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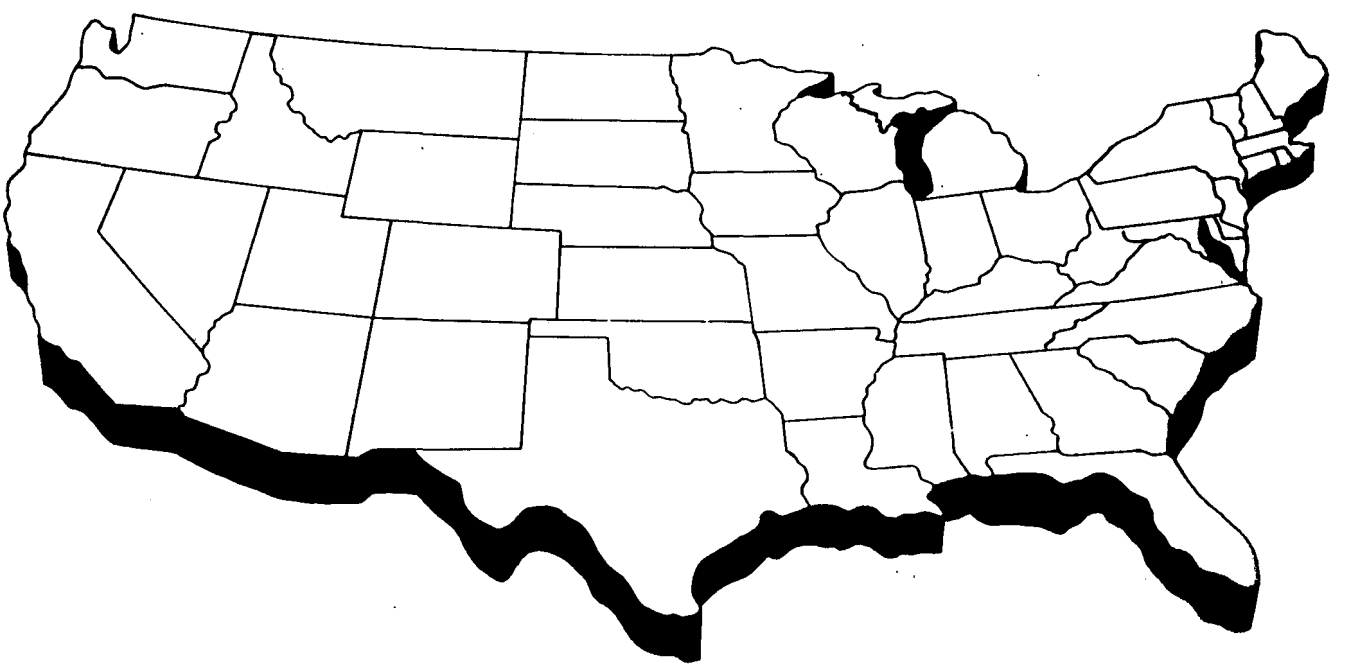
WET DEPOSITION AND SNOWPACK MONITORING OPERATIONS AND QUALITY ASSURANCE MANUAL



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WET DEPOSITION AND SNOWPACK MONITORING OPERATIONS AND QUALITY ASSURANCE MANUAL

by

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NOTICE

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ABSTRACT

This manual (user's guide) describes the quality assurance plan and operations protocols for a comparative study of snow collection instruments being conducted on Mt. Evans. Instruments to be compared include the Aerochem Metrics Model 301 wet/dry deposition collector, the Belfort Model 780-5 weighing rain gage, and 18 inch-diameter flanged bulk samplers. In addition, ground measurements are made to provide a "ground truth" standard. Primary project objectives include assessment of operational reliability, estimation of inter-instrument and temporal variability, comparison of water equivalent and matrix chemistry between the collection devices and ground measurements, and recommendation of instruments and sampling intervals for future high altitude, complex terrain monitoring. The protocols related to quality assurance, quality control, calibration, operation, maintenance, processing, analysis, and data management are described. As such, this manual is considered to be of greatest benefit to field operators, laboratory analysts, and project managers.

This manual is submitted in partial fulfillment of Contract 68-03-3249 by Lockheed-EMSCO under the sponsorship of the U.S. Enironmental Protection Agency. This manual covers operations from February 1987 to June 1987, and work will be completed as of December 1987.

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1.0 INTRODUCTION

Established acidic deposition monitoring networks largely neglect the high elevation areas of the western United States. Interest in these areas is growing, particularly for the Rocky Mountain region, because of evidence that precipitation amount, and possibly total chemical loading, is strongly correlated with elevation (Svoboda and Olson, 1986). Most monitoring equipment and siting criteria were developed for low elevation, flat-land sites. Meteorology in mountainous terrain is significantly more complex, and precipitation levels are higher than at low-elevation sites. Research on the suitability of existing instruments for use at high altitude is needed before large funding and personnel resources are committed to monitoring acidic deposition in mountainous terrain.

The National Atmospheric Deposition Program (NADP), EPA Region VIII, and U.S. Forest Service are participating in an investigation of equipment performance at high altitude. The University of Denver High Altitude Laboratory, EPA Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV), and the prime contractor for EMSL-LV, Lockheed Engineering and Management Services Company, Inc. (Lockheed-EMSCO), are responsible for equipment installation, field station operation, and data interpretation. EMSL-LV and Lockheed-EMSCO have primary responsibility for construction of the monitoring platform, installation of equipment, operator training, snow density/coring activities, data verification and interpretation, chemical analyses, and quality assurance. Instruments to be evaluated include the Aerochem Metrics Model 301 wet/dry deposition collector, the Belfort weighing rain gage, and bulk samplers. Snow density, snow coring, and event sampling also are being undertaken to provide a "ground truth" comparison. Samplers are to be evaluated in terms of reliability and ease of operation, catch efficiency, and resultant sample matrix chemistry. Meteorological sensors located on the monitoring platform will provide information on the meteorological environment surrounding the collectors.

The selected site is the High Altitude Laboratory operated by the University of Denver. The High Altitude Laboratory is located adjacent to the Mount Evans highway near Echo Lake, 14 miles south of Idaho Springs, Colorado. The site offers several advantages: the terrain is complex, and the area is subject to large amounts of precipitation and to high winds; the site is accessible even in winter, it has electrical power, and it is inhabited year-round. A National Oceanic and Atmospheric Administration (NOAA) monitoring station located near the monitoring platform can provide additional meteorological information. Monitoring is to begin as soon as possible after construction of the monitoring platform and is to continue through the winter of 1986-87. Operation is scheduled to cease in mid-June 1987.

This manual details the equipment operation, chemical analyses, and quality assurance plan for the wet deposition and snowpack monitoring project. It is designed to be of primary benefit to the station operator,

laboratory analysts, and data analysts. The protocols presented here may be revised over the course of the program to reflect necessary changes and improvements in procedures. Related documents include an operations status report which will be delivered in June 1987 and a final report on the evaluation results which will be provided in January 1988.

2.0 PROJECT DESCRIPTION

Snowpack and wet deposition monitoring on Mount Evans is being conducted to assess the suitability of selected collection devices to high altitude, complex terrain situations. Specific objectives of the project are as follows:

- Inter-instrument sampling variability for two colocated wet/dry collectors will be estimated by comparing chemistry and water equivalent for weekly samples.
- Inter-instrument sampling variability for two colocated Belfort weighing rain gages will be estimated by comparing water equivalent for event and weekly data.
- Temporal variability will be estimated by comparing chemistry and water equivalent of wet/dry collector event samples to weekly samples.
- Inter-instrument sampling variability for two colocated bulk samplers will be estimated by comparing chemistry and water equivalent for weekly samples.
- A "ground truth standard" for estimating the accuracy of all collection instruments will be estimated by comparing sample chemistry to the chemistry of snowpack cores taken to snowboards. The comparison will be made on samples collected after events.
- A "ground truth standard" for estimating the accuracy of all collection instruments will be provided by comparing water equivalent of samples collected after events and collected weekly. The comparison will be made on snow pit density measurements and on snowboard measurements.
- Instruments and sampling intervals for high altitude, complex terrain situations will be recommended based on results of all the above comparisons.
- Operational reliability will be assessed in qualitative terms of types of instrument malfunctions, length of downtime, cause and resolution of problems, ease of operation, frequency and difficulty of maintenance, and sample contamination.

Instruments to be assessed include three Aerochem Metrics Model 301 wet/dry deposition collectors, two Belfort Model 5-780 weighing rain gages, and two 18-inch-diameter flanged bulk samplers. The wet/dry collector and Belfort rain gage are the standard instruments used by NADP and by other major monitoring and research networks. The Belfort gages are unshielded;

recent studies indicate that the Alter windshield is not effective at wind speeds greater than 3 mph (Goodison et al., 1981; Goodison and Metcalfe, 1982). The bulk sampler design is identical to that used by the United States Geological Survey (USGS) in snow studies. Supplemental instrumentation includes Science Associates Models 424-1 and 424-2 wind speed/wind direction sensors and a data acquisition system (DAS) composed of an IBM at personal computer and Metrobyte logic boards. Snow coring equipment and the Taylor-LaChapelle snow-density kits used are manufactured by Hydro-Tech. Snowboards are fabricated by Lockheed-EMSCO of polyurethane-coated plywood.

The collection devices and meteorological sensors are mounted on a 20-foot-diameter octagonal wooden platform erected on a southeast-facing slope at the maximum expected snowpack height (19 feet at the point closest to the ground). Cables connect the sensors to the DAS which is located approximately 275 feet distant in a heated building. The platform is accessed by steps located on the uphill (NNE) side. The closest tree tops subtend an angle of 47° ± 3°. The nearest of several buildings is located 28 feet NNW of the platform. A fireplace in one of these buildings is a possible source of contamination; however, the building is more than 500 feet away and is shielded by other buildings and by trees.

The monitoring equipment and DAS are checked daily by an on-site operator. In addition, a Lockheed-EMSCO scientist visits the site at least once a month. During most of the study, samples are collected from two wet/dry collectors and two bulk samplers on a weekly basis or more frequently as required by event loading. Samples are collected from the third wet/dry collector daily. Snowboard cores and snow pit density measurements are taken weekly. During a 30-day period, two wet/dry collectors are operated on a daily basis, and the third is operated on a weekly basis. Snow cores and snow pit density measurements are taken daily as well as weekly during this same 30-day period.

No analyses are performed in the field. On a weekly basis, all samples are shipped frozen to Lockheed-EMSCO in Las Vegas, Nevada, where water equivalents are determined and where melted samples are processed. Processing includes pH and specific conductance measurements, which are completed immediately after melting, and filtration and preservation of aliquots for subsequent analysis. Analyses for chloride and ammonium are completed approximately every two weeks; analyses for metal cations, nitrate, and sulfate are completed every four weeks. All analyses are completed within recommended holding times for the chemical variable of interest and preservation treatment used.

Data from the field, processing laboratory, and anaytical laboratory are compiled into a single database; because of the small size of the database, an IBM-PC is used for data compilation. Quality control sample data are used to verify the data; data of poor or unknown quality are deleted.

Statistical tests, including paired t-tests, %RSD, and means, are employed to quantify the project objectives. Other interpretative schemes may be developed dependent upon the initial intra- and inter-comparison results.

An interim progress report, detailing field and laboratory operations, will be delivered in June 1987. A final project report will be available in January 1988. The final report will include interpretative results, assessment of instrument reliability, and recommendations for future snowpack monitoring and research.

3.0 QUALITY ASSURANCE PLAN

The Quality Assurance (QA) policy of EPA requires that every monitoring and measurement project have a written and approved QA project plan (Costle, 1979a and 1979b). This requirement applies to all environmental monitoring and measurement efforts authorized or supported by EPA through regulations, grants, contracts, or other formal means. The QA project plan should specify the policies, organization, objectives, functional activities, and specific quality control (QC) procedures designed to achieve the data quality goals of the project. As used herein, QC is the specific procedures and checks used to provide a quality product, while QA is the overall system used to ensure that the QC system is performing. All project personnel should be familiar with the policies and objectives outlined in the operations and QA plan to ensure proper interactions among the field operations, laboratory operations, and data management.

3.1 QUALITY ASSURANCE OBJECTIVES

QA objectives are defined in terms of precision, accuracy, completeness, representativeness, and comparability.

3.1.1 Precision and Accuracy

The QA objectives for precision and accuracy of the parameters being measured are given in Table 3-1. Precision, defined as the mutual agreement among individual measurements of the same property, is expressed in terms of percent relative standard deviation (%RSD). Precision is calculated from results of duplicate analyses and repetitive analyses of audit samples and quality control check solutions. Accuracy is the degree of agreement of a measurement with an accepted or true value. It is expressed as percent bias and is determined from the difference between recorded measurements and accepted true values of audit samples, quality control check solutions, and calibration standards.

An additional estimate of precision is provided by the two colocated wet/dry collectors, Belfort rain gages, and bulk samplers. It is common practice in many studies to designate one unit as the primary or routine sampler and the other as a secondary or duplicate sampler. This practice, in effect, designates samples from the secondary unit as QC samples.

Because one of the project objectives is estimation of inter-instrument sampling variability (i.e., quantification of precision limits), units used in this project will not receive primary and secondary designations. Consequently, a field duplicate is not included as one of the QC samples described below. Analysis of the data on colocated samplers is included in the data interpretation scheme, as discussed in Section 6.0 of this manual.

TABLE 3-1. QUALITY ASSURANCE OBJECTIVES FOR DETECTABILITY, PRECISION, AND ACCURACY

Parameter[a]	Units	Expected Range[b]	Required Detection Limits (NADP)	Precision[c] Percent Relative Standard Deviation (%RSD) Upper Limit (%)	Accuracy Max. Absolute Bias (%)
Ca^{2+}	mg/L	0.005-0.160	0.03	5	10
K^{+}	mg/L	0.010-0.30	0.01	5	10
Mg^{2+}	mg/L	0.003-0.051	0.01	5	10
Na^{+}	mg/L	0.01-0.026	0.01	5	10
Cl^{-}	mg/L	0.01-1.00	0.02	5	10
SO_4^{-2}	mg/L	0.04-0.32	0.10	5	10
NO_3^{-}	mg/L	0.002-0.120	0.02	10	10
NH_4^{+}	mg/L	0.003-0.180	0.025	5	10
pH	pH units	5.1-5.9	pH > 5.0	±0.30	±0.03
			pH < 5.0	±0.10	±0.10
Specific Conductance	µS/cm	1.78-6.10	0.6 µS/cm	10-100-3%	5%
				> 100 - 1%	2%

[a]Dissolved ions and metals are being determined.
[b]Ranges are for snowpack. Laird et al. (1986).
[c]Unless otherwise noted, this is the %RSD at concentrations approximately 10 times the instrument detection limit.
Modified from: Drouse et al. (1986).

External and internal QA and QC samples include the following:

Field Blank - A field blank is a deionized water sample meeting specifications for ASTM Type 1 reagent water (ASTM, 1984) that is poured into a clean sample bucket by the site operator and, thereafter, is treated as though it were a routine sample. One field blank accompanies each weekly sample shipment. Field blank data are used to establish the estimated system background value that can be expected for each type of chemical analysis. For data interpretation, a data point above the 95 percentile of the field blank value is considered a positive response. Blanks above the 80 percentile are investigated for contamination.

Bucket Blank - A bucket blank is a deionized water sample meeting specifications for ASTM Type I reagent water (ASTM, 1984) that is poured into a clean sample bucket in the processing laboratory and, thereafter, is processed and analyzed as though it were a routine sample. A minimum of 5 percent of each lot of washed buckets and lids are retained and

stored at the processing laboratory until the next sample shipment arrives. The bucket blanks are then prepared and incorporated into the sample batch. Bucket blank data are used to establish the estimated system background values associated with the bucket washing procedure. Data interpretation is the same as described for field blanks, above.

Audit - An audit sample is a material with known characteristics which is used to determine the accuracy of the measurement system. Several types of audit samples are used in this project and are described below.

A processing laboratory audit provides a known measure of pH and specific conductance. These samples are prepared by a group within Lockheed-EMSCO, separate and distinct from either the processing laboratory or analytical laboratory.

An analytical laboratory audit is a set of pre-prepared aliquots that are incorporated into the batch at the processing laboratory. Five synthetic audits are prepared for each of three concentration ranges for each chemical parameter.

National Bureau of Standards (NBS) audit samples are incorporated into the batch in two ways: (1) as packaged and received, and (2) diluted at the processing laboratory and packaged as an aliquot set. Six of each are used.

Field QC methods are limited to (1) sandbag weights used in the field to measure the accuracy of the Belfort weighing rain gages and to (2) periodic calibrations of the meteorological sensors and of the Belfort rain gages.

Internal laboratory QC samples for the processing and analytical laboratories include the following:

Initial Calibration - An initial calibration is performed on each day of analysis or as required for each analytical method. The concentrations of the calibration standards must bracket the expected sample concentrations. Occasionally, the standards recommended for a method must be adjusted to meet this requirement. The concentration of the low calibration standard should not be more than 10 times the detection limit. If, during the analysis, the concentration of the sample is above the linear dynamic range (LDR), two options are available. One option is to dilute and reanalyze the sample. Alternatively, two concentration ranges may be calibrated. Samples are first analyzed on the lower concentration range. Each sample with a concentration exceeding the upper end of the LDR is then reanalyzed at the higher concentration range. If the second option is taken, separate QC samples must be analyzed and reported for each range.

Quality Control Check Sample - Immediately after the instruments are calibrated, a Quality Control Check Sample (QCCS) containing the analyte of interest at a concentration that is in the middle of the calibration range must be analyzed. The QCCS may be obtained commercially, or it may be prepared by the analyst from a source which is independent of the calibration standards. The QCCS must be analyzed to verify the calibration curve prior to any other sample analyses, after every 10 samples, and after the last sample. If the measured value for a QCCS differs from the theoretical value by more than five percent (10 percent for nitrate), the instrument must be recalibrated, and all samples that were analyzed after the last acceptable QCCS must be reanalyzed.

The measured concentrations for the QCCS's also must be plotted on a control chart, and the 99 percent and 95 percent confidence intervals must be calculated. Monthly the control charts are updated, cumulative means are calculated, and new warning limits (95 percent) and control limits (99 percent) are determined. If the 99-percent control limit differs from the theoretical concentration by more than the limit given in Table 3-1, the QA manager or laboratory manager must be notified. To ensure the continuity of the control chart, all of the QCCS's must have the same theoretical concentration and must be from the same source.

Detection Limit QCCS - A sample containing the analyte of interest at a concentration two to three times the required detection limit, a detection limit QCCS, is analyzed once per batch, and the results are reported. The purpose of the detection limit QCCS is to eliminate the necessity of formally determining the detection limit on a daily basis. The measured value must be within 20 percent of the theoretical concentration. If it is not, the problem must be identified and corrected, and an acceptable result must be obtained prior to sample analysis.

Calibration Blank - A calibration blank must be analyzed once per batch, immediately after the initial calibration, to check for baseline drift. The instrument is rezeroed if necessary. The calibration blank is defined as a "0" mg/L standard and contains only the matrix of the calibration standards. The measured concentration of the calibration blank must be less than or equal to twice the required detection limit. If it is not, the calibration must be rechecked.

Duplicate Sample Analysis - One sample per batch must be prepared and analyzed in duplicate for each parameter. The %RSD is calculated as:

$$\%RSD = \frac{S}{\overline{X}} \times 100$$

$$S = \left(\frac{\Sigma(\overline{X} - X)^2}{n-1} \right)^{1/2}$$

where S = the standard deviation of the duplicate pair

X = a datum

$\overline{X}$ = the mean of the duplicate pair

n = the number of sample and duplicate (n = 2)

Control limits are set at the precision levels given in Table 3-1. If the observed precision of a duplicate pair falls outside the control limits and if the analyte concentration is greater than 10 times the detection limit, the source of the variability (e.g., instrument malfunction, calibration drift) must be sought and eliminated. A second, different sample then must be analyzed in duplicate. Further samples may not be analyzed until the duplicate sample results are within the prescribed %RSD limits, unless the QA manager gives approval.

3.1.2 Completeness

Completeness refers to the amount of valid data that is obtained from a measurement system compared to the amount expected to be obtained under normal conditions. The completeness objective for total possible field observations of event, daily, weekly, or longer term composite samples is 80 percent. Instruments that do not to meet this objective also do not meet the project objective of operational reliability.

3.1.3 Representativeness

This study is designed to achieve the objectives outlined in Section 2.0. As the objectives primarily relate to collection variability, the data are representative if sources of variability other than collection are minimized or eliminated. Independent quality control checks are associated with each step of operation, analysis, and interpretation. These checks are designed to quantify and minimize the variability inherent in each step. This process reduces sources of variability including processing, analysis, and operator variability.

Spatial variability represents an exception. Snowpack depth recordings are taken at multiple points in an attempt to quantify spatial variability. However, these measurements are taken at ground level; spatial variability across the platform, including the possible effect of the close clustering of instruments, is not quantifiable in this design. An assumption has

been made that spatial variability is insignificant in relation to collection variability.

3.1.4 Comparability

Most of the project objectives are stated in terms of comparisons, including comparisons of same and different sampling methodologies and comparisons of same and different sampling intervals. These comparisons require that the data be reported in a uniform set of units. A uniform set of procedures for the site and laboratory ensures that any observed variability is due to the variable of interest rather than to a lack of comparability in sample collection or treatment. Uniform units and procedures, coupled with data quality estimates, permit comparison of data collected in this study to data collected in other snow monitoring and research studies.

3.2 FIELD OPERATIONS QA

The field QA/QC program includes consideration of siting criteria, facilities, instrument operation, sample handling, and documentation. Avoidance of sample contamination is of particular concern because the samples are of low ionic strength; analytes introduced by simply touching the bucket interior may exceed analyte concentrations present in the sample. Continuity of field operations is ensured by adherence to documented protocols. These protocols or standard operating procedures (SOP's) are discussed in Section 4.0.

3.2.1 Siting Criteria and Facilities

The siting criteria set forth in the draft document by Svoboda and Olsen (1986) are met as closely as possible. These criteria include consideration of spacing from objects which may influence micrometeorological conditions, separation from sources of local pollutants, and orientation of collection devices. A complete site description, including photographs, is to be included in the project documentation.

Facilities requirements include adequate electrical power, site accessibility during events, accessibility to shipping facilities, heated sheltering for the DAS, cold storage for samples, and a clean area for sample handling. The selected site meets all of these needs. The University of Denver High Altitude Research Laboratory supplies electrical power and on-site heated facilities for site operator residence, DAS shelter, and sample handling. Collected samples may be stored in an unheated building since ambient temperature should provide adequate refrigeration. A United Parcel Service (UPS) facility is located in Idaho Springs, and the site access road is kept open year-round.

3.2.2 Instrument Operation

In this project, collection instruments of the same model are intra-compared to estimate sampling variability and different model instruments are compared to each other and to "ground truth" measures to estimate sampling accuracy. Instruments are also evaluated in terms of operational reliability. To achieve these objectives, it is imperative that the instruments be operated so as to achieve maximum performance and so that complete, detailed records be maintained of field operations.

Detailed SOP's that are based on manufacturers instructions and on experience gained in previous studies ensure peak performance and comparability of sampling methods. The SOP's contain instructions for calibration, QC checks, routine and preventive maintenance, operator checks, and troubleshooting. A limited spare parts inventory is maintained to minimize downtime caused by component malfunction. Supplies of consumable items are maintained and periodically are inventoried to ensure uninterrupted operation. Each instrument is operationally tested prior to deployment and again upon installation. The site operator undergoes a training program including "hands-on" experience prior to initiation of sampling. Monthly on-site visits by a Lockheed-EMSCO scientist include evaluation of operator performance and "refresher" training.

Field documentation includes outputs of the DAS, field forms that accompany sample shipment, and an operator logbook. The operator is encouraged to record all observations in the logbook. The logbook also serves as a calibration and maintenance record and tracks malfunctions from symptoms through final resolution.

3.2.3 Sample Handling

Parameters used for instrument comparisons are snow chemistry and water equivalent. It is essential that samples be handled so as to minimize potential contamination or sample loss. During the collection period, the reciprocating lid of the wet/dry collector must operate properly by exposing the wet bucket during periods of precipitation and by sealing tightly during dry periods. The foam lid seal surface also must be clean to avoid contamination. Wind scour is a potential source of sample loss for all collection devices. Wet/dry collector and bulk sampler collection vessels (buckets and bags, respectively) should be checked frequently and should be changed if nearly full. A line indicating volume is marked on the collection vessel immediately after removal, i.e., before any contents settling occurs. An antifreeze/oil mixture helps prevent wind scour and evaporative losses from the Belfort rain gages.

The site operator wears sterile or clean rubber gloves when touching

sample collection vessels. Wet/dry collector buckets are sealed with the lid accompanying the to-be-installed bucket rather than with the lid that accompanied the to-be-removed bucket. Any post-sampling in-field washing, e.g., washing of the snow density and coring equipment, is done with deionized (DI) water prior to sampling, and snow density and coring equipment are rinsed with visually clean snow of the same type that is to be sampled. All collected samples are sealed and placed in clean plastic bags for storage and shipment.

3.2.4 Documentation

Field documentation includes:

- DAS outputs
- Field forms
- Belfort rain gage charts
- Operator logbook
- Photographs

The recording medium for the DAS is floppy diskette. In addition, hardcopy outputs may be obtained from the printer. Disks are retrieved and are transported to Las Vegas by a Lockheed-EMSCO scientist monthly. Hardcopy outputs accompany weekly sample shipments.

The field form (Figure 3-1) is completed and is shipped with the samples. The form is in triplicate; one copy is retained by the site operator, and two accompany the samples. Of these, one is retained by the processing laboratory, and the other, after QA review, is submitted for data entry. Belfort rain gage charts are attached to the data entry copy and are shipped weekly.

The operator logbook contains duplicate numbered pages. All entries are carbon-copied to the duplicate page. Duplicate pages accompany each sample shipment. The operator maintains the original, bound logbook until study completion. The operator also photographs site conditions daily. Exposed film rolls are retrieved during the monthly on-site visits and are processed in Las Vegas.

3.3 PROCESSING LABORATORY QA

The processing laboratory functions include calculation of water equivalent, measurement of pH and specific conductance, preparation of aliquots for subsequent chemical analyses, and provision of field-required supplies including washed buckets. Processing laboratory protocols are

WET DEPOSITION AND SNOWPACK FIELD DATA FORM

YY MM DD Start: / / YY MM DD End: / / OPERATOR:

NTN 1 Weekly MTC MM/DD HH/MM - HH/MM:

	BUCKET	BUCKET	BUCKET	BUCKET	BUCKET	BUCKET	BUCKET
ON MMDD HHMM							
OFF MMDD HHMM							
FILL HGT. (CM.)							
BUCKET/LID WEIGHT							

NTN 2 Weekly MTC:

	BUCKET	BUCKET	BUCKET	BUCKET	BUCKET	BUCKET	BUCKET
ON MMDD HHMM							
OFF MMDD HHMM							
FILL HGT. (CM.)							
BUCKET/LID WEIGHT							

NTN 3 Weekly MTC:

	BUCKET	BUCKET	BUCKET	BUCKET	BUCKET	BUCKET	BUCKET
ON MMDD HHMM							
OFF MMDD HHMM							
FILL HGT. (CM.)							
BUCKET/LID WEIGHT							

BULK SAMPLERS

BULK 1	(USE 2ND COLUMN ONLY IF BAG REPLACED MID-WEEK)	BULK 2	(USE 2ND COLUMN ONLY IF BAG REPLACED MID-WEEK)
ON			
OFF			
FILL HGT.			
BUCKET/LID WEIGHT			

BELFORT RAIN GAGES

	UNIT 1	UNIT 2
CHART ON MMDD HHMM		
CHART OFF MMDD HHMM		
ANTIFREEZE CHANGE MMDD HHMM-HHMM		
QCCS (IN.)		

