United States
Environmental Protection
Agency

Office of Research and
Development
Washington DC 20460

EPA/600/R-94/038e
April 1994

EPA

Quality Assurance Handbook for Air Pollution Measurement Systems

Volume V: Precipitation Measurement Systems (Interim Edition)

EPA-600/R-94/038e

QUALITY ASSURANCE HANDBOOK

FOR

AIR POLLUTION MEASUREMENT SYSTEMS

Volume V -- Precipitation Measurement Systems
(Interim Edition)

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH and DEVELOPMENT
ATMOSPHERIC RESEARCH and ENVIRONMENTAL ASSESSMENT LABORATORY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

Printed on Recycled Paper

CONTENTS

CONTENTS (Continued)

Section

CONTENTS (Continued)

CONTENTS (Continued)

Section

CONTENTS (Continued)

Section

FIGURES

Figure

TABLES

Table

1.0 OVERVIEW OF THE INTERIM EDITION OF VOLUME V

The Quality Assurance (QA) Handbook is comprised of five volumes: Volume I (Principles), Volume II (Ambient Air Methods), Volume III (Stationary Source Methods), Volume IV (Meteorological Measurements), and Volume V (Precipitation Measurement Systems). Much of the material in Volumes II, III and V are out-of-date and some portions of these volumes have long been out-of-print.

EPA is now preparing an updated version of the QA Handbook series which will be available in September 1995. To meet the needs of the user community until the updated version is available, EPA has published Interim Editions of Volumes I, II, III, IV and V. Each volume of the Interim Editions, is being issued as a complete unit with out-of-date sections either deleted or modified using addendum sheets and handwritten notations in the text.

This volume and the other four volumes of the Interim Edition of the QA Handbook are available at no charge from:

USEPA/ORD
Center for Environmental Research Information
26 West Martin Luther King Drive
Cincinnati, Ohio 45268

The previous version of Volume V was published in two parts: Volume Va, Quality Assurance Manual for Precipitation Measurement Systems and Volume Vb, Operation and Maintenance Manual for Precipitation Measurement Systems. The appendices to Volume Vb contained over 200 pages of Standard Operating Procedures (SOP's) primarily concerned with the analysis of precipitation samples. For the most part, these SOP's are now out-of-date technology and were excluded from the Interim Version of Volume V. The reduced Volume Vb is now an appendix to Volume V. The titles of the excluded SOP's are:

- Aerochem Metrics Precipitation Collector Maintenance Manual
- Instruction Book for Universal Recording Rain Gauge
- Method 150.6 -- pH of Wet Deposition by Electrometric Determination
- Method 120-6 -- Specific Conductance in Wet Deposition by Electrolytic Determination

- Method 305.6 -- Acidity in Wet Deposition by Titrimetric Determination
- Method 305.2 -- Acidity (Tritrimetric)
- Method 300.6 -- Chloride, Orthophosphate, Nitrate and Sulfate in Wet Deposition by Chemically Suppressed Ion Chromatography
- Method 300.7 -- Dissolved Sodium, Ammonium, Potassium, Magnesium, and Calcium in Wet Deposition by Chemically Suppressed Ion Chromatography
- Method 375.6 -- Sulfate in Wet Deposition by Automated Colorimetric Determination Using Barium-Methylthymol Blue
- Method 353.6 -- Nitrate-Nitrite in Wet Deposition by Automated Colorimetric Determination Using Cadmium Reduction
- Method 325.6 -- Chloride in Wet Deposition by Automated Colorimetric Determination Using Thiocyanate
- Method 365.6 -- Orthophosphate in Wet Deposition by Automated Colorimetric Determination Using Ascorbic Acid reduction
- Method 340.6 -- Fluoride in Wet Deposition by Potentiometric Determination Using an Ion-Selective Electrode
- Method 350.6 -- Ammonium in Wet Deposition by Electrometric Determination Using Ion-Selective Electrode
- Method 350.7 -- Ammonium in Wet Deposition by Automated Colorimetric Determination with Phenate
- Method 200.6 -- Dissolved Calcium, Magnesium, Potassium, and Sodium in Wet Deposition by Flame Atomic Absorption Spectrophotometry
- Method 200.6 -- Dissolved aluminum, Cadmium, Copper, Iron, Lead, Manganese, and Zinc in Wet Deposition by Graphite Furnace Atomic Absorption Spectrophotometry

Copies of these SOP's can be obtained by writing to:

QA Handbook Coordinator
US EPA/ORD/AREAL/MD-77B
Research Triangle Park, NC 27711

Many of the EPA contacts and organizational units identified in Volume V are no longer correct and some of the reference materials and procedures cited have been discontinued or replaced. This type of out-of-date information is widely dispersed throughout Volume V. Rather than change every affected section, for clarity and neatness sake, we have provided below a listing of the original information and the corresponding updated information.

1) NBS is now the National Institute of Standards and Technology (NIST).

2) EMSL is now the Atmospheric Research and Exposure Assessment Laboratory (AREAL).

3) QAD is now the Quality Assurance and Technical Support Division (QATSD/AREAL).

The updated edition of Volume V which will be available in September 1995 will also contain information on quality assuring dry deposition measurement systems.

William J. Mitchell
Chief
Quality Assurance Support Branch

2.0 PROGRAM PLANNING AND OBJECTIVES

Precipitation monitoring entails extensive chemical analyses and data manipulations and requires strong interfaces between field operations, laboratory operations and the data management functions. In a program of this complexity, all elements must be carefully planned. A comprehensive "top-down" approach to planning should be adopted, starting with an experimental design and extending through to the preparation of detailed procedures.

As described below, the planning process can be broken down into three major phases:

1. Determination of Monitoring and Data Quality Objectives
2. Development of Work Plan
3. Preparation of Quality Assurance Project Plan

2.1 Determination of Monitoring and Data Quality Objectives

Data quality objectives are usually defined in terms of precision, accuracy, representativeness, comparability and completeness of the collected data. To achieve these objectives, quality assurance/quality control procedures are needed in all phases of the program from the initial planning stages through final data reporting. This involvement helps identify areas with potentially large negative impact on data quality and provides a mechanism for instituting ongoing quality control, corrective action, data validation, and external assessment of precision and accuracy.

In general, precipitation data may be considered to be complete if at least 85% of the total possible field observations of either individual events, daily, weekly, or longer term composite samples are captured. The determination of completeness for the network is calculated as a percentage of the total number of possible samples. The percentage of valid usable data will usually be 5-10% lower due to sample contamination or loss and the invalidation of some analytical results.

Tables 2-1, 2-2 and 2-3 show some precision estimates obtained from interlaboratory studies by the U. S. Geological Survey (Tables 2-1, 2-2) and a collocated sampling study from the EPRI-Sure network (Table 2-3). These results can be useful in establishing data quality objectives.

In order to establish data representativeness, stations should be sited so that they collect samples representative of both the amount and the composition of precipitation in the area. In general, monitoring sites should be classified as: (a) baseline (remote area), (b) regional (rural), or (c) urban or local area (for local impact emission sources). Also, reporting data in consistent units permits easier data comparisons. A listing of the recommended units for the most commonly sought monitoring parameters are given in Table 2-4. To facilitate intercomparison of data bases of various networks, data summaries should document, to the extent possible, field laboratory, and computational procedures utilized in data generation.

2.2 Development of Work Plan

Once the monitoring and data quality objectives have been determined, a detailed work plan should be prepared. The Work Plan should address, as a minimum, the following topics which are discussed in more detail in later sections of this manual.

1. Program Organization - identifies the organization(s) and specific personnel responsible for network operation, chemical analysis, data management and quality assurance/ quality control (Section 3.0).

2. Experimental Design - addresses the spatial and temporal measurement requirements in terms of program objectives (Section 2.0). Special consideration should be given to proper network siting (Section 5.0), and to thorough documentation of all detailed procedures to be used (Section 4.0).

3. Facilities, Equipment and Services - provides a list of resources required to carry out the monitoring program. This listing should identify the specific instruments and respective model numbers utilized in each facet

TABLE 2-1. USGS SURVEY OF SYNTHETIC PRECIPITATION SAMPLES [a]

Observable (Units)	No. of Labs	USGS Designated	Mean of Determinations	Std. Deviation	$\overline{CV}$[b]
Conductivity	10	43.5	40.7	3.32	0.082
(μmho/cm)	10	13.2	11.6	4.09	0.35
pH	10	4.35	4.22	0.124	0.029
	10	5.03	4.83	0.172	0.036
Sulfate	11	2.35	2.38	0.795	0.33
(mg/liter)	11	0.779	0.702	0.174	0.25
Nitrate	11	2.15	1.80	0.662	0.37
(mg/liter)	11	0.826	0.732	0.212	0.29
Ammonia	10	0.660	0.630	0.130	0.21
(mg/liter)	10	0.214	0.203	0.039	0.19
Chloride	11	3.27	3.18	0.249	0.078
(mg/liter)	11	0.908	0.891	0.188	0.21
Sodium	11	0.558	0.586	0.139	0.24
(mg/liter)	11	0.284	0.326	0.070	0.22
Potassium	10	0.506	0.549	0.941	0.171
(mg/liter)	10	0.156	0.198	0.106	0.53
Magnesium	11	0.226	0.273	0.0872	0.32
(mg/liter)	11	0.056	0.0752	0.0361	0.48
Calcium	11	0.654	0.652	0.0911	0.14
(mg/liter)	11	0.248	0.253	0.0585	0.23

[a] Chemical Analysis and Precipitation Study, U.S.G.S., Spring 1981; samples designated B and N.

[b] $\overline{CV}$ = Std. deviation/mean

TABLE 2-2. USGS SURVEY OF NATURAL PRECIPITATION SAMPLES [a]

Observable (Units)	No. of Labs	Mean of Determinations	Std. Deviation	$\overline{CV}$[b]
Conductivity	10	16.9	1.56	0.092
(μmho/cm)	10	28.9	1.93	0.067
pH	10	6.22	0.219	0.035
	10	6.25	0.258	0.041
Sulfate	11	0.477	0.162	0.34
(mg/liter)	11	1.52	0.606	0.40
Nitrate	11	1.23	0.436	0.35
(mg/liter)	11	2.77	1.05	0.38
Ammonia (mg/liter)	10	0.682	0.138	0.20
Chloride	11	1.81	0.349	0.19
(mg/liter)	11	2.40	0.391	0.16
Sodium	11	1.40	0.981	0.70
(mg/liter)	11	1.73	0.249	0.14
Potassium	10	0.32	0.0646	0.20
(mg/liter)	10	1.15	0.122	0.11
Magnesium	11	0.198	0.0399	0.20
(mg/liter)	11	0.307	0.0438	0.14
Calcium	11	1.11	0.210	0.19
(mg/liter)	11	1.48	0.109	0.07

a. Chemical Analysis and Precipitation Study, U.S.G.S., Spring 1981; samples designated AC and FL.

b. $\overline{CV}$ = Std. deviation/mean

TABLE 2-3. SUMMARY OF COLLOCATION RESULTS[a]

Observable	% Difference[b]
Hydrogen Ion[c]	9.0
Total Acidity[d]	24.3
Conductivity	6.0
Sulfate	5.0
Nitrate	5.3
Chloride	11.5
Ammonia	7.8
Sodium	17.6
Potassium	43.3
Calcium	16.1
Magnesium	12.5

a. From EPRI-SURE Acid Precipitation Study. The values reported represent an average of at least 1000 collocations of samplers.

b. % Difference = 100x(Median Absolute Collocated Difference/Median All Values).

c. From antilog of -pH.

d. Classical potentiometric titration

TABLE 2-4. RECOMMENDED REPORTING UNITS AND SIGNIFICANT DIGITS

Observable	Reporting Units	Significant Digits
Sample weight	g	1.0
Precipitation	cm	0.025
pH	pH units	0.01
Conductivity	μmho/cm (μS/cm)	0.1
Deposition	mg/m^2	0.1
Sulfate	mg/liter	0.01
	μeq/liter	0.2
Nitrate	mg/liter	0.01
	μeq/liter	0.2
Ammonia	mg/liter	0.001
	μeq/liter	0.05
Chloride	mg/liter	0.01
	μeq/liter	0.3
Sodium	mg/liter	0.01
	μeq/liter	0.4
Potassium	mg/liter	0.001
	μeq/liter	0.02
Magnesium	mg/liter	0.001
	μeq/liter	0.08
Calcium	mg/liter	0.001
	μeq/liter	0.05

of the measurement system (Sections 6.0 and 7.0).

4. Data Generation - specifies the measurement methods used. These include calibration techniques, frequency of calibrations, acceptability requirements for all calibration results, and action to be taken with respect to data obtained previous to an unsatisfactory calibration (Sections 6.0 and 7.0).

5. Data Processing, Validation and Reporting - describes the types of data obtained for each measurement parameter and the overall data flow from generation through reporting. Data validation methodologies, statistical analysis techniques and reporting formats should also be addressed (Section 8.0).

6. Program Evaluation and Data Quality Assessment - provides specific details of the planning and implementation of the independent quality assurance activities associated with the monitoring program (Sections 9.0, 10.0 and 2.3 below).

2.3 Preparation of Quality Assurance Project Plan

To generate and report monitoring data of the highest quality, no precipitation monitoring project should be initiated without a written, QA project plan. The QA project plan should specify QA policies, organization, objectives, functional activities, and QA/QC activities needed to achieve the data quality goals of the project. Items that should be included are:

1. Quality Assurance Policy Statement - describes the organization's policy and general approach to achieve quality results.

2. Quality Assurance Organization and Responsibility - assigns responsibility to the organization's personnel for carrying out quality related activities and defines the authority of the quality assurance officer (QAO).

3. Sampling and Analysis Procedures - defines the methods to be used both in the field and laboratory, in terms of their acceptability and applicability, and references the appropriate Standard Operating Procedures for method details.

4. Internal Quality Control Checks - describes the critical points in each measurement system and establishes a system of control and/or checks for those critical points together with a frequency for their performance.

5. Data Quality Assessment - addresses the implementation of independent program evaluations and audits to assess data quality; also establishes a schedule for these audits and a format for reporting precision, accuracy, and completeness of specific measurements.

6. Corrective Actions - indicates the methods for reporting problems, responsibility for corrections, and the documentation of action taken.

7. Quality Assurance Reporting - outlines the data quality section to be prepared as part of each data submission and final report. The report will summarize data quality assessment, reliability of the measurement system and corrective action pursued to correct the problems.

3.0 PROGRAM ORGANIZATION AND RESPONSIBILITIES

A precipitation monitoring network involves interdependent field monitoring and laboratory operations. Each operation has its own QA/QC aspects. The field monitoring sites and the laboratory can be run by independent organizations; however, the results reported are the responsibility of the program manager. The QA officer should be at the same reporting level as the program manager. Brief discussions of the qualifications and duties of the program personnel are presented below.

3.1 Program Operations

In order to oversee, coordinate and review the program as a whole the following functions are required.

Program Manager - A program manager should:

(a) Assure that data of acceptable precision and accuracy are generated within the time and funding constraints of the program.

(b) Keep abreast of all program requirements and make necessary decisions.

(c) Review data and QA reports.

(d) Issue progress reports.

(e) Analyze and interpret the results.

The program manager should have a degree in science and some experience in managing projects. Full time employment is recommended. This position can be combined with that of the field manager.

QA Officer - The QA officer should:

(a) Report directly to the program manager on inputs from other program functions.

(b) Assess the quality of the data generated.

(c) Recommend corrective actions that need to be taken.

The QA officer might be assisted by one or more QA/QC coordinators if the magnitude of the program requires it. The QA officer should have training in QA as it relates to experimental design, monitoring and data validation.

3.2 Field Operations

The personnel needed to carry out the field duties in a precipitation monitoring network include a field manager and station operators.

Field Manager - The field manager may be a member of the organization operating the stations or a member of the central laboratory staff. He should have a college degree, preferably in chemistry; should be familiar with all the field procedures; and should have experience in the operation of all equipment. His duties are:

(a) Solve field problems.

(b) Notify the program manager of such problems.

(c) Oversee and train the operators.

(d) Coordinate between field and laboratory functions.

Station operators should have a technical background but need not have a college degree. All operators should have the training to perform at the necessary level of knowledge and the skill required to obtain and report quality data. A short-term course in "hands-on" training is recommended. This should be followed by on-the-job observation immediately after the course and by a semi-annual inspection thereafter. The training should cover all pertinent aspects of the Operations and Maintenance Manual (1), which should be given to all personnel. If, at any time, an operator's performance deteriorates, additional training must be provided as soon as possible by the field manager, by a refresher course or by on-site guidance during network evaluation visits.

Station Operators - The duties of a station operator are:

(a) Operate and maintain samplers according to appropriate SOPs.

(b) Operate and maintain rain gauges according to appropriate SOP.

(c) Maintain monitoring site and its surroundings free from obstruction and dirt.

(d) Change sampling buckets at pre-assigned intervals and record activities in field logs.

(e) Perform required calibrations of measurement instruments and analyses of samples as described in SOPs.

(f) Preserve and store field samples as appropriate

(g) Ship samples to analytical laboratory at intervals specified in SOPs.

(h) Notify field manager on any problems with samplers, gauges, instruments, standards and the like.

3.3 Laboratory Operations

Each analytical laboratory should have the following types of employees: a director/supervisor, an analyst, and a QC chemist.

Laboratory Director/Supervisor - This person should have a minimum of one year's analytical experience, a degree in chemistry and be a full-time employee. His duties are:

(a) Schedule all analyses in the laboratory.

(b) Review all QC input to verify "in control" conditions.

(c) Release data to the program manager.

Laboratory Analyst - This person should be employed full-time and trained to perform with minimum supervision all routine chemical measurements on water samples. Academic training should include: completion of at least one year of college chemistry or a laboratory-oriented vocational course. A minimum of 30 days of on-the-job training in measurements performed by the organization is also highly recommended. The analyst must be supervised by an experienced professional scientist--the laboratory director, the supervisor or a similarly trained individual. His duties are:

(a) Perform instrument calibrations according to SOPs.

(b) Analyze field samples in the assigned order to meet required schedules.

(c) Notify laboratory supervisor on any problems either in the analysis or instrumentation.

