

NADP QUALITY ASSURANCE REPORT  
CENTRAL ANALYTICAL LABORATORY  
1979

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

A research program sponsored by the  
Association of State Agricultural Experiment Stations  
of the North Central Region • NC-141



The National Atmospheric Deposition Program (NADP) was organized by the North Central Region of the State Agricultural Experiment Stations to address the problem of atmospheric deposition and its effects on agriculture, forest, rangelands, and fresh water streams and lakes. It is necessary to determine both the composition and amount of atmospheric deposition and its distribution on a national scale in order to assess the magnitude of the effects, both beneficial and deleterious. It is also necessary that these measurements be carried out over an extended period of time in order to determine the long-term trends. For this purpose, the National Atmospheric Deposition Program has established a nationally distributed regional atmospheric deposition monitoring network. In addition to the State Agricultural Experiment Stations and the Department of Agriculture, programs of the NADP are now supported by the Environmental Protection Agency, the Department of the Interior, the Department of Energy, the Department of Commerce, various state agencies, public utilities, and industry.

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## United States Department of the Interior

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RESTON, VIRGINIA 22092

Dr. Gary Stensland  
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July 17, 1980

Dear Dr. Stensland:

The U.S. Geological Survey, as part of its responsibility as lead agency for quality assurance for the National Atmospheric Deposition Program (NADP), has agreed to monitor the quality control practices of the Central Analytical Laboratory and to provide an independent assessment of the quality of data produced by the laboratory. As part of this activity Dr. B. A. Malo and L. J. Schroder of the Geological Survey's Water Resources Division have reviewed the first semi-annual "Quality Assurance Report from the Central Analytical Laboratory-- March, 1980". In addition they have examined the Central Analytical Laboratory's analytical and sample handling procedures and reported on the results of the USGS-operated blind audit program.

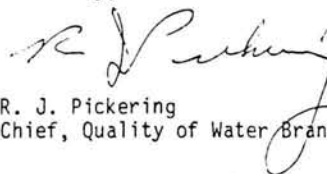
The review of the semi-annual report clearly indicated that the Central Analytical Laboratory is operating with a diverse quality control program that adequately meets the requirements of NADP. During the period represented by this first report, the level of quality control analyses exceeded 20% of the sample load. In addition to the normal reagent water blanks, reference material, and split sample analyses, the laboratory includes the analysis of the "dry-wet bucket" on a routine basis which represents a quality control measure of the system encompassing each step from sampling through laboratory analysis.

We have accepted the analytical methods employed by the Central Analytical Laboratory on an interim basis pending an inter-laboratory evaluation of their precision and bias. The limited results obtained for blind audit samples analyzed during the start-up of the external quality assurance program indicate that the data are at an acceptable level of quality. A description of the USGS blind audit program and the results obtained are contained in the semi-annual report.

Two related problem areas that effect the quality of data, particularly for non-conservative constituents, and that need to be addressed are: 1) lack of sample preservation, and 2) turn-around time in the laboratory. The sample preservation problem is an area requiring a significant research effort and is not solely the responsibility of the laboratory. Turn-around time, however, is related directly to laboratory operations, and although it is affected by sampling and shipping constraints, it should be objectively evaluated by the laboratory and the National Atmospheric Deposition Program's Technical Committee.

In summary, the quality of data resulting from the analyses by the Central Analytical Laboratory appears to be acceptable and consistent with the current state of technology. Improvements should be sought to better assure sample integrity.

Sincerely,



R. J. Pickering  
Chief, Quality of Water Branch

copy to: Dr. James H. Gibson



NADP QUALITY ASSURANCE REPORT  
CENTRAL ANALYTICAL LABORATORY

1 January 1979 to 31 December 1979

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## I. Introduction

The Atmospheric Chemistry Laboratory at the Illinois State Water Survey (ISWS) was selected in the summer of 1978 to be the Central Analytical Laboratory (CAL) for the National Atmospheric Deposition Program (NADP). CAL operations began on October 1, 1978, with 14 NADP sites sending in samples. By December 1979, 35 sites were in operation.

This is the first quality assurance report from CAL. Subsequent reports will be issued at six month intervals. This first report has two major parts: a description of the quality assurance program at CAL and tables of quality control data. Future reports will document any changes in the quality assurance program and will update the tables.

The analytical methods in use at CAL have been documented by Peden et al. (1979). This 1979 report included methods for trace metals which are not yet being monitored in NADP. Appendix A describes the methods for those parameters currently being measured in NADP. Any modifications in the CAL analytical methods will be documented in the semi-annual reports. The computerized precipitation chemistry data management system which has been implemented in the last year for use by CAL and other ISWS research projects will be described in a report now in preparation.

The United States Geological Survey (USGS) was selected by NADP to monitor the quality assurance program of CAL. Draft copies of the CAL quality assurance reports are reviewed by the USGS, by the Methods Development and Quality Assurance Subcommittee of NADP, and by the NADP Project Coordinator.

CAL is required to submit the precipitation deposition data, on a quarterly schedule, to the NADP Project Coordinator's Office. These data are to be of high quality (i.e. accurate) and are also to be screened for representativeness. Thus, this task includes both evaluating the merit of samples as they arrive at CAL from the sites and evaluating CAL's performance in measuring the chemical and physical parameters for the samples. This March 1980, report addresses mainly the latter aspect. Future CAL quality assurance reports and a data management report, in preparation, will include data and discussion of methods developed to evaluate the merit of samples being sent to CAL.

Financial support for CAL has depended on the number of operating sites. The first six months, with only about 20 sites in operation, allowed for the basic quality control measurements by CAL, but not for the manpower needed to produce a quality assurance report such as this one. This explains why the first CAL quality assurance report was not issued sooner. Also, as the project has grown, CAL has been able to carry out several special quality assurance studies to evaluate problems and to provide guidance in implementing procedural changes or in implementing additional routine quality control checks. Results from these special studies will be presented in future CAL reports. Examples of these special studies include:

- a. Sending pH and specific conductance audit solutions to the operating sites on three occasions.

- b. Remeasuring the chemical parameters on 18 NADP samples which had been stored for 6 to 12 months.
- c. Chemical analysis and data interpretation for the "DA" buckets, i.e., those from the wet-side of the sampler during weeks when no precipitation occurred.

Since late 1979, CAL has been able to devote much more attention to monitoring and evaluating the field site operation. The weekly field forms are now being screened much more thoroughly, and the sites' interaction with CAL, via letters and telephone calls, has risen dramatically.

The internal quality control procedures followed by CAL to evaluate its analytical chemistry performance are providing the data necessary to evaluate the analytical errors. However, much more remains to be done to provide data and procedures which will allow CAL to better assess the overall system errors, i.e. the merit or representativeness of data for each sample. For example, CAL was asked to develop a procedure for assessing the quality or representativeness of the data at a site based on the precipitation chemistry record there. Work on this task will be accelerated in the next year, now that some sites have over one year of data and now that our computerized data management system is operational.

## II. Description of the CAL Analytical Quality Assurance Program

### A. Precipitation Solutions

Precipitation samples are typically characterized by a low dissolved solids content ( $\sim 20 \text{ mg L}^{-1}$ ) resulting in a highly unbuffered system. Because of this, a quality assurance program for the chemical analysis of precipitation requires stringent laboratory conditions and careful control over all aspects of the analyses. Each step in the analytical flow chart shown in Figure 1 is a potential source of contamination and must be constantly monitored to assure that the final chemical determinations are not adversely affected by any processing steps. The quality control procedures adopted have been developed to provide the necessary checks at all processing stages.

### B. Laboratory Personnel Requirements

Laboratory staff members are trained in the special techniques necessary for trace analytical work. Each employee is required to adhere to documented methods which are provided for them. Continuing education seminars and training courses are encouraged for all laboratory personnel. Individual analysts are responsible for maintaining records of calibration curves, results of reference samples, and instrument performance criteria. Deviations from standard procedures or normal instrument response are documented and forwarded to the laboratory manager. In addition, each analyst is charged with dating and signing all analyses performed. Records detailing standards and reagent preparation are also documented by the laboratory staff member performing that function. All new standard solutions prepared are verified by comparison with both the old standard and with certified reference solutions before being accepted. Full-time laboratory staff are required to possess at least a baccalaureate degree in chemistry or a related discipline.

### C. General Laboratory Procedures

All laboratory glass and plastic ware are evaluated prior to use to ensure that ions of interest are neither adsorbed nor leached from the surfaces in contact with the sample. Linear polyethylene (LPE) bottles are used exclusively for sample storage prior to analysis. Pyrex or LPE containers are used for standard solution preparation and storage. All volumetric glassware is Class A. Dilutions and standards are prepared using fixed volume pipets with disposable plastic tips. The accuracy and precision of the pipets are monitored by dispensing distilled water aliquots onto a semi-micro analytical balance accurate to  $1 \times 10^{-5}$  grams. Disposable plastic pipet tips are rinsed copiously before use to remove surface impurities.

Membrane filters (Millipore type HA-0.45  $\mu\text{m}$ ) used to separate the soluble and insoluble fractions in precipitation are leached with 200 mL of deionized water prior to use. Filter blank aliquots are collected to ensure that the filtration procedure does not contribute any significant contamination to the precipitation sample. Before filters are adopted for use in a precipitation measurements program, known solutions are passed through them to check for adsorption as well as leaching phenomena. These solutions are then analyzed and recovery percentages are calculated.