SNOW CORES

Weekly Samples M CLEARING HGT. ____ S CLEARING HGT. ____

RTE HGT. DUP HGT. TAKEN MMDD HHMM

DAILY MMDD HHMM								
M HEIGHT								
S HEIGHT								
ROUTINE HEIGHT								
DUP HEIGHT								

SHIPPING INFORMATION Date Shipped: / / # of Shipping Containers:

	SAMPLE ID NUMBERS	FIELD BLANK	TOTAL
BUCKETS			
BAGS			
CORES			

Comments: _____

List Supplies Needed: _____

_____ # of clean buckets on-site: _____

Figure 3-1. Snowpack field data form.

based on procedures developed for the National Surface Water Survey (NSWS), including a snowpack survey (Chaloud et al., 1986)

3.3.1 Water Equivalent

Water equivalent is calculated from sample weight and volume. The sample depth is marked in the field; sample volume is calculated to the nearest cubic centimeter (cm^3). Weights are recorded to ±1.0 g. QA/QC checks for the scale include calibration with a minimum of three NBS-traceable weights encompassing the range of sample weights and a check of a single weight after every 10 sample weights. Calculations are made on a programmable calculator to minimize arithmetic errors. All data, including bucket tareweight, sample depth and weight, balance calibration and QC check values, and calculated volume, density, and water equivalent, are recorded in a dedicated logbook. At least 10 percent of all values are reviewed and hand-calculated to check for transcription and transposition errors.

3.3.2 pH

Because melted snow samples are at atmospheric equilibrium with respect to carbon dioxide (CO_2), all pH measurements are made on sample aliquots in centrifuge tubes or beakers (open system). Two-point temperature calibrations are performed weekly; a single-point temperature check is performed daily. The meter calibration is checked each day against pH 4.00 and 7.00 NBS-traceable standards. A pH 4.00 QCCS is checked prior to sample analysis, after every 10 samples or mid-batch (whichever is fewer), and following analysis of the last sample. One sample is measured in duplicate.

3.3.3 Specific Conductance

The conductivity meter is checked daily with NBS-traceable resistors. (The conductivity cell function is checked daily with a potassium chloride [KCl] standard and a calibration blank.) At least one QCCS, prepared from a different stock solution than the calibration standard, is checked prior to sample analysis, after every 10 samples or mid-batch (whichever is fewer), and following sample analysis. One sample is measured in duplicate. By using the calibration standard, a cell constant is calculated at the beginning and end of each batch. All measurements are made at 25°C; a temperature-controlled water bath is used to maintain constant temperature.

3.3.4 Aliquot Preparation

Filtration is performed in a clean air station set to deliver a positive flow of class 100 air. Acid-washed and non-acid washed filtration units are labeled and are separated by a plexiglass shield. Vacuum pump

pressure is checked daily. Ultrex acids and reagent-grade mercuric chloride are used as preservatives. Aliquots are prepared immediately upon completion of melting; processed aliquots are refrigerated at 4°C. A description of the aliquots is given in Table 3-2.

3.3.5 Field Support

Support of field operations includes provision of washed sample buckets and lids, DI water for field blanks, frozen gel packs, plastic bags, shipping containers, and miscellaneous consumable items. At least 5 percent of all washed buckets and lids are processed as bucket blanks as a check of the bucket washing procedure. The specific conductance of the DI water produced in the processing laboratory by the Millipore system is analyzed weekly or more often to verify that it meets the ASTM Type I requirements for specific conductance (<1 μS/cm at 25°C; ASTM, 1984).

3.3.6 Documentation

Upon receipt, shipping container temperatures are measured and are recorded on the field data form. Sample identification is verified prior to assignment of batch and sample numbers. Each laboratory procedure is documented in a bound logbook. Results, including QC data, are transcribed onto multiple-copy batch forms. One copy is retained at the processing laboratory while the original is sent to QA personnel for verification and data entry. Processing laboratory results may also be recorded on floppy disk. A shipping or chain-of-custody form accompanies aliquot transfer to the analytical laboratory.

3.4 ANALYTICAL LABORATORY QA

The analytical laboratory analysis schedule is shown in Table 3-2. Analytical protocols are fully documented and tested, having been previously used in (NSWS) (Hillman et al., 1986). QA/QC protocols also are those used in NSWS (Drouse et al., 1986).

Data reports, both hardcopy and floppy disk, are prepared monthly. These reports include analytical results, in milligrams per liter (mg/L), and QA/QC data. Copies are retained in the analytical laboratory; the originals are sent to QA personnel for verification and data entry.

3.5 DATA EVALUATION

All data are reviewed for compliance with QA objectives prior to any interpretation of results. This evaluation of data quality is completed as soon as data are received so that problems can be detected and corrected rapidly. Values associated with poor QA/QC data or outside the

TABLE 3-2. PROCESSING LABORATORY ALIQUOT DESCRIPTION AND ANALYTICAL LABORATORY ANALYSIS SCHEDULE

Analyte	Aliquot Description	Analysis Schedule
Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}	125-mL Nalgene bottles (acid washed), filtered (0.45-µm HA type filter), preserved with HNO_3 to pH < 2	monthly
NO_3^{-}, SO_4^{2-}	125-mL Nalgene bottles (non-acid washed), filtered (0.45-µm HA type filter), preserved with $HgCl_2$ (0.15 M)	monthly
Cl^{-}	125 mL-Nalgene bottles (non-acid washed), filtered (0.45-µm HA type filter), no preservative	bimonthly[a]
NH_4^{+}	125-mL Nalgene bottles (acid washed), filtered (0.45-µm HA type filter), preserved with H_2SO_4 to pH < 2	bimonthly[a]

[a]Or within required holding times.

expected range (see Table 3-1) are flagged, and the sample is reanalyzed (if possible), or the value is excluded from interpretative use.

3.5.1 Audit Sample Acceptance Criteria

Acceptance windows for single values from audit samples are based on previous interlaboratory analyses of the same sample material. The objective of creating windows is to predict intervals for acceptable single future values based on a sample mean ($\bar{x}$) and sample standard deviation (s) computed from n previously observed values. The limits of the windows are determined by using a t-statistic (t).

$$t = \frac{Z}{\sqrt{\frac{\mu}{r}}}$$ is a "Student's" t-statistic

where: Z is the standard normal variate having a normal distribution with a mean of 0 and a variance of 1

μ is a variable with chi-square distribution that has r degrees of freedom, and

Z and μ are independent.

The observed values X_1, X_2, X_3,...X_n are independent and have a normal distribution (~N) with a population mean (μ) and variance (σ^2). A $(1 - \alpha)$ prediction interval for a single future value y is needed. Let $\bar{x}$ = sample mean and s = sample standard deviation. It is known that

$$y \sim N(\mu, \sigma^2) \text{ and } \bar{x} \sim N\left(\mu, \left(\frac{\sigma^2}{n}\right)\right).$$

Therefore,

$$y - \bar{x} \sim N\left[0, \sigma^2\, 1 + \left(\frac{1}{n}\right)\right].$$

$$Z = \frac{y - \bar{x}}{\sigma\sqrt{1 + \frac{1}{n}}} \sim N(0, 1)$$

$$\mu = n\text{-}1\ \frac{s^2}{\sigma^2} \sim \chi^2\,(n\text{-}1) \text{ and}$$

$$r = n\text{-}1.$$

Substituting,

$$t = \frac{\dfrac{y - \bar{x}}{\sigma\sqrt{1 + \frac{1}{n}}}}{\sqrt{\dfrac{(n-1)s^2}{(n-1)\sigma^2}}} = \frac{y - \bar{x}}{s\sqrt{1 + \frac{1}{n}}}.$$

The upper and lower limits of the window can be formalized as follows:

$$\bar{x} + (t)(s)\sqrt{1 + \frac{1}{n}} = \text{upper limit of the window}$$

$$\bar{x} - (t)(s)\sqrt{1 + \frac{1}{n}} = \text{lower limit of the window}$$

The Student's t-value (t) has n-1 degrees of freedom. The t-value is for a 2-tailed test with a cumulative probability of 0.975 (i.e., 2.5 percent probability on either side).

For predicting future values, wider windows than the standard 95 percent confidence interval about the mean are desirable. As the number of observed values increases, more variance occurs because of chance alone. Grubbs' test (Grubbs, 1969) is applied to the data before interval estimation is used to detect outliers. The outliers are excluded from the computation of the windows.

Windows for matrix spike analysis results are computationally identical to those for audit sample results.

3.5.2 Duplicate Sample Acceptance Criteria

Acceptance criteria for the %RSD are based on the upper 95th percentile of observed values of %RSD. Because the %RSD is affected by concentration, these criteria are applied only when the mean of the duplicate analyses exceeds the detection limit by a factor of 10. Arbitrary acceptance criteria may be used until sufficient (at least 10) %RSD values have been observed.

The distribution of the %RSD values cannot be estimated accurately until the sufficient %RSD values have been observed. It is recommended that no outlier test be applied until the distribution has been estimated.

3.5.3 Blank Sample Acceptance Criteria

Field and bucket blanks must be less than five times the minimum detection limit or, failing that, must constitute less than 20 percent of the mean total analyte concentration of routine samples. Analytical blanks must be less than three times the minimum detection limit.

3.5.4 Holding Times

The processing laboratory analyses are performed within 24 hours of completion of melting. The analytical laboratory analyses of chloride

and ammonium are performed approximately every two weeks or within the the required holding time; analyses of cations (Na, K, Ca, and Mg), sulfate, and nitrate are performed every four weeks. These schedules are less than the maximum recommended holding times shown in Table 3-3.

3.5.5 Data Flags

Flags are applied to the entire batch of samples if the batch QA sample data do not meet the acceptance criteria given above. Each parameter is also flagged if internal QC checks such as matrix spike recovery, calibration and reagent blank analytical results, internal duplicate precision, instrumental detection limits, QCCS analytical results, or required holding times do not meet specifications. Flagged data are reananalyzed, if possible, or are excluded from data interpretation.

TABLE 3-3. LIST OF MAXIMUM RECOMMENDED HOLDING TIMES

Holding Time	Parameter
7 days	NO_3^-,[a] pH,[b]
14 days	Specific conductance
28 days	NH_4^+, Cl^-, SO_4^{2-}
6 months[c]	Ca, Mg, K, Na

[a]Although the EPA (U.S. EPA, 1983) recommends that nitrate in unpreserved samples (unacidified) be determined within 48 hours of collection, evidence exists that nitrate in mercuric chloride preserved samples is stable for up to 3 months (Suarez, personal communication, 1987).

[b]Although the EPA (U.S. EPA, 1983) recommends that pH be measured immediately after sample collection, evidence exists (McQuaker et al., 1983) that it is stable for up to 15 days if stored at 4°C and sealed from the atmosphere. Seven days is specified here as an added precaution.

[c]Although the EPA (U.S. EPA, 1983) recommends a 6-month holding time for these metals, this study requires that all of the metals be determined within 28 days. This is to ensure that significant changes do not occur and to obtain data in a timely manner.

4.0 FIELD OPERATIONS

The equipment installed at the monitoring site includes wet/dry collectors, Belfort rain gages, bulk samplers, wind speed and wind direction sensors, and a data acquisition system (DAS). All of these, with the exception of the DAS, are mounted on the raised sampling platform. Additional measurements are taken on the ground within a clearing. Snowboards provide a base for core samples which are collected on an event and weekly basis. Density measurements are performed in a snow pit. Responsibilities of the site operator include sample collection, handling, and shipment; instrument calibration, maintenance, and quality control checks; equipment troubleshooting and repair; and documentation of all field activities. The following sections detail each of these aspects of field operations; ground-level measurements are treated in a separate section.

4.1 EQUIPMENT AND SUPPLIES

The equipment and supplies required for operation of the monitoring site are listed in Table 4-1. Each piece of equipment is assembled and tested upon receipt and is tested again following installation on the monitoring platform. Specifications, assembly instructions, and operations tests are described below.

4.1.1 Wet/Dry Collector

The Aerochem Metrics 301 Model wet/dry deposition collector depicted in Figure 4-1 has two containers and a common lid topped by a peaked roof to minimize snow buildup. The lid seals the wet sample bucket when precipitation is not occurring and thus minimizes evaporation and contamination by dry deposition or dustfall. When precipitation occurs, the lid moves off the wet bucket and covers the dry deposition bucket.

To monitor the movement of the collector lid, an event recorder output signal is provided. A continuous 12-volt direct current (DC) signal is present during wet collection; a 0-volt DC signal is present during dry collection. Two polyethylene buckets are generally used to collect wet and dry deposition. The common lid is driven by a motor that is controlled by a rain sensor. The sensor contains a face plate with a grid closely spaced above it; when the grid and plate are shorted by a drop of water (precipitation), the motor is actuated to lift the lid from the collection bucket. The sensor contains two heating circuits: one is activated during non-event periods when ambient temperature is below 4°C; the second is activated during events to increase sensor temperature to about 55°C. The first prevents ice accumulation on the sensor grid while the second increases evaporation to permit accurate detection of the end of the event. Heating increases the rate of water evaporation from the sensor and hastens the closing of the wet bucket by the lid after precipitation ceases. This procedure minimizes the exposure time

TABLE 4-1. FIELD EQUIPMENT LIST

Equipment/Materials	Quantity
Aerochem Metrics wet/dry collector	3
Collection buckets with lids	9
Fuses 1/2 Amp (120 V AC operation)	12
Fuses 2A (for DC operation)	12
Precipitation sensor and motor box	3
Peaked aluminum snow roof	3
Belfort Rain gage (weighing type)	2
Rain gage clock	2
Rain gage chart paper	2
Rain gage ink	2
Science Associates wind speed sensor	1
Science Associates wind direction sensor	1
Cup assembly	1
Vane assembly	1
Power and distribution assembly	1
Shielded cable 500 ft	1
IBM PC AT computer	1
Sysdyne graphics adaptor	1
Sysdyne amber monitor	1
Okidata 293 printer	1
Floppy disk	1
Light bulbs 60 W	1
Teflon spray	1
Taylor Hydro-Tech snow corer and extensions	1
Snow shovel	1
Snow knife	1
Spatula	1
Taylor-LaChapelle snow density kit	1

to dry fallout. A seal between the bucket and the lid is achieved by a plastic foam gasket under the lid and by a spring load; however, with strong winds the lid may wobble, and some contamination may enter the wet bucket.

Assembly and Site Installation

Assemble the unit according to the instructions provided by the manufacturer. The counterweight is in two parts; the smaller of the two is

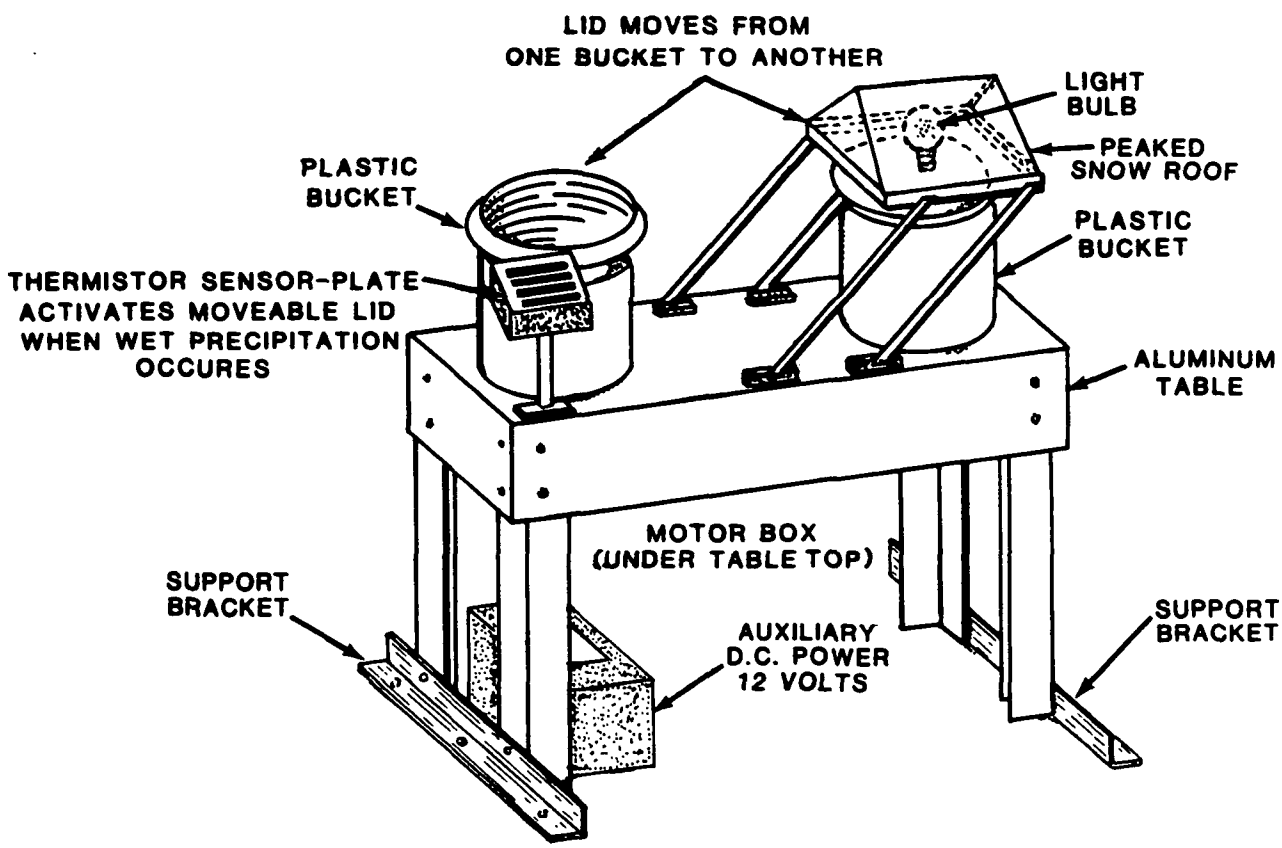

Figure 4-1. Aerochem Metrics wet/dry deposition collector.

added to counterbalance the peaked snow roof. If proper counterweighting is achieved, the lid will move to mid-position unassisted. Next, add the snow roof and recheck the balance. If necessary, add weight to the rod or existing counterweight until the lid moves to mid-position unassisted.

The wet/dry collector should be mounted so that the rims of the buckets are level and are at least 1 meter above the platform. Because of its large cross-section and relatively low weight, the wet/dry collector is susceptible to being blown over in high winds. Therefore, it is essential to anchor the unit firmly to the platform with two 5/16-inch bolts and nuts. Holes in the platform and the two sections of aluminum will have to be drilled at the site after the wet/dry collectors have been spaced. The distance between collectors or neighboring rain gages must be equal to or greater than the height of the taller object. Correct spacing will minimize interference.

Acceptance Tests

Wet/dry collector acceptance tests are conducted before the collector is used in the field. These tests include: (1) heating the sensor and checking that the lid activates when the sensor is shorted with water drops, (2) cooling the sensor and checking that the lid returns to the wet-side bucket when the water is removed (sensor may be wiped dry), (3) checking that the sensor temperature reaches 50° to 60°C when the lid is off the wet bucket, (4) checking that the sensor temperature reaches 1° to 2°C when ambient temperature falls below 4°C; and (5) checking that the lid cycling and sealing operation is correct. The procedures to be used for these acceptance tests are outlined below:

a. With the collector lid in its normal position over the wet bucket, add several drops of water to the sensor. The lid should move off the bucket within seconds and should cover the dry bucket. After the water evaporates, the lid should return to cover the wet bucket. If there is no response, check to see that the sensor is connected to the motor box and that the power is on. If the connection is complete, the sensor or motor box is probably faulty and should be replaced. To remove the box, see the instructions provided by the manufacturer.

b. Affix a temperature probe (thermistor, thermometer, or thermocouple) to the sensor plate near the screw head in the plate. Make sure the contact is good, and cover the probe with an insulating material. Short the grid and plate together with a paper clip or coin. In a few minutes the temperature should start to climb and should level off at 50° to 60°C. If the temperature setting is incorrect, it can be adjusted by turning the potentiometer screw inside the sensor box. Directions are given in the instructions provided by the manufacturer.

c. Remove the shorting object. The lid should close within a few seconds, and the temperature should fall to ambient.

d. During steps b and c, check that the lid does not cycle. Also check the lid seals.

e. If the lid does not seal the wet bucket, check to see whether or not the plastic foam gasket is secured in the correct position. To remove the seal, see the instructions provided by the manufacturer. If this is not the problem, call the manufacturer.

f. If the lid cycles while the sensor is shorted, the cause is probably a bad magnetic switch in the motor box or the lid arm that actuates the switch. The arm may be loose or may have moved too far out (more than 1 mm) from the switch as it passed the switch during lid movement. If the latter is the case, the lid arm can be adjusted and secured by tightening the 1/4 x 20 head screw in the bronze collar that secures the arm and the clutch to the motor shaft.

g. Check the sensor heating circuit at freezing temperature. The Aerochem Metrics collector has a standard heater/ammeter test plug which connects the sensor and the table cannon plugs. When the heater goes on, 0.6 to 0.7 A of current flows through the heater. The sensor can be cooled at warm temperatures by unscrewing the sensor probe from the collector table and by placing it in a refrigerator freezer compartment. A temperature probe on the sensor will give its temperature. Current should flow when the temperature falls to 0° to 2°C. The temperature setting of this circuit cannot be altered except by changing the resistor in the circuit.

If any of the above tests indicate a malfunction, the problem must be remedied or the apparatus must be returned to the manufacturer. In general, the operator can rectify the problem by replacing the sensor or the motor box. Do not replace any switches.

4.1.2 Belfort Recording Rain Gage

The Belfort 5-780 series recording rain gage is a weighing gage that converts the weight of the precipitation caught by an 8 inch diameter cylindrical collector into the curvillinear movement of a recording pen (Figure 4-2). The pen makes a trace on a rectangular paper chart that is graduated in centimeters or millimeters of precipitation.

Sensitivity: 0.01 cm of precipitation

Chart timing: within 14 minutes/week accuracy

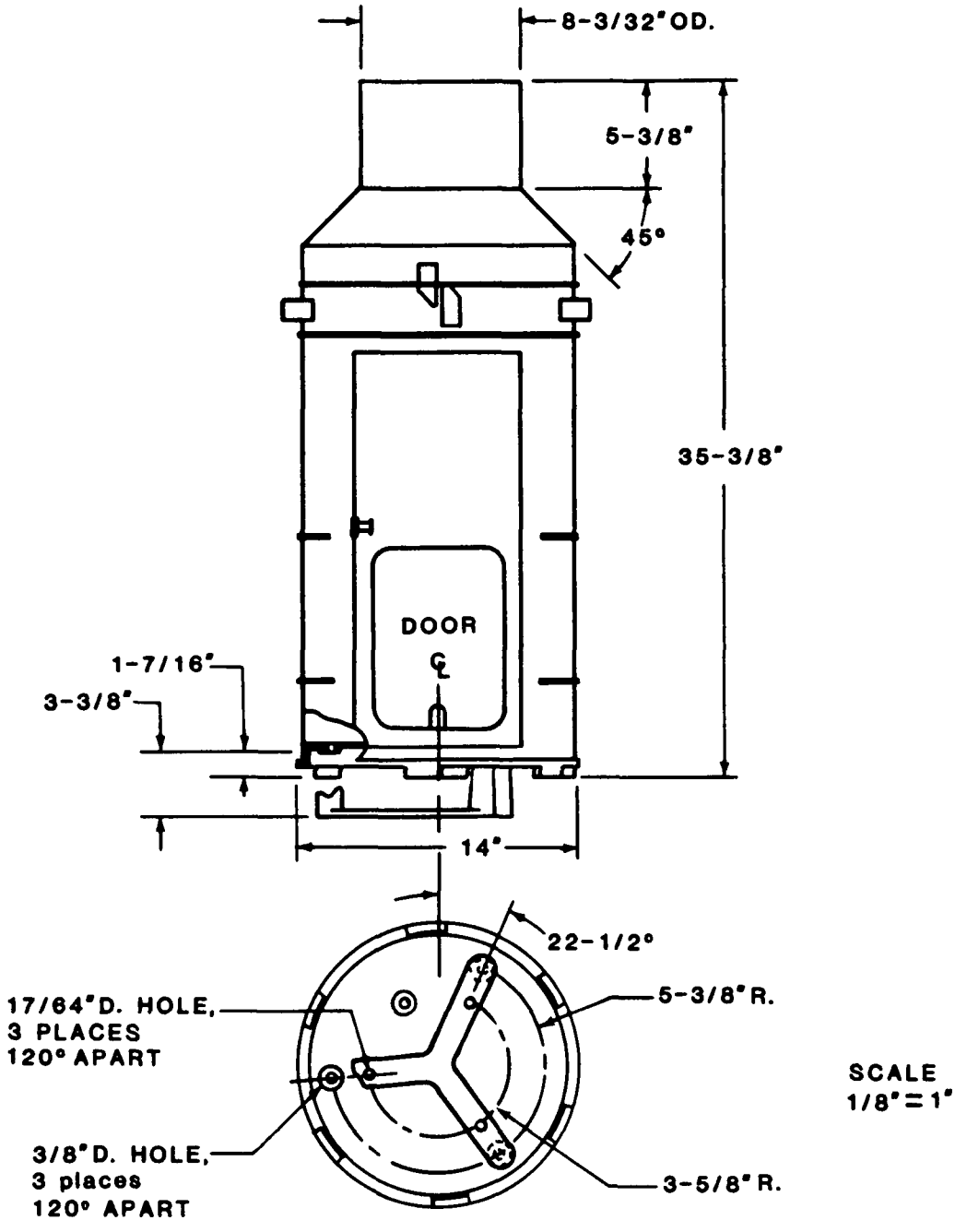

Figure 4-2. Belfort weighing rain gage.

Assembly and Site Installation

Mount the rain gage on a firmly anchored support. Make sure that its funnel rim is level and at the same height as the collector rim of the Aerochem Metrics samplers. This procedure enables comparisons of collection amounts between the two instruments. The Belfort gage can be mounted with three bolts to a level platform. The gage level can be checked with a carpenter's level placed at two intersecting positions.

Position the rain gage to prevent or minimize blowing dirt or snow from entering the access door for the chart drive. Never oil any part of the gage except the chart drive mechanism.

Acceptance Tests

Rain gage acceptance tests should include checks on the following: (1) sensitivity and accuracy, (2) clock function, (3) pen and recorder function, and (4) event pen function. The procedures to be used for these acceptance tests are outlined below.

a. With the weighing rain gage level and zeroed, add water equivalent to several inches of precipitation. For the Belfort rain gage 5-780 series, 1 inch equals 824 g of water.

b. If the rain gage does not read correctly, adjust it according to the instructions provided by the manufacturer.

c. With the pens inked and a chart in place, turn the drum to produce a zero-level trace; add water equivalent to 0.51 mm (0.02 inch) and measure the response. (For the Belfort recording rain gage 5-780 series, 0.51 mm equals 16.4 g [0.02 inch]). If there is no response or if the response is more than 1.0 mm (0.04 inch), call the manufacturer.

d. Wind the chart drive (or clock) until it is fully wound, and set it for the correct time. Let the clock run for at least 24 hours, and check the pen traces and the clock time. The time should be correct to within 0.5 hours over 24 hours. If the clock does not meet this specification, it should be replaced. If any other problems are evident, the instructions provided by the manufacturer should be consulted.