Before analysts are allowed to analyze samples, they should demonstrate their proficiency. Each new analyst should be instructed in instrument operation and should be allowed to conduct an instrument performance study. Analyst performance can be evaluated by control charts of critical QC parameters. If these charts indicate a problem, the analyst should be given further training.

Quality Control Chemist -- This individual should have a minimum of a bachelor's degree in chemistry, engineering, or mathematics with at least two years of environmental and one year of QA/QC experience. This position is under the general supervision of the laboratory director but with access to the program manager. His duties are:

(a) Implement and monitor the routine application of QC activities in the laboratory.

(b) Participate in a formal program to train new employees and to update skills of older employees.

(c) Report to laboratory supervisor status of QC checks.

This is not necessarily a full time position; it may be part time supplemented by other program duties. The percentage of the chemist's time dedicated to QC is dictated by the size and complexity of the program.

3.4 Data Management Operations

Persons involved in data acquisition, reduction and reporting are the field operator, the analyst, the data entry staff, the laboratory director, the program manager, and the QA officer. Their primary duties are:

Field Operator - His duties are:

(a) Preparation of field data forms.

(b) QC of field data form preparation before shipment to field manager.

Analyst - His duties are:

(a) Reading or transcription of strip charts

(b) Entry of data to computer.

Laboratory Supervisor - He should perform:

(a) QC check of strip chart reading.

(b) Preparation of data forms.

(c) Review of computer-generated QC information.

(d) Preparation and interpretation of control charts.

Data Processing Personnel - Duties include:

(a) Input of data from data sheets.

(b) Verification of input for keypunch errors.

(c) Update of computer files.

QA Officer - He should perform:

(a) Review of data.

(b) Preparation of QA reports.

(c) Submittal of audit data and recommendations to program manager.

3.5 Designation of QA Responsibilities and Duties

QA Officer - The QA officer, or his designee should:

(a) Review the monthly QC plots generated for each analysis to verify that QC data are acceptable and to identify any consistent bias trend.

(b) Evaluate the periodic Field Audit Report prepared by the QC chemist to assess the accuracy of field pH and conductivity measurements of test samples and to identify needs for corrective action.

(c) Review all QC information presented with each set of analytical data reported -- including data from QC reports.

(d) Evaluate laboratory and field operations by conducting program audits and reporting results to the program manager.

(e) Prepare quarterly reports to management that summarize QA activities and assess data quality in terms of precision and accuracy trends for both the field and laboratory operations.

QC Chemist - The QC chemist should:

(a) Introduce blind samples to the laboratory as an independent check on data quality.

(b) Issue a regularly-scheduled report updating control limits for all observables.

(c) Evaluate all data prior to its submission to the Laboratory Director/Supervisor.

Analyst - The analyst should:

(a) Perform all the analyses according to approved Standard Operating Procedures (SOPs).

(b) Evaluate analytical performance in real time, using readily available QC information.

(c) Reanalyze the sample if necessary.

(d) Submit data obtained "under control" conditions to the QC chemist.

Data Clerk - The data clerk should:

(a) Enter analytical and field data into the computer.

(b) Check and correct the data input.

(c) Generate reports and graphs of QC information.

3.6 Reference

1. Quality Assurance Handbook for Air Pollution Measurement Systems. Vol. V - Manual for Precipitation Measurement Systems; Part II - Operations and Maintenance Manual. U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/4-82-042b (January 1981).

4.0 DOCUMENTATION

4.1 Document Control

A system of document control should be established for all precipitation monitoring field and laboratory operations. Elements of a precipitation measurement project subject to document control should include:

1. Field operations and maintenance procedures,
2. Analysis procedures,
3. Auditing procedures,
4. Computational and data validation procedures,
5. Work plan, and
6. Quality assurance plan (if a separate document).

4.2 Internal Documentation

A central file of all data, reports, correspondence, etc. should be maintained by the program manager and a data file should be kept by the laboratory. Records in the laboratory file should meet the following requirements:

1. Records should have identification numbers and be kept in an orderly, accessible form. Records should include all raw data, calculations, QC data, and reports.
2. Data in laboratory records should include:
   - A. Sample identification number,
   - B. Sample type,
   - C. Date sample received in laboratory,
   - D. Collection data (time, date, volume, etc., if laboratory responsibility),
   - E. Date of analysis,

F. Name of analyst,

G. Results of analysis (including all raw data), and

H. Name of person receiving the analytical data.

3. The laboratory should have a sample-tracking system starting from receipt of sample through to the completion of analysis; this should include:

   A. Sampling information records (e.g., field data forms) with dates, time, site location, sample amount, etc.,

   B. Bound notebooks with numbered pages,

   C. Computer printouts or report forms verified against laboratory records before data release.

4.3 QA Documentation

QA reports should be submitted regularly to the program manager by the QA officer. They should include:

1. Periodic assessments of measurement data accuracy, precision, and completeness;

2. Results of performance audits;

3. Results of systems audits; and

4. Significant QA problems with documentation of remedial action taken or recommended solutions.

5.0 SITING

In the design of a monitoring program, the program objectives and network station density must be considered. Ideally, a complete description of the site and its surroundings (out to 20 km) should be given so that the user of the data could decide what the station is measuring or what the data represent. However, for convenience, simplified site categories (urban, remote, regional or rural) are used here.

Network station density, which helps define the spatial resolution of the data obtained, is determined by program objectives, area meteorology and topography, and budgetary constraints. Thus, it is difficult to design a network for all users of this QA manual. However, some specific guidance can be found in References 1 and 2. Points to consider for setting up a network monitoring a large geographical area are described below.

5.1 Network Design Considerations

In the design of a precipitation monitoring network, stations are located according to the objectives of the program:

1. Measurement of baseline (remote area) precipitation,
2. Measurement of representative regional (rural) precipitation, or
3. Measurement of urban area (local impact pollutant emission sources) on precipitation.

These three are generally differentiated by expected concentration levels. The background or remote station should show contamination primarily due to natural processes; the regional station would be affected primarily by long-range transport; and the urban site would show high concentrations due to a polluted local environment. In the selection of station locations, it is necessary to have detailed information on location of emission sources, regional variabilities of ambient pollutant concentrations, precipitation amounts, prevailing winds, and meteorological data. Thus, the design of a network needs to address details such as the number, location, and type of sampling stations and equipment to be used.

5.2 Site Selection Criteria

The variability and the long-range transport of pollutants make it difficult to determine whether a site is collecting precipitation data representative of any given area. In addition, the transport of air pollutants and their resultant concentrations in precipitation are complicated by topography. For example, in mountainous regions, precipitation tends to be unevenly distributed due to topographical lifting of clouds and deflection of air flows.

To optimize site locations for different station categories, the following selection criteria are suggested.

5.2.1 Baseline Station - The station should be in a location where the effects of human activities are negligible. Ideally, the station should meet as many of the following criteria as possible:

1. The station should be in an area where no significant changes in land-use practices within 100 to 1000 km (depending on prevailing wind direction) from the station are anticipated during the study period.

2. The station should be at least 50 km from major population centers, major highways, industries, air routes, and large natural sources (e.g. geysers); it should be in remote, uninhabited, or sparsely inhabited areas. If an isolated island is used, data corrections for sea salt aerosols should be made.

3. The site should not have a history of frequent local natural phenomena such as forest fires, dust and sand storms, or volcanic activities.

4. The site should have provisions, e.g. power, for setting up a meteorological and aerometric monitoring station (3,4,5,6).

5. The site should be readily accessible on a flat or gently sloping terrain (less than 20°) and sheltered from strong winds.

5.2.2 Regional Station - Ideally, site selection criteria for a regional monitoring network include criteria 3-5 for baseline stations as well as the following:

1. The general area should be free from influences of large anthropogenic sources such as cities or towns; industrial, sewage or power plants; refineries, commercial areas, and airports; and large local natural sources. Such pollutant sources should be distant enough for pollutants not to unduly affect the precipitation chemistry. If the site location must be near a large source (within 50 km), the station should be in the prevailing upwind direction from the source.

2. The site should be at least on kilometer distant from local sources such as houses, farmlands, orchards, marshes and swamps, landfills, and roads.

3. If stations are near pollutant sources, the site location should avoid undue influence by a single pollutant source.

4. If an area is characterized by a common type of land use, the collector can be near the common pollution source.

The selected site can be evaluated for representativeness and for local contamination by installing a temporary grid of neighboring satellite samplers around it. Sampling procedures for this temporary network should be comparable to those at the original site. The permanent site should be selected after evaluating the results of this temporary network.

5.2.3 Urban or Local Station - Ideally, to study urban areas or the effects of point sources on precipitation, an array of monitoring stations should be near the source in the area of interest. The stations should not be near other sources. For studying the local effect due to a single point or area source, the average interstation distance should be of the order of several kilometers. However, actual station density and interstation distance should be decided by the desired spatial resolutions.

5.3 Sampler and Rain Gauge Siting Criteria

Placements of precipitation samplers and rain gauges should assure that the site collects unbiased samples. Samplers and rain gauges should stand far enough from trees, hills, and other obstructions to minimize interference with sampling. No object, even if smaller than the collector should be within a few meters of the collector, and no object should shade the collector. An open, flat, grassy area, surrounded by trees no closer than 100m would be an ideal site.

Ideal criteria for placement of samplers and rain gauges are:

1. The horizontal distance between a large obstruction and the collector should be at least twice the obstruction height, or the top of an obstruction as viewed from the collector should be less than 30° above the horizon.

2. The horizontal distance between collocated samplers, or sampler and rain gauge should be greater than two meters.

3. The collector should be far from mobile pollution sources. Routine air, ground, or water traffic should not come within a 100m of the collector site.

4. The distance between any overhead wires and the site must be great enough not to affect the samples.

5. The collector should be at least 100m from open storage of agricultural products, fuels, or other foreign materials.

6. The ground surface around the collector should be firm and have a grass cover or gravel.

7. Wet/dry collectors should be oriented parallel to the prevailing wind direction during precipitation events, with the wet bucket upwind of the dry bucket (so that the dry bucket does not obstruct the wet bucket).

8. The rain gauge should be positioned parallel to both the collector and the direction of the prevailing wind during precipitation events. If the gauge has an access door to a recorder, weighing or drive mechanism, the door should be kept closed, and the gauge should be mounted with the door facing away from the wind.

The distance between obstructions such as growing trees and newly erected structures and the collector should be checked periodically.

5.4 Station Identification and Classification

All stations must be identified by documentation of site characteristics to facilitate evaluation of data generated from samples taken at that site. Typically, the site identification record should contain:

1. Data acquisition objective (baseline, trend, or research monitoring).

2. Station location (address, map coordinates, elevation, etc.).

3. Type of station (remote, regional, or local type; and if it is primarily an industrial, agricultural, forest, urban site, etc.).

4. Instrumentation checklist (manufacturer, model number, measurement technique, etc.).

5. Important pollutant sources (point and area sources; their pollutants and emission concentrations, proximities, etc.).

6. Topography description (trees, hills, valleys, bodies of water and type, size, proximity, orientation, of water body, etc.). Photographs of the monitoring site covering a 360° view from the precipitation collector should also be taken.

7. Site diagram properly scaled (equipment configuration, trees, man made structures, access road, electrical power lines, etc.).

All monitoring stations should be properly identified and classified as described below using a clear, concise format. This can be accomplished using forms similar to those at the end of this section or those developed by other networks such as NADP and NTN.

<u>Class I</u>

1. Station satisfies all siting criteria (Section 5.3),

2. On-site instrumentation includes
   automatic precipitation collector,
   recording rain gauge,
   pH and conductivity meters,
   meteorological sensors (windspeed and direction), and
   aerometric analyzers (SO_2 and NO/NO_x).

<u>Class II</u>

1. Station satisfies all siting criteria (Section 5.3).

2. On-site instrumentation includes
   automatic precipitation collector,
   a recording rain gauge, and
   pH and conductivity meters.

Class III

1. Station satisfies all siting criteria (Section 5.3).

2. On-site instrumentation includes
automatic precipitation collector,
nonrecording rain gauge, and
pH and conductivity meters.

Class IV

1. Station does not satisfy all siting criteria (Section 5.3).

2. On-site instrumentation identical to Class I stations.

Class V

1. Station does not satisfy all siting criteria (Section 5.3).

2. On-site instrumentation identical to Class II stations.

After initial classification, an on-site visit should be made by the QA coordinator to evaluate and certify each monitoring station as soon as possible after the start of operation to assure the quality of monitoring data. Classes IV and V must be only temporary, since they are in noncompliance with siting criteria. The program manager (or a designee) must be sure that siting deficiencies are corrected within a reasonable time. Most deficiencies should be corrected within 30 days, but for serious deficiencies, a schedule should be established for compliance attainment. When corrections are made, documentation should be provided to the QA officer and program manager and the station classification should be changed by them.

All sites should be reevaluated yearly to verify that they remain in compliance with the siting criteria. All aerometric and meteorological instrumentation should conform to standard ambient monitoring guidelines.

5.5 References

1. WMO Operational Manual for Sampling and Analysis Techniques for Chemical Constituents in Air and Precipitation, World Meteorological Organization Pub. No. 299 (1974).

2. Site Selection and Certification, National Atmospheric Deposition Program (1970).

3. Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. II - Ambient Air Specific Methods, EPA-600/4-77-027a, Research Triangle Park, NC (1977).

4. Guide to Meteorological Instrument and Observing Practices, World Meteorological Organization Pub. No.8, TP8 (1971).

5. Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD), EPA-450/1-78-019 (1978).

6. Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. I - Principles, EPA-600/9-76-005, Research Triangle Park, NC (1976).

SITE DESCRIPTION REPORT

____
Data Prepared

____
Reason (New site, change, revision)

A. DATA ACQUISITION OBJECTIVE (Description) ______________________________

____

B. SITE CATEGORY

1. Station Identification ________ 2. County __________ 3. State ______
4. Latitude _________ 5. Longitude _________ 6. Elevation _________
7. Station environment: remote ______________ rural ______________
suburban ____________ urban ____________ commercial ______________
industrial ____________
8. Available USGS Topographical Map (Yes, No) (circle)
9. Revision year ______________________________
10. Scale (1:24,000 preferred) ______________________________

C. SITE ADMINISTRATION

1. Name of official ________________________ position ______________
Mailing address ______________________________________
(number and street)

________________________________ ______________________
(city) (state) (zip) (Phone)

2. Name of Program Manager ________________________ Title ___________
Mailing address ______________________________________
(number and street)

________________________________ ______________________
(city) (state) (zip) (Phone)

3. Name of Site Operator ______________________________________
Mailing address ______________________________________
(number and street)

________________________________ ______________________
(city) (state) (zip) (Phone)

D. SITE INSTRUMENTATION

1. Precipitation Collector Type: Automatic ______ Non-automatic ______

Manufacturer ______________________

Model ____________________________ Serial No. __________________

Diameter (I.D.) of
Sample Bucket __________(cm)

2. Raingauge:

Recording ______________ Nonrecording ____________________

Type: Weighing ______ Tipping Bucket ______ Other ___________

Manufacturer ______________________

Model _____________________ Serial No. __________________

Funnel Size ________________(cm)

3. Nitrogen Oxide Monitor:

Automatic Data Acquisition _______ Stripchart recording ___________

Type: Chemiluminescent ____________ Other ________________________

Manufacturer ____

Model ________________________________ Serial No. _________________

4. Sulfur Dioxide Monitor:

Automatic Data Acquisition _______ Stripchart recording ___________

Type: Fluorescent _______________ Other __________________________

Manufacturer ____

Model ________________________________ Serial No. _________________

5. Other Aerometric Analyzers:

Sensor: ____

Recording __________________ Nonrecording ______________________

Type _______________________ Serial No. ________________________

Manufacturer _______________ Model _____________________________

6. Other Meteorological Instrument:
   a. Wind Speed Sensor: Type ______
      Manufacturer ______
      Model ______ Serial No. ______
   b. Wind Direction Sensor: Type ______
      Manufacturer ______
      Model ______ Serial No. ______
   c. Temperature Sensor: Type ______
      Manufacturer ______
      Model ______ Serial No. ______
   d. Solar Radiation Sensor: Type ______
      Manufacturer ______
      Model ______ Serial No. ______

E. ANALYTICAL INSTRUMENTATION:

1. pH Meter: Type ______ Temp Compensated ______
   Model ______ Serial No. ______
2. Conductivity Meter: Type ______ Temp. Compensated ______
   Manufacturer ______
   Model ______ Serial No. ______
3. Balance: Type ______
   Manufacturer ______
   Model ______ Serial No. ______
4. Type of low conductivity water available:
   dionized ______ distilled ______ bottled ______
5. Laboratory Space: Location ______
   Good ______ Fair ______ Poor ______
   Special problems ______
   ______

F. SITE DOCUMENTATION

1. Identify site location and major sources on local topographical map (attach to report).

2. Sketch a map to document the environment within a 1/2 mile radius of the site. Include the following information on the drawing where applicable.

    - Site diagram and equipment configuration at center of drawing
    - Roadways with names (paved and unpaved)
    - Parking areas (paved and unpaved)
    - Stationary sources (NEDS#)
    - Buildings (number of stories)
    - Tree lines or clusters
    - High power lines
    - Topographical features (valleys, hills, etc.)
    - Bodies of water
    - North direction
    - Undeveloped land (ground cover)

3. Site photographs, labelled to indicate the four compass directions.

Looking North

Looking South

Looking West

Looking East

G. POTENTIAL SOURCES OF INTERFERENCE OR CONTAMINATION AT THE SITE

1. Within 30 m of the SAMPLER identify all objects that are taller than the sampler.

a. Structures

Type ______________ Use ______________________________

Height __________(m) Distance ________(m) Direction __________

Type ______________ Use ______________________________

Height __________(m) Distance ________(m) Direction __________

b. Trees

Species ________________________ Max. Height ______________(m)

Distance __________(m) Direction ______________________________

Species ________________________ Max. Height ______________(m)

Distance __________(m) Direction ______________________________

Species ________________________ Max. Height ______________(m)

Distance __________(m) Direction ______________________________

c. Other (e.g., overhead wires, masts, etc.)

