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Atmospheric Sciences Section
Illinois State Water Survey
Urbana, Illinois 61801

PRECIPITATION SAMPLE HANDLING, ANALYSIS, AND STORAGE PROCEDURES

Research Report 4
Contract Number EY-76-S-02-1199

June 1979

by

Mark E. Peden
Loretta M. Skowron
Florence F. McGurk

Sponsored by:

United States Department of Energy
Pollutant Characterization and Safety Research Division
Office of Health and Environmental Research
Washington, D.C.

Richard G. Semonin
Principal Investigator

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PREFACE

The chemical analysis of rainwater is a relatively new tool used by atmospheric scientists researching man's impact on his environment with specific application to study of the aerosol composition of the troposphere. Precipitation, because of its unique scavenging or cleansing properties, is a useful indicator of ambient pollution levels, and its chemical analysis yields valuable data concerning inputs of both nutrients and toxic compounds to terrestrial and aquatic biota. Interest in the increased acidity of precipitation has been heightened from cases of decreased forest productivity and incidences of fish kills in lakes exhibiting lowered pH values.

The research on precipitation scavenging involved over several years on this contract from studies of radioactive wet deposition variability to current studies of energy-related pollutants. The analytical facilities also evolved moving from radioactivity counters to atomic absorption spectroscopy and automated wet chemistry techniques. The early and continuing research on atmospheric chemistry, particularly precipitation chemistry, necessitated the adaptation of existing methods for analysis of the complex precipitation water matrix, and the development of sample collection, handling, and storage procedures.

The sensitivity of the analytical quality to the entire sampling and sample handling methodology cannot be overstated. The common low levels of concentration of materials (frequently at the detection level) require extreme care of the samples in the laboratory and constant checking of instrument performance. Very early in this program, it was recognized that the time between the collection of the last precipitation to the analysis of the sample was critical for the interpretation of the results. Considerable preliminary work is completed, but much remains to be done on the problem of ionic stability in aqueous solutions.

Presently available instrumental techniques used for inorganic analysis are sufficiently refined to provide accurate determinations down to $\mu\text{g } \ell^{-1}$ levels in most cases. Because of the low ionic concentrations ($\sim 20 \text{ mg } \ell^{-1}$) routinely encountered in precipitation samples, however, biases introduced in handling and storage procedures can become the determining factors affecting reliable data acquisition and interpretation.

The procedures presented in this document were developed during the last ten years of precipitation chemistry research within the Atmospheric Sciences Section of the Illinois State Water Survey. In most cases they represent modified methods adapted specifically to meet the special requirements necessary for trace analysis of inorganic constituents in rainwater samples. All procedures have been rigorously evaluated to ensure that all aspects of collection, handling, and analysis are mutually compatible.

Detailed methodologies are outlined for all the major ions normally encountered in precipitation samples in addition to many metals also found in trace amounts in rainwater.

We hope that this report will be of use to others working in the area of precipitation chemistry research. The current emphasis on research of the chemical quality of precipitation accelerates the need for establishment of standard analytical methods to insure compatibility of data from various sources. Only with the gradual implementation of such standards can a true assessment of the changing national air and precipitation quality be achieved.

Finally, this report represents the culmination of the efforts of many scientists, particularly the dedication of the authors to the task of applying the described procedures to samples obtained during pressure-filled field experiments. However, without the continued support of Mr. Robert W. Beadl of DOE, this work would not be at the present level of sophistication we currently enjoy. His guidance throughout many hectic years is greatly appreciated and we dedicate this volume to him with gratitude.

Richard G. Semonin
Principal Investigator

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pH	17
Specific Conductance	18
NH ₄ ⁺ Ammonium	19
Cd Cadmium	23
Ca Calcium	25
Cs Cesium	27
Cl ⁻ Chloride	29
Cu Copper	33
In Indium	35
Fe Iron	37
Pb Lead	39
Li Lithium	41
Mg Magnesium	43
Mn Manganese (flame)	45
Mn Manganese (flameless)	47
NO ₃ ⁻ Nitrate	49
PO ₄ ⁼ Phosphate	53
K Potassium	57
Na Sodium	59
Sr Strontium	61
SO ₄ ⁼ Sulfate	63
Zn Zinc	67
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1. SAMPLE COLLECTION

Rainwater samples to be used for inorganic determinations are collected in linear polyethylene (LPE) vessels. All sample containers are evaluated prior to use to ensure that the plastic substrate does not leach any impurities from the walls. In addition, known synthetic and natural solutions are added to collection and storage containers and analyzed over time to make certain that ions are not adsorbed onto the vessel walls.

The collection device used is illustrated in figure 1.1. It is an electrically operated apparatus consisting of two cylindrical LPE tubs and motor driven movable cover. Built from the design published by the Department of Energy (DOE) Environmental Measurement Laboratory (EML) (Volchok and Graveson, 1975), the sampler employs a precipitation activated switch which exposes one bucket during times of rain or snow and the other during dry periods. Extraneous particulates are thereby kept out of the 'wet' side in addition to minimizing evaporation effects.

Several improvements have been made to the original design which are listed below:

1. The underside of the movable lid was covered with a foam material encased in polyethylene. This provides a tight seal with the bucket rim and allows for routine cleaning of the lid undersurface with deionized water.
2. The electronics package within the body of the sampler was placed in a waterproof metal box to ensure that it would remain moisture free under conditions of high winds and high humidities.
3. The wood frame bucket holders were replaced with a plastic double bucket configuration such that one was permanently mounted to the sampler. Screws were attached to the inside of this bucket to provide a tight fit when the actual sample bucket was inserted into it. This design kept the sample vessel in place under the most extreme high wind conditions.

The sampling duration varies based on the objectives to be achieved. Peden and Skowron (1978) have shown that dramatic concentration changes in ions such as Ca^{++} , Mg^{++} , and H^+ can occur over a relatively short time span (1-3 days) if these constituents are not somehow preserved. Other parameters such as SO_4^- , NO_3^- , and Cl^- appear to be stable over this same time period and therefore do not require the exacting sampling requirements necessary for some of the cations. In most cases, true event or daily samples are the preferred method of collection for the most representative precipitation samples. Where the more conservative chemical constituents are of main interest, weekly wet-only sampling is sometimes used.

References

- Peden, M. E. and L. M. Skowron, 1978: "Ionic stability of precipitation samples." Atmospheric Environment, Vol. 12, pp. 2343-2349.
- Volchok, H. L. and R. T. Graveson, 1975: "Wet/dry fallout collection." Proc. 2nd Federal Conf. on the Great Lakes, IL, March 25-27, 259-264.

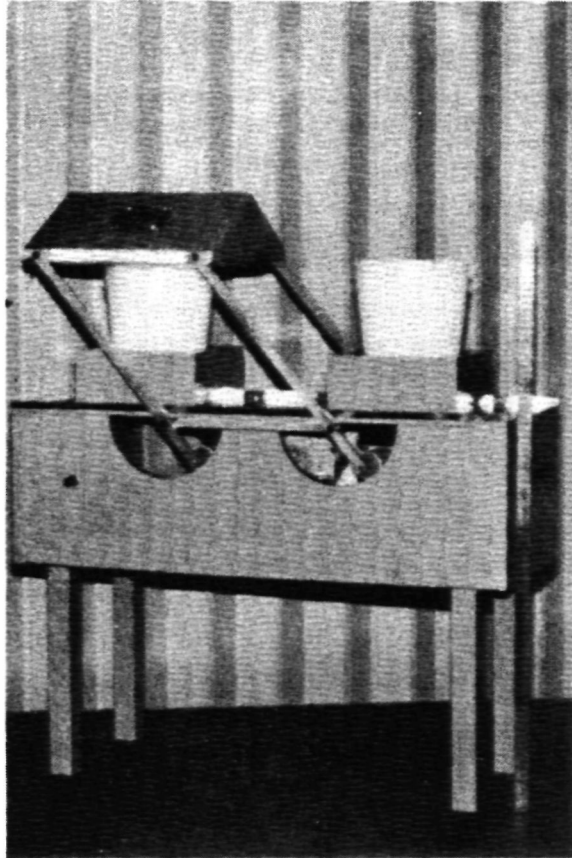


Figure 1.1 HASL type wet/dry sampler
(Volchock and Graveson, 1975)

2. SAMPLE PROCESSING AND PRELIMINARY MEASUREMENTS

Field samples brought to the laboratory are processed immediately to prevent changes in ionic composition. In cases where immediate processing is not possible, samples are stored at 4°C. The laboratory data forms shown in figures 2.1a and 2.1b are used during sample check-in. An assigned sample number includes the type of sample, location, and a sequential laboratory number for ease of identification. The forms are computer coded to facilitate direct keypunching from them. The data sheets shown in figures 2.2a and 2.2b are used for the chemical analyses and utilize only the sequential laboratory number for identification purposes. Pertinent information such as date and time on and off, field condition, precipitation amount, and comments related to visual sample observations are recorded on the first two data forms.

The flow diagram in figure 2.3 illustrates the laboratory processing procedure for both wet and dry samples. Wet samples are first weighed to determine the total precipitation amount. Specific conductance and pH are then determined prior to filtration. Details of the specific conductance and pH measurements are included in the Methods Section. Samples are then filtered through a 0.45 µm membrane filter (Millipore HA) to separate the soluble fraction from the insoluble material.

Figure 2.4 illustrates the filtering apparatus used. It was designed to facilitate leaching contaminants from the filter and the glass funnel prior to actual sample filtration. In operation, the plexiglass top is removed and a linear polyethylene bottle is placed in its holder. The top is replaced and the empty bottle rotated to position 'A' to avoid collecting any leach water. The filter funnel with filter is then placed into the hole in the top. The interior surface of the filter funnel is rinsed with 200 mL of deionized water with the vacuum on. The sample is then filtered, after rotating the receiving bottle to position 'B'. The stopcock at the base is used to drain the leach water. This procedure has proven effective in avoiding contamination to the water soluble portion of the samples for Na, K, Ca, Mg, NO₃, SO₄, Cl, NH₄, PO₄, Li, Cs, Sr, Mn, Fe, Cu, Cd, In, and Pb. In addition, the filter has been shown to absorb none of the ions above when known amounts are filtered through it.

As seen in the flow diagram, a portion of the filtrate is acidified to pH 2 with HNO₃ (Environmental Protection Agency, 1974) to stabilize the trace metals. Previous work by Peden and Skowron (1978) has shown that filtration alone is sufficient to stabilize the constituents H, K, Na, Ca, Mg, NO₃, SO₄, PO₄, Cl, and NH₄. The detailed methodologies for all chemical parameters are outlined in the Methods Section.

The insoluble material remaining on the filter is oven-dried at 60°C for 1 hour and stored in glass vials until an acid dissolution is performed. The dissolution procedure is outlined in Section Three.

