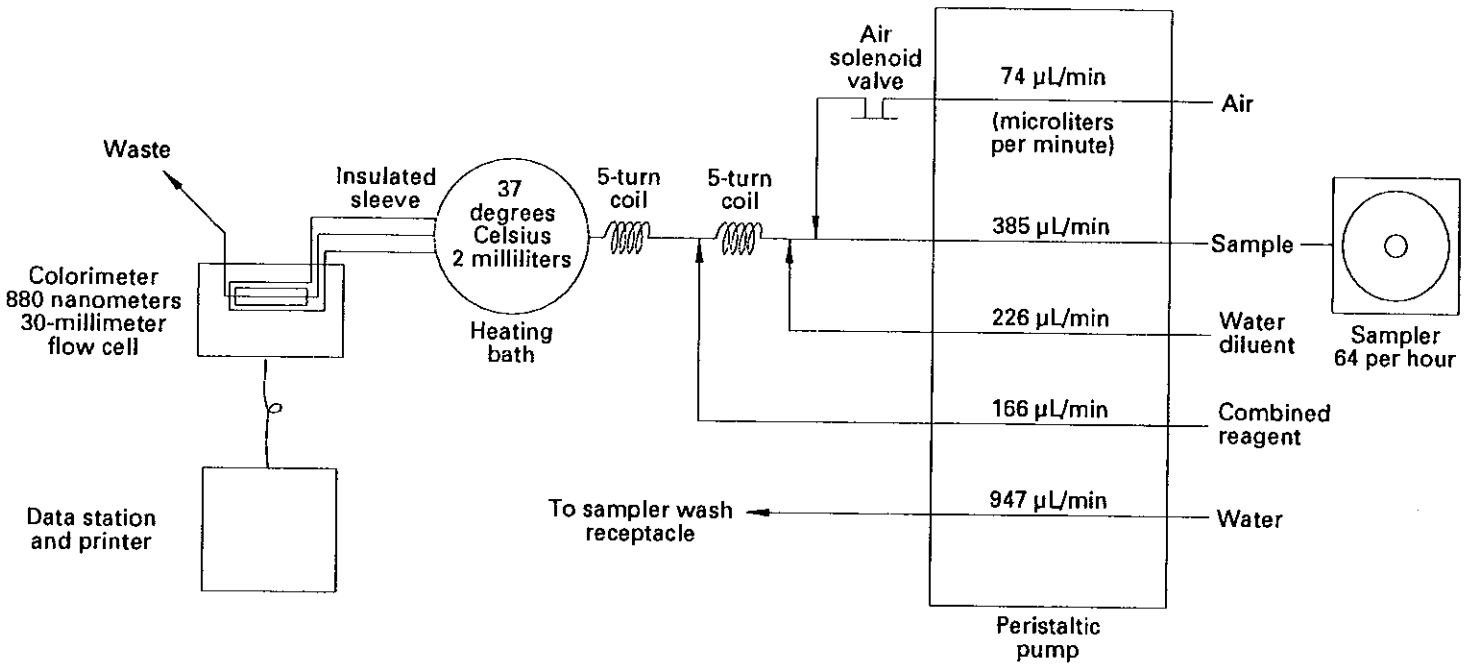

Figure 11.—Phosphorus, orthophosphate, low ionic-strength water, phosphomolybdate manifold.

6.4 Place the most concentrated working solution in two cups before analysis. As the peaks appear on the recorder, adjust the STD CAL control until the peak obtains 95 percent of full scale.

6.5 When the system is clear of all working solutions, determine a dwell time using the most concentrated working solution.

6.6 Place a complete set of working solutions and a blank in the first positions of the sample tray beginning with the most concentrated working solution. Place individual working solutions of differing concentrations in about every eighth position of the tray following the accepted protocol. Fill the remainder of each tray with unknown samples.

6.7 Begin analysis.

7. Calculations

7.1 Prepare an analytical curve either by plotting the voltage of each working solution peak in relation to its respective orthophosphate-phosphorus concentration, or by using the RFA Softpac data reduction package. See operation manuals for complete details (Alpkem Corp., 1986).

7.2 Compute the concentration of dissolved orthophosphate-phosphorus in each sample either by comparing its voltage to the analytical curve or by using the software. Any baseline drift needs to be accounted for when computing the voltage of a sample or working solution peak; the RFA software automatically corrects for baseline drift.