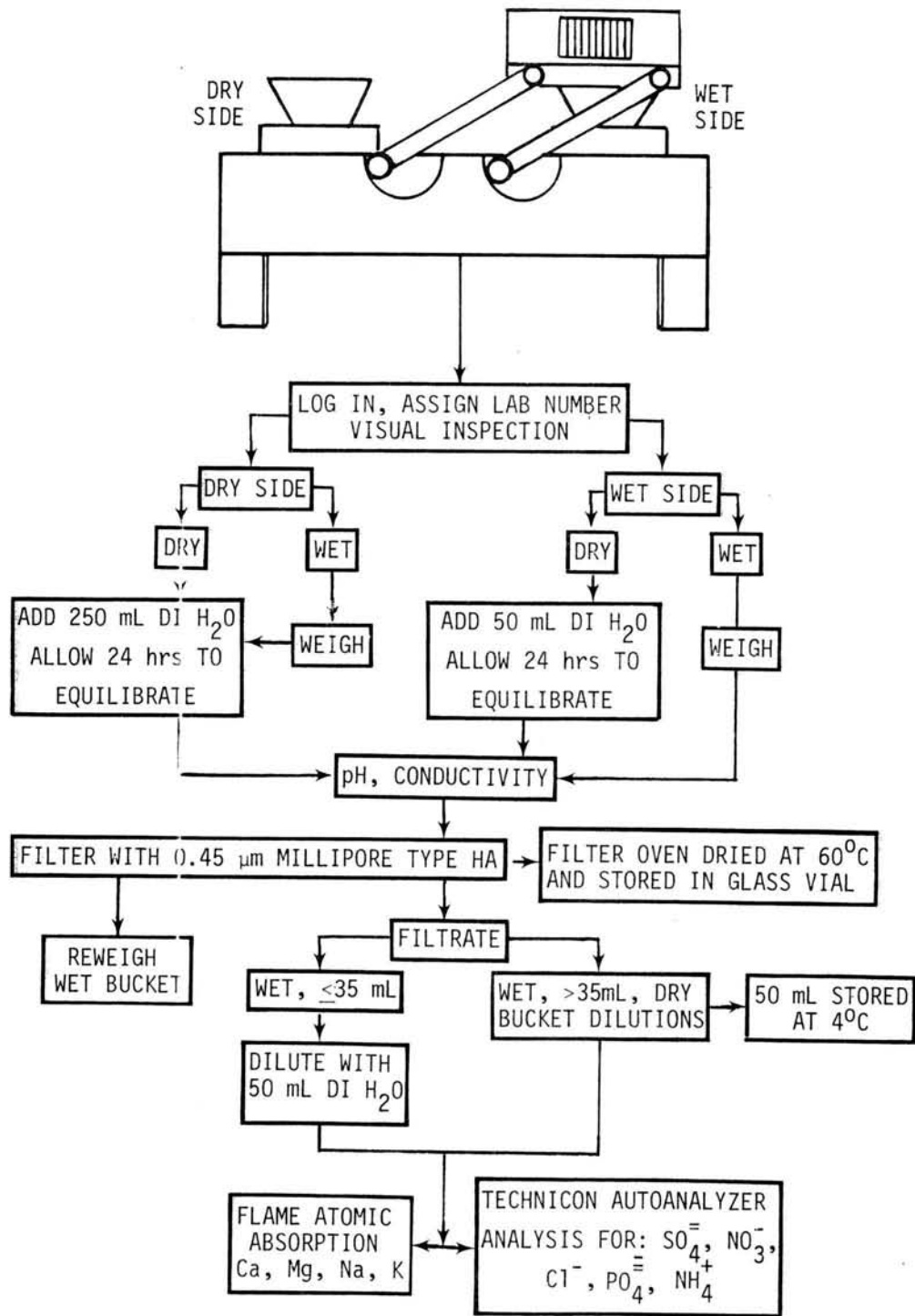


Figure 1. Sample processing flow chart

Laboratory deionized water used for cleaning and solution preparation purposes must be free of dissolved minerals and have a specific conductance  $< 1.0 \mu\text{mho cm}^{-1}$ . Purity is monitored by in line resistance meters which display megohm readings. Mixed bed ion exchange cartridges and a  $0.2 \mu\text{m}$  filter cartridge are installed at point of use locations for final polishing. Cartridges are changed at six month intervals or sooner if water quality degrades or pressure drop increases. Deionized water samples are collected weekly for analysis to verify water purity.

All chemicals used are American Chemical Society (ACS) approved. Baker Ultrex<sup>R</sup> nitric acid is used for preservation of samples for trace metal analyses. At this time trace metals are not being measured for the NADP precipitation samples. Glassware is cleaned with 20% reagent grade  $\text{HNO}_3$ . The glassware is soaked in this solution for 24 hours, followed by a 72 hour soak in deionized water. New plastic bottles used for sample and standard solution storage are rinsed with deionized water three times before use. The plastic bottles to store precipitation samples are used only once.

#### D. Instrumental Procedures

Quality control procedures for monitoring instrument performance involve documentation of standard calibrations, of maintenance, and of analyses of certified reference materials.

An electronic top loading balance with a 4400 gram capacity and a triple beam balance with a 20 kilogram capacity, both used for weighing incoming samples, are checked weekly for accuracy with a 2000 gram IOLM weight. A semi-micro analytical balance which is used for standard and reagent preparation is monitored for proper operation and accuracy with 50 mg and 100 mg NBS class S weights on a per use basis. Servicing is provided by the Instrument Repair Division of the University of Illinois Measurement Program. Analytical balances are serviced at six month intervals or more frequently if the test weight values are not within the manufacturers' instrumental specification.

The pH meters are calibrated with NBS certified buffers of 4.01 and 7.00 units. Automatic temperature compensation is employed. Electrode slope is monitored daily to ensure proper performance. As an additional check the working combination electrode is checked weekly against a standby combination electrode. The standby electrode replaces the working electrode when its performance deteriorates, and a new electrode is then put into service as the standby electrode.

Specific conductance is measured with a manually balanced AC Wheatstone bridge. The glass cell is visually inspected for platinum black integrity and cleaned monthly in an ultrasonic bath containing a mild detergent solution. The cell constant is calculated weekly using a  $75 \mu\text{mho cm}^{-1}$  KCl in water standard. Accuracy of both pH and specific conductance measurements is checked weekly using a low ionic strength synthetic solution which approximates values common to precipitation samples. This procedure is especially important in identifying combination pH electrodes which need to be reconditioned or replaced. Our experience has shown that a faulty electrode may behave properly during calibration with buffered solutions but then give erroneous readings for low ionic strength solutions, such as precipitation samples.

Calibrations curves for flame atomic absorption analyses are established by using a blank and five standards. Standard solutions are stored in linear polyethylene (LPE) bottles. Both blanks and standards are made to match sample matrices and acidified to pH 2 with HNO<sub>3</sub> for stability. New calibration standards must have concentrations within 1.0% of known standards before they are accepted for routine use. The calibration curves are maintained as straight lines by using the instrument's internal curvature correction feature. Concentrations are read directly from the instrument display panel and the standards' values are recorded whenever analyzed. Cumulative curves with standard deviations are drawn with computer aid at three month intervals and maintained in the laboratory files. During the course of normal analyses, a complete set of standards is run every 36 samples with a single point check on the highest standard being made every 12 samples.

A blank and four standards are used for analyses performed on the Technicon AutoAnalyzer. Calibration curves are derived from data represented on an attached strip chart recorder. Curves are retained in an identical manner to the atomic absorption procedure. Blanks and standards are formulated in a deionized water matrix. Phosphate working standards are made daily to avoid degradation of the orthophosphate. SO<sub>4</sub>, NO<sub>3</sub>, PO<sub>4</sub>, Cl, and NH<sub>4</sub> standards are stored in amber borosilicate glass bottles. A complete set of standards with a blank is analyzed every 36 samples and a single point check every twelfth sample.

The detection limit for a given parameter is defined as the concentration level that is twice the standard deviation of the baseline or instrument noise. This is determined by performing an analysis of a blank solution ten times and calculating the minimum detectable concentration with the derived data.

Accuracy is monitored through the use of US EPA water quality reference samples supplied through the Cincinnati Environmental Monitoring and Support Laboratory. These are diluted further after initial ampule dilutions to achieve concentrations normally encountered in precipitation samples. Analysis of reference samples takes place before and after each sample run. Values measured must be  $\pm 5\%$  of the known concentrations. If they fail to meet this criterion, the instrument is recalibrated and the samples, both reference and precipitation, are reanalyzed. Additional checks for accuracy are the introduction of 'blind' samples received through participating NADP sites. The blind audit program is administered by the U.S. Geological Survey (USGS) National Water Quality Laboratory in Denver, Colorado. These samples undergo routine handling and analysis, with results sent to and tabulated by the USGS.