Reference

U.S. Environmental Protection Agency, 1974: Manual of Methods for Chemical Analysis of Water and Wastes. Office of Technology Transfer, Washington, DC.

ISWS ATM. CHEM. DATA FORM: JAN. 1979

TIME: CST CDT EST GET				DATE	TIME	DATE	TIME	LAB	LAB	WEIGHT	DRY	LAB	LAB	LAB	LAB	LAB	
SAMPLE	NUMBER	DATE	TIME	OH	CH	OFF	OFF	COND.	GROSS	AFTER	BOTTLE	PH	CONDUCT.	TEMP.	RESERVED	DATE	
11	2-6	7 8 9-12	14-19	21-24	26-31	33-36	37-39	40-44	46	48-51	53	55-58	60	62	64-65	66-69	71
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(a)

ISWS ATM. CHEM. DATA FORM: JAN. 1979

SAMPLE	NUMBER	SAMPLE	FINAL	FIELD	FIELD	FIELD	WEEKLY	COMMENTS	DATE
11	2-6	7 8 9-12	14-20	22-27	29-32	34-36	38-40		79
X	XXXX	X	XXXX	XXXX	X	X	XX	00-78	93
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(b)

Figure 2.1 Laboratory data forms. (a) - Preliminary lab measurements, (b) - Comment form

ISWS ATE. CHEM. DATA (MG/L) FORM: JAN. 1979

SAMPLE NUMBER	CA		MG		NA		K						II DI
	71 81	9-115-	16-120-	23-127-	30-134-	37-141-	44-148-	51-155-	58-162-	65-169-	72-176-	79-183-	
11 X XXXX	X X	11 115 XXXXXX	16 120 XXXXXX	23 127 XXXXXX	30 134 XXXXXX	37 141 XXXXXX	44 148 XXXXXX	51 155 XXXXXX	58 162 XXXXXX	65 169 XXXXXX	72 176 XXXXXX	79 183 XXXXXX	91 01
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(a)

ISWS ATE. CHEM. DATA (MG/L) FORM: JAN. 1979

SULFATE AS SO4; NITRATE AS NO3; AMMONIUM AS NH4; PHOSPHATE AS PO4

SAMPLE NUMBER	SC4		NO3		CL		NH4		PO4				II DI
	71 81	9-115-	16-120-	23-127-	30-134-	37-141-	44-148-	51-155-	58-162-	65-169-	72-176-	79-183-	
11 X XXXX	X X	11 115 XXXXXX	16 120 XXXXXX	23 127 XXXXXX	30 134 XXXXXX	37 141 XXXXXX	44 148 XXXXXX	51 155 XXXXXX	58 162 XXXXXX	65 169 XXXXXX	72 176 XXXXXX	79 183 XXXXXX	91 01
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(b)

Figure 2.2 Chemistry data forms. (a) - Atomic absorption measurements, (b) - Wet chemistry measurements.

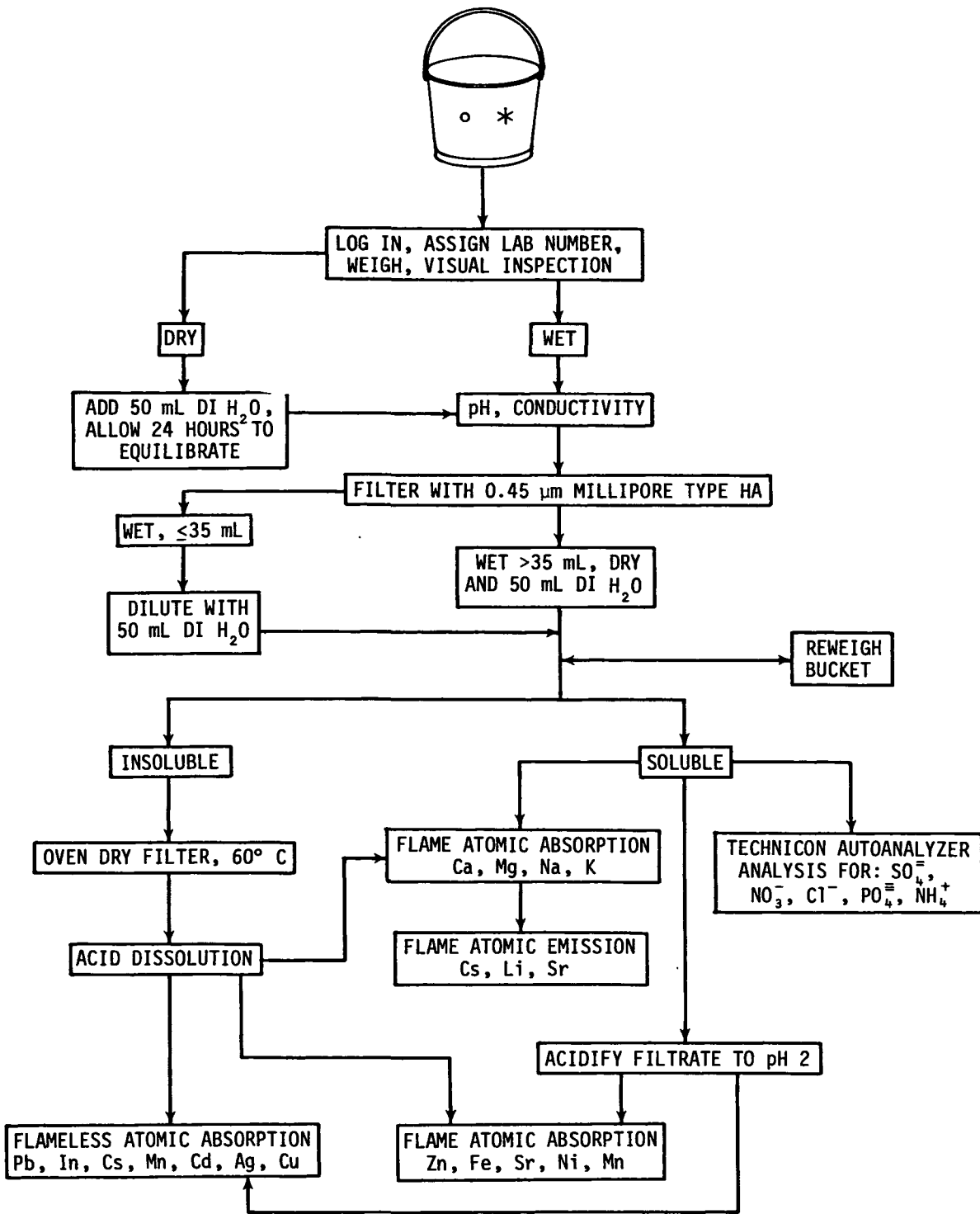


Figure 2.3 Sample processing flow chart

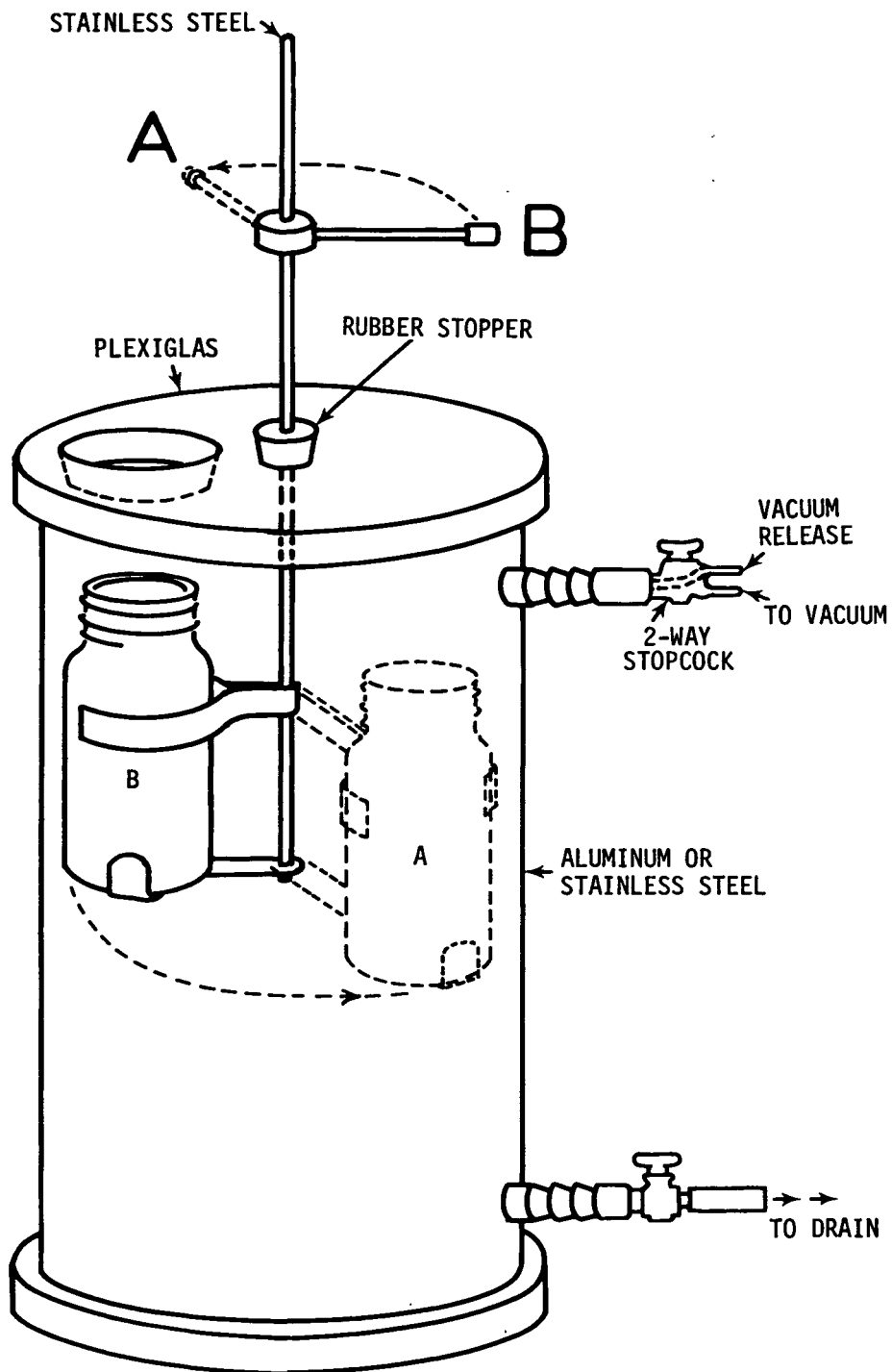


Figure 2.4 Sample filtration apparatus

3. ACID DISSOLUTION PROCEDURE

The heterogeneous nature of insoluble particulate matter found in precipitation samples presents a problem in finding a suitable dissolution procedure prior to atomic absorption analysis. An acceptable technique must possess the properties of: 1) minimal chemical interferences, 2) low reagent blank, 3) high rate of decomposition, and 4) the ability to dissolve a varied matrix consisting of metals, carbon, resins, pollen, fungi, bacteria, oxides, fluorides, silicates, and other inorganic and organic species such as leaves, insects, and bird droppings. A suitable procedure has been developed consisting of HF, H₂SO₄, and HNO₃ whereby the resultant solution can be satisfactorily used in the flame and flameless atomic absorption determination of 15 metallic elements, including the atmospheric tracers In, Li, and Cs.