8. Report

Report concentrations of phosphorus, orthophosphate, dissolved (00671), as follows: less than 0.10 mg/L, three decimals; 0.10 mg/L and greater, two significant figures.

9. Precision

Single operator precision for dissolved orthophosphate-phosphorus, as determined for natural-water samples expressed as standard deviation and percentage relative standard deviation, is as follows:

Number of determinations	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
22	0.16	0.001	6.2
22	.189	.003	1.6
22	.196	.002	1.0

References

Alpkem Corp., 1986, Rapid flow analyzer operator's manual: ALPKEM, methodology section.

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. 1363-1368.

Murphy, J., and Riley, J.P., 1962, A modified single-solution method for the determination of phosphorus in natural waters: Analytica Chimica Acta, v. 27, p. 31-36.

Pai, Su-Cheng, Yang, Chung-Cheng, and Riley, J.P., 1990, Effects of acidity and molybdate concentration on the kinetics of the formation of the phosphoantimonylmolybdenum blue complex: Analytica Chimica Acta, v. 229, p. 115-120.

Phosphorus, orthophosphate, colorimetry, phosphomolybdate, automated-segmented flow

Parameter and Code:
Phosphorus, orthophosphate, dissolved, I-2601-90 (mg/L as P): 00671

1. Application

This method is used to analyze most samples of water, wastewater, and brines containing from 0.01 to 1.0 mg/L of orthophosphate-phosphorus. Concentrations greater than 1.0 mg/L must be diluted. This modified method was implemented in the National Water Quality Laboratory in March 1988.

2. Summary of method

Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Murphy and Riley, 1962; Gales and others, 1966; Pai and others, 1990).

3. Interferences

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

3.2 Arsenic as arsenate (AsO_4^{-3}) produces a color similar to phosphate (Murphy and Riley, 1962) and might cause a positive interference. Arsenic concentrations as much as 100 µg/L do not interfere.

4. Apparatus

4.1 *Alpkem rapid flow analyzer (RFA)*, consisting of sampler, peristaltic pump, analytical cartridge, heating bath, colorimeter, data station, and printer.

4.2 With this equipment, the following operating conditions are satisfactory for the range from 0.01 to 1.0 mg/L phosphorus:

Flow cell .....10 mm
Wavelength.....880 nm
Sample time.....24 seconds
Sampling rate.....90 per hour
Wash time.....16 seconds
Heating bath (2 mL).....37°C
Pecking .....ON
Damp (RC).....1 second

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 in 800 mL demineralized water and dilute to 1 L.

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

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

Sulfuric acid, 2.45*M* ..... 100 mL
Ammonium molybdate solution..... 30 mL
Ascorbic acid solution..... 60 mL
Antimony potassium tartrate solution..... 10 mL

5.5 *Phosphorus 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.

5.6 *Phosphorus standard solution II*, 1.00 mL = 0.001 mg P: Dilute 10.0 mL standard solution I to 1,000 mL with demineralized water.

5.7 *Phosphorus working solutions*: Prepare a blank and 250 mL each of a series of working solutions by appropriate dilution of phosphorus standard solution II and working solutions as listed in the following table. If the samples to be analyzed are preserved, the phosphorus working solutions need to contain an equivalent concentration of the same preservative.

Working solution No.	Solution added (mL)	Solution used	Phosphorus concentration (mg/L)
1	250	Standard solution II	1.00
2	125	Standard solution II	.50
3	50	Standard solution II	.20
4	25	Standard solution II	.10
5	25	Working solution No. 2	.05
6	25	Working solution No. 4	.01

5.8 *Sodium lauryl sulfate solution*, 15 percent w/w: Dissolve 30 g sodium lauryl sulfate in 170 mL of demineralized water. Place flask in an ultrasonic bath to aid in dissolving sodium lauryl sulfate. CAUTION: Solid sodium lauryl sulfate is a nasal irritant; work in a well-ventilated hood.

5.9 *Sulfuric acid, 2.45M*: 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 1,000 mL with demineralized water.

5.10 *Water diluent*: Dissolve 2.5 g NaCl in 400 mL demineralized water. Add 10 mL of sodium lauryl sulfate solution (paragraph 5.8) and dilute to 500 mL with demineralized water.

6. Procedure

6.1 Set up manifold (fig. 12).

6.2 Allow colorimeter, recorder, and heating bath to warm for at least 10 minutes or until the temperature of the heating bath is 37°C.