(1) Object ____

Height ________(m) Direction ________ Distance ________(m)

(2) Object ____

Height ________(m) Direction ________ Distance ________(m)

(3) Object ____

Height ________(m) Direction ________ Distance ________(m)

(4) Object ____

Height ________(m) Direction ________ Distance ________(m)

(5) Object ____

Height ________(m) Direction ________ Distance ________(m)

d. Is public road access to site in

summer Good ___ Fair ___ Poor ___

and winter Good ___ Fair ___ Poor ___

e. Type of public road surface? ______________________________

f. How far from the public road will collector be sited? ______(m)

g. Is there other than public road access to the site? If so, please describe.

____

____

____

h. How close can a vehicle approach the collector? __________(m)

i. How is site secured against vandalism, etc.? ____________

j. Are there any special logistical problems? Please describe.

____

____

____

2. Within 200 m of the site identify:

a. Predominate land use in the area:

Use 1 _____, _____% Use 2 _____, _____% All Others __________%
(cultivated, orchard, lawn, pasture, forest, water, swamp, residential)

b. Unpaved roads and parking areas:

Unpaved road: Distance ____(km,m) Direction from sampler _____
Traffic: Heavy _____, Medium _____, Light _____
Unpaved road: Distance ____(km,m) Direction from sampler _____
Traffic: Heavy _____, Medium _____, Light _____
Parking lot: Distance ____(km,m) Direction from sampler _____
Unpaved __________ Surface material __________
Use: continuous _____ intermittent ______ car volume ________
large truck volume __________
Parking lot: Distance ____(km,m) Direction from sampler _____
Unpaved __________ Surface material __________
Use: continuous _____ intermittent ______ car volume ________
large truck volume __________

3. Within 1 km of the site identify significant agricultural operations such as feedlots, dairy barns, cultivated fields, etc.

   Type ____
   Distance ________(km,m) Direction from sampler ______________
   Type ____
   Distance ________(km,m) Direction from sampler ______________

4. Within 10 km of the site identify transportation related sources.

   a. Main highways or expressways: Traffic volume ____________
      Direction from sampler ____ Distance ____(km,m) Route #_____
      Main highways or expressways: Traffic volume ____________
      Direction from sampler ____ Distance ____(km,m) Route #_____

   b. Other paved roads: Distance ___(km,m) Direction from sampler__
      Traffic: Heavy ___, Medium ___, Light ___ Traffic Volume ____
      Other paved roads: Distance ___(km,m) Direction from sampler__
      Traffic: Heavy ___, Medium ___, Light ___ Traffic Volume ____

   c. Lake/river or rail traffic:
      Distance ____(km,m) Direction from sampler ______________
      barge ____, lake steamer ____, ocean vessels ____, rail ______
      Traffic: Heavy ___, Medium ___, Light ___ Traffic Volume ____

   d. Airport: Distance _____(km,m) Direction from sampler ________
      Traffic: Heavy _____, Medium _____, Light _____

   e. Other transportation related sources ____________________
      ____

5. Within 60 km of the site identify stationary sources:

   a. Power plant(s):
      Name ____
      Distance ________(km) Direction from sampler ______________
      Fuel ___________ Electrical capacity ____________(KW_e, MW_e)
      Name ____
      Distance ________(km) Direction from sampler ______________
      Fuel ___________ Electrical capacity ____________(KW_e, MW_e)

b. Industry:

Type/product ______________________________

Distance _________(km) Direction from sampler ____________

Comment ______________________________

Type/product ______________________________

Distance _________(km) Direction from sampler ____________

Comment ______________________________

c. Other stationary sources:

Type/product ______________________________

Distance _________(km) Direction from sampler ____________

____

____

____

____

6. Within 60 km of the site identify significant area sources:

Type/product ______________________________

Distance _________(km) Direction from sampler ____________

____

____

____

____

H. PERSON WHO FILLED OUT THIS FORM

Name ______________________________

Position ______________________________

Phone # ______________________________

Address ______________________________

Affiliation ______________________________

Signature ______________________________

6.0 FIELD OPERATIONS

6.1 Facilities

All field facilities should be accessible and should have a clean shelter, a level table, deionized or distilled water (conductivity less than 2.0 μmho/cm), and a sink or drain. A refrigerator and a 110v AC outlet are highly desirable. The former is necessary to preserve samples until they are shipped. For weekly sampling, the samples should be shipped within 24 hours of collection.

The precipitation collector and the recording rain gauge can be run on either 12v DC storage batteries or 110v AC. Both means have advantages and disadvantages. If large current usage is required (e.g., for heating), batteries are not recommended.

6.2 Method Selection

6.2.1 Precipitation Collectors and Rain Gauges - The rain gauge and the precipitation collector serve different functions. The rain gauge measures the amount of precipitation. The precipitation collector collects a sample for chemical analysis. The two devices are not interchangeable.

Precipitation Collectors -- The precipitation collectors should have the following characteristics:

(a) Reliable automatic operation - collector opens at start of precipitation and closes after event ends.

(b) Prevent contamination of wet sample by dry deposition.

(c) Minimize evaporation.

(d) Inert to sample constituents of interest.

Collectors, meeting these criteria are available. The most satisfactory collector is one based on the design of the Department of Energy's Health and Safety Laboratory (HASL)(1). However, the sampler is not very efficient for collecting snow.

The first three criteria are met by means of a precipitation sensor and a motor-driven, tight-fitting lid for the collector container. When the grid and plate of the sensor are shorted by a drop of water, the motor is activated, lifting the lid from the container. The sensor has two heating circuits. One operates to melt snow or ice (on the sensor) when the temperature is below 2°C. When the lid lifts off the sample bucket, the other circuit heats the sensor to about 55°C to increase the rate of evaporation of water from the sensor. (Heat hastens the sealing of the sample by the lid after precipitation ceases, thus minimizing the exposure times to dry fallout and to snow blowout from the collector.) A seal between the container and the lid is achieved by a plastic foam gasket under the lid and by a spring load. However, in strong winds the lid can wobble and may permit contaminants to enter the sample bucket.

To ensure inertness to major constituents in acid precipitation, polyethylene sample buckets (1,2) are usually used, because of their low cost, durability, and availability, high-density linear polyethylene containers can be used for collecting and shipping samples. Glass or metal can affect inorganic sample integrity, but should be used if organic compounds are being monitored.

Subevent or sequential samplers separate samples on either a volume or time-of-collection basis, but the same requirements as above hold. In volume-based sampling, precautions must be taken to minimize mixing or carry over of samples. For time-based sampling, there should be provision for overflow during heavy rainfalls. For sequential sampling, the time corresponding to each subevent specimen must be known for correlations with other data. Sequential samplers vary greatly in sophistication from a series of connected bottles to completely automated and electrically operated designs (3-8). One of the latter is available commercially(8).

Rain Gauges -- A standard, a rain gauge is used to record the quantity of precipitation. Recording rain gauges are of two basic operational designs--the weighing type and the tipping bucket type. Both types of gauges should be capable of measuring precipitation to approximately 0.25 mm (0.01 in). Weighing gauges measure within ±0.76 mm (0.03 in), and their accuracy (1% of full scale) is independent of precipitation rate. The accepted accuracy for tipping bucket gauges is 1% for precipitation rates of 25 mm/h (1 in/h) or less, 4% for 75 mm/h (3 in/h), and 6% up to 150 mm/h (6 in/h). Rates are measured either directly or derived from the cumulative data.

The recording weighing rain gauge should have an event marker pen to indicate when the collector is open and closed. Such a pen typically rises from its baseline when the collector lid opens, and remains actuated until the lid closes at which time the pen falls to its baseline position. To prevent the event marker pen from interfering with the weighing trace pen, the two must be offset on the time axis. Thus only one pen can be set at the correct time, and care must be taken to use the correct beginning and ending times. Since the operator is seldom present to observe collector operation during an event, the event pen marker is an invaluable aid in indicating sampler malfunction or a power outage.

For windy areas and especially where snowfall constitutes more than 20% of the mean annual precipitation, an Alter-type windshield should be installed around the rain gauge. The shield should be level and its top should be 1.3 cm (0.5 in) above the level of the gauge collecting orifice. In addition, the shield should be concentric with the gauge. Installation instructions for the improved Alter-type windshield can be obtained from the U.S. Weather Bureau (9). Alternatively, a Nipher-shielded snow gauge can be used for snow depth measurement.

6.2.2 <u>pH and Conductivity Apparatus, Temperature Probe</u> - The pH and conductivity of a 20 ml aliquot of the precipitation sample should be withdrawn and measured at the field station as soon as possible after the sample is collected but only after it is at the temperature of the calibration solutions. The sample and the aliquot should be protected from contamination during this time.

pH Apparatus -- The pH meter and electrode must be capable of measuring with a precision within ± 0.03 unit and with an accuracy of 0.05 unit. Meters should have an impedance of at least 10^{11} ohms. A combination glass and reference electrode of the nongel type with an unprotected membrane bulb is preferred. The combination electrode requires less sample and fewer washings than two separate electrodes; electrodes with shielded bulbs are more difficult to clean, and are thus more prone to yield errors. When a new electrode is obtained, it should be equilibrated overnight and stored in the solution recommended by the manufacturer.

Conductivity Apparatus -- The conductivity meter and cell must have a measurement range of 0 to 1000 µmho/cm, a precision of ±0.5% of range, and an accuracy of ±1.0% of range. The range most frequently used is 10-100 µmho/cm. A temperature-compensated cell with a cell constant of 1.0 is preferred.

Temperature -- A thermistor, thermocouple, or thermometer can be used to measure solution temperature. The temperature probe must have an accuracy of at least 1°C and a precision of ±0.5°C.

6.2.3 Balance or Graduated Cylinders - The amount of precipitation sample collected can be measured with a balance or with graduated cylinders. Since the density of rain samples is approximately 1.0 g/ml at 20°C, the weight of the sample (in grams) can be taken to equal its volume (in ml). The measurement of sample volume by graduated cylinders increases the chance of contamination, so a balance is preferred.

The precipitation sample volume can be compared to that recorded by the rain gauge (e.g., with the Aerochem Metrics collector, 16.2 g of sample = 0.01 in. = 0.25 mm) to calculate the collection efficiency of the sampler (Section 8.4.2). Differences between the field and the laboratory weight values (container plus sample shipped to the laboratory) indicate either loss of sample during shipment or a weighing error.

For weekly sampling, the balance should have a capacity of 20 kg with a accuracy of at least ±10 g. Triple beam balances meeting these requirements are readily available. The balance should be kept on a sturdy, level table, and it should be zeroed daily before weighing. The balance should be checked initially in the laboratory with 1.0 and 5.0 kg test weights. For event and sequential sampling, a 2.6 kg capacity triple beam balance with a sensitivity of at least ±1 g should be used.

Graduated cylinders are not recommended, but if they are used, they should be plastic. To measure within ±10 ml, the graduated cylinder should not be more than 1000 ml in capacity. The graduated cylinder should be checked before use for accuracy in the laboratory by weighing known volumes of water and comparing the results to the volume measurement after converting the weight to volume by multiplying by the density of the water.

6.3 Acceptance Testing

All precipitation collectors, rain gauges, pH and conductivity meters, and electrodes should be functionally tested before they are used in the field. Acceptance tests should cover the essential operations of the instruments. Collectors and rain gauges should be tested on site. It is convenient to test meters and electrodes in a central laboratory, where common standards and procedures are available. Procedures for this acceptance testing are detailed below. Procedures for carrying out these tests are in the Operations and Maintenance Manual (10).

6.3.1 Precipitation Collectors and Rain Gauges - Collector tests should include:

(a) sensor heating and actuating of the lid,

(b) sensor cooling and return of the lid,

(c) sensor temperature attainment when the lid is raised,

(d) sensor temperature with lid closed when ambient temperature is below freezing, and

(e) observation of lid cycling and sealing.

Rain gauge tests should include:

(a) sensitivity and accuracy,

(b) clock function, and

(c) pen and recorder functions.

6.3.2 pH and Conductivity Meters - Erroneous pH measurements may not be revealed by conventional two-point calibration procedures. The majority of standard buffer solutions have a similar total ionic strength. However, precipitation samples differ in ionic strength from the standardizing buffers, which might introduce a bias in the measurement.

For these reasons it is advisable for the electrode systems used in acid precipitation pH measurements to be used exclusively for this task and to be monitored with respect to their performance with known reference solutions intended to simulate the unknown samples. However, for documentation purposes, calibration with the certified buffer solution is essential (11,12).

For each of the tests indicated below a total of ten solutions are measured, and an average value and a standard deviation are calculated. These tests should include:

(a) Evaluation of conductivity meter and cell using 0.0003M KCl. System is acceptable if within 2% of 44.6 µmho/cm at 25°C, and the standard deviation is less than 2%.

(b) Evaluation of field pH meters using a certified laboratory pH electrode. System is acceptable if the average pH and standard deviation are within 0.03 pH unit of the documented values obtained using two certified buffer solutions.

(c) Evaluation of pH electrodes using pH electrode reference solution. System is acceptable if the average pH is within 0.1 pH unit of the known value and the standard deviation is less than 0.05 pH unit, when using reference solutions which simulate the ionic strength of precipitation samples.

6.4 Sampler and Rain Gauge Installation and Operation

The precipitation collector should be mounted on the ground so that the rim of the mouth or opening is level and at least 1 m above the ground, and it should be properly anchored against strong winds (cement blocks can be used as weights). The collector may be shielded from the wind, but it should not be put in an area where there will be excessive turbulence caused by the shield or where there are obstructive objects such as trees and buildings close by. In the winter, loss of snow from the collector can occur due to blow out. Also, in windy areas the bucket should be secured to the sampler by means of a spring or elastic tie down cord hooked to the bucket handle and collector table.

The sampler installation and operation are described in the manufacturer's instructions and in the Operations and Maintenance Manual (10). The precipitation collector requires no calibration, but proper functioning should be checked frequently. The rain gauge should be calibrated according to the manufacturer's instructions after installation and checked at least annually.

The rain gauge should be mounted on a firmly anchored support or base, e.g., cement blocks, so that the funnel rim is level and at about the same height as the collector bucket rim to enable comparisons of collection amounts between the two. The gauge level can be checked with a carpenter's level placed at two intersecting positions. The gauge mouth should be high enough not to be covered by snow.

6.4.1 Routine Checks on Collector, Rain Gauge and Site - Some tests should be carried out routinely on the precipitation collector and the rain gauge. The detailed procedures for these tasks and a checklist for conducting them are provided in the Operations and Maintenance Manual (10).

6.4.2 Corrective Action - Any indication of a malfunction should be recorded in the logbook, and the field manager should be notified. An attempt to diagnose and correct the problem should be made with the aid of the Operations and Maintenance Manual (10) as soon as possible. If the problem cannot be corrected, the field manager or equipment manufacturer should be asked for advice and direction. Any action taken should be recorded in the logbook.

6.5 Sampling Methodology

This section gives the methodology for sample collection, handling, measurement, and preservation. The procedures used to accomplish each of the above-mentioned tasks are given in the Operations and Maintenance Manual (10).

6.5.1 Sample Collection and Schedule - The choice of sampling schedule depends on the program objective and the available funds. To correlate precipitation data with aerometric and/or meteorological data, event or daily sampling must be used. To measure the amount of deposition and/or its effects, a weekly sample may be sufficient. Sampling periods longer than one week are not advised because significant changes in sample chemistry can occur as the sample stands in the collector.

6.5.2 Handling of Plastic Containers - Treatment of plastic containers depends on the species to be measured, the container's previous use, and its cleanliness. In most cases, the cleaning of the bucket, lid and gasket should be done in the laboratory.

The container should be capped with a clean lid and kept in a plastic bag until immediately before use, and it must be resealed immediately after use. When a bucket is to be returned to the laboratory with or without a sample, it should not be sealed with its original lid. Instead, the sample should be covered with the lid from a new bucket which is replacing the old bucket in the collector. Thus the chance of contamination from the stored lid is eliminated.

An alternative approach used by the Canadians (13,14) that eliminates the washing of buckets and lids is the use of laminated nylon-polyethylene bags inserted into the buckets. When the bag is placed in the bucket, plastic gloves are worn and no contact with the interior of the bag further than 7.5 cm inside is made. A fold of 7-10 cm is extended down over the outside surface of the bucket. When removing the bag containing a sample, the bag is grasped by the fold. The bag is sealed below the fold with a cable tie (13) or by heat (13,14). Up to 500 ml of sample is emptied from the bag into a polyethylene bottle by cutting a prewashed and dried corner off the bag with a clean scissors and pouring the sample directly into the bottle.

6.5.3 Sample Handling - The sample bucket must be checked for precipitation at the time and frequency set by the schedule. However, if a snowfall occurs, the sample should be removed as soon as possible and replaced with a new bucket to minimize snow loss by overflow and blow out.

6.5.4 Sample Preservation and Storage - Sample degradation can occur due to chemical interactions (e.g., with particulates or gases) or to biochemical reactions. In addition, losses of potassium and some trace metals by adsorption on polyethylene walls have been reported (15). Preservation of sample integrity can be maximized by filtration, sealing, and storage in the dark at about 4°C. After pH and conductivity measurements, filtration should be done with a 0.45 µm organic membrane filter (16), if inorganic species are to be analyzed. Although biocides such as toluene or chloroform might be effective in stopping biochemical activity, they may interfere in the various measurements or analyses (2) and thus should not be added to the sample. If certain species must be preserved, an aliquot of the sample can be mixed with a preservative in a separate container.

6.6 Field Measurements

Field measurement of pH, specific conductance, and temperature are discussed in general terms in this section; detailed procedures are given in the Operations and Maintenance Manual (10). Sample pH and conductivity are measured in both the field and the laboratory to detect sample changes and errors in measurement. Results of field measurements should be recorded on a Field Data Form that will accompany the sample to the laboratory.

6.6.1 pH Determination Method - Since rain samples generally have pH values between 3.0 and 6.0, the pH meter should be calibrated with pH 3.0 and 6.0 standard buffers. For other less acidic samples, pH 4.0 and 7.0 buffers should be used, and for basic samples, pH 5.0 and 8.0 buffers should be used. Each station should receive the needed calibration buffer solutions from the central laboratory. The stations should notify the laboratory when the buffer supply is nearly exhausted or if it appears to be contaminated by algae growth.