Required Reagents

1. HF, 48.9% Dissolve silicates by the formation of volatile SiF₄ producing a Si free sample.
2. H₂SO₄, 96.7% Decompose and remove organic material.
3. HNO₃, 70.6% Solvent for inorganic phase.
4. Deionized water (DI) Dilute dissolved sample.

Apparatus

1. Teflon TFE (polytetrafluoroethylene) beakers, 50 mL; cleaned by soaking in 4N HNO₃ for 12 hours, then rinsed with deionized water.
2. Eppendorf micropipets with disposable polyethylene tips, rinsed in 4N HNO₃.
3. Laminar flow clean air bench and fume hood.
4. Corning hot plate with pyroceram top.

Experimental Procedure

1. Add one mL of HF to the beak containing the filter. Heat at 120°C* until dry (~1.25 hr).
2. Add two mL of H₂SO₄, and let stand until filter decomposes (0.25 hr).

*Manufacturer's values for top temperature.

3. Add two mL of H_2O_2 slowly in 0.25 mL increments to avoid foaming. Solution should become clear at this point.
4. Heat sample at 210°C for 1 hr or until solution begins to turn yellow. Avoid charring.
5. Remove beaker from hot plate and cool for 10 min. Add 1 mL of H_2O_2 in 0.25 increments to clear solution..
6. Heat sample at 210°C for ~0.5 hr to boil off the H_2O resulting from H_2O_2 decomposition.
7. Add one mL HNO_3 and heat at 120°C for 0.5 hr, and then at 260°C until the dense white fumes of SO_3 begin to evolve (0.5 hr). The HNO_3 will have boiled off prior to SO_3 fumes.
8. Remove beaker from hot plate and cool for 10 min. Add 1 mL of HNO_3 to prevent possible precipitation of the alkaline earth sulfates after dilution. Rotate beakers carefully to wash down the interior walls and add ~20 mL of deionized water. Rinse again and transfer contents to a 25 mL volumetric flask. Bring to volume with deionized water and transfer to a 60 mL polyethylene bottle.

This procedure has been tested and found to give quantitative (97% - 105%) recoveries of Ca, Mg, Na, K, Li, Mn, Fe, Cu, Zn, Sr, Cd, In, Cs, and Pb at the $1 \mu\text{g mL}^{-1}$ level. The rationale behind this method is to keep the analyte blank at the lowest possible level in all steps. Therefore, a minimum volume of acids was used. Samples containing a large amount of particulate material may require additional amounts of one or more of the reagents.

Since a clean air hood is used to exhaust the fumes, the beakers do not require covers; however, when using a conventional fume hood, teflon (TFE) beaker covers should be used to partially cover the beaker to protect it from particles introduced from unfiltered laboratory air. Completely covering the beakers and refluxing the sample assists in the dissolution of refractory particles when either type of fume hood is used. When refluxing with small volumes of acids, the cover should occasionally be tapped to make the acid droplets fall back into the sample solution.

4. QUALITY ASSURANCE

Precipitation samples are typically characterized by a low dissolved solids content (~20 mg L⁻¹) resulting in a highly unbuffered system. Because of this, a quality control program for rainwater analysis requires stringent laboratory conditions and a careful check on all aspects of the analyses. Each step in the analytical flow chart shown in figure 2.5 is a potential source of contamination and must be constantly monitored to guarantee that the final chemical analyses are not adversely affected by any processing steps.

Sample collection and storage containers are evaluated for impurities and absorption phenomena on a routine basis. Reagent grade or Ultrex chemicals are used for all laboratory analyses. Reagent purity is monitored by the use of extensive 'blanks' to ensure that trace contaminants do not interfere with analytical determinations. Membrane filter extracts are also assayed to check for soluble impurities.

Known water reference samples provided by the U.S. Environmental Protection Agency, Water Quality Branch are checked each time a particular constituent is being determined. These values are used to generate accuracy and precision data for each parameter measured. In addition, participation in interlaboratory comparisons of unknown samples provides a constant check on overall laboratory performance.

Routinely, 5% of the samples are split and analyzed as blind duplicates. Four-point calibrations are used for all parameters except pH and specific conductance. A full calibration is made after every 36 samples with a one point calibration check being made every 12 samples. Standard addition procedures are utilized in methods development to investigate any interference effects.

After being transcribed to the laboratory data forms, chemical determinations are computer checked for ionic balance and calculated versus measured specific conductance. Ionic balance is calculated on an equivalent basis using the formula:

$$\frac{\text{Anions} - \text{Cations}}{\text{Anions} + \text{Cations}} \times 100$$

Analyses differing by more than 10% are re-analyzed for all parameters. Calculated conductance is derived from the sum of the equivalent conductances of each measured ion. Differences of more than 10% between measured and calculated values are subjected to reanalysis.

5. STANDARD CONDITIONS FOR THE DETERMINATIONS OF IONS IN PRECIPITATION

The following procedures are used in our laboratory for the analysis of soluble and insoluble components of precipitation samples. The operating conditions are optimal, based on experience with a given ion in a specific matrix. A complete listing of the instrumentation employed is given at the end of the methods documentation.

Each chemical parameter is detailed separately and includes the instrumental mode, reagent requirements, working ranges, and recommended instrument settings. The three basic methods employed include: 1) glass electrode, 2) atomic absorption, and 3) automated wet chemistry. Glass electrode systems are used for pH and specific conductance measurements. These two parameters are outlined first in the method descriptions. The remaining constituents are listed alphabetically by chemical name.

All metal determinations are made by atomic absorption spectroscopy using both the flame and flameless mode. The format for all atomic absorption determinations is similar and gives detailed operating parameters for the specific equipment listed.

The ions $\text{SO}_4^{=}$, NO_3^- , Cl^- , $\text{PO}_4^{=}$, and NH_4^+ are determined using a Technicon AutoAnalyzer system. Instrument settings are given separately for each module of the Technicon system in addition to reagent preparation guidelines.

In many cases, the methods used represent departures from the manufacturer's recommended operating parameters. These modifications were made to lower the working range to the $\text{ng} \cdot \text{mL}^{-1}$ level which is necessary for accurate precipitation analyses.

PH

The pH measurements are made on unfiltered aliquots after the sample has equilibrated with room temperature (25°C). One mL of sample is first dispensed into a clean polystyrene vial. Direct insertion of the electrode into the whole sample is not permitted to prevent introducing any contamination that might affect the accuracy of the ensuing elemental determinations. A microcombination electrode connected to a pH meter which reads to ± 0.01 pH units is used for all determinations. Care should be taken to keep the sample away from acid or ammonia fumes, which can be absorbed and alter the true pH value.

The pH meter is standardized by dispensing two certified buffers which bracket the expected pH values. A pH 7 and pH 4 buffer are generally adequate for precipitation samples. The electrode is first rinsed in deionized water and then inserted into the pH 7 buffer. Any excess water remaining on the electrode bulb should be blotted with a Kimwipe before insertion into the buffer. After a 1-2 minute equilibration time, the calibration control should be set to read 7.00. The electrode is now removed, rinsed as before and placed in the pH 4 buffer. After another 1-2 minutes, the slope control knob should be carefully adjusted to read 4.00. The pH 7 should now be checked again and must read 7.00 ± 0.01 . If not, repeat the calibration procedure until the buffers agree. Instruments with temperature compensation should be pre-set to room temperature before the calibration procedure is begun.

Once the instrument is calibrated, sample measurements are made using a 2 minute equilibration period followed by careful rinsing of the electrode before each determination. Results are reported to the nearest 0.01 pH unit. The standard deviation of replicate determinations is 0.05 pH unit.

Electrodes are stored in 3 molar KCl when not in use. The level of the electrolyte solution is checked daily and filled as necessary with saturated KCl. Electrodes are reconditioned by immersion in ammonium hydroxide with ultrasonic agitation for 0.5 hour. This has proven effective in cleaning clogged diaphragms, the most common cause of trouble with combination electrodes. After cleaning, electrodes are rinsed well in deionized water and refilled with new electrolyte solution.