6.3 After all reagents are on line, adjust the sample output of the photometer to 5 V. Then switch the photometer to "absorbance" mode and use the reference detector "fine gain" control to adjust the baseline absorbance to about 0.2 V. See operation manuals for complete details (Alpkem Corp., 1986).

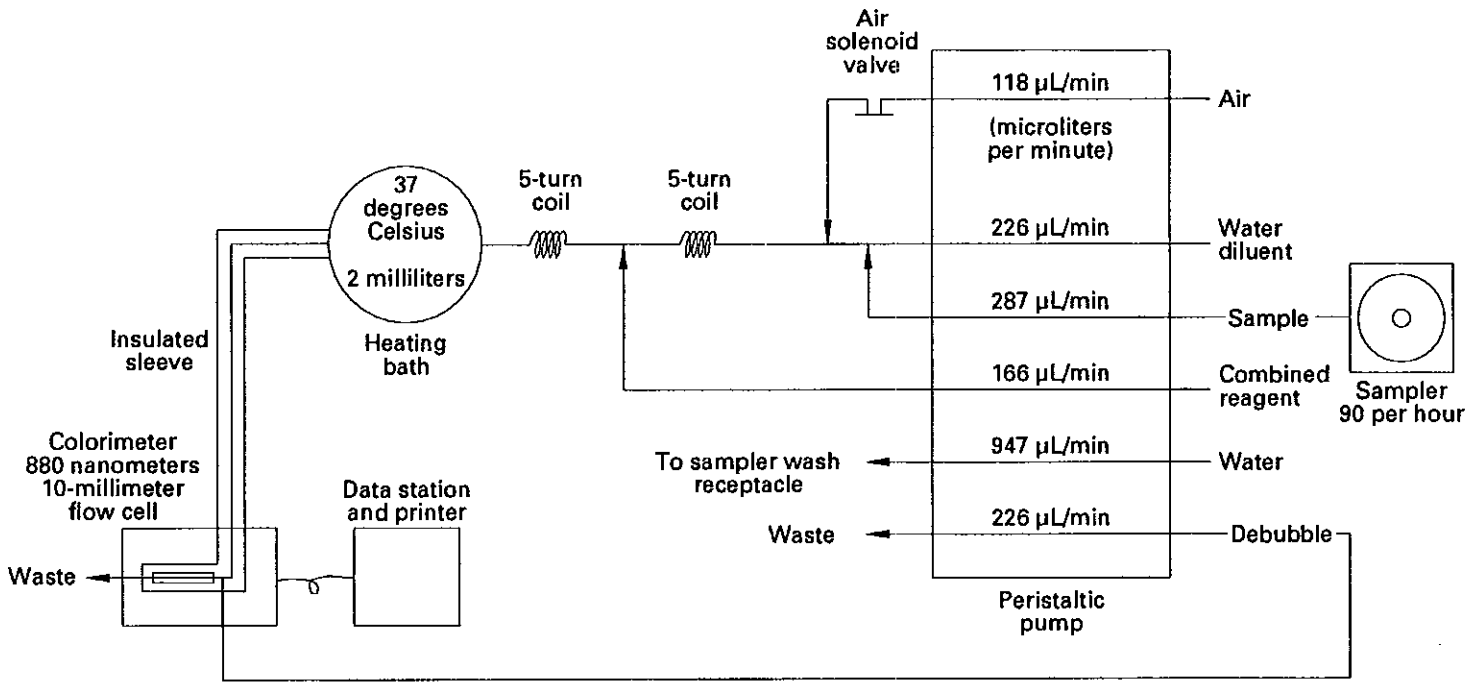

Figure 12.—Phosphorus, orthophosphate, phosphomolybdate manifold.

6.4 Place the most concentrated working solution in two cups before analysis. As the peaks appear on the recorder, adjust the STD CAL control until the peak obtains 95 percent of full scale.

6.5 When the system is clear of all working solutions, determine a dwell time using the most concentrated working solution.

6.6 Place a complete set of working solutions and a blank in the first positions of the sample tray beginning with the most concentrated working solution. Place individual working solutions of differing concentrations in about every tenth position of the sample tray following the accepted protocol. Fill the remainder of each tray with unknown samples.