4.1.3 Bulk Sampler

The bulk sampler is an 18-inch by 6-foot galvanized metal cylinder. A hose clamp permits attachment of a polyethylene bag. The top of the cylinder is open to the atmosphere. No special assembly or acceptance tests are required. The bulk samplers may be mounted to the platform by

means of a tie-strap secured to the platform. Alternatively, the sampler may be lowered through a hole cut in the platform and may be secured from below.

4.1.4 Science Associates Wind Speed and Wind Direction Sensors

The Science Associates Model 424-1 wind speed and 424-2 wind direction sensors are the same types used by NOAA for airport observations under severe conditions.

The wind speed transmitter is essentially a direct current, permanent magnet generator with a cup-wheel directly attached to its armature shaft. The output voltage of this unit, which is directly proportional to the rate of cup-wheel rotation, is applied to a remotely located voltmeter indicator that has been calibrated to indicate wind speed in terms of miles per hour or in terms of knots, depending upon the measurement system selected. (The output of the transmitter has been set up at such a value that an additive constant can be used for all wind speeds.) This constant correction is applied by changing the rest position of the indicator pointer from 0 to 2.0. The transmitter-indicator system is entirely self contained and requires no external source of electrical power for operation.

The wind direction transmitter contains a resistance coil in toroid form; two brushes spaced 180° apart move around the edge of the coil. The brushes are attached to the wind vane shaft and turn with the shaft. The energizing voltage, 12 volts DC, is introduced into the coil by means of these brushes, and movement of the brushes causes varying voltages to appear at the three equally spaced taps on the toroid coil. These voltage changes are transferred to the indicator where three coils mounted at equally spaced intervals around a circular iron core are located. A small permanent magnet, which is located at the center of the iron core and which supports the indicator pointer shaft, follows the magnetic field through the coils and causes the pointer to indicate the direction of the wind. Prime power for operation of the wind direction system is obtained from a 115 volt, 60 cycle source. This is converted to the required 12 volts of DC power through a step-down transformer and a dry disc rectifier located in the power supply and distribution assembly.

Assembly and Site Installation

Wind Speed Transmitter Installation--

Unpack the cup-wheel and transmitter body with care. This is especially important in the case of the cup-wheel which is capable of withstanding wind speeds of 170 mph without damage but which easily can be thrown out

of balance and calibration if subjected to rough handling. After inspecting the components for damage and for loose parts, remove the adaptor from the case of the transmitter body and install it on the supporting pipe. Do not remove the length of two conductor cords soldered to the connector in the adaptor. Use the connector to splice to the connecting cable from the power and distribution assembly. With the adaptor installed, remove the cap nut from the top of the transmitter body shaft and place the cup-wheel in position on the shaft. Tighten the lateral set screw in the cupwheel hub and replace the cap nut firmly. Place the transmitter on the adaptor and rotate the transmitter until proper seating of the coupling connectors takes place, which is indicated by a sudden lowering of the transmitter body to a full seated depth on the adaptor. Lock the transmitter body in place on the adaptor by securing the two hexagonal lock screws in the body.

Wind Direction Transmitter Installation--

As with the wind speed transmitter components, exercise care in unpacking the wind vane and transmitter body. This is important in the case of the wind vane; rough handling can cause misalignment. After inspecting the equipment, remove the adaptor from the transmitter body and place it on the IPS 1 1/4-inch pipe support. Lock it firmly in place by means of the two hexagonal cap screws. Use the length of five conductor cables attached to the adaptor to splice to the main connecting cable from the power and distribution assembly. Remove the cap nut from the transmitter shaft and place the wind vane in position on the shaft. Tighten the locking screw on the wind vane hub, taking care that the screw binds firmly on the flat side of the transmitter shaft.

Mount the transmitter on the adaptor and secure it by tightening the locking screws that are similar to the screws on the wind speed transmitter. For proper orientation, the alignment marks on the transmitter body must match the mark on the adaptor. The mark on the adaptor is normally oriented to magnetic north.

Connections

All joints (wire splices) are made by soldering and taping in an approved manner. Note the color coding of the conductors that are used for the wire splices and connect them to the power and distribution assembly as follows:

Wind speed transmitter	Power and dist. assembly
A	F
B	G

Wind direction transmitter	Power and dist. assembly
A	A
B	B
C	C
D	D
E	E

The power and distribution assembly is located in a temperature-controlled area with the DAS. Connect the power and distribution assembly to a 110 V AC source. Outputs from this assembly are as follows:

Wind speed	Wind direction
L	H
M	J
	K

Additional signal conditioning may be required for the wind direction output before it is recorded by the DAS.

Acceptance Tests

Acceptance tests are limited to calibration, as described in Section 4.4, and to verification of proper interface to the DAS.

4.1.5 Data Acquisition System

The DAS consists of (1) an IBM-PC AT computer with a 12-V DC battery backup (to be used in the event of station power failure) and a 360-KB floppy disk drive, (2) a DAS-8 interface for analog to digital conversion and timing, (3) a PIO-12 interface for digital input/output signals, and (4) a SRA-01 module board with the IDC-05 solid state input/output modules to sense and convert higher than 5-V DC voltages to TTL level signals. Other instrumentation and software that support the computer include a math coprocessor 80287, PC DOS, graphics adaptor module, Sysdyne amber monitor, and Okidata 293 printer.

Assembly and Site Installation

Assembly instructions are contained in the manuals provided by the manufacturer. At the field site, the DAS is housed in a temperature-controlled building and is connected to the monitoring instruments via a buried cable.

Acceptance Tests

Most of the equipment from Metrabyte and IBM have internal system

diagnostics programs. These system diagnostic checks are performed after the equipment arrives. Some other areas of concern are data conversion and timing accuracy, memory capacity, recovery of data from disk, and power failures.

Data conversion and timing accuracy involves applying a constant voltage source to all analog inputs, then allowing the DAS to scan all input channels at specific intervals, to record the data on disk and to provide a printout copy to the user.

To minimize the effect of power failures, an uninterruptable power source (PS) is connected to the DAS. PS is expected to keep the system running for not longer than 30 minutes.

4.2 CALIBRATION, MAINTENANCE, AND QUALITY CONTROL

Calibration, maintenance, and QC checks are all elements of the field QA/QC program. Calibration is adjustment of an instrument response to known values of standards. A QC check is a periodic check, without adjustment, of instrument response to a known-value standard. Generally, QC checks are performed more frequently and employ different standards than do calibration checks. Maintenance consists of tasks performed on a set schedule to ensure operational reliability. Some maintenance tasks are specific to winter operations.

4.2.1 Wet/Dry Collector

There are no calibration or QC check procedures.

Maintenance

Weekly, test the precipitation sensor by placing two or three drops of water on the sensor grid. The top will then expose the wet-side collector, and the event signal will indicate a logic high (+ 12-V DC at the unit or a logic high [1] at the DAS). Within several minutes, the top will return to its original position, and the event signal will indicate a logic low (0) at the DAS or a 0-V DC level at the precipitation collector. Faulty sensors should be removed and replaced, and the faulty sensor should be returned to Aerochem Metrics for repair or exchange.

Weekly, wash the sensor grid with clean water to remove any accumulation of materials that would close the circuit and would present a false event signal. A shorted sensor can be verified by unscrewing the cannon plug connector at the motor box. When the sensor is disconnected, the cover will always position itself over the wet-side bucket. To clean

the space between the sensor grid and the plate, cut a strip of cardboard or manila folder to a width of about 1.8 inch and pass it between the sensor grid and plate.

Weekly, clean the Aerochem Metrics sampler cover and dry-side bucket rim with deionized water (if temperatures permit) and wipe it with a clean laboratory tissue. This procedure removes loose dirt on the cover and removes any excess buildup that would contaminate the samples. Replace the dry-side bucket every 3 weeks.

Winter Operation

The two most common problems encountered during winter operation of the Aerochem Metrics sampler are that the collector lid freezes to one of the buckets and that the lid is immobilized because of heavy snow or ice accumulation.

To help prevent both of these problems, the peaked snow roof has been modified for heating capability: a light bulb has been installed which must be checked periodically or changed to ensure proper heating operation. Increasing the rating of the light bulb will increase the heating capability.

Gaiters or boots may be installed on the cover arm to prevent freezing of the joint. Weekly, lubricate the moveable joints with Teflon or graphite spray. Spraying should be done only when the sampler lid is covering the dry-side bucket and there is not a bucket in the wet side.

4.2.2 Belfort Rain Gage

Because winter operation includes use of an antifreeze-oil mixture that must be emptied to perform calibration or QC checks, the schedule for these activities may be shifted slightly to coincide with needed antifreeze replacements.

Calibration

Two types of calibrations are recommended for the Belfort 5-780. A single-point check should be performed monthly; and a multipoint calibration should be conducted twice a year, at initial setup and 6 months later.

1. Once a month, add several known weights to the rain gage to measure the accuracy. For the Belfort weighing gage, 824 g will equal 1 inch of displacement according to the chart drive. It is recommended that for the 0- to 6-inch range, a mid-scale reading of 3 inches be used. (3 inches of water will be approximately 2,472 g).

a. Place several calibration weights, which are equal to 2,472 g, in the center of the bucket platform.

b. Loosen the set screw which fastens the lever to the Pen Arm shaft and rotate the Pen Arm shaft to put the recording pen in the center of the chart; retighten the set screw.

c. Remove the calibration weights from the bucket, and set the pen to the zero-line of the chart. Rotate the thumbscrews clockwise to lower the pen and counterclockwise to raise it.

d. Place the calibration weights on the bucket to determine whether or not the pen position is within accuracy tolerance (0.333 percent of fullscale or 0.02 inch of precipitation). If the pen position is not within accuracy tolerance, perform steps (a) through (d) again, then recheck accuracy tolerance. Call the manufacturer if the accuracy tolerance cannot be attained.

e. Remove weights from the bucket, and set up equipment for normal operation.

2. At 6-month intervals after the inital setup (unless the test described above shows that it is necessary to do so sooner), calibrate and adjust the weighing rain gage at each 1-inch level according to instructions provided by the manufacturer.

In the winter, approximately 2 inches of an antifreeze and oil mixture must be added to the weighing gage bucket to capture and melt the snow. Thus, a prolonged storm can bring the gage to the 5- to 7-inch level. If a problem occurs with the calibration in this range, it is recommended that the bucket be emptied whenever the 5-inch range is approached and that new antifreeze and oil be added.

Linearity Test

Level, in.	Calibration weight in bucket, g
1	824
2	1,648
3	2,472
4	3,296
5	4,120
6	4,944

Quality Control Check

The QC check is performed exactly like calibration except that

sandbag weights prepared by the Las Vegas laboratory are substituted for the standard weights. Two weights are supplied, corresponding to 1- and 5-inch precipitation. Place the smaller weight in the catch bucket first; record the value on the chart after stabilization. Add the larger weight without removing the smaller; record the value corresponding to 6-inch precipitation. If either value is not within ±0.05 inch, perform a full calibration and then recheck the QC check weights. This QC check is performed every time that the antifreeze-oil mixture is changed or, at a minimum, every 2 weeks.

Maintenance

Routine checks must be performed at daily, weekly, or monthly intervals, as appropriate, to ensure proper operation.

1. Whenever the antifreeze-oil mixture is replaced, adjust the zero setting with the fine-adjustment screw if necessary. The zero setting will fluctuate slightly with temperature but generally not more than 0.75 mm or 0.03 inch.

2. When the rain gage pail is removed, be sure that it is replaced correctly so that it is level.

3. Weekly, wind the clock on the weighing gage and correct the time setting if necessary. (Record any changes in the station logbook.) Be sure to correct for backlash and to set the time correctly with respect to a.m. and p.m.

4. Daily, inspect the ink level and check that the pen is writing on the chart paper. If it is not, clean the pen, refill the pen reservoir; and, using a flat toothpick, make the ink from the pen reservoir form a small pool at the point of contact between the pen and the chart.

5. Weekly, remove the old chart paper by removing the chart cylinder thumbnut and by lifting the chart cylinder from its spindle. Release the chart clip that holds the paper. Install the new chart and chart clip. Replace the cylinder in its original position on the starting point of the new week; and replace the cylinder thumbnut. The winding mechanism for the clock is exposed when the chart cylinder is removed. Make sure that the cylinder gears mesh. Close the access door.

6. At weekly intervals, measure the gage level to ensure that it is still horizontal. The check can be performed by placing a machinist's level across the mechanism base that supports the bucket.

Winter Operation

Blowing snow causes the biggest problem in the winter operation of the rain gage. Besides the inaccurate measurement of precipitation caused by wind scour out of the gage, the dash pot may be damaged if snow enters the weighing mechanism. Both problems may be prevented by the following procedure:

Remove the funnel that is fixed to the bottom of the collector by rotating the funnel until it clears the pins in the collector tube. Empty the catch bucket, replace it in the gage, and add to it an antifreeze solution composed of 2 pints of ethylene glycol and 3 pints of methyl alcohol. Add 6 ounces of motor oil to the solution to reduce evaporation. Replace mixture whenever the gage indicates more than 9 inches of precipitation (5 inches if calibration in mid-range is poor). Empty the mixture into an approved disposal can. Do not make any zeroing adjustment to the gage after adding the antifreeze and oil mixture to the bucket. The gage will indicate a precipitation level of approximately 2 2/3 inch. Approximate freezing temperatures of the antifreeze solution, when diluted by additional water content to the gage levels indicated, are as follows:

Gage level, inch	Temperature, (°C)
6	-40
7	-30
8	-23
10	-13
12	-4

4.2.3 Bulk Samplers

There are no calibration procedures or quality control checks for this instrument. Maintenance consists of weekly replacement of the collection bag. Each bag must be rinsed three times with deionized water prior to installation. Two bags are used in each sampler, one inside the other. Approximately one meter below the top, the bags are constricted and wrapped with strapping tape to form a funnel approximately 23 cm diameter.

4.2.4 Science Associates Meteorological Sensors

The meteorological sensors are located on a pole approximately 2 meters above the platform. A stepladder or step-box is provided to access the sensors.

Wind Speed Calibration

The wind speed transmitter is calibrated monthly by using a synchronous motor and by adjusting the output of the generator. The following three revolutions per minute (RPM) speeds have been selected to determine linearity of the wind speed transmitter:

RPM	MPH	Knots	Volts (DAS)
300	32.4 ± 1	28.1 ± 1	1.50
600	62.4 ± 1	54.2 ± 1	2.90
900	92.5 ± 1	80.3 ± 1	4.28

Remove the transmitter from the supporting structure. Remove the cap nut and cup-wheel assembly from the wind speed transmitter. Attach the synchronous motor to the shaft and apply power to the synchronous motor. This motor will rotate at a speed of 300 RPM, which corresponds to an output voltage of 1.50 V. Repeat for remaining RPM points. If the output of the wind speed transmitter is not within ±0.05 V for any point, adjust the generator. To do so, loosen the two binder head screws that overlap the metal brush mounting ring. Turn the ring to change the output voltage of the transmitter. Adjust the brush ring until proper indication is obtained, and secure the ring in this position by tightening the binder screws. Recheck calibration after securing the ring; in tightening the screws, the ring may have rotated slightly. If the transmitter will not calibrate, check the terminal resistance and swamping resistance before proceeding further. Using an ohm meter, check the terminal resistance which should read 40 ohms. The swamping resistor should have a value of 8 ohms. If the terminal resistance is not correct, replace the brushes according to the procedures given in the instruction manual.

Wind Direction Calibration

Calibrate the wind direction transmitter by using a circular plexiglass template with at least eight marks or lines at 45° spacing to indicate the eight cardinal compass directions.

Remove the wind direction transmitter from the supporting structure, and place it on the calibration stand. Secure it to the stand by tightening the locking screws on the transmitter body. Connect a voltmeter to the output of the power and distribution assembly or to the signal conditioning circuit. Rotate the vane until a north reading is observed on the voltmeter, and rotate the calibration template until the north mark is also aligned with the vane position. Secure the template against changing position. Position the vane at each of the 45° marks, and record the readings from the voltmeter. Accuracy within 3° is acceptable.

After calibration has been completed for both transmitters, install them on the 1 1/4-inch pipe on the supporting structure. Place the vane directly over the scribed line on the side of the case. This line corresponds to north. Rotate the wiper-arm assembly so that the resistance between terminal and wiper arm is at minimum resistance. Use the low-range scale on the ohm meter. Fasten the wiper-arm assembly in that position securely. Check alignment with a compass or landmark, and secure case to pole.

Quality Control Check

There are no QC check procedures.

Maintenance

Routine maintenance of the wind speed and wind direction transmitters consists of checking calibration, lubricating moving parts, and replacing defective or worn parts at regular intervals. Calibration of the wind speed transmitter is checked at monthly intervals, and the bearings are cleaned and lubricated at 6-month intervals.

Calibration of the wind direction transmitter is checked at monthly intervals, and the commutator torroid resistor unit and contact brushes are checked at 6-month intervals.

Replacement of defective or worn parts is performed as necessary, according to the instructions provided by the manufacturer.

Winter Operation

Snow buildup or freezing of the transmitters can cause inaccurate information to be recorded. To reduce or prevent snow accumulation on the wind speed and wind direction transmitters, lightly coat the units with a Teflon spray. It is recommended that this procedure be performed indoors or be performed outdoors when the air is calm, provided that the outside temperature is within the specified limits of the Teflon spray.

4.2.5 Data Acquisition System

Calibration

A constant voltage source is used to ensure proper recording of inputs; the recording process is checked as part of the initial acceptance tests, during installation and at 6-month intervals thereafter. On site, the constant voltage source is connected to the cable end on the monitoring platform to check the cable and the DAS.

Quality Control Check

There is no specific QC check for the DAS. Instead, the DAS-recorded values of meteorological sensor calibrations are compared to recorded voltmeter or ohm-meter readings. Clock accuracy is verified weekly against standard time.

Maintenance

Routine maintenance includes replacement of printer paper and periodic hard disk downloading. See Appendix A or the instructions provided by the manufacturer for specific procedures.

Winter Operation

Because the DAS is housed in a temperature-controlled shelter, specific procedures for winter operation are not necessary.

4.3 TROUBLESHOOTING

Copies of manufacturer manuals are maintained on site to provide troubleshooting guidance. Further troubleshooting aid is provided by Lockheed-EMSCO engineers who may be called through the project supervisor at 1-800-322-8844 or (702) 734-3227. Spare parts and test equipment are provided on site.

All malfunctions from initial symptoms through final resolution are tracked in the site operator's logbook. Analysis of malfunctions is included in the assessment of instrument operational reliability.

4.4 SAMPLE COLLECTION, HANDLING, AND SHIPMENT

Sample collection, handling, and shipment procedures are structured to ensure that contamination and sample loss are minimized.

The following discussion is limited to the physical samples shipped to Las Vegas for processing and analysis. Included are snow cores and samples from the wet/dry collectors and bulk samplers. The documentation included with each shipment, including Belfort rain gage charts, DAS outputs, site operator's logbook entries, and field forms, are discussed in greater detail in Section 4.6.

Samples are collected in accordance with the sampling schedule unless heavy precipitation necessitates more frequent replacement of collection vessels. Specific guidelines are as follows:

1. Change bucket or bag if it is observed to be more than 3/4 full during daily checks and if snow or winds are forecast.

2. Change bucket or bag if it is more than 1/2 full and if forecasts predict heavy snowfall (more than 6 inches) in the next 24 hours.

In all cases when multiple buckets or bags represent a single sample interval, identify each container chronologically (i.e., indicate date removed, and indicate that the vessel is 1 of x, 2 of x, x of x).

Change the sampling bucket in the wet/dry collector as follows:

1. Approach the collector from and work from the downwind side (if possible) to minimize windblown contaminants from entering the buckets. Open one of the shipping containers, and, wearing gloves, remove the new lid from the plastic bag. Do not touch surfaces that will come in contact with the precipitation sample. Place the lid on the bucket to be removed. With masking tape or a similar tape, temporarily fasten the lid on the bucket. With a permanent marker, record sample identification information on the bucket lid, and mark snow depth on the outside of the bucket. Remove the bucket with the lid from the collector, and secure the lid by snapping in place or by striking the edges with a rubber mallet. Place the bucket in the plastic bag and then in the shipping container. Secure the bucket so that it will not tip over and leak.

   Perform weekly instrument maintenance tasks after removing the bucket and prior to installing a new bucket.

2. Place the new bucket on the collector after removing the plastic bag in which it was shipped. Buckets are not to be removed from plastic bags until they have been taken to the sampling site and are ready to be placed on the collector. This procedure helps avoid dust and other contamination of the bucket before it is installed. Note times of bucket removal and placement.

   NOTE: If possible, change buckets only when no precipitation is occurring.

   Change the bag in the bulk sampler as follows:

   1. Wearing lab gloves and working from the downwind side, lift bags by edges protruding from the hose clamp which secures the bags to the rim. Remove the bags and twist the top closed; secure the bag with twist tie or a cable tie. Mark the snow depth with a permanent marker. Place the bags inside a plastic garbage bag, and close the garbage bag with twist tie. Attach the sample identification label. Replace the bags with clean, washed double-bags without touching any part of the inside surface except the top edge. Note times of removal and replacement.

2. If the volume is too large to place into a shipping container, measure and record the fill height, then carefully transfer the contents to sample buckets. Perform the transfer in an area out of the wind, such as the unheated barn. Record the sample identification information on the bucket lids with a permanent marker.

   Samples are shipped once each week. Until that day, collected samples are stored in an unheated or refrigerated area. On the shipping date, place four to eight frozen gel packs around samples, enclose related documentation in a Ziploc bag, and tape the tab to the shipping container lid. Seal the shipping container. Label each container, and ship by designated carrier (UPS). Retain a copy of the bill of lading provided by the carrier or a copy of a similar document. By telephone, notify the project supervisor of the shipment; provide the project supervisor with the sample identifications, the number of containers, and the identification number provided by the carrier.

4.5 DAILY OPERATOR ACTIVITIES

The following section details the checks, observations, and tasks to be performed each day of operation. Calibrations, maintenance, QC checks, and sample collection activities all are dictated by schedules. Therefore, the first task to be performed each day is to check these schedules to determine the specific tasks to be performed on that day. Note the task to be performed, and refer to the relevant section of this manual for the specific procedures. In addition, the following tasks are to be performed each day:

1. Obtain a weather forecast for the next 24 hours. It may be necessary to change sample collection vessels and to empty the Belfort rain gage catch bucket if heavy snowfall is predicted. If an event is in progress but is scheduled to end within the next 2 hours, delay sample collection (if possible) until event conclusion.

2. Check the most recent outputs of the DAS (see Appendix A for procedure). Note the indicated wind speed and wind direction and the wet/dry collector open/closed position. Upon ascending the platform, verify that actual instrument status corresponds to recorded data.

3. Inspect each instrument. Check fill levels of wet/dry collectors, bulk samplers, and Belfort rain gages; change collection vessels and empty rain gage catch bucket if needed. Check for joint freezing; lubricate as needed.

   NOTE: Before applying spray lubricant, cover all collection vessels.

4. Check Belfort rain gage chart trace. Re-ink pens if chart trace is light.

5. Photograph the area in each of the four directions, beginning on the north side and proceeding clockwise.

6. Clear the accumulated snow from the monitoring platform and steps.

   NOTE: Cover all collection vessels.

Before descending from the platform, make a last check of each instrument to ensure that covers are removed, wet/dry collectors are in the correct open/closed position, and meteorological sensors are positioned and are responding properly.

4.6 DOCUMENTATION

Field documentation includes the site operator logbook, Belfort rain gages charts, DAS outputs, photographs, and a field data form.

4.6.1 Site Operator's Logbook

The site operator's logbook is the permanent history of all field activities. Each day the operator records the following information: date, time of site checks, names of personnel on site, all tasks performed, calibration values, results of QC checks, weather observations, problems and resolutions, samples collected, and personal observations. The logbook is doublepaged and numbered. Duplicate (carbon copy) pages are submitted with each weekly shipment; the original bound pages are maintained on site.

4.6.2 Belfort Rain Gage Charts

Chart changing procedures are described in Section 4.2.2. Annotation on the chart includes rain gage identification, dates and times of installation and removal, dates and times of calibrations, QC checks, and antifreeze-oil mixture replacement. Charts are submitted weekly with the sample shipment. Copies may be retained on site if duplicating services are available.

4.6.3 Data Acquisition System

DAS outputs include floppy disks, graphics, and hardcopy outputs from the printer. Hardcopy outputs are submitted weekly with the sample shipment and are annotated with the following information: time period covered, dates and times of wet/dry collector and meteorological sensor calibration, QC checks, maintenance, dates and times of sample collection, and notation of malfunctions. Floppy disks of DAS outputs are created

monthly during site visits by a Lockheed-EMSCO scientist. They are hand-carried back to Las Vegas. Copies of each disk are kept on site. All graphics are produced in duplicate; one set accompanies sample shipments, and the other set is kept on-site. These graphics are used for data analysis purposes and are annotated with the site operator's interpretation of the data.

4.6.4 Photographs

Photographs are taken daily to document site conditions. The site operator records the date, time, direction, and number of frames taken in the site operator logbook. The first and last frames are pictures of a chalkboard or other surface annotated with date and time. Exposed film rolls are kept on site until they are hand-carried to Las Vegas after a visit by a Lockheed-EMSCO scientist. Processed slides are identified by date, time, and direction and are filed in protective sheets.

4.6.5 Field Data Form

The field data form (Figure 3-1) is described in Section 3.2.4. The site operator records requested information daily. On the date of sample shipment, the final information is recorded, and the site operator reviews the form for completeness, legibility, and accuracy. The last copy is removed and filed on site; the original and first copy are included in the sample shipment.

4.7 SNOW CORING, SNOW PIT DENSITY MEASUREMENTS, AND SNOWBOARDS

In addition to the use made of the instruments located on the monitoring platform, measurements are made manually at ground level. The site operator receives 2 weeks of training in performance of these measurements. Training is conducted by a Lockheed-EMSCO scientist familiar with these techniques. Particular attention is given to performance of these methods during monthly site visits.

4.7.1 Snow Coring

Snow coring is performed weekly, except during the intensive sampling period when samples are taken daily as well as weekly. The purpose in snow coring is to establish on a weekly or daily basis a "ground truth" value for the mean chemical composition of snow after deposition occurs. Snowboards are the standard for quantitative comparison of snow accumulation in both hydrological and glaciological studies. This study incorporates the snowboard as the base for vertical cores to ensure that they are representative of the same sampling interval as collected by the platform-mounted instruments.

The snowboard base limits the migration of chemical species vertically through the pack, except in situations of fairly high liquid water content flowing through the snow (greater than 5 percent liquid water). The base of the board also serves as a very effective event marker or time stratigraphic marker.

During weekly sampling periods for the Aerochem Metrics samplers, vertical snow coring also is performed weekly. The field sampler takes two vertical cores to the base of a snowboard on the day that the NTN sample buckets are sealed. The "pusher" is used to extrude the core from the core barrel into the standard sample buckets. The pusher can be used to tamp the sample into the buckets in order to maximize the amount of snow core shipped in one bucket. The snow core depth is recorded in the field notebook for each core. This measurement can be calculated later to a snow density that is determined from the diameter of the corer and from the sample weight recorded by the processing laboratory. It is important that duplicate cores be taken to establish an estimate of the spatial variability of the ground truth data. These two cores should be taken as close together temporally as logistical constraints allow. Usually, one core should be taken directly after the other, unless the first sample freezes solid in the core barrel. In that case, the cores must be brought inside, and the snow sample must be melted into the bucket. This should be noted in the field book and the sample logbook, because melting and subsequent refreezing of samples may precipitate out materials that will be filtered out of the sample during processing in Las Vegas.

