ANALYTICAL METHODS

of the U.S. Geological Survey's New York District Water-Analysis Laboratory

U.S. GEOLOGICAL SURVEY
Open-File Report 95-416

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By Gregory B. Lawrence, Tricia A. Lincoln, Debra A. Horan-Ross, Mark L. Olson, and Laura A. Waldron

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Conversion Factors and Abbreviations

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, avoirdupos
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 the following equation:

$$°F = \frac{9}{5}(°C) + 32$$

Abbreviated Units of Measurement

M	Molar
M/L	moles per liter
M Ω-cm	megohm-centimeter
mg/L	milligrams per liter
min	minutes
mL	milliliter
mm	millimeter
mM	millimolar
mV	millivolt
N	normal
nm	nanometer
ppm	parts per million
psi	pounds per square inch
µeq/L	microequivalents per liter
µL	microliters
µm	micrometers
µmol/L	micromoles per liter
µS/cm	microsiemens per centimeter

Other Abbreviations

AAS	atomic-absorption spectrophotometry
ANC	acid-neutralizing capacity
DI water	deionized water
DIC	dissolved inorganic carbon
DOC	dissolved organic carbon
DQO	data-quality objective
ECD	electron-capture detector
FIA	flow-injection analyzer
GC	gas chromatograph
HPLC	high-performance liquid chromatography
ISWS	Illinois State Water Survey
LIMS	Laboratory Information Management System
LRTAP	Long-Range Transport of Atmospheric Pollutants
NEAP	Northeast Area Program
NED	N-(1-naphthyl)ethylenediamine dihyhydrochloride
NIST	National Institute for Standards and Technology
NWIS	National Water Information System
QC-high	high-concentration quality-control sample
QC-low	low-concentration quality-control sample
SWRS	Standard Water Reference Sample
TCD	thermal-conductivity detector
TISAB	total-ionic-strength adjustment buffer
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

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Abstract

The New York District of the U.S. Geological Survey (USGS) in Troy, N.Y., operates a water-analysis laboratory for USGS watershed-research projects in the Northeast that require analyses of precipitation and of dilute surface water and soil water for major ions; it also provides analyses of certain chemical constituents in soils and soil-gas samples.

This report presents the methods for chemical analyses of water samples, soil-water samples, and soil-gas samples collected in watershed-research projects. The introduction describes the general materials and techniques for each method and explains the USGS quality-assurance program and data-management procedures; it also explains the use of cross reference to the three most commonly used methods manuals for analysis of dilute waters. The body of the report describes the analytical procedures for (1) solution analysis, (2) soil analysis, and (3) soil-gas analysis. The methods are presented in alphabetical order by constituent. The method for each constituent is preceded by (1) reference codes for pertinent sections of the three manuals mentioned above, (2) a list of the method's applications, and (3) a summary of the procedure. The methods section for each constituent contains the following categories: instrumentation and equipment, sample preservation and storage, reagents and standards, analytical procedures, quality control, maintenance, interferences, safety considerations, and references. Sufficient information is presented for each method to allow the resulting data to be appropriately used in environmental investigations.

INTRODUCTION

The New York District of the U.S. Geological Survey (USGS) operates a laboratory for chemical analysis of low-ionic-strength water. This laboratory operates in support of USGS projects in the Northeast that require chemical analyses of precipitation, dilute surface water and soil water, shallow ground water, stream water, and lake water collected in upland watersheds. Although the laboratory's primary role is to provide analyses of low-ionic-strength water samples, it provides other services, including soil-gas analysis and soil-water extractions.

This report documents the analytical methods used by the laboratory. The methods have been selected to meet the needs of USGS watershed research in the Northeast and to be consistent with methods used in similar studies conducted by the USGS elsewhere and by other agencies.

Purpose and Scope

This report documents the instrumentation and equipment, sample preservation and storage, reagents and standards, analytical procedures, quality control, and equipment maintenance for each constituent . The applications listed for each constituent are those used by the New York District laboratory and do not include all possible applications of the methods. Other information given for each constituent describes general laboratory materials and techniques, the data-quality-assurance program, data-reporting protocols, and data-base management.

Cross Referencing to Other Methods Manuals

The method for each constituent represented herein is cross referenced to three methods manuals–the U.S. Environmental Protection Agency (USEPA) *Handbook of Methods for Acid Deposition Studies* (USEPA, 1987), Illinois State Water Survey (ISWS) *Methods for Collection and Analysis of Precipitation* (Peden and others, 1986), and the The USGS *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments* (Fishman and others, 1989). The first two manuals were selected for cross referencing because they are the most frequently cited methods manuals used in studies of low-ionic-strength water; the USGS manual is referenced so that USGS method codes can be associated with the methods described herein.

Methods for sample preservation and storage by the New York District laboratory may differ from those listed in these EPA, ISWS, and USGS manuals. If no directly comparable method for a specific constituent is listed in the EPA, ISWS, or USGS manuals, no cross-reference is given for that constituent in this manual.

Materials and Techniques

Materials and techniques used for processing water, soil-water, and soil-gas samples are selected to minimize contamination of low-concentration samples.

Deionized Water

The Megohmetrics[1] ultra-pure water system is used to provide deionized (DI) water for washing labware. The Megohmetrics system is made up of one carbon tank, a 1-µm filter, and two cation-anion mixed-bed resin tanks and is equipped with an inline conductivity meter between the resin tanks. When the conductivity meter detects a conductance of 1.0 µS/cm or greater, a red indicator light is deactivated. The first mixed resin tank (upstream of the conductivity meter) is then replaced with the second tank, and a new tank is installed downstream of the conductivity meter. The light is checked daily. The filter is replaced with every tank change, and the carbon tank is replaced every 6 months. This system provides water that meets the specifications of TYPE III water (American Society of Testing and Materials, 1984).

TYPE I DI water (American Society of Testing and Materials, 1984), used for the preparation of standards and reagents, is produced by a Millipore Milli-Q Plus system. The system's feed water is pretreated by the Megohmetrics system. The Millipore system first prefilters the water with a 0.5-µm filter, then treats it with activated carbon, nuclear-grade ion-exchange resin, and the Organex-Q organic scavenger mixture. Final filtration is then done at the dispensing point with a 0.22-µm filter. An electronic-resistivity meter is monitored daily, and the cartridges are replaced when the resistivity drops below 16.5M Ω-cm.

Labware

Sample containers:. High-density polyethylene and Teflon are used for sample storage and handling, except for samples to be analyzed for dissolved organic carbon (DOC) and inorganic carbon (DIC), for which glass is used. Glass is preferable for DOC analysis because it is less costly than Teflon and because organic carbon can leach from polyethylene; it also is less gas permeable than plastic and therefore is

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1. Use of a trade, product, or firm name in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

preferable for DIC analysis. Certain elements, including silicon, sodium,and potassium can leach out of glass, however, and glass also has a negative surface charge that can remove cations such as aluminum from solution.

Pipettes: Volumetric pipettes are washed between uses with a 2-percent solution of hydrochloric acid. The acid is in contact with the labware for 15 to 20 min. Pipettes are then rinsed three times with DI water, then filled with DI water and allowed to soak for a minimum of 24 hours. Before use, the pipettes are rinsed again and dried.

Other labware: All other labware is rinsed by the above procedure, but without acid washing.

Equipment-Calibration Checks

Balances are internally calibrated yearly by service representatives using National Institute for Standards and Technology traceable weights. The balance calibrations are checked monthly by laboratory personnel. Pipettors used for dispensing reagents and standard solutions are calibrated monthly by weighing 10 additions of deionized water. Refrigerator temperatures are checked daily. Logbooks are kept for all equipment checks.

Quality Assurance

Quality-assurance data are based on (1) analyses of environmental samples collected for New York District projects, (2) participation in sample-exchange programs with other laboratories, and (3) analyses of laboratory blanks.

Internal Quality-Assurance Samples

To assure data quality, 1 triplicate (environmental samples), 1 analysis blank, and 1 filter blank are included in each 50 samples. Analytical precision is documented by plotting triplicate results on control charts. Samples for triplicate analysis are selected on a rotating basis to encompass the range of sample concentrations analyzed by the laboratory. Filter blanks are samples of DI water that are processed (including filtration) and analyzed in the same manner as all other samples. Analysis of filter blanks indicates whether any sources of contamination were present during sample processing and analysis. Analysis blanks are samples of DI water that are processed and analyzed like all other samples, except that the filtration step is omitted. Comparison between filter blanks and analysis blanks identifies potential contamination caused specifically by filtration. Results of filter blanks and analysis blanks are plotted on control charts.

External Quality-Assurance Samples

In addition to analyzing internal quality-assurance samples, the New York District Laboratory also participates in three interlaboratory quality-assurance programs—Environment Canada, Long-Range Transport of Atmospheric Pollutants (LRTAP, 30 samples per year), the USGS Standard Water Reference Sample Program (SWRS, 2 samples per year), and the USGS Blind Sample Program (50 samples per year). In each of these programs, results from the New York District laboratory are compared with a most probable value determined by averaging data from all laboratories participating in the respective programs. In the LRTAP and SWRS programs, the identity of quality-assurance samples is known by the analyst; in the USGS Blind Sample Program, sample identities are unknown to the analyst.

Quality-Assurance Reporting

Other quality-assurance procedures include plotting results for quality-control samples on control charts and computing charge balances. A quality-control sample is analyzed every 10 to 17 samples, depending on the type of analysis. Although the primary function of quality-control samples is to determine when reanalysis is needed, plotting these data on control charts provides temporal information on analysis accuracy and identifies directional biases. Charge balances are useful for summarizing the overall accuracy of a complete analysis for all major ions. If all ion concentrations are measured, a charge imbalance indicates a bias in one or more analyses. Often in low-ionic-strength environmental samples, however, the total charge of all ions cannot be measured; in particular, the total charge of organic anions and both organic and inorganic monomeric aluminum cannot be measured directly. Presence of these constituents can result in charge imbalances of up to 200 µeq/L (Lawrence and Fernandez, 1991). Biases of both cations and anions can also cancel each other and result in an erroneous balance. Interpretation of charge-balance data for quality-assurance purposes must consider these complications.

Reporting limits for all methods described in this report are listed in table 1 (p. 6). A reporting limit is defined as the lowest concentration for which chosen data-quality objectives (DQO's) for both accuracy and precision can be expected to be achieved. Reporting limits differ from detection limits in that detection limits generally refer to the lowest concentration at which an analytical method can determine the presence of a constituent, without regard to specified DQO's. Measured concentrations below the reporting limit are flagged in the data base and are not used in quality-assurance summaries. High- and low-concentration DQO's for accuracy and precision are included in table 1. Accuracy is based on quality-control samples, and precision is based on environmental-sample triplicates. DQO's for filter and analysis blanks are also given in table 1. All DQO's listed in table 1 are based on results of 5,000 analyses completed in the New York District Laboratory

A quality-assurance summary report is published annually by the New York District Laboratory. This report includes a brief discussion of quality-assurance results and control charts of all internal and external quality-assurance samples analyzed for that year.

Data-Base Management

Constituent concentrations are entered into the laboratory data base in units of micromoles per liter (µmol/L) except for pH, and acid-neutralizing capacity, which is given in microequivalents per liter, and carbon dioxide and nitrous oxide, which are given in parts per million. Micromoles per liter is useful for expressing concentrations of constituents that have an unknown molecular charge, such as dissolved organic carbon. Data for all analyses are reported to within 0.1 µmol unless this results in more than 3 significant figures, in which case only 3 significant figures are used. One exception is total aluminum, for which concentrations are reported to 0.01 µmol/L. If concentrations must be converted to other units before being reported, rules for arithmetic operations involving significant figures are followed.

All laboratory data capture, processing and management are done through a networked laboratory information-management system (LIMS). Laboratory instruments, except the Dohrmann Carbon Analyzer (which analyzes dissolved organic and dissolved inorganic carbon) and the Shimadzu Gas Chromatograph, are connected to personal computers that capture data using software specific to that instrument. Upon completion of an analysis run, the analyst processes the data using the instrument software. Data produced by the Dohrmann Carbon Analyzer and the Shimadzu Gas Chromatograph is manually entered into the laboratory data base. Once processing is completed, the data are transferred into the network data-base program (CHEMLAB), written in SAS screen-control language. CHEMLAB

updates the laboratory data base with the new data using a preassigned sample serial number. Duplicate sample serial numbers and out-of-limits data are rejected by CHEMLAB. Out-of-limits data are measurements whose values exceed the range that is realistically expected (for example pH > 10). CHEMLAB stores the data by date of analysis and includes quality-control sample concentrations and flags that provide details of the analysis.

CHEMLAB also merges laboratory data with field data for the respective sample serial numbers and outputs data for entry into the USGS National Water Information System data base. All field data are typed into the computer twice so that the SAS procedure PROC COMPARE can be used to identify discrepancies. Once the laboratory data have been merged with the field data, the data are reviewed by project chiefs to identify missing and questionable values. When the review and necessary corrections are complete, the data are placed in a read-only file accessible to project personnel. All data reside on a dedicated Data General workstation. These data are backed up daily on the network server and weekly on tape.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, Section II, Water: Philadelphia, American Society of Testing and Materials, v. 11.01, 750 p.

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

Lawrence, G.B., and Fernandez, I.J., 1991, Biogeochemical interactions between acidic deposition and a low elevation spruce-fir stand in Howland, Maine: Canadian Journal of Forest Research, v. 21, p. 147-65.

Peden, M.E., and others, 1986, Methods for collection and analysis of precipitation: Champaign, Ill., Illinois State Water Survey, Contract Report 381 (variously paged).

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies - laboratory analyses for surface water chemistry: Washington D.C., U.S. Environmental Protection Agency, EPA 600/4-87/026 (variously paged).

Table 1. Reporting limits and data-quality objectives for accuracy, precision, and blanks for analyses performed by the U.S. Geological Survey's New York District Laboratory

[DQO, data-quality objective. µmol/L, micromoles per liter. cv, coefficient of variation. ANC, acid-neutralizing capacity. Numbers in "dividing value" column are concentrations that divide high range from low range of precision DQO's. pH and ANC values (in parentheses) are in pH units and microequivalents per liter, respectively.]

Consttuent or property	Reporting limit (µmol/L)	Accuracy				Precision			Filter and analysis blanks DQO (µmol/L)
		Low-concentration quality-control sample		High-concentration quality-control sample					
		DQO (percent error)	Concentration (µmol/L)	DQO (percent error)	Concentration (µmol/L)	Low-concentration range DQO (cv)	Dividing value (µmol/L)	High-concentration range DQO (cv)	
ANC †	none	10	(-39.9)	10	(125)	10	none	10	none
Al, total	1.0	15	1.8	10	28	15	1	5	0.5
Al, total monomeric	1.5	10	7.4	10	18.5	15	5	10	0.75
Al, organic monomeric*	1.5	none	none	none	none	15	5	10	0.75
NH_4^+	2.0	15	7.1	10	17.5	15	5	10	1.0
Cl^-	2.0	10	8.5	10	85	15	8	10	0.5
NO_3^-	2.0	10	5	10	50	15	5	10	0.3
SO_4^{2-}	2.0	10	8.3	10	83	15	8.3	10	0.3
Ca^{2+}	2.0	10	25	10	100	15	10	10	1.0
Mg^{2+}	1.0	10	8.2	10	33	15	5	10	0.5
Na^+	1.0	10	8.7	10	35	15	15	10	1.0
K^+	1.0	10	5.1	10	20	15	5	10	0.5
Br^-	2.0	10	20	10	150	15	8	10	0.5
C, dissolved inorganic ‡	41.0	15	83	10	415	15	83	10	18
C, dissolved organic ‡	41.0	15	83	10	415	15	83	10	18
F, total †	0.5	15	1.6	none	none	10	none	10	none
pH †	none	10	(4.41)	20	(6.88)	10	(6.00)	20	none
Total Si	6.0	15	35.6	10	107	15	50	10	3
NO_2^-	5.0	10	14.3	10	28.6	10	none	10	none
NO_2^- plus NO_3^-	5.0	12	42.9	10	100	10	none	10	none
CO_2 ††	80	10	732	10	1000.4	10	none	10	none
N_2O ††	0.10	15	0.462	10	0.701	10	none	10	none

† ANC: Values in parentheses are in microequivalents per liter (µeq/L). For values within ±20 µeq/L, an absolute data-quality objective of ± 6 µeq/L is used for precision, rather than a coefficient of variation of 10 for values outside this range. Blanks are not run for ANC.

pH: Values in parentheses are standard pH units. Percent error and coefficient of variation determined from $[H^+]$. Blanks are not run for pH.

F, total: No data yet available for precision. Blanks are not run for total fluoride.

* Quality-control samples for organic monomeric Al are unavailable.

‡ Concentrations are expressed as µmol C/L.

ANALYTICAL METHODS

A. SOLUTION ANALYSIS

ACID-NEUTRALIZING CAPACITY (ANC)

Cross references:

USGS Method Code: -- none
ISWS Method Code: -- none
EPA Section # 5.0

Applications.—This method is used to measure acid-neutralizing capacity in dilute surface water and soil water. It is applicable for water samples that are buffered by aluminum and weakly acidic organic acids.

Summary.—ANC of water is determined electrometrically through an open-atmosphere strong-acid titration. Three to five increments of acid are added beyond an estimated equivalence point. The equivalence point and ANC are then calculated by the method of Gran (1952).

INSTRUMENTATION AND EQUIPMENT

- Radiometer VIT 90 Video Titrator with temperature compensator and stirrer
- Radiometer ABU 93 Triburette
- Radiometer SAC 80 Sample Changer
- Corning combination pH electrode with flowing reference junction
- Computer for calculating ANC values

SAMPLE PRESERVATION AND STORAGE

Samples are stored in acid-washed polyethylene bottles at 4°C without filtration.

REAGENTS AND STANDARDS

Buffers.—pH 4.00 and 7.00, purchased commercially, are used to calibrate the titrator.

Titrant.—0.02N volumetric sulfuric acid (H_2SO_4) is purchased commercially. Normality of each batch of titrant is checked by titrating a sodium carbonate (Na_2CO_3) solution of known concentration.

Quality-Control (QC) Stock Solution for QC-Low-Concentration Standard.—0.1N sulfuric acid (H_2SO_4) is purchased commercially. Each lot received is titrated to ensure that the concentration is accurate.

QC Stock Solution for QC-High-Concentration Standard.—Prepare a solution of 0.025M potassium phosphate, monobasic (KH_2PO_4)/0.025M sodium phosphate, dibasic heptahydrate ($Na_2HPO_4 \cdot 7H_2O$) by dissolving 3.4023 g potassium phosphate, monobasic and 6.6961 g sodium phosphate, dibasic heptahydrate in a 1,000-mL volumetric flask. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare as needed.

Saturated KCl Electrode Filling Solution.—Purchased commercially.

QC Samples.—Pipet desired volume of QC stock solution into a 1,000-mL volumetric flask. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare as needed.

QC-low concentration:	-39.9 µeq/L	0.40 mL QC-low stock
QC-high concentration:	125 µeq/L	5.0 mL QC-high stock

PROCEDURE

1. Turn on the computer and start the titration program. Verify that the program includes the following parameter settings:
   - titrant increment volume—0.1 mL
   - stability criterion for recording pH— < 0.001 change in pH per second
   - minimum time between titrant additions—45 seconds
   - titration termination pH—3.5
2. Flush the burette using the VIT 90.
3. Unplug fill hole on pH probe.
4. Calibrate the pH probe using pH 4.00 and 7.00 buffer solutions.
5. Record the temperature and millivolts of the buffers, and sensitivity of the calibration in the instrument logbook.
6. Fill titrant reservoir with volumetric 0.02N sulfuric acid.
7. Fill two rinse cups with DI water and place them in positions 19 and 20 on the autosampler tray.
8. Measure 40.0 mL of a QC sample in a graduated cylinder, pour into a sample cup, and place on the autosampler tray.
9. Start the run.
10. If the QC is acceptable, proceed with the sample analysis. If the QC fails, reanalyze it.
11. If the QC is acceptable after reanalysis, then proceed with the run. If the QC fails after reanalysis, then recalibrate.
12. Record sample serial numbers on the instrument bench sheet.
13. Between samples, the instrument immerses the electrode in two DI rinse cups for 10 seconds each.

QUALITY CONTROL

- The computer software calculates ANC, in µeq/L, according to the method of Gran (1952).
- A QC sample is analyzed at the start of a sample tray, after 17 samples, and at the end of the run. A quality-control sample is acceptable if the analyzed value is within 10 percent of the QC theoretical value. Samples are reanalyzed if they are associated with a QC sample that has failed.
- ANC values are stored along with the sample's tray location in the computer data file. Sample serial numbers corresponding to tray locations are entered into the data file. A printout of the computer's data are produced. The data are then imported electronically into the SAS network data base, where they are verified against the computer printout, and flags are assigned. A database printout is then produced to provide hard-copy documentation of the data entry.
- The electrode response is verified by ensuring that the electrode potential for pH 7.00 buffer is ±30 mV, and the electrode potential for pH 4.00 buffer is about160 mV greater than for pH 7.00 buffer.

MAINTENANCE

- Store the electrode in pH 7.00 buffer when not in use.
- If the probe will be stored for longer than 1 week, it should be stored in saturated KCl fill solution
- The pH bulb/reference junction should not be allowed to dry out.
- When the internal fill solution level falls to 2.5 cm below the fill hole, add saturated KCl fill solution until the level reaches the fill hole.

- Plug the fill hole when the electrode is not in use.
- Rinse off any salt deposits with DI water before using the electrode.

INTERFERENCES

None.

SAFETY CONSIDERATIONS

Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

Gran, G., 1952, Determination of the equivalence point in potentiometric titrations - Part II: Analyst, v. 77, p. 661-671.

Metcalf, R.C., and Peck, D.V., 1991, Dilute, neutral pH standard of known conductivity and acid-neutralizing capacity Analyst, v. 116, p. 221-231.