All chemical analyses are reported to the same number of significant figures as justified by the sensitivity of a given analytical method. The odd/even rule is employed when rounding is necessary. Numbers ending in 0-4 keep the preceding digit the same. Numbers ending in 6-9 have the preceding digit increased by one. Numbers ending in a 5 are rounded up if the preceding digit is an odd integer and left the same if the preceding digit is an even integer.

#### E. Analytical Blanks

To ensure that CAL procedures are not contributing contaminants to a precipitation sample, several checks are made at various stages of the

processing flow chart (Figure 1). The collection buckets and lids used at the field sites are cleaned and individually wrapped at the Central Analytical Laboratory.

The cleaning procedure consists of scrubbing and rinsing each bucket with deionized water that has a conductance of less than two micromho  $\text{cm}^{-1}$ . A natural sponge is used for scrubbing previously exposed buckets. The scrubbing procedure is followed by multiple rinsings until the conductance of the rinse water is less than two micromho  $\text{cm}^{-1}$ . Excess water is shaken from the buckets and they are immediately placed into plastic bags. Buckets are not allowed to air dry to avoid contamination from airborne dust particles. To make certain that the deionized water washing procedure is removing all soluble impurities, randomly selected clean buckets are equilibrated with 50, 150, and 500 mL aliquots of deionized water on a weekly basis. The water remains in the buckets for 24 hours and is then transferred to 60 mL LPE bottles for subsequent analysis. All parameters routinely determined on precipitation samples are measured on these bucket blanks. Results are summarized on a semi-annual schedule.

The quality of deionized water is assayed by collecting 50 mL aliquots and storing them in LPE bottles. These water blanks are not filtered, but are otherwise handled as though they were a precipitation sample. Water samples are collected on a weekly basis and results are summarized semi-annually.

Filter blank solutions consist of aliquots collected on a weekly basis during a normal filtration procedure. The blanks consist of two sequential 50 mL aliquots collected after the filter has been leached with 200 mL of deionized water. Analysis results are tabulated similarly to bucket and deionized water blanks.

#### F. Replicate Samples

Four percent of the sample load, excluding standards and reference materials, consists of replicate (split or duplicate) samples. The replicates are physically separated on the sample trays which hold about 100 samples, but will typically be analyzed within a few hours of each other during the subsequent measurements of the various ions. Results of replicate sample analyses are compiled on a semi-annual basis and used to generate precision statistics for all measured parameters.

#### G. Data Verification

In addition to the quality control measures implemented during sample handling and processing, precipitation samples are subjected to computer verification. Raw chemical results are entered into the data management system by keypunching directly from laboratory data forms. Key punching errors are essentially eliminated by entering a line of data for each of 25 samples and then reentering all the data a second time, with the data being accepted only if the two entries agree. Control checks within the computer programs ensure that data are in the proper form and that all necessary information is provided. For example, the program checks that the sample location, which is part of the sample number, matches a site location stored in the master file. The ionic balance is calculated for each sample. Additionally the percentage difference between calculated versus measured specific conductance is

tabulated. Samples are machine selected for reanalysis based on the pre-determined control limits for ion balance and specific conductance differences. A complete reanalysis is carried out on all samples selected and original versus repeat values are compared. The laboratory manager and data analyst then determine which values, if any, justify change based on consultation with individual laboratory analysts. If values are changed, the original, repeat and corrected final data are all maintained in the computerized data base.

In order to detect systematic or consistent trends in the data, graphical summaries are produced for each set of analyses in the form of scatter plots and histograms. The histograms display ion balance data and specific conductance differences, and are used to detect any persistent bias or shifts from one set of analyses to another. In this way, overall data quality can be monitored as a function of time. Scatter plots comparing conductance and ion balance data as a function of sample pH were used to formulate the control limits for sample acceptance. These limits were chosen such that about 8 percent of the total sample load would be selected by the computer program for reanalysis. The control limits, presently being used are not constant, but instead vary with the sample pH. This subject will be the topic of a separate chapter in the next CAL Quality Assurance Report. For now we will simply state that for samples with a CAL measured pH < 4.7, the ion balance must exceed  $\pm 13\%$  for the sample to be selected for reanalysis. Reanalyzed samples are also compared with original values with scatter plots to quickly identify outliers which require further investigation by the data analyst and laboratory manager.

The measurement set for a sample is never completely replaced by the reanalyzed sample data. Rather, the typical situation is that only one or possibly two of the original parameter measurements will be replaced by the reanalysis values. Less than 1% of the original samples ultimately have a chemical parameter corrected.



### III. Quality Control Data

#### A. Discussion of Results

This section presents the data for the various quality control samples. The glossary proceeding the tables defines terms and lists mathematical formulas which were used for the calculations. As mentioned earlier the tables will be cumulative, i.e., contain data for the current reporting period as well as previous reporting periods.

Tables 1-11 report the CAL analytical accuracy. The unbuffered CAL quality control samples referred to in Tables 1 and 2 are sulfuric and nitric acid solutions which simulate unbuffered precipitation samples. The concentrations (activities) of these synthetic solutions, in pH units, are calculated from the normality of the reagent being diluted and are cross checked by measuring the sulfate and nitrate levels in the solutions. Corrections are made for incomplete acid dissociation if ion concentrations warrant such treatment (e.g., the  $pK_a$  of  $HSO_4^-$  is 1.92 at 25°C and thus has a small effect for a pH = 3 sulfuric acid solution). The specific conductances in the middle column of Table 2 are determined as the product of the equivalent concentration of the ions in the synthetic solutions and the tabulated equivalent conductance values (at infinite dilution). Empirical (Kohlrausch) corrections are made in these equivalent conductance values if the concentrations of ions are large enough to introduce a measurable error.

Tables 3-11 present the precision and bias for the rest of the ions being measured for NADP precipitation samples. Chloride is the only ion with a statistically significant bias. The bias is small and our calculations indicate that it is accounted for by interference from the fluoride levels in the EPA reference samples.

Tables 12-20 present the analysis of the replicate (split or duplicate) samples. Every 25th precipitation sample, or the first one thereafter having sufficient volume, is filtered into two LPE containers to provide the replicate set. The RMS percent deviation of these replicate analyses provides a measure of precision at CAL which can be compared to the precision column for the corresponding Tables 1-11. The agreement is good except for chloride, which is somewhat higher on Table 21 than on Table 10.

A more straight-forward procedure to estimate precision is to do multiple measurements on a standard solution or even a precipitation sample. The advantage of using split samples for this quality control procedure is that all the various types of precipitation samples are randomly being included in the study and also data are accumulated on essentially every ion analysis day instead of a few days a year.

Tables 23-25 present results for the analytical blanks. The water blanks and filter blanks display the pattern we have come to expect in our laboratory. For the filter blanks the ions likely to be associated with human contamination, namely Na, K, and Cl, are detectable in 1 to 3 percent of the samples. The median precipitation sample volume for the NADP sites ranges from about 500 to 2000 mL, and this explains the choice of 500 mL as the normalized volume for presenting the blank data.

The bucket blank quality control procedure has only very recently been standardized at CAL. The limited data presented in Table 25 was accumulated before this standardization and is included to indicate that no significant problems are expected from this processing step. The procedure currently in use for both the filter blanks and the bucket blanks includes more than one aliquot volume in order to identify the aliquot volume at which the values above the detection limit will completely disappear.

B. Glossary of Terms for the Tables

Accuracy Degree of conformity of measured values with true value; accuracy includes both bias (systematic error) and precision (random error)<sup>1</sup>.

Bias Persistent positive or negative deviation of measured value from true value, expressed as 
$$\frac{(\text{mean value measured} - \text{certified value})}{\text{certified value}} \times 100\%$$

The quantity in parentheses in the bias column of the tables is the limit-of-error<sup>2</sup> in the calculated bias. If the absolute value of the bias exceeds the absolute value of this quantity, the bias is taken to be significant; conversely, if the error exceeds the bias, the bias can be taken to be insignificant.

Significant values of the bias can often be accounted for by chemical species which interfere with the analysis of the constituent under consideration. These interfering species may be part of the chemical matrix of the standard solution used for accuracy determinations but might not be present at interfering levels in precipitation samples. In this instance no bias would follow for precipitation measurements. On the contrary, analyses which suggest no bias with the standard solution may in fact exhibit bias for precipitation samples because of the presence of some interfering chemical not part of the standard matrix.

Calculated Concentration Table 1 only - hydrogen ion activity (pH units) calculated from strong mineral acid dilutions.

Calculated Conductance Table 2 only - calculated specific conductance for strong mineral acid dilutions; empirical (Kohlrausch) corrections made where appropriate.

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<sup>1</sup>U.S. Dept. of the Interior, Geological Survey, 1978: Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments, Open-File Report 78-679, pp. 5-25.

<sup>2</sup>David P. Shoemaker and Carl W. Garland, 1967: Experiments in Physical Chemistry, McGraw-Hill Book Company, New York, pp. 30-35.