Specific
Conductance

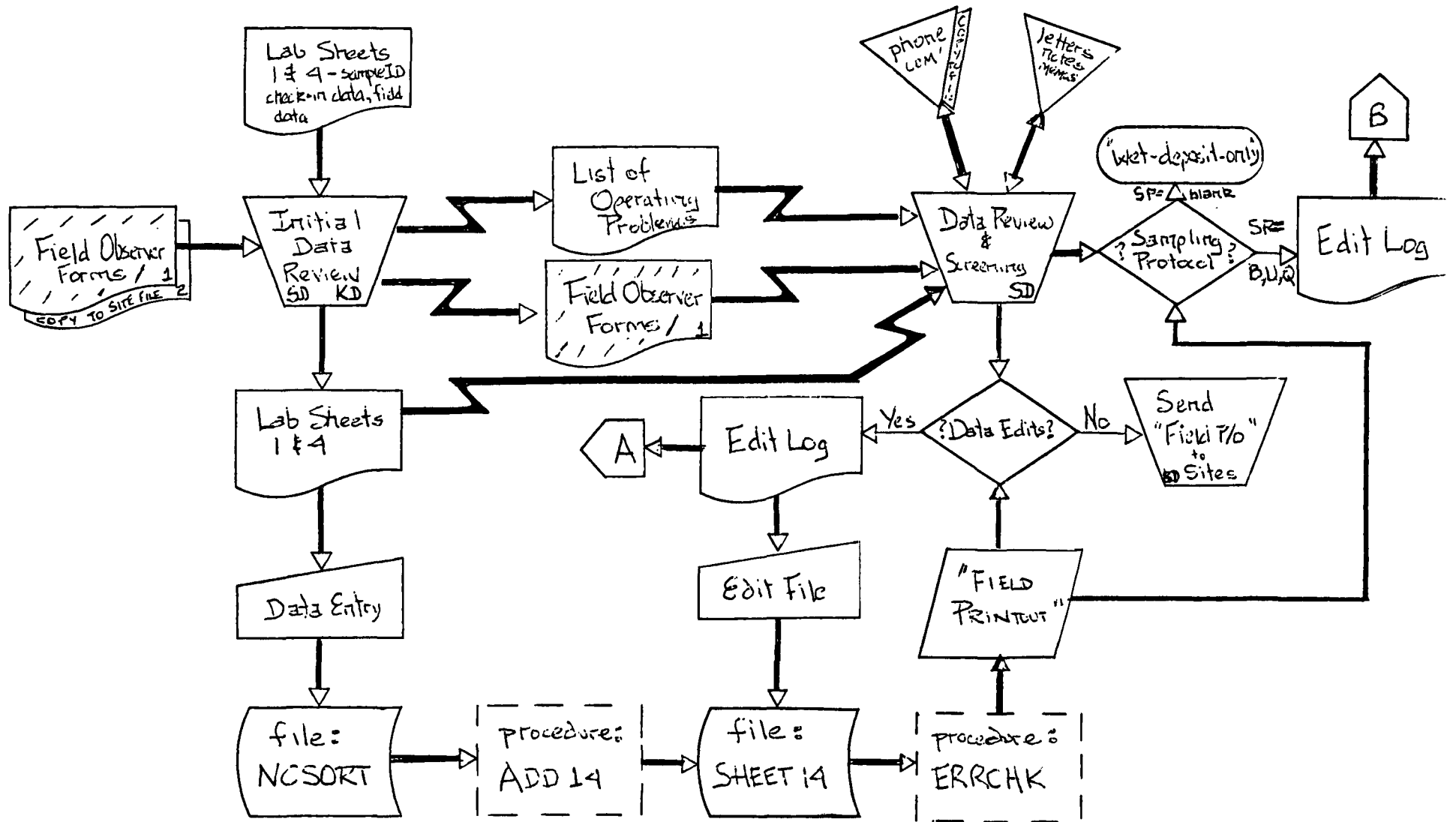
Conductivity measurements are made with an inverted Pyrex conductance cell connected to a manually balanced AC bridge. A three mL sample volume of unfiltered precipitation is dispensed into the cell and readings are taken ~ 5 minutes later. These values are multiplied by the cell constant (K) to obtain the specific conductance, expressed in microSiemens/cm ($\mu\text{S cm}^{-1}$). Contamination is minimized by rinsing the cell three times with deionized water between samples, and shaking off the excess water.

Since the specific conductance varies about 2% per degree Celsius, the reported value is normalized to 25°C. The measurements, however, can be made at room temperatures between 20° and 30°C, and the following equation used to calculate the specific conductance at 25°C:

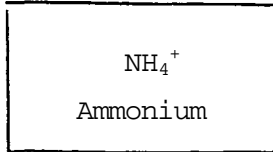
$$\text{Specific conductance} = \frac{717.8 \times R_{\text{KCl}}}{R_s} \frac{\mu\text{S}}{\text{cm}}$$

where R_{KCl} and R_s are the resistances, in ohms, of a standard potassium chloride solution (0.005M) and the sample, respectively.

Rainwater exhibits, a relatively low specific conductance, usually ranging from 10 to 60 $\mu\text{S cm}^{-1}$ with a mean value of 25.



Schematic of "Field Printout" Generation and Assignment of Sampling Protocol Designations.
 NADP/CAL - ILLINOIS STATE WATER SURVEY.



Method : Automated Colorimetric Phenate

Instrumental Mode: Technicon Auto Analyzer II System

Auto Sampler III

No. of Samples/Hr: 60

Sample/Wash: 6/1

Sample Volume, mL: 0.5-1.0

GILSON 2" Pump

Pump Manifold Tubes

<u>Color</u>	<u>Flow Rate (mL/min⁻¹)</u>	<u>Application*</u>
Grn/Grn	2.00	DI to sampler wash receptacle
Red/Red	0.80	Complexing reagent
Orn/Wht	0.23	Air
Orn/Orn	0.42	Sample
Orn/Orn	0.42	Alkaline Phenol
Blk/Blk	0.32	Sodium Hypochlorite
Orn/Orn	0.42	Sodium Nitroprusside
Blu/Blu	1.60	From flow cell to waste

Ammonium Cartridge Manifold

Heating Bath, °C: 37

Mixing Coils : (2) 20 turns

*See Technicon AA II Method No. 154-71W for schematic diagram.

Single Channel Colorimeter with Voltage Stabilizer

Reversing Switch : Direct (D) Wavelength, nm: 630
Flow Cell Path Length, mm: 15 F/C ID, mm : 2
Standard Calibration : 0.6-1.0 Damp : Normal

Houston Instruments 10 in. Omniscribe Recorder

Chart Paper Units, CPU: 0 - 100
Chart Paper Speed : 1 cm/min
Voltage Setting, mv : 100 (The standard calibration on the colorimeter is adjusted to set the recorder response at 80-85 CPU for the 8.0 mgL⁻¹ standard).

Typical Standard Curve

<u>mgL⁻¹ NH₄⁺</u>	<u>peak height (CPU)</u>
.25	2.5
.50	6
1.00	11.5
2.00	22
3.00	33
5.00	54
8.00	80

Limit, Range, and Interferences

Detection Limit, mgL⁻¹ : 0.02
Working Range, mgL⁻¹ : 0.0-8.0
Interferences : No significant interferences.

Reagents

Complexing Reagent. Dissolve 33 grams of potassium sodium tartrate ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) and 24 grams of sodium citrate ($\text{HOC}(\text{COONa})\text{CH}_2\text{COONa} \cdot 2.2\text{H}_2\text{O}$) in 950 mL of deionized water. Adjust the pH to 5.0 with 2.5 mL conc. H_2SO_4 . Dilute to one liter with DI.

Alkaline Phenol. Add 35 grams of sodium hydroxide (NaOH) to 250 mL DI slowly and with stirring. Allow to cool and slowly add 85 mL of an 88% phenol solution (carbolic acid). Dilute to 500 mL with DI. Add 0.25 mL Brij-35. Filter through glass wool. Store in an amber glass bottle. Stability is three days.

Sodium Hypochlorite Solution (NaOCl). Filter and dilute 100 mL of any household bleach (5.25% available chlorine) with 200 mL deionized water. Prepare daily.

Sodium Nitroprusside. Dissolve 0.5 grams sodium nitroprusside ($\text{NaFe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$) in 900 mL DI. Dilute to one liter with DI.

Sampler Rinse Water. Add 0.5 mL Brij-35 to one liter DI.

Stock Standard, 1000 mgL^{-1} NH_4^+ . Dissolve 2.9654 grams of dried ammonium chloride (NH_4Cl) and dilute to one liter with deionized water.

Summary of Method

Technicon Auto Analyzer Colorimetric measurements using the Berthelot reaction (Bolleter et al., 1961), (O'Brien and Fiore, 1962), (Tetlow and Wilson, 1965).

Procedure

Analysis. This automated procedure for the determination of ammonia uses the Berthelot reaction. The precipitation sample containing ammonium ions is introduced into the system and mixed with the complexing agent to prevent the formation of heavy metal hydroxide precipitates. The alkaline phenol and sodium hypochlorite solutions are added and react with the ammonium ions to form a blue-colored compound. Sodium nitroprusside is added to intensify this blue color. The resulting solution is then passed through a 37°C constant temperature bath. The intensity of the blue-colored complex is determined colorimetrically at 630 nm. The concentration of this compound is proportional to the concentration of ammonium ions present in the precipitation sample. Sample concentrations are determined from a graph of NH_4^+ standards concentration versus peak height.

Shut-down. At the end of each period of analysis, flush the system for 20-30 min. with deionized water.

References

- Bolleter, W. T., C. J. Bushman, and P. N. Tidwell, 1961: Spectrophotometric determination of ammonia as indophenol. Anal. Chem. 33, 592.
- O'Brien, J. E., and J. Fiore, 1962: Ammonia determination by automatic analysis. Waste Engineering, 33, 352.
- Tetlow, J. A., and A. L. Wilson, 1965: An absorptiometric method for determining ammonia in boiler feed-water. Analyst, 89, 453.

Cd Cadmium

Instrumental Mode : Non-flame atomic absorption, carbon tube atomizer;
simultaneous background correction

Wavelength, nm : 228.8 Bandpass, nm : 1

Light Source : Cd HCL Lamp Current, ma : 3
H HCL 6

Photomultiplier Tube: R446 Photomultiplier Voltage, v: 800

.64N HNO₃⁻

.016N NHO₃ matrix

1.44N H₂SO₄, matrix

Sheath Gas : Argon Argon

Flow Rate, L min⁻¹: 5 10

Sample Volume, µL : 5 5

Time, sec. Temperature, °C

Dry-Pyrolyze: 30 400

Atomize : 3 1700

Reagents :

Stock Standard Solution;

Dissolve 1.8546 grams of Cd SO₄ in a minimal amount of 16N HNO₃ and dilute to a volume of 1 liter with deionized water. Final concentration is 1000 µg mL⁻¹ Cd.

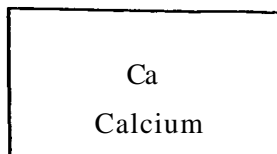
Working Standards;

Dilute stock solution to 1, .5, and .25 ng mL⁻¹ with .016N HNO₃ or .64N HNO₃/1.44N H₂SO₄ for sample soluble and acid dissolved insoluble phases, respectively.

Procedure:

Dispense 5 µL of sample into the carbon tube and initiate atomization sequence. Peak height is measured on a strip chart recorder having a full scale response time of .5 second or less. Sample concentrations are determined from a calibration curve of standard concentration versus peak heights.

	<u>.016N HNO₃ matrix</u>	<u>.64N HNO₃⁻</u> <u>1.44N H₂ SO₄ matrix</u>
Sensitivity, grams :	2 x 10 ⁻¹³	1 x 10 ⁻¹²
Detection Limit, grams:	1 x 10 ⁻¹³	5 x 10 ⁻¹³



Instrumental Mode : Flame atomic absorption

Wavelength, nm : 422.7 Bandpass, nm : 0.24

Light Source : Ca HCL Lamp Current, ma : 6

Photomultiplier Tube: R446 Photomultiplier Voltage, v: 700

Burner : Single slot Burner Height, mm : 9

Combustion Mixture : Air-Acetylene; Stoichiometric Flame

Reagents:

Stock Standard Solution;

Dissolve 2.4973 grams of CaCO_3 , in a small amount of 6M HCl and dilute to a volume of 1 liter with deionized water. Final concentration is $1000 \text{ } \mu\text{g mL}^{-1}$ Ca.

Working Standards;

Dilute stock solution to 10, 5, 1, and $.5 \text{ } \mu\text{g mL}^{-1}$ with .016N HNO_3 /1.44N H_2SO_4 for sample soluble and acid dissolved in soluble phases, respectively. Surface waters require a 1:10 dilution prior to analysis in this range of standards.