Orion Research Incorporated, 1990, Ross pH electrode instruction manual: Boston, Orion Research, Laboratory Products Groups, 25 p.

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies - laboratory analysis for surface water chemistry: Washington, D.C., U.S. Environmental Protection Agency, EPA 600/4-87/026 (variously paged).,

ALUMINUM, TOTAL

Cross references:

USGS Method Code: --none
ISWS Method Code: --none
EPA Section # -- none

Applications.—This method is used to measure aluminum concentrations in precipitation and dilute surface water and soil water.

Summary.—Aluminum analysis is performed by graphite-furnace atomic absorption spectroscopy (AAS). A 20-µL portion of the sample is placed on a L'vov platform in a pyrocoated graphite tube. The sample is then dried, charred, and atomized. The beam from an aluminum hollow cathode lamp is directed through the tube and onto the detector that measures radiant energy. Absorption is measured at a wavelength of 309.3 nm.

INSTRUMENTATION AND EQUIPMENT

- Perkin-Elmer 1100 B atomic absorption spectrophotometer (AAS) that includes:
  - HGA 700 Graphite Furnace
  - AS-70 Autosampler
  - Pyrocoated graphite tubes
  - L'vov Platforms
  - 2-mL sample cups
- Computer for data retrieval

SAMPLE PRESERVATION AND STORAGE

Samples are acidified to a pH < 1 with reagent-grade nitric acid (HNO_3) for preservation and stored in acid-washed polyethylene bottles.

REAGENTS AND STANDARDS

Argon Gas.—Use 4.5-grade argon, purchased commercially.

Aluminum Standard Stock Solution, 1,000 mg Al/L.—Use a 1,000-mg/L aluminum atomic absorption standard, purchased commercially.

Aluminum Standard Substock Solution, 50 mg Al/L.—Pipet 25.0 mL aluminum stock into a 500-mL volumetric flask. Add 1 mL nitric acid (HNO_3) to maintain a pH of <1. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare every 6 months.

Aluminum Working Standards.—Pipet desired amount of standard substock into a 500-mL volumetric flask. Add 1 mL nitric acid (HNO_3) to maintain a pH <1. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare every 6 months.

Standard 3:	7.41 µmol/L (200 µg/L)	2.0 mL substock
Standard 2:	3.71 µmol/L (100 µg/L)	1.0 mL substock
Standard 1:	1.85 µmol/L (50 µg/L)	0.5 mL substock
Standard blank:	0.00 µmol/L (0.000 µg/L)	0.0 mL substock

Aluminum Quality-Control (QC) Stock Solution, 1,000 mg Al/L.—Use a 1,000-mg/L aluminum atomic absorption standard, purchased commercially. This stock must be from a manufacturer or lot different from that of the standard stock.

Aluminum QC Substock Solution, 13.5 mg Al/L.—Pipet 6.75 mL aluminum QC stock into a 500-mL volumetric flask. Add 1 mL nitric acid (HNO_3) to maintain a pH of <1. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare every 6 months.

Aluminum QC Samples.—Pipet desired amount of QC substock solution into a 500-mL volumetric flask. Add 1 mL nitric acid (HNO_3) to maintain a pH of <1. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare monthly.

QC-low concentration:	1.0 µmol/L (27 µg/L)	1.0 mL QC substock
QC-high concentration:	15 µmol/L (405 µg/L)	15.0 mL QC substock

PROCEDURE

1. Turn on hood and open valve to argon tank. Record regulator pressures in the instrument notebook.
2. Clean Al hollow-cathode lamp with lens paper, then place in location 1, making sure it is properly aligned in the 3 o'clock position.
3. Turn on furnace, AAS, and computer.
4. On AAS, enter date, set baud rate to 1200, and check tube alignment, tube condition, and sample delivery. Change "END OF LINE" default softkey to "CARRIAGE RETURN" softkey.
5. Recall aluminum program with background correction, confirm wavelength of 309.3 nm, and enter standard and sample location. Operating parameters are as follows:

Technique: AA-BG
Lamp Current (mA): 18
Signal (sig.) Processing: PA
Integration Time (sec.): 6.0
Read Delay (sec.): 0.0

Printer: Data + Suppl.
Replicates: 2
Plot Full Scale: Auto.
Background Full Scale: Auto
Calibration: Auto

	Sample Locations		
	Location	Volume (µL)	Blank Volume (µL)
Std. Blank	40	20	0
Standard 1	37	20	0
Standard 2	38	20	0
Standard 3	39	20	0
Samples	1 to 36	5	15

Wavelength Al: 309.3 nm

Step	Operating Parameters				
	Furnace temperature. (°C)	Time		Internal gas flow (mL/min)	Read (sec)
		Ramp (sec)	Hold (sec)		
1. Drying	180	5	30	300	--
2. Charring	1700	5	20	300	--
3. Atomization	2500	0	4	0	-1.5
4. Conditioning	2650	1	3	300	--
5. Cooling	30	1	30	300	--

6. Fill blank container with standard blank and place in location #40.
7. Turn on cooling water.
8. Place AAS in run mode and turn on printer.
9. Autozero instrument by analyzing the blank until acceptable replication is produced.
10. Reset autosampler.
11. Place working standard 3 in location #39, standard 2 in location #38, and standard 1 in location #37.
12. Press the ON/OFF sampler softkey to activate sampler program.
13. Place filled sample cups in sampler tray and record tray location and sample serial number on bench sheet.
14. After an acceptable calibration, identify sample locations through printer and begin analysis of samples.

QUALITY CONTROL

- The Perkin-Elmer software automatically calculates the linear standard curve and computes the aluminum concentration of the samples. The calibration is set up in the "auto" mode, and a correlation coefficient of 0.999 or greater is acceptable.
- Samples and standards are analyzed in duplicate, and the average is recorded. A relative standard deviation of <10 percent is acceptable.
- Quality-control samples are analyzed at the start of a run, after every 10th sample during the run, and at the end of the run. A quality-control sample is acceptable if the analyzed value is within 10 percent of the QC-high theoretical values and within 20 percent of the QC-low theoretical values.
- Samples are diluted and reanalyzed if they exceed the concentration of the highest standard or if they are associated with a quality-control sample that failed.
- All samples are diluted 1 part sample to 3 parts DI water automatically by the instrument because the concentration of most samples exceeds the concentration of highest standard. If a sample concentration exceeds the highest standard concentration after the automatic dilution, a second manual dilution is done. Dilution factors are accounted for automatically when analysis results are transferred to the network database.
- The data are edited on the computer data file by entering the sample serial numbers corresponding to tray locations. A data-file printout is produced. The data are imported into the SAS network data base, where they are verified against the printout. Flags are assigned, and any automatic flags are resolved.

A data-base printout is then produced to provide hard-copy documentation of the data entry.

MAINTENANCE

- Graphite tubes last from 60 to 100 samples. When a new graphite tube is installed, it must be conditioned through the aluminum-conditioning program as outlined in the operator's manual. L'vov platforms will last through the life of three graphite tubes.
- Clean quartz windows and check furnace alignment at least once every 6 months.

INTERFERENCES

With flameless atomization, background correction is necessary at wavelengths below 350 nm. Gaseous molecular species, salt particles, and smoke can absorb radiant energy emitted by the lamp. This effect may vary between samples and standards. Deuterium arc background correction ensures that an artificially high absorbance is not measured.

SAFETY CONSIDERATIONS

Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

Perkin-Elmer, 1982, Analytical methods for atomic absorption spectrophotometry operators manual B303-0152: Norwalk, Conn., Perkin-Elmer (variously paged).

----- 1985, Techniques in graphite furnace atomic absorption spectrophotometry operators manual B017-4195: Norwalk, Conn., Perkin-Elmer (variously paged).

----- 1990, HGA-700 graphite furnace operators manual B3205: Norwalk, Conn., Perkin-Elmer (variously paged).

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies - laboratory analysis for surface water chemistry: Washington, D.C., U.S. Environmental Protection Agency, EPA/600/4-87/026 (variously paged).

ALUMINUM, TOTAL MONOMERIC

Cross references:

USGS Method Code: -- none
ISWS Method Code: -- none
EPA Section # 8.0

Applications.—This method is used to measure concentrations of total monomeric aluminum in dilute surface waters and soil waters. Separation between monomeric and polymeric aluminum is determined by complexation with pyrocatechol violet. Total monomeric aluminum is operationally defined as the fraction of total aluminum species that will complex with pyrocatechol violet. In environmental waters, this fraction is primarily aluminum monomers complexed with inorganic and organic ligands.

Summary.—The analysis for total monomeric aluminum is an automated colorimetric reaction. Each sample is systematically introduced into the flow- injection analyzer (FIA) reaction manifold. The sample is initially mixed with a 1,10 phenanthroline/hydroxylamine hydrochloride reagent, which eliminates the interference of iron. The sample subsequently reacts with a pyrocatechol violet (PCV) solution that turns blue-gray in the presence of monomeric aluminum. Aluminum polymers and strongly complexed Al monomers will not react with PCV. A hexamethylenetetramine buffer is added to adjust pH to about 6.2. The absorbance of the color complex is measured at a wavelength of 580 nm.

INSTRUMENTATION AND EQUIPMENT

- Lachat QuikChem Automated Analyzer System consisting of:
  - XYZ sampler
  - Diluter
  - Pump
  - Injection module
  - Reaction module
  - Total Monomeric Al reaction manifold
  - Photometer
  - QuikChem AE software and compatible computer
- Replacement pump tubes
- Sample tubes

SAMPLE PRESERVATION AND STORAGE

Samples are stored in acid-washed polyethylene bottles at 4°C without being filtered or acidified.

REAGENTS AND STANDARDS

Degassed Deionized (DI) Water.—DI water is degassed by bubbling with commercial-grade helium for about 2 min. Degassed DI water is used for carrier water and for preparation of all reagents.

1-10 Phenanthroline/Hydroxylamine Hydrochloride Reagent.—Add 7.6 g hydroxylamine hydrochloride ($H_2NOH{\cdot}HCl$; 99+ percent purity) to about 500 mL DI water in a 1,000-mL volumetric flask. Stir until all crystals have dissolved. Add 0.56 g anhydrous 1,10 phenanthroline ($C_{12}H_8N_2$; 99+ percent purity) and stir until dissolved (about 20 min). Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C.

Pyrocatechol Violet (PCV).—Add 0.386 g PCV (about 90 percent purity) to a 1,000-mL volumetric flask containing 500 mL DI water. Swirl until the PCV has dissolved. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. This reagent should be prepared fresh daily.

Hexamethylenetetramine Buffer.—Add 84.0 g hexamethylenetetramine [$(CH_2)_6N_4$); 99+ percent purity] to about 800 mL DI water in a 1,000-mL volumetric flask. Mix until all solid is dissolved. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C.

Hydrochloric Acid (1.0 M).—Add 82.5 mL concentrated hydrochloric acid (HCl) to a 1,000-mL volumetric flask containing about 500 mL DI water. Swirl, then fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle.

Cleaning Solution.—Add 65 g sodium hydroxide (NaOH) to a 1,000-mL volumetric flask containing about 800 mLDI water. Swirl the flask until all pellets have dissolved. Add 6 g disodium ethylenediamine tetraacetic acid dihydrate ($Na_2EDTA{\cdot}2H_2O$) to the flask. Cool, then fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle.

Aluminum Standard Stock Solution, 1,000 mg Al/L.—Use a 1,000-mg/L aluminum atomic absorption standard purchased commercially.

Aluminum Standard Substock Solution, 50 mg Al/L.—Pipet 25.0 mL aluminum standard stock into a 500-mL volumetric flask. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare every 6 months.

Aluminum Working Standards.—Pipet desired amount of standard substock into a 100-mL volumetric flask. Add 0.1 mL 1.0M HCl. Fill to the mark with DI water and mix thoroughly. Store standards in polyethylene bottles at 4°C. Prepare every other day

Standard A:	37.06 µmol/L (1.00 mg/L)	2.0 mL substock
Standard B:	27.80 µmol/L (0.75 mg/L)	1.5 mL substock
Standard C:	18.53 µmol/L (0.50 mg/L)	1.0 mL substock
Standard D:	11.12 µmol/L (0.30 mg/L)	0.6 mL substock
Standard E:	7.41 µmol/L (0.20 mg/L)	0.4 mL substock
Standard F:	3.71 µmol/L (0.10 mg/L)	0.2 mL substock
Standard G:	1.85 µmol/L (0.05 mg/L)	0.1 mL substock
Standard H:	0.00 µmol/L (0.00 mg/L)	0.0 mL substock

Quality-Control (QC) Stock Solution, 1,000 mg Al/L.—Use a 1,000-mg/L aluminum atomic absorption standard purchased commercially. This stock must be from a manufacturer or lot different from the standard stock.

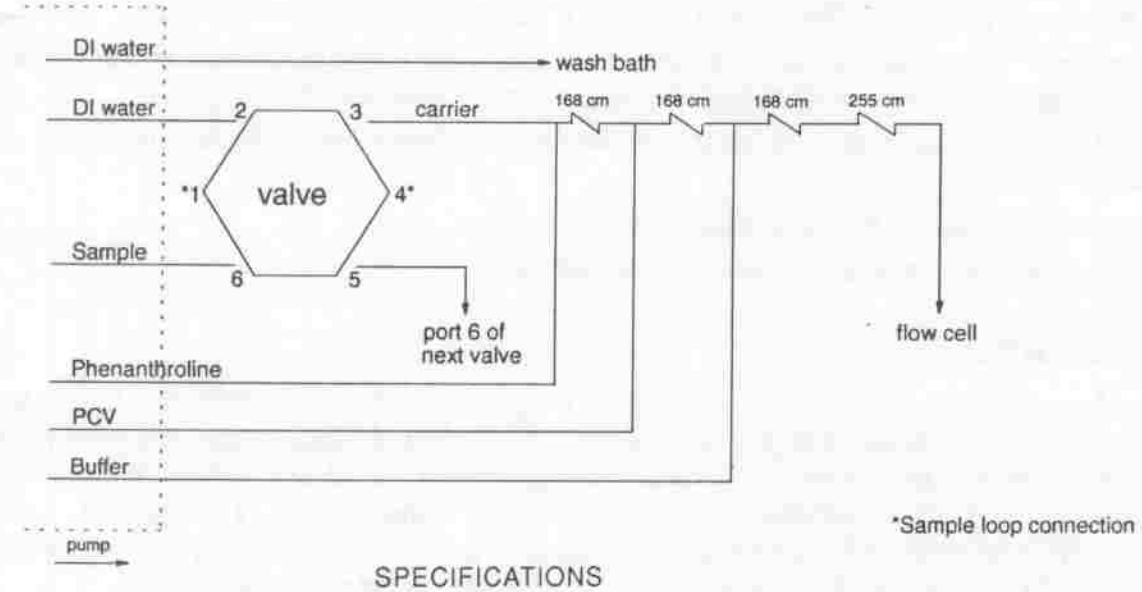
Aluminum QC Substock Solution, 50 mg Al/L.—Pipet 25.0 mL aluminum QC stock into a 500 mL-volumetric flask. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare every 6 months.

Aluminum QC Samples.—Pipet desired amount of QC substock into a 250-mL volumetric flask. Add 0.25 mL 1.0M HCl. Fill to the mark with DI water and mix thoroughly. Store QC samples in polyethylene bottles at 4°C. Prepare every other day

QC-low concentration:	7.41 µmol/L (0.20 mg/L)	1.0 mL QC substock
QC-high concentration:	18.53 µmol/L (0.50 mg/L)	2.5 mL QC substock

PROCEDURE

1. Turn the power on for all components of the Lachat system. After the main menu appears on both monitor screens, download the appropriate aluminum method.[1]
2. Install the total monomeric aluminum reaction manifold onto the second reaction module. See manifold flow chart (fig. 1).



SPECIFICATIONS

Manifold tubing: 0.8mm i.d.
Sample loop: 150 cm (754 µL)
Flow cell: 10 mm
Interference filter: 580 nm
Pump setting: 35

Pump tubes:
DI water/wash bath: 2.00 mL/min (green)
DI water/carrier: 1.60 mL/min (blue)
Sample: 2.00 mL/min (green)
Phenanthroline: 0.32 mL/min (black)
PCV: 0.32 mL/min (black)
Buffer: 0.80 mL/min (red)

Figure 1. Schematic diagram of total monomeric aluminum flow-injection manifold

3. Put all reagent lines into a beaker of degassed DI water.
4. Adjust the tension levers on the individual pump tube cassettes. Set the pump to "OVERRIDE STANDBY."
5. After all air has been pumped out of the system, place each reagent line into its respective container.
6. Continue to pump the reagents through until the baseline has stabilized. Return the pump to standby speed.

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1. The New York District Laboratory Lachat system is capable of determining concentrations of up to three constituents concurrently. Generally the analysis for total monomeric Al concentrations is run together with the analysis for organic monomeric Al concentrations.

7. Place the diluter line into a container of DI water.
8. Place standards A-H, QC-high range, and QC-low range in their containers in the order specified on the sample tray labeled "STANDARDS." Put empty sample tubes into the dilution tray labeled "EMPTY TUBES."
9. Start the calibration.
10. Check the calibration curve. If the calibration fails, repeat the calibration procedure.
11. If the calibration is acceptable, load samples into the first tray labeled "SAMPLES" and type in the sample serial numbers in the tray identification window.
12. Submit the tray.
13. At the end of the run(s), rinse the ends of all reagent lines and put all lines into a beaker of DI water. Set the pump speed to "OVERRIDE STANDBY." Let the system flush for 5 min.
14. Place the PCV line into the cleaning solution to remove the brown discoloration that forms in the reaction manifold. Remove the line after 1 min and place it back into DI water.
15. Pump DI water through all lines for 15 min. Remove the lines from the beaker and let the system pump air to dry.
16. Release the tension on the pump-tube cassettes.
17. Turn off the power to all components of the system.

QUALITY CONTROL

- Standard-curve and data-verification calculations are performed by the QuikChem AE software package supplied by Lachat. The standard curve is a linear plot of standard concentration vs. average absorbance. The standard curve is separated into two segments–the first is calculated from Standards A-D (37.06 µmol/L - 11.12 µmol/L), and the second from Standards D-H (11.12 µmol/L - 0.00 µmol/L). The best-fit line is drawn for each segment, and the curve is accepted if the correlation coefficient is 0.995 or greater for the high range and 0.990 or greater for the low range.
- Quality-control samples are analyzed at the start of a run, after every 10 samples during the run, and at the end of the run. A quality-control sample is acceptable if the analyzed value is within 10 percent of the QC-high-range theoretical value and 15 percent of the QC-low-range theoretical value.
- Samples are diluted and reanalyzed if the measured concentration exceeds the concentration of the highest standard. Dilution factors are calculated and applied by the instrument software, and dilution reruns are performed automatically by the instrument. Samples are also reanalyzed if they are associated with a quality-control sample that failed.
- Sample serial numbers are entered in the computer before the sample tray is submitted. A real-time printout is produced as the run progresses, to monitor the peak integrity factors for each sample. At the conclusion of the run, the sample serial numbers and concentration values are electronically combined into a data file that is printed. This file is electronically transferred into the SAS network data base, where it is verified against the data-file printout. Any necessary flags are assigned at this time. A data-base printout is then produced to provide hard-copy documentation of the data entry.

MAINTENANCE

- All pump tubes must be replaced as they become worn or stretched. The frequency will depend upon the number of samples analyzed. The sample and wash-bath pump tubes should be changed monthly.
- Interference filters should be cleaned with lens paper whenever they are changed.

- Manifold tubing must be replaced as it becomes discolored or clogged.
- Sample tubes are rinsed, then soaked in DI water overnight, and oven dried between uses.
- Buildup and clogging may require periodic replacement of the waste lines.
- Effluent pH needs to be checked weekly to ensure that the pH is between 6.1 and 6.3.

INTERFERENCES

Fe^{3+} interferes with this method. Fe^{3+} is reduced to Fe^{2+} by hydroxylamine hydrochloride and then chelated by 1,10-phenanthroline to eliminate the interference. Samples should not be acidified because this will change the aluminum speciation. Chelating agents and inorganic ions that are strong complexers also interfere with the PCV color development.

SAFETY CONSIDERATIONS

All concentrated acids and bases should be mixed in a hood. Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

Lachat Instruments, 1990, Methods manual for the QuikChem automated ion analyzer - Method no. 10-113-33-1-A: Milwaukee, Wisc., Lachat Instruments (variously paged).

Peden, M.E. and others, 1989, Evaluation of aluminum speciation using synthetic and natural samples - final report: Champaign, Ill., Illinois State Water Survey Contract Report 463,

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies - laboratory analysis for surface water chemistry, Washington, D.C., U.S. Environmental Protection Agency, EPA 600/4-87/026 (variously paged).

ALUMINUM, ORGANIC MONOMERIC

Cross references:

USGS Method Code: -- none
ISWS Method Code: -- none
EPA Section # 8.0

Applications.—This method is used to measure organic monomeric aluminum concentrations in dilute surface waters and soil waters. Organic and inorganic monomeric aluminum are differentiated by their reactivity with strongly acidic cation-exchange resin. Organic monomeric aluminum is operationally defined as the fraction of aluminum species that will complex with pyrocatechol violet but will not adsorb to the cation-exchange resin. In environmental waters this fraction is primarily aluminum monomers complexed with organic ligands.

Summary.—The analysis of organic monomeric aluminum is an automated colorimetric reaction. This method is identical to the total monomeric aluminum method except for the addition of a cation-exchange column. Each sample is systematically introduced into the flow-injection analyzer (FIA) reaction manifold. The sample is passed through the column that removes inorganic aluminum and is then mixed with a 1,10 phenanthroline/hydroxylamine hydrochloride reagent, which eliminates the interference of iron. The sample subsequently reacts with a pyrocatechol violet (PCV) solution that turns blue-gray in the presence of monomeric aluminum. Aluminum polymers and strongly complexed Al monomers will not react with PCV. A hexamethylenetetramine buffer is added to adjust the pH to about 6.2. The absorbance of the color complex is measured at a wavelength of 580 nm.