The procedure is altered slightly during daily event sampling of the NTN monitors. Each day, one vertical core is taken to the snowboard base, is extruded into a sample bucket, and is shipped as above. Once each week (to split up tasks, the day before sample shipping) a second daily vertical core sample is taken in order to estimate the natural variability associated with daily "ground truth" samples. During the 30-day daily sampling period on the day of sample shipping, two weekly cores are taken in addition to the core taken daily. This procedure should ensure comparability of weekly event chemistry in the unlikely situation that chemical processes affect samples left on snowboards for a week differently than they affect samples left on the boards for a day.

4.7.2 Snow Pit Density

Density measurements compose the primary "ground truth" to determine incoming precipitation water-equivalent volumes. In order to quantify the natural variability between measurements, two complete sets of snow pit density measurements are made from the snow surface to the pit bottom each week. It should be recognized that stratigraphic layers may not always lie flat, but may slope. For these situations, a comparsion of densities of layers at equal depths from the snow surface (or height

above the ground surface) will be in error. Only stratigraphically similar snow samples should be compared for density.

The north- or northwest-facing snow pit walls should be scraped with a shovel from the snow surface to the ground to form a nearly perpendicular surface. Then a snow shovel or snow knife is used to trim the walls visibly smooth. The Hydro-Tech Taylor-LaChapelle snow density kit is opened on the floor of the pit or, if snow depth necessitates, on a shelf cut into a side wall. First, place the three thermometers into the snow at about equal intervals. Insert the stem of the thermometer perpendicular to the pit wall until the dial is flush with the pit wall. Allow 5 minutes for the thermometers to come to equilibrium before recording temperatures in the field book. Make certain to record the label identification for each thermometer and the height above the ground. Use the folding ruler supplied with the kit to make the measurement. This procedure ensures that temperature calibration errors are not randomly superposed on the data. Temperature is measured to obtain a rapid, indirect indication of liquid water in the pack. The presence of liquid water is inferred from 0°C temperatures. At temperatures below 0°C, liquid water is assumed to be below 1 percent by volume, which is below the limit of detection by standard field techniques.

Remove the larger of the two "cookie cutters" from the density kit, and insert it into the snow pack until a full sample is taken. Visually confirm that the sample is full, then empty the sample into the weighing pan on the upper surface of the analytical balance. Weigh the sample, and record the weight in the field book. Use the volume of the "cookie cutter" to compute sample weight to density.

The hand lens estimate of snow grain shape and metamorphic changes is used to evaluate intervals throughout the snow pack (LaChapelle, 1969). As with the distribution of thermometers, the purpose of the interval evaluation is to acquire qualitative data (in this case on snow grain shapes) that can be correlated with vertical coring chemistry data collected throughout the study. These correlations provide preliminary information on changes in pollutant distribution on snow grains during diagenetic changes in the snow pack.

It is especially important to note in the field logbook the presence and potential variability of water within the pack. The presence of water is a potential source of variability which will not be obvious during subsequent interpretation of the data and field notes. Only air temperature, snow temperature, and the field observer's comments will help identify that water was present in the sample.

4.7.3 Snowboard Precipitation Amount Sampling

Two snowboards with 1.30 meter center posts ruled in centimeters are

used to collect daily samples during intensive sampling and to collect weekly samples throughout the monitoring study. When there is no measurable precipitation in progress, a measurement of accumulation is entered into the field logbook. The boards are painted white with satin-finish polyurethane. This treatment minimizes melt absorption by the wood and prevents heat absorption from affecting thin layers of snow significantly.

Four snowboards are needed to quantify independently the variation in "ground truth" accumulation in the study plot. Lockheed-EMSCO will provide two snowboards for use in the area surrounding the sampling platform and two for the snow study clearing, 60 meters further south. Because snow accumulation rates are not always the same for different clearings, separate accumulation "ground truth" measurements are needed for the platform clearing and the snow pit clearing.

During the measurement period, the following items should be entered in the field logbook for each set of measurements:

1. Observer's general impression of the wind speed during the previous 24 hours:

   a. high (greater than 30 MPH)

   b. medium (10 to 30 MPH)

   c. low (less than 10 MPH)

2. Tendency for redeposition or scouring (check for YES, blank for no):

_____ Saltation of snow grains along snow surface

_____ Blowing snow moving in suspension 10 cm above the snow surface

_____ Blowing snow moving in suspension 50 cm above the snow surface

_____ Blowing plumes of snow observed going onto or over the sampling deck of the platform

_____ Presence of dunes or ridges on snow surface

_____ Evidence of wind erosion on snowboard sample surface

_____ If yes, specify which snowboard.

3. Platform Clearing - snow accumulation:

_____ Depth of snow on board A, (cm)

which are ruled in centimeters are used to collect daily measurements

_____ Depth of snow on board B, (cm)

_____ Presence of ice layers in snow on boards

_____ Snowmelt refrozen

_____ Rain refrozen

_____ Ice layer in sample, origin not obvious

4. Snow pit clearing - snow accumulation:

_____ Depth of snow on board C, (cm)

_____ Depth of snow on board D, (cm)

_____ Presence of ice layers in snow on boards

_____ Snow melt refrozen

_____ Rain refrozen

_____ Ice layer in sample, origin not obvious

5. Date of observation: _____

6. Time of observation: _____

7. Weather conditions in relation to ability to complete field observations: _____

(1-10; 1 = excellent conditions
5 = average conditions
10 = normal protocols not possible)

5.0 ANALYTICAL OPERATIONS

All analytical activities are performed by Lockheed-EMSCO in facilities provided by EPA EMSL-LV. Processing operations, including water equivalent determination, aliquot preparation, specific conductance and pH measurements, and field operations support, are conducted in laboratory facilities at 4675 Valley View, Las Vegas, Nevada, under the direction of D. J. Chaloud, Laboratory Operations Supervisor. Analyses of chloride, ammonium, nitrate, sulfate, and cations are performed on instrumentation located at 944 East Harmon, Las Vegas, Nevada, under the direction of D. C. Hillman, Methods Development Supervisor. Weekly processing activities are initiated immediately upon receipt of samples and are concluded within 48 hours of receipt of frozen samples. Every two weeks, the aliquots that have been prepared and accumulated for chloride and ammonium determinators are analyzed; every four weeks the accumulated aliquots for cations (Na, K, Ca, and Mg) and nitrate and sulfate determinations are analyzed. The accumulated aliquots that are analyzed at one time are considered a unique batch.

5.1 PROCESSING ACTIVITIES

Samples are received weekly via UPS. Initial measurements are taken, then samples are permitted to melt. Conductivity and pH measurements and aliquot preparation are performed upon completion of melting. Clean sample buckets and field supplies are shipped to the field station via UPS weekly or as needed.

5.1.1 Sample Handling

1) Sample Receipt

The UPS shipping form is checked to verify receipt of all samples. Each sample is then checked against the field data form to verify complete identification of each sample. A log is maintained showing sample identification, bucket ID, and relevant comments such as incomplete lid seal, leakage, or partial melting. Measurements (weight and volume) for determination of water equivalent are taken. Samples are then placed on snowmelt racks and are left undisturbed until the next morning. Bucket blanks are prepared and placed on the snowmelt racks with samples.

2) Batch Organization

Buckets are shaken to determine if the snow has melted. When melting is complete, bucket lids are removed by using a specially designed metal tool which does not contact any internal surfaces. Sample ID numbers are randomly assigned and comments (e.g., low volume, debris) are noted.

Audits and blanks are incorporated according to the schedule supplied by QA personnel. Audits and blanks are described in Section 3.1. Blanks and audits are assigned sample ID numbers randomly. A Batch/QC Field Data Form is initiated which makes use of sample codes below:

R = routine

B = field blank

BB = bucket blank

Audits F L I - XXX

- ID number (sequential)
- concentration lot number
- concentration level
  - S = synthetic
  - L = low NBS
  - H = high NBS
- audit type
  - L = lab
  - F = field

3) Sample Preparation

The bucket is transferred to the clean-air station where an analyst, wearing a lab coat and gloves, prepares the sample for analyses by following these steps in the order given:

a) pH and specific conductance. Obtain four 50-mL centrifuge tubes (not acid-washed [NAW]) which have been soaked in deionized water for 24 hours. Swirl the contents of the bucket and mix. Rinse the tubes three times with sample (if the sample volume is low, rinse twice with deionized water and a third time with sample).

   Swirl the bucket, and pour 25 mL of the sample into each tube. Cap the tubes, and label two of the tubes with an "R." The contents of these tubes are to be used as a rinse for each method.

b) Filtration and Preservation. Rinse a Cubitainer or a 500-mL NAW aliquot bottle three times with sample (rinse twice with deionized water and once with sample if the sample volume is low). The remaining sample volume is transferred to the Cubitainer by using a funnel which has been soaked in deionized water for 24 hours.

4) Sample Storage and Transfer

Prepared aliquots are kept refrigerated at 4°C until they are received by analytical personnel. On the date of transfer, a shipping form is completed and is signed by the analyst receiving the aliquots.

5.1.2 Water Equivalent Determination

1) Balance Standardization

Check standardization prior to each use of the balance. Select weights encompassing the range for which the balance is used. Wear gloves. Do not touch the weights with anything but forceps (or a gloved hand for weights over 1 kg). Tare balance, and record reading for each weight in the logbook. If weight values and balance readings do not agree, consult the guide provided by the manufacturer for adjustments.

2) Weight and Volume

Record weight of clean, empty bucket prior to shipment to field. Upon return from field, record weight of sealed bucket. Subtract the bucket tare weight and the average lid weight; record net sample weight.

With the sealed bucket on a level surface, measure height to the fill level marked by the site operator (see Section 4.4), and record that height (centimeters). Determine volume (cm^3) by:

$$\text{volume} = \pi r^2 \cdot \text{height}$$

Record volume.

3) Snow Density and Water Equivalent Calculation
Calculate snow density (SD) by:

$$SD = \frac{\text{net sample weight, g}}{\text{sample volume, } cm^3}$$

Snow density is used as a cross-check of snow pit density measurements (see Section 4.7) computed on-site.

Calculate water equivalent (we) by:

$$we = \frac{\text{net sample weight, g}}{\text{density of water, g/cm}^3 \times \text{surface area*, cm}^2}$$

*of bucket base, bulk sampler funnel, or core barrel.

For these calculations, the density of water is assumed to be 1.00 g/cm^3. Record both snow density and water equivalency values in the logbook.

5.1.3 Specific Conductance

1) Summary of Method

The specific conductance in samples is measured with a conductance meter and conductivity cell. The meter and cell are calibrated with potassium chloride standards of known specific conductance (U.S. EPA, 1983).

Samples are preferably analyzed at 25°C. If they cannot be analyzed at 25°C, temperature corrections are made, and results are reported at 25°C. A water bath may be used to maintain constant temperature.

2) Interferences

Temperature variations represent the major source of potential error in specific conductance determinations. To minimize this error, calibration standards and samples must be measured at the same temperature.

The samples may contain substances (suspended solids, etc.) which may build up on the conductivity cell. Such a buildup interferes with the operation of the cell and must be removed periodically by following the recommendations provided by the cell manufacturer.

3) Apparatus and Equipment

° Specific Conductance Meter--Digital meter with the following minimum specifications:

Range--0.1 to 1,000 µS/cm
Readability--0.1 µS/cm
Maximum error--1 percent of reading
Maximum imprecision--1 percent of reading

- Conductivity Cell--High quality glass cell with a cell constant of 1.0 cm^{-1} or 0.1 cm^{-m}. Cells containing platinized electrodes are recommended.

- Thermometer--NBS-traceable thermometer with a range of 0 to 40°C and divisions of 0.1°C.

- Water bath (Optional) with heating/cooling apparatus capable of maintaining constant temperature of 25°C ± 0.1°C.

4) Reagents and Consumable Materials

- Potassium Chloride Stock Calibration Solution (0.01000M KCl)--Dissolve 0.7456 g potassium chloride (KCl, ultrapure, freshly dried for two hours at 105°C and stored in a desiccator) in water, and dilute the solution to 1.000 L. Store the final solution in a tightly sealed container.

  NOTE: Prepare two stocks. Label one as Calibration Stock, the other as QCCS stock.

- Potassium Chloride Calibration Solution (0.001000M KCl)--Dilute 10.00 mL KCl stock calibration solution to 100.00 mL with water. This solution has a theoretical specific conductance of 147.0 µS/cm at 25°C.

- Potassium Chloride QC Solution (0.000500M KCl)--Dilute 5.00 mL 0.0100M KCl solution (independent of the KCl stock calibration solution) to 100.00 mL with water. This solution has a theoretical specific conductance of 73.9 µS/cm at 25°C.

- Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

- Glassware - Class A volumetric.

5) Calibration and Standardization

Step 1--Measure and record the specific conductance of the KCl calibration solution.

Step 2--Calculate the corrected cell constant, K_C, with the following equation:

$$K_C = \frac{147.0\ \mu S/cm}{KCl_m}$$

where: KCl_m = measured specific conductance for the KCl calibration solution.

The corrected cell constant, K_c, includes the calculation for the cell constant and for the temperature correction to 25°C.

NOTE: See SOP (Appendix B) for quality control checks.

6) Procedure

Step 1--Follow the instructions for the operation of the meter and cell which are provided by the manufacturer.

Step 2--Allow the samples and calibration standard to equilibrate to room temperature.

Step 3--Measure the sample temperature. If different from the standard temperature, allow more time for equilibration.

Step 4--Rinse the cell thoroughly with water.

Step 5--Rinse the cell with a portion of the sample to be measured. Immerse the electrode in a fresh portion of sample, and measure its specific conductance.

Step 6--Rinse the cell thoroughly with water after use. Store the cell in water.

If the readings become erratic, the cell may be dirty or may need replatinizing. Consult the operating manual provided by the manufacturer for guidance.

7) Calculations

Calculate the corrected specific conductance (S_c) for each sample with the following equation:

$$S_c = (K_c)\ (S_m)$$

where: K_c = corrected cell constant

S_m = measured specific conductance

Report the results as specific conductance: µS/cm at 25°C if using a constant temperature water bath. If analysis is not at 25°C, report µS/cm at temperature of analysis.

8) Precision and Accuracy

Forty-one analysts in 17 laboratories analyzed 6 synthetic samples containing increments of inorganic salts, with the following results (U.S. EPA, 1983):

Increment, as Specific Conductance (µS/cm)	Precision, as Standard Deviations (µS/cm)	Accuracy, as Bias (%)	Accuracy, as Bias (µS/cm)
100	7.55	-2.02	-2.0
106	8.14	-0.76	-0.8
808	66.1	-3.63	-29.3
848	79.6	-4.54	-38.5
1,640	106	-5.36	-87.9
1,710	119	-5.08	-86.9

In a single laboratory (EMSL-Cincinnati) analyzing surface-water samples with an average conductivity of 536 µS/cm at 25°C, the standard deviation was 6 µS/cm (U.S. EPA, 1983).

5.1.4 pH

NOTE 1: Because of the length of the detailed SOP for the determination of pH, only an overview of the method is presented here. The SOP is included in this document as Appendix C.

NOTE 2: This SOP is written specifically for the Orion Model 611 pH meter and Orion Ross combination pH electrode and is based on instructions provided by the manufacturer (Orion, 1983).

1) Summary of Method

The pH of samples is measured with a pH meter and electrode. The meter and electrode are calibrated with commercially available, NBS-traceable buffers.

2) Interferences

No interferences are known.

3) Apparatus and Equipment

° Orion Model 611 pH meter.
° Orion Ross combination pH electrode.
° 50-mL plastic centrifuge tubes.

4) Reagents and Consumable Materials

- pH Calibration Buffers (pH 4.00 and 7.00)--Commercially available NBS-traceable.
- Potassium Chloride (3 M)--Dissolve 70 g KCl in 1 L of DI water.
- Water--Water used in all preparations must conform to ASTM specifications for Type I water (ASTM, 1984). It is obtained from the Millipore water system.

5) Calibration and Standardization

Weekly, calibrate the temperature function of the pH meter and electrode by using a two-point calibration (4°C and room temperature) and by following the instructions provided by the manufacturer.

Daily, calibrate the pH function of the pH meter and electrode by using a two-point calibration (pH 7 and 4) and by following the instructions provided by the manufacturer. Generally, the calibration involves setting the meter calibration control while measuring pH 7 buffer and setting the slope control while measuring pH 4 buffer. After calibration, the calibration accuracy is checked according to the following procedure:

Step 1--Copiously rinse the electrode with water. Immerse the electrode in 20 mL pH 7 buffer, and stir it for 30 to 60 seconds. Discard the original buffer and replace it with an additional 40 mL pH 7 buffer. While gently stirring the solution, measure and record the pH.

Step 2--Repeat step 1 with the pH 4 buffer.

Step 3--Compare the pH values obtained for the pH 7 and 4 buffers in steps 1 and 2 to the certified values of the buffers. If either observed value differs from the certified value by more than ±0.02 pH units, repeat the electrode calibration. If acceptable results cannot be obtained, replace the electrode.

NOTE: See SOP (Appendix C) for quality control checks.

6) Procedure

Step 1--Calibrate the pH meter and electrode.

Step 2--Equilibrate samples to room temperature.

Step 3--Perform the required QC analysis. Proceed with sample analyses if acceptable results are obtained.

Step 4--Immerse the pH electrode in the 50-mL centrifuge tube designated as the rinse for 5 to 10 seconds. Measure pH in the second tube, allowing the pH to stabilize over a 2-minute interval. The pH is stable when the value does not change more than 0.02 pH units in one direction over a 2-minute interval.

Step 5--Rinse the electrode copiously with water between samples.

Step 6--At the end of the day, store the electrode in 3 M KCl.

7) Calculations

No calculations are required.

Record pH and temperature values in the logbook.

5.1.5 Aliquot Preparation

NOTE: Because of the length of the detailed SOP for filtration and preservation, only an overview of the method is presented here. The SOP is included in this document as Appendix D.

1) Summary of Method

Samples are filtered to remove the biotic and abiotic particles which exceed 0.45 μm in size. This procedure is necessary to prevent changes in particular chemical parameters prior to analysis. The preparation of the sample and the preservation used depends on the parameter being measured; the sample-preservative design ensures sample stability until analysis is complete. Aliquots are prepared within approximately 12 hours following completion of snow melting. Aliquots are prepared as follows:

Aliquot	Chemical Parameter	Container	Preservative
1	Na, K, Ca, Mg	125 mL AW*	HNO_3 to pH < 2
2	NO_3, SO_4	125 mL NAW*	$HgCl_2$
3	Cl	125 mL NAW*	none
4	NH_4	125 mL AW*	H_2SO_4 to pH < 2

*Smaller bottles or reduced volume or both may be substituted for low volume samples (AW = acid-washed, NAW = not acid-washed).

2) Apparatus and Equipment

Filtration Apparatus--Includes filter holder, vacuum chamber, and vacuum pumps.

Pipets--Calibrated over range 40 to 200 µL(2) and 1 to 5 mL(1).

3) Reagents and Consumable Materials

- Nitric Acid (HNO_3, 12 M, Baker Ultrex grade or equivalent).
- Sulfuric Acid (H_2SO_4, 18 M, Baker Ultrex grade or equivalent).
- Mercuric chloride ($HgCl_2$, 5 percent, reagent grade or equivalent).
- Water--Water used in all preparations must conform to ASTM specifications for Type I water (ASTM, 1984). It is obtained from the Millipore Milli-Q water system.
- Aliquot Bottles--Clean aliquot bottles are required for the four aliquots prepared from each sample and for any split samples. The bottles are cleaned and are supplied by an outside contractor.
- Indicating pH Paper (Range pH 1 to 3).
- Membrane Filters (0.45-µm pore size).

4) Procedure

Preparation of the four aliquots and any split samples is described in this section. All filtrations are performed in the laminar-flow clean work station.

a) Preparation of Aliquots 1 and 4

Step 1--Complete aliquot labels for aliquots 1 and 4, and attach labels to containers. Assemble the filtration apparatus with a waste container as a collection vessel. Apply vacuum (pressure must not exceed 12 inches Hg). Thoroughly rinse the filter holder and membrane filter in succession with 20 to 40 mL DI water, 20 mL 5 percent HNO_3 (Baker Instra-Analyzed grade), and 40 to 50 mL DI water.

Step 2--Rinse the filter holder and membrane with 10 to 15 mL of the sample to be filtered.

Step 3--Turn off vacuum. Replace the waste container with the aliquot 1 container. Reapply vacuum and filter 10 to 15 mL of sample. Remove the vacuum. Rinse the aliquot 1 container with the 15 mL of filtered sample by slowly rotating the bottle so that the sample touches all internal surfaces. Discard the rinse sample, and replace the container under the filter holder.

Step 4--Filter sample into the container until the container is full.

Step 5--Transfer filtered sample into the aliquot 4 container (previously labeled) after first rinsing the container with 10 to 15 mL of filtered sample.

Step 6--Return the aliquot 1 container to the filtration apparatus, and collect additional filtered sample until the container is full.

If it is necessary to replace a membrane (because of clogging) before adequate filtered sample has been obtained, rinse the new membrane with 15 to 20 mL of water, 10 to 15 mL of 5 percent HNO_3, 40 to 50 mL of water, and 10 to 15 mL of sample prior to collecting additional sample.

Step 7--Between samples, remove the membrane and thoroughly rinse the filter holder with water.

Step 8--Preserve the sample by adding concentrated HNO_3 to aliquot 1 and concentrated H_2SO_4 to aliquot 4 in 0.100-mL increments until the pH <2 (U.S. EPA, 1983). Check the pH by using a clean pipet tip to place a drop of sample on indicating pH paper.

Step 9--Store aliquots 1 and 4 at 4°C until ready to transfer.

b) Preparation of Aliquots 2 and 3

Step 1--Soak filter holders for 24 hours in deionized water prior to first use and weekly thereafter.

Step 2--Complete aliquots 2 and 3 labels, and attach labels to the aliquot bottles. Assemble the filtration apparatus with a waste container as a collection vessel. Thoroughly rinse the filter holder and membrane filter with three 25-mL portions of water followed by a final rinse with 10 to 15 mL of the sample to be filtered.

Step 3--Replace the waste container with the aliquot 3 container, and filter an additional 15 mL of sample. Remove the container, and rinse it by slowly rotating the bottle so that the sample touches all internal surfaces. Discard the rinse sample, and replace the container under the filter holder.

Step 4--Filter sample into the container until cubitainer is full.

Step 5--Transfer filtered sample into the aliquot 2 container (previously labeled) after first rinsing the container with 10 to 15 mL of filtered sample.

Step 6--Return the aliquot 3 container to the filtration apparatus, and collect additional filtered sample until the container is completely full. Cap the container tightly to ensure that all headspace is removed.

If it is necessary to replace a membrane (because of clogging), rinse the membrane with three 20-mL portions of water followed by a final rinse with 15 mL of sample.

Step 7--Between samples, remove the membrane and thoroughly rinse the filter holder with water.

Step 8--Preserve aliquot 2 by adding 0.1 mL 5 percent mercuric chloride. No preservation is required for aliquot 3.

Step 9--Store at 4°C until ready to ship.

5.1.6 Field Support

Items supplied by the laboratory to the field include clean, tared sampling buckets and lids, DI water, and various consumable items. The DI water is used for rinses and field blanks. Consumable items may include such things as sterile laboratory gloves, freeze-gel packs, spare parts, bulk sampler bags, field forms, and other items defined on an as-needed basis.

All buckets and lids are initially leached in DI water for at least 72 hours, and three DI water rinses and a wipe down with a natural sponge follow. Each bucket is assigned a unique ID number and is weighed prior to each use. Prior to the first use, 20 lids will be weighed; if the standard deviation is less than 1 g, a mean lid weight will be used in weight calculations. Each bucket and lid is placed in a large plastic bag and is closed with a twist tie. They are shipped to the field in styrofoam containers along with freeze-gel packs and other

required consumable items. After each use, the cleaning procedure is repeated for each used bucket; lids are not reused.

All shipping is by UPS.

5.2 ANALYTICAL PROCEDURES

The most economical means of providing analyses is to analyze a large number of samples at one time. However, chemical changes may occur in a sample over time. Filtration, preservation, and storage at 4°C aid in maintaining sample integrity over a discrete period, defined as the holding time. Because of the small number of raw samples received weekly, samples from successive weeks are grouped or batched for analysis. The holding times determine the analysis schedule; aliquots 3 (Cl^-) and 4 (NH_4^+) are analyzed every two weeks while aliquots 1 (metals) and 2 (NO_3^-, SO_4^{2-}) are analyzed every 4 weeks. Analysis procedures were developed for NSWS and, except for the use of preservatives, closely mirror those used by CAL for NADP samples. The procedures presented in the sections below are reprinted with minor modification from the NSWS Eastern Lake Survey (Phase I-Synoptic Chemistry) Analytical Methods Manual (Hillman et al., 1986).

5.2.1 Determination of Ammonium

NOTE: An alternate method using flow injection analysis (FIA) may be used if sample concentrations are low. The FIA method is presented in Appendix E.

1) Scope and Application

This method covers the determination of ammonium in natural surface waters in the range of 0.01 to 2.6 mg/L NH_4^+. This range is for photometric measurements made at 630 to 660 nm in a 15-mm or 50-mm tubular flow cell. Higher concentrations can be determined after sample dilution. Approximately 20 to 60 samples per hour can be analyzed.

2) Summary of Method

Alkaline phenol and hypochlorite react with ammonium to form an amount of indophenol blue that is proportional to the ammonium concentration. The blue color formed is intensified with sodium nitroprusside (U.S. EPA, 1983).

3) Interferences

Calcium and magnesium ions may be present in concentrations sufficient to cause precipitation problems during the analysis. A

5 percent EDTA solution is used to prevent the precipitation of calcium and magnesium compounds.

Sample turbidity may interfere with this method. Turbidity is removed by filtering the sample at the processing laboratory.

Sample color that absorbs in the photometric range used also interferes.

4) Safety

The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use protective clothing (lab coat and gloves) and safety glasses when preparing reagents.

5) Apparatus and Equipment

° Technicon AutoAnalyzer Unit (AAI or AAII) consisting of sampler, manifold (AAI) or analytical cartridge (AAII), proportioning pump, heating bath with double-delay coil (AAI), colorimeter equipped with 15-mm tubular flow cell and 630- to 660-nm filters, recorder, and digital printer for AAII (optional).

6) Reagents and Consumable Materials

° Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

° Sulfuric Acid (5N), Air Scrubber Solution--Carefully add 139 mL concentrated sulfuric acid to approximately 500 mL ammonia-free water. Cool the solution to room temperature, and dilute it to 1 L with water.

° Sodium Phenolate Solution--Using a 1-L Erlenmeyer flask, dissolve 83 g phenol in 500 mL water. In small increments, cautiously add with agitation 32g NaOH. Periodically cool flask under flowing tap water. When it is cool, dilute the solution to 1 L with water.

° Sodium Hypochlorite Solution--Dilute 150 mL of a bleach solution containing 5.25 percent NaOCl (such as Clorox) to 500 mL with water. The concentration of available chlorine should be approximately 2 to 3 percent. Clorox is a proprietary product, and its formulation is subject to change. The analyst must remain alert to any variation in this product which is significant to its use in this procedure. Because of the instability of this product, storage over an extended period should be avoided.

- Disodium Ethylenediaminetetraacetate Acid (EDTA) (5 percent w/v)--Dissolve 50 g EDTA (disodium salt) and approximately six pellets NaOH in 1 L water.

- Sodium Nitroprusside (0.05 percent w/v)--Dissolve 0.5 g sodium nitroprusside in 1 L deionized water.

- NH_4^+ Stock Standard Solution (1,000 mg/L)--Dissolve 2.9654 g anhydrous ammonium chloride, NH_4Cl (dried at 105°C for 2 hours), in water, and dilute the solution to 1,000 mL.

- Standard Solution A (10.00 mg/L NH_4^+)--Dilute 10.0 mL NH_4^+ stock standard solution to 1,000 mL with water.