Concentration	Tables 3 thru 11 only - EPA certified concentrations or dilutions thereof
Detection Limit	Twice the standard deviation of baseline noise
Number of Analyses	Number of individual measurements
Number of Days of Analyses	Number of separate days on which individual measurements were made
Period	Time period over which analyses were performed
Precision	Degree of agreement of repeated measurements <sup>1</sup> expressed as standard mean value $+(2 \times \text{deviation/observed}) \times 100\%$ . For cases in which the instrumental error exceeds two times the standard deviation this quantity is substituted for the numerator in the above formula and the resulting precision is reported in parentheses (instrumental error is governed by the practical limitations of the apparatus and its output and is equal to one half of the sensitivity)
Replicate Samples	Precipitation samples which are split to provide identical samples for analysis
Sensitivity	Minimum reported difference between measurements
Unbuffered CAL Samples	Synthetic solutions which simulate pH and specific conductance levels typical of precipitation samples

Equations:

Percent Deviation	$= \pm [(\text{value2}-\text{value1})/(\text{value2}+\text{value1})/2]100\%$
Mean Percent Deviation	$= \pm \frac{\sum}{n}   \text{percent deviation}_i / n$
Root Mean Square (RMS) Percent Deviation	$= \pm \frac{(\sum(\text{percent deviation}_i^2)/n)^{1/2}}{n}$

C. Data Tables

1. Tables for Accuracy

Table 1. Hydrogen Ion Analysis - Analytical Accuracy Based on Unbuffered CAL Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Calculated Concentration (pH units)	Sensitivity (pH units)	Precision* (percent)	Bias* (percent)
1/79 - 12/79	14	14	3.06	±.01	+ 3.0	+3.4(±4.1)
"	14	12	4.08	±.01	+ 10.1	+4.5(±8.6)

\*For hydrogen ion activities

Table 2. Conductance Analysis - Analytical Accuracy Based on Unbuffered CAL Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Calculated Conductance (µS/cm)	Sensitivity (µS/cm)	Precision (percent)	Bias (percent)
1/79 - 12/79	9	9	35.5	±.1	+ 9.7	+1.0(±8.1)
"	14	14	401	+ 1	+ 2.3	+0.6(±1.3)

Table 3. Calcium Analysis - Analytical Accuracy Based on EPA Mineral Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	9	6	.35	.02	+4.0	+4.4(±3.8)
"	6	5	.53	.02	+5.3	+4.3(+4.5)
"	24	15	1.45	.02	+2.6	+3.1(±2.6)

Table 4. Magnesium Analysis - Analytical Accuracy Based on EPA Mineral Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	9	6	.114	.002	+3.1	+2.0(+3.3)
"	6	5	.171	.002	+2.1	+1.3(+2.8)
"	24	15	.300	.002	+2.0	-0.2(+2.1)

Table 5. Sodium Analysis - Analytical Accuracy Based on EPA Mineral Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	5	2	.157	.004	+1.4	+0.4(+2.4)
"	6	5	.314	.004	+5.0	-0.2(+4.2)
"	5	4	.472	.004	+2.6	-0.2(+3.0)
"	25	14	.500	.004	+1.5	-0.1(+1.9)

Table 6. Potassium Analysis - Analytical Accuracy Based on EPA Mineral Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	5	2	.033	.004	+10.7	-7.4(+6.7)
"	6	5	.067	.004	+ 6.8	-1.1(+5.0)
"	3	3	.100	.004	+ 2.3	+0.9(+2.8)
"	29	15	.270	.004	+ 3.1	+0.5(+2.7)

Table 7. Ammonium Analysis - Analytical Accuracy Based on EPA Nutrient Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	24	18	.30	.02	$\pm 10.1$	+1.1( $\pm 6.2$ )
"	23	17	2.05	.02	$\pm 3.3$	+0.1( $\pm 2.7$ )

Table 8. Sulfate Analysis - Analytical Accuracy Based on EPA Mineral Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	31	26	1.20	.10	$\pm (2.1)$	+0.1( $\pm 1.9$ )
"	24	22	5.12	.10	$\pm 1.7$	+0.3( $\pm 2.1$ )
"	18	16	10.24	.10	$\pm 1.2$	-0.2( $\pm 1.8$ )

Table 9. Nitrate Analysis - Analytical Accuracy Based on EPA Nutrient Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	38	26	.49	.02	$\pm (5.1)$	+1.6( $\pm 3.6$ )
"	40	26	1.68	.02	$\pm 3.6$	-0.5( $\pm 2.8$ )

Table 10. Chloride Analysis - Analytical Accuracy Based on EPA Mineral Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	3	3	1.41	.05	+1.4	+4.6(+2.0)
"	21	16	2.81	.05	+2.1	+4.4(+2.2)
"	19	16	4.32	.05	+1.2	+4.9(+1.9)

Table 11. Orthophosphate Analysis - Analytical Accuracy Based on EPA Nutrient Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	16	14	.058	.003	+3.4	+0.6(+2.4)
"	17	14	.080	.003	+4.0	-1.4(+3.1)



2. Tables for Precision from Replicate Samples

Table 12. Hydrogen Ion Analysis - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (pH units)	Median Concentration (pH units)	Sensitivity (pH units)	RMS Percent Deviation*	Mean Percent Deviation*
1/79 - 12/79	34	3.63-4.99	4.29	±.01	+ 2.8	+1.4
"	11	5.00-6.56	5.71	±.01	+17.4	+8.3

\*For hydrogen ion activities

Table 13. Conductance Analysis - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (µS/cm)	Median Concentration (µS/cm)	Sensitivity (µS/cm)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	44	<100	20.0	±.1	+3.8	+1.5
"	1	100-117	117	± 1	0.0	0.0

Table 14. Calcium - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	27	<.20	.10	.02	+6.6	+3.2
"	18	.20-1.60	.41	.02	+0.5	+0.1

Table 15. Magnesium - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	12	<.020	.015	.002	<u>+4.6</u>	<u>+1.8</u>
"	33	.020-.302	.045	.002	<u>+2.2</u>	<u>+1.2</u>

Table 16. Sodium - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	3	<.040	.038	.004	<u>+3.8</u>	<u>+3.1</u>
"	42	.040-1.89	.183	.004	<u>+2.7</u>	<u>+1.3</u>

Table 17. Potassium - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	26	<.040	.020	.004	<u>+6.5</u>	<u>+4.7</u>
"	19	.040-.341	.083	.004	<u>+4.3</u>	<u>+2.4</u>

Table 18. Ammonium - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	15	<.20	.08	.02	<u>+5.0</u>	<u>+1.7</u>
"	29	.20-1.54	.38	.02	<u>+5.6</u>	<u>+2.2</u>

Table 19. Sulfate - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	5	<1.00	.88	.10	<u>+2.6</u>	<u>+1.1</u>
"	40	1.00-14.60	2.75	.10	<u>+2.5</u>	<u>+1.6</u>

Table 20. Nitrate - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	1	<.20	.10	.02	0.0	0.0
"	44	.20-7.85	1.38	.02	<u>+2.8</u>	<u>+1.3</u>

Table 21. Chloride - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	37	<.50	.19	.05	<u>+14.8</u>	<u>+10.5</u>
"	6	.50-1.75	.92	.05	<u>+ 3.8</u>	<u>+ 2.3</u>

Table 22. Orthophosphate - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	2	<.030	.006	.003	0.0	0.0
"	1	.030-.338	.338	.003	0.0	0.0

3. Tables for Analytical Blanks

Table 23. Water Blank Analyses for the Period 1/79 through 12/79

Ion	Number of Analysis	Number of Days of Analyses	Typical Detection Limit (mg/L)	Frequency of Detection Limit* (percent)	Percentile*	
					90th (mg/L)	95th (mg/L)
Ca	10	10	.02	100	<.02	<.02
Mg	10	10	.002	100	<.002	<.002
Na	10	10	.004	100	<.004	<.004
K	10	10	.004	100	<.004	<.004
NH <sub>4</sub>	10	10	.02	100	<.02	<.02
SO <sub>4</sub>	10	10	.10	100	<.10	<.10
NO <sub>3</sub>	10	10	.02	100	<.02	<.02
Cl	10	10	.05	100	<.05	<.05
PO <sub>4</sub>	10	10	.003	100	<.003	<.003

\*Ion concentrations normalized to 500 mL sample volume

Table 24. Filter Blank Leachate Analysis for the Period 1/79 through 12/79

Ion	Number of Analysis	Number of Days of Analyses	Typical Detection Limit (mg/L)	Frequency of Detection Limit* (percent)	Percentile*	
					90th (mg/L)	95th (mg/L)
Ca	348	282	.02	100	<.02	<.02
Mg	348	282	.002	100	<.002	<.002
Na	348	282	.004	97	<.004	<.004
K	348	282	.004	99	<.004	<.004
NH <sub>4</sub>	348	282	.02	100	<.02	<.02
SO <sub>4</sub>	348	282	.10	100	<.10	<.10
NO <sub>3</sub>	348	282	.02	100	<.02	<.02
Cl	348	282	.05	99	<.05	<.05
PO <sub>4</sub>	348	282	.003	100	<.003	<.003