INSTRUMENTATION AND EQUIPMENT

- Lachat QuikChem Automated Analyzer System consisting of:
  - XYZ sampler
  - Diluter
  - Pump
  - Injection module
  - Reaction module
  - Organic monomeric Al reaction manifold
  - Photometer
  - QuikChem AE software and compatible computer
- Replacement pump tubes
- Sample tubes

SAMPLE PRESERVATION AND STORAGE

Samples are stored in acid-washed polyethylene bottles at 4°C, without being filtered or acidified.

REAGENTS AND STANDARDS

Degassed Deionized (DI) Water.—DI water is degassed by bubbling with commercial-grade helium for about 2 min. Degassed DI water is used for carrier water and in preparation of all reagents.

1-10 Phenanthroline/Hydroxylamine Hydrochloride Reagent.—Add 7.6 g hydroxylamine hydrochloride ($H_2NOH{\cdot}HCl$; 99 percent purity) to about 500 mL DI water in a 1,000-mL volumetric flask. Stir until all

crystals have dissolved. Add 0.56 g anhydrous 1,10 phenanthroline ($C_{12}H_8N_2$; 99+ percent purity) and stir until dissolved (about 20 min). Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C.

Pyrocatechol Violet (PCV).—Add 0.386 g PCV (about 90 percent purity) to a 1,000-mL volumetric flask containing 500 mL DI water. Swirl until the PCV has dissolved. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene container. This reagent should be prepared fresh daily.

Hexamethylenetetramine Buffer.—Add 84.0 g hexamethylenetetramine ($(CH_2)_6N_4$); 99+ percent purity) to about 800 mL DI water in a 1,000-mL volumetric flask. Mix until all solid is dissolved. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C.

Hydrochloric Acid (1.0 M).—Add 82.5 mL concentrated hydrochloric acid (HCl) to a 1,000-mL volumetric flask containing about 500 mL DI water. Swirl, then fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle.

Sodium Chloride (1 mM).—Add 0.058 g sodium chloride (NaCl) to a 1,000-mL flask containing about 500 mL DI water. Swirl to mix. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle.

Resin (pH about 5.0).—Add 100 mL DI water to a 250-mL beaker containing 100 g Amberlite IR-120(plus) ion-exchange resin-sodium form and 1.00 g Amberlite IR-120(plus) ion-exchange resin- acidic form. Mix thoroughly and decant the liquid. Wash again with DI water and then twice with 100-mL portions of 1 mM NaCl. Store the resin in a wide-mouth container at 4°C. Prepare every 6 months.

Cation-Exchange Column.—Remove the fittings and foam plugs at both ends of the glass column and rinse the column with DI water. Replace the foam plug at one end using forceps. Draw about 10 cc resin and supernatent into a 20-cc syringe. With the plugged side down, inject the resin into the top of the column in one motion without allowing air into the column. Once the column is full, cover the bottom end with a finger and plug the top end with foam. Replace the fitting on the top end, then turn the column over and replace the fitting on the other end. Keep the column closed until the system is ready for the column addition. If the fittings are not in place, the liquid will drain out, and the column must be repacked. If air bubbles are introduced during the packing procedure, the column must be rinsed and repacked. The column is packed daily. The used resin is not regenerated.

Cleaning Solution.—Add 65 g sodium hydroxide (NaOH) to a 1,000-mL volumetric flask containing about 800 mL DI water. Swirl the flask until all pellets have dissolved. Add 6 g disodium ethylenediamine tetraacetic acid dihydrate ($Na_2EDTA \cdot 2H_2O$) to the flask. Fill to the mark with DI water and mix. Store in a polyethylene bottle.

Aluminum Standard Stock Solution, 1,000 mg Al/L.—Use a 1,000-mg/L aluminum atomic absorption standard purchased commercially.

Aluminum Standard Substock, 50 mg Al/L.—Pipet 25.0 mL aluminum standard stock into a 500-mL volumetric flask. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare every 6 months.

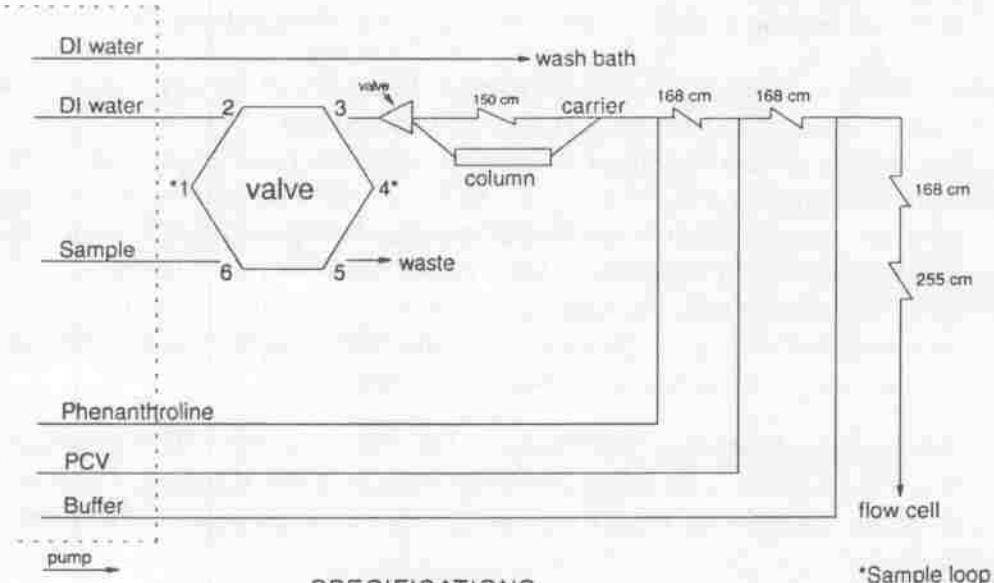
Aluminum Working Standards.—Pipet desired amount of standard substock into a 100-mL volumetric flask. Add 0.1 mL 1.0M HCl. Fill to the mark with DI water and mix thoroughly. Store standards in polyethylene bottles at 4°C. Prepare every other day.

Standard A:	37.06 µmol/L (1.00 mg/L)	2.0 mL substock
Standard B:	27.80 µmol/L (0.75 mg/L)	1.5 mL substock
Standard C:	18.53 µmol/L (0.50 mg/L)	1.0 mL substock
Standard D:	11.12 µmol/L (0.30 mg/L)	0.6 mL substock
Standard E:	7.41 µmol/L (0.20 mg/L)	0.4 mL substock
Standard F:	3.71 µmol/L (0.10 mg/L)	0.2 mL substock
Standard G:	1.85 µmol/L (0.05 mg/L)	0.1 mL substock
Standard H:	0.00 µmol/L (0.00 mg/L)	0.0 mL substock

Aluminum Quality-Control (QC) Samples.—QC samples are not currently available for the organic monomeric aluminum analysis. Total monomeric aluminum QC's are also analyzed in the organic monomeric aluminum analysis as a check on column efficiency. The column should remove all aluminum from the QC sample. If the QC produces a peak, the column is emptied and repacked with new resin.

PROCEDURE

1. Turn on the power for all components of the Lachat system. After the main menu appears on both monitor screens, download the appropriate aluminum method.[1]
2. Install the organic monomeric aluminum reaction manifold onto the third reaction module. See manifold flow chart (fig. 2).



SPECIFICATIONS

Manifold tubing: 0.8 mm i.d.
Sample loop: 150 cm (754 µL)
Flow cell: 10 mm
Interference filter: 580 nm
Pump setting: 35

Pump tubes:
DI water/wash bath: 2.00 mL/min (green)
DI water/carrier: 1.60 mL/min (blue)
Sample: 2.00 mL/min (green)
Phenanthroline: 0.32 mL/min (black)
PCV: 0.32 mL/min (black)
Buffer: 0.80 mL/min (red)

Figure 2. Schematic diagram of organic monomeric aluminum flow-injection manifold.

1. The New York District Laboratory Lachat system is capable of determining concentrations of up to three constituents concurrently. Generally the analysis for organic monomeric Al concentrations is run together with the analysis for total monomeric Al concentrations.

3. Put all reagent lines into a beaker of degassed DI water. Turn the three-way valve to the position that bypasses flow through the column.
4. Adjust the tension levers on the individual pump-tube cassettes. Set the pump to "OVERRIDE STANDBY."
5. After all air has been pumped out of the system, turn the valve back to the position that allows flow through the column. Remove one fitting from the packed column and attach this end to the column fitting on the manifold that is closest to the valve. Remove the other fitting and attach this end to the remaining manifold column fitting. The column is now in line.
6. Return the valve to the position that bypasses the column and place each reagent line into its respective container.
7. Continue to pump the reagents through until the baseline has stabilized. Return the pump to standby speed.
8. Place the diluter line into a container of DI water.
9. Place standards A-H, QC-high, and QC-low in their containers in the order specified on the sample tray labeled "STANDARDS." Put empty sample tubes into the dilution tray labeled "EMPTY TUBES."
10. Start the calibration. Flow through the column should be bypassed during the calibration procedure.
11. Check the calibration curve. If the calibration fails, repeat the calibration procedure.
12. If the calibration is acceptable, turn the valve to allow flow through the column.
13. Load samples into the first tray labeled "SAMPLES" and type the sample serial numbers in the tray-identification window.
14. Submit the tray.
15. At the end of the run(s), turn the valve to bypass flow through the column.
16. Rinse off the ends of all the reagent lines and put all lines into a beaker of DI water. Set the pump speed to "OVERRIDE STANDBY." Let the system flush for 5 min.
17. Place the PCV line in the cleaning solution to remove the brown discoloration that forms in the reaction manifold. Remove the line after 1 min and place it back in DI water.
18. Pump DI water through all lines for 15 min.
19. Remove the column from the manifold. Remove the plugs and flush the column with DI water. Place the column back in line.
20. Remove the lines from the beaker and let the system pump air to dry.
21. Release the tension on the pump-tube cassettes.
22. Turn off the power to all components of the system.

QUALITY CONTROL

- Standard curve and data-verification calculations are performed by the QuikChem AE software package supplied by Lachat. The standard curve is a linear plot of standard concentration vs. average absorbance. It is separated into two segments–the first is calculated from Standards A-D (37.06 µmol/L - 11.12 µmol/L); the second is calculated from Standards D-H (11.12 µmol/L - 0.00 µmol/L). The best-fit line is drawn for each segment, and the curve is accepted if the correlation coefficient is 0.995 or greater for the high concentrations and 0.990 or greater for the low concentrations.

- Samples are diluted and reanalyzed if they exceed the concentration of the highest standard. Dilution factors are calculated and applied by the software, and dilution reruns are performed automatically by the instrument. Samples are also reanalyzed if they are associated with a total monomeric aluminum quality-control sample that failed. (See total monomeric aluminum method.)
- Sample serial numbers are entered in the computer before the sample tray is submitted. A real-time printout is produced as the run progresses to monitor the peak integrity factors for each sample. At the conclusion of the run, the sample serial numbers and concentrations are electronically combined into a data file that is printed. This file is electronically transferred into the SAS network data base, where it is verified against the data-file printout. Any necessary flags are assigned at this time. A data-base printout is then produced to provide hard-copy documentation of the data entry.

MAINTENANCE

- All pump tubes must be replaced as they are worn or stretched; the frequency will depend upon the number of samples analyzed. The sample and wash-bath pump tubes should be changed once a month.
- Interference filters should be cleaned with lens paper whenever they are changed.
- Manifold tubing must be replaced as it becomes discolored or clogged.
- Sample tubes are rinsed, soaked in DI water overnight, and oven dried between uses.
- Buildup and clogging in the waste lines may require periodic replacement of the lines.
- Effluent pH should be checked weekly and should be in the range from 6.1through 6.3.

INTERFERENCES

Fe^{3+} interferes with this method. Fe^{3+} is reduced to Fe^{2+} by hydroxylamine hydrochloride and then chelated by 1,10-phenanthroline to eliminate the interference. Samples should not be acidified because this will change the aluminum speciation. Chelating agents and inorganic ions that are strong complexers also interfere with the PCV color development.

SAFETY CONSIDERATIONS

All concentrated acids and bases should be mixed in a hood. Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

Lachat Instruments, 1990, Methods manual for the QuikChem automated ion analyzer Method no. 10-113-34-1-B: Milwaukee, Wisc., Lachat Instruments (variously paged).

Peden, M.E., and others, 1987, Evaluation of aluminum speciation using synthetic and natural samples - final report: Champain, Illinois State Water Survey Contract Report 463 (variously paged).

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies - laboratory analysis for surface water chemistry Washington, D.C., U.S. Environmental Protection Agency EPA 600/4-87/026 (variously paged).

AMMONIUM

Cross references:

USGS Method Code: I-4523-85
ISWS Method Code: I-350.7
EPA Section # 10.0

Applications.—This method is used to measure ammonium concentrations in precipitation, surface water, soil water, and forest-soil extracts.

Summary.—The ammonium analysis is an automated colorimetric reaction. Samples are systematically introduced into the flow-injection analyzer (FIA) reaction manifold. The sample is initially mixed with an ethylenediamine tetraacetic acid (EDTA) buffer to prevent the precipitation of magnesium and calcium as hydroxides. The sample subsequently reacts with phenol and hypochlorite to form an indophenol blue complex. The intensity of the blue complex is enhanced by mixing with nitroferricyanide. The mixture is heated to 60°C to ensure optimal color development. The sample flows through a debubbler to remove any gas bubbles that develop. Absorbance of the color complex is measured at a wavelength of 630 nm.

INSTRUMENTATION AND EQUIPMENT

- Lachat QuikChem Automated Analyzer System consisting of:
  - XYZ sampler
  - Diluter
  - Pump
  - Injection module
  - Reaction module
  - Ammonium reaction manifold
  - Photometer
  - QuikChem AE software and compatible computer
- Replacement pump tubes
- Sample tubes

SAMPLE PRESERVATION AND STORAGE

- Samples are stored in acid-washed polyethylene bottles in a freezer without being filtered or acidified.
- Samples should be analyzed as soon as they are thawed.

REAGENTS AND STANDARDS

Degassed Deionized (DI) Water.—DI water is degassed by bubbling with commercial-grade helium for about 2 min. Degassed DI water is used for carrier water and for preparation of all reagents.

EDTA Buffer.—Add 50.0 g disodium ethylenediamine tetraacetic acid dihydrate ($Na_2EDTA{\cdot}2H_2O$) and 5.5 g sodium hydroxide (NaOH) to a 1,000-mL volumetric flask containing about 800 mL DI water. Stir until all solids have dissolved. Dilute to the mark and mix thoroughly. Store in a polyethylene bottle.

Sodium Phenolate.—Add 88 mL liquefied phenol (C_6H_5OH) to a 1,000-mL volumetric flask containing about 700 mL DI water. Add 32 g sodium hydroxide (NaOH) to the solution and swirl to mix. After the

pellets have dissolved, cool, fill to the mark with DI water, and mix thoroughly. Store in an amber bottle at 4°C. Prepare every other day.

Sodium Hypochlorite.—Dilute 500 mL household bleach containing at least 5.25 percent sodium hypochlorite (NaOCl) to 1,000 mL in a 1,000-mL volumetric flask. Mix thoroughly and store in a polyethylene bottle at 4°C. Prepare every 3 days.

Sodium Nitroferricyanide.—Add 3.50 g sodium nitroferricyanide dihydrate ($Na_2Fe(CN)_5NO{\cdot}2H_2O$) to a 1,000-mL volumetric flask containing about 500 mL DI water. Swirl to dissolve and fill to the mark with DI water. Mix thoroughly and store in an amber bottle at 4°C. This solution is stable for 3 months.

Cleaning Solution (1M HCl).—Add 82.5 mL concentrated hydrochloric acid (HCl) to a 1,000-mL volumetric flask containing about 700 mL DI water. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle.

Ammonium Standard Stock Solution, 1,000 mg NH_4^+/L (as N).—Dry about 5 g ammonium chloride (NH_4Cl) at 110°C for 2 hours and allow to cool in a desiccator. Add 1.9095 g ammonium chloride to a 500-mL volumetric flask containing about 250 mL DI water. Swirl to dissolve the solid. Fill to the mark with DI water. Mix thoroughly and store in a polyethylene bottle at 4°C. Prepare every 6 months.

Ammonium Substock Solution, 5 mg NH_4^+/L (as N).—Pipet 1.25 mL of the standard stock solution into a 250-mL volumetric flask containing 100 mL DI water. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare every 3 months.

Ammonium Working Standards.—Pipet desired amount of standard substock into a 100-mL volumetric flask. Fill to the mark with DI water and mix thoroughly. Store standards in polyethylene bottles at 4°C. Prepare every other day.

Standard A:	35.70 µmol/L (0.500 mg/L)	10.0 mL substock
Standard B:	26.77 µmol/L (0.375 mg/L)	7.5 mL substock
Standard C:	17.85 µmol/L (0.250 mg/L)	5.0 mL substock
Standard D:	10.71 µmol/L (0.150 mg/L)	3.0 mL substock
Standard E:	7.14 µmol/L (0.100 mg/L)	2.0 mL substock
Standard F:	3.57 µmol/L (0.050 mg/L)	1.0 mL substock
Standard G:	1.78 µmol/L (0.025 mg/L)	0.5 mL substock
Standard H:	0.00 µmol/L (0.000 mg/L)	0.0 mL substock

Ammonium Quality-Control (QC) Stock, 1,000 mg NH_4^+/L (as N).—Use an ammonium chloride (NH_4Cl) stock from a different manufacturer or a different lot from the standard stock. Dry about 5 g ammonium chloride at 110°C for 2 hours and allow to cool in a desiccator. Add 3.819 g ammonium chloride to a 1,000-mL volumetric flask containing about 500 mL DI water. Swirl to dissolve the solid. Fill to the mark with DI water and store in a polyethylene bottle at 4°C. Prepare every 6 months.

Ammonium QC Substock, 5 mg NH_4^+/L (as N).—Pipet 1.25 mL of QC stock into a 250-mL volumetric flask containing 100 mL DI water. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare every 3 months.

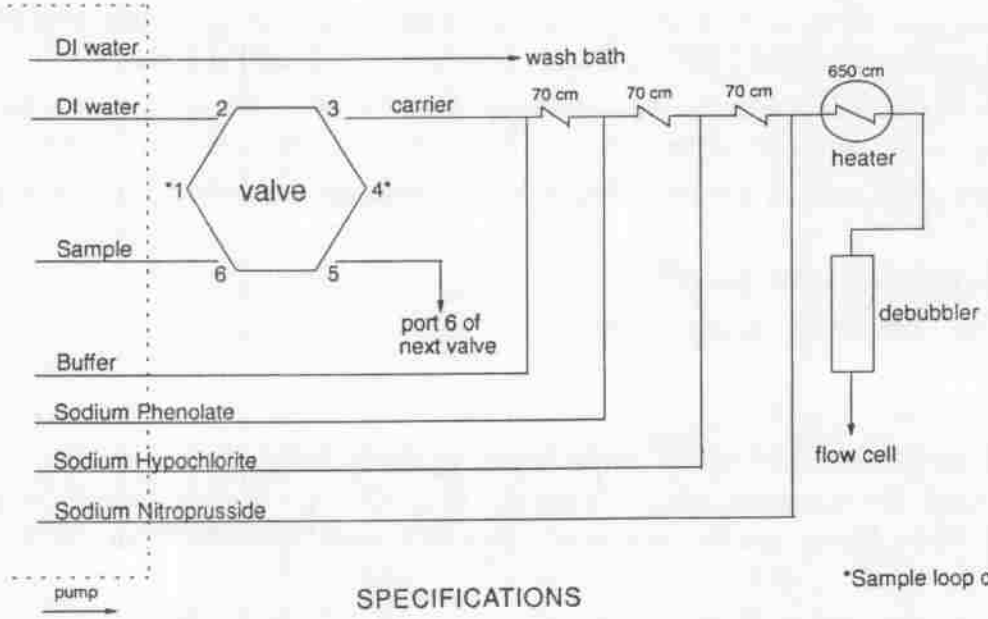
Ammonium QC Samples.—Pipet desired amount of QC substock into a 500-mL volumetric flask. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare every other day.

QC-low concentration	7.14 µmol/L (0.100 mg/L)	10.0 mL substock
QC-high concentration	17.85 µmol/L (0.250 mg/L)	25.0 mL substock

NOTE: When ammonium concentrations of soil extracts are being determined, the working standards and QC samples are prepared in a 1M KCl matrix The carrier and diluent are also 1M KCl, not DI water.

PROCEDURE

1. Turn on the power on for all components of the Lachat system. After the main menu appears on both monitor screens, download the appropriate ammonium method.[1]
2. Install ammonium-reaction manifold onto the first reaction module. See manifold flowchart (fig. 3).



SPECIFICATIONS

Manifold tubing: 0.8 mm i.d.
Sample loop: 150 cm (754 µL)
Flow cell: 10 mm
Interference filter: 630 nm
Pump setting: 35
Heater: 60°C
Debubbler: 50 mm glass tubing with 0.8 mm i.d.

Pump tubes:
DI water/wash bath: 2.00 mL/min (green)
DI water/carrier: 1.00 mL/min (gray)
Sample: 2.00 mL/min (green)
Buffer: 0.80 mL/min (red)
Sodium Phenolate: 0.42 mL/min (orange)
Sodium Hypochlorite: 0.32 mL/min (black)
Sodium Nitroprusside: 0.42 mL/min (orange)

Figure 3. Schematic diagram of ammonium flow-injection manifold.

1. The New York District Laboratory Lachat system is capable of determining concentrations of up to three constituents concurrently. Generally, concentrations of ammonium, nitrite, and nitrite plus nitrate in soil extracts are determined concurrently.