- Standard Solution B (1.000 mg/L NH_4^+)--Dilute 10.0 mL standard solution A to 100.0 mL with water.

Using standard solutions A and B, prepare (fresh daily) the following standards in 100-mL volumetric flasks:

NH_4^+ (mg/L)	mL Standard Solution/100 mL
	Solution B
0.01	1.0
0.02	2.0
0.05	5.0
0.10	10.0
NH_4^+ (mg/L)	mL Standard Solution/100 mL
	Solution A
0.20	2.0
0.50	5.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

7) Sample Collection, Preservation, and Storage

Samples are filtered and preserved (addition of H_2SO_4 until pH <2) in the processing laboratory. The samples must be stored in the dark at 4°C when not in use.

8) Calibration and Standardization

Analyze the series of ammonium standards by following the procedure described in Section 10. Prepare a calibration curve by plotting the peak height versus standard concentration.

9) Quality Control

The required QC is described in Section 3.1.

10) Procedure

Since the intensity of the color used to quantify the concentration is pH-dependent, the acid concentration of the wash water and the standard ammonium solutions should approximate that of the samples. For example, if the samples have been preserved with 2 mL concentrated H_2SO_4/L, the wash water and standards should also contain 2 mL concentrated H_2SO_4/L.

Step 1--For a working range of 0.01 to 2.6 mg/L NH_4^+ (AAI), set up the manifold as shown in Figure 5-1. For a working range of 0.01 to 1.3 mg/L NH_4^+ (AAII), set up the manifold as shown in Figure 5-2. Higher concentrations may be accommodated by sample dilution.

Step 2--Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through the sample line.

Step 3--For the AAI system, sample at a rate of 20/hr, 1:1. For the AAII system, use a 60/hr 6:1 cam with a common wash.

Step 4--Load sampler tray with samples.

Step 5--Switch sample line from water to sampler, and begin analysis.

Step 6--Dilute and reanalyze samples which have an ammonium concentration exceeding the calibrated concentration range.

11) Calculations

Compute concentration of samples by comparing sample peak heights with calibration curve. Report results in mg/L NH_4^+.

12) Precision and Accuracy

In a single laboratory (EMSL-Cincinnati), by using surface-water samples at concentrations of 1.41, 0.77, 0.59, and 0.43 mg NH_3-N/L, the standard deviation was ±0.005 (U.S. EPA, 1983).

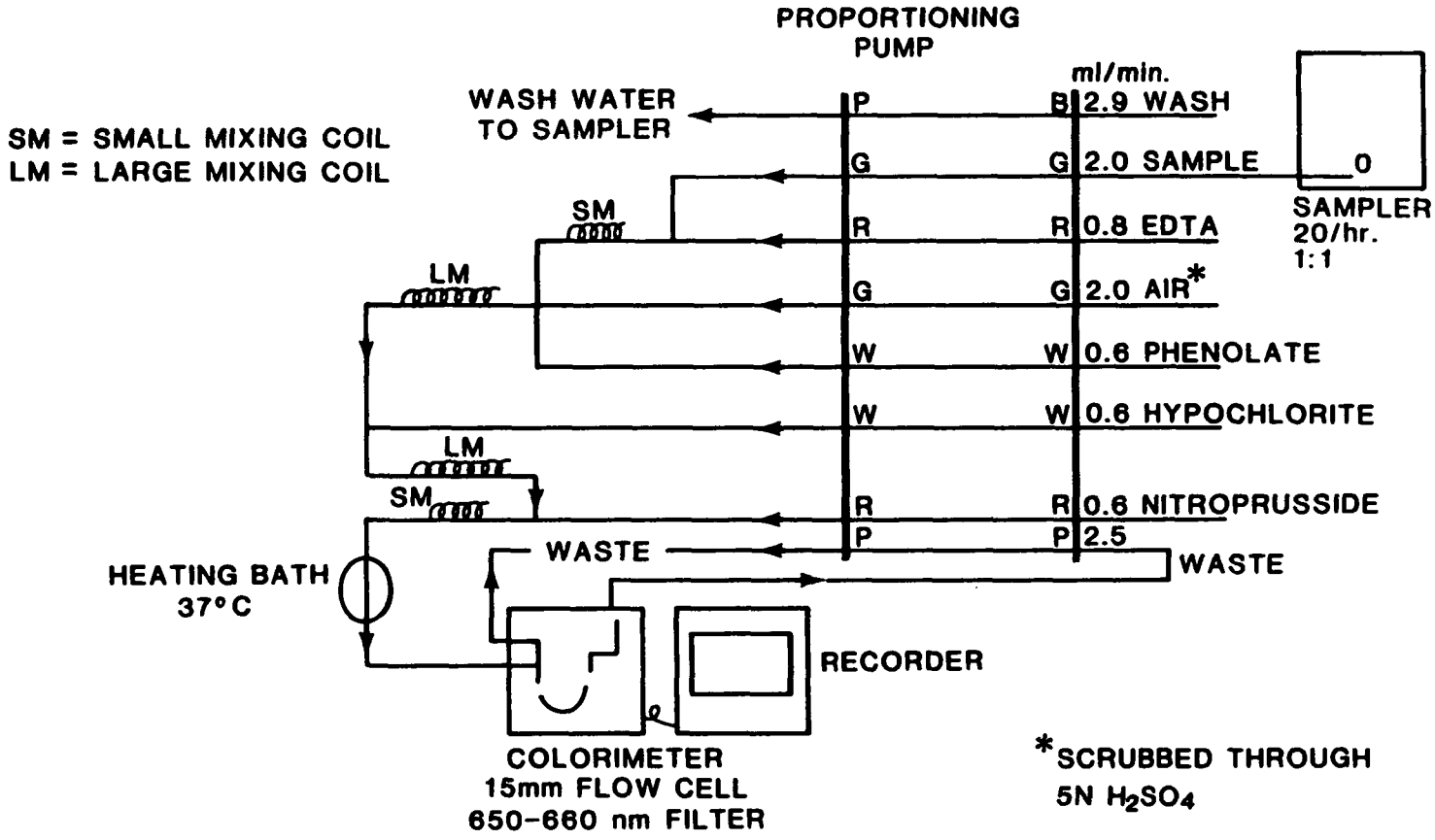

Figure 5-1. Ammonia Manifold AAI.

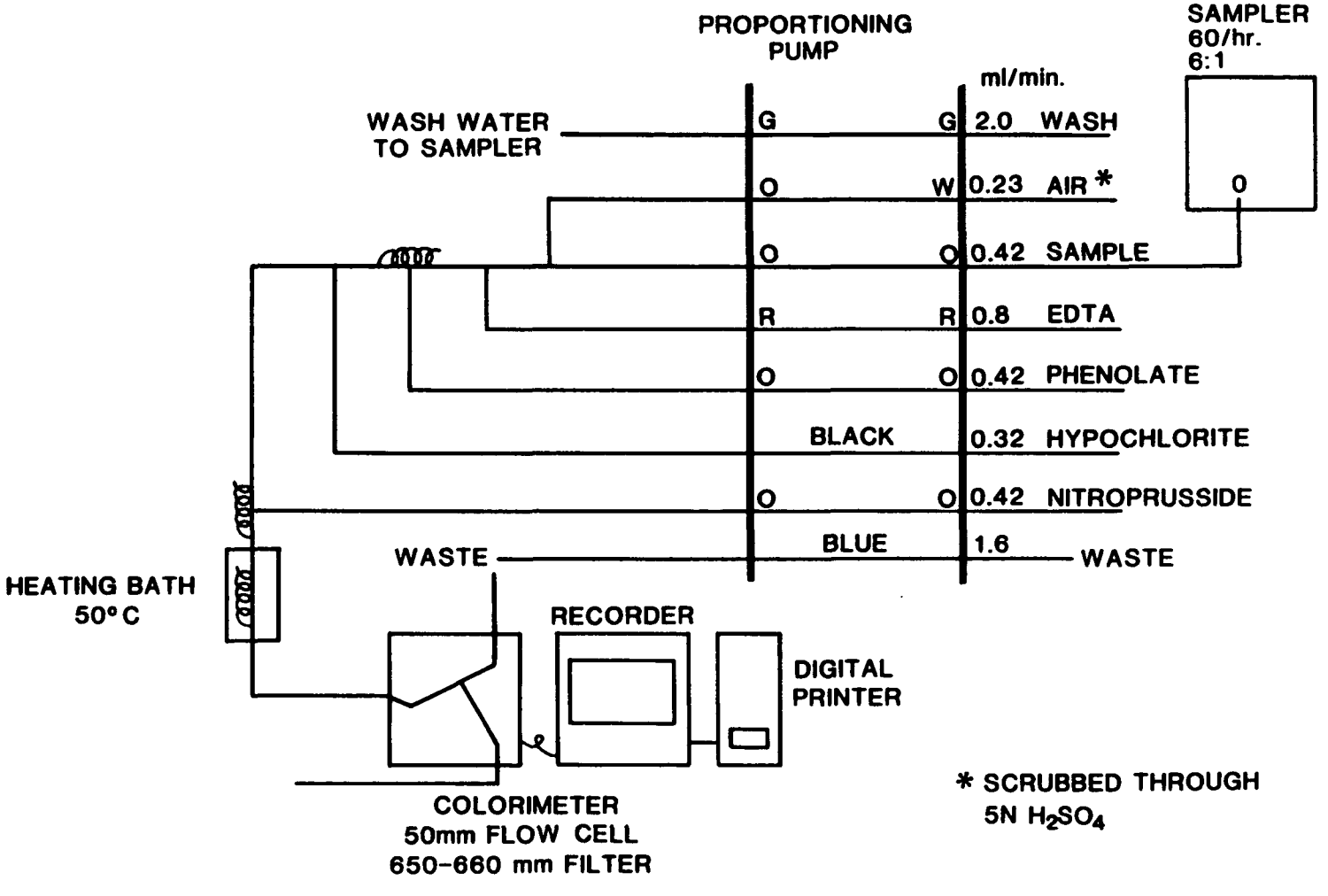

Figure 5-2. Ammonia Manifold AAII.

In a single laboratory (EMSL-Cincinnati), with surface-water samples at concentrations of 0.16 and 1.44 mg NH_3-N/L, recoveries were 107 percent and 99 percent, respectively (U.S. EPA, 1983). These recoveries are statistically significantly different from 100 percent.

5.2.2 Determination of Chloride, Nitrate, and Sulfate by Ion Chromatography

1) Scope and Application

This method is applicable to the determination of chloride, nitrate, and sulfate in natural surface waters by ion chromatography (IC).

It is restricted to use by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram.

2) Summary of Method

Samples are analyzed by IC. IC is a liquid chromatographic technique that combines ion exchange chromatography, eluent suppression, and conductimetric detection.

A filtered sample portion is injected into an ion chromatograph. The sample is pumped through a precolumn, separator column, suppressor column, and a conductivity detector. The precolumn and separator column are packed with a low-capacity anion exchange resin. The sample anions are separated in these two columns with separation being based on their affinity for the resin exchange sites.

The suppressor column reduces the conductivity of the eluant to a low level and converts the sample anions to their acid form. Typical reactions in the suppressor column are represented as follows:

$$\underset{\text{(high-conductivity eluant)}}{Na^+ HCO_3^- + R - H} \longrightarrow \underset{\text{(low conductivity)}}{H_2CO_3 + R - Na}$$

$$Na^+ A^- + R - H \longrightarrow HA + R - Na$$

Three types of suppressor columns are available: the packed-bed suppressor, the fiber suppressor, and the micromembrane suppressor. The packed-bed suppressor contains a high-capacity cation exchange resin in the hydrogen form. It is consumed during analysis and must be periodically regenerated off-line. The latter two suppressors are based on cation exchange membranes. These suppressors are continuously regenerated throughout the analysis. Also, their dead volume is substantially less than that of a packed-bed suppressor. For these two reasons, the latter two suppressors are preferred.

The separated anions in their acid form are measured with a conductivity cell. Anion identification is based on retention time. Quantification is performed by comparing sample peak heights to a calibration curve generated from known standards (ASTM, 1984; O'Dell et al., 1984; Topol and Ozdemir, 1984).

3) Interferences

Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. The samples are not expected to contain any interfering species. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution or spiking can be used to solve most interference problems.

The water dip or negative peak that elutes near and that can interfere with the chloride peak can be eliminated by the addition of the concentrated eluant so that the eluant and sample matrix are similar.

Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in ion chromatograms.

Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

4) Safety

Normal, accepted laboratory safety practices should be followed during reagent preparation and instrument operation. The calibration standards, samples, and most reagents pose no hazard to the analyst. Protective clothing and safety glasses should be worn when handling concentrated sulfuric acid.

5) Apparatus and Equipment

- Ion Chromatograph--Analytical system complete with ion chromatograph and all accessories (conductivity detector, autosampler, data recording system, etc.).

- Anion Preseparator and Separator Columns--Dionex Series AG-4A and AS-4A are recommended for use with the 2000i ion chromatographs. AG-3 and AS-3 columns are recommended for older ion chromatographs.

- Suppressor Column--Dionex AFS fiber suppressor or AMMS membrane suppressor is recommended.

6) Reagents and Consumable Materials

Unless stated otherwise, all chemicals must be ACS reagent grade or better. Also, salts used in preparation of standards must be dried at 105°C for 2 hours and must be stored in a desiccator until they are weighed.

- Deionized Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

- Eluant Solution (0.0028M $NaHCO_3$/0.0020M Na_2CO_3)--Dissolve 0.94 g sodium bicarbonate (NaHCO3) and 0.85 g sodium carbonate (Na_2CO_3) in water and dilute to 4 L. This eluant strength may be adjusted for different columns according to the recommendations provided by the manufacturer.

- Fiber Suppressor Regenerant (0.025 H_2SO4)--Add 2.8 mL concentrated sulfuric acid (H_2SO_4, Baker Ultrex grade or equivalent) to 4 L water.

- Stock Standard Solutions--Store stock standards in clean polyethylene bottles (cleaned without acid) at 4°C. Prepare monthly.

  a) Bromide Stock Standard Solution (1,000 mg/L Br^-)--Dissolve 1.2877 g sodium bromide (NaBr) in water and dilute to 1.000 L.

  b) Chloride Stock Standard Solution (200 mg/L Cl^-)--Dissolve 0.3297 g sodium chloride (NaCl) in water and dilute to 1.000 L.

  c) Fluoride Stock Standard Solution (1,000 mg/L F^-)--Dissolve 2.2100 g sodium fluoride (NaF) in water and dilute to 1.000 L.

  d) Nitrate Stock Standard Solution (200 mg/L NO_3^-)--Dissolve 0.3261 g potassium nitrate (KNO_3) in water and dilute to 1.000 L.

  e) Phosphate Stock Standard Solution (2,000 mg/L P)--Dissolve 4.3937 g potassium phosphate (KH_2PO_4) in water and dilute to 1.000 L.

f) Sulfate Stock Standard Solution (1,000 mg/L SO_4^{2-})--Dissolve 1.8141 g potassium sulfate (K_2SO_4) in water and dilute to 1.000 L.

° Mixed Resolution Sample (mg/L F^-, 2 mg/L Cl^-, 2 mg/L NO_3^-, 2 mg/L P, 2 mg/L Br^-, 5 mg/L SO_4^{2-}).

Prepare by appropriate mixing and dilution of the stock standard solutions.

7) Sample Collection, Preservation, and Storage

Samples are filtered in the processing laboratory. Nitrate and sulfate are preserved with mercuric chloride. Store samples at 4°C when not in use.

8) Calibration and Standardization

Each day (or work shift) analyze a blank and a series of standards for each analyte, which bracket the expected analyte concentration range. Suggested concentrations for the dilute standards are given in Table 5-1.

TABLE 5-1. SUGGESTED CONCENTRATION OF DILUTE CALIBRATION STANDARDS

	Concentration (mg/L)		
Standard	Cl^-	NO_3^-	SO_4^{2-}
1	0	0	0
2	0.020	0.020	0.20
3	0.10	0.10	0.50
4	0.50	0.50	2.00
5	1.00	1.00	5.00
6	3.00	3.00	10.00

Prepare a calibration curve for each analyte by plotting peak height versus standard concentration.

9) Quality Control

General QC procedures are described in Section 3.0.

After calibration, perform a resolution test. Analyze the mixed standard containing fluoride, chloride, nitrate, phosphate, bromide, and sulfate. Resolution between adjacent peaks must equal or exceed 60 percent. If it does not, replace or clean the separator colunn and repeat calibration.

10) Procedure

Step 1--Set up the IC for operation. Typical operating conditions for a Dionex 2010i IC are given in Table 5-2. Other conditions may be used depending upon the columns and system selected.

TABLE 5-2. TYPICAL IC OPERATING CONDITIONS

IC: Dionex 2010i Sample Loop Size: 250 µL

Precolumn: AG-4A

Separator Column: AS-4A

Suppressor Column: AMMS

Eluant: 0.75mM $NaHCO_3$/2.0mM Na_2CO_3

Eluant Flow Rate: 2.0 mL/min

Regenerant: 0.025N H_2SO_4

Regenerant Flow Rate: 3 mL/min

Ion	Typical Retention Time (min.)
Cl^-	1.8
NO_3^-	4.9
SO_4^{2-}	8.1

Step 2--Adjust detector range to cover the concentration range of samples.

Step 3--Load injection loop (manually or via an autosampler) with the sample (or standard) to be analyzed. Load 5 to 10 times the volume required to flush the sample loop thoroughly. Inject the

sample. Measure and record (manually or with a data system) the peak heights for each analyte.

Step 4--Dilute and reanalyze samples which have an analyte concentration exceeding the calibrated concentration range.

11) Calculations

Compute the sample concentration by comparing the sample peak height with the calibration curve. Report results in mg/L.

12) Precision and Accuracy

Typical single operator results for surface water analyses are listed in Table 5-3 (O'Dell et al., 1984).

TABLE 5-3. SINGLE-OPERATOR ACCURACY AND PRECISION (O'Dell et al., 1984)[a]

Ion	Spike (mg/L)	Number of Replicates	Mean % Recovery	Standard Deviation (mg/L)
Cl^-	1.0	7	105	0.14
NO_3^-	0.5	7	100	0.0058
$SO^2_4^-$	10.0	7	112	0.71

[a]The chromatographic conditions used by O'Dell were slightly different than those listed in Table 5-2. However, the results are typical of what is expected.

5.2.3 Determination of Metals (Ca, K, Mg, Na) by Atomic Absorption Spectroscopy

NOTE: An alternate method for Ca and Mg determination using Inductively Coupled Plasma (ICP) Emission Spectroscopy may be used if sample concentrations are low. The ICP method is presented in Appendix F.

1) Scope and Application

Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to the determination of Ca, K, Mg, and Na in natural surface waters.

Detection limits, sensitivity, and optimum ranges of the metals vary with the makes and models of atomic absorption spectrophotometers. The data listed in Table 5-4, however, provide some indication of the actual concentration ranges measurable by direct aspiration (flame) techniques. In the majority of instances, the concentration range shown in the table for analysis by direct aspiration may be extended much lower with scale expansion and, conversely, may be extended upward by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and through solvent extraction techniques. The concentration ranges given in Table 5-4 are somewhat dependent on equipment such as the type of spectrophotometer, the energy source, and the degree of electrical expansion of the output signal.

TABLE 5-4. ATOMIC ABSORPTION CONCENTRATION RANGES[1]

	Flame		
Metal	Detection Limit (mg/L)	Sensitivity (mg/L)	Optimum Concentration Range (mg/L)
Calcium	0.01	0.08	0.2 to 7
Magnesium	0.001	0.007	0.02 to 0.5
Potassium	0.01	0.04	0.1 to 2
Sodium	0.002	0.015	0.03 to 1

[1]The concentrations shown are obtainable with any satisfactory atomic absorption spectrophotometer.

2) Summary of Method

In direct aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp, whose cathode is made of the element to be determined, is directed through the flame into a monochromator and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy. A monochromator isolates the characteristic radiation from the hollow

cathode lamp, and a photo-sensitive device measures the attenuated transmitted radiation. Dissolved metals (Ca, K, Mg, and Na) are determined in a filtered sample (aliquot 1) by flame atomic absorption spectroscopy (U.S. EPA, 1983).

3) Definitions

- Optimum Concentration Range--This is a range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and with the operating conditions employed.

- Sensitivity--Sensitivity is the concentration in milligrams of metal per liter that produces an absorption of 1 percent.

- Dissolved Metals--Dissolved metals are those constituents (metals) which can pass through a 0.45-μm membrane filter.

4) Interferences

The most troublesome type of interference in direct aspiration atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome the phosphate interference in the magnesium and calcium determinations.

Chemical interferences may also be eliminated by separating the metal from the interfering material. While complexing agents are primarily from the interfering material employed to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess of an easily ionized element.

Although quite rare, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of

the element of interest. The results of the determination will then be erroneously high because of the contribution of the interfering element to the atomic absorption signal. Also, interference can occur when resonant energy from another element in a multi-element lamp or from a metal impurity in the lamp cathode falls within the bandpass of the slit setting and when that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

5) Safety

The calibration standards, sample types, and most reagents pose no hazard to the analyst. Use protective clothing (lab coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated hydrochloric acid should be restricted to a hood.

Follow the safety precautions recommended by the manufacturer when operating the atomic absorption spectrophotometer.

Follow good laboratory practices when handling compressed gases.

6) Apparatus and Equipment

- Atomic Absorption Spectrophotometer--The spectrophotometer used shall be a single- or dual-channel, single or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip chart recorder.

- Burner--The burner recommended by the particular instrument manufacturer should be used. For certain elements, the nitrous oxide burner is required.

- Hollow Cathode Lamps--Single element lamps are preferred. Electrodeless discharge lamps may also be used when available.

7) Reagents and Consumable Materials

General reagents used in each metal determination are listed in this section. Reagents specific to particular metal determinations are listed in the particular procedure description for that metal.

- Concentrated Hydrochloric Acid (12M HCl)--Ultrapure grade (Baker InstraAnalyzed or equivalent) is required.

- HCl (1 percent v/v)--Add 5 mL concentrated HCl to 495 mL water.

- Nitric Acid (0.5% v/v HNO - Ultrapure grade, Baker Instra-Analyzed or equivalent)--Carefully dilute HNO_3 in water in the ratio of 0.5 to 100.

- Stock Standard Metal Solutions--Prepare as directed in the individual metal procedures. Commercially available stock standard solutions may also be used.

- Dilute Calibration Standards--Prepare a series of standards of the metal by dilution of the appropriate stock metal solution to cover the concentration range desired.

- Fuel and Oxidant--Commercial grade acetylene is generally acceptable if replaced at 100 lbs pressure. Air may be supplied from a compressed air line, from a laboratory compressor, or from a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

- Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

8) Sample Collection, Preservation, and Storage

Samples are processed in the processing laboratory. The sample for dissolved metals (aliquot 1) is filtered through a 0.45-µm membrane filter and is then preserved by acidifying to a pH <2 with nitric acid. After processing, the samples are transferred to the analytical laboratory.

9) Calibration and Standardization

The calibration procedure varies slightly with the various atomic absorption instruments.

For each analyte, calibrate the atomic absorption instrument by analyzing a calibration blank and a series of standards and by following the instructions in the instrument operating manual.

The concentration of standards should bracket the expected sample concentration. However, the linear range of the instrument should not be exceeded.

When indicated by the matrix spike analysis, the analytes must be quantified by the method of standard additions. In this method, equal volumes of sample are added to a deionized water blank and to

three standards containing different known amounts of the test element. The volume of the blank and of each standard must be the same. The absorbance of each solution is determined and is then plotted on the vertical axis of a graph; the concentrations of the known standards are plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of intersection of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 5-3. The method of standard additions can be very useful; however, for the results to be valid, the following limitations must be taken into consideration:

- The absorbance plot of sample and standards must be linear over the concentration range of concern. For best results, the slope of the plot should be nearly the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20 percent), caution should be exercised.

- The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

- The determination must be free of spectral interference and must be corrected for nonspecific background interference.

10) Quality Control

The required QC procedures are described in Section 3.1.

11) Procedure

General procedures for flame atomic absorption analysis are given in Section 11a. Detailed procedures for determinating Ca, K, Mg, and Na are given in Sections 11b through 11e.

a) Flame Atomic Absorption Spectroscopy

Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the operating instructions which are provided by the manufacturer for the particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, the lamp should be allowed to warm up for a minimum of 15 minutes. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current

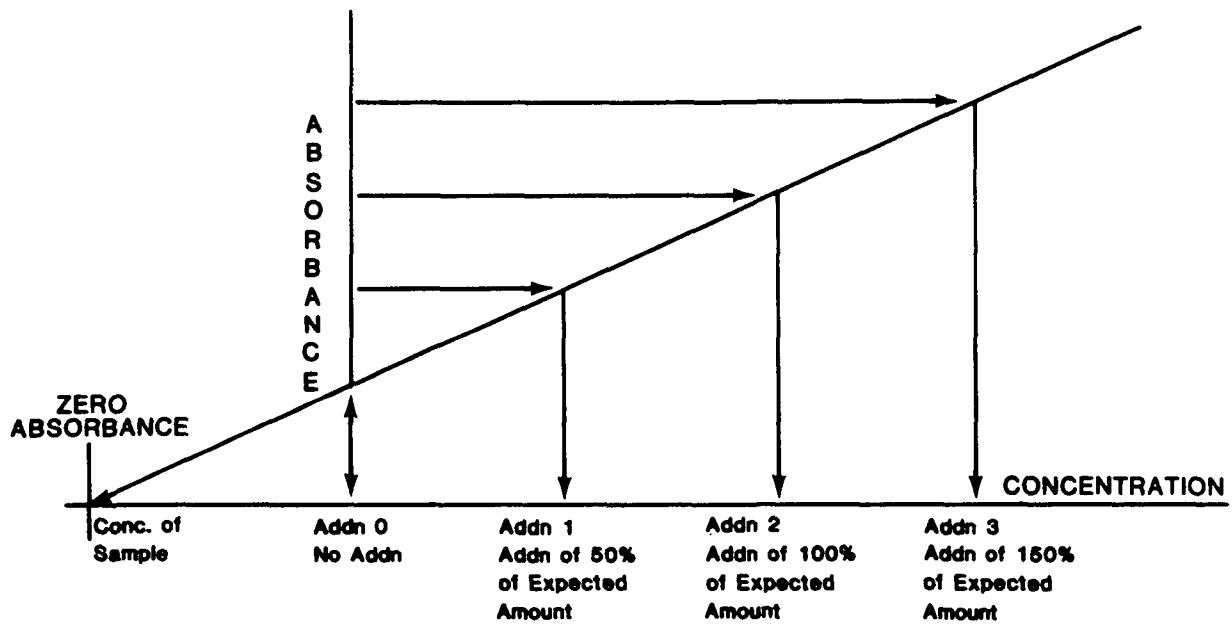

Figure 5-3. Standard Addition Plot.

by following the recommendations of the manufacturer. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the element under analysis, and calibrate the instrument.

Aspirate the samples, and determine the concentrations either directly (if the instrument reads directly in concentration units) or from the calibration curve.

b) Procedure for Determination of Dissolved Calcium

Samples for determination of dissolved calcium (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy for calcium (U.S. EPA, 1983).

1) Preparation of Reagents

Lanthanum chloride matrix modifier solution ($LaCl_3$)--Dissolve 29 g La_2O_3, slowly and in small portions, in 250 mL concentrated HCl (Caution: Reaction is violent), and dilute to 500 mL with water.

2) Preparation of Calcium Standard Solutions

Calcium stock solution (500 mg/L Ca)--Suspend 1.250 g $CaCO_3$ (analytical reagent grade, dried at 180°C for 1 hour before weighing) in water, and dissolve it cautiously with a minimum of dilute HCl. Dilute the solution to 1,000 mL with water.