The pH meter should be calibrated before and after each measurement or a series of measurements at one time. If the initial and final calibrations have changed by more than 0.02 unit, the measurements must be repeated. If this change reoccurs, a problem exists with the apparatus, and it should be remedied.

Each electrode should be assigned an identification number so that its calibration can be traced. To check for electrode problems (aging and loss of sensitivity), each site should periodically receive from the central laboratory a polyethylene bottle of electrode reference solution with pH and conductivity similar to those of rain samples. The pH of this sample is measured and reported to the central laboratory. The field pH value should agree within ±0.10 pH unit of the assigned value if the electrode is operating properly.

Electrode performance can also be determined by observing the time needed to attain a stable reading, where a stable reading is defined as a constant pH value (±0.02 units) for a period of 1 min. The time required to attain stability should be less than 5 min. for a well-behaved electrode. Results of these tests should be guides for the measurement technique and the equilibration time to be used for precipitation sample measurement. If an electrode test at any time exhibits out-of-control behavior (as indicated by the above criteria), the electrode and/or solution should be replaced.

6.6.2 Specific Conductance Determination Method - The conductivity (or resistance) of a solution varies with electrode area and spacing as well as with temperature and ion concentration. Therefore, the measuring apparatus has to be calibrated to obtain the cell constant or to adjust the meter. For calibration, a KCl solution of known conductivity should be used. The temperature of the KCl standard and the precipitation sample should be the same. For rain samples, a 0.00050M KCl solution is ideal. All conductances should be reported in µmho/cm corrected to 25°C.

The conductivity apparatus should be calibrated before and after each measurement or series of measurements at one time. If a change of more than 5% occurs, the measurements should be repeated. If the drift persists, a problem exists with the apparatus. In general, stable values occur in about 30 sec. Conductivity of the samples can be measured on the same aliquot used for pH. IF THIS IS DONE, THE CONDUCTIVITY MUST BE MEASURED BEFORE pH TO AVOID ERROR DUE TO SALT CONTAMINATION FROM THE ELECTRODE.

The conductivity cell generally has few problems. However, the working conductivity standard (0.0005M KCl) may degrade slowly or become contaminated. To minimize errors due to changes in the calibration standard, the working solution should be replaced quarterly. When a new working standard is received, it should be checked against the old working standard, and the two values should agree within 4.0%. If they do not, the laboratory which supplied the standard to the site should be notified.

Conductivity standards should be sealed and stored in a refrigerator to minimize changes. Generally, changes of less than 2% monthly may be ignored; if greater than 2%, the field values can be corrected for the larger changes by prorating with time in a linear manner. Another means of evaluating the working conductivity standard is the use of unknown quality control test samples submitted periodically from the laboratory to determine the accuracy and precision of the station's specific conductance measurements. If the laboratory finds that the station's conductivity measurement differs from the laboratory's by more than 5%, the laboratory should inform the field and quality assurance personnel and should replace the old conductivity standard or the meter.

6.6.3 Temperature Measurements - Each field thermometer or temperature probe should be assigned an identification number so that it will be possible to trace its certification. The temperature probe should be washed and dried before the solution temperature is measured. It should never be placed in a solution on which pH and conductivity measurements will subsequently be made.

The central support laboratory should maintain and store an NBS-calibrated thermometer as a primary standard, and one field thermometer should be certified against this as a secondary standard. All field thermometers or temperature probes should be calibrated against the certified (secondary) thermometer in a circulating water bath in the 0° to 25°C range. After initial calibration, the temperature probes should be recalibrated at least once per year.

6.6.4 Gravimetric Measurements - For weighing rain buckets, the balance should be in a room free from drafts and on a table that minimizes vibrations. The balance should be level.

Before being shipped to the field, each balance should be calibrated with NBS traceable weights in the central support laboratory. Annually, a full calibration should be performed by weighing two NBS traceable weights (1.0 and 5.0 kg) on the field balance. The actual reference weight, measured weight, and weight difference should be recorded. The rain gauges can be calibrated using a set of weights generally available from its supplier.

6.7 Documentation

All data, observations, and changes or modifications must be dated and documented on data forms and/or in logbooks in triplicate and duplicate, respectively (carbon paper may be used). One copy of each should be kept in the station records, and another shipped with the sample; the third copy (of the data form) should be mailed to the laboratory separately from the sample to help trace a missing sample.

Samples must be labeled so that they can be readily and correctly matched with their data forms. The label should contain station, date, and sample weight marked with a pencil or a ball point pen so that it is legible if it should gets wet.

Forms for use in documenting the data are provided in the Operations and Maintenance Manual(10).

6.8 References

1. J.N. Galloway and G.E. Likens, Water, Air and Soil Pollut. 6, 241 (1976).

2. J.N. Galloway and G.E. Likens, Tellus 30, 71 (1978).

3. H.B.H. Cooper, Jr., J.A. Lopez, and J.M. Demo, Water, Air Soil Pollut. 6, 351 (1976).

4. D.F. Gatz, R.F. Selman, R.K. Langs, and R.B. Holtzman, J. Appl. Meteorol. 10, 341 (1971).

5. J.J. Morgan and H.M. Liljestrand, "The Measurement and Interpretation of Acid Rainfall in the Los Angeles Basin," California Institute of Technology Report, No. AC-2-80 (February 20, 1980).

6. J.K. Robertson, T.W. Dolzine and R.C. Graham, "Chemistry and Precipitation from Sequentially Sampled Storms," EPA report to be published.

7. G.S. Raynor and J.P. McNeil, "The Brookhaven Automatic Sequential Precipitation Sampler," BNL-50818, Brookhaven National Laboratory (January 1978); Atmos. Environ. 13, 149 (1979).

8. P.B.S.K. Associates, P.O. Box 131, State College, PA. 16801, Bulletin 177.6801.

9. Installation Instructions for Improved Alter-Type Windshield, U.S. Dept. of Commerce, Weather Bureau, Instrumental Engineering Division (November 1957).

10. Quality Assurance Handbook for Air Pollution Measurement Systems - Vol. V - Manual for Precipitation Measurement Systems. Part II - Operations and Maintenance Manual. U. S. Environmental Protection Agency, Research Triangle Park, N.C., EPA-600/4-82-042b (January 1981).

11. G. Masinenko and W.F. Koch, "A Critical Review of Measurement Practices for the Determination of pH and Acidity Atnospheric Precipitation," NBSIR 84-2866. To be published by Environment International (1984).

12. J.A. Illingworth, "A Common Source of Error in pH Measurements," Biochem. J., 195, 259-262 (1981).

13. Acidic Precipitation in Ontario Study, Technical and Operating Manual APIOS Deposition Monitoring Program, W.S. Bardswick, Ed. Ontario Ministry of the Environment, Toronto, Ontario, Canada (April 1983).

14. T. Jarv, "Acid Rain Studies at Ontario Hydro: Air, Aerosol and Precipitation Chemistry Measurements for 1981," Report No. C82-81-K, Ontario Hydro Research Division, Toronto, Ontario, Canada (Sept. 2, 1982).

15. W.H. Chan, F. Tomassini and B. Loescher, "The Evaluation of Sorption Properties of Precipitation Constituents on Polyethyelene Surfaces," Atmos. Environ. 17, 1779 (1983).

16. M.E. Peden and L.M. Skowron, "Ionic Stability of Precipitation Samples," Atmos. Environ. 12, 2343 (1978).

7.0 LABORATORY OPERATIONS

7.1 Analytical Reagents

7.1.1 Purity Requirements - Water having a conductivity less than 2.0 µmho/cm (resistivity greater than 0.5 megohm/cm) is acceptable for analysis of major constituents in rainwater. In the past, high purity has been obtained by distilling water; however, distillation systems have several drawbacks. Even double- or triple-distilled water contains easily detectable impurities. Stills require periodic shutdown and careful cleaning, and water production is relatively low. If distilled water is used then it must be passed through an ion exchange column before use.

Ion exchange systems, on the other hand, provide high quality water, are relatively maintenance free, and provide water on demand. The only maintenance required is to change cartridges periodically. It is preferable to pretreat the feed water with a reverse osmosis system to remove a high percentage of ionic impurities and to prolong the life of the ion exchange beds. In the last stage of treatment, a 0.2-micron filter should be used to remove microorganisms and particles. A meter to monitor the conductivity of the water should be installed inline directly before the spigot, and the system should be checked if the conductivity becomes greater than 2.0 µmho/cm. If trace organics are to be determined, an activated charcoal filter should also be used for purification.

Reagents used for analyses must meet standards of quality denoted by the terms "analytical reagent grade," "reagent grade," and "ACS analytical reagent grade." All of these grades are equivalent, and they identify reagents which conform to current specifications of the Committee on Analytical Reagents of the American Chemical Society (1).

It may not be possible to obtain dyes of analytical reagent grade for automated colorimetric ammonium and phosphate analyses. For these, a statement of purity should be obtained from the manufacturer and, if necessary, the weights of dye used in reagent preparation should be adjusted.

The lanthanum nitrate used as a flame buffer in atomic absorption should be "atomic absorption grade."

7.1.2 Storage Requirements - Analytical reagents have a finite shelf life, so all chemicals should be dated by the receiving clerk and labeled "Do not use after...". Unless otherwise specified by the manufacturer, inorganic chemicals have a shelf life of 5 yr at room temperature.

Concentrations of reagents in solution may change due to: (1) biological action, (2) chemical reaction (e.g., oxidation), (3) evaporation, and (4) adsorption-desorption phenomena on container surfaces. All of these effects can be slowed by refrigeration. Guidelines for reagent storage can be found in references 2, 3 and 4.

7.2 Laboratory Support for the Field

The laboratory must prepare standards for calibrating field instruments and for field testing the quality control samples. Clean sample containers and shipping materials should be supplied as needed. This section discusses reference solutions, laboratory evaluation of field equipment, and routine supply of materials. Detailed procedures for preparation of solutions are in the Operations and Maintenance Manual (5).

Accuracies of field conductivity and pH measurements should be evaluated with audit samples. At scheduled intervals, an audit sample should be prepared using the procedures in the Operations and Maintenance Manual (5).

All meters and electrodes should be tested in the laboratory before they are shipped to the field. Meters usually have a serial number affixed, but electrodes do not, so an identification number should be affixed to each electrode. Acceptance tests are described in the Operations and Maintenance Manual (5).

[illegible] Agency

[illegible] d, 12th Floor

7.3 Laboratory Logistics

7.3.1 Sample Handling in the Laboratory - All samples received by the laboratory should be checked in by a receiving clerk who: (1) records the site, date, and other identification; (2) checks the field data form against sample labels to identify discrepancies; (3) assigns a laboratory identification number to the sample and records the number and the date of arrival on the data form and in the logbook; and (4) examines the data form and the sample for certain conditions and codes the information on the data form. These codes, which may be useful later in interpreting the data, should be stored with the sample data in the computer. Table 7-1 suggests some information to be coded. After logging-in the samples, the receiving clerk should refrigerate them immediately and retain the data forms received with the samples.

The receiving clerk should replace the old sample bucket or containers with clean, sealed, bagged ones, and should ship the new ones in shipping cartons to the field sites with other required materials. These can be sent by ground transport since each site should have a several-week supply on hand.

After all analyses have been completed and the results checked, the sample can be transferred into a 125 ml polyethylene bottle for storage in a refrigerator or freezer for 6 mo to 1 yr for other tests or analyses. Stability tests over several months indicate that storage at either 4°C (6,7) or 0°C (7) will preserve the sample.

7.3.2 Laboratory Documentation - The following documents should be reviewed regularly by the laboratory analyst and the supervisor to determine if the documents are up-to-date and are being followed.

1. Laboratory Standard Operating Procedure - instructions on laboratory and instrument operations.

2. The Laboratory Quality Assurance Plan - laboratory QA protocol, including personnel responsibilities and use of QC samples.

TABLE 7-1. SAMPLE INFORMATION TO BE CODED

Snow/ice
Mixed: snow/rain; hail/rain
Sample contaminated
Possible sample leakage in shipping
Sampler inoperative - no sample
Insufficient sample for complete measurement
Rain gauge inoperative
Noticeable suspended particulates
Lid cycling
Field pH and conductivity measured x days after scheduled sample removal or end of event
pH/conductivity/temperature meter inoperative
Sample partially frozen
Unusual condition in area
Collocated samples
Sequential samples

3. List of In-House Samples - dates for completion of analysis to allow the analyst to schedule further analyses.

4. Instrument Performance Study Information - information on baseline noise, calibration standard response, precision as a function of concentration, and detection limits used by analyst and supervisor to evaluate daily instrument performance.

5. Quality Control Charts - Once a month, update all control limits to include data from analyses of the previous month; generate plots of all QC samples and curve parameters.

6. Data Sheet Quality Control Report - generate a QC report after data for each analysis are placed in the computer (preferably within 1 day of analysis); present information for all QC parameters; flag all data which exceed the statistically established QC limits; have the supervisor review this report to decide what is to be done for out-of-control samples; and if necessary, reanalyze samples.

7. The Analyst's Spike Plot - daily when the analysis is set up, the first sample analyzed should be the analyst spike; percentage recovery for this sample should be calculated and plotted by the analyst in real time.

7.3.3 Traceability of Calibration Standards - For chemical traceability all calibration standards must be prepared from ACS reagent grade salts, and the accuracy of calibration standard preparations must be checked. With procedures proposed here, accuracy is checked by running an independently prepared analyst spike with each analysis and by checking each new set of stock standards against the old.

For gravimetric measurements, NBS traceability is provided by daily balance checks with weights traceable to NBS-certified weights, so each laboratory should maintain a set of NBS-traceable weights. The recommended procedure is to purchase weights traceable to NBS from a commercial supplier and to have them certified by an NBS-approved laboratory; it is unnecessary and expensive to have NBS calibrate a set of weights directly.

7.3.4 Preparation of Analyst's Spikes - When preparing calibration standards, the analyst should prepare an analyst's spike from a different stock solution. The concentration of the spike should be approximately at the midpoint of the calibration curve; however, if the majority of samples have concentrations below the midstandard, the spike should be prepared within that range.

7.3.5 Analytical Data Computations - The concentrations of the various constituents in each sample are based on calibration standards, which should be run at the beginning and end of the analysis and periodically during the analysis. Sample data are calculated from linear least squares fit parameters of the bracketing calibration standards. The linear least squares fit yields the following parameters: slope (m), intercept (b), error of fit (e) and correlation coefficient (r). The slope and intercept predict a relationship between concentration standards and instrument response:

$$y_{pi} = mx_i + b \quad (r \geq 0.9990) \qquad 7\text{-}1$$

where y_{pi} is the predicted instrument response, based on the calibration constants, and x_i is the concentration of standard i.

Equation 7-1 yields the preferred fit where major components of random variance are assumed to occur primarily in instrument response. If the range of concentrations observed is very large, it might not be possible to use a single equation. Concentration ranges should then be defined with separate linear least square fit.

Rearrangement of Equation 7-1 yields the sample concentration corresponding to an instrumental measurement (Equation 7-2):

$$x_j = (y_{aj} - b)/m \qquad 7\text{-}2$$

where x_j is the calculated concentration for a sample, y_{aj} is the actual instrument response for a sample, and m and b are the calculated slope and intercept from the latest calibration standards run.

The error term is calculated from the difference between the predicted instrument response, y_{pi}, and the actual instrument response, y_{ai}, for a given calibration standard (Equation 7-3):

$$e=\left\{\left[\sum_{i=1}^{n}(y_{ai}-mx_i-b)^2\right]/(n-2)\right\}^{\frac{1}{2}} \qquad 7\text{-}3$$

where n is the number of calibration standards.

This term, which indicates how much random scatter is in the calibration, has the same units as the y variable (instrument response) and thus should be directly compared between calibrations only when all setup parameters (scale factor, concentration range, etc.) are identical.

7.4 Quality Control Program

When analytical data are reported, it is essential to specify their quality. Statements about quality should refer to the particular data set being reported, not to laboratory analyses in general. To accomplish this, an internal QC program should be implemented. Internal QC includes calibration and real-time control by the analyst, preparation of special QC samples by the QC chemist, analysis of those samples by the analyst, review of the data by the laboratory supervisor and QA coordinator, scheduled data checking for transcription errors by data processing personnel, and a final review of all QC data by the QA coordinator before final reporting.

This section specifies QC samples to be analyzed, and discusses responsibilities for evaluation of the QC data. Control charts for both analyst review and managerial review are stressed. Procedures require real-time review of analytical performance by the analyst, and QC review of all data directly after input to the computer.

7.4.1 Real-Time Quality Control Procedures - These procedures are designed to spot problems during the analysis so that corrections can be made immediately. A brief description of the recommended procedures for each measurement is provided below:

(a) Real-Time Plotting of Analyst Spike Data -- After each instrument is calibrated, the analyst should immediately run an analyst spike to ensure that calibration standards were correctly prepared and that no degradation of the standards has occurred. After the analyst spike sample has been run, its value should be calculated by using the first calibration curve of the day. The percentage recovery should be calculated and plotted as indicated in Figure 7-1. (For pH and conductivity, the absolute magnitude, not the percentage recovery, should be plotted.) The horizontal average recovery and control limit lines (Figure 7-1) are those calculated in the most recent monthly QC report. If an out-of-limits data point is noted, an explanation should be sought. If eight successive values fall on one side of the average line, the indicated bias should be evaluated.

(b) Gravimetric Measurements -- The analytical balance should be calibrated frequently against Class-S weights, and the Balance Calibration Log should be completed. The balance should be zeroed before each use.

(c) pH Measurement -- The pH meter should be calibrated as indicated in the Operations and Maintenance Manual (5). The first sample analyzed after calibration should be the pH electrode reference solution. The analyst should plot and evaluate the pH value. Backup electrodes should always be in the laboratory to check the first electrode(s) if the reading differs from the previous analysis of the reference solution by more than ±0.03 units. Calibration drift should be evaluated after 20 samples are analyzed. If the drift is more than ±0.02 pH unit, the analysis should be stopped, and the meter and electrodes should be checked.