3. Put all reagent lines into a beaker of degassed DI water.
4. Adjust the tension levers on the individual pump-tube cassettes. Set the pump to "OVERRIDE STANDBY."
5. After all air has been pumped out of the system, place each reagent line into its respective container.
6. Continue to pump the reagents through until the baseline has stabilized. Turn the debubbler over to expel all air to waste. Return the debubbler to its original position. Return the pump to standby speed.
7. Place the diluter line in a container of DI water.
8. Place standards A-H, QC-high, and QC-low in their containers in the order specified on the sample tray labeled "STANDARDS." Put empty sample tubes into the dilution tray labeled "EMPTY TUBES."
9. Start the calibration.
10. Check the calibration the curve. If the calibration fails, repeat the calibration procedure.
11. If the calibration is acceptable, load samples into the first tray labeled "SAMPLES" and type in the sample serial numbers in the tray-identification window.
12. Submit the tray.
13. At the end of the run(s), rinse off the ends of all the reagent lines and put all lines into a beaker of DI water. Set the pump speed to "OVERRIDE STANDBY." Let the system flush for 5 min.
14. Place the reagent lines int a beaker containing the cleaning solution to remove any discoloration that forms in the lines after the heater. Remove the lines after 2 min and place them back in DI water.
15. Pump the DI water through all lines for 15 min. Remove the lines from the beaker and let the system pump air to dry.
16. Release the tension on the pump-tube cassettes.
17. Turn off the power to all components of the system.

QUALITY CONTROL

- Standard curve and data-verification calculations are performed by the QuikChem AE software package supplied by Lachat. The standard curve is a linear plot of standard concentration vs. average absorbance. The best-fit line is drawn, and the curve is accepted if the correlation coefficient is 0.999 or greater.
- Quality-control samples are analyzed at the start of a run, after every 10 samples during the run, and at the end of the run. A quality-control sample is acceptable if the analyzed value is within 10 percent of the QC-high theoretical value and 15 percent of the QC-low theoretical value.
- Samples are diluted and reanalyzed if their concentration exceeds the concentration of the highest standard. Dilution factors are calculated and applied by the instrument software, and dilution reruns are performed automatically by the instrument. Samples are also reanalyzed if they are associated with a quality-control sample that failed.
- Sample serial numbers are entered into the computer before the sample tray is submitted. A real-time printout is produced as the run progresses to monitor the peak integrity factors for each sample. At the conclusion of the run, the sample serial numbers and concentrationsare electronically combined into a data file that is printed. This file is electronically transferred into the SAS network data base, where it is verified against the data-file printout. Any necessary flags are assigned at this time. A data-base printout is then produced to provide hard-copy documentation of the data entry.

MAINTENANCE

- All pump tubes must be replaced as they become worn or stretched. The frequency will depend on the number of samples analyzed. The sample and wash-bath pump tubes should be changed once a month.
- Interference filters should be cleaned with lens paper whenever they are changed.
- Manifold tubing must be replaced as it becomes discolored or clogged.
- Sample tubes are rinsed, soaked in DI water overnight, and oven dried between cases.
- Waste lines may need to be replaced periodically due to build-up and clogging.

INTERFERENCES

Sample color may interfere with this method and cause abnormally high ammonium measurements. High concentrations of calcium and magnesium may cause precipitation of hydroxides.

SAFETY CONSIDERATIONS

- All concentrated acids and bases should be mixed in a hood.
- Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis. Prepare the phenol in a hood and keep the bottles closed at all times.

REFERENCES

Fishman, M.J. and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A5, 545 p.

Lachat Instruments, 1990, Methods manual for the QuikChem automated ion analyzer: Method no. 10-107-06-1-B: Milwaukee, Wisc., Lachat Instruments (variously paged).

Peden, M.E., and others, 1986, Methods for collection and analysis of precipitation: Champaign, Ill., Illinois State Water Survey Contract Report 381 (variously paged).

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies - laboratory analysis for surface water chemistry: Washington, D.C., U.S. Environmental Protection Agency, EPA 600/4-87/026 (variously paged).

ANIONS: CHLORIDE, NITRATE, AND SULFATE

Cross references:

USGS Method Code, chloride, sulfate: I-2057-90
USGS Method Code, nitrate: -- none
ISWS Method Code: 300.6
EPA Section # 11.0

Applications.—This method is used for analysis of chloride, nitrate, and sulfate concentrations in precipitation and dilute surface waters and soil waters.

Summary.—Chloride, nitrate, and sulfate are separated chromatographically after sample injection into an anion exchange column. Ions are separated on the basis of their affinity for the exchange sites of the resin. The separated anions are detected with an electrical conductivity cell. Anions are identified on the basis of their retention times in relation to those of known standards. The peak area is measured and compared with a standard curve to determine concentrations.

INSTRUMENTATION AND EQUIPMENT

- Ion chromatograph, Model DX 100, equipped with Dionex AI450 data station
- Guard and separator columns, Dionex AG4A and AS4A
- Anion micromembrane suppressor, Dionex AMMS-II
- Autosampler, Dionex Model ASM-2
- Sample loop about 15 µL
- Computer equipped with Dionex AI450 software

SAMPLE PRESERVATION AND STORAGE

Samples are filtered through a 0.4-µm polycarbonate filter and stored at 4°C in polyethylene bottles that have been rinsed, then leached with DI water.

REAGENTS AND STANDARDS

Nitrogen Gas.—Use standard-grade nitrogen (N_2), purchased commercially.

Eluent Solution, 0.0015M sodium bicarbonate/0.0016M sodium carbonate.—Dissolve 0.25 g sodium bicarbonate ($NaHCO_3$) and 0.35g sodium carbonate (Na_2CO_3) in helium-sparged DI water and dilute to 2,000 mL. Prepare daily.

Regenerant, 0.025N sulfuric acid.—Add 2.8 mL concentrated sulfuric acid (H_2SO_4) to DI water and dilute to 4,000 mL. Prepare as needed.

Mixed-Anion Standard Stock Solution, 1,000 mg Cl^-/L, 1,000 mg NO_3^-/L, 2,500 mg SO_4^{2-}/L.—All salts must be dried at 105°C for 3 hours and cooled in a desiccator. Add 1.6484 g sodium chloride (NaCl), 1.3707 g sodium nitrate ($NaNO_3$), and 4.5355 g potassium sulfate (K_2SO_4) to a 1,000-mL volumetric flask containing 500 mL DI water. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare every 6 months.

Mixed-Anion Working Standards.—Pipet appropriate amounts of standard stock solutions into volumetric glassware and fill to the mark with DI water. Prepare every month.

Standard A:	chloride:	112.88 µmol/L (4.0 mg/L)	pipet 2.0 mL standard stock per 500 mL
	nitrate:	64.512 µmol/L (4.0 mg/L)	
	sulfate:	104.1 µmol/L (10.0 mg/L)	
Standard B:	chloride:	56.44 µmol/L (2.0 mg/L)	pipet 1.0 mL standard stock per 500 mL
	nitrate:	32.256 µmol/L (2.0 mg/L)	
	sulfate:	52.05 µmol/L (5.0 mg/L)	
Standard C:	chloride:	14.11 µmol/L (0.5 mg/L)	pipet 0.5 mL standard stock per 1,000 mL
	nitrate:	8.064 µmol/L (0.5 mg/L)	
	sulfate:	13.01 µmol/L (1.25 mg/L)	
Standard D:	chloride:	5.644 µmol/L (0.2 mg/L)	pipet 0.2 mL standard stock per 1,000 mL
	nitrate:	3.226 µmol/L (0.2 mg/L)	
	sulfate:	5.205 µmol/L (0.5 mg/L)	

Mixed-Anion Quality-Control (QC) Stock, 300 mg Cl^-/L, 300 mg NO_3^-/L, 800 mg SO_4^{2-}/L.—Prepare a mixed-anion QC stock solution from salts obtained from a manufacturer or lot different from that of the those used to prepare the standard stock solutions. All salts must be dried at 105°C for 3 hours and cooled in a desiccator. Add 0.4945 g sodium chloride (NaCl), 0.4112 g sodium nitrate ($NaNO_3$), and 1.4514 g potassium sulfate (K_2SO_4) to a 1,000-mL volumetric flask containing 500 mL DI water. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare every 3 months.

Anion QC Samples.—Pipet desired amount of mixed-anion QC stock into a volumetric flask. Fill to the mark with DI water and mix thoroughly. Prepare every 6 months.

QC-low concentration:	chloride	8.47 µmol/L (0.3 mg/L)	1.0 mL QC stock per 1,000 mL
	nitrate	4.838 µmol/L (0.3 mg/L)	
	sulfate	8.33 µmol/L (0.8 mg/L)	
QC-high concentration:	chloride	84.66 µmol/L (3.0 mg/L)	5.0 mL QC stock per 500 mL
	nitrate	48.384 µmol/L (3.0 mg/L)	
	sulfate	83.3 µmol/L (8.0 mg/L)	

PROCEDURE

1. Turn on nitrogen gas to pressurize eluent and regenerant reservoirs. Regenerant reservoir pressure should be about 7 psi, eluent reservoir pressure about 3 psi.
2. Turn on eluent pump; set to a flow rate of 2.0 mL/min. Allow instrument to stabilize (about 30 min).
3. When stable, the conductivity should be 10-20 µS/cm, with no drifting or fluctuating.
4. Load appropriate "Method" and "Schedule" software into system.
5. Analyze one standard to verify that retention times and peak shapes are acceptable. Typical retention times are as follows:

   Chloride ≅ 1.60 min Nitrate ≅ 3.75 min Sulfate ≅ 8.50 min

6. Analyze mixed-anion working standards from lowest to highest concentrations. If the calibration is acceptable, proceed to the next step. If calibration is not acceptable, recalibrate.
7. Produce printout of the calibration curves.
8. Analyze one QC-low and one QC-high sample. If the samples meet the acceptance criteria, proceed by loading a DI blank and 10 samples into the autosampler. If the QC samples do not meet the acceptance criteria, rerun one or both of them. If the QCs meet the acceptance criteria, proceed with the run. If the QCs do not meet the acceptance criteria, recalibrate the instrument.
9. If the instrument is set to run overnight, set the pump pressure "LOW LIMIT" to 30 psi.

QUALITY CONTROL

- The AI450 software determines best-fit line and correlation coefficients. An acceptable standard curve has a correlation coefficient of at least 0.997 for each analyte.
- Quality-control samples are analyzed at the start of a run, after every 10 samples during the run, and at the end of the run. A quality-control sample is acceptable if the analyzed value is within 10 percent of the theoretical value.
- Samples are diluted and reanalyzed if their concentration exceeds the concentration of the highest standard. Any necessary dilutions are done manually. Samples are also reanalyzed if they are associated with a quality-control sample that failed.
- As the samples are loaded into the autosampler, an instrument bench sheet is created to record the order of samples. When the run is completed, a batch file is created, printed, and checked to determine if any samples need to be rerun. The serial numbers of acceptable samples are entered into the batch file and edited. A printout of the edited batch file is produced and checked, then the file is electronically transferred into the network SAS data base, where it is verified against the batch-file printout. Any necessary flags are assigned at this time. A data-base printout is produced to provide hard copy documentation of the data entry.

MAINTENANCE

- Column deterioration is indicated by an increase in system pressure above 3,000 psi and(or) decrease in retention times.
- An increase in system pressure may indicate the need to change bed supports in the guard columns, to clean the columns with 1M HCl, or to replace either guard or separator columns.
- A decrease in retention times, especially of sulfate, indicates that the columns need to be cleaned with 1M HCl or replaced.

INTERFERENCES

Samples containing significant amounts of organic acids produce peaks that are eluted just prior to the chloride peak and make the integration of chloride erroneously high. Using a weaker eluent or decreasing the flow rate will help correct this problem.

SAFETY CONSIDERATIONS

Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory - Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations book 5, chap. 1, 545 p.

Peden, M.E., and others, 1986, Methods for collection and analysis of precipitation: Champaign, Ill., Illinois State Water Survey Contract Report 381 (variously paged).

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies - laboratory analysis for surface water chemistry: Washington, D.C., U.S. Environmental Protection Agency , EPA 600/4-87/026 (variously paged).

BASIC CATIONS: CALCIUM AND MAGNESIUM

Cross references:
USGS Method Code: Calcium: I-3152-85
USGS Method Code: Magnesium: I-3447-85
ISWS Method Code: 200.6
EPA Section Calcium # 16.5.5
EPA Section Magnesium # 16.5.7

Applications.—This method is used to measure calcium and magnesium concentrations in precipitation and in dilute surface waters and soil water.

Summary.—Calcium and magnesium analysis is performed by direct aspiration atomic absorption spectrophotometry. The sample is aspirated and atomized in an air-acetylene reducing flame for calcium and in an oxidizing flame for magnesium. A lanthanum chloride/nitric acid solution is added to the sample to minimize possible interferences. The beam from a hollow-cathode lamp is directed through the flame and onto the detector that measures radiant energy not absorbed in the flame. Calcium is measured at a wavelength of 422.7 nm, and magnesium at 285.2 nm.

INSTRUMENTATION AND EQUIPMENT

- Perkin-Elmer 1100 B atomic absorption spectrophotometer (AAS)
  - AS-90 Autosampler
  - AS-90 Controller
- Sample tubes
- Computer for data retrieval

SAMPLE PRESERVATION AND STORAGE

Samples are acidified to pH < 2 with reagent-grade nitric acid (HNO_3) for preservation and are stored in acid-washed polyethylene bottles.

REAGENTS AND STANDARDS

Lanthanum Chloride Solution.—Dissolve 66.0 g lanthanum chloride heptahydrate ($LaCl_3 \cdot 7H_2O$) in a 500-mL volumetric flask. Add 250 mL hydrochloric acid. Fill to the mark with deionized (DI) water and mix thoroughly. Store in a polyethylene bottle.

Acetylene.—Use atomic absorption-grade acetylene, purchased commercially.

Compressed Air.—Any compressed-air source is acceptable.

Calcium Standard Stock Solution, 1,000 mg Ca^{2+}/L.—Use a 1,000-mg/L calcium atomic absorption standard, purchased commercially.

Magnesium Standard Stock Solution, 1,000 mg Mg^{2+}/L.—Use a 1,000-mg/L magnesium atomic absorption standard, purchased commercially.

Mixed-cation Standard Substock, 80 mg Ca^{2+}/L 20 mg Mg^{2+}/L.—Pipet 80 mL calcium standard stock, 20 mL magnesium standard stock, 30 mL sodium standard stock, and 20 mL potassium standard stock

into a 1,000-mL volumetric flask. Add 1 mL concentrated nitric acid (HNO_3) to maintain a pH <2. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare every 6 months.

Calcium and Magnesium Working Standards.—Pipet desired amount of mixed-cation substock solution into a 500-mL volumetric flask. Add 0.5 mL nitric acid (NHO_3) to maintain a pH <2. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare fresh monthly.

	Calcium	Magnesium	
Auto zero:	0.0 µmol/L (0.0 mg/L)	0.00 µmol/L (0.0 mg/L)	0.0 mL substock
Standard 1:	10.0 µmol/L (0.4 mg/L)	4.11 µmol/L (0.1 mg/L)	2.5 mL substock
Standard 2:	29.9 µmol/L (1.2 mg/L)	12.34 µmol/L (0.3 mg/L)	7.5 mL substock
Standard 3:	49.9 µmol/L (2.0 mg/L)	20.57 µmol/L (0.5 mg/L)	12.5 mL substock
Standard 4:	99.8 µmol/L (4.0 mg/L)	41.14 µmol/L (1.0 mg/L)	25 mL substock
Standard 5:	199.6 µmol/L (8.0 mg/L)	82.28 µmol/L (2.0 mg/L)	50 mL substock
Standard 6:	299.6 µmol/L (12.0 mg/L)	----------	75 mL substock (if necessary)

Calcium Quality-Control (QC) Stock Solution, 1,000 mg Ca^{2+}/L.—Use a 1,000-mg/L calcium atomic absorption standard purchased commercially. This stock must be from a different manufacturer or a different lot than the standard stock.

Magnesium QC Stock Solution, 1,000 mg Mg^{2+}/L.—Use a 1,000-mg/L magnesium atomic absorption standard purchased commercially. This stock must be from a different manufacturer or a different lot than the standard stock.

Mixed-cation QC Samples.—Pipet desired amount of QC stock solution into a 1,000-mL volumetric flask. Add 1 mL nitric acid to maintain pH <2. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare monthly.

QC-low concentration:	calcium	25 µmol/L (1.0 mg/L)	1 mL QC stock
	magnesium	10.3 µmol/L (0.25 mg/L)	0.25 mL QC stock
QC-high concentration:	calcium	99.8 µmol/L (4.0 mg/L)	4 mL QC stock
	magnesium	41.14 µmol/L (1.0 mg/L)	1.0 mL QC stock

PROCEDURE

1. Turn on hood, acetylene, and compressed air. Record regulator pressures in the instrument logbook.
2. Turn on AAS, autosampler, and computer.
3. Clean appropriate hollow-cathode lamp with lens paper, then place lamp in location #1, making sure it is properly aligned in the 3 o'clock position.
4. On AAS enter date, set baud rate to 1200 and press "CARRIAGE RETURN" softkey.
5. Recall appropriate program and verify wavelength (calcium 422.7 nm, magnesium 285.2nm), standard concentrations, tray type, and sample locations.
6. Using an automatic pipette, dispense 0.5 mL 4-percent lanthanum chloride into each sample tube.
7. Record tray location and sample number on bench sheet.

8. Using an automatic pipette, dispense 5.0 mL of samples and QC standards into sample tubes. Injection must be done rapidly to ensure proper mixing with the lanthanum chloride solution.
9. Change pipette tip between samples.
10. Using an automatic pipette, dispense 2.0 mL lanthanum chloride into blank and standard tubes. These are the 50-mL tubes located in positions #1 through #6 on the sample tray.
11. Using an automatic pipette, dispense 20 mL of blank and standards into their respective locations.
12. Fill rinse container with deionized water and place in location #0.
13. Place AAS in run mode and turn printer on.
14. Light flame and verify that it is burning clearly. If not, turn off flame and allow burner head to cool, then clean.
15. Adjust burner-head position to achieve desired sensitivity.
16. Reset autosampler to rinse sample probe.
17. Press the ON/OFF sampler softkey to activate sampler program.
18. After an acceptable calibration, identify sample locations and begin analysis.

QUALITY CONTROL

- The Perkin-Elmer software automatically calculates a linear standard curve and computes the concentrations. The calibrations are set up in the "auto" mode, and a correlation coefficient of 0.999 or greater is acceptable.
- Quality-control samples are analyzed at the start of a run, after every 10 samples during the run, and at the end of the run. A quality-control sample is acceptable if the analyzed value is within 10 percent of the QC-high and QC-low theoretical value.
- Samples and standards are analyzed in tripilicate, and the average is recorded. A relative standard deviation of <10 percent is acceptable. The data are edited on the computer data file by entering the sample serial numbers corresponding to tray locations. A data-file printout is produced. The data are imported into the SAS network data base, where they are verified against the printout. Flags are assigned, and any automatic flags are resolved. A data-base printout is then produced to provide hard-copy documentation of the data entry.
- Samples are diluted and reanalyzed if their concentration exceeds the concentration of the highest standard. Any necessary dilutions are done manually. Samples are also reanalyzed if they are associated with a quality-control sample that failed.

MAINTENANCE

- Nebulizer flow rate needs to be checked weekly and adjusted if necessary.
- Clean flame assembly every 6 months.

INTERFERENCES

The effect of reduced sensitivity on the calcium signal from aluminum, beryllium, phosphorus, silicon, titanium, vanadium, and zirconium is controlled by the addition of 4-percent lanthanum chloride. Concentrations of magnesium above 1,000 mg/L cause a low bias for calcium. The addition of lanthanum chloride controls the depression of the magnesium signal from aluminum, silicon, titanium and phosphorus.

SAFETY CONSIDERATIONS

Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

Peden M.E., and others., 1986, Methods for collection and analysis of precipitation: Champaign, Ill., Illinois State Water Survey Contract Report 381 (variously paged).

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

Perkin-Elmer, 1982, Analytical methods for atomic absorption spectrophotometry: Norwalk, Conn., Perkin-Elmer, Operators Manual B017-4145 (variously paged).

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies, laboratory analysis for surface water chemistry: Washington, D.C., U.S. Environmental Protection Agency, EPA 600/4-87/026 (variously paged).

BASIC CATIONS: SODIUM AND POTASSIUM

Cross references:
USGS Method Code: Sodium: I-3735-85
USGS Method Code: Potassium: I-3630-85
ISWS Method Code: 200.6
EPA Section: Sodium: # 16.5.10
EPA Section: Potassium: # 16.5.9

Applications .—This method is used to measure sodium and potassium concentrations in precipitation and in dilute surface waters and soil water.

Summary.—Sodium and potassium analysis is performed by direct aspiration atomic absorption spectroscopy. The sample is aspirated and atomized in an air-acetylene oxidizing flame. The beam from a sodium or potassium hollow cathode lamp is directed through the flame and onto the detector that measures radiant energy not absorbed in the flame. Sodium is measured at a wavelength of 589.0 nm, and potassium at a wavelength of 766.5 nm.

INSTRUMENTATION AND EQUIPMENT

- Perkin-Elmer 1100 B atomic absorption spectrophotometer (AAS)
  - AS-90 Autosampler
  - AS-90 Controller
- Sample tubes
- Computer for data retrieval

SAMPLE PRESERVATION AND STORAGE

The samples are acidified to pH < 2 with reagent-grade nitric acid (HNO_3) for preservation and are stored in an acid-washed polyethylene bottle.

REAGENTS AND STANDARDS

Acetylene.—Use atomic absorption-grade acetylene, purchased commercially.

Compressed Air.—Any compressed-air source is acceptable.

Sodium Standard Stock Solution, 1,000 mg Na^+/L.—Use a 1,000 mg/L sodium atomic absorption standard, purchased commercially.

Potassium Standard Stock Solution. 1,000 mg K^+/L.—Use a 1,000-mg/L potassium atomic absorption standard, purchased commercially.