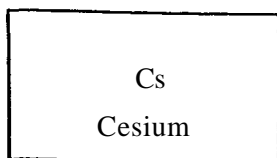
Releasing Agent Stock Solution;

Dissolve 117.28 grams of La_2O_3 in 500 mL of 6 N HCl and dilute to a volume of 1 liter with deionized water. Final concentration is $100,000 \text{ } \mu\text{g mL}^{-1}$ La. Lanthanum prevents interference from phosphates, aluminum, and silicates.

Procedure : Combine .02 mL of releasing agent to 2 mL of samples, standards, and blanks. Concentration is read directly on the instrumental digital display.

Sensitivity : 4.5×10^{-8} gram mL⁻¹

Detection Limit: 2×10^{-8} gram mL⁻¹



Instrumental Mode : Flame emission, yellow optical filter placed between flame and monochromator entrance slit

Wavelength, nm : 852.1 Bandpass, nm : .86

Light Source : None required Lamp Current, ma : n.a.

Photomultiplier Tube : R406 Photomultiplier Voltage, v: 1000

Burner : Single slot Burner Height, mm : 10

Combustion Mixture : Air-Acetylene; Stoichiometric Flame

Reagents:

Stock Standard Solution; Dissolve 1.4665 grams of CsNO₃ in deionized water to a volume of 1 liter. Final concentration is 1000 µg mL⁻¹.

Working Standards; Dilute stock solution to 10 µg mL⁻¹ with .016N HNO₃ or .64N HNO₃/1.44N H₂SO₄ for sample soluble and acid insoluble phases, respectively. Cs concentrations in natural waters are generally below the detection limit of this method, however, it is useful in determining the behavior of Cs in natural matrices by standard addition techniques.

Radiation Buffer Ionization Suppressant Stock Solution; Dissolve 190.67 grams of KCl in deionized water to a final volume of 1 liter. Final concentration is 100,000 µg mL⁻¹ K.

Procedure : Combine .02 mL of radiation buffer to 2 mL of samples, standards, and blanks. Scan 2 nm across the Cs 852.1 line at a rate of 5 nm min⁻¹ recording the resultant peak on a strip chart recorder. Sample concentrations are determined from a calibration curve of standard concentrations versus peak height.

Sensitivity : n.a.

Detection Limit: 5 x 10⁻⁹ gram mL⁻¹

Cl ⁻ Chloride

Method : Automated Colorimetric Thiocyanate

Instrumental Mode: Technicon Auto Analyzer II System

Auto Sampler III

No. of Samples/Hr: 60

Sample/Wash: 6/1

Sample Volume, mL: 1.0-1.5

GILSON 2" Pump

Pump Manifold Tubes

<u>Color</u>	<u>Flow Rate (mL/min⁻¹)</u>	<u>Application*</u>
Grn/Grn	2.00	DI to sampler wash receptacle
Gry/Gry	1.00	Sample
Orn/Wht	0.23	Air
Orn/Grn	0.10	Diluent Water
Wht/Wht	0.60	Debubbler to waste
Orn/Wht	0.23	Air
Gry/Gry	1.00	Color Reagent
Gry/Gry	1.00	From flow cell to waste (collected in a separate container)

Chloride Cartridge Manifold

Mixing Coils: 5 and 14 turns

* See Technicon AA II Method No. 99-70W for schematic diagram.

Reagents

Mercuric Thiocyanate Stock Solution. Add 4.17 grams of mercuric thiocyanate ($\text{Hg}(\text{SCN})_2$) per liter methanol (CH_3OH). Mix and filter through filter paper.

Ferric Nitrate, 20.2% Stock Solution. Place 202 grams of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in 500 mL of deionized water. Shake until the ferric nitrate is dissolved and carefully add 31.5 mL conc, nitric acid (HNO_3). Dilute to 1 liter with DI. Filter through filter paper and store in an amber reagent bottle.

Chloride Color Reagent. Mix 150 mL of stock mercuric thiocyanate and 150 mL of 20.2% ferric nitrate solution and dilute to 1 liter with DI. Add 1.0 mL Brij-35.

Diluent Water. Add 2 mL Brij-35 to 1 liter DI.

Sampler Rinse Water. Add 0.5 mL Brij-35 to 1 liter DI.

Thioacetamide, 13% Solution. Dissolve 13 grams of thioacetamide (CH_3CSNH_2) per 100 mL DI. Store in a closed glass container. Stability is one year.

Stock Standard Solution, $1000 \text{ mgL}^{-1} \text{ Cl}^-$. Dissolve 1.6485 grams of dried sodium chloride (NaCl) and dilute to 1 liter with deionized water.

Single Channel Colorimeter with Voltage Stabilizer

Reversing Switch : Direct (D) Wavelength, nm: 480
Flow Cell Path Length, mm: 15 F/C ID, mm : 2
Standard Calibration : 0.5-0.8 Damp : 2

Houston Instruments 10 in. Omniscribe Recorder

Chart Paper Units, CPU: 0 - 100
Chart Paper Speed : 1 cm/min
Voltage Setting, mv : 10 (The standard calibration on the colorimeter is adjusted to set the recorder response at 85 - 90 CPU for the 5.0 mgL⁻¹ standard.)

Typical Standard Curve

<u>mgL⁻¹ Cl⁻</u>	<u>peak height (CPU)</u>
.10	1.5
.50	7.5
1.00	15
2.50	40
5.00	80

Limit, Range, and Interferences

Detection Limit, mgL⁻¹ : 0.05
Working Range, mgL⁻¹ : 0.0 - 5.0
Interferences : No significant interferences.

Summary of Method

Technicon Auto Analyzer Colorimetric measurements of liberated thiocyanate ion from mercuric thiocyanate in the presence of ferric ion (O'Brien, 1962).

Procedure

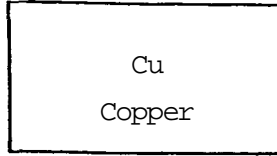
Analysis. The precipitation sample containing chloride ions is introduced into the system and diluted with diluent water. The color reagent is added and soluble, but unionized mercuric chloride (HgCl_2) is formed, liberating mercuric thiocyanate. In the presence of ferric ions from the color reagent, the liberated thiocyanate forms a colored ferric thiocyanate complex. The intensity of the ferric thiocyanate complex is determined colorimetrically at 460 nm. The concentration of the complex is equivalent to the original chloride ions. Sample concentrations are determined from a graph of the Cl^- standards concentrations vs. peak height.

Collection of Chloride Waste. Waste from the chloride channel should be collected in a container of known volume. When the container is full, remove it from the system and place it in a hood. Add 20 mL of 13% thioacetamide per liter of chloride waste. Mix thoroughly and cap the container. A precipitate of mercuric sulfide will form. After 24 hours, filter (in a hood) the solution through a Buchner filter. Discard the clear filtrate. Store the residue of mercuric salt in a tightly stoppered glass container.

Shut-down. At the end of each period of analysis, flush the system for 20-30 min. with deionized water.

References

O'Brien, J. E., December 1962: Automatic analysis of chloride in sewage. Waste Engineer, 33, 670-672.



Instrumental Mode : Non-flame atomic absorption, Tantalum ribbon atomizer

Wavelength, nm : 324.7 Bandpass, nm : .5

Light Source : Cu HCL Lamp Current, ma : 5

Photomultiplier Tube : R446 Photomultiplier Voltage, v: 460

.64N HNO₃⁻

.016N NH₃ matrix

1.44N H₂SO₄ matrix

Sheath Gas : Argon Argon

Flow Rate, L min⁻¹ : 5 5

Sample Volume, μL : 50 50

Time, sec. Temperature, °C

Dry-Pyrolyze: 60 350

Atomize : 5 1700

Reagents :

Stock Standard Solution:

Dissolve 1 gram of Cu metal in a slight excess of 10M HNO₃ and dilute to 1 liter with deionized water. Final concentration is 1000 μg mL⁻¹ Cu.

Working Standards; Dilute stock solution to 10, 5, and 1 ng mL⁻¹ with .016N HNO₃ or .64N HNO₃/1.44N H₂SO₄ for sample soluble and acid dissolved insoluble phases, respectively.

Extraction Reagents; Dithizone in carbon tetrachloride 250 mgL⁻¹.
16 M HNO₃

Procedure: Cu is extracted into Dithizone-Carbon Tetrachloride from a HNO₃ solution of pH 1-2. pH adjustments are made by addition of .01 mL hHNO₃ per mL of .016N HNO₃ and by a 1:10 dilution of .64N HNO₃/1.44N H₂SO₄ samples.

After extraction for two minutes with .1 mL of D₂/CCl₄, 50 μL of the organic layer is dispensed into tantalum receptacle and atomization sequence initiated. Resultant peak is recorded on a strip chart recorder having a full scale response of .5 second or less.

.64N HNO₃⁻

0.16N HNO₃ matrix

1.44N H₂SO₄ matrix

Sensitivity, grams : 1 x 10⁻¹¹ 1 x 10⁻¹¹

Detection Limit, grams: 1 x 10⁻¹¹ 1 x 10⁻¹¹

In Indium

Instrumental Mode : Non-flame atomic absorption, modified tantalum ribbon atomizer

Wavelength, nm : 303.9 Bandpass, nm : 1

Light Source : In HCL Lamp Current, ma : 10

Photomultiplier Tube: R446 Photomultiplier Voltage, v: 460

.64N HNO₃⁻

.016N HNO₃ matrix

1.44N H₂SO₄ matrix

Sheath Gas : Argon Argon

Fow Rate, L min⁻¹ : 5 10

Sample Volume, μL: 50 50

Time, sec. Temperature, C

Dry-Pyrolyze: 60 350

Atomize : 3 2700

Reagents :

Stock Standard Solution;

Dissolve 1 gram of In metal in a slight excess of HCL and dilute to 1 liter with deionized water. Final concentration is 1000 ug mL⁻¹ In.

Working Standards; Dilute stock solution to .5, .25, .1, and .05 ng mL⁻¹ with .016N HNO₃ or .64N HNO₃/1.44N H₂SO₄ for sample soluble and acid dissolved particulate phases, respectively.

Extraction Reagents; Acetylacetone - Chloroform, 1:1
Sodium Citrate - Deionized Water, 1:10
1.5N NH₃OH
Acetate Buffer, dissolve 164 grams NaC₂H₃O₂ and 150 mL glacial acetic acid in deionized water to a volume of 1 liter

- Procedure:
1. Tantalum ribbon is narrowed in the center to achieve atomization temperature of 2700°C.
 2. Add .25 mL of NH₄OH per mL of acid dissolved particulates.
 3. Add .25 mL of acetate buffer and .1 mL of citrate to sample filtrate and acid dissolved particulate samples respectively.
 4. Extract for two minutes with .25 mL of HAA/CMCL₃ per 4 mL of sample and dispense 50 µL of the organic layer into the tantalum receptacle and initiate atomization sequence.
 5. Record peak on a strip chart recorder having a full scale response time of .5 second or less.