(d) Strong Acid and Acidity Measurements -- For strong acid determination, each day when sample measurements are begun, three conditioning solutions (if applicable) and an analyst spike should be measured and calculated using the linear least squares fit, as described in the procedure in the Operations and Maintenance Manual (5). If correlation coefficients from the calculation are less than 0.9990, the indicated problem should be eliminated. The value of V_e (the equivalent volume of base added) for each conditioning solution and the analyst spike percentage recovery should be plotted and obtained as indicated in the Operations and Maintenance Manual (5). At the end of the day, an analyst spike and a conditioning solution sample (if applicable) should be analyzed. The initial conditioning solution potential for each sample (if applicable) should be within 1.2 mv of the potential for the conditioning solution. According to the Operations and Maintenance Manual (5), an analyst spike should be analyzed before and after samples are determined and these values should be plotted daily.

(e) Conductivity Measurement -- Each day, the conductivity apparatus should be calibrated before and after samples are analyzed. The first sample should be an aliquot of a 0.0003M KCl (conductivity = 44.6 µmho/cm at 25° C) or the pH electrode reference solution. The analyst should calculate the conductivity and then plot and evaluate the conductivity of this reference sample.

(f) Automated Colorimetric Analysis -- This instrument should be set up, and the baseline noise and instrument response should be evaluated by comparison with data from the instrument performance study. Any problem noted should be investigated. The instrument should be calibrated as

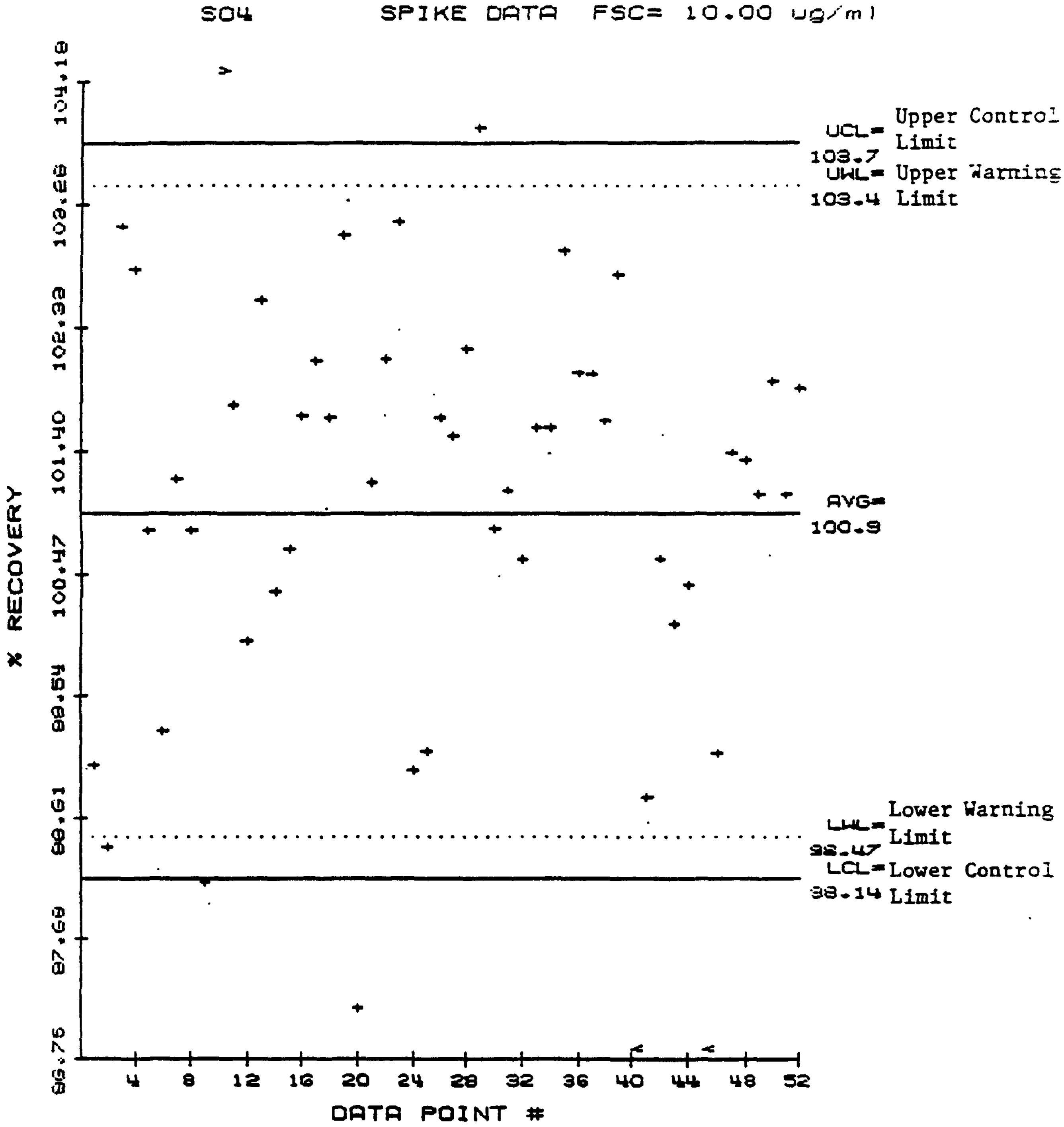

Figure 7-1. Analyst Spike Plot for $SO_4^=$ Analysis

described in the Operations and Maintenance Manual (5). For real-time QC, the first calibration curve should be checked for linear response and adequate detection limit by using a linear least squares fit of the first calibration curve and by determining a detection limit. Linearity should not be less than 0.9990; the detection limit should be within the statistically established control limits. The first sample analyzed should be the analyst spike. Concentrations of this sample should be calculated from the first calibration curve, and the value obtained should be plotted and evaluated. In addition, the calibration response during analysis should be checked to see that it is changing less than 5% from one calibration curve to the next. If a greater change is noted, the analysis should be stopped and an explanation sought.

(g) Ion Chromatographic Analysis -- Calibration procedures are in the Operations and Maintenance Manual (5). For real-time QC the baseline noise and the response of the first standard at setup time should be monitored. The first sample analyzed should be the analyst spike; it should be calculated from the first calibration curve, and the value should be plotted and evaluated. Linearity of the least square fit should be no less than 0.995 (to allow for IC non-linearity in calibration curve).

(h) Atomic Absorption Analysis -- Atomic absorption calibration procedures are in the Operations and Maintenance Manual (5). For real-time QC, the first calibration curve should be analyzed, and the linear least squares fit of response vs concentration should be calculated. The correlation coefficient should be 0.9995 or greater, and the detection limit should be within the statistically established limits. The first sample analyzed should be the analyst spike; it should be plotted in real time.

7.4.2 Analysis and Evaluation of Quality Control Samples - At least once each analysis day, a reagent blank, an old sample, a duplicate sample, an analyst spike, and a blind sample should be analyzed following the recommendations below:

(a) Reagent Blank -- This deionized water QC sample, which is subjected to the same preparation procedure as the routine samples, should be analyzed to check for random contamination which may have occurred in sample preparation or analysis.

(b) Old Sample -- This randomly chosen, previously analyzed QC sample (if no sample degradation has occurred) provides information on analytical precision for different days of analysis; it may provide information on sample stability, but this is not its primary purpose. Sample degradation can be corroborated by a repeat measurement at another time and the value in the QC data noted accordingly.

(c) Duplicate Sample -- This randomly chosen QC sample is a reanalysis of a sample analyzed during the same analytical run. If preparation is necessary before analysis, it is prepared twice. The result may be used to calculate analytical precision for the measurement method.

(d) Analyst Spike -- This QC sample prepared by the analyst from a stock solution independent of that used to prepare the calibration standards provides information on the accuracy of the calibration standard and the precision of analysis. The analyst spike should be analyzed at the beginning of the run; results should be calculated and plotted in real time.

(e) Blind Sample -- This QC sample is a standard of known authority (NBS, USGS, or EPA). It is inserted into the analytical run as a blind sample by the laboratory supervisor. The purpose of this QC sample is to assess data quality independently of analyst judgment.

7.4.3 Data Screening Tools - For most precipitation measurements, 100% QC of each sample cannot be attained. However, with QC procedures properly implemented for each analysis batch, adequate screening of continued, proper instrument functioning can be achieved. Recommended data checks for routine screening of measurement data include the following:

1. Calibrations -- provide statistics for evaluating the analytical method. Duplicate calibrations, performed before and after analysis of field samples, yield data on instrument reproducibility and drift. Statistics from routine calibration data include:

Slope (m) and Intercept (b) - of the least squares fit of the data for a technique and instrument range should be fairly constant. Visual inspection of values from successive days or comparison with values obtained during method validation can be used for quality control.

Correlation Coefficient (r) - is often used in a semi-quantitative way to evaluate goodness of fit of the relation of one variable with respect to another. Values near +1.0 and -1.0 are good and values near 0 are poor. The actual range of good fit values will depend on the particular measurement or test. For most instrumental techniques employed for analysis of precipitation samples, $r \geq 0.9990$ would be acceptable.

Residual Error (e) - is a measure of the scatter of data points off the regression line indicating "noise" in the calibration. Such scatter is related to the expected precision of the analysis. For analysis of precipitation samples, $e \leq 2\%$ of full scale of instrument response, for a given concentration range, is acceptable.

2. Spikes, Duplicates and Reagent Blanks -- are the primary tools for monitoring the integrity of the analysis. As a minimum, at least one QC spike, one duplicate and one reagent blank should be included with every sample batch. If calibrations are performed before and after each batch of samples for optimum control, a QC spike of known value should be run at the beginning, after calibration is completed. If a large batch of samples is run, analysis of the QC spike should be repeated after every twenty samples. The concentration values of the spikes, duplicates and reagent blanks should be entered into the computer before analysis, so that control limits can be checked as the analysis results are keyed into the computer. Detailed discussion on computation of control limits is given in Section 7.4.4 below.

3. Old Samples -- are reanalyzed to obtain information on sample stability, which varies from sample to sample. Analytes such as H^+, NH_4^+, PO_4^{-3}, and NO_3^- are susceptible to degradation, and if degradation is observed (i.e., lower analytical results are obtained for an ion), sample handling and preservation techniques should be examined. Old sample data may be used to calculate control limits using a mathematical approach similar to that discussed in 7.4.4 below.

7.4.4 Control Limits Determination - QC data are stored, tabulated and sometimes plotted as a function of time. The abscissa is the chronological order of analysis, and the ordinate may be either the range, absolute magnitude, value of the difference of replicates, or percentage recovery. The data are used for the determination of expected values and the associated control limits. These are plotted as the average-value line and the control limit lines when constructing control charts (2) such as the one given in Figure 7-1.

Computer calculation and data evaluation with or without plotting may be substituted for manually plotting the data. Because the purpose of establishing control limits is to flag potential problems as soon as possible, a computer can be easily programmed to recognize control criteria without having to plot the data manually. Even in those instances where a laboratory has such computer capabilities, a visual inspection of QC data is still a valuable tool, and any out of control situation should be examined without delay. Two types of limits are frequently used to identify such situations. These are:

1. Control Limits - corresponding to the 99% confidence interval for the mean value of the control parameter. Thus the upper control limit (UCL) and the lower control limit (LCL), given by the mean $\pm 3\ S_d$ (standard deviations), imply that for normal data distributions, less than 1% of valid data is flagged due to random error alone and that other flagged data may be assumed to indicate nonrandom error, i.e., malfunction or contamination which requires immediate action.
2. Warning Limits - corresponding to the 95% confidence interval for the mean value of the control parameter. Thus it includes about 95% of the expected random variation about the mean u for normal distributions, i.e., $u \pm 2S_d$. However, simple probability predicts that there is less than a 1% probability that two independently chosen values for the controlled parameter will exceed the upper warning limit (UWL) or the lower warning limit (LWL) due to chance alone. Thus two successive values which exceed the warning limits should be reason for investigation of analytical control. Also, probability predicts that there is less than a 1% chance of eight independent, consecutive values occurring on the same side of the mean value line. Thus, eight or more such values would indicate a systematic bias in the measurement.

For precipitation monitoring there are five key parameters that are useful for controlling the field and the laboratory measurement processes. Control and warning limits for each of those parameters should be determined as follows (Equation 7-4):

(a) Spike Recovery -- best determined by utilizing reference standards (such as NBS or EPA). The analyst spike data are used to calculate an average percent recovery (Equation 7-4):

$$\%\overline{R} = \frac{1}{N}\sum_{i=1}^{N} \frac{X_i}{C_i} \times 100 \qquad 7\text{-}4$$

where, $\%R$ is the average percent recovery, X_i is the found spike concentration, C_i is the known spike concentration, and N is the number of spikes used for constructing the control limits.

The standard deviation of the percent recoveries will be given by:

$$S_{\%\overline{R}} = \left\{ \frac{1}{N-1}\left[\sum_{i=1}^{N}\left(\frac{X_i}{C_i}\right)^2 - \frac{1}{N}\left(\sum_{i=1}^{N} \frac{X_i}{C_i}\right)^2\right]\right\}^{1/2} \qquad 7\text{-}5$$

and the appropriate warning and control limits are:

$$\begin{pmatrix}\text{UWL}\\ \text{LWL}\end{pmatrix}_{\%R} = \%\overline{R} \pm D_5\, S_{\%R} \qquad \begin{pmatrix}\text{UCL}\\ \text{LCL}\end{pmatrix}_{\%R} = \%\overline{R} \pm D_4\, S_{\%R} \qquad 7\text{-}6$$

Table 7-2 presents the numerical values of the various factors for computing control limits (i.e., control chart lines).

(b) <u>Range of Duplicates</u> - determined by utilizing the absolute differences of duplicate analyses of selected samples. These data are used to calculate an average range (r)

$$\overline{r} = \frac{1}{K}\sum_{i=1}^{K}|X_{i1} - X_{i2}| \qquad 7\text{-}7$$

where, X_{i1} and X_{i2} are the results of the duplicate analysis of the ith sample, and K is the number of duplicates used to construct the average. The corresponding warning and control limits for the range are:

$$\begin{pmatrix}\text{UWL}\\ \text{LWL}\end{pmatrix}_{r} = \begin{pmatrix}D_5\overline{r}\\ D_6\overline{r}\end{pmatrix} \qquad \begin{pmatrix}\text{UCL}\\ \text{LCL}\end{pmatrix}_{r} = \begin{pmatrix}D_4\overline{r}\\ D_3\overline{r}\end{pmatrix} \qquad 7\text{-}8$$

When utilizing Table 7-2 for duplicate analysis, N=2; N>2 only if a larger number of replicate analyses of the <u>same</u> sample are performed.

(c) <u>Detection Limits</u> -- determined by running either a series of ten non-consecutive reagent blanks (for AA analyses) or ten standards of the same

TABLE 7-2. FACTORS FOR COMPUTING CONTROL LIMITS[a]

Number of Observations, N	Factor D_3	Factor D_4	Factor D_5	Factor D_6
2	0	3.27	2.51	0
3	0	2.57	2.05	0
4	0	2.28	1.85	0.15
5	0	2.11	1.74	0.26
6	0	2.00	1.67	0.33
7	0.08	1.92	1.62	0.38
8	0.14	1.86	1.58	0.42
9	0.18	1.82	1.55	0.45
10	0.22	1.78	1.52	0.48
11	0.26	1.74	1.50	0.50
12	0.28	1.72	1.48	0.52
13	0.31	1.69	1.46	0.54
14	0.33	1.67	1.45	0.55
15	0.35	1.65	1.43	0.56
16	0.36	1.64	1.42	0.58
17	0.38	1.62	1.41	0.59
18	0.39	1.61	1.40	0.59
19	0.40	1.60	1.40	0.60
20	0.41	1.59	1.39	0.61
21	0.42	1.58	1.38	0.62
22	0.43	1.57	1.38	0.62
23	0.44	1.56	1.37	0.63
24	0.45	1.55	1.36	0.63
25	0.46	1.54	1.36	0.64

[a] Based on EPA-APTD-1132, "Quality Control Practices in Processing Air Pollution Samples," March 1973.

concentration, at 10% of working curve (for ion chromatographic and colorimetric analyses). For each series of runs, a standard deviation (S_d) is determined with the detection limit (DL) defined as $DL=3S_d$. When reagent blanks (B) are part of the analytical run, the control limit should be set such that $B \leq 2DL$ for each of the observables.

The notification that a sample is below the detection limit of the analytical method for a given analyte range should be available immediately after raw data entry. The analyst then has two options: to reanalyze the sample on an instrument scale of greater sensitivity; or to accept and flag data as being below the detection limit.

(d) <u>(Field - Laboratory) pH</u> -- determined by comparing the measurements performed in the field by the individual site operators to those performed at the central network laboratory upon sample receipt. The warning limits for this comparison are:

$$\begin{aligned} |pH_{field} - pH_{lab}| &\geq 0.2 \quad \text{Sample pH} \leq 5.00 \\ |pH_{field} - pH_{lab}| &\geq 0.3 \quad \text{Sample pH} > 5.00 \end{aligned} \tag{7-9}$$

If those limits are exceeded, the laboratory reanalyzes the sample and the field measurement is investigated (i.e. pH electrode, buffer solutions, etc.). The control limit for this difference has been set at 0.5 pH unit. If this is exceeded the sample should be reanalyzed and the data flagged as suspicious.

(e) <u>(Field - Laboratory) Conductivity</u> -- determined by comparing the conductivity (COND) measurements performed in the field by the individual site operators to those performed at the central network laboratory upon sample receipt. The control limits for this comparison are:

$$\begin{aligned} &COND_{field} - COND_{lab}| \geq 3\mu mho/cm && COND \leq 15\mu mho/cm \\ &\frac{COND_{field} - COND_{lab}|}{COND_{lab}} \times 100 \geq 20\% && COND > 15\mu mho/cm \end{aligned} \tag{7-10}$$

If those limits are exceeded, the laboratory reanalyzes the sample and the field measurement is investigated (i.e. conductivity cell, KCl standards, etc.). If the laboratory reconfirms its initial analysis, the field value is flagged as suspicious.

7.4.5 Evaluation of QC Data - Data for QC samples should be calculated and compared to control limits established in the most recent monthly QC chart. After input, a Data Sheet QC Report is printed by the computer. If no computer is available, this procedure can be done manually. The report on the performance of the QC samples should be given to the laboratory supervisor for evaluation to see if the data are acceptable for reporting or if reanalysis is necessary.