Mixed-cation Standard Substock, 30 mg Na^+/L 20 mg K^+/L.—Pipet 30 mL sodium standard stock and 20 mL potassium standard stock into a 1,000-mL volumetric flask. Add 1 mL concentrated nitric acid (HNO_3) to maintain a pH <2. Fill to the mark with deionized (DI) water and mix thoroughly. Store in a polyethylene bottle. Prepare every 6 months.

Sodium and Potassium Working Standards.—Pipet desired amount of mixed-cation substock solution into a 500-mL volumetric flask. Add 0.5 mL nitric acid (HNO_3), maintaining a pH <2. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare fresh monthly

	Sodium	Potassium	
Auto zero:	0.0 µmol/L (0.00 mg/L)	0.00 µmol/L (0.00 mg/L)	0.0 mL substock
Standard 1:	6.5 µmol/L (0.15 mg/L)	2.56 µmol/L (0.10 mg/L)	2.5 mL substock
Standard 2:	19.6 µmol/L (0.45 mg/L)	7.67 µmol/L (0.30 mg/L)	7.5 mL substock
Standard 3:	32.6 µmol/L (0.75 mg/L)	12.79 µmol/L (0.50 mg/L)	12.5 mL substock
Standard 4:	65.2 µmol/L (1.50 mg/L)	25.58 µmol/L (1.00 mg/L)	25 mL substock
Standard 5:	130.5 µmol/L (3.00 mg/L)	51.16 µmol/L (2.00 mg/L)	50 mL substock

Sodium Quality-Control (QC) Stock Solution, 1,000 mg Na^+/L.—Use a 1,000-mg/L sodium atomic absorption standard, purchased commercially. This stock must be from a different manufacturer or lot than the standard stock.

Potassium QC Stock Solution, 1,000 mg K^+/L.—Use a 1,000-mg/L potassium atomic absorption standard, purchased commercially. This stock must be from a different manufacturer or lot than the standard stock.

Mixed-cation QC Samples.—Pipet desired amount of QC stock solutions into a 1,000-mL volumetric flask. Add appropriate amounts of calcium and magnesium QC stock solutions. Add 1 mL nitric acid (HNO_3). Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare monthly.

QC-low concentration:	sodium	8.7 µmol/L (0.2 mg/L)	0.2 mL QC stock
	potassium	5.12 µmol/L (0.2 mg/L)	
QC-high concentration:	sodium	43.5 µmol/L (1.0 mg/L)	1.0 mL QC stock
	potassium	25.58 µmol/L (1.0 mg/L)	

PROCEDURE

1. Turn on hood, acetylene, and compressed air. Record regulator pressures in the instrument logbook.
2. Turn on AAS, autosampler, and computer.
3. Clean appropriate hollow cathode lamp with lens paper; then place lamp in location #1, making sure it is properly aligned in the 3 o'clock position.
4. On AAS, enter date, set baud rate to 1200, and press "CARRIAGE RETURN" softkey.
5. Recall appropriate program and verify wavelength (sodium 589.0 nm, potassium 766.5 nm), standards, tray type, and sample locations.
6. Record tray location and sample number on bench sheet (for manual operation, go to step 15).
7. Pour standards and samples into tubes on the sampler tray.
8. Fill rinse container with DI water.
9. Place AAS in run mode and turn printer on.
10. Light flame and verify that the flame is burning clearly. If not, turn off flame and allow burner head to cool, then clean.
11. Adjust burner-head position to achieve desired sensitivity.
12. Reset autosampler to rinse sample probe.

13. Press the ON/OFF sampler softkey to activate sampler program.
14. After an acceptable calibration, identify sample locations and begin the analysis.
15. For manual operation, skip steps 7, 8, 12, 13, and 14. Samples may be aspirated directly, and the printer may be used to identify the sample serial numbers.

QUALITY CONTROL

- The Perkin-Elmer software automatically calculates the standard curve and computes the sample concentration. The calibration is set up in the "auto" mode for sodium and "linear" mode for potassium. A correlation coefficient of 0.999 or greater is acceptable.
- Quality-control samples are analyzed at the start of a run, after every 10 samples during the run, and at the end of the run. A quality-control sample is acceptable if the analyzed value is within 10 percent of the QC-high and QC-low theoretical value.
- Samples and standards are analyzed in tripilicate, and the average is recorded. A relative standard deviation of <10 percent is acceptable. The data are edited on the computer data file by entering the sample serial numbers corresponding to tray locations. A data-file printout is produced. The data are imported into the SAS network data base, where they are verified against the printout. Flags are assigned, and any automatic flags are resolved. A data-base printout is then produced to provide hard-copy documentation of the data entry.
- Samples are diluted and reanalyzed if their concentration exceeds the concentration of the highest standard. Any necessary dilutions are done manually. Samples are also reanalyzed if they are associated with a quality-control sample that failed.

MAINTENANCE

- Check nebulizer flow rate and adjust weekly.
- Clean flame assembly every 6 months.

INTERFERENCES

Sodium can potentially interfere with potassium, but this effect is negligible in dilute waters.

SAFETY CONSIDERATIONS

Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

Peden, M.E., and others, 1986, Methods for collection and analysis of precipitation: Champaign, Ill., Illinois State Water Survey Contract Report 381 (variously paged).

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

Perkin-Elmer, 1982, Analytical methods for atomic absorption spectrophotometry: Operators Manual B017-4145, Norwalk, Conn., Perkin-Elmer (variously paged).

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies - laboratory analysis for surface water chemistry: Washington, D.C., U.S. Environmental Protection Agency EPA 600/4-87/026 (variously paged).

BROMIDE

Cross references:
USGS Method Code: I-2058-85
ISWS Method Code: -- none
EPA Section #-- none

Applications.—This method is used to measure bromide concentrations in dilute surface waters and soil waters.

Summary.—Bromide is separated chromatographically after sample injection into an anion-exchange column and is detected with an electrical conductivity cell. The bromide peak area is measured and compared with a standard curve to determine concentrations.

INSTRUMENTATION AND EQUIPMENT

- Ion chromatograph, model DX 100, equipped with Dionex AI450 data station
- Guard and separator columns, Dionex, AG4A and AS4A
- Anion micro-membrane suppressor, Dionex AMMS-II
- Autosampler, Dionex model ASM-2
- Sample loop about 15 µl
- Computer equipped with Dionex AI450 software

SAMPLE PRESERVATION AND STORAGE

Samples are filtered through a 0.4-µm polycarbonate filter and stored at 4°C in polyethylene bottles that have been rinsed, then leached with DI water.

REAGENTS AND STANDARDS

Nitrogen Gas.—Use standard-grade nitrogen (N_2), purchased commercially.

Eluent Solution, 0.0014M sodium bicarbonate/0.0016M sodium carbonate.—Add 0.25 g sodium bicarbonate ($NaHCO_3$) and 0.35 g sodium carbonate (Na_2CO_3) to 2,000 mL helium-sparged deionized (DI) water. Prepare daily.

Regenerant, 0.025N sulfuric acid.—Add 2.8 mL concentrated sulfuric acid (H_2SO_4) to DI water and dilute to 4,000 mL. Prepare as needed.

Bromide Standard Stock Solution, 1,000 µmol Br/L.—Dry about 0.100 g lithium bromide (LiBr) at 105°C for 3 hours and cool in a desiccator. Add 0.08684 g lithium bromide to a 1,000-mL volumetric flask containing about 500 mL DI water. Fill to the mark with DI water and mix thoroughly. Prepare every 6 months.

Working Standards.—Pipet desired amounts of stock solution into a 100-mL volumetric flask and fill to the mark with DI water. Prepare monthly.

Standard A:	200.0 µmol/L	20.0 mL stock
Standard B:	150.0 µmol/L	15.0 mL stock
Standard C:	100.0 µmol/L	10.0 mL stock
Standard D:	50.0 µmol/L	5.0 mL stock
Standard E:	20.0 µmol/L	2.0 mL stock
Standard F:	10.0 µmol/L	1.0 mL stock

Bromide Quality-Control (QC) Stock Solution, 1,000 µmol Br^-/L.—Prepare a bromide QC stock solution from salts obtained from a source or lot number other than those used to prepare the bromide standard stock solutions. Dry about 0.100 g lithium bromide (LiBr) at 105°C for 3 hours and cool in a desiccator. Add 0.08684 g lithium bromide to a 1,000-mL volumetric flask containing about 500 mL DI water. Fill to the mark with DI water and mix thoroughly. Prepare every 6 months.

Bromide QC samples.—Pipet desired amount of bromide QC stock solution into a 100-mL volumetric flask. Fill to the mark with DI water and mix thoroughly.

QC-low concentration:	20.00 µmol/L	2.0 mL stock
QC-high concentration:	150.00 µmol/L	15.0 mL stock

*NOTE:Bromide is occasionally measured together with three major anions: chloride, nitrate, and sulfate. In that case, bromide is added to mixed-anion standard and QC samples.

PROCEDURE

1. Turn on nitrogen gas to pressurize eluent and regenerant reservoirs. Regenerant reservoir pressure should be about 7 psi, eluent pressure about 3 psi.
2. Turn on eluent pump; set flow rate of 2.0 mL/min. Allow instrument to stabilize (about 30 min).
3. When stable, the conductivity should be 10 to 20 µS, with no drifting or fluctuating.
4. Load appropriate "Method" and "Schedule" software into system.
5. Analyze one standard to verify that retention times and peak shapes are acceptable. A typical retention time for bromine ≅ 2.75 min.
6. Analyze bromide standards from smallest to greatest concentrations. If the calibration is acceptable, proceed to the next step. If the calibration is not acceptable, recalibrate.
7. Produce a printout of the calibration curve.
8. Analyze one QC-low and one QC-high sample. If the samples meet the acceptance criteria, proceed by loading a DI blank and 10 samples into the autosampler. If the QC samples do not meet the acceptance criteria, rerun one or both of them. If the QC's meet the acceptance criteria, proceed with the run. If the QC's do not meet the acceptance criteria, recalibrate the instrument.
9. If the instrument is to run overnight, set the pump pressure "LOW LIMIT" to 30 psi.

QUALITY CONTROL

- The AI450 software determines best-fit linear and correlation coefficients. An acceptable curve has a correlation coefficient of at least 0.997.

- Quality-control samples (QC-low and QC-high) are analyzed at the start of a run, after every 10 samples during the run, and at the end of the run. A quality-control sample is acceptable if the analyzed value is within 10 percent of the theoretical value.
- Samples are diluted and reanalyzed if their concentration exceeds the concentration of the highest standard. Any necessary dilutions are done manually. Samples are also reanalyzed if they are associated with a quality-control sample that failed.
- As the samples are loaded into the autosampler, an instrument bench sheet is created to record the order of samples. When the run is completed, a data-file printout is created, printed, and checked to determine whether any samples need to be rerun. The serial numbers of acceptable samples are entered into the data file and edited. A printout of the edited data file is produced and checked. Any necessary flags are assigned at this time. The file is not electronically transferred to the network SAS data base because Br concentrations are not routinely analyzed in all samples.

MAINTENANCE

- Replace anion-exchange column when system pressure exceeds 3,000 psi.
- Life of the anion-exchange column can sometimes be prolonged. Retention times can be increased by replacing bed supports or passing 1M HCl through the column, thereby increasing the life of the column.
- Column deterioration is indicated by an increase in system pressure and(or) decrease in retention times. An increase in system pressure may indicate the need to change bed supports, to clean the column with 1M HCl, or to replace the column. A decrease in retention times indicates that the columns need to be cleaned with 1M HCl or replaced.

INTERFERENCES

No significant interferences are specific to the analysis of bromide by ion chromatography.

SAFETY CONSIDERATIONS

All concentrated acids should be mixed in a hood. Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory - Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations book 5, chap. 1, 545 p.

Peden, M.E., and others, 1986, Methods for collection and analysis of precipitation: Champaign, Ill., Illinois State Water Survey Contract Report 381 (variously paged).

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies - laboratory analysis for surface water Chemistry, EPA 600/4-87/026: Washington, D.C., U.S. Environmental Protection Agency EPA 600/4-87/026 (variously paged).

CARBON, DISSOLVED INORGANIC

Cross references:
USGS Method Code: --none
ISWS Method Code: --none
EPA Section # 13.0

Applications .—This method is used to measure concentrations of inorganic carbon in a gaseous or solution phase in dilute surface waters and soil water. This method does not involve sample filtration and is therefore not used for samples that have measurable amounts of inorganic carbon in the mineral phase.

Summary.—The sample is manually injected into the acidified reaction chamber where all forms of dissolved inorganic carbon (DIC) are converted to carbon dioxide. Carbon dioxide is measured by an infrared detector.

INSTRUMENTATION AND EQUIPMENT

- Dohrmann DC 80 consisting of:
  - Reaction module
  - Detector module
  - Printer
  - ASM-1 autosampler
- 1-mL syringe
- Replacement pump tubes

SAMPLE PRESERVATION AND STORAGE

The sample is collected and stored in a glass bottle with a septum cap, void of head space.

REAGENTS AND STANDARDS

Degassed Deionized (DI) water.—DI water is degassed by bubbling with commercial-grade helium for about 2 min. Degassed DI water is used to prepare standards and QC samples.

Oxygen.—Use zero-grade oxygen, purchased commercially.

Reaction Chamber Solution.—Add 50 mL concentrated phosphoric acid (H_3PO_4) to a 1,000-mL volumetric flask containing about 800 mL DI water. Swirl, then fill to the mark with DI water, and mix thoroughly.

DIC Standard Stock Solution, 1,000 mg C/L.—Dry about 5 g sodium bicarbonate ($NaHCO_3$) at 105°C for 2 hours and allow to cool in a desiccator. Dissolve 0.7000 g dried $NaHCO_3$ in a 100-mL volumetric flask containing about 80 mL degassed DI water. Fill to the mark with DI water and mix thoroughly. Prepare fresh daily.

DIC Working Standards.—Pipet desired amount of DIC standard stock solution into a 100-mL volumetric flask. Fill to the mark with degassed DI water and mix thoroughly. Prepare fresh daily.

Standard A:	1666 µmol/L (20.0 mg/L)	2.0 mL stock
Standard B:	833 µmol/L (10.0 mg/L)	1.0 mL stock
Standard C:	416 µmol/L (5.0 mg/L)	0.5 mL stock
Standard D:	167 µmol/L (2.0 mg/L)	0.2 mL stock
Standard E:	83 µmol/L (1.0 mg/L)	0.1 mL stock
Standard F:	0 µmol/L (0.0 mg/L)	0.0 mL stock

DIC Quality-Control (QC) Stock Solution, 1,000 mg C/L.—Prepare QC stock solution as described for standard stock solution. Use $NaHCO_3$ from a manufacturer or lot different from that of the the $NaHCO_3$ used for the standard stock.

DIC QC Samples.—Pipet desired amount of QC stock solution into a 100-mL volumetric flask. Fill to the mark with degassed DI water and mix thoroughly. Prepare fresh daily.

QC-low concentration	83 µmol/L (1.0 mg/L)	0.1 mL QC stock
QC-high concentration	416 µmol/L (5.0 mg/L)	0.5 mL QC stock

PROCEDURE

1. Drain reaction chamber and fill with reaction-chamber solution.
2. Turn on autosampler and set in "MANUAL" mode.
3. Remove shut-off magnet from autosampler tray.
4. Open zero-grade oxygen valve and record regulator and in-line pressure in instrument logbook.
5. Clean pump pressure fingers and lock into place.
6. Turn on reaction module and pump.
7. Check reaction chamber and gas/liquid flow routes for leaks. Clean and repair if necessary.
8. Turn on detector module and allow reading to stabilize for 30 min.
9. Press "GO" on the auto sampler. This should stop gas flow through the sparging tubes.
10. Once the sample has cycled through, and the detector has reached "READY," record baseline in instrument logbook.
11. Press the "CALIBRATE" button on the detector module so the light is off. "NO CAL -- 1ML" will be printed on the printer paper.
12. Prepare standard B for injection by rinsing the syringe three times with the standard and drawing 1.0 mL into the syringe. The sample in the syringe must be free of bubbles.
13. Press "START" on the detector. Inject the sample into the injection port on the reaction module.
14. Wait for detector to reach "READY."
15. Repeat steps 12 through 14 three times.
16. Once the detector has reached "READY" after the fourth standard, press and hold the "CALIBRATE" button until the light comes on. "CAL -- 1ML," the average of the 4 standards, and the adjusted value will be printed. Record the average in the instrument logbook.
17. Inject each standard twice, starting with the highest concentration.

18. Record peak heights on bench sheet.
19. Once control criteria have been met, analysis of samples may begin.
20. At the end of the run, turn off the oxygen, detector, lamp, pump, reaction module and autosampler.

QUALITY CONTROL

- Standard calibration-curve data are entered into a LOTUS linear-regression program in which standard concentrations are plotted in relation to peak height. A correlation coefficient of 0.995 or greater is acceptable. Record the correlation coefficient, slope, and intercept in the instrument logbook.
- Quality-control samples are analyzed at the start of a run, after every 10 samples during the run, and at the end of the run. A quality-control sample is acceptable if the analyzed value is within 10 percent of the QC-high theoretical value and 15 percent of the QC-low theoretical value.
- Samples are diluted and reanalyzed if their concentration exceeds the concentration of the highest standard. Any necessary dilutions are done manually. Samples are also reanalyzed if they are associated with a QC sample that exceeded control limits.
- The instrument responses are transcribed from the instrument printout to the bench sheet. Data are entered into the SAS network data base, where instrument responses are converted to concentrations. Any necessary flags are added at this time. A data-base printout is produced, and the data are verified against the instrument printout.

MAINTENANCE

- The pressure finger for the reaction-chamber solution pump tube (black) should be locked when the system is off to prevent the reaction chamber from overflowing when not in use.
- Check rate of gas flow from detector weekly and adjust to 200 mL/min (10 mL in 3 sec.).
- Record previous and adjusted flow rates in instrument logbook.
- All pump tubes should be replaced every 3 months or when they are worn, stretched, or flattened. Frequency will depend on instrument use.
- The tin and copper in the scrubber should be replaced every 6 months or when discolored.
- The perma-drier tube in the reaction module should be inspected periodically and replaced if necessary.

INTERFERENCES

None.

SAFETY CONSIDERATIONS

All concentrated acids should be mixed in a hood. Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

Rosemount Analytical Division, 1989, Dohrmann DC-80 total organic carbon systems manual: Santa Clara, Calif., Xertex Corporation (variously paged).

U.S. Environmental Protection Agency. 1987. Handbook of methods for acid deposition studies - laboratory analysis for surface water chemistry: Washington, D.C., U.S. Environmental Protection Agency EPA 600/4-87/026 (variously paged).

CARBON, DISSOLVED ORGANIC

Cross references:
USGS Method Code: -- none
ISWS Method Code: -- none
EPA Section # 14.0

Applications .—This method is used to measure dissolved organic carbon (DOC) concentrations in precipitation and dilute surface waters and soil water. This method measures nonvolatile organic carbon with an oxidation state of less than +4 that will pass through a Whatman GF/F filter.

Summary.—The sample is poured into a glass test tube, acidified with phosphoric acid, and then sparged twice with zero-grade oxygen prior to analysis. This removes inorganic carbon from the sample. Dissolved organic carbon is then converted by ultraviolet radiation and persulfate oxidation to carbon dioxide, which is measured by an infrared detector.

INSTRUMENTATION AND EQUIPMENT

- Dohrmann DC 80 consisting of:
  - Reaction module
  - Detector module
  - Printer
  - ASM-1 Auto sampler
  - 1-mL sample loop
- Glass test tubes: 18 x 150 mm
- Replacement pump tubes

SAMPLE PRESERVATION AND STORAGE

The sample is filtered from the collection bottle through a Whatman GF/F glass-fiber filter into a glass vial with a Teflon seal. The sample is not acidified for preservation.

REAGENTS AND STANDARDS

Oxygen.—Use zero-grade oxygen, purchased commercially.

Phosphoric Acid.—Use reagent-grade concentrated phosphoric acid (H_3PO_4), purchased commercially.

Potassium Persulfate.—Dissolve 20.0 g potassium persulfate ($K_2S_2O_8$) in a 1,000-mL volumetric flask containing about 800 mL deionized (DI) water. Add 2 mL phosphoric acid (H_3PO_4). Fill to the mark with DI water and mix thoroughly. Place in a 4,000-mL carboy on top of instrument. Prepare when necessary.

DOC Standard Stock Solution, 1,000 mg C/L.—Dry about 10 g potassium biphthalate (KHP) at 105°C for 2 hours and allow to cool in a desiccator. Dissolve 2.1254 g dried KHP in a 1,000-mL volumetric flask containing about 800 mL DI water. Add 1 mL phosphoric acid (H_3PO_4). Fill to the mark with DI water and mix thoroughly. Store in a glass bottle at 4°C. Prepare every 6 months.

DOC Working Standards.—Pipet desired amount of DOC standard stock solution into a 100-mL volumetric flask. Fill to the mark with DI water and mix thoroughly. Prepare fresh daily.

Standard A:	1666 µmol/L (20.0 mg/L)	2.0 mL stock
Standard B:	833 µmol/L (10.0 mg/L)	1.0 mL stock
Standard C:	416 µmol/L (5.0 mg/L)	0.5 mL stock
Standard D:	167 µmol/L (2.0 mg/L)	0.2 mL stock
Standard E:	83 µmol/L (1.0 mg/L)	0.1 mL stock
Standard F:	0 µmol/L (0.0 mg/L)	0.0 mL stock

DOC Quality-Control (QC) Stock Solution, 1,000 mg C/L.—Prepare QC stock solution as described for standard stock solution. Use KHP from a manufacturer or lot different from that of the the KHP used for the standard stock.

DOC QC Samples.—Pipet desired amount of QC stock solution into a 1,000-mL volumetric flask. Fill to the mark with DI water and mix thoroughly. Store in glass bottles at 4°C. Prepare monthly.