Dilute calibration standards--Prepare a series of dilute Ca standards from the calcium stock solution to span the desired concentration range. These stocks are stable for two weeks or longer.

3) Suggested Instrumental Conditions (General)

Lamp--Ca, hollow cathode
Wavelength--422.7
Fuel--acetylene
Oxidant--air
Flame--reducing

4) Analysis Procedure

Step 1--To each 10.0 mL volume of dilute calibration standard, blank, and sample, add 1.00 mL $LaCl_3$ solution (e.g., add 2.0 mL $LaCl_3$ solution to 20.0 mL sample).

Step 2--Calibrate the instrument as directed by the manufacturer.

Step 3--Analyze the samples.

Step 4--Dilute and reanalyze any samples which have a concentration exceeding the calibrated range.

Report results as mg/L Ca.

NOTE 1: Phosphate, sulfate, and aluminum interfere but are masked by the addition of lanthanum. Because low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute acid solution. Concentrations of magnesium greater than 1,000 mg/L also cause low calcium values. Concentrations of up to 500 mg/L each of sodium, potassium, and nitrate cause no interference.

NOTE 2: Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.

NOTE 3: The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to the sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame.

5) Precision and Accuracy--In a single laboratory (EMSL-Cincinnati), with distilled water spiked at concentrations of 9.0 and 36 mg Ca/L, the standard deviations were ±0.3 and ±0.6, respectively. Recoveries at both these levels were 99 percent.

c) Procedure for Determination of Dissolved Magnesium

The samples for determination of dissolved magnesium (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy.

1) Preparation of Reagents

Lanthanum chloride solution ($LaCl_3$)--Dissolve 29 g La_2O_3, slowly and in small portions, in 250 mL concentrated HCl (Caution: Reaction is violent), and dilute the solution to 500 mL with water.

2) Preparation of Magnesium Standard Solutions

Stock solution (500 mg/L Mg)--Dissolve 0.829 g magnesium oxide, MgO (analytical reagent grade), in 10 mL of HNO_3, and dilute the solution to 1 L with water.

Dilute calibration standards--Daily, prepare from the Mg stock solution a series of Mg standards that span the desired concentration range.

3) Suggested Instrumental Conditions (General)

Lamp--Mg, hollow cathode
Wavelength--285.2 nm
Fuel--acetylene
Oxidant--air
Flame--oxidizing

4) Analysis Procedure

Step 1--To each 10.0 mL dilute calibration standard, blank, and sample, add 1.00 mL $LaCl_3$ solution (e.g., add 2.0 mL $LaCl_3$ solution to 20.0 mL sample).

Step 2--Calibrate the instrument as directed by the manufacturer.

Step 3--Analyze the samples.

Step 4--Dilute and reanalyze any samples which have a concentration exceeding the linear range.

Report results as mg/L Mg.

5) Precision and Accuracy--In a single laboratory (EMSL-Cincinnati), with distilled water spiked at concentrations of 2.1 and 8.2 mg/L Mg, the standard deviations were ±0.1 and ±0.2, respectively. Recoveries at both of these levels were 100 percent.

d) Procedure for Determination of Dissolved Potassium

The samples for determination of dissolved potassium (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy for potassium (U.S. EPA, 1983).

1) Preparation of Potassium Standard Solutions

Potassium stock solution (100 mg/L K)--Dissolve 0.1907 g KCl (analytical reagent grade, dried at 110°C) in water, and bring volume of solution to 1 L.

Dilute calibration standards--Daily, prepare a series of calibration standards spanning the desired concentration range. Match the acid content of the standards to that of the samples (ca. 0.1 percent [v/v] HNO_3).

2) Suggested Instrumental Conditions (General)

Lamp--K, hollow cathode
Wavelength--766.5 nm
Fuel--acetylene
Oxidant--air
Flame--slightly oxidizing

3) Analysis Procedure

Step 1--Calibrate the instrument as directed by the manufacturer.

Step 2--Analyze the samples.

NOTE: In air-acetylene or other high-temperature flames (>2,800°C), potassium can experience partial ionization which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and can thereby enhance analytical results. The ionization suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement which is due to sodium can be stabilized by adding excess sodium (1,000 µg/mL) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks should be analyzed to correct for potassium impurities in the buffer stock.

4) Precision and Accuracy--In a single laboratory (EMSL-Cincinnati), with distilled water samples spiked at concentrations of 1.6 and 6.3 mg/L K, the standard deviations were ±0.2 and ±0.5, respectively. Recoveries at these levels were 103 percent and 102 percent, respectively.

e) Procedure for Determination of Dissolved Sodium

The samples for determination of dissolved sodium (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy for sodium (U.S. EPA, 1983).

1) Preparation of Sodium Standard Solutions

Sodium stock solution (1,000 mg/L Na)--Dissolve 2.542 g NaCl (analytical reagent grade, dried at 140°C) in water, and bring the volume of the solution to 1 L.

Dilute calibration standards--Daily, prepare a series of calibration standards spanning the desired concentration range. Match the acid content of the standards to that of the samples (ca. 0.1 percent [v/v] HNO_3).

2) Suggested Instrumental Conditions (General)

Lamp--Na, hollow cathode
Wavelength--589.6 nm

NOTE: The 330.2-nm resonance line of sodium, which has a relative sensitivity of 185, provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.

Fuel--acetylene
Oxidant--air
Flame--oxidizing

3) Analysis Procedure

Step 1--Calibrate the instrument as directed by the manufacturer.

Step 2--Analyze the samples.

Step 3--Dilute and reanalyze any samples which have a concentration exceeding the calibrated range.

Report results as mg/L Na.

NOTE: Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1,000 mg/L) to both standards and samples.

4) Precision and Accuracy--In a single laboratory (EMSL-Cincinnati), with distilled water samples spiked at levels of 8.2 and 52 mg/L Na, the standard deviations were ±0.1 and ±0.8, respectively. Recoveries at these levels were 102 percent and 100 percent.

6.0 DATA MANAGEMENT

Most data for this program are provided on floppy disk. A limited amount of data must be manually entered (e.g., Belfort rain gage data). Hand entered data are reviewed for transcription accuracy. Evaluation of data quality is described in Section 3.0. Following this evaluation, data of poor or unknown quality are removed from the data base. Operator records are reviewed, and data corresponding to calibrations, quality control checks, maintenance activities, or malfunctions are removed.

The remaining verified data are analyzed and interpreted in accordance with the project objectives. Inter-instrument comparisons are made for instruments of the same model operating over the same sampling interval. These include the two Belfort rain gages, the two bulk samplers, duplicate weekly and daily snow cores, paired weekly wet/dry collectors, and paired daily wet/dry collectors. Comparisons are made of the water equivalent and chemistry results. Specific comparisons include computation of means, range, %RSD, and paired t-tests.

Comparisons between different instrument models employ statistical tests similar to those described above. All instruments operating over the same sampling interval are intercompared with intercomparison being based on water equivalent and chemistry results. In addition, comparisons are made of same model and different model instruments operating over different sampling intervals. This comparison of daily and weekly samples is made possible by integration of daily samples to create a "synthetic" weekly sample. Graphics are also used to illustrate temporal variability results.

The water equivalent and chemistry results of each instrument are also compared to ground truth measurements. The ground truth measurements include snow pit density measurements (water equivalent only) and snow cores (chemistry and water equivalent). To make these comparisons, the inter-instrument and spatial variability must be quantified; comparisons between instruments and ground truth measurements are generally made on means rather than on individual sample data.

Operational reliability is assessed on the basis of field documentation and data quality. Statistical analyses, comparison to ground truth, and operational reliability are all considered in the evaluation of recommended instruments and sampling intervals; this is the substance of the final project objective.

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APPENDIX A

DAS OPERATION

A.0 PROGRAM: SAMPLER

Version Documented: 2.00
Date: 11 February 1987

A.1 Introduction

SAMPLER is a program designed to acquire meteorological data continuously in analog and digital form in a remote setting. It is to operate in a relatively severe environment with unreliable electrical power. Therefore it is designed to be self starting and automatic with as much data file protection as possible.

A.2 Hardware Environment

SAMPLER is designed to operate on an IBM PC or compatible computer. The computer must be equipped with a MetroByte DAS-8 Analog to Digital (A/D) converter board.

A.3 Operating SAMPLER

To start SAMPLER, type the command

SAMPLER<cr>

from any directory on the computer ("<cr>" means "press the Carriage Return or ENTER key"). The program will immediately take its first sample, enter it into a file for that day, display a summary of the sample on the console, and wait for about one minute. Then the process repeats.

Normally, a command to start the program will automatically be given whenever power is first applied to the computer (or when it is reset). This is done by including the command SAMPLER in the AUTOEXEC.BAT file, which includes a variety of startup commands. Therefore, the starting sequence given above is only necessary after the program has been intentionally halted.

Please refer to section (7) for precautions to guarantee that the date (which is important for data file generation) is maintained properly.

A.4 Stopping SAMPLER

To halt SAMPLER, press the ESCape key (on the top left of the keyboard for the "new-style" IBM PC/AT keyboard). Within about a second, the prompt

Terminate [Y/N]?

will appear. You must press the "y" key (either upper or lower case) within approximately two seconds to terminate. No <cr> is needed.

When the program is stopped, the computer can be used for any other desired purpose, such as copying data files to floppy disk. When the other activity has been completed, restart SAMPLER as indicated in (3).

A.5 Other Keyboard Input

The design of SAMPLER assumes that the computer is usually completely dedicated to data acquistion and that it is often untended. To minimize the danger of tampering, "busy fingers," or carelessness, keystrokes other than ESCape are rejected and produce an audible tone and the message "Keyboard input ignored." Also, the same response is given after an ESCape if there is no response within about two seconds or if the response is other than "y" or "n."

If the program has been terminated properly, the following functions may be accessed:

Function	Command
view data files:	type YYMMDD.DAT
print data files:	print YYMMDD.DAT
format the disk:	
(for drive A):	format A:/s
(for drive B):	format B:/s
copy to disk:	
(for drive A):	copy *.DAT A:
(for drive B):	copy *.DAT B:
restart "Sampler Ver. 2.0"	(easiest method) press ALT, DEL,CTRL keys simultaneously

A.6 Data Files

SAMPLER places its records into a file whose name is derived from the current date. The file name is of the form

YYMMDD.DAT

where YY, MM, and DD are year, month, and day numbers. For example, files 870101.DAT and 871231.DAT would be used for 1 January 1987 and 31 December 1987, respectively.

At each new record, the current day's file is opened (or created if it

does not exist), a new record is appended at its end, and it is closed. This assures file integrity in the event of power failure.

Note that if the program is halted and then restarted, data will continue to be appended to the current day's file if it existed before the restart and if it was not deleted or renamed.

The data files are standard MS-DOS "ASCII" (American Standard Code for Information Interchange) files. They can be viewed or printed with the MS-DOS "TYPE" or "PRINT" commands or processed with any text editor. The file format is

hh:mm:ss www.w ddd X X X<cr>

where "hh," "mm," and "ss" are sample time hours, minutes, and seconds, "www.w" is wind speed in meters/second (m/s) (to a precision of 0.1 m/s), "ddd" is wind direction bearing in degrees (0 to 359), and "X X X" is the state of three moisture detectors. The states are "W" for wet (high signal level) or "D" for dry (low signal level).

A.7 Maintaining the Proper Date

SAMPLER obtains the date from MS-DOS when it is first started, and MS-DOS in turn obtains it from an internal clock/calendar whenever the computer is reset or powered up. As the time of day passes midnight (23:59:59 to 00:00:00), the internal copy of the date of SAMPLER is updated to the next day.

A.8 Sample Timing

SAMPLER spends most of its time in a delay loop in a procedure named Wait-for-1-Minute. This procedure makes 60 calls to an internal procedure named Delay that waits for (approximately) 1,000 milliseconds (one second). This delay value is established in a constant named OneSecond that is currently set to 1,000. If required, this constant can be raised or lowered to adjust the sampling interval. If it is changed, the program will need to be recompiled (Section 13).

A.9 Hardware Configuration

SAMPLER assumes that the DAS-8 A/D converter is used as follows (Pin numbers refer to the 37-pin connector on the DAS-8 board):

A/D Converter Analog Channels:

Channel	Pin Number Signal	Ground	Purpose
0	37	18	Wind Direction Signal
1	Not used		
2	Not used		
3	34	15	Wind Speed Indicator Output
4-7	Not used		

Binary Inputs

Inputs	Pin Number	Purpose
1	25	Moisture Detector No. 1
2	26	Moisture Detector No. 2
3	27	Moisture Detector No. 3

The computer is also equipped with a parallel interface card that provides additional binary inputs. SAMPLER does not use that card at the present time, but it could be modified to do so if necessary.

A.10 Obtaining the Wind Direction

The wind direction indicator is powered by a 5.0 volt d.c. source and produces an output of 0 to 360 degrees proportionate to 0 to 5.0 volts.

volts	degrees
0.0	0.0
1.25	90.0
2.50	180.0
3.75	270.0
4.97	359.0

A.11 Wind Speed

The wind speed indicator contains a generator that produces an output voltage proportional to wind speed. Three calibration values were provided by data from the manufacturer:

Rotation Speed (RPM)	Wind Speed Miles/Hr	Knots	Meters/sec	Output Voltage (volts)
300	32.4	28.1	14.48	1.50
600	62.4	54.2	27.90	2.90
900	92.5	70.3	41.35	4.28

The output voltage is clearly nonlinear with respect to rotation speed.

However, when wind speed is plotted as a function of output voltage (Figure A-1), the relation is as nearly linear as can be observed from the three points. Therefore, a simple scaling constant is used to derive wind speed from its sample (on A/D converter channel 2):

1. Sample channel 2
2. Convert to the equivalent voltage in volts
3. Multiply this by the constant "MetersPerSecondPerVolt" = 41.35/ 4.28 = 9.6612

A.12 Moisture Detection

The Wet (high) or Dry (low) status of three moisture detectors must be monitored. This can be accommodated by the DAS-8 A/D converter hardware, which makes three TTL-compatible binary input signals available. SAMPLER uses these. The sampling procedure is simple; it is documented in the DAS-8 manual and in the appropriate procedure in the source code for SAMPLER.

A.13 Program Elements for SAMPLER

SAMPLER is written in Turbo Pascal, Version 3.02, and is compiled into a executable file. Both source and executable forms are in directory C:\FISHER. The program elements are

SAMPLER.PAS: Pascal source code
SAMPLER.COM: Executable form

Directory C:\FISHER also contains the Turbo Pascal system, which includes the compiler and a full-screen editor. These files are TURBO.COM (the compiler/editor) and TURBO.MSG (an error message file).

A.14 Generating SAMPLER.COM

If SAMPLER.PAS is modified, it must be recompiled to produce a new executable file SAMPLER.COM. To do this, a "Compile into .COM file" option must be invoked in TURBO (otherwise the program is compiled only into memory). To do this,

1. Set the current directory to C:\FISHER with the command

   CD\FISHER<cr>

2. Start the TURBO system by giving the command

   TURBO<cr>

3. Select the "Compile to .COM file" option with the following command sequences (only the first letter is used; no <cr> is used):

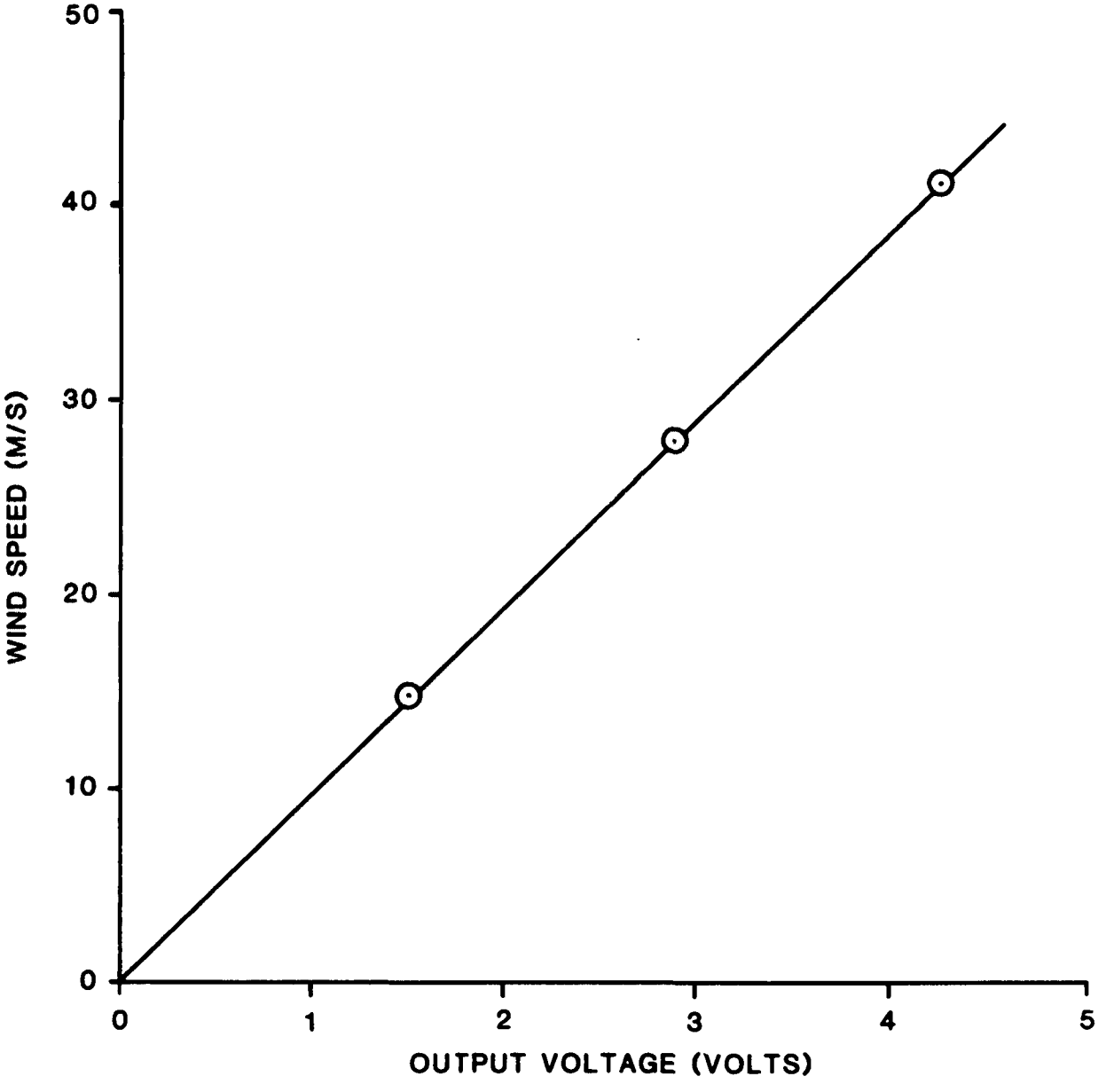

Figure A-1. Windspeed indicator calibration.

```
O     (for "Options")
C     (for "Compile to .COM file")
Q     (for "Quit Options")
W     (for "Workfile")
SAMPLER (to specify the file to compile)
C     (to compile it, creating a new SAMPLER.COM)
Q     (to exit from TURBO.)
```

A.15 General Remarks About SAMPLER

The program is written in normal Pascal style, with a number of procedures defined first, followed finally by a brief main program which is merely a collection of procedure calls. The procedures are generally straightforward and are heavily commented, so little needs to be added here.

Access to the registers of the DAS-8 board are handled by "Port" instructions that write to or read from an Input/Output port on the computer. The DAS-8 programmers' manual describes the use of the registers in detail, and the source code of SAMPLER also elaborates on them.

APPENDIX B

PROCESSING LABORATORY CONDUCTIVITY METHOD
(Modified from Chaloud et al., 1986, unpublished document)

B.0 INTRODUCTION

Conductivity is a measure which often can be linearly correlated with the ionic strength of a solution. Conductivity can be used to generate a synthetic ionic balance which can be used as a check on measured ionic concentrations.

The Beckman Instruments Model RC-20 conductivity bridge employs a Wheatstone bridge in which the values of three out of four resistances are known. Conductivity is determined by measuring the reciprocal of the unknown resistance when a constant voltage is delivered across the conductivity cell.

B.1 Instrument Set-up

NOTE 1: Never acid wash any containers used for conductivity measurement. Rinse the containers three times with deionized water, or soak them in deionized water overnight before use.

NOTE 2: Store the conductivity probe in fresh deionized water daily. Substances which build up on the probe (e.g., suspended solids, etc.) should be removed periodically according to the recommendations provided by the manufacturer. Probe replatinization is also required periodically; consult the instruction manual for the proper method.

NOTE 3: An analyst pours the snow melt into the conductivity tubes after completion of melting.

NOTE 4: See the conductivity flowchart (Figure B-1).

1) Unscrew both of the leads connecting the probe to the conductivity meter to break the circuit and to prevent capacitance shunting between calibrating resistors and probe.

2) Check the electronic function of the conductivity meter by plugging in the resistors and by reading the conductivity at the appropriate ranges (RES MULT/CONDMULT Switch).

   Readings should be within 1 percent of the theoretical value. Record the values in the logbook. If the values are not within 1 percent, consult the guide provided by the manufacturer.

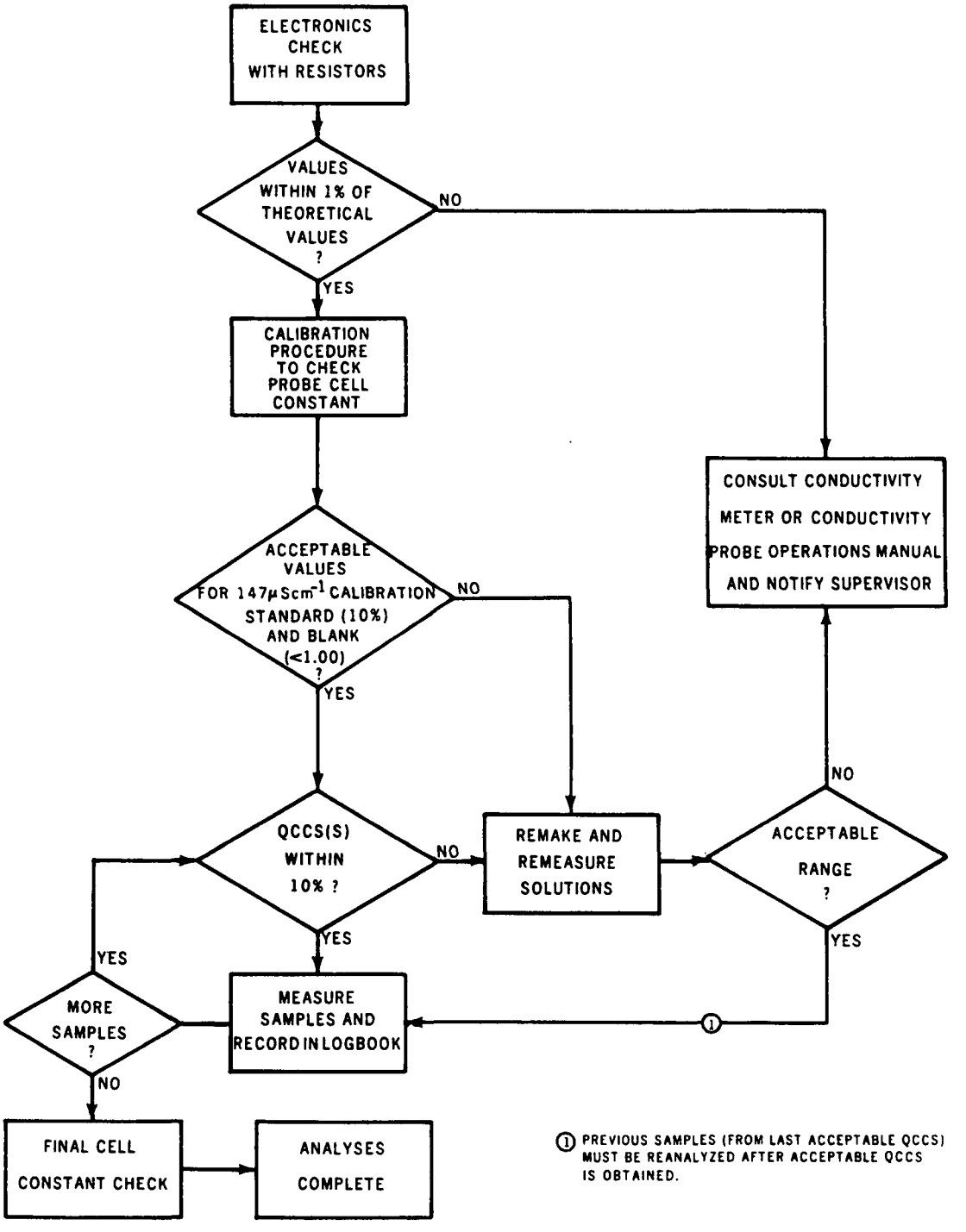

Figure B-1. Flowchart for conductivity.

B.2 Reagents

B.2.1 Potassium Chloride Stock Solution (1 M KCl)

NOTE 1: Prepare as needed and refrigerate at 4.0°C.

NOTE 2: This stock solution is used to make the following standards:

147 $\mu S\ cm^{-1}$ calibration standard,
14.7, 74, 147 $\mu S\ cm^{-1}$ QC standards.

NOTE 3: This stock solution should be made up in at least 1-L batches to minimize weighing and dilution errors. The 1 M KCl stock solution has a theoretical electrical conductivity of 111,900 $\mu S\ cm^{-1}$ at 25°C. This value should be verified by measuring at least three 35-mL samples contained in 50-mL centrifuge tubes.

1) Fill a clean 1-L volumetric flask with approximately 500 mL of deionized water.

2) Weight 74.553 g of potassium chloride (KCl, ultrapure, dried for 2 hours at 105°C, and ampulated).

3) Completely dissolve the KCl in deionized water, and dilute to the 1-L mark. Mix again thoroughly.

4) Store the stock solution in 500-mL bottles (not acid washed) which have been rinsed three times with the 1 M KCl solution. Label the bottles "1 M KCl Stock Solution," and refrigerate them at 4.0°C.

B.2.2 Calibration Blank

NOTE 1: Two centrifuge tubes (deionized water leached) are required for each of the calibration, QCCS, and blank solutions. Label the tubes accordingly, and designate one of each pair as the rinse.

NOTE 2: It cannot be assumed that the deionized water has a negligible conductivity; therefore, the blank conductivity value is subtracted from all standards.

NOTE 3: Be consistent in obtaining deionized water. Obtain deionized water from the same reverse osmosis (RO) system from which all standards are made.

1) Rinse two clean, labeled 50-mL centrifuge tubes three times with deionized water, and then fill them with 30 to 40 mL deionized water.

B.2.3 Calibration Standard - 147 $\mu S\ cm^{-1}$

NOTE: Prepare Daily

1) Fill a clean labeled 1-L volumetric flask with approximately 500 mL of deionized water. Obtain a 50-mL disposable beaker, rinse the beaker three times with 1 M KCl stock solution (2 to 3 mL rinse), and fill it with 5 to 10 mL of stock solution. Use this stock solution to make calibration and QCCS solutions.

2) Use a calibrated 100 to 2,000 µL pipet (rinse pipet tip one time with solution) to deliver 1.000 mL of stock solution to the 1-L flask. Mix and dilute to 1-L mark, and mix again.

3) Rinse two clean, labeled 50-mL centrifuge tubes three times with calibration standard, and pour 30 to 40 mL in each tube.

B.2.4 QC Standards - 14.7, 74, 174 $\mu S\ cm^{-1}$

NOTE: Prepare daily.