The analyst spike and the blind sample data are also calculated and the results given to the QC chemist, who tabulates the data and calculates the percent recoveries. The QC chemist routinely gives the blind sample data to the laboratory director, who reviews this before reporting the analytical data to the program manager. The QC chemist reviews the blind sample data with the analyst monthly.

Once a month, the QC chemist should combine all QC sample data and calibration curve parameters obtained during the month with all previous data for the same parameters and plot the data to yield new control limits are calculated. A copy of the monthly QC plot should be given to the laboratory supervisor, the QC chemist, and each analyst.

A Data Quality Control Report should be given to the laboratory supervisor on a regular basis. This report should flag any out-of-limits conditions for the analysis. The analyst or the supervisor should check to see that any out-of-limits conditions are not results of manual transcription errors. If a transcription error is found, the transcription of all data on the data form should be checked, a corrected data form should be input and a new QC report issued. The problem should be carefully documented and the old data form and QC report should be filed with the corrected forms. The new QC data should replace the old in the computer QC data base (if applicable). If the out-of-limits conditions are not due to transcription errors, another explanation should be sought.

The most critical parameters are the calibration curve parameters, because any problem with them directly affects the data. If an explanation cannot be found for out-of-limits calibration parameters, all samples analyzed in the time interval between the questionable calibration curves should be reanalyzed.

If only one of several QC samples is out-of-limits, an explanation should be sought. However, if one cannot be found, no action is needed. The supervisor may assume that the problem was with the particular QC sample itself, but he may retain the out-of-limits data in the QC data base. If several QC samples are out-of-limits and an explanation is not found, all samples analyzed with the QC samples should be reanalyzed.

In any case, an out-of-limits QC sample requires evaluation and an explanation by the supervisor. The explanation may be noted on the QC report. If samples are to be reanalyzed, the supervisor should note this on the data form and in the QC report. At the time of the reanalysis, it should be noted on the data form that the samples are being reanalyzed, and the date of the first and the repeat analyses should be given.

The supervisor also evaluates the QC plots when they are periodically generated. Since the supervisor has already evaluated out-of-limits conditions in the QC reports, all out-of-limits conditions should have been explained or eliminated (by reanalysis) before the monthly plots are generated. Accordingly, the monthly plots should be examined primarily for systematic bias. If no systematic bias is present, all plotted values should be evenly distributed about the average-value line.

7.5 Evaluation of Laboratory Performance

The QC procedures (Section 7.3) stress the supervisor's role in evaluating QC data and in scheduling reanalyses until data are acceptable for reporting. This section discusses the QC chemist's role in evaluating laboratory performance by independent QC checks and by external audits.

7.5.1 Independent Internal Quality Control - The QC chemist ensures that QC procedures are implemented and provides independent judgment on the accuracy and precision of the data generated in the laboratory. These are checked by analyst spikes and synthetic rainwater samples which have been inconspicuously added to the sample analysis stream. Blind samples can be prepared by the QC chemist from NBS-SRMs, from reagent grade salts or from reference samples obtained from EPA, USGS, or other reliable sources and routinely submitted to the laboratory as blind samples to be analyzed in the same manner as a routine sample. The data should be flagged in the data set by the QC chemist when checking for out-of-limits conditions before the reports are reviewed by the laboratory director.

7.5.2 Laboratory Audits - Laboratories analyzing rainwater samples should regularly conduct both systems and performance audits of their operations. A complete description of the schedule, scope and methods for conducting both types of audits is included in Section 10.0 of this document.

7.6 References

1. Reagent Chemicals, American Chemical Society Specifications, 5th Edition, American Chemical Society, Washington, D.C. (1974).

2. "Standard Methods for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis", from Part 31 of 1976 Book of ASTM Standards, American Society for Testing and Materials, Philadelphia (1977).

3. Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Association, New York (1971).

4. M. Reichgott, "Organic Coatings and Plastic Chemistry," Vol. 41, 1979, Paper presented at 178th National Meeting of the American Chemical Society, Washington, D.C. Sept. 9-14, 1979.

5. Quality Assurance Handbook for Air Pollution Measurement Systems - Vol. V - Manual for Precipitation Measurement Systems. Part II - Operations and Maintenance Manual. U.S. Environmental Protection Agency, Research Triangle Park, N.C., EPA-600/4-82-042b (January 1981).

6. M.E. Peden, and L.M. Skowran, "Ionic Stability of Precipitation Samples," Atmos. Environ. 12, 2343 (1978).

7. J.E. Rothert, Battelle Pacific Northwest Laboratories, Richland, Washington, MAP3S Program, private communication.

8.0 DATA HANDLING, VALIDATION, AND REPORTING

All data collected by a monitoring program from both field and laboratory activities must accurately represent the concentrations of measured constituents, i.e., the data must be valid. Validity depends on control of error and bias, and such validity is assured only by careful screening during all phases of data handling from field and analytical results to final reporting. Thus, the field operator, laboratory analyst, data entry staff, laboratory director, program manager and QA officer all contribute to data validity by screening data generated or processed by their respective areas.

8.1 Data Logistics

Ideally, data should go directly from an instrument to a machine-readable raw data base to avoid transcription errors. Not all laboratories have computer facilities, so manual data-recording techniques are discussed, but all calculations and data-processing steps in this section can be performed by either manual or automated processing.

If output from the analytical instrument is not recorded automatically, a data form must be prepared. Each analyst should keep a bound notebook to record all analytical data, and the notebook should have carbons so copies can be pulled for data reduction. Typical data forms for each analytical procedure are in the Operations and Maintenance Manual (1).

Whenever data forms are prepared from strip charts, transcriptions should be checked by recalculating 5% of all values. If errors are found, all data should be reprocessed. Manual data-recording practices for several typical techniques used in precipitation analysis are described briefly below:

(a) pH and Conductivity -- The pH and conductivity measurements read directly from meters are recorded on a prepared data form. The baseline reading category is ignored.

(b) Ion Chromatography for Chloride, Phosphate, Nitrate and Sulfate -- Peak heights on strip charts are a measure of response. Baselines should be carefully drawn and each peak height read from the baseline with a clear plastic ruler. Each peak height is recorded on the strip chart and also on the data form. Because this is a chromatographic technique, care must be exercised in drawing the baseline, particularly where the peak of one anion is resting on the tail of another due to extreme differences in concentration. In all cases, the method used when drawing the baselines should be identical for both standards and samples.

(c) Automated Colorimetry for Ammonium and Phosphate -- The data on the strip charts should be read at the midpoint of the flat-topped peaks and a straight line drawn between baseline points on the chart. Each peak height should be read from the baseline using a clear plastic ruler, and the data on both the strip chart and the data form recorded.

(d) Atomic Absorption for Sodium, Potassium, Calcium, and Magnesium -- The data should be processed the same as for automated colorimetry.

(e) Strong Acid by Gran Method -- In the microtitration, the electrical potential (mv) or pH is recorded as a function of the volume of base added to the sample. As a QC procedure, the initial potential reading of the conditioning solution (if applicable) before addition of sample is recorded on the data form. The final temperature of the sample before titration should also be recorded.

(f) Acidity -- The sample is titrated potentiometrically with a basic solution to an end point of pH 8.3. The normality (N) of the base and the volume (ml) required are recorded on the data form. As a QC measure, it is suggested that the base be standardized at least monthly in an acceptable manner (such as NaOH standardized with potassium biphthalate).

(g) Volume -- In determining the amount of precipitation sample, a density of 1.0 gm/ml is assumed; thus the ratio of mass (g) to volume (ml) is 1.0. The mass is recorded directly on the data form.

8.2 Software Requirements

Data handling from raw data input through finished report should be computerized as much as possible to facilitate data management. All software used by an organization to process data should be well documented. Current source code listings should be available to responsible personnel and such code should include sufficient comment statements to explain and describe both algorithms and data transfer steps. As a further QC measure, it is recommended that, during execution, the software version identifiers be printed on each generated report. Typically these include date and time of generation and the name of the program used to make the calculations. Such identifiers will increase the efficiency of tracking when data problems occur. The software employed should have the characteristics and capabilities described below.

8.2.1 <u>Data Input</u> - Data can be input manually or automatically. For manual data entry, the data clerk should screen all of the terminal input by comparison of the computer printout with the original data forms or by duplicate entry of the same data batch. For automated entry, errors can be detected by monitoring the data display while the data are being taken and by occasional spotchecks of the data acquisition apparatus. Such checks might include the introduction of a dummy data set or the introduction of a known voltage to the instrument from which data are being taken.

8.2.2 <u>Data Storage and Indexing</u> - At a minimum, acid precipitation data bases should be stored on a computer readable medium (disk, tape or cassette) which can be efficiently accessed. A duplicate backup file, stored in a different location, should be maintained so that lost data files can be retrieved or reconstructed. Special file attributes, such as random access, keys, and indexing, can be useful for efficient data management. Acid precipitation data bases may be handled efficiently by any one of a number of commercially available data base management systems. Such systems decrease the necessity of writing vast amounts of software and are available for any size computer installation from a small microcomputer to mainframe. Most include sufficient provisions for the development of audit trails.

8.2.3 <u>Precipitation Data Bases</u> - Acid precipitation measurement data from the following networks: NADP, CANSAP, APIOS, MAP3S, EPRI SURE, and EPRI UAPSP network are currently stored at Pacific Northwest Laboratory (PNL) in Richland, WA. The use of this data base can be helpful when developing QA procedures for an acid rain network's software.

Data are also available in hard copy format. Data are obtained from the various networks in one-year increments, but input data are reorganized by region and not maintained by network. Reports may be obtained detailing network inventories of precipitation-weighted concentrations by site, area, analyte and the time period. Although not yet available at the time of this writing, PNL is developing a spatial distribution map for precipitation data and is working to standardize isopleth derivation from sparse amounts of network data. Both of these will be available soon. The PNL data base currently serves as a repository for all data collected from the National Atmospheric Deposition Program (NADP)/National Trends Network (NTN). The PNL data bank is not currently available by dial up (interactive mode). However, interested contributor/user organizations may contact the individual noted below for assistance in obtaining the proper data summaries. One extremely useful feature of this data base is that PNL will prepare data sets for organizations in a custom-tailored magnetic tape format. (Contact: A.R. Olsen (Statistical or Data Inquiries) or C. Watson (Data base use and tape formats), Pacific Northwest Laboratory, Richland, WA, 509/376-2227.)

8.3 Data Handling and Preliminary Screening

In an acid precipitation monitoring network, data handled both in the field and in the laboratory must be critically reviewed to identify and isolate errors. Data should be validated at each step of the measurement process, beginning with sample validation in the field and followed by a preliminary physical screening process when the sample is received at the laboratory. Once data have been entered into the storage-retrieval system, more critical screening procedures should be implemented.

In establishing statistical screening procedures, it is necessary to recognize characteristics of the chemical analyses. For the most part, analyses are done in a batch mode. A batch may contain several dozen samples with multipoint calibrations performed before and after the samples. In an efficiently run laboratory, most analyses are automatically sequenced with data recorded by direct computer interface or continuously recorded onto strip charts.

8.3.1 Quality Control of Data Handling - Table 8-1 summarizes the data handling steps and the corresponding QC procedures to be utilized at each step. A range check is sometimes effective as an additional screen against keypunch errors. The data handling steps outlined are self explanatory and are designed for computerized data reduction systems for analytical results. If completely automatic data acquisition systems are utilized, the first two data handling steps should be modified to verify the integrity of the digitization of the analog signal output from the analytical instrumentation and the computer interface.

TABLE 8-1. SUGGESTED QC SPOTCHECK OF DATA HANDLING

Data Handling Step	QC Procedure
Manual reading of strip chart	Duplicate reading of 5% of the data
Transfer of analytical raw data and results to data sheet	Spotcheck transfer accuracy for 5% of data
Input of data (field or analytical form) into computer	Enter both data sheets from above into separate files, followed by computer comparison of 100% of data
Electronic digitization of strip chart	Check 5 to 8% for proper baseline determination and for accurately and properly recorded retention times
Field report record of event time and amount.	Check 100% vs rain gauge strip chart.

8.3.2 <u>Treatment of Outliers</u> - This section will discuss treating data which fall outside of certain control limits. In doing this, it is important to understand the difference between outliers and erroneous data and how each should be handled. Outliers have two origins: random errors and operational errors. Random errors can occur in the physical condition being measured and in the measurement system itself. Operational errors originate in numerous technical problems such as sample handling, difficulty in accurately weighing chemicals for standard solutions, and shift of a decimal point in manual transcription of numbers. Operational errors contribute systematic errors or the bias component of the measurement data.

There are basically three ways of dealing with outliers:

(a) Reject them as invalid;

(b) Subject them to special scrutiny, and reject or adjust them only if documentary evidence of errors is found; and

(c) Do nothing.

If outliers are rejected, a great deal of care should be exercised. It is not recommended to directly reject the highest X% of the data points, since this would artificially bias the averages low, and quite possibly would weaken the ability to detect correlations in the data by throwing out valid but high-valued data. This danger of rejecting valid data is the motivation behind statistical methods for detecting "true" outliers.

It is advisable to check outlying data points for data handling errors. Since no data should be rejected without documentary evidence of handling errors, there is no serious consequence if some good data are checked. However, outlier-specific spot-checking should not be used to completely replace all random-selection spot-checking. Outlier-specific spot checking alone could fail to detect a procedural or computer software error. Fully randomized spot-checking is discussed further in 8.6. Outlier-specific screening methods can be based on examination of the most extreme values of a variety of computed parameters, such as calibration slopes, collocation differences, total anion - cation balance, etc., as discussed in Section 7.

The most commonly used outlier-detection statistics assume that the normal fluctuations (in both the measurement error and the physical condition being measured) are well-approximated by a Gaussian distribution (3). It is also assumed that there is at most one outlier due to systematic bias. The mean and standard deviation are calculated from the data, and the chance that the most outlying value from that Gaussian distribution would be as large as the most outlying value observed is determined. If this chance is less than a selected statistical significance level, then the outlier is declared to be caused by an operational error. Details on applying this statistical procedure are given elsewhere (3).

These methods suffer from the problem of "masking". If the sample of data points has two outliers that are far from the majority of data points, then the computed standard deviation is increased, and no outliers are detected. There is another method called backward elimination, which eliminates the masking problem. However, it still has the assumption that the normal fluctuation fits a Gaussian distribution. In most cases a log-normal or other transformation of the parent data distribution has proven adequate. The chance of experiencing any particular extreme value is under-predicted by all Gaussian-based methods. Therefore, rejection of data points on the basis of those statistical outlier detection methods should be undertaken with great care and only after examining in detail the distributional characteristics of the entire measurement data.

8.4 Data Validation Criteria

Data validation based on a set of criteria is the process of evaluating the data after its preliminary screening, and either accepting or rejecting them. Validation in this sense also includes the investigation of anomalies. Procedures in this section are used after the preliminary screening of the analytical runs has been completed. They are designed to flag questionable data for subsequent investigation based on some key physical properties of precipitation samples.

8.4.1 Detection Limit Flag - If a sample concentration is below detection limits, a flag should be entered into the data base indicating that the result is below the detection limit. With a fully automated system, this flagging could serve as an additional QC procedure because the analyst cannot mistakenly enter data which are below the detection limit if the computer program is written to question and flag all such entries. Statistical handling and reporting of below-detection-limit data are discussed below in Section 8.5.3.

8.4.2 Comparison of Sampler and Rain Gauge Performance - At stations equipped with duplicate samplers or with a sampler and a rain gauge, sampler performance can be evaluated by comparing the quantity of precipitation measured by the two instruments. In most stations a sampler and a rain gauge are present. The rain gauge is used as the reference to measure both the sampler capture ratio and its collection efficiency. The percent capture (%CAP), which indicates sampler down time, is given by

$$\%\text{CAP} = (\text{No. of samples collected}/\text{Total No. of events}) \times 100 \qquad 8\text{-}1$$

The total number of events are counted from the rain gauge charts, and the failure of the sampler to capture an event is detected either by direct observation of the sample bucket or by counting the event pen markings for a given collection period. In the 1982 Utility Acid Precipitation Study Program (UAPSP), a percent capture of 98% was found (5) for over 2200 events at 20 sites.

The sampler collection efficiency (COL.EFF.) is given by the ratio of the sample amounts collected by the sampler and the rain gauge:

$$\text{COL.EFF.} = \text{Sample Depth (cm)}/\text{Rain Gauge Reading (cm)} \qquad 8\text{-}2$$

The Aerochem Metrics bucket sample weight can be converted to cm(in) by the relation, 1 cm = 640 g (1 in = 1625 g). When a sample is not collected due to either sampler or rain gauge down time, the event is not included in the efficiency average. An overall sampler efficiency of 1.04 was found for UAPSP (5) and indicates that the samplers, on the average, collected 4% more precipitation than the rain gauges. For rain events greater than 0.25 cm (0.1 in), amounts which differ by more than 15% between the collector and rain gauge should be flagged for investigation of faulty collector function. Light rainfalls generally yield high rain gauge capture vs. the sampler, and heavy rainfalls (and wind) yield high sampler capture vs. tipping bucket gauges. For snow with no windshield present, differences of 30% or more between the sampler and the rain gauge are frequent. It is recommended that the sample be rejected if

$$\text{Ratio} = \frac{\text{Rain Gauge Reading (cm)} - \text{Sample Depth (cm)}}{\text{Rain Gauge Reading (cm)}} > 0.5 \qquad 8\text{-}3$$

The Ratio in Equation 8-3 applies directly to both rain and snow when the rain gauge is of the weighing type; if another rain gauge is used the snow should be melted before rain gauge reading is utilized. If the sampler volume is greater than the rain gauge volume, the reason for the difference in sample amount captured by the rain gauge and sampler should be adequately resolved before a decision is made as to which quantity will be used in reporting precipitation amounts.

As an additional check on data validity, the stripchart record of the precipitation gauges should be compared with the field data form. If discrepancies in time of event or precipitation amount are noted, they must be resolved before the data are reported.

8.4.3 Unusual Ion Ratios - Another check on data validity is to inspect the ratios of ions in individual samples. Table 8-2 shows average and typical ion weight ratios for different geographical locations. Average values for sea water (6) should apply to those areas within 50 km of a sea coast, but those for the earth's crust (7) cannot be assumed to represent any specific region. The range data (last column) are based on a 1968 national study (8).