QC-low concentration	83 µmol/L (1.0 mg/L)	1.0 mL QC stock
QC-high concentration	416 µmol/L (5.0 mg/L)	5.0 mL QC stock

PROCEDURE

1. Turn on auto sampler and place in "MANUAL" mode.
2. Remove shut-off magnet from autosampler tray.
3. Open zero-grade oxygen valve and record regulator and in-line pressure in the instrument logbook.
4. Clean pump pressure fingers with a tissue and lock into place.
5. Turn on reaction module and pump.
6. Check reaction chamber and gas/liquid flow routes for leaks. Clean and repair if necessary.
7. Close reaction-module door and turn on lamp.
8. Turn on detector module and allow to stabilize for 30 min.
9. Fill test tubes about two-thirds full with standards and samples as stated below:

Location	Standard
42 - 43	DI water
44 - 47	Standard B
48 - 49	Standard A
50 - 51	Standard B

Location	Standard
52 - 53	Standard C
54 - 55	Standard D
56 - 57	Standard E
58 - 60	Standard F

10. Dispense 0.1 mL phosphoric acid in each test tube.
11. Rotate autosampler clockwise so that the sampling probe is above location #42.
12. Press "GO" on the autosampler. If probe does not descend, be sure probe is aligned over location #42.
13. Once sample has cycled through, the sample probe is above location #43, and the detector has reached "READY," press "GO" again.
14. Observe flow of DI water through sampling line and loop. Sample should rinse loop and reach the pump tube prior to injection.

15. Once detector has reached "READY," record baseline in instrument logbook.
16. Press the "CALIBRATE" button on the detector module so the light is off. "NO CAL -- 1ML" will be printed on the printer paper.
17. Press "GO" to cycle through locations #44-47.
18. Once the detector has reached "READY" after the fourth standard, press and hold the "CALIBRATE" button until the light comes on. "CAL -- 1ML," the average of the 4 standards, and the adjusted value will be printed. Record the average in the instrument logbook.
19. Press "AUTO" on the autosampler.
20. Record tray location and sample numbers on the bench sheet.
21. Place QC-high and QC-low samples in locations #1 and #2.
22. Place 10 samples in locations #3 through #12.
23. Dispense 0.1 mL phosphoric acid to all QC and sample test tubes.
24. Record instrument responses on bench sheet.
25. Once control criteria have been met, analysis of samples may begin.
26. For overnight runs, the instrument can be automatically shut off by placing the magnet in line with the sample tubes 3 locations behind the last sample. The instrument can be shut off manually by turning off the detector, lamp, pump, reaction module, autosampler, and oxygen valve.

QUALITY CONTROL

- Standard calibration-curve data are entered into a LOTUS linear-regression program in which standard concentrations are plotted in relation to peak height. A correlation coefficient of 0.995 or greater is acceptable. Record the correlation coefficient, slope, and intercept in the instrument logbook.
- Quality-control samples are analyzed at the start of a run, after every 10 samples during the run, and at the end of the run. A quality-control sample is acceptable if the analyzed value is within 10 percent of the QC-high theoretical value and 15 percent of the QC-low theoretical value.
- Samples are diluted and reanalyzed if their concentration exceeds the concentration of the highest standard. Any necessary dilutions are done manually. Samples are also reanalyzed if they are associated with a QC sample that exceeded control limits.
- The instrument responses are transcribed from the instrument printout to the bench sheet. Data are entered into the SAS network data base, where instrument responses are converted to concentrations. Any necessary flags are added at this time. A data-base printout is produced, and the data are verified against the instrument printout.

MAINTENANCE

- The pressure finger for persulfate pump tube (black) should be locked when system is off. This prevents the reaction chamber from overflowing.
- Check rate of gas flow from detector outlet weekly and adjust to 200 cc/min (10 mL in 3 sec).
- Record previous and adjusted flow rates in instrument logbook.
- All pump tubes should be replaced every 3 months or when they are worn, stretched, and(or) flattened. Frequency will depend on instrument use.
- The tin and copper in the scrubber should be replaced every 6 months or when it becomes discolored.

- The 3-way valve on the auto sampler should be cleaned annually.
- The perma-drier tube in the reaction module should be inspected every 6 months and replaced if necessary.

INTERFERENCES

None.

SAFETY CONSIDERATIONS

All concentrated acids should be mixed in a hood. Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

Rosemount Analytical Division, 1989, Dohrmann DC-80 total organic carbon systems manual: Santa Clara, Calif., Xertex Corporation (variously paged).

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies - laboratory analysis for surface water chemistry: Washington, D.C., U.S. Environmental Protection Agency EPA 600/4-87/026 (variously paged).

FLUORIDE

Cross references:
USGS Method Code: I-4327-85
ISWS Method Code: 340.6
EPA Section # 15.0

Applications .—This method is used to measure total fluoride concentrations in dilute surface water and soil water.

Summary.—Total fluoride in a sample is determined electrometrically by a combination fluoride ion-selective electrode (ISE) after addition of total-ionic-strength adjustment buffer (TISAB) to the sample . The TISAB adjusts sample ionic strength and pH and decomplexes fluoride so that it can be detected as F^-. The electrical potential of the fluoride ISE varies logarithmically with the fluoride concentration according to the Nernst equation. Computer software determines sample concentrations by associating sample millivolt readings with the calibration curve.

INSTRUMENTATION AND EQUIPMENT

- Analog-to-digital converter that reads the electrical potential of the fluoride electrode
- XYZ-type autosampler
- Orion Ross combination fluoride electrode
- Oxford Automatic Pipet, 5- to 10-mL capacity
- Repipet II dispenser, 5.0-mL capacity
- Chem-Feed adjustable-flow pump
- Computer for autosampler operation and data calculations
- Deionized (DI) water reservoir
- Teflon sample cups

SAMPLE PRESERVATION AND STORAGE

Samples are stored at 4°C in polyethylene bottles. They are not filtered or acidified.

REAGENTS AND STANDARDS

TISAB III.—Total Ionic Strength Adjustment Buffer, available commercially.

Combination Fluoride Electrode Filling Solution.—Available commercially from Orion Ross.

Fluoride Standard Stock Solution, 100 mg F^-/L.—Use a 100-mg/L fluoride standard, purchased commercially.

Fluoride Standard Substock, 1 mg F^-/L.—Pipet 1.0 mL fluoride stock into a 100-mL polyethylene volumetric flask. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare monthly.

Fluoride Working Standards.—Pipet desired amount of standard substock into a 100-mL polyethylene volumetric flask. Fill to the mark with DI water and mix thoroughly. Prepare weekly

Standard A:	1.050 µmol/L (0.02 mg/L)	2.0 mL substock
Standard B:	2.630 µmol/L (0.05 mg/L)	5.0 mL substock
Standard C:	5.263 µmol/L (0.10 mg/L)	10.0 mL substock

Fluoride Quality-Control (QC) Stock Solution, 100 mg F^-/L.—Use a fluoride 100-mg/L standard purchased commercially. This stock must be from a manufacturer or a lot other than that of the standard stock.

Fluoride QC substock, 1 mg F^-/L.—Pipet 1.0 mL QC stock solution into a 100-mL polyethylene volumetric flask. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare monthly.

Fluoride QC Sample.—Pipet desired amount of fluoride QC substock into a 100-mL polyethylene volumetric flask. Fill to the mark with DI water and mix thoroughly. Prepare weekly.

QC:	1.58 µmol/L (0.03 mg/L)	3.0 mL QC substock

PROCEDURE

1. Flush the fluoride electrode with filling solution several times. Make sure no air bubbles are trapped in the electrode.
2. Turn on the computer and autosampler motor.
3. Access the appropriate sampling program on the computer. Immerse the fluoride electrode in DI water. After about 20 min, record the value in the instrument logbook.
4. Prepare fluoride working standards by dispensing 1.0 mL TISAB solution from a Repipet II into 3 separate Teflon cups. Pipet 9.0 mL each of the 3 fluoride working standards into the Teflon cups. Place the cups in the first three positions of the autosampler tray, from least to greatest concentration.
5. Start the run.
6. Prepare a fluoride QC sample by dispensing 1.0 mL TISAB solution from a Repipet II into a Teflon cup. Pipet 9.0 mL of fluoride QC sample. Place on the autosampler tray.
7. Using a calculator, check the standard curve parameters by plotting the $\log_{10}$ [standard concenration] (in µmol/L) against the corresponding millivolt readings. Record the correlation coefficient, slope, and intercept on the bench sheet.
8. If the calibration curve is acceptable, proceed to the analysis of the QC sample. If the calibration is not acceptable, recalibrate.
9. Using a calculator, determine the measured value of the QC sample.
10. If the QC sample value is acceptable, proceed with sample analysis. If the QC sample fails, reanalyze it.
11. If the QC sample value is acceptable after reanalysis, then proceed with the run. If the QC sample fails after reanalysis, recalibrate.
12. The probe is automatically rinsed with DI water for 1 min between samples.

QUALITY CONTROL

- The best-fit line is drawn, and the curve is accepted if the correlation coefficient is at least 0.995. The slope of the millivolt values of the standards, plotted as a function of $\log_{10}$ [standard concentration], should be between -30 and -56.
- A QC sample is analyzed at the start of a run, after about 10 samples, and at the end of the run. A QC sample is acceptable if the analyzed value is within 10 percent of the theoretical value.
- Samples are diluted and reanalyzed if their concentration exceeds the concentration of the highest standards. Any necessary dilutions are done manually. Samples are also reanalyzed if they are associated with a QC sample that has failed.
- Sample serial numbers are typed into the computer as the sample tray is loaded. At the end of the run, an instrument printout of sample serial numbers and concentrations is produced. The data are then imported into the network SAS data base, where they are checked against the instrument printout, and any necessary flags are assigned. A data-base printout is then produced to document the data entry.

MAINTENANCE

- External filling solution should be drained and replaced daily.
- When not in use, electrode should be stored dry with external filling solution removed.

INTERFERENCES

The optimum pH for measurement of fluoride is between 5.0 and 8.5. Below pH 5.0, fluoride is complexed by hydronium, and above pH 8.5 it is complexed by hydroxide. Polyvalent cations such as Fe^{3+}, Al^{3+}, and silicon are also capable of complexing fluoride. The addition of TISAB minimizes these potential interferences.

SAFETY CONSIDERATIONS

Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

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

Orion Research Incorporated, 1990, Ross fluoride electrode instruction manual: Boston, Mass., Orion Research Inc., Laboratory Products Group, 23 p.

Peden, M.E., and others, 1986, Methods for collection and analysis of precipitation: Champaign, Ill., Illinois State Water Survey Contract Report 381 (variously paged).

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies - laboratory analysis for surface water chemistry: U.S. Environmental Protection Agency, EPA 600/4-87/026, Washington, D.C. (variously paged).

pH

Cross references:

USGS Method Code: -- none
ISWS Method Code: -- none
EPA Section # -- none

Application.—This method is used to measure pH in precipitation, dilute soil waters, and surface waters that are at or near equilibrium with atmospheric carbon dioxide concentrations or have a pH <5.0.

Summary.—pH is defined as the negative logarithm of hydrogen-ion activity. Solution pH is determined by relating electrical potential of an electrode placed in a standard buffer solution to the electrical potential of the electrode in a sample through the Nernst equation. Measurements are made with an autosampler that transfers the electrode from one sample to the next. Stability of pH measurements is evaluated by computer software.

INSTRUMENTATION AND EQUIPMENT

- Accumet 925 pH/ion meter with temperature compensator
- Technicon Sampler IV, with modifications to accommodate necessary sample cup size
- Orion Ross combination pH electrode
- Chem-Feed adjustable-flow pump
- Computer for autosampler operation and data retrieval
- Deionized (DI) water reservoir
- Teflon sample cups

SAMPLE PRESERVATION AND STORAGE

Samples are stored in acid-washed polyethylene bottles in the refrigerator at 4°C and are not filtered.

REAGENTS AND STANDARDS

Buffers.—pH 4.00, 7.00, and 10.00 buffers, purchased commercially.

pH-Electrode Storage Solution.—Add 1 g potassium chloride (KCl) to 200 mL pH 7.00 buffer.

pH Quality-Control (QC) Stocks:

QC-Low-Concentration Stock Solution, 0.1N volumetric sulfuric acid.—Purchased commercially. Each lot is titrated to verify the listed concentration.

QC-High-Concentration Stock Solution.—Prepare a 0.025M potassium phosphate, monobasic (KH_2PO_4)/0.025M potassium phosphate, dibasic heptahydrate ($Na_2HPO_4 \cdot 7H_2O$) solution by dissolving 3.4023 g potassium phosphate, monobasic and 6.6961 g potassium phosphate, dibasic heptahydrate in a 1,000-mL volumetric flask containing 800 mL DI water. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare as needed.

pH QC Samples.—Pipet desired volume of QC stock solution into a 1,000-mL volumetric flask. Fill to

the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare as needed.

QC-low concentration	pH 4.44	0.4 mL QC-low stock
QC-high concentration	pH 6.88	5.0 mL QC-high stock

PROCEDURE

1. Turn on the computer and autosampler.
2. Access the appropriate sampling program on the computer.
3. Unplug fill hole on pH probe.
4. Calibrate the meter using pH 4.00 and 7.00 buffer solutions. (Occasionally pH 7.00 and 10.00 buffers are used, depending on the expected sample range).
5. Record temperature and millivolt readings of the buffers in the instrument logbook.
6. On the meter, press "PRINT INTERVAL" and then press "ENTER" twice to establish communication between the meter and computer.
7. Place a QC sample on the autosampler tray.
8. Start the run.
9. The electrode will record a pH measurement and advance to the next sample when sample measurement time is at least 5 min and the variance in pH values is less than 0.005 pH units in 4 min. If these criteria are not met in 60 min, the current reading is accepted, and the electrode is advanced to the next sample.
10. If the QC sample passes, proceed with the sample analysis. If the QC sample fails, reanalyze it.
11. If the QC sample passes after reanalysis, then proceed with the run.
12. If the QC sample fails after reanalysis, then recalibrate.
13. The probe is automatically rinsed with DI water for 1 min between samples.

QUALITY CONTROL

- The electrode response is verified by ensuring that the electrode potential for pH 7.00 is ±30 mV and the electrode potential for pH 4.00 buffer is about 160 mV greater than for pH 7.00 buffer.
- A QC sample is analyzed at the start of a run, after about 10 samples, and at the end of the run. A QC sample is acceptable if the analyzed value is within 20 percent of the QC-high theoretical value and within 10 percent of the QC-low theoretical value, when expressed in hydrogen ion concentration.
- Samples are reanalyzed if they are associated with a QC sample that failed.
- Sample serial numbers are entered into the computer software as the sample tray is loaded. At the end of the run, a printout of sample serial numbers and pH's is produced. The data are then imported into the SAS network data base where they are verified to the original printout, and any necessary flags are assigned. A data-base printout is then produced to provide hard-copy documentation of the data entry.

MAINTENANCE

- Store the electrode in the pH-electrode storage solution when not in use.
- The reference junction should not be allowed to dry out.

- When the internal fill solution level falls to 2.5 cm (1 inch) below the fill hole, add the fresh fill solution supplied with the electrode until the level reaches the fill hole.
- Plug the fill hole when the electrode is not in use.
- Rinse off any salt deposits with DI water before using the electrode.

INTERFERENCES

None.

SAFETY CONSIDERATIONS

Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

Metcalf, R.C., and Peck, D.V., 1991, Dilute, neutral pH standard of known conductivity and acid-neutralizing capacity: Analyst, v. 116, p. 221-231.

Orion Research Incorporated, 1990, Ross pH electrode instruction manual: Boston, Orion Research, Laboratory Products Groups, 21 p.

SILICON

Cross references:
USGS Method Code: I-2700-85
ISWS Method Code: -- none
EPA Section # 22.0

Applications .—This method is used to measure silicon concentrations in dilute surface water and soil water.

Summary.—The analysis for silicon is an automated colorimetric reaction. Samples are systematically introduced into the flow-injection analyzer (FIA) reaction manifold. The sample is initially mixed with an acidified ammonium molybdate solution. The reactive silicon in the sample (as orthosilicic acid) forms a yellow silicomolybdate complex in the acidic solution. Oxalic acid is introduced into the flow to minimize the formation of a phosphomolybdate complex. The silicomolybdate complex is reduced by ascorbic acid to form a blue color . The intensity of the blue complex is measured at a wavelength of 820 nm.

INSTRUMENTATION AND EQUIPMENT

- Lachat QuikChem Automated Analyzer System consisting of:
  - XYZ sampler
  - Diluter
  - Pump
  - Injection module
  - Reaction module
  - Silicon reaction manifold
  - Photometer
  - QuikChem AE software and compatible computer
- Replacement pump tubes
- Sample tubes

SAMPLE PRESERVATION AND STORAGE

Samples are poured directly from the collection bottle. They are stored in polyethylene bottles at 4°C. They are not filtered or acidified.

REAGENTS AND STANDARDS

Degassed Deionized (DI) Water.—DI water is degassed by bubbling with commercial-grade helium for about 2 min. Degassed DI water is used for carrier water and for preparation of all reagents.

Ammonium Molybdate.—Pipet 2.8 mL concentrated sulfuric acid (H_2SO_4) into a 1,000-mL volumetric flask containing about 600 mL DI water. Swirl to mix. Add 10.0 g ammonium molybdate tetrahydrate ($(NH_4)_6\ Mo_7O_{24}{\cdot}4H_2O$) to the solution and stir until the solid dissolves. Fill to the mark with DI water and mix thoroughly. Store in an amber polyethylene bottle at 4°C. Prepare weekly.

Oxalic Acid.—Add 50.0 g oxalic acid dihydrate ($C_2H_2O{\cdot}2H_2O$) to a 1,000-mL volumetric flask containing about 700 mL DI water. Stir to dissolve the solid. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C.

Ascorbic Acid.—Add 50 mL acetone to a 1,000-mL volumetric flask containing 800 mL DI water. Add 17.6 g ascorbic acid ($C_6H_8O_6$) to the solution and stir to dissolve. Fill to the mark with DI water and mix thoroughly. Store in an amber polyethylene bottle. Prepare daily.

Silicon Standard Stock Solution, 1,000 mg Si/L.—Add 10.119 g sodium metasilicate nonahydrate ($NaSiO_3 \cdot 9H_2O$) to a 1,000-mL polyethylene volumetric flask containing about 800 mL DI water. Swirl to dissolve the solid. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare every 6 months.

Silicon Working Standards.—Pipet desired amount of standard stock into a 100-mL polyethylene volumetric flask. Fill to the mark with DI water and mix thoroughly. Store standards in polyethylene bottles at 4°C. Prepare every other day.

Standard A:	178.0 µmol/L (5.00 mg/L)	0.5 mL stock
Standard B:	142.4 µmol/L (4.00 mg/L)	0.4 mL stock
Standard C:	106.8 µmol/L (3.00 mg/L)	0.3 mL stock
Standard D:	71.2 µmol/L (2.00 mg/L)	0.2 mL stock
Standard E:	35.6 µmol/L (1.00 mg/L)	0.1 mL stock
Standard F:	17.8 µmol/L (0.50 mg/L)	10.0 mL 5.00 mg/L standard
Standard G:	7.12 µmol/L (0.20 mg/L)	10.0 mL 2.00 mg/L standard
Standard H:	0.00 µmol/L (0.00 mg/L)	0.0 mL stock

Silicon Quality-Control (QC) Stock, 1,000 mg Si/L.—Use a sodium metasilicate nonahydrate ($NaSiO_3 \cdot 9H_2O$) stock from a manufacturer or lot other than those of the standard stock. Add 10.119 g sodium metasilicate nonahydrate to a 1,000-mL polyethylene volumetric flask containing about 500 mL DI water. Swirl to dissolve the solid. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare every 6 months.

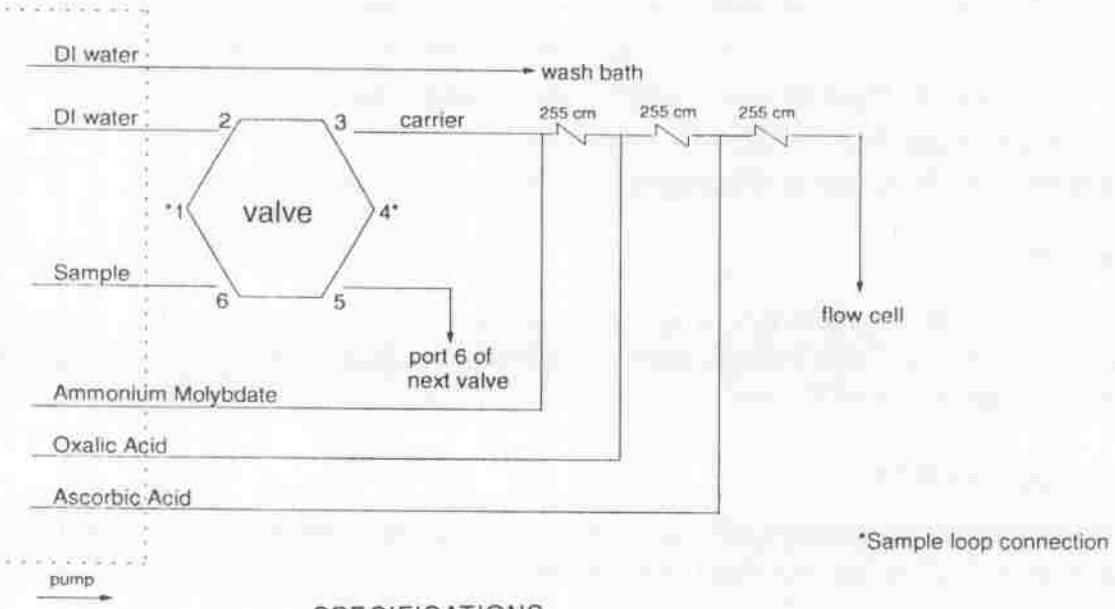
Silicon QC Samples.—Pipet desired amount of QC stock into a 250-mL polyethylene volumetric flask. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare every other day.