6.7 Begin analysis.

7. Calculations

7.1 Prepare an analytical curve either by plotting the voltage of each standard peak in relation to its respective orthophosphate-phosphorus concentration, or by using the RFA Softpac data reduction package. See operation manuals for complete details (Alpkem Corp., 1986).

7.2 Compute the concentration of dissolved orthophosphate-phosphorus in each sample either by comparing its voltage to the analytical curve or by using the software. Any baseline drift needs to be accounted for when computing the voltage of a sample or working solution peak; the RFA software automatically corrects for baseline drift.

8. Report

Report concentrations of phosphorus, orthophosphate, dissolved (00671), as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and greater, two significant figures.

9. Precision

Single operator precision for dissolved orthophosphate-phosphorus, as determined for natural-water samples expressed as standard deviation and percentage relative standard deviation, is as follows:

Number of determinations	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
147	0.06	0.001	1.7
193	.18	.001	.56
252	.48	.006	1.2
240	.72	.013	1.8
180	.95	.008	.84

References

Alpkem Corp., 1986, Rapid flow analyzer operator's manual: ALPKEM, methodology section.

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. 1363-1368.

Murphy, J., and Riley, J.P., 1962, A modified single-solution method for the determination of phosphorus in natural waters: Analytica Chimica Acta, v. 27, p. 31-36.

Pai, Su-Cheng, Yang, Chung-Cheng, and Riley, J.P., 1990, Effects of acidity and molybdate concentration on the kinetics of the formation of the phosphoantimonylmolybdenum blue complex: Analytica Chimica Acta, v. 229, p. 115-120.

Silver, atomic absorption spectrophotometry, graphite furnace

Parameters and Codes:
Silver, dissolved, I-2724-89 (µg/L as Ag): (01075)
Silver, whole water recoverable, I-4724-89 (µg/L as Ag): (01077)

1. Application

1.1 This method is used to determine silver in samples of water and water-suspended sediment with a specific conductance not greater than 10,000 µS/cm. With Zeeman background correction and a 20-µL sample, the method is applicable in the range from 1 to 10 µg/L. Sample solutions that contain silver concentrations greater than 10 µg/L must be diluted or be analyzed by an alternate method. This method was implemented in the National Water Quality Laboratory in May 1989.

1.2 The analytical range and detection limit can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings.

1.3 Whole water recoverable silver in samples of water-suspended sediment must undergo preliminary digestion by method I-3485 before being determined.

2. Summary of method

Silver is determined by atomic absorption spectrophotometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). Whole water recoverable silver samples are evaporated to dryness and then brought back to volume with 0.1*N* HNO_3 prior to introduction to the graphite furnace. A sample is placed on the graphite platform, and a matrix modifier is added. The sample then is evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal produced during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences for samples with specific conductances less than 10,000 µS/cm normally are small. In addition, the use of the graphite platform reduces the effects of many interferences.

3.2 Hydrochloric acid added to the water-suspended samples during the digestion process causes false silver signals. A concentration of 30 µL HCl per milliliter of water will cause false readings of 2 to 3 µg/L of silver.

Concentrations increase proportionately with increased additions of HCl. Evaporate digested samples to dryness to remove excess HCl.

3.3 Special precautionary measures to prevent contamination are used during sample collection and laboratory determination.

4. Apparatus

4.1 *Atomic absorption spectrophotometer*, for use at 328.1 nm and equipped with Zeeman background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer needs to have high-temperature ramping and controlled argon-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize operations and instrumental performance. A 20-µL sample with a 10-µg/L concentration of silver should yield a signal of approximately 0.59 absorbance-second. This absorbance signal is based on silver's characteristic mass of 1.5 pg for a signal of 0.0044 absorbance-second. A 20-µL sample generally requires 30 seconds at 130°C to dry. Samples that have a complex matrix might require a longer drying or charring time. Peak shapes may be used to detect insufficient drying, charring, or atomization times or temperatures.

4.1.2 *Graphite furnace*, capable of reaching a temperature of 1,800°C sufficient to atomize silver. Warning: dial settings frequently are inaccurate, and newly conditioned furnaces need to be temperature-calibrated.

4.1.3 *Graphite tubes and platforms*, pyrolytically coated graphite tubes and platforms are suggested.