\*Ion concentrations normalized to 500 mL sample volume

Table 25. Bucket Blank Leachate Analyses for the Period 1/79 through 12/79

Ion	Number of Analysis	Number of Days of Analyses	Typical Detection Limit (mg/L)	Frequency of Detection Limit* (percent)	Percentile*	
					90th (mg/L)	95th (mg/L)
Ca	12	12	.02	100	<.02	<.02
Mg	12	12	.002	100	<.002	<.002
Na	12	12	.004	100	<.004	<.004
K	12	12	.004	100	<.004	<.004
NH <sub>4</sub>	12	12	.02	91	<.02	.03
SO <sub>4</sub>	12	12	.10	100	<.10	<.10
NO <sub>3</sub>	12	12	.02	91	<.02	.03
Cl	12	12	.05	100	<.05	<.05
PO <sub>4</sub>	12	12	.003	100	<.003	<.003

\*Ion concentrations normalized to 500 mL sample volume

#### IV. Results of USGS/NADP Blind Audit Program<sup>a</sup>

The blind audit portion of the USGS/NADP Quality Assurance Program began with the distribution of samples to the field in October 1979. This part of the quality assurance program depends on the cooperation of NADP site operators for the submission of known reference material samples to the Central Analytical Laboratory (CAL). Instructions to the site operators indicate that they should transfer the reference sample to a clean bucket, fill out the normal field form and submit the sample to the laboratory in the same manner that they would their normal samples. The quality assurance or blind audit samples are submitted during those one-week periods when no wet deposition occurs at a cooperating site. In order to control the flow of audit samples to CAL, the Geological Survey has limited the number of samples distributed to field sites at any one time. There are a number of unknowns controlling sample flow in the blind audit program. The principle one is the weather. Since samples are only submitted during dry weeks, there is no way to precisely control the number of samples received by the laboratory in a given period. The goal of the program is to achieve a submission of one reference sample for each two-week period, thus insuring that each batch of analyses that go through CAL contains one audit sample. To date we have not been able to achieve this level. Table 26 presents the blind-audit analysis that have been completed at CAL. The analytical values determined by CAL are compared to calculated or expected values for the given reference samples. The term calculated value is used since the reference materials currently employed by the program are quantitative dilutions of Standard Reference Water Samples employed by the Geological Survey in their methods development and quality assurance investigations.

Examination of Table 26 indicates that the CAL analysis compared extremely well with the expected values from the reference samples. The sample submission scheme includes potential errors from contamination sources attributable to the field transfer of reference materials and CAL's cleaning of the sample container. The differences between the CAL analysis and the expected values are minimal.

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<sup>a</sup>This section of the report was provided by B. A. Malo and L. J. Schroder of the USGS, Denver, CO.

Table 26. Blind Sample Analysis by CAL of USGS Rain Water Reference Samples.

Species	CAL analysis mg/L	Calculated values mg/L	CAL analysis mg/L	Calculated value mg/L	CAL analysis mg/L	Calculated value mg/L	CAL analysis mg/L	Calculated value mg/L
Calcium	2.59	2.67	2.52	2.44	4.83	4.89	2.55	2.67
Magnesium	.574	.662	.56	.56	1.04	1.03	.67	.67
Sodium	2.16	2.2	2.55	1.45	4.93	4.95	2.10	2.20
Potassium	.432	.43	.36	.32	.33	.34	.47	.44
Sulfate	6.30	5.97	4.45	3.52	9.75	9.60	6.23	5.97
Chloride	.72	.88	1.45	1.40	3.72	3.87	.90	.88
Ortho-phosphate	.08	.10	.03	--	.08	.09	.054	1.05
pH			6.93	7.10	7.14	8.0	7.11	7.2
Specific Conductance	32.8	32.6	31.6	16.2	62	53	32.3	30.0
CAL Sample ID	N1450A0WMC25		N1414A0HC022		N1589A0JCA58		N1315A0JH116	
Date Off Collector	10/16/79		10/09/79		11/13/79		1/02/80	



V. CAL Staff

As of March, 1980, the following ISWS employees contributed a fraction of their time to the CAL project.

<u>Name</u>	<u>Activity</u>
Van Bowersox	Data Management
Susan Engroff	Student Assistant
Florence F. McGurk	Chemical Analyst
Mark E. Peden	Laboratory Manager
Sara Reed	Student Assistant
Herminio Reyes	Student Assistant
Richard G. Semonin	Project Co-Principal Investigator
Loretta M. Skowron	Chemical Analyst
Michael Slater	Chemical Analyst
Randall K. Stahlhut	Computer Programmer
Gary J. Stensland	CAL Director and Project Co-Principal Investigator

Other ISWS support staff members contribute to the project, including those in graphic arts, keypunching, the machine shop, the electronics shop, and typing.

VI. References

- Peden, M. E., L. M. Skowron, F. F. McGurk, 1979: Precipitation Sample Handling, Analysis and Storage Procedures. Research Report 4 to U.S. Dept. of Energy, Contract EY-76-S-02-1199, pp. 71.
- Shoemaker D. P., and C. W. Garland, 1967: Experiments in Physical Chemistry, McGraw-Hill Book Company, New York, pp. 30-35.
- U.S. Dept. of the Interior, Geological Survey, 1978: Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments, Open-File Report 78-679, pp. 5-25.
- Weast, R. C., 1968/1969: Handbook of Chemistry and Physics, 49th Edition, The Chemical Rubber Co., Cleveland, OH, p. D-91.

APPENDIX A

CENTRAL ANALYTICAL LABORATORY METHODS



## SAMPLE PROCESSING AND PRELIMINARY MEASUREMENTS

Field samples sent to the laboratory are processed immediately to prevent changes in ionic composition. The laboratory data forms shown in figures 1a and 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 2a and 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.

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 descriptions. Samples are then filtered through a 0.45  $\mu\text{m}$  membrane filter (Millipore HA) to separate the soluble fraction from the insoluble material.

Figure 3 illustrates the filtering apparatus used. It was designed to facilitate leaching contaminants from the filter and the glass funnel prior to actual sample filtration. The interior surface of the filter funnel is rinsed with 200 mL of deionized water with the vacuum on prior to placing the filtrate collection bottle in place. The plexiglass top is then removed and a 250 mL bottle is placed under the funnel outlet. Approximately 250 milliliters of samples are collected. The bottle is then removed and the remaining sample is filtered to collect all of the insoluble material on the filter substrate. The stopcock at the base of the filtration assembly is used to drain the leach and excess sample water. The insoluble material remaining on the filter is oven-dried at 60°C for one hour and stored in glass vials.

Fifty mL of the filtrate are transferred to 60 mL bottles and stored at room temperature for subsequent chemical analysis. The remaining portion is refrigerated at 4°C. Previous work by Peden and Skowron (1978) has shown that filtration alone is sufficient to stabilize the constituents H, K, Na, Mg,  $\text{NO}_3$ ,  $\text{SO}_4$ , Cl, and  $\text{NH}_4$ .

The pages which follow, detail the procedures for pH, specific conductance,  $\text{Ca}^{++}$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{=}$ , respectively. Following these descriptions is a list of abbreviations on page A27 and an equipment list on page A28.

ISWS ATM. CHEM. DATA FORM: JAN. 1979

TIME: CST	CDT	EST	GMT	SAMPLE NUMBER	DATE ON	TIME ON	DATE OFF	TIME OFF	LAB COND.	LAB GROSS WEIGHT	WEIGHT AFTER ALIQUOT	DRY BOTTLE WEIGHT	LAB PH	LAB CONDUCT	LAB MEASUREMENT	I	D				
11				2-6	71 81	9-12	14-19	21-24	26-31	33-36	37-39	40-44	44-51	53-55	58-60	62-65	66-69	71-73	78-80	79-80	
11	XXXX	X	X	XXXX	XXXXXX	XXXX	XXXXXX	XXXX	XXXX	XXXX	XXXX	XXXX	XXXX	XXXX	XXXX	XXXX	XXXX	XXXX	XXXX	XXXX	XXXX
01																					
02																					
03																					
04																					
05																					
06																					
07																					
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16																					
17																					
18																					
19																					
20																					
21																					
22																					
23																					
24																					
25																					

(a)

ISWS ATM. CHEM. DATA FORM: JAN. 1979

SAMPLE NUMBER	SAMPLE TYPE	FINAL FIELD WT.	FIELD CONDUCT.	FIELD PH	WEEKLY PRECIP.	COMMENTS	I	D
11	2-6	71 81	14-20	22-27	29-32	34-36		
11	XXXX	X	XXXX.X	XXXX.X	X.XX	XX.XX		
01								
02								
03								
04								
05								
06								
07								
08								
09								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
21								
22								
23								
24								
25								

(b)

Figure 1. Laboratory data forms. (a) - Preliminary lab measurements, (b) - Comment form

ISWS ATM. CHEM. DATA (MG/L)												FORM: JAN. 1979		
SAMPLE NUMBER				CA	HG	NA	K							ID
11	2-6	71	8	9-112	16-120	23-127	30-134	37-141	44-148	51-155	58-162	65-169	72-176	7
X	XXXXX	X	X	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	9
01														3
02														
03														
04														
05														
06														
07														
08														
09														
10														
11														
12														
13														
14														
15														
16														
17														
18														
19														
20														
21														
22														
23														
24														
25														

(a)

ISWS ATM. CHEM. DATA (MG/L)												FORM: JAN. 1979		
SAMPLE NUMBER				SC4	NO3	CL	NH4	PO4						ID
11	2-6	71	8	9-112	16-120	23-127	30-134	37-141	44-148	51-155	58-162	65-169	72-176	7
X	XXXXX	X	X	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	XXXXXXXX	9
01														2
02														
03														
04														
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(b)

Figure 2. Chemistry data forms. (a) - Atomic absorption measurements, (b) - Wet chemistry measurements.