.64N HNO₃⁻

.016N HNO₃ matrix

1.44N H₂SO₄, matrix

Sensitivity, grams

4 x 10⁻¹¹

4 x 10⁻¹¹

Detection Limit, grams:

1 x 10⁻¹¹

1 x 10⁻¹¹

Fe Iron

Instrumental Mode : Flame atomic absorption

Wavelength, nm : 248.3 Bandpass, nm : .24

Light Source : Fe HCL Lamp Current, ma : 8

Photomultiplier Tube: R446 Photomultiplier Voltage, v: 700

Burner : Single slot Burner Height, mm : 8

Combustion Mixture : Air-Acetylene; Lean Flame

Reagents:

Stock Standard Solution;

Dissolve 4.840 grams of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in deionized water to a volume of 1 liter. Final concentration is $1000 \mu\text{g mL}^{-1}$ Fe.

Working Standards;

Dilute stock solution to 2, 1, .5, .2, and .1 $\mu\text{g mL}^{-1}$ with .016N HNO_3 or .64N $\text{HNO}_3/1.44 \text{H}_2\text{SO}_4$ for sample soluble and acid dissolved insoluble phases, respectively.

Procedure : Concentration is read directly on the instrumental digital display. Iron in precipitation is virtually all in the dissolved particulate phase at pH values above 4.5. Soluble iron exists at concentrations at or below the detection limit of this method.

Sensitivity : 5×10^{-8} gram mL⁻¹

Detection Limit: 5×10^{-9} gram mL⁻¹

Pb Lead

Instrumental Mode : Non-flame atomic absorption, carbon tube atomizer,
simultaneous background correction

Wavelength, nm : 217.0 Bandpass, nm : 1

Light Source : Pb HCL Lamp Current, ma : 7
H HCL 7

Photomultiplier Tube: R446 Photomultiplier Voltage, v: 800

.64N HNO₃⁻

.016N HNO₃ matrix

1.44N H₂SO₄ matrix

Sheath Gas : Argon Argon

Flow Rate, L min⁻¹: 5 10

Sample Volume, µL: 10 10

Time, sec. Temperature, °C

Dry-Pyrolyze; 90 450

Atomize : 5 1300

Reagents :

Stock Standard Solution;

Dissolve 1.598 grams of Pb (NO₃)₂
in deionized water to a volume of
1 liter. Final concentration is
1000 µg mL⁻¹ Pb.

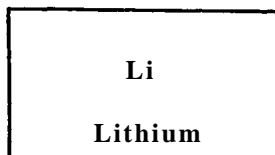
Working Standards:

Dilute stock solution to 50, 25, 10, 5, and 1 ng mL⁻¹ with .016N HNO₃ or .64N HNO₃/1.44 H₂SO₄ for sample soluble and acid dissolved insoluble phases, respectively.

Procedure:

Dispense 10 µL of sample into the carbon tube and initiate atomization sequence. Peak height is measured on a strip chart recording having a full scale response time of .5 second or less. Sample concentrations are determined from a calibration curve of standard concentrations versus peak heights.

	<u>.016N HNO₃ matrix</u>	<u>.64N HNO₃⁻</u> <u>1.44N H₂SO₄ matrix</u>
Sensitivity, grams :	2 x 10 ⁻¹¹	4 x 10 ⁻¹¹
Detection Limit, grams:	9 x 10 ⁻¹²	1.5 x 10 ⁻¹¹



Instrumental Mode : Flame emission; yellow optical filter placed between flame and monochromator entrance slit

Wavelength, nm : 670.8 Bandpass, nm : .24

Light Source : None required Lamp Current, ma : n.a.

Photomultiplier Tube: R446 Photomultiplier Voltage, v: 1000

Burner : Single slot Burner Height, mm : 10

Combustion Mixture : Air-Acetylene; Stoichiometric Flame

Reagents:

Stock Standard Solution;

Dissolve 5.3240 grams Li_2CO_3 in a minimum amount of HCl and dilute to a volume of 1 liter with deionized water. Final concentration is 1000 pg mL^{-1} .

Working Standards;

Dilute stock solutions to 1, .5, and $.1 \text{ ng mL}^{-1}$ with .016N HNO_3 or .64N HNO_3 / 1.44N NH_2SO_4 for sample soluble and acid dissolved insoluble phases, respectively. Surface waters require standard concentrations of 10, 5, and 1 ng mL^{-1} .

Radiation Buffer - Ionization Suppressant Stock Solution

Dissolve 254.20 grams of NaCl in deionized water to a volume of 1 liter. Final concentration is $100,000 \text{ } \mu\text{g mL}^{-1} \text{ Na}$.

Dissolve 25.42 grams of NaCl in deionized water to a volume of 1 liter. Final concentration is $10,000 \text{ } \mu\text{g mL}^{-1} \text{ Na}$.

Procedure : Combine .02 mL of ionization suppressant to 2 mL of samples, standards, and blanks. The higher Na concentration is for use with surface samples where more Na is needed to equalize the ionization suppressing effects of the endogenous alkali metals.

Scan 2 nm across the 670.8 Li line at a rate of 5 nm min⁻¹ recording the resultant peak on a strip chart recorder. Sample concentrations are determined from a calibration curve of standard concentration versus peak height (see Figure 4).

Sensitivity : n.a.

Detection Limit: 2×10^{-11} gram mL⁻¹

Mg Magnesium

Instrumental Mode : Flame atomic absorption

Wavelength, nm : 285.2 Bandpass, nm : 0.24

Light Source : Mg HCl Lamp Current, ma : 3

Photomultiplier Tube: R446 or R372 Photomultiplier Voltage, v: 620

Burner : Single slot Burner Height, mm : 9

Combustion Mixture : Air-Acetylene; Stoichiometric Flame

Reagents:

Stock Standard Solution;

Dissolve 1 gram of Mg metal in a slight excess of 12M HCl and dilute to a volume of 1 liter with deionized water. Final concentration is 1000 $\mu\text{g mL}^{-1}$ Mg.

Working Standards;

Dilute stock solution to 1.0, .5, and .1 $\mu\text{g mL}^{-1}$ with .016N HNO_3 or .64N $\text{HNO}_3/1.44\text{N H}_2\text{SO}_4$ for sample soluble and acid dissolved insoluble phases, respectively. Surface waters require a 1:10 dilution prior to analysis in this range of standards.

Releasing Agent Stock Solution;

Dissolve 117.28 grams of La_2O_3 in 500 mL of 6N HCl and dilute to a final volume of 1 liter with deionized water. Final concentration is 100,000 $\mu\text{g mL}^{-1}$ La. Lanthanum prevents interference from phosphates, aluminum and silicates.

Procedure : Combine .02 mL of releasing agent to 2 mL of samples, standards, and blanks. Concentration is read directly on the instrumental digital display.

Sensitivity : 2×10^{-9} gram mL⁻¹

Detection Limit: 1×10^{-9} gram mL⁻¹

Mn Manganese

Instrumental Mode : Flame atomic absorption; simultaneous background correction

Wavelength, nm : 279.5 Bandpass, nm : 0.86

Light Source : Mn HCl Lamp Current, ma : 5
H HCl 25

Photomultiplier Tube : R446 Photomultiplier Voltage, v: 800

Burner : Single slot Burner Height, mm : 9

Combustion Mixture : Air-Acetylene; Stoichiometric Flame

Reagents:

Stock Standard Solution;

Dissolve 1 gram of Mn metal in a minimum amount of HCl and dilute to 1 liter with deionized water. Final concentration is $1000 \text{ } \mu\text{g mL}^{-1}$ Mn.

Working Standards;

Dilute stock solution to 50, 20, 10, and $5 \text{ } \mu\text{g mL}^{-1}$ iwth .016N HNO₃ or .64N HNO₃/1.44N H₂SO₄ for sample soluble and acid dissolved insoluble phases, respectively.

Procedure	:	Ten second integrated concentrations are read directly on the instrumental digital display.
Sensitivity	:	2×10^{-8} gram mL ⁻¹
Detection Limit:		2×10^{-9} gram mL ⁻¹

Mn Manganese

Instrumental Mode : Non-flame atomic absorption, carbon tube atomizer;
simultaneous background correction

Wavelength, nm : 279.5 Bandpass, nm : .3

Light Source : Mn HCl Lamp Current, ma : 3
H HCl 28

Photomultiplier Tube : R446 Photomultiplier Voltage, v: 1000

	<u>.016N HNO₃ matrix</u>	<u>.64N HNO₃⁻ 1.44N H₂SO₄ matrix</u>
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Sheath Gas :	Argon	Argon
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Flow Rate, L min ⁻¹ :	5	10
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Sample Volume, μL :	10	10
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	Time, sec.	Temperature, °C
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Dry-Pyrolyze:	85	450
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Atomize :	5	1600
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Reagents:

Stock Standard Solution;

Dissolve 1 gram of Mn metal in a minimum amount of HCl and dilute to 1 liter with deionized water. Final concentration is 1000 μg mL⁻¹ Mn.

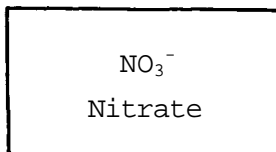
Working Standards;

Dilute stock solution to 20, 10, 5, and 1 ng mL⁻¹ with .016N HNO₃ or .64N HNO₃. 1.44N H₂SO₄ for sample soluble and acid dissolved insoluble phases, respectively.

Procedure:

Dispense 10 µL of sample into the carbon tube and initiate atomization sequence. Peak height is measured on a strip chart recorder having a full scale response time of .5 second or less. Sample concentrations are determined from a calibration curve of standard concentrations versus peak heights.

	<u>.016N HNO₃ matrix</u>	<u>.64N HNO₃⁻</u> <u>1.44N H₂SO₄ matrix</u>
Sensitivity, grams :	4 x 10 ⁻¹³	1 x 10 ⁻¹²
Detection Limit, grams:	1 x 10 ⁻¹³	5 x 10 ⁻¹³



Method : Automated Colorimetric Cadmium Reduction

Instrumental Mode: Technicon Auto Analyzer II System

Auto Sampler III

No. of Samples/Hr: 40

Sample/Wash: 6/1

Sample Volume, mL: 0.5-1.0

GILSON 2" Pump

Pump Manifold Tubes

<u>Color</u>	<u>Flow Rate (mL/min⁻¹)</u>	<u>Application*</u>
Grn/Grn	2.00	DI to sampler wash receptacle
Orn/Wht	0.23	Air
Yel/Yel	1.20	Ammonium Chloride Reagent
Blk/Blk	0.32	Sample
Orn/Wht	0.23	Air
Wht/Wht	0.60	Debubbler to waste
Blk/Blk	0.32	Color Reagent
Gry/Gry	1.00	From flow cell to waste

Nitrate Cartridge Manifold

Column Type : Copper-Cadmium Reduction

Column Size : 14 in. long x 2 mm ID, U-shaped glass or
.081 ID (PUR/PUR) pump tubing

Mixing Coils: 5 and 20 turns

*See Technicon AA II Method No. 100/70W for schematic diagram.