4.2 *Labware*. Many trace metals at small concentrations adsorb rapidly to glassware. To preclude this problem, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternatively, glassware, particularly flasks and pipets, can be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co.), according to the manufacturer's instructions. Check autosampler cups for contamination. Lancer polystyrene disposable cups are satisfactory after acid rinsing. Alternatively, reusable Teflon or FEP cups can be purchased.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen also can be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Matrix modifier solution,* 6.9 g/L $NH_4H_2PO_4$ and 1.005 g/L $Mg(NO_3)_2 \cdot 6H_2O$: Add 13.8 g $NH_4H_2PO_4$ to 950 mL water; mix and dilute to 1,000 mL. Add 2.01 g $Mg(NO_3)_2 \cdot 6H_2O$ to 950 mL water; mix and dilute to 1,000 mL. Mix the two solutions together 1 + 1. Analyze 20 µL of matrix modifier to determine if silver contamination is present. If the silver reading is more than 0.005 absorbance-second, purify the solution by chelation with ammonium pyrrolidine dithiocarbamate (APDC) followed by extraction with methyl isobutyl ketone (MIBK) (NOTE 1). Analyze 20 µL of the purified solution. Repeat extractions until the silver level is reduced to the acceptable level. DO NOT ADD ACID TO THE PURIFIED MATRIX MODIFIER SOLUTION.

NOTE 1. To purify matrix modifier solution, pour the solution into a Teflon or FEP container. While stirring, adjust the solution to pH 2.9 by dropwise addition of concentrated HNO_3 (sp gr 1.41). Add 10.0 g APDC to 1 L of water and mix well. Add 5.0 mL of the APDC solution to each 100.0 mL of matrix modifier. Shake vigorously for 10 minutes. Add 10 mL MIBK/100 mL of solution and shake vigorously for at least 10 minutes. Separate MIBK by draining through separatory funnel. Repeat process. Since some MIBK will remain in the solution, boil for 10 minutes in a silicone-treated or acid-rinsed container covered with a watch glass.

5.2 *Nitric acid,* concentrated, ultrapure (sp gr 1.41): J.T. Baker Ultrex brand HNO_3 is adequately pure; however, check each lot for contamination. Analyze acidified water (paragraph 5.9) for silver. Add 1.5 mL of concentrated HNO_3 per liter of water, and repeat analysis. Integrated signal should not increase by more than 0.001 absorbance-second.

5.3 *Nitric acid,* 0.1*N*: Add 6.4 mL ultrapure concentrated HNO_3 to water and dilute to 1 L.

5.4 *Silver standard solution I,* 1.00 mL = 1,000 µg Ag: A commercially prepared and certified silver standard can be used. An alternate method is to dissolve 1.0000 g silver wire in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 4 mL ultrapure concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with water.

5.5 *Silver standard solution II,* 1.00 mL = 10.0 µg Ag: Dilute 10.0 mL silver standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified water (paragraph 5.9) to make dilutions. Store all standards in sealed Teflon or FEP containers. Rinse each container twice with a small volume of standard solution before filling the storage container. Standard stored for 6 months in FEP containers yielded values equal to freshly prepared standards.

5.6 *Silver standard solution III,* 1.00 mL = 1.00 µg Ag: Dilute 100.0 mL silver standard solution II to 1,000 mL with acidified water. Prepare fresh monthly.

5.7 *Silver working solution IV,* 1.00 mL = 0.010 µg Ag: Dilute 10.0 mL silver standard solution III to 1,000 mL with acidified water. Prepare fresh monthly.

5.8 *Silver working solution V,* 1.00 mL = 0.005 µg Ag: Dilute 5.0 mL silver standard solution III to 1,000 mL with acidified water. Prepare fresh monthly.

5.9 *Water, acidified:* Add 4 mL ultrapure concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.10 *Water:* All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

6. Procedure

6.1 The autosampler and the graphite furnace need to be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1*N* HNO_3 solution.

6.3 For dissolved silver, proceed to paragraph 6.4. Follow instructions in paragraph 6.3.1 for whole water recoverable silver.

6.3.1 Pipet 1.0 mL of each digested sample into autosampler cups. Add 100 µL concentrated HNO_3 and 100 µL matrix modifier solution.

6.3.2 In a clean hood environment, allow samples to evaporate to dryness. Temperatures as great as 50°C can be used to speed the process.

6.3.3 Add 1.0 mL 0.1*N* HNO_3 and allow samples to sit overnight in a closed container to avoid evaporation. Proceed with paragraph 6.4 (except do not rinse sample cups).

6.4 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.