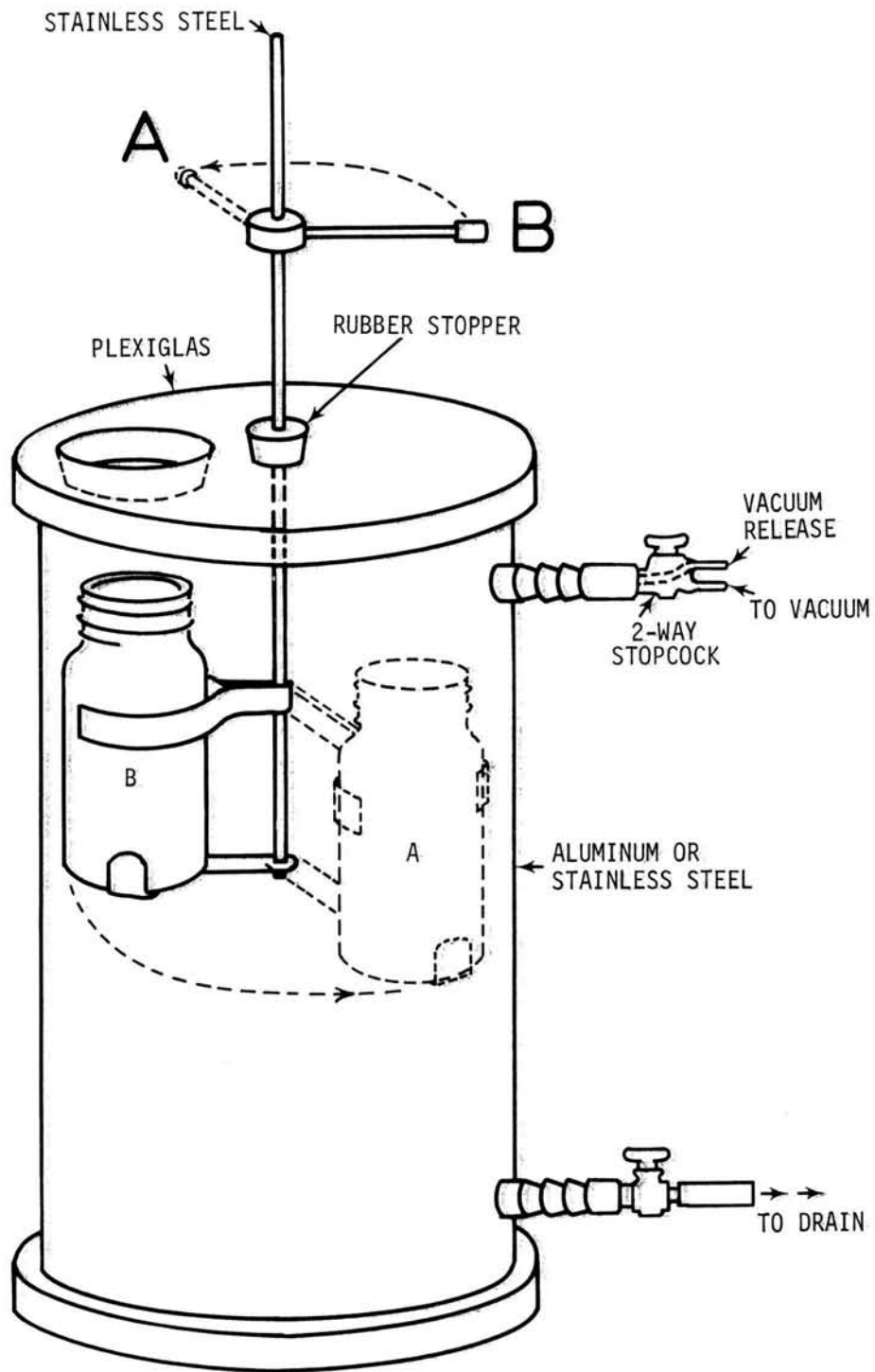


Figure 3. Sample filtration apparatus



## STANDARD CONDITIONS FOR THE DETERMINATIONS OF IONS IN PRECIPITATION

The following procedures are used in our laboratory for analysis of the soluble 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 parameters 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 symbol.

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

The ions  $\text{SO}_4^{=}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{=}$ , and  $\text{NH}_4^+$  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  $\text{ng mL}^{-1}$  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). 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. All determinations are made in 4 mL polystyrene vials.

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 3 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 3 minutes, the slope control knob should be carefully adjusted to read 4.01. The pH 7 should now be checked again and must read  $7.00 \pm 0.01$ . 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, the electrode is rinsed thoroughly with deionized water followed by a final rinse with a separate aliquot from the sample to be measured. A 3-4 minute equilibration period is used for each sample determination. Results are reported to the nearest 0.01 pH unit. The standard deviation of replicate determinations is 0.05 pH unit.

The accuracy of the measurements is checked weekly by measuring the pH of a synthetic dilute acid solution in the range of 4.00-4.50. The composition of this solution approximates that found in precipitation samples. In addition, the electrode response is monitored daily by tabulation of the percent slope necessary to calibrate the meter.

Electrodes are stored in pH 7 buffer 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 0.25 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, refilled with new electrolyte solution, and allowed to soak in pH 7 buffer for 24 hours before use.

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, in addition to a final rinse with the sample to be measured.

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°C and 30°C, and the following equation used to calculate the specific conductance at 25°C:

$$\text{Specific conductance} = \frac{75 \times R_{\text{KCl}}}{R_{\text{S}}} \frac{\mu\text{S}}{\text{cm}}$$

where  $R_{\text{KCl}}$  and  $R_{\text{S}}$  are the resistances, in ohms, of a standard potassium chloride solution (0.0005 M) 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.

Ca <sup>++</sup> Calcium
-----------------------------

Instrumental Mode: Flame atomic absorption

Wavelength, nm : 422.7 Bandpass, nm : 5 (interference filter)

Light Source : Ca HCL Lamp Current, ma : 7

Photomultiplier Tube : R955 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 dried calcium carbonate (CaCO<sub>3</sub>) in a small amount of 6 N HCl and dilute to a volume of 1 liter with deionized water. Final concentration is 1000  $\mu\text{g mL}^{-1}$  Ca.

Releasing Agent Stock Solution: Dissolve 117.28 grams of lanthanum oxide (La<sub>2</sub>O<sub>3</sub>) in 500 mL of 6 N HCl and dilute to a volume of 1 liter with deionized water. Final concentration is 100,000  $\mu\text{g mL}^{-1}$  La. Lanthanum prevents interference from sulfates, phosphates, aluminum, and silicates.

Working Standards: Dilute stock solution to 3.00, 2.25, 1.50, 0.75, and 0.30  $\mu\text{g mL}^{-1}$  with 0.016 N HNO<sub>3</sub>. Add 1.0% by volume La solution; final La concentration is 1000  $\mu\text{g mL}^{-1}$ . A blank is prepared with 0.016 N HNO<sub>3</sub> diluted 1.0% with La stock solution.

Sample Preparation: Combine 25.0  $\mu\text{L}$  of releasing agent to 2.5 mL of sample. Concentration is read directly on the instrumental digital display.

Sensitivity : 0.05  $\mu\text{g mL}^{-1}$ .

Detection Limit : 0.02  $\mu\text{g mL}^{-1}$ .

Cl <sup>-</sup> Chloride
-----------------------------

Method: Automated Colorimetric Thiocyanate

Instrumental Mode:

Auto Sampler III.

No. of Samples/Hr.: 60

Sample/Wash: 6/1

Sample Volume, mL: 1.0-1.5

Gilson "minipuls 2" Peristaltic Pump Tubes.

Color	Flow Rate (mL/min)	Application*
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.

Mixing Coils: 5 and 14 turns

Single Channel Colorimeter.

Reversing Switch: Direct (D)

Wavelength, nm: 480

Flow Cell Path Length, mm: 15

F/C ID, mm: 2

Damp: 2

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

Strip Chart Recorder. 1 cm/min Chart Speed

Typical Standard Curve:

mgL <sup>-1</sup> Cl <sup>-</sup>	Peak Height (cm)
.20	.60
.50	1.85
1.00	4.10
2.00	8.40
2.50	10.55
5.00	21.30

Limit, Range, Interferences:

Detection Limit, mgL<sup>-1</sup>: 0.05

Working Range, mgL<sup>-1</sup>: 0.0-5.00

Interferences: No significant interferences.

Summary of Method:

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

Procedure:

Analysis. The precipitation sample containing chloride ions is introduced into the system and diluted with diluent water. Color reagent is added, and soluble, but unionized mercuric chloride (HgCl<sub>2</sub>) is formed, liberating mercuric thiocyanate. In the presence of ferric ions, the liberated thiocyanate forms a colored ferric thiocyanate complex. The intensity of this complex is determined colorimetrically at 480 nm and is proportional to the concentration of chloride ions in the precipitation sample.