The seawater ratio of $SO_4^{=}/Na^{+}$ in the table is sometimes used in coastal areas to correct measured $SO_4^{=}$ values for seawater contribution.

$$(SO_4^{=})_{corrected} = (SO_4^{=})_{measured} - 0.25\ (Na^{+})_{measured} \qquad 8\text{-}4$$

However, the ratio of sulfate to sodium in spray has been shown to exceed that in seawater by 10% to 30% (9). The $SO_4^{=}/Na^{+}$ ratio is preferred to $SO_4^{=}/Cl^{-}$ because there are non-sea sources of Cl^{-} and because loss of atmospheric Cl^{-} occurs by oxidation.

TABLE 8-2. ION RATIOS FOR VARIOUS SOURCES

Geochemical Ratio	Primary Source	Average Value(6,7) (µg/g)	Precipitation Area	Acceptable Range(8) (µg/g)
Cl^{-}/Na^{+} [a]	seawater	1.8	industrial area	1.8 - 3.5
			seacoast	1.5 - 1.8
	earth's crust	0.01	arid region (soil particles)	0.8 - 1.0
Na^{+}/K^{+} [a]	seawater	27.8	seacoast	6 - 13
	earth's crust	1.1	inland	1.2 - 4
Mg^{++}/Ca^{++} [a]	seawater	3.2	seacoast	0.1 - 1.0
	earth's crust	0.6	inland	0.03 - 0.3
$SO_4^{=}/Na^{+}$ [b]	seawater	0.25	seacoast	0.25

a. Do not test if either number is at detection limit.
b. To correct $SO_4^{=}$ for seawater $SO_4^{=}$ contribution.

8.4.4 Comparison of Anion and Cation Equivalents - The principle of electroneutrality requires that total anion equivalents equal total cation equivalents. The Anion Equivalents (AE) are

$$AE = \sum_{i=1}^{N_A} \frac{C_{Ai}}{(Eq.Wt.)_i} \qquad 8\text{-}5$$

where C_{Ai} denotes the concentration of the ith anion in mg/liter, $(Eq.Wt.)_i$ is the equivalent weight for the corresponding species as given in Table 8-3, and N_A is the number of anions used to compute the Anion Equivalents.

The cation equivalents (CE) are:

$$CE = 10^{(3-pH)} + \sum_{i=1}^{N_c} \frac{C_{ci}}{(Eq.Wt.)_i} \qquad 8\text{-}6$$

where C_{Ci} is the concentration of the ith cation in mg/liter, $(Eq.Wt.)_i$ is the same as in Equation 8-5, and N_c is the number of cations, excluding H^+, used in computing the Cation Equivalents.

Using Equations 8-5 and 8-6 above, we obtain the % difference for the discrepancy between the cations and anions.

$$\text{Ion \% Difference} = \left[\frac{CE - AE}{0.5(CE+AE)}\right] \times 100 \qquad 8\text{-}7$$

For the EPRI Utility Acid Precipitation Study Program (5) the observed Ion % Difference (Equation 8-7) had a median of 4.6% for 3061 samples (HCO_3^- was accounted for). The greatest spread in data occurred at low concentrations. If the % discrepancy significantly exceeds 0, it suggests that errors exist in the data and/or that important constituents, such as bicarbonate HCO_3^- or organic anions, have not been analyzed. For solutions in equilibrium with atmospheric CO_2 at 25°C, the bicarbonate concentration is given by (7):

$$(HCO_3^-) = K(H_2CO_3)/(H^+) = 4.45 \times 10^{-7}\ (11.56 \times 10^{-6})/(H^+) \qquad 8\text{-}8$$

TABLE 8-3. CONVERSION FACTORS and EQUIVALENT WEIGHTS

Analyte	Equivalent Weight	Factor[a]
Cl^-	35.46	28.2
NO_3^-	62.01	16.1
$SO_4^=$	48.03	20.8
PO_4^{-3} as $H_2PO_4^-$	96.98	10.3
HCO_3^-	61.0	16.4
H^+	1.01	990.1
NH_4^+	18.04	55.4
Na^+	22.99	43.5
K^+	39.10	25.6
Mg^{++}	12.15	82.3
Ca^{++}	20.04	49.9

a. (μeq./liter) = (mg/liter) x Factor

Expressing the concentration of HCO_3^- and H^+ in µeq./liter, we find $(HCO_3^-) = 5.1/(H^+)$. Thus, bicarbonate is negligible for solutions more acidic than a pH of about 5.0, i.e. for $H^+ = 10$ µequiv./liter, $HCO_3^- = 0.031$ mg/liter. It can also be shown that carbonate $(CO_3^=)$ can be expressed as follows: $(CO_3^=) = K_1 K_2 (H_2CO_3)/(H^+)^2$. If we substitute the (H_2CO_3) concentration from the solubility of CO_2 at 25°c, and K_1 and K_2 respectively for the two dissociation constants of carbonic acid we would obtain $(CO_3^=) = 2.9 \times 10^{-22}/(H^+)^2$ moles/liter. This shows that $CO_3^=$ is negligible for solutions more acidic than a pH of about 7.7 ($H^+ = 0.02$ µeq./liter).

The anion-cation balance criteria used for reanalysis by the National Atmospheric Deposition Program are presented in Table 8-4. This information may prove to be a useful starting point for those organizations wishing to use this information in screening and validating data.

TABLE 8-4. NADP REANALYSIS CRITERIA[a]

1. Ion Balance		
Anions + Cations (µeq/liter)	Ion % Difference	Frequency of Check
<50	>±60	All samples at monthly intervals
≥50 < 100	>±30	
>100	>±15	
2. Specific Conductance Balance		
Measured Conductance (µmho/cm)	Conductance % Difference	Frequency of Check
<5	> 50	All samples at monthly intervals
>5 < 30	> 30	
≥30	> 20	

a. From Illinois State Water Survey for National Atmospheric Deposition Program

8.4.5 Comparison of Measured and Calculated Conductances - For dilute solutions (below 10^{-3}M) of known composition, the equivalent conductance is the sum of the equivalent ionic conductances at infinite dilution (Table 8-5). From the relation between equivalent and specific conductance

$$\Lambda = 1000\kappa/N \qquad 8\text{-}9$$

the conductance in mho/cm can be calculated as follows:

$$\kappa = N_i \sum_{i=1}^{N_T} \lambda_i/1000 \qquad 8\text{-}10$$

where $N_i = z_i M_i$ with M_i = g. moles of ion i/liter, z_i = valence or charge of ion i, and N_T is the total number of species used in the computation. For the major ionic constituents in precipitation this will become:

$$\kappa = [10^{-pH}(350) + 2(SO_4^=)(79.0) \pm (NO_3^-)(70.6) + (Cl^-)(75.5) +$$

$$(NH_4^+)(74.5) + (Na^+)(50.9) + (K^+)(74.5) + 2(Ca^{+2})(60)] \times 10^{-3}$$

where the parentheses denote the ionic concentrations in moles/liter. With Equation 8-10 and Table 8-5, the calculated specific conductance of a solution containing

H^+ = 7×10^{-5} mol/liter, NH_4^+ = 4×10^{-5} mol/liter,
$SO_4^=$ = 4×10^{-5} mol/liter, and NO_3^- = 3×10^{-5} mol/liter.

is

$$\begin{aligned}1000\kappa &= 7\times10^{-5}(350)+4\times10^{-5}(74.5)+2(4\times10^{-5})(79.0)+3\times10^{-5}(70.6)\\ &= 3592\times10^{-5}\ \text{mho/cm}\end{aligned}$$

or

$$\kappa = 35.9\ \mu\text{mho/cm}.$$

The calculated specific conductance (COND) values can be compared with the measured values for precipitation samples, which are generally 10^{-4}M or less, by the relation

$$\text{Conductance \% Difference} = \left[\frac{\text{COND}_{\text{calc'd}} - \text{COND}_{\text{meas}}}{\text{COND}_{\text{meas}}}\right] \times 100 \qquad \text{8-11}$$

For the EPRI-UAPSP study (5), the median value of the Conductance % Difference was -0.8% and, as expected, the greatest spread occurred at low conductivities. The H^+ ion is the chief contributor to the specific conductance of a solution, and any significant error in the H^+ concentration will generally be evident in a comparison of the specific conductances and the anion/cation equivalents. The conductivity criteria used by the National Atmospheric Deposition Program for reanalysis of samples are given in Table 8-4.

TABLE 8-5. EQUIVALENT CONDUCTANCE AT INFINITE DILUTION, 25°C (7)

Ion	λ_i(mho/cm)	Ion	λ_i(mho/cm)
H^+	350.0	1/2 Ca^{+2a}	60.0
NH_4^+	74.5	1/2 $SO_4^{=a}$	79.0
Na^+	50.9	NO_3^-	70.6
K^+	74.5	Cl^-	75.5
1/2Mg^{+2a}	53.1	HCO_3^-	41.5

a. 1/2 = value for 1 gram equivalent

8.5 Data Reporting

Directly measured observables typically reported by an organization are pH, specific conductance, concentrations of major constituents and the amount of precipitation. Recommended reporting units are

pH - unitless;

conductivity - µS/cm or µmho/cm;

concentration of ion - mg/liter or µeq./liter; and

precipitation - cm (1 in = 2.54 cm).

Table 8-3 provides the relation and the transformation factors for converting mg/liter to µeq./liter for the ions of interest. Specifics on the computational procedures and/or flagging practices used in precipitation data reporting are provided below.

8.5.1 Average Concentrations and Deposition - Precipitation-weighted mean concentrations, $\bar{C}_i$ for various ions are generally reported for a given time interval (month, quarter, or year).

$$\bar{C}_i = \sum_{j=1}^{N_E} P_j C_{ij} / \sum_{j=1}^{N_E} P_j \qquad 8\text{-}12$$

where P_j is the amount of precipitation in event j (cm), C_{ij} is the concentration of constituent i for event j (mg/liter), and N_E is the number of events.

For pH or H^+ concentration, the cumulative value is calculated, and the precipitation weighted pH value is obtained by converting the cumulative H^+ back to pH.

$$\overline{pH} = -\log \left[\frac{\sum_{j=1}^{N_E} \left(P_j \; 10^{-pH_j} \right)}{\sum_{i=1}^{N_E} P_j} \right] \qquad 8\text{-}13$$

The average concentration at each site can be used to study the distribution of the constituents as a function of time (month or season) and/or geographic location. It might also be useful to report the site-specific, precipitation-weighted standard deviation of the means (S_{pi}) as an indicator of constituent variability for different seasons and geographical locations. A proposed equation for S_{pi} (10,11) is

$$S_{pi} = \left[\frac{1}{N_E} \left(\sum_{j=1}^{N_E} P_j \, (C_{ij} - \bar{C}_i)^2 \Big/ \sum_{j=1}^{N_E} P_j \right) \right]^{1/2} \qquad \text{8-14}$$

Total deposition of the ith analyte D_i per unit area (mg/m^2) in a precipitation event or time interval is calculated as:

$$D_i = 10 \sum_{j=1}^{N_E} P_j \, C_{ij} \qquad \text{8-15}$$

where P_j is the precipitation amount of event j in cm, C_{ij} is the concentration of the ith analyte in mg/liter, N_E is the total number of events, and the conversion factor is 10^4 cm^2/m^2.

8.5.2 Median Concentrations - Average values are also reported in terms of the median (50th percentile value). The medians and their respective confidence intervals are estimated from the ordered observations obtained from the independent precipitation samples. The advantages of medians over means is that extreme values (outliers) have much less effect on medians than on means, and it is possible to readily compute confidence intervals for medians. In computing confidence intervals for the medians, let

$$X^{(1)} \leq X^{(2)} \leq \ldots \leq X^{(r)} \leq \ldots \leq X^{(s)} \leq \ldots \leq X^{(n)}$$

represent the ordered set of observations. The number of observations in a given set is n and $1 \leq r < s \leq n$, where r and s represent the lower and upper bound elements, respectively, of the confidence interval of the median.

(a) For $n \leq 20$, Table 8-6 may be used to find r and s. The table was constructed such that the confidence level is at least 0.90. The exact confidence level, P, can be computed from the appropriate α given in the table i.e., $P = 1-\alpha$, where α denotes the significance level.

(b) For $n > 20$, the approximations below may be used to obtain the confidence intervals at the 0.95 confidence interval.

$$r^* = 1/2\ (n - 1.96\sqrt{n}) \qquad \text{8-16a}$$

$$s^* = 1/2\ (n + 1.96\sqrt{n}) \qquad \text{8-16b}$$

In general r^* and s^* will not be integers. Let r and s be the integers obtained by rounding r^* and s^* upward to the next higher integer.

For example, for a set of 30 precipitation samples we obtain 29 pH, 22 $SO_4^=$, and 19 NH_4^+ values. In order to compute the appropriate medians and confidence intervals for each of the three observable parameters, the following procedure is followed:

(a) Order the observed values for each of the three observables starting with the lowest and going to the highest.

(b) For pH: the median will be the value of the 15th element. The lower and upper bounds of the confidence interval ($P = 0.95$), obtained from equations 8-16a and 8-16b, are the values of the 10th ($r^* = 9.22$) and 20th ($s^* = 19.77$) elements, respectively.

(c) For $SO_4^=$: the median will be the average of the 11th and 12th elements. The lower and upper bounds of the confidence interval ($P = 0.95$), obtained from equation 8-16a and 8-16b, are the values of the 7th ($r^* = 6.4$) and 16th ($s^* = 15.59$) elements, respectively.

(d) For NH_4^+: the median will be the value of the 10th element. The lower and upper bounds of the confidence interval ($P = 0.94$), obtained from Table 8-6, are the values of the 6th and 14th elements, respectively.

TABLE 8-6. CONFIDENCE BOUNDS FOR MEDIANS OF SMALL SAMPLES $(n \leq 20)$[a]

Sample Size (n)	Confidence Interval Bounds (element number) Lower (r)	Upper (s)	α[b]
5	1	5	0.062
6	1	6	0.031
7	1	7	0.016
8	2	7	0.070
9	2	8	0.039
10	2	9	0.021
11	3	9	0.065
12	3	10	0.039
12	4	10	0.092
14	4	11	0.057
15	4	12	0.035
16	5	12	0.077
17	5	13	0.049
18	5	14	0.031
19	6	14	0.064
20	6	15	0.041

a. Based on Table A3 in W. J. Conover, Practical Nonparametric Statistics, 2nd Edition, John Wiley & Sons, New York (1980).

b. Significance Level

8.5.3 Reporting and Treating Below-Detection-Limit Data - Data below the detection limit (BDL) or the minimal detectable limit for the analytical method used should be flagged with a code both in the printouts and in all computer readable data forms. Table 8-7 provides as an example the minimum detection limit criteria used in the NADP program for Laboratory measurements.

TABLE 8-7. NADP MINIMUM DETECTION LIMIT CRITERIA FOR LABORATORY MEASUREMENTS

Chemical	Measurement Technique	Detection limit (mg/liter)
Na	Flame AA	0.01
K	Flame AA	0.01
Ca	Flame AA	0.03
Mg	Flame AA	0.004
NH_4	Colorimetry	0.025
SO_4	Ion Chromatography	0.1
NO_3	Ion Chromatography	0.02
PO_4	Ion Chromatography	0.02
Cl	Ion Chromatography	0.02

8.5.4 Reporting Out-of-Control Data - Analytical data obtained from a sample batch in which an out-of-control QC sample is found should be flagged in the data base as suspect and should not be used unless the laboratory supervisor determines that the cause of the out-of-control condition did not affect the analytical results. Data reported as invalid should not be used in summaries, statistics, analyses, or other interpretation. For data stored or reported on computer readable media, it is often best to use a character or code to indicate out-of-control, missing, BDL, and other such data.

8.6 QC Checks on Final Data

As part of the ongoing QC program, data intended for use in such summaries should be checked for the parameters indicated below and any discrepancies brought immediately to the attention of the person with overall program responsibilities.

8.6.1 Time and Dates of Sampling - Since acid precipitation networks may be scattered over a large geographic area containing sites in different time zones, it is useful to reference all event times and dates to one time zone, e.g. Eastern Standard Time. Such necessary changes from the local times usually recorded on field data sheets to this standard reporting time zone should be checked.

8.6.2 Codes, Flags and Identifiers - Where a code such as that described in Section 8.1 is employed for field observations and where a similar coding system has been employed for laboratory operations, the accurate transcription of subcodes should be checked at the 10% level.

8.6.3 Overall Transcription Checks - Other observables including rain gauge vs. sample precipitation amounts, field measurements (pH, cond.) and other transcribed information should be checked against field data sheets at the 10% level.

8.6.4 Spotcheck/Recalculation of Data - The laboratory supervisor should regularly check and recalculate 5% of the data points which can be spread over the total sites in the monitoring network and should include the specially difficult analyses and extreme values.

8.6.5 QC Checks for Data Summaries - Where quarterly or less frequent data summaries are prepared, the calculations (made by the person with program responsibility or at his direction) should be verified as being correct from previously screened, clean, raw data. Usually, one or two sites within the summary period are selected at random and for those sites one or two analytes are checked. This is equally important for both manually and computer derived summaries. Quality control checks on such summaries should include verification of

1. calculation of precipitation-weighted means

2. calculation of depositions

3. derivation of medians

4. 95% confidence bounds on the medians

5. reporting of maximum and minimum values.

If yearly summaries derived from quarterly or monthly data are reported, checks should be made for consistency between the four quarterly summaries or the twelve monthly summaries and the data reported for the year.

8.7 References

1. Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. V - Manual for Precipitation Measurement Systems; Part II - Operations and Maintenance Manual. U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/4-82-042b (January 1981).

2. Handbook for Analytical Quality Control in Water and Wastewater Laboratories, United States Environmental Protection Agency, Cincinnati, OH, EPA-600/4-79-019 (1979).

3. Quality Assurance Handbook for Air Pollution Measurement Systems- Vol. I- Principles, United States Environmental Protection Agency, Research Triangle Park, NC, EPA-600/9-76-005 (1976) Appendix F.

4. T.R. Fitz-Simons and D.M. Holland, The Maximum Likelihood to Probabilistic Modeling of Air Quality Data, United States Environmental Protection Agency, Research Triangle Park, NC, EPA-600/4-79-044 (1979).