6.5 In sequence, inject 20-µL aliquots of blank and a minimum of two standards (NOTE 3) in duplicate. Construct the analytical curve from the integrated peak areas (absorbance-seconds).

NOTE 3. The automatic sampler is programmed to inject 5.0 µL of matrix modifier along with blank, standards, and samples.

6.6 Similarly, inject and analyze the samples in duplicate. Every tenth sample cup needs to contain either a standard, blank, or a reference material.

6.7 Restandardize as required, although with the use of L'vov platforms, restandardization generally is not necessary. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, 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 silver in each sample from the digital display of printer output. Dilute those samples containing concentrations of silver that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factor.

8. Report

Report concentrations of silver, dissolved (01075), and whole water recoverable (01077), as follows: less than 10 µg/L, the nearest 1 µg/L; 10 µg/L and greater, two significant figures.

9. Precision

9.1 Analysis of six samples for dissolved silver by a single operator is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
39	1.0	0	0
7	1.1	.04	3.6
38	2.2	.70	31.8
7	5.2	.09	1.7
33	6.6	.88	13.3
34	10.2	1.22	12.0

9.2 Analysis of three samples for whole water recoverable silver is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
7	1.2	0.16	13.3
11	2.0	.71	35.5
10	6.2	.50	8.1

9.3 The precision and bias for dissolved silver was tested on several standard reference water samples. A known amount of silver was added to each sample, and single operator precision and bias for the samples are as follows:

Amount present (µg/L)	Number of replicates	Amount added (µg/L)	Found (µg/L) (NOTE 4)	Standard deviation (percent)	Relative standard deviation (percent)	Percent recovery
2.1	6	4.5	4.2	0.4	0.9	93.3
2.1	6	1.6	1.5	.1	3.1	98.8
2.2	6	3.1	3.0	.8	2.6	96.8
5.9	6	3.3	2.8	.4	13.7	84.8
6.1	6	5.5	5.1	.2	4.3	92.7

NOTE 4. The amount originally present has been subtracted.

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 45-47.

Hinderberger, E.J., Kasser, 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.

(p 211 follows)

Vanadium, colorimetry, catalytic oxidation, automated-segmented flow

Parameter and Code:
Vanadium, dissolved, I-2880-90 (µg/L as V): 01085

1. Application

This method is used to analyze samples of most water containing from 1.0 to 40 µg/L vanadium, provided that the interferences identified below are not exceeded. Concentrations of vanadium greater than 40 µg/L must be reduced by dilution. This modified method was implemented in the National Water Quality Laboratory in August 1990.

2. Summary of method

Small concentrations of vanadium catalyze the acid-persulfate oxidation of gallic acid. This reaction proceeds rapidly in the presence of vanadium but only 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 (Jarabin and Szarvas, 1961; Fishman and Skougstad, 1964; Weigo, 1983).

3. Interferences

3.1 Chloride, bromide, and iodide interfere when their concentrations exceed 200 mg/L (chloride), 250 µg/L (bromide), and 250 µg/L (iodide). Iron(II), iron(III), and copper(II) interfere when their concentrations exceed 300 µg/L [iron(II)], 500 µg/L [(iron(III)], and 50 µg/L [copper(II)]. The concentrations of other ions are rarely large enough to interfere.

3.2 Results are erratic for samples preserved with nitric acid.

4. Apparatus

4.1 *Continuous flow autoanalyzer*, consisting of sampler, peristaltic pump, analytical cartridge, heating coil, colorimeter, voltage stabilizer, recorder, and hardware/software package with personal computer for data acquisition and processing.

4.2 With this equipment, the following operating conditions are satisfactory for the range from 1 to 40 µg/L vanadium:

Flow cell ..... 50 mm
Wavelength..... 410 nm
Rate of analysis 30/h (1:1)
Heating-coil temperature.... 60°C

5. Reagents

5.1 *Water*: All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

5.2 *Ammonium persulfate-phosphoric acid reagent*: Dissolve 10.0 g $(NH_4)_2S_2O_8$ in 100 mL water. Heat solution at just below boiling for 5 minutes. Split the persulfate reagent into two equal volumes and transfer to 250-mL volumetric flasks. Immediately add 50 mL of concentrated H_3PO_4 (sp gr 1.69) to each flask. Let stand for 24 h. Just before use add 98 mL water and 2 mL of sodium lauryl sulfate solution. These two reagent portions will allow for two consecutive days of analyses.