1) Fill three clean, labeled 500-mL volumetric flasks each with approximately 250 mL deionized water.

2) Use the beaker of 1 M KCl stock solution (see Section B.2.3, Step 1) to prepare the following solutions:

   a) 14.7 $\mu S\ cm^{-1}$. Use a calibrated 40- to 200-µL pipet to deliver 0.050 mL of stock solution to the volumetric flask labeled "14.7 $\mu S\ cm^{-1}$ QC Standard."

   b) 74 $\mu S\ cm^{-1}$. Use a calibrated 200- to 1,000-µL pipet to deliver 0.250 mL of stock solution to the volumetric flask labeled "74 $\mu S\ cm^{-1}$ QC Standard."

   c) 147 $\mu S\ cm^{-1}$. Use a calibrated 200- to 1,000-µL pipet to deliver 0.500 mL of stock solution to the volumetric flask labeled "174 $\mu S\ cm^{-1}$ QC Standard."

3) Mix and dilute each of the three standards to the 500-mL mark, and mix them again.

4) Rinse each clean, labeled, centrifuge tube three times with the appropriate standard (two centrifuge tubes for each standard, with one tube designated as rinse). Fill each tube with its corresponding standard (30 to 40 mL).

5) Cap and store each standard, and all poured centrifuge tubes, at room temperature.

B.3 Probe Calibration Check

NOTE 1: Turn conductivity meter "OFF" when removing probe from solution. Follow the guidelines provided by the manufacturer for operation of the conductivity bridge. The following procedure is modified from the Beckman instruction manual.

NOTE 2: When measuring the conductivity of a solution, do not allow the probe to touch the sides or the bottom of the plasticware. Hold the cell upright. Be sure the vent holes are covered by solution and that there are no air bubbles around the electrode.

NOTE 3: Rinse the probe in deionized water between each measurement.

NOTE 4: Always measure the blank first.

1) Connect the probe leads to the instrument at CELL binding posts 2 and 3.

2) Instrument settings: set MODE switch to COND/RES. position; set FREQ switch to IKHZ bridge frequency; set CAP COARSE and CAP FINE switches to zero.

3) Turn instrument on by actuating the ON-BAT check switch.

4) The conductivity measurements are made without temperature compensation when a water bath is employed. If not using a temperature bath, consult the guide provided by the manufacturer for information about alternative methods. Set the TEMP COMP switch to NONE, and adjust the BALANCE control to give a counter reading of 1.05.

5) To balance the meter, set the COND MULT selector to 0.1 (the balance meter pointer will deflect left of zero). Increase the multiplier value step by step until the balance meter pointer deflects to the right of zero, and then return the multiplier dial one step so that the pointer deflects left again. Turn the BALANCE control until the balance meter pointer reads zero. Set MODE selector to the CAP setting. If the balance meter pointer deflects less than one major division (five minor divisions) to either side of zero, the meter is balanced. If the one division limit is exceeded, rotate the CAP FINE switch to bring balance meter pointer toward zero. The CAP COARSE switch is used if the CAP FINE switch fails to bring the pointer toward zero (return CAP FINE to zero before using CAP COARSE). Alternate the MODE switch between COND/RES and CAP as described

above until COND/RES balance equals zero, and the CAP balance is within one major division of zero.

6) To determine the conductivity value, place the probe into the container with the solution to be measured and use the BALANCE control to obtain the measured conductivity. The measured conductivity value is the counter reading at balance multiplied by the COND MULT setting.

Determine the value of the cell constant as follows:

$$K_C = \frac{147.0\ \mu S\ cm^{-1}\ \text{Theoretical value of calibration standard at 25°C}}{\text{Measured value of calibration standard at 25°C} - \text{Measured value of blank at 25°C}}$$

B.4 QCCS Check

NOTE 1: Measure 14.7, 74, and 147 $\mu S\ cm^{-1}$ QC standards after every 10 samples and at the end of the batch which follows the trailer duplicate, and do the calculations as described below in Step 2. Record all calculations in the logbook.

NOTE 2: If any QCCS solution is not in range, try repouring the standard. If it still is not in range, remake the standard, and make a note in the logbook under the comment section indicating exactly when this occurred. Record the data.

1) Measure the conductance of the three QCCS solutions (prepared in Section B.2.4).

2) Determine the conductivity values of QCCS solutions as described in Section B.3, Step 6. Multiply the measured value (counter reading x COND MULT setting) by the cell constant (K_C) value calculated in B.3, Step 7. Subtract the measured value of the blank (counter reading x COND MULT setting x K_C) to determine the actual value of the QCCS solutions. The actual values must be within 10 percent of the theoretical values.

B.5 Sample Measurement

1) Sample conductivity is determined, and measured conductivity is calculated as follows: measured conductivity x COND MULT setting x K_C. Do not subtract the temperature adjusted blank value from the result. Record all computations in the logbook.

2) The trailer duplicate is measured last. The trailer duplicate values must be within 10 percent of each other.

B.7 Clean-up

1) Make sure that the conductivity meter is in the "OFF" position. Place the probe in fresh deionized water, and cover the container with Parafilm.

2) Clean all glassware used for the preparation of the standard solutions by rinsing them three times with deionized water.

APPENDIX C

LABORATORY pH DETERMINATION (OPEN SYSTEM)
(modified from Chaloud et al., 1986, unpublished document)

C.0 INTRODUCTION

The pH of an aquatic environment is regulated by both abiotic (inorganic CO_2 equilibria, surficial geology, and anthropogenic pollutants) and biotic (photosynthesis, respiration, and decomposition) factors. A pH balance is usually maintained by the presence of buffering reactions within the aquatic system. If this balance is shifted, both chemical and biotic repercussions may result.

In the processing laboratory, pH is measured with Orion Model 611 pH/millivolt meters and Orion Ross combination electrodes. Measurements of snow samples are made with an open system because snow samples are assumed to be at equilibrium with respect to CO_2 gas transfer between the water sample and the laboratory atmosphere.

The pH is defined as the negative logarithm of the activity of hydrogen ions (H^+). The H^+ activity is a measure of the "effective" concentration of hydrogen ions in solution, and it is always equal to or less than the true concentration of hydrogen ions in solution. Values usually range from pH 1 to pH 14, with pH 1 being most acidic, pH 7 neutral (at 25°C), and pH 14 most alkaline. Each pH unit represents a tenfold change in H^+ activity. For example, a pH 4 solution is 10 times as acidic as a pH 5 solution.

When the pH of a sample solution is measured, the hydrogen ions come into equilibrium with the ion exchange surface (glass) of a calibrated pH electrode which creates an electrical potential. This voltage difference is measured by the pH meter in millivolts and is then converted and displayed as pH units.

C.1 Reagents

NOTE 1: See the flowcharts for pH determinations (Figures C-1 and C-2).

NOTE 2: Use deionized water obtained from the same RO system throughout all reagent preparation.

C.1.1 pH 4.00 QCCS Solution (0.0001 N H_2SO_4)

NOTE: pH 4.00 QCCS must be prepared daily.

1) Fill a clean 1-L volumetric flask with approximately 500 mL deionized water.

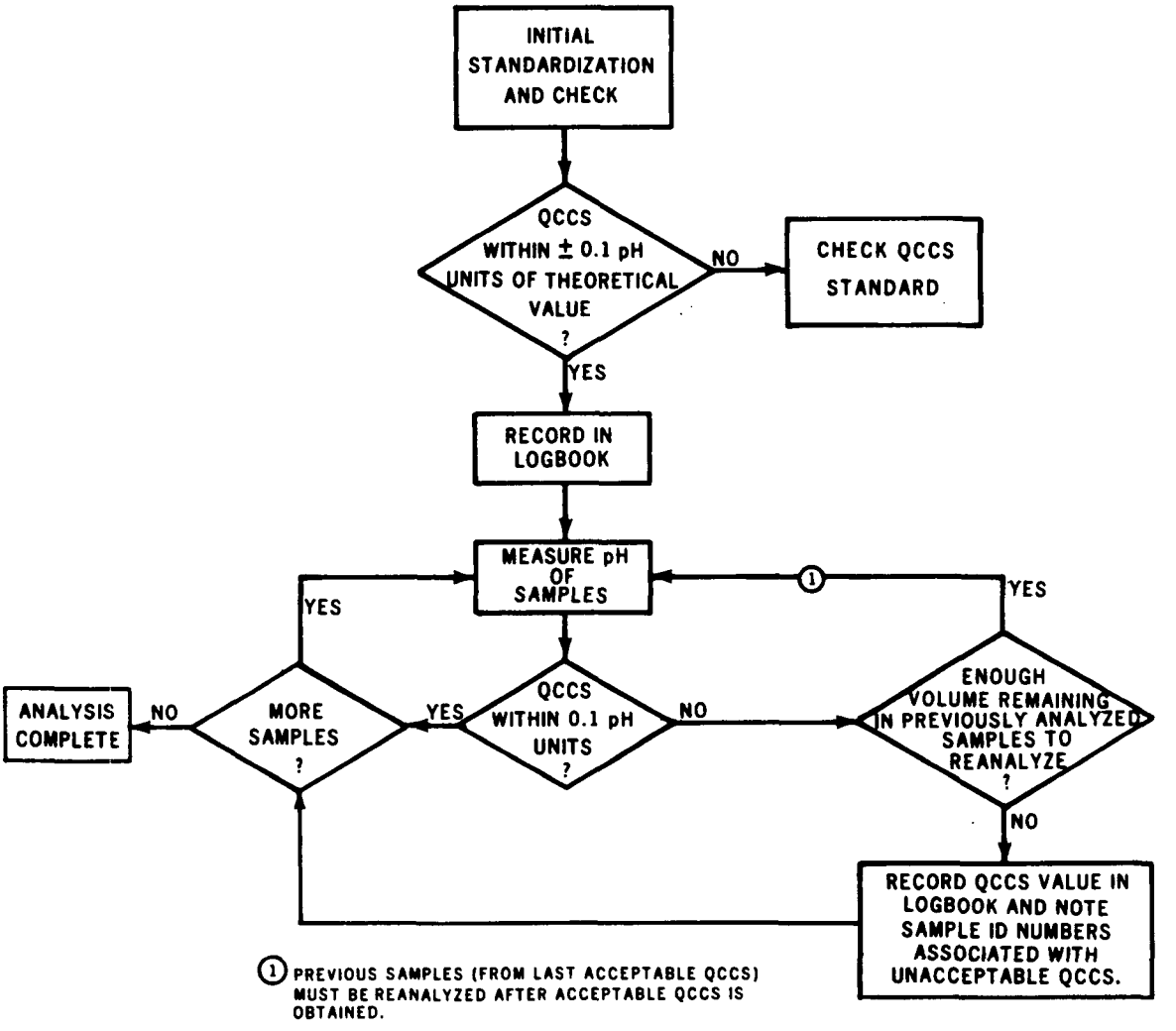

Figure C-1. Flowchart for laboratory pH determination.

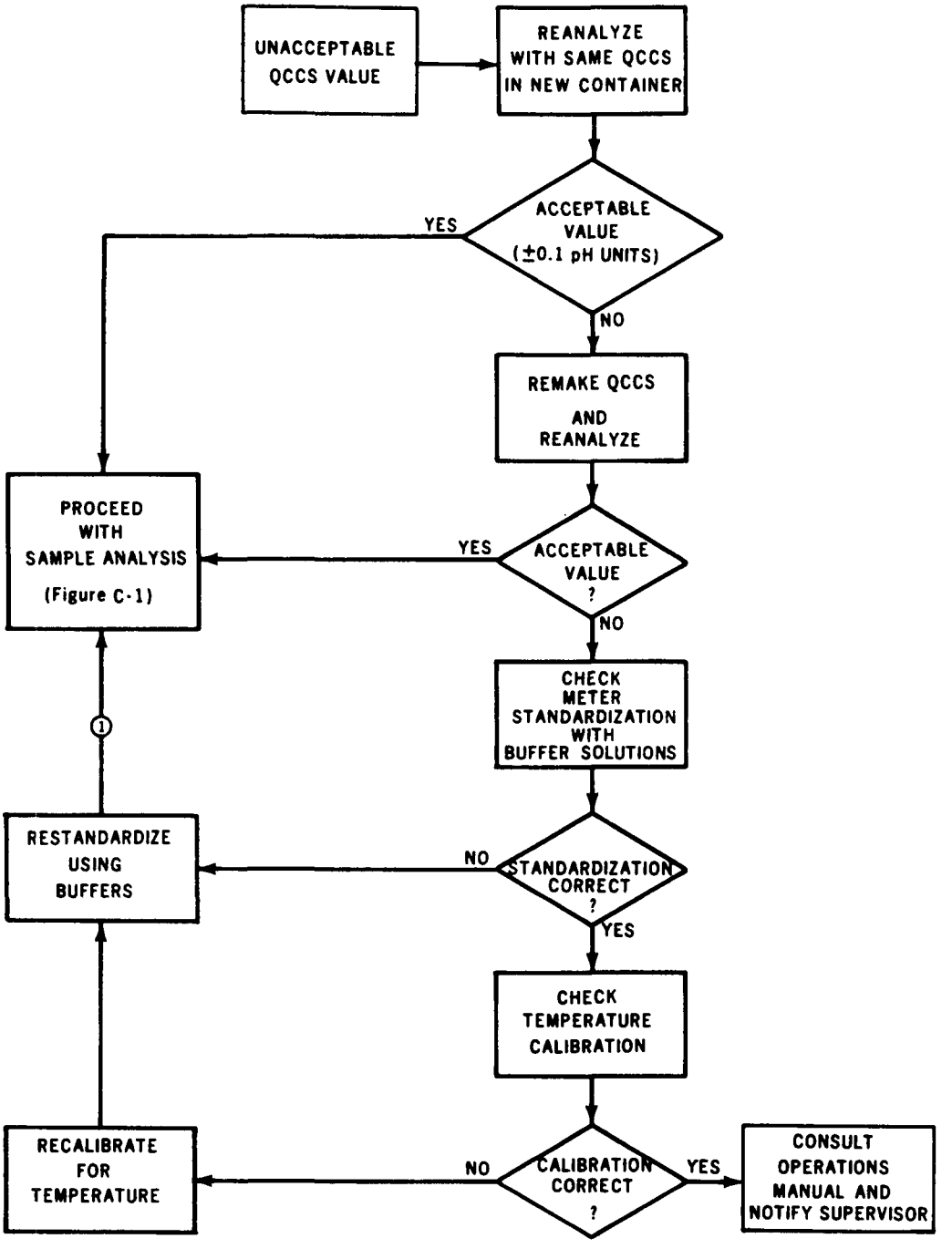

Figure C-2. Troubleshooting flowchart for pH determination.

2) Pour approximately 5 mL 0.1 N H_2SO_4 into a 50-mL disposable beaker.

3) Using a calibrated 200- to 1,000-µL pipet, add 1.000 mL of 0.1 N H_2SO_4 to the volumetric flask. Stopper the flask, and mix the solution thoroughly by inversion. Dilute to the 1-L mark with deionized water to produce 0.0001 N H_2SO_4. Mix the solution again, and label the flask "QCCS-pH 4.00."

C.1.2 NBS-Traceable Buffers

Two commercially prepared buffer solutions (pH 4.00 and pH 7.00) are required.

C.1.3 Dilute pH 7.00 Buffer Intermeter Comparability Solution

NOTE: The dilute pH 7.00 buffer must be prepared daily; the theoretical pH value is 7.31 ± 0.07.

1) Fill a clean, labeled, 1-L volumetric flask with approximately 500 mL deionized water.

2) Tare the balance containing a 50-mL beaker, and measure 5.000 ± 0.001 g of NBS pH 7.00 buffer. Add the volume to the 1-L flask. Stopper the flask, and mix the solution thoroughly by inversion. Dilute to the 1-L mark with deionized water. Mix the solution again.

C.2 Instrument Preparation

NOTE 1: It is mandatory that all personnel operating the pH meter be familiar with its operating procedures before using the instrument.

NOTE 2: Always leave the pH meter on "STD BY" when the electrode is removed from a solution, when rinsing the electrode, or when the meter is not in use.

1) Plug in the instrument, and verify that the control knob is on "STD BY." Allow at least 30 minutes for instrument warm-up prior to use.

2) Connect the Orion Ross combination electrode to the meter. Consult the pH electrode manual for the proper procedure.

3) Verify that the level of reference filling solution (3 M KCl) in the electrode is just below the fill hole and that the fill hole is uncovered during measurement (slide the plastic sleeve down).

4) Calibrate the meter for temperature weekly by using a two-point standardization (one point at approximately 5°C to 10°C and the other point at room temperature).

a) Room Temperature: Place the electrode and an NBS thermometer into deionized water which is at room temperature. Swirl the electrode for 5 to 10 seconds.

b) Turn the knob on the meter to "TEMP." With a small screw driver, adjust the "TEMP ADJ" screw on back of pH meter until the display corresponds to the temperature reading of the thermometer.

c) Cold Temperature: Place the probe and the NBS thermometer into a 250-mL beaker containing cold deionized water (5 to 10°C). Repeat Step b by adjusting the display with the "TEMP SLOPE" screw on the back of the meter.

d) Continue Steps a through c until no further adjustments are necessary, and record all values in the logbook.

C.3 Daily Instrument Standardization

C.3.1 Temperature Standardization

1) Check the calibration of the temperature meters daily with a beaker of room temperature deionized water and with an NBS thermometer as described in Section C.2, Steps 4a and 4b.

2) If the meter reading differs from the NBS thermometer by more than 1.0°C, adjust the display to that of the thermometer by using the "TEMP ADJ" screw.

C.3.2 Standardization with NBS-Traceable Buffers

NOTE: The pH meter is standardized <u>daily</u> with two NBS pH buffers (pH 7.00 and pH 4.00).

1) Pour fresh pH 7.00 and pH 4.00 buffer solutions into labeled 50-mL beakers (one "RINSE," one "CALIBRATION," and one "CHECK" beaker for each buffer). Rinse all beakers three times, and fill them with the appropriate buffer solutions.

2) Rinse the electrode with deionized water. Place the electrode into the pH 7.00 "RINSE" beaker, and swirl the beaker for 30 seconds. Place the electrode into the "CALIBRATION" beaker, turn the knob to "pH," swirl the beaker for 30-60 seconds (or until the pH reading is stable), and read the value on the display. Consult the pH-temperature chart, Table C-1. Use the "CALIBRATE" knob to adjust the pH reading on the meter to the theoretical pH of the buffer solution at the appropriate temperature.

TABLE C-1. pH VALUES OF BUFFERS AT VARIOUS TEMPERATURES
(from Orion Research Instruction Manual, 1983).

NBS buffer, nominal value at 25°C	Temperature										
	0°C	5°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C
1.68	1.67	1.67	1.67	1.67	1.68	1.69	1.71	1.72	1.74	1.77	1.79
3.78	3.86	3.84	3.82	3.79	3.77	3.75	3.75				
4.01	4.00	4.00	4.00	4.00	4.02	4.03	4.06	4.08	4.13	4.16	4.21
6.86	6.98	6.95	6.92	6.87	6.85	6.84	6.83	6.84	6.85	6.86	6.88
7.00*	7.11	7.08	7.06	7.01	6.98	6.97	6.97				
7.41	7.53	7.50	7.47	7.43	7.40	7.38	7.37				
9.18	9.46	9.40	9.33	9.23	9.14	9.07	9.01	8.96	8.92	8.89	8.85
10.01	10.32	10.25	10.18	10.06	9.97	9.89	9.83				

*Non-NBS Phosphate buffer

3) Repeat Step 2 for pH 4.00 buffer adjust the "% SLOPE" knob to adjust the pH reading.

4) Repeat Steps 2 and 3 until both the pH 7.00 and the pH 4.00 buffers agree with the theoretical pH of the buffer solution at the appropriate temperature.

5) Check the standardization with the buffer solutions in the "CHECK" beakers. If the values differ by more than ±0.03 units from the theoretical value, repeat the standardization process (see Section C.3.2, Steps 1-5). When the meter standardization is acceptable, record the pH and temperature readings for each buffer solution in the pH logbook.

C.4 Sample Analysis

NOTE 1: At the beginning of each survey, a primary meter must be designated. This meter is to be used when only one meter is necessary to analyze a batch.

NOTE 2: If the batch size is equal to or greater than 20 samples, a

secondary meter may be used, and additional procedures are involved (see Section C.5).

NOTE 3: pH is not measured in field blanks, lab blanks, or lab audits.

NOTE 4: Allow samples to warm to room temperature before measuring pH.

C.4.1 Initial QCCS Check

1) Rinse and fill two beakers with pH 4.00 QCCS.

2) Rinse the electrode by swirling it in the rinse beaker for 15 to 30 seconds.

3) Insert electrode into the QCCS beaker.

4) Turn the knob to pH and start the stopwatch. Record the initial pH, temperature, and time (0:00) in the pH logbook.

5) Wait until the reading seems fairly consistent, and then note the time and pH values on a loose sheet of paper. If the pH reading does not vary by more than 0.02 pH units in one direction throughout a 1-minute interval, the reading is considered stable. Record the stable pH and temperature readings, and the total elapsed time in the logbook.

C.4.2 Sample Measurement

1) Rinse the electrode copiously with deionized water, and then rinse it in the sample tube marked "Rinse."

2) Determine sample pH by following the instructions in Section C.4.1.

C.4.3 Routine QCCS Determination

NOTE: The pH 4.00 QCCS is always analyzed at the beginning of a batch and at the end of a batch. The QCCS is also analyzed at intervals within the batch; the intervals depend on the batch size and on the number of pH meters used. The criteria necessary for determining when a QCCS should be analyzed are listed below:

- If the batch is less than 20 samples, use only the meter designated as the primary meter. Run a QCCS in the middle of the batch.

- If the batch is less than or equal to 5 samples, a QCCS does not need to be analyzed mid-batch.

- If the batch is greater than or equal to 20 samples and if one pH meter is used, analyze a QCCS after every 10 samples.

1) Measure and record the QCCS by following the instructions in Section C.4.1.

2) If the measured QCCS pH is acceptable (pH 4.00 ± 0.10), proceed with routine sample pH determinations.

3) If the QCCS pH is not acceptable, follow the steps below until an acceptable value is obtained.

   a) Repour the pH 4.00 QCCS into a beaker and reanalyze.

   b) Remake the pH 4.00 QCCS (see Section C.1.1), and reanalyze the QCCS.

   c) Repeat the standardization steps (see Section C.3), and reanalyze the QCCS.

   d) If an acceptable reading is still not obtained, consult the laboratory supervisor.

4) If the pH meter requires recalibration to obtain an acceptable QCCS reading, make a notation in the pH logbook. Determine which samples must be reanalyzed.

   a) Reanalyze all samples back to the last acceptable QCCS.

C.5 Data Reporting

Trailer Duplicate (TD) Pair. One sample is analyzed in duplicate. The pH value of the duplicate sample must be within 0.1 pH unit of the routine sample value. If the value is outside the acceptable range, record the values and notify the laboratory supervisor for the appropriate procedure.

C.6 Instrument Care and Clean-up

NOTE: Read the instructions provided by the manufacturer for the maintenance of the pH meter and electrode.

C.6.1 Daily Clean-up

1) Copiously rinse the electrode and glassware with deionized water.

2) Cover the fillhole of the electrode with the plastic sleeve, and store the electrode in 3 M KCl.

3) Make sure the meter is on "STD BY."

C.6.2 Weekly Maintenance

1) Drain the 3 M KCl filling solution from the electrode by using a disposable pipet with Teflon tubing attached.

2) Refill the electrode chamber with the 3 M KCl filling solution, and rinse it by inverting the electrode. Drain the solution as in Step 1.

3) Refill the electrode with the filling solution to just below the fill hole.

4) Gently spin the electrode overhead by the leader for approximately 1 minute to remove any air bubbles. Be careful to stand clear of any obstacles when swinging the electrode.

C.6.3 pH Meter Electronic Checkout

NOTE: This procedure should be performed whenever a new pH meter is set up or when calibration problems occur.

1) Connect the shorting strap by following the instructions in Orion pH meter manual.

2) Turn the "TEMP ADJ" and "TEMP SLOPE" screws fully counterclockwise and record the display pH value (turn knob to "pH" position).

3) Turn the "TEMP SLOPE" screw 7.5 turns clockwise, and record the display pH value. The difference between the "TEMP SLOPE" value in Step 2 and Step 3 should be between 7.0 and 15.0.

4) Turn the "TEMP ADJ" screw until a value between 50.0 ± 0.1 appears on display.

5) Press the test button. A value of 42.2 ± 2.0 should appear on display when the knob is in the "TEMP" positon. If this value is not displayed, keep depressing the test button and use the "TEMP SLOPE" screw to adjust the reading to 40.0 ± 0.1. Release the test button and use the "TEMP ADJ" screw to obtain reading of 50.0 ± 0.1. Press the test button again. The reading should be 42.2 ± 2.0. Repeat this procedure several times if the value is not in range.

6) If the meter still will not calibrate, consult the laboratory supervisor.

C.6.4 Electrode Etching Procedure

CAUTION: Use Extreme Caution when using the NaOH pellets. Be sure to wear gloves, protective glasses, and a rubber apron.

NOTE 1: If the electrode response is sluggish or if the instrument cannot be standardized, the following procedure is recommended for cleaning the ceramic junction of the electrode and for improving the electrode response time. Consult the laboratory supervisor before performing this procedure.

NOTE 2: Etch electrodes in groups of three when possible. Prepare a fresh NaOH solution for each group of electrodes.

1) Drain the filling solution from the electrode.

2) Rinse the filling chamber with deionized water, and drain it.

3) Refill the chamber with deionized water.

4) Prepare a 50 percent (weight to volume) NaOH solution by slowly adding 30 g NaOH to 30 mL deionized water.

5) Gently stir the solution with up to three electrodes to dissolve the NaOH. The solution will be very hot and may boil and splatter, and CAUTION MUST BE USED.

6) Stir the solution for an additional 2 minutes with the electrodes.

7) Rinse the electrodes with deionized water.

8) Rinse the electrodes in pH 7.00 buffer for 2 minutes.

9) Drain the deionized water from the filling chambers.

10) Refill each electrode with 3 M KCl, agitate the electrodes, and drain the chambers.

11) Refill the chambers once more with 3 M KCl, and spin each electrode from the leader to remove air bubbles.

12) Soak electrode in pH 7 buffer for 24 hours prior to checking performance.

APPENDIX D

FILTRATION, PRESERVATION, AND SHIPPING
(Modified from Chaloud et al., 1986, unpublished document)

D.0 INTRODUCTION

Samples are filtered to remove the biotic and abiotic particles which exceed 0.45 μm in size. This procedure is necessary to prevent changes in particular chemical parameters prior to processing at the analytical laboratory. The parameter being measured at the analytical laboratory dictates what the preparation and preservation procedure performed by the processing laboratory will be in order to ensure sample stability until analysis is complete. Aliquot preparation takes priority in the laboratory in that the samples must be processed after completion of melting but before sample temperature exceeds 4°C.

D.1 Filtered Aliquots - Acid-Rinsed Units (Aliquots 1 and 4)

D.1.1 Filtration Unit Assembly

NOTE 1: There are two 4-apparatus filtration set-ups in each clean air station.

NOTE 2: A slight positive (blowing into the laboratory) air flow should be maintained in the clean air station. Air flow can be regulated by turning the adjustment screw located centrally above the sash. Check for positive air flow by taping a Kimwipe strip to the bottom of the glass window.

1) Four filtration units in a series constitute a set-up. Counting inward from the side of the hood, the first three units are acid-rinsed. The fourth, in the center of the hood and isolated by a Plexiglas divider, is not acid-rinsed. This unit is also identified by the presence of a strip of blue tape.