Collection of Chloride Waste. Waste from the chloride channel should be collected in a container of known volume. When the container is full, place it in a hood and add 20 mL of 13% thioacetamide per liter of chloride waste. Mix well and cap the container. A precipitate of mercuric sulfide will form. After 24 hours, filter (in a hood) the solution through a Buchner funnel. 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 30 min. with deionized water.

Reagents:

Stock Standard Solution, 1000 mgL<sup>-1</sup> Cl<sup>-</sup>. Dissolve 1.6485 grams of dried sodium chloride (NaCl) and dilute to 1 liter with deionized water.

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

Mercuric Thiocyanate Stock Solution. Add 4.17 grams of mercuric thiocyanate ( $\text{Hg}(\text{SCN})_2$ ) per liter methanol ( $\text{CH}_3\text{OH}$ ). 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 ( $\text{HNO}_3$ ). 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.

Thioacetamide, 13% Solution. Dissolve 130 grams of thioacetamide ( $\text{CH}_3\text{SCNH}_2$ ) per liter DI. Store in a closed glass container. Stability is one year.

Reference:

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

$K^+$ Potassium
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Instrumental Mode: Flame atomic absorption

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

Light Source : K HCL      Lamp Current, ma : 6

Photomultiplier Tube : R955      Photomultiplier Voltage, v : 530

Burner : Single slot      Burner Height, mm: 8

Combustion Mixture : Air-Acetylene; Stoichiometric Flame

Reagents:

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

Releasing Agent Stock Solution: Dissolve 31.67 grams of dried cesium chloride (CsCl) in deionized water to a volume of 250 mL. Final concentration is  $100,000 \mu\text{g mL}^{-1}$  Cs.

Working Standards: Dilute stock solution to 1.000, 0.750, 0.500, 0.250, and  $0.100 \mu\text{g mL}^{-1}$  with  $0.016 \text{ N HNO}_3$ . Add 1.0% by volume CsCl stock solution; final Cs concentration is  $1000 \mu\text{g mL}^{-1}$ . A blank is prepared with  $0.016 \text{ N HNO}_3$  diluted 1.0% with CsCl stock solution.

Sample Preparation: Combine  $25.0 \mu\text{L}$  of ionization suppressant to 2.5 mL of sample. Concentration is read directly on the instrumental digital display.

Sensitivity :  $0.02 \mu\text{g mL}^{-1}$ .

Detection Limit :  $0.004 \mu\text{g mL}^{-1}$ .



Mg <sup>++</sup> Magnesium
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Instrumental Mode: Flame atomic absorption

Wavelength, nm : 285.2      Bandpass, nm : 1.0

Light Source : K HCL      Lamp Current, ma : 6

Photomultiplier Tube : R372      Photomultiplier Voltage, v : 530

Burner : Single slot      Burner Height, mm: 8

Combustion Mixture : Air-Acetylene; Stoichiometric Flame

Reagents:

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

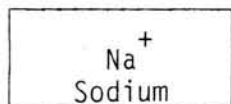
Releasing Agent Stock Solution: Dissolve 117.28 grams of lanthanum oxide ( $\text{La}_2\text{O}_3$ ) in 500 mL of 6 N HCL and dilute to a final volume of 1 liter with deionized water. Final concentration is 100,000  $\mu\text{g mL}^{-1}$  La. Lanthanum prevents interference from phosphates, aluminum and silicates.

Working Standards: Dilute stock solution to 1.000, 0.750, 0.500, 0.250, and 0.100  $\mu\text{g mL}^{-1}$  with 0.016 N  $\text{HNO}_3$ . Add 1.0% by volume La solution; final La concentration is 1000  $\mu\text{g mL}^{-1}$ . A blank is prepared with 0.016 N  $\text{HNO}_3$  diluted 1.0% with La stock solution.

Sample Preparation: Combine 25.0  $\mu\text{L}$  of releasing agent to 2.5 mL of sample. Concentration is read directly on the instrumental digital display.

Sensitivity : 0.003  $\mu\text{g mL}^{-1}$ .

Detection Limit : 0.002  $\mu\text{g mL}^{-1}$ .



Instrumental Mode: Flame atomic absorption

Wavelength, nm	: 589.0	Bandpass, nm	:	0.5
Light Source	: Na HCL	Lamp Current, ma	:	7
Photomultiplier Tube	: R446 or R372	Photomultiplier Voltage, v	:	700
Burner	: Single slot	Burner Height, mm:	:	8

Combustion Mixture : Air-Acetylene; Stoichiometric Flame

Reagents:

Stock Standard Solution: Dissolve 2.5420 grams of dried sodium chloride (NaCl) in deionized water and dilute to a volume of 1 liter. Final concentration is 1000  $\mu\text{g mL}^{-1}$  Na.

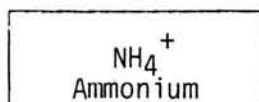
Releasing Agent Stock Solution: Dissolve 31.67 grams of cesium chloride (CsCl) in deionized water to a volume of 250 mL. Final concentration is 100,000  $\mu\text{g mL}^{-1}$  Cs.

Working Standards: Dilute stock solution to 1.000, 0.750, 0.500, 0.250, and 0.100  $\mu\text{g mL}^{-1}$  with 0.016 N  $\text{HNO}_3$ . Add 1.0% by volume CsCl solution; final Cs concentration is 1000  $\mu\text{g mL}^{-1}$ . A blank is prepared with 0.016 N  $\text{HNO}_3$  diluted 1.0% with CsCl stock solution.

Sample Preparation: Combine 25.0  $\mu\text{L}$  of ionization suppressant to 2.5 mL of sample. Concentration is read directly on the instrumental digital display.

Sensitivity : 0.010  $\mu\text{g mL}^{-1}$ .

Detection Limit : 0.004  $\mu\text{g mL}^{-1}$ .



Method: Automated Colorimetric Phenate

Instrumental Mode:

Auto Sampler III.

No. of Samples/Hr.: 60

Sample/Wash: 6/1

Sample Volume, mL : 0.5-1.0

Gilson "minipuls 2" Peristaltic Pump Tubes.

Color	Flow Rate (mL/min)	Application*
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.

Mixing Coils: (2) 20 turns

Heating Bath: 50°C

Single Channel Colorimeter.

Reversing Switch: Direct (D)

Wavelength, nm: 630

Flow Cell Path Length, mm: 15

F/C ID, mm: 2

Damp: Normal

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

Strip Chart Recorder. 1 cm/min Chart Speed

Typical Standard Curve:

mgL <sup>-1</sup> NH <sub>4</sub> <sup>+</sup>	Peak Height (cm)
.10	.65
.25	2.45
1.00	9.70
2.00	19.75

Limit, Range, Interferences:

Detection Limit, mgL<sup>-1</sup>: 0.02

Working Range, mgL<sup>-1</sup>: 0.0-2.0

Interferences: No significant interferences.

Summary of Method:

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

Procedure:

Analysis. The precipitation sample containing ammonium ions is introduced into the system and mixed with the complexing agent to prevent formation of heavy hydroxide precipitates. Alkaline phenol and sodium hypochlorite solutions are added and react with the ammonium ions to form a blue-colored complex. Sodium nitroprusside is added to intensify the blue color. The resulting solution is then pumped through a 50°C constant temperature bath. The intensity of the blue-colored complex is determined colorimetrically at 630 nm and is proportional to the concentration of ammonium ions present in the precipitation sample.

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

Reagents:

Stock Standard Solution, 1000 mgL<sup>-1</sup> NH<sub>4</sub><sup>+</sup>. Dissolve 2.9654 grams of dried ammonium chloride (NH<sub>4</sub>Cl) and dilute to 1 liter with deionized water.

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

Complexing Reagent. Dissolve 33 grams of potassium sodium tartrate (KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·4H<sub>2</sub>O) and 24 grams of sodium citrate --(HOC(COONa)- (CH<sub>2</sub>(COONa)<sub>2</sub>·2H<sub>2</sub>O)-- in 950 mL of deionized water. Adjust the pH to 5.0 with 2.5 mL conc. H<sub>2</sub>SO<sub>4</sub>. Dilute to 1 liter with DI.

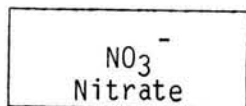
Alkaline Phenol. Add 35 grams of sodium hydroxide (NaOH) to 250 mL DI slowly and with stirring. Allow to cool and slowly add 85 mL of an 88% phenol solution (carbolic acid). Dilute to 500 mL with DI. Add 0.25 mL Brij-35. Filter through glass wool. Store in an amber glass bottle. Stability is three days.

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 1 liter with DI.

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.



Method: Automated Colorimetric Cadmium Reduction

Instrumental Mode:

Auto Sampler III.

No. of Samples/Hr.: 40

Sample/Wash: 4/1

Sample Volume, mL: 0.5-1.0

Gilson "minipuls 2" Peristaltic Pump Tubes.

Color	Flow Rate (mL/min)	Application*
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.

Mixing Coils: 5 and 20 turns

Column Type: Copper-Cadmium Reduction

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

Single Channel Colorimeter.