5.3 *Sodium hydroxide solution, 5.0N*: Dissolve with stirring and cooling 200 g NaOH in water. Allow to cool and dilute to 1 L.

5.4 *Sodium lauryl sulfate (SLS) solution*, 15 percent w/w: Dissolve 30 g of SLS in 170 mL of water. Place flask in an ultrasonic bath to aid in dissolving SLS. CAUTION: Sodium lauryl sulfate is a nasal irritant; work in a well-ventilated hood.

5.5 *Gallic acid solution*, 20 g/L: Weigh 4.0 g gallic acid monohydrate and transfer to a 200-mL volumetric flask. Add 2 mL of 5*N* NaOH and bring up to about 180 mL with water. To dissolve, set volumetric flask in an ultrasonic vibrator for 30 minutes. Bring to volume and mix. Prepare fresh daily.

5.6 *Mercuric nitrate solution*, 332 mg/L: Dissolve 350 mg $Hg(NO_3)_2 \cdot H_2O$ in about 900 mL water and dilute to 1 L.

5.7 *Vanadium standard solution I*, 1.00 mL = 100 µg V: Dissolve 0.2309 g ammonium metavanadate (NH_4VO_3) in water and dilute to 1,000 mL.

5.8 *Vanadium standard solution II*, 1.00 mL = 1.0 µg V: Dilute 10.0 mL vanadium standard solution I to 1,000 mL with water.

5.9 *Vanadium standard solution III,* 1.00 mL = 0.1 µg V: Dilute 100.0 mL vanadium standard solution II to 1,000 mL with water.

5.10 *Vanadium working solutions*: Prepare 1-L volumes each of a series of vanadium working solutions by appropriate quantitative dilution of vanadium standard solutions II and III, as follows:

Vanadium standard solution (mL)	Vanadium concentration (µg/L)
10 of III	1
50 of III	5
100 of III	10
20 of II	20
30 of II	30
40 of II	40

6. Procedure

6.1 Set up manifold (fig. 13).

6.2 Allow colorimeter, recorder, and heating coil to warm up for at least 30 minutes or until the temperature of the heating coil reaches 60°C.

6.3 Adjust the baseline to near zero scale divisions on the recorder with all reagents on line.

6.4 Before beginning analysis, aspirate three cups of the most concentrated working solution. Set reaction plateaus (peaks) to 95 percent on the recorder by adjusting STD CAL on the colorimeter.

6.5 Pour a tray of working solutions, blanks, water reference materials, and samples according to preselected protocol. Begin analysis.

7. Calculations

All vanadium concentrations are calculated automatically by the mathematical algorithms of the analytical software package. These tasks include calibrations and curve regressions followed by corrections for baseline drift.