Single Channel Colorimeter with Voltage Stabilizer

Reversing Switch : Direct (D) Wavelength, nm: 520
Flow Cell Path Length, mm: 15 F/C ID, mm : 2
Standard Calibration : 0.0 Damp : Normal

Cole Parmer 10 in. Recorder

Chart Paper Units, CPU : 0 - 100
Chart Paper Speed : 1 cm/min
Full Scale Response, mv: 100 (attenuation is adjusted to set the recorder response at 85-90 CPU for the 10 mgL⁻¹ standard).

Typical Standard Curve

<u>mgL⁻¹ NO₃⁻</u>	<u>peak height (CPU)</u>
.5	4
2.0	18
4.0	36
7.0	65
10.0	88

Limit, Range, and Interferences

Detection Limit, mgL⁻¹ : 0.02
Working Range, mgL⁻¹ : 0.0-10.0
Interferences : high concentrations of metal ions,
high concentration of Cl⁻,
air bubbles in reduction column,
exhaustion of the reduction column

Reagents

Alkaline Water, pH 8.5. Add 1.8 mL of ammonium hydroxide (NH_4OH) per liter of deionized water.

Ammonium Chloride Reagent, pH 8.5. Dissolve 10 grams of ammonium chloride (NH_4Cl) in 1 liter Alkaline Water. Add 0.25 mL Brij-35.

Color Reagent. To 400 mL DI add 5 grams of sulfanilamide ($\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$), 50 mL phosphoric acid (H_3PO_4), and 0.25 grams of N-1-Naphthylethylenediamine dihydrochloride ($\text{C}_{12}\text{H}_{14}\text{N}_2 \cdot 2\text{HCl}$). Dilute to 500 mL with DI. Add 0.25 mL Brij-35. Store in an amber bottle. Refrigerate. Stability is one month.

Copper Sulfate, 2% solution. Dissolve 2 grams of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) per 100 mL DI.

Diluted CuSO_4 Solution. Dilute 1 part 2% CuSO_4 with 4 parts DI.

Hydrochloric Acid, 1N. Add 83 mL concentrated hydrochloric acid (HCl) to 900 mL DI. Dilute to 1 liter with DI.

Cadmium Filings, 99.99% pure. Wash cadmium filings with 1N HCl and then with multiple rinses of DI. Allow metal to air dry and store in a closed container.

Stock Standard Solution, 1000 mgL^{-1} NO_3^- . Dissolve 1.6306 grams of potassium nitrate (KNO_3) per liter of deionized water.

Preparation of Column

Fill the reductor column with deionized water. Add the cadmium filings. Stopper each end of the U-tube with glass wool. Attach the column to a PUR/PUR pump tube and pump 1N HCl for 2 min. Follow with a 2 min. DI rinse. Pump the 1:5 CuSO_4 solution through one side of the U-tube for 2.5 min. and rinse with DI for 2.5 min. Turn the column and pump CuSO_4 through the other side for 2.5 min. Follow with a DI rinse for 2.5 min. If there are any trapped air bubbles in the column, repeat the column preparation procedure. All pump tubes should be filled with reagents before putting the column in the analytical stream. For initial activation of the column, pump a 100 mgL^{-1} NO_3^- standard for 5 min. then rinse with DI for 30 min. A column thus prepared and activated should last for 200 - 300 samples.

Summary of Method

Technicon Auto Analyzer Colorimetric measurements of nitrate after reduction of nitrate and complexation with sulfanilamide (Armstrong et al., 1967).

Procedure

Analysis. The precipitation sample containing nitrate ions is introduced into the system, mixed with ammonium chloride, and channeled through a copper-cadmium reduction column which reduces the nitrate ions to nitrite ions. The nitrite ions are mixed with the color reagent forming a reddish-purple dye which passes through the colorimeter. The intensity of this dye, measured at 520 nm, is proportional to the nitrite ion concentration. Sample concentrations are determined from a graph of the NO_3^- standards concentration vs. peak height.

Shut-down. At the end of each period of analysis, remove the reduction column from the system and pump deionized water for 20-30 min. to remove any contaminants in the system.

References

Armstrong, F. A., C. R. Stearns, and J. D. Strickland, 1967: The Measurements of upwelling and subsequent biological processes by means of the Technicon Auto Analyzer and Associate Equipment. Deep Sea Research, 14, 381-389.

Single Channel Colorimeter with Voltage Stabilizer

Reversing Switch : Direct (D) Wavelength, nm: 880
Flow Cell Path Length, mm: 50 F/C ID, mm : 1.5
Standard Calibration : 0.0 Damp : Normal

Cole Parmer 10 in. Recorder

Chart Paper Units, CPU : 0 - 100
Chart Paper Speed : 1 cm/min
Full Scale Response, mv: 10 (the attenuation is adjusted to set the recorder response at 55-60 CPU for the 100 μL^{-1} standard).

Typical Standard Curve

<u>$\mu\text{gL}^{-1} \text{PO}_4^-$</u>	<u>peak height (CPU)</u>
10	5
25	13
50	29
100	60

Limit, Range, and Interferences

Detection Limit, μgL^{-1} : 3.0
Working Range, μgL^{-1} : 0.0 - 100
Interferences : No significant interferences.

Reagents

Sulfuric Acid, 4.9 N Stock Solution. Add 136 mL of concentrated sulfuric acid (H_2SO_4) to 800 mL DI. Cool and then dilute to one liter with DI. Store in a LPE bottle.

Ammonium Molybdate Stock Solution. Dissolve 40 grams of ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) in 800 mL DI. Dilute to 1 liter with DI. Store in a LPE bottle. Refrigerate.

Ascorbic Acid Stock Solution. Dissolve 18 grams of U.S.P. quality ascorbic acid ($\text{C}_6\text{H}_7\text{O}_6$,) in 800 mL of DI. Dilute to 1 liter with DI. Store in a LPE bottle. Refrigerate. Stability is 2 months.

Antimony Potassium Tartrate Stock Solution. Dissolve 3 grams of antimony potassium tartrate ($\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2\text{H}_2\text{O}$) in 800 mL DI. Dilute to 1 liter with DI. Store in a LPE bottle. Refrigerate.

Combined Working Reagent. Allow the above stock solutions to reach room temperature before combining in the following order:

- 50 mL sulfuric acid
- 15 mL ammonium molybdate
- 30 mL ascorbic acid
- 5 mL antimony potassium tartrate

This combined reagent is stable for 8 hours. We found 100 mL of working reagent sufficient for approximately 7 hours of operation.

Sampler Rinse Water. Add 0.5 mL LEVOR V to 1 liter DI.

Stock Standard, $100 \text{ mgL}^{-1} \text{PO}_4^{=}$. Dissolve 143.47 mg potassium phosphate (KH_2PO_4) in DI. Dilute to 1 liter with deionized water. Add 1 mL chloroform (CHCl_3).

Summary of Method

Technicon Auto Analyzer Colorimetric measurements of molybdenum blue complex after reduction with ascorbic acid (Murphy and Riley, 1962).

Procedure

Analysis. The precipitation sample containing phosphate ions is introduced into the system and mixed with an acidified solution of ammonium molybdate containing ascorbic acid and antimony. A blue-colored phosphomolybdenum complex is formed. The blue color is enhanced by the antimony. The solution is pumped through a constant temperature bath and the intensity of the blue-colored compound is then determined colorimetrically at 880 nm. The concentration of phosphate ions present in the precipitation sample. Sample concentrations are determined from a graph of $\text{PO}_4^{=}$ standards concentration vs. peak height.

Shut-down. At the end of each period of analysis, flush the system for 20-30 min. with deionized water.

References

Murphy, J. and J. Riley, 1962: A modified single solution for the determination of total phosphorus in water. J. AWWA, 58, no. 10, 1363.

K Potassium

Instrumental Mode : Flame atomic absorption

Wavelength, nm : 766.5 Bandpass, nm : 5 (Interference filter)

Light Source : K HCl Lamp Current, ma : 8

Photomultiplier Tube: R406 Photomultiplier Voltage, v: 620

Burner : Single slot Burner Height, mm : 6

Combustion Mixture : Air-Acetylene; Stoichiometric Flame

Reagents:

Stock Standard Solution; Dissolve 1.9067 grams of KCl in deionized water to a volume of 1 liter. Final concentration is $1000 \mu\text{g mL}^{-1}$.

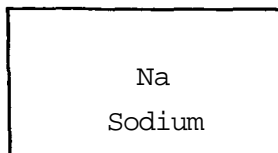
Working Standards; Dilute stock solution to 4, 2, 1, and $.5 \mu\text{g mL}^{-1}$ with $.016\text{N HNO}_3$ or $.64\text{N HNO}_3/1.44\text{N H}_2\text{SO}_4$ for sample soluble and acid dissolved insoluble phases, respectively.

Ionization Suppressant Stock Solution; Dissolve 12.67 grams of CsCl in deionized water to a volume of 1 liter. Final concentration is $10,000 \mu\text{g mL}^{-1}$ Na.

Procedure : Combine .02 mL of ionization suppressant to 2 mL of samples, standards, and blanks. Concentration is read directly on the instrumental digital display.

Sensitivity : 5×10^{-8} gram mL⁻¹

Detection Limit: 2×10^{-8} gram mL⁻¹



Instrumental Mode : Flame atomic absorption

Wavelength, nm : 589.0 Bandpass, nm : .24
330.2

Light Source : Na HCl Lamp Current, ma : 8

Photomultiplier Tube: R446 Photomultiplier Voltage, v: 700

Burner : Single slot Burner Height, mm : 10

Combustion Mixture : Air-Acetylene; Stoichiometric Flame

Reagents:

Stock Standard Solution;

Dissolve 2.5420 grams of NaCl in deionized water to a volume of 1 liter. Final concentration is 1000 yg mL^{-1} Na.

Working Standards;

Dilute stock solution to 2, 1, .5, and $.1 \text{ yg mL}^{-1}$ with .016N HNO₃ or .64N HNO₃/1.44 H₂SO₄ for sample soluble and acid dissolved insoluble phases, respectively. Surface waters require standard concentrations of 20, 10, 5, and $1 \text{ } \mu\text{g mL}^{-1}$.

Ionization Suppressant Stock Solutions;

Dissolve 190.67 grams of KCl in deionized water to a volume of 1 liter. Final concentration is $100,000 \text{ yg mL}^{-1}$ K.