QC-low concentration	35.6 µmol/L (1.00 mg/L)	0.25 mL QC stock
QC-high concentration	106.8 µmol/L (3.00 mg/L)	0.75 mL QC stock

PROCEDURE

1. Turn on the power for all components of the Lachat system. After the main menu appears on both monitor screens, download the silicon method.
2. Install the silicon-reaction manifold onto the second reaction module. See manifold flow chart (fig. 4).
3. Put all reagent lines into a beaker of degassed DI water.
4. Adjust the tension levers on the individual pump tube cassettes. Set the pump to "OVERRIDE STANDBY."
5. After all air has been pumped out of the system, place each reagent line into its respective container.

6. Continue to pump the reagents through until the baseline has stabilized. Return pump to standby speed.
7. Place the diluter line into a container of DI water.
8. Place standards A-H, QC-high, and QC-low in their containers in the order specified on the sample tray labeled "STANDARDS." Put empty sample tubes into the dilution tray labeled "EMPTY TUBES."
9. Start the calibration.
10. Check the calibration curve. If the calibration fails, repeat the calibration procedure.
11. If the calibration is acceptable, load samples into the first tray labeled "SAMPLES" and type in the sample serial numbers in the tray-identification window.
12. Submit the tray.
13. At the end of the run(s), rinse off the ends of all the reagent lines and put all lines into a beaker of DI water. Set the pump speed to "OVERRIDE STANDBY." Let the system flush for 15 min.
14. Remove the lines from the beaker and let the system pump air to dry.
15. Release the tension on the pump tube cassettes.
16. Turn off the power to all components of the system.



SPECIFICATIONS

Manifold tubing: 0.8 mm i.d.
Sample loop: 150 cm (754 µL)
Flow cell: 10 mm
Interference filter: 820 nm
Pump setting: 35

Pump tubes:
DI water/wash bath: 2.00 mL/min (green)
DI water/carrier: 1.20 mL/min (yellow)
Sample: 2.00 mL/min (green)
Ammonium Molybate: 0.42 mL/min (orange)
Oxalic Acid: 0.32 mL/min (black)
Ascorbic Acid: 0.42 mL/min (orange)

Figure 4. Schematic diagram of silicon flow-injection manifold.

QUALITY CONTROL

- Standard-curve and data-verification calculations are performed by the QuikChem AE software package supplied by Lachat. The standard curve is a linear plot of standard concentration vs. average absorbance. The best-fit line is drawn, and the curve is accepted if the correlation coefficient is 0.995 or greater.
- QC samples are analyzed at the start of a run, after every 10 samples during the run, and at the end of the run. A quality-control sample is acceptable if the analyzed value is within 10 percent of the QC-high theoretical value and 15 percent of the QC-low theoretical value.
- Samples are diluted and reanalyzed if they exceed the concentration of the highest standard. Dilution factors are calculated and applied by the instrument software, and dilution reruns are performed automatically by the instrument. Samples are also reanalyzed if they are associated with a quality-control sample that failed.
- Sample serial numbers are entered into the computer before the sample tray is submitted. A real-time printout is produced as the run progresses to monitor the peak integrity factors for each sample. At the conclusion of the run, the sample serial numbers and concentration values are electronically combined into a data file that is printed. This file is electronically transferred into the SAS network data base, where it is verified against the data-file printout. Any necessary flags are assigned at this time. A data-base printout is then produced to provide hard-copy documentation of the data entry.

MAINTENANCE:

- All pump tubes must be replaced as they are worn or stretched. The frequency will depend upon the number of samples analyzed. The sample and wash-bath pump tubes should be changed once a month.
- Interference filters should be cleaned with lens paper whenever they are changed.
- Manifold tubing must be replaced as it becomes discolored or clogged.
- Sample tubes are rinsed, then soaked in DI water overnight, and oven dried between uses.
- Waste lines may need to be replaced periodically as buildup and clogging develop.

INTERFERENCES

Phosphate interferes with this method by forming a phosphomolybdate complex with ammonium molybdate. The addition of oxalic acid decreases this interference. Significant concentrations of sulfides and iron may also interfere with the analysis.

SAFETY CONSIDERATIONS

All concentrated acids and bases should be mixed in a hood. Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

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

Lachat Instruments, 1990, Methods manual for the QuikChem automated ion analyzer: Method no. 10-114-27-1-A, Milwaukee, Wisc., Lachat Instruments (variously paged).

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies - laboratory analysis for surface water chemistry: Washington, D.C., U.S. Environmental Protection Agency, EPA 600/4-87/026 (variously paged).

ANALYTICAL METHODS

B. SOIL-EXTRACT ANALYSIS

NITRITE

Cross references:
USGS Method Code: I-2540-90
ISWS Method Code: -- none
EPA Section # -- none

Applications .—This method is used to measure nitrite concentrations in forest-soil extracts. Soil nitrite is extracted with 1M potassium chloride to produce a high ionic-strength solution.

Summary.—The nitrite analysis is an automated colorimetric reaction. Samples are systematically introduced into the flow-injection analyzer (FIA) reaction manifold. An acidified sulfanilamide and N-(1-naphthyl)ethylenediamine dihydrochloride (NED) reagent is introduced into the flow. Sulfanilamide forms a diazo linkage with nitrite in the sample. The diazo compound couples with NED and forms a water-soluble red dye. The absorbance of the dye is read at a wavelength of 520 nm.

INSTRUMENTATION AND EQUIPMENT

- Lachat QuikChem Automated Analyzer System consisting of:
  - XYZ sampler
  - Diluter
  - Pump
  - Injection module
  - Reaction module
  - Nitrite reaction module
  - Photometer
  - QuikChem AE Software and compatible computer
- Replacement pump tubes
- Sample tubes

SAMPLE PRESERVATION AND STORAGE

Soil extracts are frozen in polyethylene bottles until analysis. Samples should be analyzed as soon as they are thawed.

REAGENTS AND STANDARDS

Degassed Deionized (DI) Water.—DI water is degassed by bubbling with commercial-grade helium for about 2 min. Degassed DI water is used for carrier water and for preparation of all reagents.

Sulfanilamide/NED reagent.—Add 100 mL 85-percent phosphoric acid (H_3PO_4) to a 1,000-mL volumetric flask containing about 600 mL DI water. Swirl to mix. Add 40.0 g sulfanilamide and 1.0 g NED to the solution. Stir until the solids have dissolved (about 20 min). Fill to the mark with DI water and mix thoroughly. Store in an amber polyethylene bottle at 4°C. Prepare monthly.

1M KCl.–Add 74.55 g potassium chloride (KCl) to a 1,000-mL volumetric flask containing about 800 mL DI water. Swirl to dissolve the solid. Fill to the mark and mix thoroughly. Store in a polyethylene bottle.

4M KCl.—Add 298.20 g potassium chloride (KCl) to a 1,000-mL volumetric flask containing about 800 mL DI water. Swirl to dissolve the solid. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle.

Nitrite Standard Stock Solution, 2000 mg NO_2^-/L (as N).—Add 9.8600 g sodium nitrite ($NaNO_2$) formula to a 1,000-mL volumetric flask containing about 800 mL DI water. Swirl to dissolve the solid. Pipet 2.0 mL chloroform into the flask. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare monthly.

Nitrite Standard Substock, 20 mg NO_2^-/L (as N).—Pipet 2.5 mL of standard stock into a 250-mL volumetric flask containing about 100 mL DI water. Fill to the mark with DI water and mix thoroughly. Prepare monthly.

Nitrite Working Standards.—Pipet desired amount of standard substock into a 100-mL volumetric flask containing 25 mL 4M KCl. Fill to the mark with DI water and mix thoroughly. Store in polyethylene bottles at 4°C. Prepare every other day.

Standard A:	142.78 µmol/L (2.00 mg/L)	10.0 mL substock
Standard B:	107.08 µmol/L (1.50 mg/L)	7.5 mL substock
Standard C:	71.39 µmol/L (1.00 mg/L)	5.0 mL substock
Standard D:	42.83 µmol/L (0.60 mg/L)	3.0 mL substock
Standard E:	28.60 µmol/L (0.40 mg/L)	2.0 mL substock
Standard F:	14.28 µmol/L (0.20 mg/L)	1.0 mL substock
Standard G:	7.14 µmol/L (0.10 mg/L)	0.5 mL substock
Standard H:	0.00 µmol/L (0.00 mg/L)	0.0 mL substock

Nitrite Quality-Control (QC) Stock, 2,000 mg NO_2^-/L (as N).—Use a sodium nitrite stock from a manufacturer or lot other than that of the standard stock. Add 9.8600 g sodium nitrite to a 1,000-mL volumetric flask containing about 800 mL DI water. Swirl to dissolve the solid. Pipet 2.0 mL chloroform into the flask. Fill to the mark with DI water and mix thoroughly. Store in polyethylene bottles at 4°C. Prepare monthly.

Nitrite QC Substock, 20 mg NO_2^-/L (as N).—Pipet 2.5 mL of QC stock into a 250-mL volumetric flask containing about 100 mL DI water. Fill to the mark with DI water and mix thoroughly. Store in polyethylene bottles at 4°C. Prepare monthly.

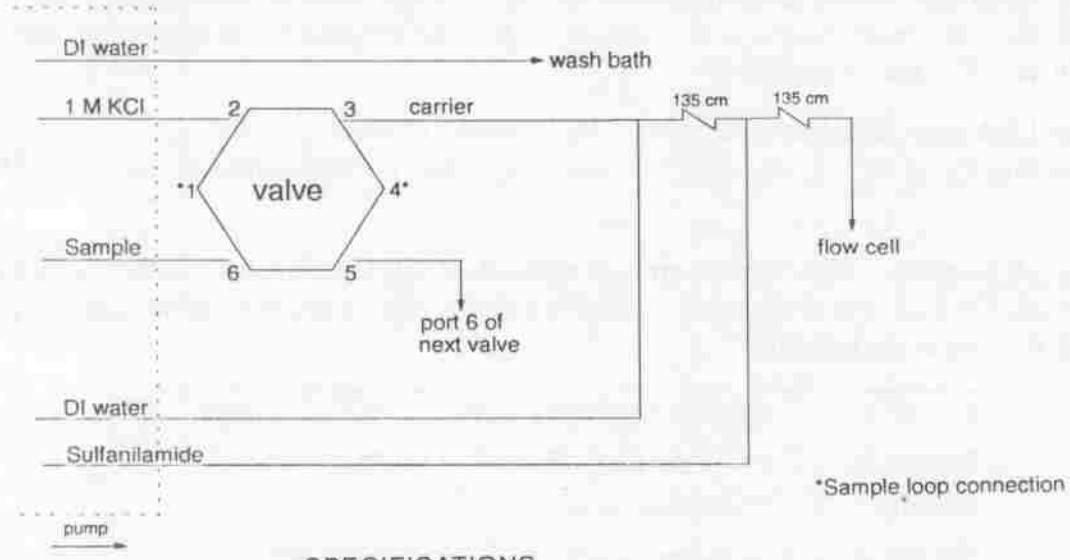
Nitrite QC Samples.—Pipet desired amount of QC substock into a 500-mL volumetric flask containing 125 mL 4M KCl. Fill to the mark with DI water and mix thoroughly. Store in polyethylene bottles at 4°C. Prepare every other day.

QC-low concentration	14.28 µmol/L (0.20 mg/L)	5.0 mL QC stock
QC-high concentration	28.60 µmol/L (0.40 mg/L)	10.0 mL QC stock

PROCEDURE

1. Turn the power on for all components of the Lachat system. After the main menu appears on both monitor screens, download the appropriate nitrite method.[1]
2. Install the nitrite-reaction manifold onto the second reaction module. (See manifold flowchart, fig. 5.)

[1] The New York District Laboratory Lachat system is capable of determining concentrations of up to three constituents concurrently. Generally, concentrations of nitrite, nitrate plus nitrite, and ammonium are determined concurrently.



SPECIFICATIONS

Manifold tubing: 0.8 mm i.d.
Sample loop: 17 cm (86µL)
Flow cell: 10 mm
Interference filter: 520 nm
Pump setting: 35

Pump tubes:
DI water/wash bath: 2.00 mL/min (green)
1 M KCl/carrier: 0.42 mL/min (orange)
Sample: 2.00 mL/min (green)
DI water: 1.40 mL/min (yellow/blue)
Sulfanilamide: 0.60 mL/min (white)

Figure 5. Schematic diagram of nitrite flow-injection manifold.

3. Put all reagent lines into a beaker of degassed DI water.
4. Adjust tension levers on the individual pump tube cassettes. Set pump to "OVERRIDE STANDBY."
5. After all air has been pumped out of the system, place each reagent line in its respective container.
6. Continue to pump the reagents through until the baseline has stabilized. Return the pump to standby speed.
7. Place the diluter line in a container of 1M KCl.
8. Place standards A-H, QC-high, and QC-low in their containers in the order specified on the sample tray labeled "STANDARDS." Put empty sample tubes into the dilution tray labeled "EMPTY TUBES."
9. Start the calibration.
10. Check the calibration curve. If the calibration fails, repeat the calibration procedure.
11. If the calibration is acceptable, load samples into the first tray labeled "SAMPLES" and type in the sample serial numbers in the tray-identification window.
12. Submit the tray.
13. At the end of the run(s), rinse off the ends of all reagent lines and put all lines into a beaker of DI water. Set the pump speed to "OVERRIDE STANDBY." Let the system flush for 15 min.
14. Remove the lines from the beaker and let the system pump air to dry.
15. Release the tension on the pump-tube cassettes.
16. Turn off the power to all components of the system.

QUALITY CONTROL

- Standard-curve and data-verification calculations are performed by the QuikChem AE software package supplied by Lachat. The standard curve is a linear plot of standard concentration in relation to average absorbance. The best-fit line is drawn, and the curve is accepted if the correlation coefficient is 0.999 or greater.
- Quality-control samples are analyzed at the start of the run, after every 10 samples during the run, and at the end of the run. A quality-control sample is acceptable if the analyzed value is within 10 percent of the QC-high and QC-low theoretical values.
- Samples are diluted and reanalyzed if their concentration exceeds the concentration of the highest standard. Dilution factors are calculated by the instrument software, and dilution reruns are performed automatically by the instrument. Samples are also reanalyzed if they are associated with a quality-control sample that failed.
- Sample serial numbers are entered into the computer before the sample tray is submitted. A real-time printout is produced as the run progresses to monitor the peak integrity factors for each sample. At the conclusion of the run, the sample serial numbers and concentrations are electronically combined into a data file, which is printed. This file is electronically transferred into the SAS network data base, where it is verified against the data-file printout. Any necessary flags are assigned at this time. A data-base printout is then produced to provide hard-copy documentation of the data entry.

MAINTENANCE

- All pump tubes must be replaced as they are worn or stretched. The frequency will depend on the number of samples analyzed. The sample and wash-bath pump tubes should be changed once a month.
- Interference filters should be cleaned with lens paper whenever they are changed.
- Manifold tubing must be replaced as it becomes discolored or clogged.
- Sample tubes are rinsed, then soaked in DI water overnight, and oven dried between uses.
- Waste lines may need to be replaced periodically as buildup and clogging develop.

INTERFERENCES

Any oxidizing reagents present will interfere by oxidizing nitrite to nitrate.

SAFETY CONSIDERATIONS

All concentrated acids and bases should be mixed in a hood. Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis.

REFERENCES

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory - Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Lachat Instruments, 1990, Methods manual for the QuikChem automated ion analyzer - Method no. 10-107-04-1-C: Milwaukee, Wisc., Lachat Instruments (variously paged).

NITRITE PLUS NITRATE

Cross references:
USGS Method Code: I-2545-90
ISWS Method Code: -- none
EPA Section # -- none

Applications.—This method is used to measure nitrate concentrations in forest-soil extracts. Soil nitrate is extracted with 1M potassium chloride to produce a high ionic-strength solution.

Summary.—The nitrite-plus-nitrate analysis is an automated colorimetric reaction. Samples are systematically introduced into the flow-injection analyzer (FIA) reaction manifold. The sample passes through a copperized cadmium column that reduces any nitrate present to nitrite. An acidified sulfanilamide and N-(1-naphthyl)ethylenediamine dihydrochloride (NED) reagent is introduced into the flow. Sulfanilamide forms a diazo linkage with nitrite in the sample. The diazo compound couples with NED and forms a water-soluble red dye. The absorbance of the dye is read at 520 nm. The results represent the amount of nitrate and the original nitrite concentration in the sample.

INSTRUMENTATION AND EQUIPMENT

- Lachat QuikChem Automated Analyzer System consisting of:
  - XYZ sampler
  - Diluter
  - Pump
  - Injection module
  - Reaction module
  - Nitrite plus Nitrate reaction module
  - Photometer
  - QuikChem AE software and compatible computer
- Replacement pump tubes
- Sample tubes

SAMPLE PRESERVATION AND STORAGE

Soil extracts are frozen in polyethylene bottles until analysis. Samples are analyzed as soon as they are thawed.

REAGENTS AND STANDARDS

Degassed Deionized (DI) Water.—DI water is degassed by bubbling with commercial-grade helium for about 2 min. Degassed DI water is used for carrier water and for preparation of all reagents.

Ammonium Chloride Buffer, pH 8.5.—Add 210 mL concentrated hydrochloric acid (HCl) to a 2,000-mL volumetric flask containing about 1,200 mL DI water. Swirl to mix. Slowly add 190 mL ammonium hydroxide (NH_4OH) to the flask. Swirl to mix and allow smoke to vent. Add 2.0 g disodium ethylenediamine tetraacetic acid dihydrate ($Na_2EDTA \cdot 2H_2O$) to the solution. Fill to the mark with DI water and mix thoroughly. Allow to cool before use. Store in a polyethylene bottle at 4°C.

Sulfanilamide/NED reagent.–Add 100 mL 85-percent phosphoric acid (H_3PO_4) to a 1,000-mL volumetric flask containing about 600 mL DI water. Swirl to mix. Add 40.0 g sulfanilamide and 1.0 g NED to the solution. Stir until the solids have dissolved (about 20 min). Fill to the mark with DI water and mix thoroughly. Store in an amber polyethylene bottle at 4°C. Prepare monthly.

1M KCl.—Add 74.55 g KCl to a 1,000-mL volumetric flask containing about 800 mL DI water. Swirl to dissolve the solid. Fill to the mark and mix thoroughly. Store in a polyethylene bottle.

4M KCl.—Add 298.20 g KCl to a 1,000-mL volumetric flask containing about 800 mL DI water. Swirl to dissolve the solid. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle.

Hydrochloric Acid (1 M).—Pipet 82.5 mL concentrated hydrochloric acid (HCl) into a 1,000-mL volumetric flask containing about 700 mL DI water. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle.

2-percent Copper Sulfate Solution.—Add 20 g copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) to a 1,000-mL container containing about 700 mL DI water. Stir until the solid dissolves. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle.

Cadmium Copperization.—Pour about 15 g coarse cadmium powder (0.3 - 1.5 mm diameter) into a 250-mL beaker. Add 50 mL acetone to the beaker and stir with a glass stirring rod. Decant the liquid. Wash with 100 mL DI water and decant. Add 50 mL 1M HCl to the beaker, stir, decant, and repeat. Wash the cadmium 4 times with DI water. Add 50 mL 2-percent copper sulfate solution, stir for about 5 min, and decant the liquid. Repeat. Rinse with 5 additions of 50 mL ammonium chloride buffer. Store the cadmium in buffer in a closed wide-mouth container. Used cadmium may be washed and recopperized by this method.

Cadmium-Reduction Column.—Remove the fittings and foam plugs at both ends of the glass column. Rinse the column with DI water. Replace the foam plug at one end of the column using forceps. Draw about 10 cc ammonium chloride supernatent into a 20-cc syringe. Inject the liquid into the column, expelling any air bubbles. Once the column is full, replace the fitting on the bottom end. Holding the column over the container of copperized cadmium, scoop cadmium granules with a spatula and drop them into the top of the glass column. Tap the column lightly after adding a few centimeters of cadmium to ensure good packing. After the column is full, replace the foam plug and the fitting at the top of the column. Keep the column closed until the system is ready for the column addition. If the fittings are not in place, the liquid will drain from the column and must be repacked. If air bubbles are introduced during the packing procedure, the column must be rinsed and packed again. The column is packed weekly.

Nitrite Standard Stock Solution, 2000 mg NO_2^-/L (as N).—Add 9.8600 g sodium nitrite ($NaNO_2$) to a 1,000-mL volumetric flask containing about 800 mL DI water. Swirl to dissolve the solid. Pipet 2.0 mL chloroform into the flask. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare monthly.

Nitrite Standard Substock, 20 mg NO_2^-/L (as N).—Pipet 2.5 mL of standard stock into a 250-mL volumetric flask containing about 100 mL DI water. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle. Prepare monthly.

Nitrite Working Standards.—Pipet desired amount of standard substock into a 100-mL volumetric flask containing 25 mL 4M KCl. Fill to the mark with DI water and mix thoroughly. Store in polyethylene bottles and at 4°C. Prepare every other day

Standard A:	142.78 µmol/L (2.00 mg/L)	10.0 mL substock
Standard B:	107.08 µmol/L (1.50 mg/L)	7.5 mL substock
Standard C:	71.39 µmol/L (1.00 mg/L)	5.0 mL substock
Standard D:	42.83 µmol/L (0.60 mg/L)	3.0 mL substock
Standard E:	28.60 µmol/L (0.40 mg/L)	2.0 mL substock
Standard F:	14.28 µmol/L (0.20 mg/L)	1.0 mL substock
Standard G:	7.14 µmol/L (0.10 mg/L)	0.5 mL substock
Standard H:	0.00 µmol/L (0.00 mg/L)	0.0 mL substock

Nitrate Quality-Control (QC) Stock, 2,000 mg NO_3^--L (as N).—Add 14.4400 g potassium nitrate (KNO_3) to a 1,000-mL volumetric flask containing about 800 mL DI water. Swirl to dissolve the solid. Pipet 2.0 mL chloroform into the flask. Fill to the mark with DI water and mix thoroughly. Store in a polyethylene bottle at 4°C. Prepare monthly.