Reversing Switch: Direct (D)      Wavelength, nm: 520

Flow Cell Path Length, mm: 15      F/C ID, mm: 2

Damp: Normal

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

Strip Chart Recorder. 40 cm/hr. Chart Speed

Typical Standard Curve:

mgL <sup>-1</sup> NO <sub>3</sub> <sup>-</sup>	Peak Height (cm)
.10	.25
.50	1.55
1.00	3.50
2.00	7.90
4.00	15.75
5.00	19.50

Limit, Range, Interferences:

Detection Limit, mgL<sup>-1</sup>: 0.02

Working Range, mgL<sup>-1</sup>: 0.0-5.00

Interferences: High concentrations of Cl<sup>-1</sup> and metal ions  
Air bubbles in reduction column, exhaustion of column

Summary of Method:

Technicon Auto Analyzer Colorimetric measurement 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. The intensity of this dye, measured at 520 nm, is proportional to the nitrite ion concentration.

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

Reagents:

Stock Standard Solution, 1000 mgL<sup>-1</sup> NO<sub>3</sub><sup>-</sup>. Dissolve 1.3707 grams of sodium nitrate (NaNO<sub>3</sub>) per liter of deionized water.

Sampler Rinse Water. Deionized water.

Alkaline Water, pH 8.5. Add 1.8 mL of ammonium hydroxide (NH<sub>4</sub>OH) per liter of deionized water.

Ammonium Chloride Reagent, pH 8.5. Dissolve 10 grams of ammonium chloride (NH<sub>4</sub>Cl) in 1 liter Alkaline Water. Add 0.25 mL Brij-35.

Color Reagent. To 400 mL DI add 5 grams of sulfanilamide ( $C_6H_8N_2O_2S$ ), 50 mL phosphoric acid ( $H_3PO_4$ ), and 0.25 grams of N-1-Naphthylethylenediamine dihydrochloride ( $C_{12}H_{14}N_2 \cdot 2HCl$ ). 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 ( $CuSO_4 \cdot 5H_2O$ ) 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.

#### Preparation of Reductor Column:

Fill the reductor column with DI. 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 end of the U-tube for 2.5 min. and rinse with DI for 2.5 min. Then pump  $CuSO_4$  through the other end 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. For initial activation of the column, pump a  $100 \text{ mgL}^{-1} \text{ NO}_3^-$  standard for 5 min.

#### Reference:

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.



PO<sub>4</sub><sup>3-</sup>  
Phosphate

Method: Automated Colorimetric Ascorbic Acid Reduction

Instrumental Mode:

Auto Sampler II.

No. of Samples/Hr.: 30

Sample/Wash: 2/1

Sample Volume, mL: 1.5-2.0

Gilson "minipuls 2" Peristaltic Pump Tubes.

Color	Flow Rate (mL/min)	Application*
Grn/Grn	2.00	DI to sampler wash receptacle
Wht/Wht	0.60	Sample
Orn/Grn	0.10	Air
Orn/Wht	0.23	Debubbler to waste
Orn/Grn	0.10	Air
Orn/Grn	0.10	Color Reagent
Orn/Wht	0.23	From F/C to waste

Phosphate Cartridge.

Mixing Coils: (2) 5 turns

Heating Bath: 37°C

Single Channel Colorimeter.

Reversing Switch: Direct (D)      Wavelength, nm: 880

Flow Cell Path Length, mm: 50      F/C ID, mm: 1.5

Damp: Normal

\*See Technicon AA II Method No. 155-71W for schematic diagram. We modified the Technicon procedure to determine lower PO<sub>4</sub><sup>3-</sup> concentrations.

Strip Chart Recorder. 30 cm/hr. Chart Speed

Typical Standard Curve:

mgL <sup>-1</sup> PO <sub>4</sub> <sup>3-</sup>	Peak Height (cm)
.010	2.30
.025	5.50
.050	11.70
.100	24.40

Limit, Range, Interferences:

Detection Limit, mgL<sup>-1</sup>: .003

Working Range, mgL<sup>-1</sup>: 0.0-.100

Interferences: No significant interferences

Summary of Method:

Technicon Auto Analyzer Colorimetric measurement of molybdenum blue complex after reduction with ascorbic acid (Murphy and Riley, 1962) (Lennox, 1979).

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. The intensity of the blue-colored compound is determined colorimetrically at 880 nm and is proportional to the concentration of phosphate ions present in the precipitation sample.

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

Reagents:

Stock Standard Solution, 100 mgL<sup>-1</sup>PO<sub>4</sub><sup>3-</sup>. Dissolve 143.47 mg potassium phosphate (KH<sub>2</sub>PO<sub>4</sub>) in DI. Dilute to 1 liter with deionized water. Add 1 mL chloroform (CHCl<sub>3</sub>).

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

Sulfuric Acid, 4.9 N Stock Solution. Add 136 mL of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) to 800 mL DI. Cool and then dilute to 1 liter with DI. Store in a LPE bottle.

Ammonium Molybdate Stock Solution. Dissolve 40 grams of ammonium molybdate ((NH<sub>4</sub>)<sub>6</sub> Mo<sub>7</sub> O<sub>24</sub>·4H<sub>2</sub>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 ( $C_6H_8O_6$ ) 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 ( $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$ ) 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:

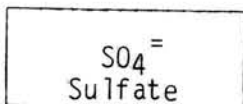
50 mL sulfuric acid  
15 mL ammonium molybdate  
30 mL ascorbic acid  
5 mL antimony potassium tartrate

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

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.

Lennox, L. J., 1979: An automated procedure for the determination of phosphorus. Water Research, 13, 1329-1333, Pergamon Press Ltd.



Method: Automated Colorimetric Barium-Methythymol Blue Complex

Instrumental Mode:

Auto Sampler II.

No. of Samples/Hr.: 30

Sample/Wash: 6/1

Sample Volume, mL: 3.0-3.5

Gilson "minipuls 2" Peristaltic Pump Tubes.

Color	Flow Rate (mL/min)	Application*
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.

Mixing Coils: 22, 20, and 7 turns

Column Type: Ion Exchange Resin

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

Single Channel Colorimeter.

Reversing Switch: Inverse (I)      Wavelength, nm: 460

Flow Cell Path Length, mm: 15      F/C ID, mm: 2

Damp: 2

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

Strip Chart Recorder. 30 cm/hr. Chart Speed

Typical Standard Curve:

mgL <sup>-1</sup> SO <sub>4</sub> <sup>=</sup>	Peak Height (cm)
0.50	.65
1.00	1.50
2.50	4.25
5.00	9.20
7.00	14.20
10.00	21.10

Limit, Range, Interferences:

Detection Limit, mgL<sup>-1</sup>: 0.10

Working Range, mgL<sup>-1</sup>: 0.0-10.00

Interferences: Anions such as PO<sub>4</sub> and SO<sub>3</sub> could result in a positive error. Cations such as calcium, aluminum, and iron are removed by the ion exchange column.

Summary of Method:

Technicon Auto Analyzer Colorimetric measurement 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. Excess barium ions react with an equivalent concentration of methylthymol blue to form a blue-colored chelate. The intensity of the unchelated MTB is determined colorimetrically at 460 nm. The concentration of unchelated MTB ions is equal to the initial sulfate ion concentration.

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.

Reagents:

Stock Standard Solution, 1000 mgL<sup>-1</sup>SO<sub>4</sub><sup>=</sup>. Dissolve 1.4789 grams of sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) in 900 mL of deionized water. Dilute to 1 liter with DI.

Sampler Rinse Water. Deionized water.

Barium Chloride Stock Solution. Dissolve 1.526 grams of barium chloride (BaCl<sub>2</sub>·2H<sub>2</sub>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<sub>2</sub> Stock Solution and 4 mL of 1 N HCl to 0.1182 grams of methylthymol blue (3'3" - Bis-N, N-bis (carboxymethyl) - amino methylthymolsulfonephthalein 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<sub>4</sub>Cl) and 57 mL conc. ammonium hydroxide (NH<sub>4</sub>OH) 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).

#### Preparation of Column:

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

#### Reference:

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

LIST OF ABBREVIATIONS

ACS	American Chemical Society
HCL	Hollow cathode lamp
IL	Instrumentation Laboratory, Inc. Wilmington, MA.
LPE	Linear polyethylene
ma	Milliampere
mm	Millimeter
nm	Nanometer ( $10^{-9}$ meter)
Sensitivity	Amount of analyte necessary to give an absorption signal of 1% (.0044 absorbance)
n.a.	Not applicable
mL	Milliliter (.001 L)
$\mu$ L	Microliter ( $10^{-6}$ L)
DI	Deionized water

EQUIPMENT LIST

1. Orion Model 811 pH meter with Beckman Futura microcombination electrode.
2. Metrohm Model 103 pH meter with microcombination electrode.
3. Yellow Springs Instrument Company manually balanced AC bridge with glass microelectrode; cell constant = 1.
4. Technicon AutoAnalyzer (5 units).
5. Instrumentation Laboratory Models 353 and 151 Atomic Absorption Spectrophotometers.
6. Sartorius Model 2474 microbalance.
7. Ohaus Model 1119-D solution balance.
8. Mettler Model 4400 electronic balance.
9. Millipore glass filtration system.

References to specific brand names, products, or manufacturers do not constitute endorsement by the Illinois State Water Survey or the National Atmospheric Deposition Program.