2) Attach the vacuum line from the vacuum pump via a waste filter flask to the outlet on the first filtration base. Turn on the vacuum. Adjust the vacuum pump to 10 to 12 inches Hg.

   CAUTION: Do not exceed 12 inches Hg under any circumstances.

   Be sure that the waste flask remains upright and that it is emptied on a regular basis.

3) Two sets of Teflon forceps are needed. One set is acid-rinsed. Label one pair of this set "ACID-CLEAN" and the other "ACID-DIRTY."

Mark these with red tape. One set is not acid-rinsed. Label one pair of this set "NONACID-CLEAN" and the other "NONACID-DIRTY." Mark these with blue tape.

D.1.2 Between Sample Rinsing - Acid-Rinsed Units

NOTE: Each filter apparatus must be rinsed completely before a new sample is processed. See Figure D-1 for a diagram of the filtration unit.

1) Place a 250-mL plastic beaker (for waste) under each filter funnel.

2) Rinse the filter funnel once with deionized water from a 1-L wash bottle. Be sure water flows evenly over all interior surfaces of the filter cup; turn the cup one complete revolution while rinsing the sides.

3) Rinse the filter funnel once with 5 percent HNO_3 (Baker Instra-Analyzed grade) from 1-L wash bottle. Turn the cup one complete revolution while rinsing the sides.

4) Rinse the filter funnel three times with deionized water from a 1-L wash bottle. Turn the cup one complete revolution for each rinse, and allow the water to drain completely.

D.1.3 Filter Rinsing Procedure - Acid-Rinsed Units

NOTE 1: The 0.45 µm membrane filter should be replaced before a new sample is to be filtered. Be sure that the filter is centered and that it lies smoothly on the filter screen with no tears.

NOTE 2: Make sure the blue filter separators are removed before placing the filter on the screen. Do not touch the filter to any object other than clean Teflon forceps or the filter screen. If the filter does touch another object, discard the filter and obtain a new one.

NOTE 3: Empty the waste beaker that is under the filtration apparatus into a second waste beaker to be dumped outside the hood. Never remove the apparatus waste beaker from the clean air station.

1) Unscrew the filter cup from the filter holder. Make sure that it separates properly and that the O-rings are secure and in place.

2) Lift the cup. Using clean, acid-rinsed Teflon forceps, place a 0.45 µm membrane filter onto the screen. Moisten the filter with deionized water (from wash bottle), and apply the vacuum to seal the

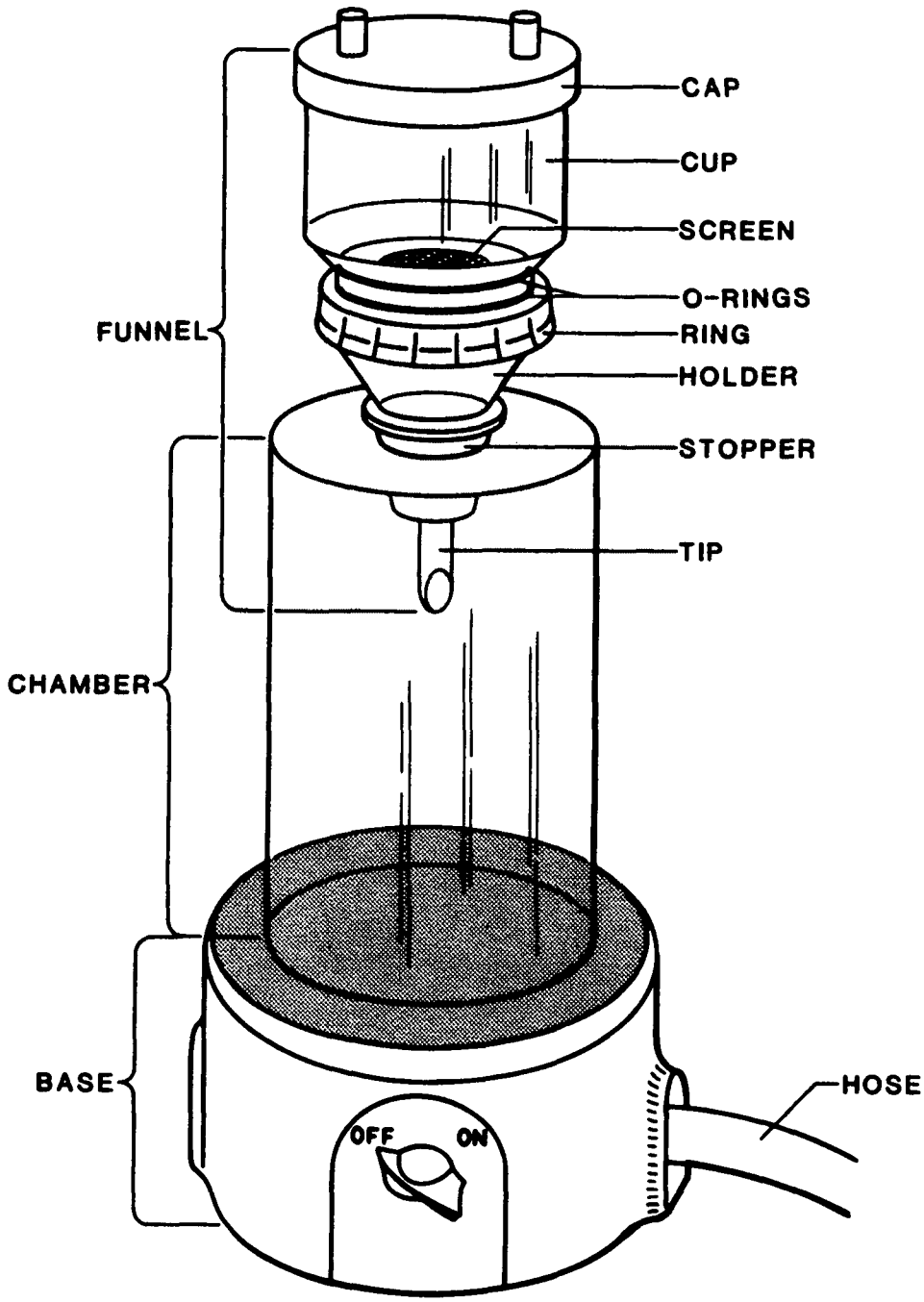

Figure D-1. Filtration apparatus.

filter to the screen. Be sure that the filter is centered and that it lies smoothly with no tears.

3) Replace the cup onto the holder without disturbing the filter. Tighten the ring securely. If the ring is not properly tightened, it may leak while filtering. If this happens, obtain a new aliquot bottle of the same type, and reprocess the aliquot.

4) Rinse the filter with 5 mL of deionized water, and follow that with a 5-mL rinse of 5 percent HNO_3, and follow that with two 5-mL rinses with deionized water. A third rinse with deionized water should cover the sides of the cup as well as the filter.

5) Shut off the vacuum. Break the seal, and thoroughly rinse the filter funnel tip with deionized water.

D.1.4 Sample Filtration - Acid-Rinsed Units

NOTE 1: The cap is kept on the aliquot bottles until the bottle is placed under the funnel to avoid any possible contamination from the chamber.

NOTE 2: If the Cubitainer cap (or its white paper liner) is dropped at any time, rinse it one time with deionized water and one time with sample and then continue processing.

NOTE 3: Keep the hood area clean. Wipe up spills after they occur.

1) Agitate the Cubitainer. Pour no more than 10 mL of sample into the filter cup.

2) Turn on the vacuum, and filter the sample into the waste beaker. Turn off the vacuum.

3) Lift the chamber and remove the waste beaker. Empty the beaker, and place it behind the apparatus out of the way. Loosen the lid of the Aliquot 1 bottle. Lift the chamber, and set the Aliquot 1 bottle on the base. Remove the cap, and lower the chamber back onto the base. Set the cap upright next to apparatus in a clean spot.

4) Agitate the Cubitainer. Pour no more than 10 mL of sample into the filter cup.

5) Turn on the vacuum. Filter the sample into the Aliquot 1 bottle, and turn off the vacuum.

6) Lift the chamber, and replace the cap on the Aliquot 1 bottle. Remove the bottle, and tighten down the cap. Rinse the bottle thoroughly by

shaking and rotating. Pour the rinse sample into the waste beaker. Loosen the cap, lift the chamber, and replace the bottle under the funnel. Remove the cap, and set the chamber on its base.

7) Agitate the Cubitainer. Pour 200 mL of the sample into the filter cup. Apply vacuum pressure, and filter the sample into the Aliquot 1 bottle. Turn off the vacuum.

8) Only the Aliquot 1 bottle is used to collect the filtered sample. Aliquot 4 is poured from Aliquot 1.

D.2 Filtered Aliquots - Units Which are not Acid-Rinsed (Aliquots 2 and 3)

NOTE 1: Use the filtration apparatus which is not acid-rinsed to filter Aliquot 2 and 3. All components of this unit (except the base) should be soaked in deionized water for 48 hours prior to the initial set-up, and each component should be labeled with blue tape.

NOTE 2: If any part of the apparatus is contaminated by acid, replace the entire apparatus with a clean one. Soak the dirty one in deionized water for 48 hours.

1) Follow the same set-up and rinsing procedures described in Section D.1.2 through D.1.4. However, eliminate the 5 percent HNO_3 rinse in all steps, rinsing three times with deionized water only.

2) Aliquot 2 is poured from aliquot 3.

3) The aliquot 3 bottle should be filled to the brim and should be capped tightly so that no headspace exists. To break the pressure in the chamber and to avoid losing sample, carefully insert a gloved finger between the stopper and the funnel.

D.3 Filter Changing Procedure

1) If it is necessary to change the filter before filling all aliquots from one sample because the filter has become clogged, use the following procedure:

   a) Shut off the vacuum. Lift the chamber, cap the aliquot bottle, and remove it; replace it with the waste beaker.
   b) Unscrew the filter cup, remove the dirty filter with the "DIRTY" forceps, and replace it with a clean filter by using the "CLEAN" forceps.

   c) For aliquots prepared with the acid-rinsed units, rinse the

filter by following the instructions in Section D.1.3. For Aliquots 2 and 3 (which make use of the filtration unit which is not acid rinsed), follow the same procedure except eliminate the 5 percent HNO_3 wash; instead, rinse three times with deionized water.

D.5 Preservation

NOTE 1: Prepare and attach the appropriate labels to the aliquot bottles prior to sample arrival; the label color reflects the appropriate preservation procedure.

Aliquot No.	Label Color	Acid used for Preservation
1	Pink	HNO_3
2	Blue	$HgCl_2$
3	White	None
4	Yellow	H_2SO_4

1) Use two 40- to 200-µL micropipets, one labeled for nitric acid (red tape) and one labeled for sulfuric acid (yellow tape). Add 100 µL of the appropriate Ultrex acid to the sample as follows:

   Aliquot 1 is preserved with Ultrex HNO_3.

   Aliquot 4 is preserved with Ultrex H_2SO_4.

2) After the acid is added, tighten the caps and mix the solution thoroughly.

3) Loosen the aliquot bottle caps, and using a fresh capillary tube for each bottle, collect and place a drop of preserved sample on Whatman pH paper (type CS, 1.8 to 3.8). The pH should be less than 2.

4) It may be necessary to add more than 100 µL of acid for the pH to be less than 2. If this situation occurs, continue adding the appropriate acid in 100-µL increments until the pH is less than 2, using a new capillary tube each time the pH is tested.

5) Write the total amount of acid added to the sample on the aliquot label and in the logbook.

6) Dissolve 50 g $HgCl_2$ in 1 L of deionized water.

   CAUTION: $HgCl_2$ is hazardous. Wear gloves when weighing $HgCl_2$.

7) Use one 40- to 200-µL pipet to add 100 µL 5 percent $HgCl_2$ to aliquot 2. Cap the aliquot tightly, and indicate amount of 5 percent $HgCl_2$ on the aliquot label and in the logbook.

D.6 Preparation of Aliquots for Shipping

1) Refrigerate all aliquots for at least 1 hour at 4°C before shipping. Check that all labels are correct, and tighten the caps firmly. Tape each cap in a clockwise direction with electrical tape. Place each each aliquot or centrifuge tube to be shipped in an individual plastic bag, and tie them with a twist-tie.

2) Place each set of aliquot bottles into a 1-pint Ziploc bag. Face the labels in the same direction for easy sample identification. Remove the air from the bag, seal it, and place the bag in the refrigerator or directly into the prepared shipping coolers.

D.7 Shipping Instructions

NOTE 1: Samples are delivered to the analytical laboratory the day before analysis.

NOTE 2: Styrofoam containers are used to ship the aliquots. Be sure that the containers are sturdy.

1) Place eight frozen gel packs into each large shipping container, lining the inside of the container. Use four gel packs for the smaller shipping containers.

2) Place 12 sets of aliquots in a container. If there are less than 12 sets to be shipped, fill the excess space with gel packs or newspaper.

3) A four part shipping form is completed by the laboratory coordinator, and it contains all aliquot information for the batch. The pink and gold copies are placed inside a Ziploc bag and are placed inside the shipping box on the cooler lid. The yellow copy is sent to QA personnel. The original (white) is retained in the processing laboratory.

4) Samples are hand delivered to the analytical laboratory.

APPENDIX E

DETERMINATION OF AMMONIUM BY FLOW INJECTION ANALYSIS

E.0 Scope and Application

This method covers the determination of ammonium in the range of 0.01 to 0.150 mg/L NH_4^+. This range is for photometric measurements made at 630 to 660 nm in a 10-mm tubular flow cell. Higher concentrations can be determined by sample dilution. Approximately 60 samples per hour can be analyzed.

E.1 Summary of Method

Alkaline phenol and hypochlorite react with ammonium to form an amount of indophenol blue that is proportional to the ammonium concentration. The blue color formed is intensified with sodium nitroprusside.

E.2 Interferences

Calcium and magnesium ions may be present in concentration sufficient to precipitate during the analysis. A 5 percent EDTA solution is used to prevent the precipitation of calcium and magnesium ions.

Sample turbidity may interfere with this method. Turbidity is removed by filtration at the processing laboratory. Sample color that absorbs in the photometric range used also interferes.

E.3 Safety

The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use protective clothing (lab coat and gloves) and safety glasses when preparing reagents.

E.4 Apparatus and Equipment

Tecator FIAstar flow injection analyzer or equivalent consisting of:

Sampler
Analytical manifold with 200-µl sample loop
In-line heater
Colorimeter equipped with a 10-mm flow cell
Printer

E.5 Reagents and Consumable Materials

Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

Acidified water--To a 2-L volumetric flask containing 1500 mL water, pipet 0.70 mL of concentrated H_2SO_4 (Ultrex or equivalent). Dilute to 2 L and mix.

Sodium Phenate Solution--Using a 400-mL Griffen beaker, dissolve 20.7 g phenol in 200 mL water. Add 8 g NaOH by stirring occasionally. Add water to the 250-mL mark and stir. The final solution should be a light amber color. Pour the solution into a 250-mL amber plastic bottle and store the bottle in a hood until used.

Sodium Hypochlorite Solution--Using a 500-mL Erlenmeyer flask, dilute 100 mL of a commercial bleach solution (Chlorox or equivalent, 5 percent NaOCl, minimum) with 100 mL water.

Disodium Ethylenediaminetetraacetate Acid (EDTA)--Dissolve 50 g EDTA (disodium salt) and approximately 6 pellets of NaOH in 1 L water and store the solution in a 1 L plastic bottle. To facilitate solution, use of a mechanical shaker is recommended.

Sodium Nitroprusside--Dissolve 0.5 g sodium nitroprusside in 1 L water. Store the solution in a 1-L plastic bottle.

Ammonium Stock Solution (1000 mg/L NH_4^+)--In a 1-L volumetric flask, dissolve 3.6624 g $(NH_4^+)\ 2SO_4$ (dried at 105°C for 2 hours) in water, add 0.35 mL concentrated H_2SO_4 (Ultrex or equivalent), and dilute the solution to 1 L. Store it in a 1-L plastic bottle.

Standard Solutions (10 mg/L NH_4^+)--In a volumetric flask, dilute 1 mL of ammonium stock solution to 100 mL with acidified water.

Working Standards--Using the standard solution and diluting with acidified water, prepare the following standards in 100-mL volumetric flasks:

NH_4^+ (mg/L)	mL standard solution /100 mL
0.010	0.100
0.025	0.250
0.050	0.500
0.100	1.00
0.150	1.50

E.6 Sample Collection, Preservation, and Storage

Samples are filtered and preserved (addition of H_2SO_4 to pH <2) in the processing laboratory. The samples must be stored at 4°C when not in use.

E.7 Calibration and Standardization

Analyze the series of standards described above.

The calibration curve is calculated by the instrument. Follow the instructions provided by the manufacturer for creating calibration curves.

E.8 Quality Control

The following special sample types are used for quality control. A batch is defined herein as the number of samples, excluding the standards and QC samples, accommodated by the analyzer at any one time. For the FIAstar, this is approximately 25 samples.

Quality control check standard (QCCS) is a standard having a concentration of approximately the midpoint of the calibration range. Use 0.100 ppm concentration for this procedure. The QCCS is analyzed after the calibration standards (before any samples), then after every tenth sample and as the last sample of any batch of samples. The QCCS must be within the prescribed accuracy limits (within 10 percent of actual concentration). If a QCCS is not within the prescribed limit, all samples analyzed since the last good QCCS are reanalyzed. Prepare the QCCS from an ammonium stock made of ammonium sulfate from a different lot than that used for the ammonium stock used to prepare the standards.

Detection limit standard (DL) is a standard 2 to 5 times the required detection limit. Use a 0.050 ppm solution for this standard. The DL is analyzed after the first QCCS and before the first sample and must be within the prescribed accuracy limit (within 20 percent of actual concentration).

A blank is run once per batch of samples. The blank is a sample of the acidified water used to make up the standards.

External standards from the National Bureau of Standards or the EPA are analyzed twice in any batch of samples.

An internal standard (IS) or calibration standard is run three times in a batch, the first time before the first sample. The additional IS's are spaced at approximately equal intervals in the sample batch. The IS assists in compensating for any drift that may occur during the analysis.

One sample in any batch is analyzed in duplicate.

E.9 Procedure

Turn the power to the analyzer and to data station on for at least 30 minutes before use.

Set up the ammonium manifold, and pump water through the manifold and lines while making the standards.

Prepare the reagents, standards, and QC samples.

Check the photometer reference and sample dark current. Consult the owners manual for specific instructions for this adjustment.

Load the standards, QC, and samples in the sample trays.

Enter the required information about the standards into the analyzer.

Begin the analysis.

Dilute any samples which are outside the calibration range.

E.10 Calculations

The concentrations of the samples are computed by the data station.

E.11 Precision and Accuracy

In a single laboratory (LEMSCO-Las Vegas) with standards at concentrations of 0.125, 0.104 (EPA reference sample WP486 No. 1), 0.100, and 0.050 mg/L NH_4^+, the average %RSD was 5.65 (Pia, personal communication, 1987).

Bias for the same samples were 102, 106, 105, 106, respectively.

E.12 References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specifications for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadephia, Pennsylvania.

Pia, S. H., 1987. Personal Communication.

APPENDIX F

DETERMINATION OF DISSOLVED METALS (Ca and Mg) BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY (modified from Hillman et al., 1986)

F.0 Scope and Application

This method is applicable to the determination of dissolved Ca and Mg in natural surface waters and precipitation.

Table F-1 lists the recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization for the specified elements. Actual working detection limits are sample-dependent, and as the sample matrix varies, these concentrations may also vary.

Because of the differences among makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

F.1 Summary of Method

The method describes a technique for the simultaneous or sequential determination of Ca and Mg in natural surface waters and precipitation samples. The method is based on the measurement of atomic emission by optical spectroscopy. Samples are nebulized to produce an aerosol. The aerosol is transported by an argon carrier stream to an inductively coupled argon plasma (ICP), which is produced by a radio frequency (RF) generator. In the plasma (which is at a temperature of 6,000 to 10,000°K), the analytes in the aerosol are atomized, ionized, and excited. The excited ions and atoms emit light at their characteristic wavelengths. The spectra from all analytes are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed by a computer system. The signal is proportional to the analyte concentration and is calibrated by analyzing a series of standards (U.S. EPA, 1983; Fassel, 1982).

A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during sample analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and must reflect the same

TABLE F-1. RECOMMENDED WAVELENGTHS[a] AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength (nm)	Estimated detection limit (µg/L)[b]
Calcium	317.933	2-3
Magnesium	279.079	2-3

[a]The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

[b]The estimated instrumental detection limits as shown are taken from Fassel, 1982. They are given as a guide for an instrumental limit. The actual method detection limits are sample-dependent and may vary as the sample matrix varies.

change in background intensity as occurs at the analyte wavelength measured. Generally, each instrument has different background handling capabilities. The instrument operating manual should be consulted for guidance.

The possibility of additional interferences named in Section F.2 should also be recognized, and appropriate corrections should be made.

F.2 Interferences

Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They are summarized in Sections F.2.1 through F.2.3.

F.2.1 Spectral Interferences

Spectral interferences can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from the line emission of high-concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the

instrument array. Listed in Table F-2 are some interference effects for the recommended wavelengths given in Table F-1. The interference information is expressed as analyte concentration eqivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interfering element. The values in the table are only approximate and should be used as a guide for determining potential interferences. Actual values must be determined for each analytical system when necessary.

Only those interferences listed were investigated. The blank spaces in Table F-2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table F-3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2 to 5 percent of the peaks generated by the analyte concentrations (also listed in Table F-3).

F.2.2 Physical Interferences

Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples that contain high dissolved solids or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample or by utilization of standard addition techniques.

High dissolved solids may also cause salt buildup at the tip of the nebulizer. This affects aerosol flow rate and causes instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem.

It has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

F.2.3 Chemical Interferences

Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are negligible with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (i.e., incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and on the specific analyte element.

TABLE F-2. ANALYTE CONCENTRATION EQUIVALENTS (mg/L) ARISING FROM INTERFERENCES AT THE 100-mg/L LEVEL

Analyte	Wavelength (nm)	Interference				
		Al	Ca	Cr	Cu	Fe
Calcium		--	--	0.08	--	0.01
Magnesium		--	0.02	0.11	--	0.13
		Interference				
		Mg	Mn	Ni	Ti	V
Calcium		0.01	0.04	--	0.03	0.03
Magnesium		--	0.25	--	0.07	0.12

F.2.4 Interference Tests

Whenever a new or unusual sample matrix is encountered, a series of tests should be performed prior to reporting concentration data for analyte elements. These tests, as outlined in sections F.2.4.1 through F.2.4.4, will ensure that neither positive nor negative interference effects are operative on any of the analyte elements, in a way that would distort.

F.2.4.1 Serial Dilution--If the analyte concentration is sufficiently high (minimally a factor of 9 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 percent of the original determination (or within some acceptable control limit that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

F.2.4.2 Spiked Addition--The recovery of a spiked addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect.

TABLE F-3. INTERFERENCE AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR INTERFERENCE MEASUREMENTS IN TABLE F-2

Analytes	(mg/L)	Interferences	(mg/L)
Ca	1	Al	1,000
Mg	1	Ca	1,000
		Cr	200
		Cu	200
		Fe	1,000
		Mg	1,000
		Nn	200
		Ni	200
		Ti	200
		V	200

CAUTION: The standard addition technique does not detect coincident spectral overlap. If overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

F.2.4.3 Comparison with Alternate Method of Analysis--When investigating a new sample matrix, a comparison test may be performed with other analytical techniques such as atomic absorption spectrometry or other approved methodology.

F.2.4.4 Wavelength Scanning of Analyte Line Region--If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

F.3 Safety

Generally, the calibration standards, sample types, and most reagents pose no hazard to the analyst. Protective clothing (lab coats and gloves) and safety glasses should be worn when handling concentrated acids.

Follow the safety recommendations for the instrument provided by the manufacturer for the operation of the ICP.

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of

OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (DHEW, 1977; OSHA, 1976; ACS, 1979) for the information of the analyst.

F.4 Apparatus and Equipment

- Inductively Coupled Plasma-Atomic Emission Spectrometer.

- Computer-controlled ICP emission spectrometer with background correction capability.

F.5 Reagents and Consumable Materials

- Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent (e.g., Baker Ultrex grade or SeaStar Ultrapure grade).

  a. Hydrochloric Acid, concentrated (sp gr 1.19).

  b. Hydrochloric Acid (50 percent v/v)--Add 500 mL concentrated HCl to 400 mL water and dilute to 1 L.

  c. Nitric Acid, concentrated (sp gr 1.41).

  d. Nitric Acid (50 percent v/v)--Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 L.

- Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

- Standard Stock Solutions--Solutions should be purchased or alternatively may be prepared from ultra-high purity grade chemicals or metals. All salts must be dried for 1 hour at 105°C unless otherwise specified.

  CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

  a. Calcium Stock Standard Solution (100 mg/L)--Suspend 0.2498 g $CaCO_3$ (dried at 180°C for 1 hour before weighing) in water and dissolve the mixture cautiously with a minimum amount of 50 percent HNO_3. Add 10.0 mL concentrated HNO_3 and dilute the solution to 1,000 mL with water.

b. Magnesium Stock Standard Solution (100 mg/L)--Dissolve 0.1658 g MgO in a minimum amount of 50 percent HNO_3. Add 10.0 mL concentrated HNO_3 and dilute the solution to 1,000 mL with water.

F.6 Sample Handling, Preservation, and Storage

For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Labware should be thoroughly acid-washed.

Samples are collected and processed in the field and processing laboratory. A portion (aliquot 1) of each sample is filtered and acidified (0.1-mL increments) with nitric acid until the pH <2. The processed samples are then sent to the lab and are analyzed (as is) for dissolved metal (Ca and Mg) content.

F.7 Calibration and Standardization

Prepare a calibration blank and a series of dilute calibration standards from the stock solutions so that the expected sample concentration range is spanned. Match the acid content of the standards to that of the samples (written on the sample label, ca. 0.2 percent). A multi-element standard may be prepared.

The calibration procedure varies with the various ICPES instruments. Calibrate the ICPES for each analyte by following the instrument operating conditions.

F.8 Quality Control

The required QC procedures are described in Section 3.

F.9 Procedure

Step 1--Set up instrument as recommended by the manufacturer or as experience dictates. The instrument must be allowed to become thermally stable before beginning (10 to 30 minutes).

Step 2--Profile and calibrate instrument according to the recommended procedures for the instrument provided by the manufacturer. Flush the system with the calibration blank between each standard. (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

Step 3--Begin sample analysis, flushing the system with the calibration blank solution between each sample. Remember to analyze required QC samples.

Step 4--Dilute and reanalyze any samples with a concentration exceeding the calibration range.

F.10 Calculations

Generally, instruments are calibrated to output sample results directly in concentration units. If not, then a manual calibration curve must be prepared, and sample concentrations must be determined by comparing the sample signal to the calibrated curve. If dilutions were performed, the appropriate factor must be applied to sample values. Report results as mg/L for each analyte.

F.11 Precision and Accuracy

In an EPA round-robin study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates; Ca and Mg, however, were not included. Table F-4 lists the true value, the mean reported value, and the mean %RSD (U.S. EPA, 1983).

TABLE F-4. ICP PRECISION AND ACCURACY DATA[1]

	Sample 1			Sample 2		
Element	True Value (µg/L)	Mean Reported Value (µg/L)	Mean %RSD	True Value (µg/L)	Mean Reported Value (µg/L)	Mean %RSD
Mn	350	345	2.7	15	15	6.7
Fe	600	594	3.0	20	19	15

	Sample 3		
Element	True Value (µg/L)	Mean Reported Value (µg/L)	Mean %RSD
Mn	100	99	3.3
Fe	180	178	6.0

[1]Not all elements were analyzed by all laboratories.
Ca and Mg were not determined.

F.12 References

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