Nitrate QC Substock, 20 mg NO_3^-/L (as N).—Pipet 2.5 mL of standard stock into a 250-mL volumetric flask containing about 100 mL DI water. Fill to the mark with DI water and mix thoroughly. Prepare monthly.

Nitrite QC Stock, 2,000 mg NO_2^-/L (as N).—Use a sodium nitrite ($NaNO_2$) stock from a different manufacturer or a different lot from the standard stock. Add 9.8600 g sodium nitrite to a 1,000-mL volumetric flask containing about 800 mL DI water. Swirl to dissolve the solid. Pipet 2.0 mL chloroform into the flask. Fill to the mark with DI water and mix thoroughly. Store in polyethylene bottles at 4°C. Prepare monthly.

Nitrite QC Substock, 20 mg NO_2^-/L (as N).—Pipet 2.5 mL of QC stock into a 250-mL volumetric flask containing about 100 mL DI water. Fill to the mark with DI water and mix thoroughly. Store in polyethylene bottles at 4°C. Prepare monthly.

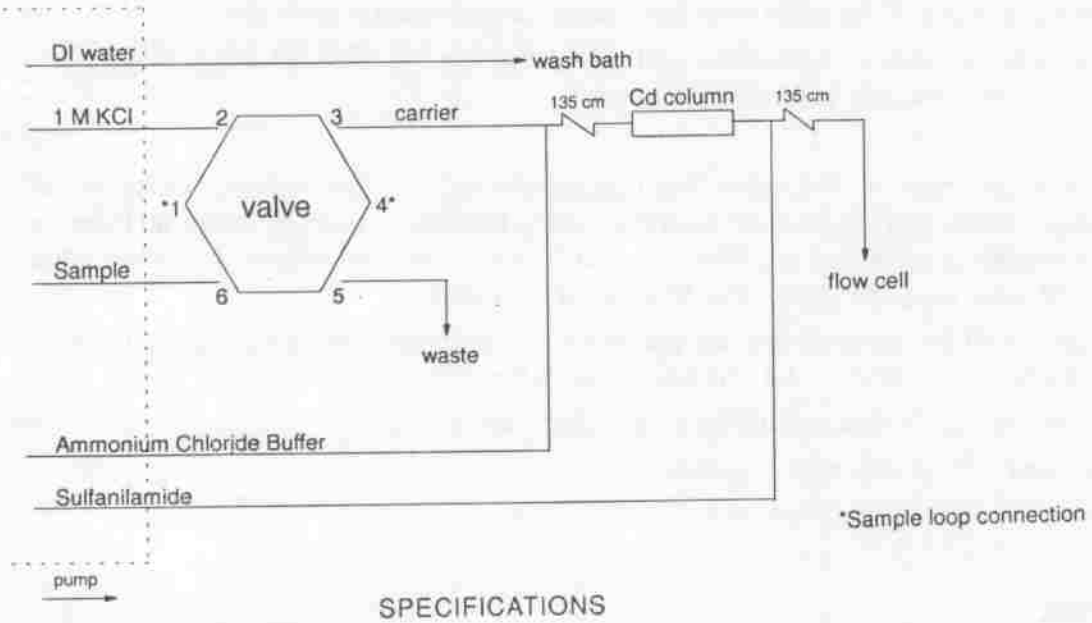
Nitrite plus Nitrate QC Samples.—Pipet desired amount of QC substock into a 500-mL volumetric flask containing 125 mL 4M KCl. Fill to the mark with DI water and mix thoroughly. Store in polyethylene bottles at 4°C. Prepare every other day.

QC-low concentration:	42.88 µmol/L (0.60 mg/L)	10.0 mL nitrate substock;	5.0 mL nitrite substock
QC-high concentration:	99.99 µmol/L (1.40 mg/L)	25.0 mL nitrate substock;	10.0 mL nitrite substock

PROCEDURE

1. Turn the power on for all components of the Lachat system. After the main menu appears on both monitor screens, download the appropriate nitrite plus nitrate method.[1]

[1] The New York District Laboratory Lachat system is capable of determining concentrations of up to three constituents concurrently. Generally, concentrations of nitrite plus nitrate, nitrite, and ammonium are determined concurrently.



SPECIFICATIONS

Manifold tubing: 0.8 mm i.d.
Sample loop: 17 cm (86 µL)
Flow cell: 10 mm
Interference filter: 520 nm
Pump setting: 35

Pump tubes:
DI water/wash bath: 2.00 mL/min (green)
1 M KCl/carrier: 0.42 mL/min (orange)
Sample: 2.00 mL/min (green)
Ammonium Chloride Buffer: 1.40 mL/min (yellow/blue)
Sulfanilamide: 0.60 mL/min (white)

Figure 6. Schematic diagram of nitrite plus nitrate flow-injection manifold.

2. Install the nitrite plus nitrate reaction manifold onto the third reaction module. The union fitting must be in place at the column position. (See manifold flowchart, fig. 6.)
3. Put all reagent lines into a beaker of degassed DI water.
4. Adjust the tension levers on the individual pump tube cassettes. Set the pump to "OVERRIDE STANDBY."
5. After all air has been pumped out of the system, place each reagent line into its respective container.
6. Continue to pump the reagents through until the baseline has stabilized. Return the pump to standby speed.
7. Remove the union fitting from the column position on the manifold.
8. Remove one fitting from the packed column and attach this end to the manifold column fitting that is closest to the valve. Remove the other fitting and attach this end to the remaining manifold column fitting. The column is now in line.
9. Set the pump to "OVERRIDE STANDBY" and continue to pump at this speed until the baseline has stabilized. Return the pump to standby speed.
10. Place the diluter line into a container of 1M KCl.
11. Place standards A-H, QC-high, and QC-low in their containers in the order specified on the sample tray labeled "STANDARDS." Put empty sample tubes into the dilution tray labeled "EMPTY TUBES."
12. Start the calibration.

13. Check the calibration curve. If the calibration fails, repeat the calibration procedure.
14. If the calibration is acceptable, load samples into the first tray labeled "SAMPLES" and type the sample serial numbers in the tray-identification window.
15. Submit the tray.
16. At the end of the run(s), remove the column from the manifold fitting that is closest to the waste. Place the old column fitting on this end. Remove the column from the remaining manifold fitting and place the other column fitting on this end of the column. The column must be stored with the column fittings in place. Put the union fitting back in line on the manifold.
17. Rinse off the ends of all the reagent lines and put all lines into a beaker of DI water. Set the pump speed to "OVERRIDE STANDBY." Let the system flush for 15 min.
18. Remove the lines from the beaker and let the system pump air to dry.
19. Release the tension on the pump-tube cassettes.
20. Turn off the power to all components of the system.

QUALITY CONTROL

- Standard-curve and data-verification calculations are performed by the QuikChem AE software package supplied by Lachat. The standard curve is a linear plot of standard concentration in relation to average absorbance. The best-fit line is drawn, and the curve is accepted if the correlation coefficient is 0.999 or greater.
- Quality-control samples are analyzed at the start of a run, after every 10 samples during the run, and at the end of the run. A quality-control sample is acceptable if the analyzed value is within 10 percent of the QC-high theoretical value and 12 percent of the QC-low theoretical value.
- Samples are diluted and reanalyzed if their concentration exceeds the concentration of the highest standard. Dilution factors are calculated by the instrument software, and dilution reruns are performed automatically by the instrument. Samples are also reanalyzed if they are associated with a quality-control sample that failed.
- Sample serial numbers are entered into the computer before the sample tray is submitted. A real-time printout is produced as the run progresses to monitor the peak integrity factors for each sample. At the conclusion of the run, the sample serial numbers and concentration values are electronically combined into a data file that is printed. This file is electronically transferred into the SAS network data base, where it is verified against the data-file printout. Any necessary flags are assigned at this time. A data-base printout is then produced to provide hard-copy documentation of the data entry.

MAINTENANCE

- All pump tubes must be replaced as they become worn or stretched. The frequency will depend on the number of samples analyzed. The sample and wash-bath pump tubes should be changed once a month.
- Interference filters should be cleaned with lens paper whenever they are changed.
- Manifold tubing must be replaced as it becomes discolored or clogged.
- Sample tubes are rinsed, then soaked in DI water overnight, and oven dried between uses.
- Waste lines may need to be replaced periodically as buildup and clogging develop.

INTERFERENCES

High concentrations of iron, copper, or other metals may interfere with the reaction and cause abnormally low results. The EDTA in the buffer decreases this interference. The presence of sulfides will destroy the column efficiency from the formation of cadmium sulfide.

SAFETY CONSIDERATIONS

All concentrated acids and bases should be mixed in a hood. Gloves, safety glasses, and lab coats should be worn when preparing for and performing this analysis. All cadmium preparations should be done in a hood. Waste cadmium should be collected and stored in a hazardous waste container.

REFERENCES

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory - Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open File Report 93-125, 217 p.

Lachat Instruments, 1990, Methods manual for the QuikChem automated ion analyzer - Method no. 10-107-04-1-C: Milwaukee, Wisc., Lachat Instruments (variously paged).

ANALYTICAL METHODS

C. SOIL-GAS ANALYSIS

CARBON DIOXIDE

Cross references:
USGS Method Code: -- none
ISWS Method Code: -- none
EPA Section # -- none

Applications .—This method is used to measure gaseous concentrations of carbon dioxide in forest soils.

Summary.—The analysis of carbon dioxide is performed with a gas chromatograph (GC). Each sample is injected through a desiccant into a six-point valve. GC-grade helium then delivers the sample into a separator column maintained at 70°C, and then through a thermal conductivity detector (TCD) maintained at 120°C.

INSTRUMENTATION AND EQUIPMENT

- Shimadzu GC-14A gas chromatograph consisting of:
  - Modular flow control
  - TCD
  - Column oven
  - Six-point valve modular injection system
  - Microprocessor detector keypad controller
- Shimadzu CR501 integrator
- Chromatography-grade helium
- Anhydrous magnesium perchlorate (desiccant)
- High-performance liquid-chromatography (HPLC) split/splitless injector
- Porapack Q 80/100 mesh, 10 feet, packed column
- SESI 20-mL nylon syringes
- Cole-Parmer 3-way port stopcocks

SAMPLE PRESERVATION AND STORAGE

Samples are collected and stored in 20-mL nylon syringes with 3-way stopcocks. Rubber bands are used to maintain positive pressure on the plunger of the syringe. The gas samples contain no additives.

REAGENTS AND STANDARDS

Carbon Dioxide Working Standards.—Carbon dioxide standards are purchased balanced with helium. The commercial supplier certifies standards in the range of 89.2 to 385.0 ppm to be within ±10 percent of the stated concentration, and standards in the range of 732.1 to 9,990 ppm to be within ±5 percent of the stated concentration.

PROCEDURE

1. Turn on the carrier gas flow. Let flow for 10 min at about 40 mL/min.
2. Turn on power for the gas chromatograph and the integrator.
3. Load the program file containing preset parameters and time programs previously saved for the TCD (file = "CO2").

4. Turn on the heater to the column oven and the detector oven.
5. Set the TCD detector temperature to 120°C, the column oven temperature to 70°C, and the injector temperature to 100°C on the GC keypad.
6. Set the TCD detector polarity and current settings on the GC keypad. (Polarity = 1, Current = 85). The TCD current should be set before conditioning (see below) and should be turned off when the TCD is not in use. Temperature-sensitive filaments can be damaged if the TCD current is set too high, left on while the TCD is not in use, or if carrier gas is turned off before the current is set to zero. A warning signal will occur if current is set too high. A reference graph is attached to the side of the gas chromatograph displaying current settings for various TCD temperatures and type of carrier gases.
7. Condition the TCD detector with carrier gas flowing previously at set temperatures for a minimum of 1 hour.
8. Immediately before analysis, automatic slope adjustment should be performed on the integrator for the TCD detector. The slope adjustment is a function of the integrator used for automatic calculation and setting of the peak processing parameter (slope). A higher slope setting (>1,000) delivers a decrease in sensitivity for peak detection.
9. Inject an air sample into the injection port to identify peak retention time. Enter the peak retention time in the ID file for the TCD parameter settings (TCD file = 9).
10. Calibration is performed by a two-point calibration curve using 385.0 ppm and 2431.7 ppm carbon dioxide balanced in helium. Three injections of each standard are used for calibration of the TCD detector on the integrator. External standard concentration (ppm) is a function of peak areas based on the calibration.
11. At the end of analysis, the heater to the gas chromatograph and the integrator are turned off, and the current to the TCD is set to zero. The gas chromatograph and carrier gas may be turned off once the temperatures of the detector, injection port, and column oven are about room temperature.

QUALTY CONTROL

- A series of certified analysis gas standards are used to verify calibration. Concentrations of these gas samples are as follows: 89.2 ppm, 385.0 ppm, 732.1 ppm, 1,000.1 ppm, and 2,431.7 ppm of carbon dioxide balanced in helium. The calibration is accepted if all standards are measured within an error of ±10 percent.
- A quality-control sample of 1,000.1 ppm carbon dioxide is analyzed at the start of the analysis run, after every 10 samples during the run, and at the end of the run. A quality-control sample is accepted when the analyzed value is within 10 percent of the certified analysis concentration. Samples are reanalyzed if the quality-control sample fails to meet the 10-percent criteria.
- Quality-assurance samples are used to detect errors that result from defective syringes, transport of samples, or extended holding times. For every 50 samples, two syringes are filled with a quality-control sample at the approximate time of field-sample collection and analyzed with the regular samples. Quality-assurance samples must be within 10 percent of the certified analysis value to meet the data-quality objectives of this analysis.
- Data entry into the data base is performed manually. Sample concentration values are transcribed from the integrator report to the bench sheet. The sample concentrations are entered into the data base in units of ppm. A printout is generated from the data base, and the values are compared to those in the integrator reports.

MAINTENANCE:

- The column oven temperature is increased to 200°C to purge any contamination that may have built up on the packed columns from excessive use. The TCD detector oven temperature is increased to 240°C to remove contamination. The period of contamination removal ranges from 24 to 48 hours. Removal of any contamination is performed with TCD current set at zero.
- The desiccant is replaced each week in which an analysis is performed or when excessive moisture peaks develop during analysis. The anhydrous magnesium perchlorate is replaced within the high-performance liquid-chromatography split/splitless injector.

INTERFERENCES

Moisture interferes with baseline stability. The desiccant removes sufficient quantities of moisture before analysis. Once excessive moisture causes an increased and unstable baseline, analysis is terminated until the next day.

SAFETY CONSIDERATIONS

The gas chromatograph has automatic shut-off functions for temperature malfunctions of the column oven, injector, and detector. The maximum temperature for the TCD oven is set at 250°C. Maximum temperature for the column oven is set at 250°C.

REFERENCES

Shimadzu Corporation, 1989, CR501 Chromatopac instruction manual 233-00142: Kyoto, Japan, Shimadzu Corporation Analytical Instruments Division (variously paged).

------ 1989, Gas Chromatograph GC-14A instruction manual 221-20818: Kyoto, Japan, Shimadzu Corporation Analytical Instruments Division (variously paged).

NITROUS OXIDE

Cross references:
USGS Method Code: -- none
ISWS Method Code: -- none
EPA Section # -- none

Applications .—This method is used to measure gaseous concentrations of nitrous oxide in forest soils.

Summary.—The analysis of nitrous oxide is performed with a gas chromatograph (GC). Each sample is injected through a desiccant into a six-point valve. Carrier gas consisting of 5 percent methane and 95 percent argon delivers the sample through a separator column maintained at 70°C. The sample is then passed from the column into the electron- capture detector (ECD) maintained at 320°C.

INSTRUMENTATION AND EQUIPMENT

- Shimadzu GC-14A Gas Chromatograph consisting of:
  - Modular flow control
  - ECD with ^{63}Ni radioactivity
  - Column oven
  - Six-point valve modular injection system
  - Microprocessor detector keypad controller
- Shimadzu CR501 Integrator
- Indicating moisture trap
- Chromatography-grade p5 mixture gas (5 percent methane, 95 percent argon)
- Anhydrous magnesium perchlorate (desiccant)
- High Performance Liquid Chromatography (HPLC) split/splitless injector
- Porapack Q 80/100 mesh, 10 feet, packed column
- SESI 20-mL nylon syringes
- Cole-Parmer 3-way port stopcocks

SAMPLE PRESERVATION AND STORAGE

Samples are collected and stored in 20-mL nylon syringes with 3-way stopcocks. To maintain positive pressure within the syringe, rubber bands are used to maintain pressure on the plunger of the syringe. The gas samples contain no additives.

REAGENTS AND STANDARDS

Low-concentration (about 0.1 ppm, 0.3 ppm, 0.5 ppm, 0.7 ppm) and high-concentration (1.0 ppm and 10.0 ppm) gas samples of nitrous oxide balanced in nitrogen are purchased. The lowest concentration gas sample, 0.092 ppm nitrous oxide, has a certificate of analysis from the commercial supplier for ±5 percent accuracy. 0.3 ppm, 0.5 ppm, and 0.7 ppm nitrous oxide gas samples are certified from the commercial supplier for ±2 percent accuracy. High-level concentration standards from the commercial supplier have an analytical accuracy of ±5 percent from the certified concentration.

PROCEDURE

1. Turn on the carrier gas and let flow for 10 min at about 40 mL/min.
2. Turn on power for the gas chromatograph and the integrator.
3. Load the program file containing preset parameters and time programs previously saved for the ECD (file = "N2O").
4. Turn on the heater to the column oven and the detector oven.
5. Set the ECD detector temperature to 320°C, the column oven temperature to 70°C, and the injector temperature to 100°C on the GC keypad.
6. Set the ECD detector range and current settings on the GC keypad (Range = 1, Current = 0.5).
7. Condition the ECD detector with carrier gas flowing at previously set temperatures for a minimum of 24 hours.
8. Immediately before analysis, automatic slope adjustment should be performed on the integrator for the ECD detector. The slope adjustment is a function of the integrator used for automatic calculation and setting of the peak processing parameter (slope). A higher slope setting (>1,000) delivers a decrease in sensitivity for peak detection.
9. Inject an air sample into the injection port to identify peak retention time. Enter the peak retention time in the ID file for the ECD parameter settings (ECD file = 0).
10. Calibration is performed by a two-point absolute calibration curve using 0.296 ppm and 0.475 ppm nitrous oxide balance in nitrogen. Three injections of each standard are used for calibration of the ECD detector on the integrator. External standard concentration is a function of peak areas based on the calibration.
11. At the end of analysis, the heater to the gas chromatograph and the integrator are turned off. Once the temperatures of the detector, injection port, and the column oven have reached room temperature, the gas chromatograph and carrier gas may be turned off.

QUALITY CONTROL

- To verify the calibration, a series of certified analysis standards are injected into the gas chromatograph. Concentrations of these standards are as follows: 0.092 ppm, 0.296 ppm, 0.475 ppm, and 0.701 ppm nitrous oxide balanced in nitrogen. The calibration is accepted if all of these standards are measured within an error of ±10 percent.
- A quality-control sample of 0.462 ppm nitrous oxide balance in air is analyzed at the start of the analysis run, after every 10 samples during the run, and at the end of the run. A quality-control sample is accepted when the analyzed value is within 10 percent of the certified analysis concentration. Samples are reanalyzed if the quality-control sample fails to meet the 10-percent criterion.
- Quality-assurance samples are used to detect any errors that may result from defective syringes, transporting samples, or extended holding times. For every 50 samples, two syringes are filled with a quality-control sample at the appropriate time of field-sample collection and analyzed with the regular samples. Quality-assurance samples must be within 10 percent of the certified analysis value to meet the data-quality objective of this method.
- Data entry into the data base is performed manually. Sample concentration values are transcribed from the integrator report to the bench sheet. The sample concentrations are entered into the data base in units of ppm. A printout is generated from the data base, and the values are compared with those on the integrator reports.

MAINTENANCE

- The indicating moisture trap is in line between the carrier gas and the gas chromatograph. This trap removes any moisture that may be in the carrier gas. The moisture trap will change from blue to pink when replacement is needed.
- The column oven temperature is increased to 240°C to purge any contamination that built up on the packed columns from excessive use. The ECD-detector oven temperature is increased to 340°C to remove contamination. The period of contamination removal ranges from24 to 48 hours.
- The desiccant is replaced each week in which an analysis is performed or when excessive moisture peaks develop during analysis. The anhydrous magnesium perchlorate is replaced within the high-performance liquid-chromatography split/splitless injector.

INTERFERENCES

Moisture interferes with baseline stability. The desiccant removes sufficient quantities of moisture prior to analysis. Once excessive moisture causes an increased and unstable baseline, analysis is terminated until the next day.

SAFETY CONSIDERATIONS

- Medical Industrial Systems Consultants, Inc. performs radiation-leakage tests on the ^{63}Ni in the ECD every 6 months. If leakage is detected, the ECD detector is to be returned to Shimadzu Scientific Instruments, Inc. for repair or replacement. When the ECD ^{63}Ni cell has become soiled, cleaning is performed by Shimadzu Scientific Instruments, Inc.
- If malfunctions in the temperature of the column oven, injector, and detector occur, the GC has automatic shut-off functions. The gas chromatograph has automatic shut-off functions. The maximum temperature allowance for the ECD oven is set at 350°C. Maximum temperature allowance for the column oven is set at 250°C.

REFERENCES

Shimadzu Corporation, 1989, CR501 Chromatopac instruction manual 233-00142: Kyoto, Japan, Shimadzu Corporation Analytical Instruments Division (variously paged).

----- 1989, Gas Chromatograph GC-14A instruction manual 221-20818: Kyoto, Japan, Shimadzu Corporation Analytical Instruments Division (variously paged).