Dissolve 12.67 grams of CsCl in deionized water to a volume of 1 liter. Final concentration is $10,000 \text{ yg mL}^{-1}$ Cs.

Procedure : Combine .02 mL of ionization suppressant to 2 mL of samples, standards, and blanks. Rainwater requires the use of $10,000 \mu\text{g mL}^{-1}$ Cs stock solution to keep the amount of Na contributed by this reagent at an insignificant level. The NaCl ionization suppressant and the less sensitive 330.2 resonance line are used for surface water samples. Concentration is read directly on the instrumental digital display.

Sensitivity : 4×10^{-9} gram mL^{-1} at 589.0 Na line
 2×10^{-6} gram mL^{-1} at 330.2 Na line

Detection Limit: 1×10^{-9} gram mL^{-1} at 589.0 Na line
 1×10^{-6} gram mL^{-1} at 330.2 Na line

Sr Strontium

Instrumental Mode : Flame emission; ultraviolet optical filter placed
between flame and monochromator entrance slit

Wavelength, nm : 460.7 Bandpass, nm : 0.24

Light Source : none required Lamp Current, ma : n.a.

Photomultiplier Tube: R446 Photomultiplier Voltage, v: 1000

Burner : Single slot Burner Height, mm : 10

Combustion Mixture : Air-Acetylene; Lean Flame

Reagents:

Stock Standard Solution; Dissolve 1.685 grams of SrCO_3 in a slight excess of 6M HCl and dilute to 1 liter with deionized water. Final concentration is 1000 ug mL^{-1} Sr.

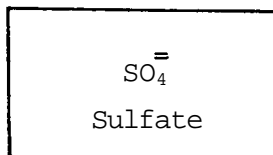
Working Standards; Dilute stock solution to .2, .1, .05, and $.01 \text{ ug mL}^{-1}$ with .016N HNO_3 or .64N $\text{HNO}_3/1.44 \text{ H}_2\text{SO}_4$ for sample soluble and acid dissolved insoluble phases, respectively.

Releasing Agent Stock Solution; Dissolve 117.28 grams of La_2O_3 in 500 mL of 6N HCl and dilute to a volume of 1 liter with deionized water. Final concentration is $100,000 \text{ ug mL}^{-1}$ La. Lanthanum prevents interference from phosphates, aluminum, and silicates.

Procedure : Combine .02 mL of releasing agent to 2 mL of samples, standards and blanks. Scan 2 nm across the 460.7 Sr line at a rate of 5 nm min⁻¹ recording the resultant peak on a strip chart recorder. Sample concentrations are determined from a calibration curve of standard concentrations versus peak height.

Sensitivity : n.a.

Detection Limit: 2 x 10⁻⁹ gram mL⁻¹



Method : Automated Colorimetric Barium - Methylthymol Blue Complex

Instrumental Mode: Technicon Auto Analyzer II System

Auto Sampler II

No. of Samples/Hr: 30

Sample/Wash: 6/1

Sample Volume, mL: 3.5-4.0

GILSON 2" Pump

Pump Manifold Tubes

<u>Color</u>	<u>Flow Rate (mL/min⁻¹)</u>	<u>Application*</u>
Pur/Pur	2.90	DI to sampler wash receptacle
Blu/Blu	1.60	Sample
Wht/Wht	0.60	Debubbler to waste
Orn/Wht	0.23	Air
Wht/Wht	0.60	Methylthymol Blue Reagent
Orn/Orn	0.42	Sodium Hydroxide
Yel/Blu	1.40	From flow cell to waste

Sulfate Cartridge Manifold

Column Type : Ion Exchange Resin

Column Size : .09 cm ID x 10 cm long, U-shpaed glass or a .09 ID (PUR/BLK) pump tubing.

Mixing Coils: 22, 20, and 7 turns

* See Technicon AA II Method No. 226-72W for schematic diagram.

Single Channel Colorimeter with Voltage Stabilizer

Reversing Switch : Inverse (I) Wavelength, nm: 460
Flow Cell Path Length, mm: 15 F/C ID, mm : 2
Standard Calibration : 0.0 Damp : 2

Cole Parmer 10 in. Recorder

Chart Paper Units, CPU : 0 - 100
Chart Paper Speed : 30 cm/hr
Full Scale Response, mv: 10 (The attenuation is adjusted to set the recorder response at 95-100 CPU for the 11 mgL⁻¹ standard.)

Typical Standard Curve

<u>mgL⁻¹SO₄⁼</u>	<u>peak height (CPU)</u>
0.40	2.5
1.00	6
2.50	16
5.00	35
7.00	53
9.00	72
11.00	95

Limit, Range, and Interferences

Detection Limit, mgL⁻¹: 0.10
Working Range, mgL⁻¹ : 0.0-11.0
Interferences : Anions such as PO₄⁼, and SO₃⁼ could result in a positive error. Cations such as calcium, aluminum, and iron are removed by the ion exchange column.

Reagents

Barium Chloride Stock Solution. Dissolve 1.526 grams of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in DI. Dilute to 1 liter with deionized water. Store in a brown polyethylene bottle.

Sodium Hydroxide. Dissolve 7.2 grams of sodium hydroxide (NaOH) in 900 mL DI. Dilute to 1 liter with DI.

Hydrochloric Acid, 1 N. Add 83 mL conc, hydrochloric acid (HCl) to 900 mL DI. Dilute with DI to 1 liter.

Methylthymol Blue Reagent Solution. Add 25 mL BaCl_2 Stock Solution and 4 mL of 1 N HCl to 0.1182 grams of methylthymol blue (3'3" - Bis-N,N-bis (carboxymethyl) - amino methylthymolsul - fonephthalein pentasodium salt). Mix and dilute to 500 mL with 95% ethanol. Prepare daily.

Buffer pH 10.1. Add 6.75 grams of ammonium chloride (NH_4Cl) and 57 mL conc, ammonium hydroxide (NH_4OH) to 900 mL DI. Dilute to 1 liter with DI.

Buffered EDTA. Add 40 grams of tetrasodium EDTA to 1 liter of pH 10.1 Buffer. Store in a brown polyethylene bottle.

Ion Exchange Resin. Bio-Rex (70, 20-50 mesh, sodium form).

Stock Standard Solution, 1000 $\text{mgL}^{-1}\text{SO}_4^-$. Dissolve 1.4789 grams of sodium sulfate (Na_2SO_4) in 900 mL of deionized water. Dilute to 1 liter with DI.

Preparation of Column

Soak the ion exchange resin overnight in deionized water. Stir and decant the finer acrticles. Store covered with DI. Draw the resin into the column. Place glass wool at one of the column to prevent the resin from escaping into the sytem. If air bubbles are trapped in the ion exchange column, prepare the column over again. Replace daily.

Summary of Method

Technicon Auto Analyzer Colorimetric measurements of barium-methylthymol blue complex (Lazrus et al., 1966).

Procedure

Analysis. The precipitation sample containing sulfate ions is introduced into the system, channeled through the ion exchange column for removal of interfering cations, and then reacted with barium chloride at pH 2.5-3.0 to form barium sulfate. Sodium hydroxide is added to increase the pH to 12.5-13. The excess barium ions react with an equivalent concentration of methylthymol blue to form a blue-colored chelate. The intensity of the uncomplexed MTB is determined colorimetrically at 460 nm. The concentration of uncomplexed MTB ions is equivalent to the initial sulfate ion concentration. Sample concentrations are determined from a graph of the SOT standards vs. peak height.

Shut-down. At the end of each period of analysis, the system should be washed with the Buffered EDTA solution. Place the MTB and NaOH reagent feed lines in the EDTA solution for 10 min. Follow with a 15 min. deionized water rinse before shutting down.

References

Lazrus, A. L., K. C. Hill, and J. P. Lodge, 1965: A new colorimetric microdetermination of sulfate ion. Automation in Analytical Chemistry, Technicon Symposia, Mediad, 1966, 291-293.

Zn Zinc

Instrumental Mode : Flame atomic absorption; simultaneous background correction

Wavelength, nm : 213.9 Bandpass, nm : ,86

Light Source : Zn HCl Lamp Current, ma : 10
H HCl 8

Photomultiplier Tube: R446 Photomultiplier Voltage, v: 700

Burner : Single slot Burner Height, mm : 6

Combustion Mixture : Air-Acetylene; Rich Flame

Reagents:

Stock Standard Solution; Dissolve 1 gram of Zn metal in a minimum amount of 12M HCl and dilute to 1 liter with deionized water. Final concentration is $1000 \mu\text{g mL}^{-1}$.

Working Standards; Dilute stock solution to .050, .025, and $.010 \mu\text{g mL}^{-1}$ with .016N HNO₃ or .64N HNO₃/1.44N H₂SO₄ for sample soluble and acid dissolved insoluble phases, respectively.

Procedure : Background absorption occurs at the 213.9 region when determining zinc in the acid dissolved particulate phase necessitating the use of the hydrogen continuum lamp to correct for this absorption. Concentration is read directly on the instrumental digital display.

Sensitivity : 3×10^{-8} gram mL⁻¹

Detection Limit: 5×10^{-9} gram mL⁻¹

6. EQUIPMENT LIST

1. Metrohm Model 103 pH meter with microcombination electrode.
2. Yellow Springs Instrument Company manually balanced AC bridge with glass microelectrode; cell constant = 1.
3. Technicon AutoAnalyzer (2 units).
4. Instrumentation Laboratory Models 353 and 151 Atomic Absorption Spectrophotometers.
5. Varian Techtron Model 63 Carbon Rod Atomizer.
6. Instrumentation Laboratories Flameless Atomizer 455.
7. Sartorius Model 2474 microbalance.
8. Ohaus Model 1119-D solution balance.
9. Milipore glass filtration system.

References to specific brand names, products, or manufacturers do not constitute endorsement by the Illinois State Water Survey or the U.S. Department of Energy.

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APPENDIX

LIST OF ABBREVIATIONS

ACS	American Chemical Society
D.L.	Detection limit, concentration that gives twice the standard deviation of the baseline noise.
Dz	Dithizone (Diphenylthiocarbazone)
HAA	Acetylacetone (2, 4, Pentanedione), organic solvent and chelating agent
HCL	Hollow cathode lamp
IL	Instrumentation Laboratory, Inc., Wilmington, MA.
LPE	Linear polyethylene
ma	Milliampere
nm	Nanometer (10^{-9} meter)
Sensitivity	Amount of analyte necessary to give an absorption signal of 1% (.0044 absorbance)
VT	Varian Techtron, Inc., Palo Alto, CA.
n.a.	Not applicable.
mL	Milliliter (.001 L)
μ L	Microliter (10^{-6} L)
DI	Deionized water