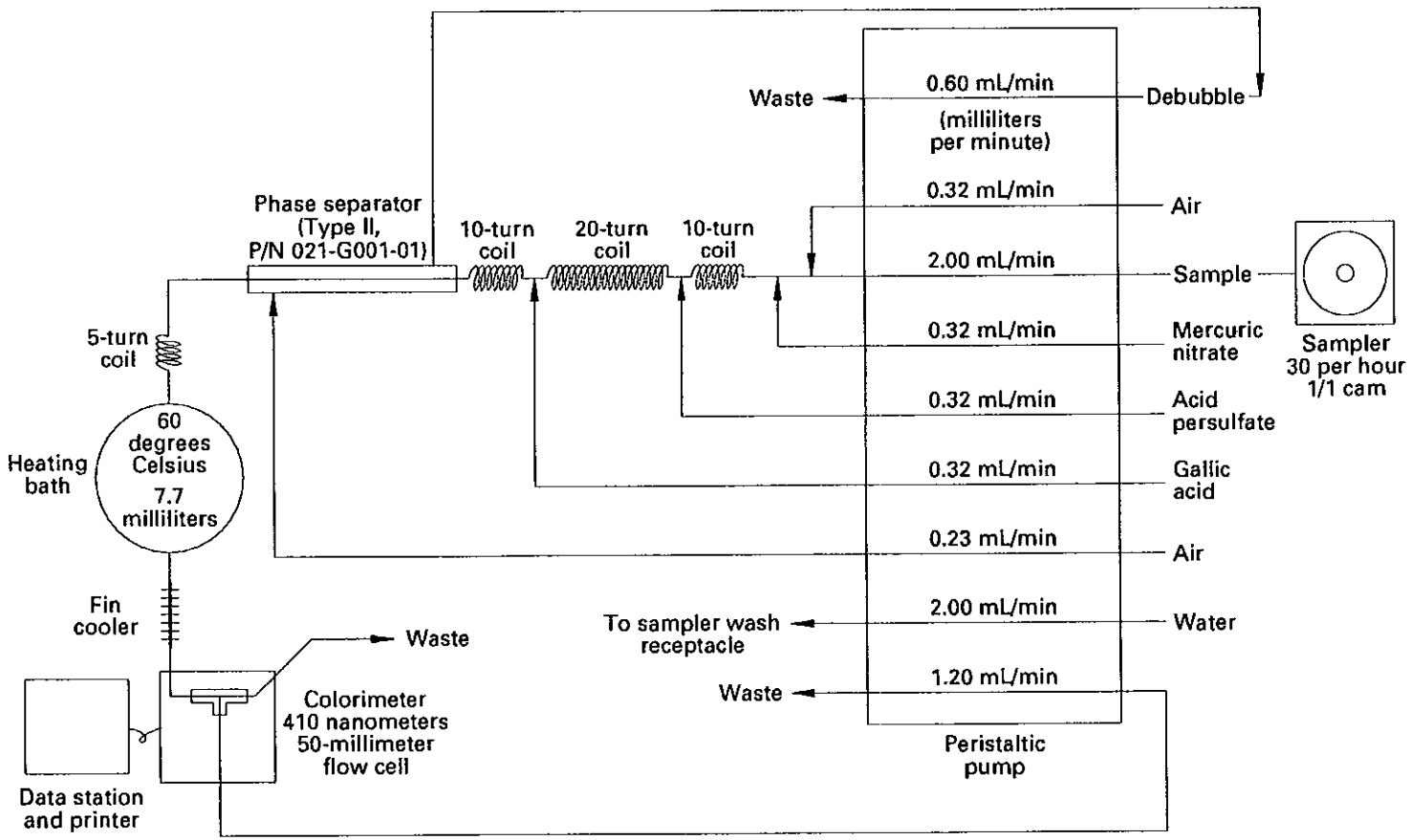

Figure 13.—Vanadium, catalytic oxidation manifold.

8. Report

Report concentrations of vanadium, dissolved (01085), as follows: less than 10 µg/L, nearest 1 µg/L; 10 µg/L and greater, two significant figures.

9. Precision and matrix recovery

9.1 Single operator precision for dissolved vanadium for seven samples, expressed as standard deviation and percentage relative standard deviation, is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
5	2.8	0.11	4
6	6.4	.19	3
7	6.8	.41	6
5	9.5	.19	2
7	25.1	.25	1
7	27.4	.82	3

9.2 Recovery of vanadium on seven samples spiked with vanadium is as follows:

Sample No.	Measured (µg/L)	Added (µg/L)	Found (µg/L)	Recovery (percent)
1	6.41	4.37	10.81	101
	6.38	4.84	10.63	88
	6.57	4.84	10.75	86
	6.42	4.75	10.78	92
2	6.50	4.37	10.79	98
	6.65	4.84	10.83	86
	.29	4.44	10.47	94
	6.24	4.34	10.59	100
3	26.83	9.83	37.07	104
	26.76	9.64	37.22	109
	26.98	9.89	36.22	93
	26.98	9.58	37.48	113
4	2.89	1.95	4.69	92
	2.89	1.94	4.77	97
5	25.25	9.83	35.61	105
	25.31	9.64	35.75	108
	25.12	9.68	34.73	99
	25.14	9.50	35.22	106
6	9.54	4.37	13.90	100
	9.54	4.84	13.98	92
7	9.47	4.37	13.88	101
	9.60	4.84	13.81	87

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 45-47.

Fishman, M.J., and Skougstad, M.W., 1964, Catalytic determination of vanadium in water: Analytical Chemistry, v. 36, p. 1643-1646.

Jarabin, Z., and Szarvas, P., 1961, Detection of small amounts of vanadium by catalytic reaction with the addition of gallic acid: Acta University Debrecen, v. 7, p. 131; Chemical Abstracts, 1962, v. 57, 9192c.

Weigo, Q., 1983, Determination of trace vanadium in water by a modified catalytic-photometric method: Analytical Chemistry, v. 55(13), p. 2043-2047.

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