5. Electric Power Research Institute, "The Utility Acid Precipitation Study Program: Annual Report on Operations and Results for 1982." Contract U101-1, Rockwell International Environmental Monitoring and Services Center (1983).

6. J.L. Mero, The Mineral Resources of the Sea, Elsevier Publ., New York, NY (1964) p. 25.

7. Handbook of Chemistry and Physics, 48th ed. Edited by R.C. Weast, The Chemical Rubber Co., Cleveland, OH 44128, 1967-68.

8. J.P. Lodge, Jr., J.B. Pate, W. Basbergill, G.S. Swanson, K.C. Hill, E. Lorange and A.L. Lazrus, "Chemistry of United States Precipitation," Final Report on the National Precipitation Sampling Network, National Center for Atmospheric Research, Boulder CO, (August 1968).

9. J.A. Garland, "Enrichment of Sulphate in Maritime Aerosols," Atmos. Environ. 15, 787 (1981).

10. J.M. Miller, "A Statistical Evaluation of the U.S. Precipitation Chemistry Network," in Precipitation Scavenging, P.B. Semonin and R.W. Beadle, eds., CONF-741003 (1974); pp. 639-659. Technical Information Center, Energy Research and Development Administration, Springfield, VA.

11. H.M. Liljestrand and J.J. Morgan, "Error Analysis Applied to Indirect Methods for Precipitation Acidity," Tellus, 31, 421-431 (1979).

12. G. Nehls and G. Akland, J. Air Pollut. Control. Assoc., 23, 180 (1973).

9.0 DATA QUALITY ASSESSMENT

The determination of the precision and accuracy of precipitation data is the principal means employed to quantitatively assess data quality. Specific procedures developed for determining precision and accuracy for the measurement methods used in precipitation monitoring are presented below. In general, data generation is a three-step process; the first two are functions of field operations, and the third one is part of laboratory operations. These are:

1. Collection of the sample in a suitable sampler.
2. Initial field analyses for pH, specific conductance, and weight.
3. Expanded chemical analyses in the laboratory.

Data quality should be routinely assessed for each step in the measurement system. Precision of the measurement system is estimated from data obtained by using collocated samplers and employing identical sampling, handling and analysis protocols for all samples. Field measurement accuracy is determined by regular test sample audits. Precision of field and laboratory analytical methods can be derived from multiple analyses of certain samples. Accuracy of laboratory analyses is derived from laboratory analysis of internal and/or external blind audit samples.

9.1 Evaluation of Field Operations

9.1.1 Measurement System Precision - Precision is estimated by duplicate sampling with collocated precipitation samplers. Each network of sites operated by an organization should have a minimum of one duplicate sampler of the type used for routine monitoring. The collocated sampler(s) should be operated during routine sampling and be installed consistent with the siting criteria (Section 5.0).

Sampling precision is known to vary among sites and during different seasons (1). Each organization should therefore develop a schedule for the deployment of the collocated sampler(s) such that all the possible site/season combinations are satisfied (2).

In order to derive a precision estimate, data from the collocated sampler(s) and data from the station sampler are compared. The measured differences in pH (pH units), conductivity (μmho/cm), total mass captured and concentrations of the various analytes (mg/liter or μeq/liter) are then used to calculate precision. For each pair of measurements, the signed (SCD) and absolute (ACD) collocation differences are calculated:

$$(SCD)_{ik} = y_i - x_{ik}, \text{ and} \qquad 9\text{-}1$$

$$(ACD)_{ik} = |y_{ik} - x_{ik}|$$

where y_{ik} is the observable determined for the duplicate sampler for the ith species and kth collocation event, and x_{ik} is the observable determined for the corresponding station sampler for the same species and collocation event.

Quarterly, the mean, $\overline{SCD}_{ij}$, and the standard deviation, S_{ij}, are estimated for the SCDs of each observable (i) obtained from the jth site having collocated samplers:

$$\overline{SCD}_{ij} = \frac{1}{k_j} \sum_{k=1}^{k_j} (SCD)_{ijk} \qquad 9\text{-}2$$

$$S_{ij} = \left\{ \frac{1}{2(k_j-1)} \sum_{k=1}^{k_j} \left[(SCD)_{ijk} - (\overline{SCD})_{ij} \right]^2 \right\}^{1/2} \qquad 9\text{-}3$$

where k_j is the number of collocation events at the jth site during a calendar quarter.

Equations 9-2 and 9-3 could also be used for summarizing the ACDs, if appropriate. If the network contains more than one site with collocated samplers, a mean, $(\overline{SCD})_i$, and a pooled standard deviation, S_{ai}, for each observable should be computed quarterly:

$$(\overline{SCD})_i = \sum_{j=1}^{n} k_j \, (\overline{SCD})_{ij} \Big/ \sum_{j=1}^{n} k_j \qquad 9\text{-}4$$

$$S_{ai} = \left[\sum_{j=1}^{n} (k_j - 1)\, S_{ij}^{2} \Big/ \sum_{j=1}^{n} (k_j - 1) \right]^{1/2} \qquad 9\text{-}5$$

where n is the number of sites having collocated measurements within the network. Equations 9-4 and 9-5 can also be used for summarizing the ACDs, if appropriate.

An analysis of the distributions of SCDs for the different observables in precipitation monitoring reveals that they are symmetrical but may not be derived from a Gaussian (normal) population. Therefore, statistical prediction methods based solely on the assumption of a normal distribution may lead to erroneous predictions. To illustrate, consider the summary of upper and lower SCD limits presented in Table 9-1 for an event sampler network. The entries in the table correspond to the observed (O) 95% SCD population limits, i.e. the 97.5th percentile is the upper limit (UL) and the 2.5th percentile is the lower limit (LL). The table also presents the computed ratio (P/O) where the predicted value (P) was derived for a normal distribution. The range of P/O is 0.96 to 23.9 with the majority between 1.00 and 3.00. This indicates that using a normal distribution to estimate the upper and lower limits for the SCDs would not be very accurate in this case.

The usual Gaussian approach, which brackets 95% of the SCD population, is:

$$\begin{aligned} UL &= \overline{(SCD)}_{ij} + 1.96\, S_{ij} && \text{for a site} \\ &= \overline{(SCD)}_{i} + 1.96\, S_{ai} && \text{for a network} \qquad 9\text{-}6 \end{aligned}$$

$$\begin{aligned} LL &= \overline{(SCD)}_{ij} - 1.96\, S_{ij} && \text{for a site} \\ &= \overline{(SCD)}_{i} - 1.96\, S_{ai} && \text{for a network} \qquad 9\text{-}7 \end{aligned}$$

Each network should maintain at least one pair of collocated samplers. For large national networks it might prove more useful to form regional clusters of sites for the purpose of precision estimation. The collected samples should be tagged in a consistent manner so their respective measurements in the field and the laboratory can be easily traced and used to quantitatively assess monitoring precision.

TABLE 9-1. NETWORK SUMMARY OF UPPER AND LOWER LIMITS OF THE SCDs FOR DAILY SAMPLING

Observables (units)	No. of Collocation Events	Observed 95%* Population Limits		Predicted/Observed (P/O)**	
		LL	UL	LL	UL
pH (pH units)	936	-0.44	0.39	1.12	1.21
Hydrogen Ion (mg/liter)	936	-0.07	0.06	0.96	1.13
Total Acidity (mg/liter)	847	-0.06	0.06	1.09	0.94
Conductivity (μmho/cm)	935	-13.9	13.4	1.43	1.50
Sulfate (mg/liter)	912	-1.07	1.09	1.05	1.03
Nitrate (mg/liter)	912	-0.72	0.62	1.04	1.18
Chloride (mg/liter)	910	-0.44	0.58	2.20	1.75
Ammonium (mg/liter)	897	-0.22	0.26	10.6	8.74
Sodium (mg/liter)	886	-0.33	0.44	1.60	1.21
Potassium (mg/liter)	887	-0.21	0.30	2.87	1.97
Calcium (mg/liter)	885	-0.20	0.30	3.78	2.29
Magnesium (mg/liter)	886	-0.03	0.05	2.52	1.60
Phosphate (mg/liter)	904	-0.04	0.05	23.9	17.8

* Observed (O) values based on the 2.5 and 97.5 percentiles of the SCDs for the lower (LL) and upper (UL) limits, respectively.

** P/O ratio obtained from predicted values based on 95% probability limits of a normal distribution, i.e. P = mean ± 1.96 std. dev.

A quarterly precision assessment report containing the descriptors below should be prepared. These summaries should pertain to entire networks or regional clusters of sites, as appropriate:

1. SCDs, ACDs and associated standard deviations for each observable following Equations 9-1 through 9-3.
2. Network averages (SCD), (ACD), and the corresponding pooled standard deviations for each observable, following Equations 9-4 and 9-5.
3. Upper (UL) and lower (LL) precision probability limits for each observable, either for a given site or for the entire network, following Equations 9-6 and 9-7.

These quarterly summaries should be reviewed by program management, and out of control conditions identified and corrected. The precision summaries should be submitted together with the monitoring data to the accountable organization.

9.1.2 Accuracy of pH and Conductivity Measurements - To assess the accuracy of field measurements of pH and conductivity, audits should be conducted using test samples prepared and sent from the central laboratory each month. The samples should be measured at the site as soon as possible after receipt, and the results should be returned to the laboratory. The laboratory should analyze the test sample before the sample is sent to the field. The results of the laboratory analyses should be included with the field analysis results. The QA officer should record all the data on the Monthly Field Audit Report (Section 9.4). The acceptance criteria to be used as control limits on potential sample degradation are given in Table 9-2.

Accuracy for each measured variable is estimated by computing the differences:

$$d_j = f_j - (l_{ij} + l_{fj})/2 \qquad 9\text{-}8$$

where d_j is the difference in measurements for jth site (appropriate units), f_j is the field analysis of observable for jth site, l_{ij} is the initial laboratory analysis of observable before shipment to the jth site, and l_{fj} is the final laboratory analysis of the observable after return from the jth site. Equation 9-8 should be used only if $|l_{ij} - l_{fj}|$ is less than the acceptable control limits (Table 9-2). If a site value of d_j in equation 9-8 exceeds the acceptance criteria in part b of Table 9-2, this should alert the program manager that the pH electrode or conductivity standard solution may require replacing.

TABLE 9-2. ACCEPTANCE CRITERIA FOR TEST SAMPLE QUALITY AND FIELD ANALYTICAL ACCURACY.

(a) Laboratory Before and After Audit Measurements (one-asterisk flag if exceeded)		
pH $\leq$ 5.00	$\lvert \text{Before} - \text{After} \rvert$	$\leq$0.1 pH unit
pH > 5.00	$\lvert \text{Before} - \text{After} \rvert$	$\leq$0.2 pH unit
Cond. $\leq$ 15 μmho/cm	$\lvert \text{Before} - \text{After} \rvert$	$\leq$2 μmho/cm
Cond. > 15 μmho/cm	$\frac{\lvert \text{Before} - \text{After} \rvert}{\text{After}} \times 100$	$\leq$ 15%
(b) Lab vs. Field Measurement Comparison (two-asterisk flag if exceeded)		
pH $\leq$ 5.0	$\lvert \text{avg. field} - \text{average lab} \rvert$	$\leq$0.2
pH > 5.00	$\lvert \text{avg. field} - \text{average lab} \rvert$	$\leq$0.3
Cond. $\leq$ 15 μmho/cm	$\lvert \text{average field} - \text{avg. lab} \rvert$	$\leq$ 3 μmho/cm
Cond. > 15 μmho/cm	$\frac{\lvert \text{avg. field} - \text{avg. lab} \rvert}{\text{avg. lab}} \times 100$	$\leq$ 20%

Data should be summarized in the Monthly Field Audit Report by the QA officer, who also computes an average monthly network difference $\bar{d}_m$ for the observed pH and conductivity

$$\bar{d}_m = (1/m) \sum_{j=1}^{m} d_j \tag{9-9}$$

and the monthly variance, S_m^2, or standard deviation, Sm.

$$S_m^2 = \left[\frac{1}{(m-1)} \cdot \sum_{j=1}^{m} (d_j-\bar{d}_m)^2\right]^{\frac{1}{2}} \tag{9-10}$$

where $\bar{d}_m$ is the average monthly network difference for a given variable, d_j is as defined in equation 9-8 above, and m is the number of sites audited during the month. Monthly results should be summarized in a quarterly report (Section 9.3).

9.1.3 Sampling Bucket Blanks - Sampling bucket blanks should be obtained to ascertain the levels of constituents that contaminate the bucket over a period of time when there is no precipitation. This contamination can be due to poor techniques used for bucket cleaning and handling in the laboratory and field, or may be due to dry deposition entering the bucket around the lid seal. A bucket blank is obtained by cleaning a sample bucket that has been in the collector for seven consecutive days without an event occurring and analyzing the rinse solution. A known amount of distilled or deionized water, e.g., 100 g, is used to rinse the bucket, and this rinse is analyzed for the constituents $SO_4^=$, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{+2} and Mg^{+2}. The ionic quantities measured should be corrected for the deionized water blank.

The bucket blanks serve as a quality control check in two respects. First, any increase in bucket blank contamination over time may indicate the presence of a problem. Second, data from bucket blanks may be used as a correction for event concentrations or deposition averages. Bucket blanks are expected to vary from site to site and season to season with the largest values occurring at arid, windy sites with poor lid seals. Thus blank averages are most useful if they have been derived for a site over a significant time period, such as a quarter of the year.

The blank deposition can be used as an indicator of a problem. The blank deposition is calculated from equation 9-11 with P given by W/k(cm), where W is the weight of the deionized water rinse and k is the conversion factor for sample weight to centimeters, e.g., 640 g/cm for the Aerochem Metrics bucket.

The blank deposition then is

$$D_b\ (\mathrm{mg/m^2}) = 10\ P\ C = 10\ (W/k)\ C \tag{9-11}$$

where C is the analyzed concentration of the ion in mg/liter.

Since C and W are inversely proportional, the deposition is independent of the amount of rinse water. In contrast, concentration varies with the amount of water used and would have to be calculated as a function of W for comparisons. After a data base of blank values has been accumulated for each site and quarter, a mean or a median can be obtained and updated. The median ion deposition in blanks is generally less than 8% of the median precipitation values (1). The occurrence of extreme blank values, e.g., those greater than the lowest 5% of event sample values, or, alternatively, greater than 3 to 10 times the blank median, can be used as an indication of unduly high contamination. The actual upper limit will vary with the analyte, site and season.

The blank values can also be used to correct event value averages. However, this is not a straightforward procedure since the conditions under which the blanks and the event samples were obtained may be quite different. Corrections should be made only on an individual site and seasonal basis. To simplify matters, the median or average blank values for the analyte for a particular quarter is subtracted from the median or average event value for the same quarter and site. For concentration, the median bucket blank value for the ith analyte $\bar{C}_i$, must be corrected for the rinse water blank and calculated for the median precipitation quantity $\bar{P}$, i.e:

$$\bar{C}_i(\mathrm{mg/liter}) = (C_B - C_W)W/\bar{P} \tag{9-12a}$$

or

$$\bar{C}_i(\mu\mathrm{eq/l}) = 10^3\bar{C}_i(\mathrm{mg/liter})/\mathrm{Eq.Wt.} \tag{9-12b}$$

where C_B and C_W are the measured concentrations in mg/l for the analyte in the bucket rinse and the deionized water, respectively, P denotes the median precipitation volume (ml) or weight (g) for the quarter, Eq. Wt. is the equivalent weight of the analyte, and W has been defined above.

If a daily sampling schedule is followed, the above $\bar{C}$, which is for a weekly time interval, should be divided by the average number of daily samples per week. (It is assumed here that the chief source of contamination is deposition of dust in the bucket while in the sampler and that deposition increases uniformly with time.) Table 9-3 shows the medians of both the absolute analyte blank values and the relative magnitude of these blanks expressed as percentage of the median precipitation values, for the 1982-1983 UAPSP network (3). The blank data are for 224 weekly samples taken in the last quarter of 1982 through October 1983 from most of the sites, whereas the precipitation medians are for approximately 1600 daily samples from the entire network for 1982. The blank data have been normalized for a median precipitation volume of approximately 500 ml but have not been corrected for the average time interval between samples. Since the number of samples per week averaged slightly less than two, the concentrations listed should be halved.

The data indicate that the cations generally have larger blank contributions than sulfate and nitrate, and are consistent with soil dust being the chief source of contamination. However, even without the time correction, the largest bucket blank median value (for potassium) is only 6% of its median precipitation concentration. Thus, these blank contributions to the precipitation averages are small and can be neglected. For specific sites and time intervals the blank concentration may not always be negligible, in which case the blank concentration should be subtracted from the average.

For those sites which frequently show large blank values, the sampler lid seals should be checked and/or replaced as necessary. If the seal is functioning properly, the problem may be caused by excessive winds. The pressure of the seal can be increased as indicated by the sampler manufacturer. If neither of the above corrects the problem, bucket preparation and handling techniques should be evaluated and changed as necessary.

TABLE 9-3. ABSOLUTE AND RELATIVE BLANK VALUES.

Observable	Median Blank Values[a,b] (mg/liter)	Relative Median Blank Values[c] (%)
SO_4	0.0086	0.5
NO_3	0.0068	0.5
Cl	0.0043	3.0
NH_4	0.0068	3.0
Na	0.0009	1.5
K	0.0012	6.0
Ca	0.0048	5.0
Mg	0.0010	5.0

a. (Blank - D.I. H_2O)Concn. x Rinse vol. /500

(Median precipitation volume ~ 500 ml)

b. For 224 samples

c. expressed as median blank value as a percent of median concentration in approximately 1600 precipitation samples.

9.2 Evaluation of Laboratory Operations

The QA officer should routinely assess the reproducibility, precision, and accuracy of laboratory chemical analyses of precipitation samples in order to obtain a representative indication of overall data quality.

9.2.1 Analytical Precision - To estimate the contribution of analytical variability to total variability, duplicate analyses should be performed on approximately 10% of all the precipitation samples routinely analyzed by the laboratory. Samples randomly selected for replicate analyses by the QC chemist should contain a large quantity of precipitation. The split samples should be properly identified, and the results of such duplicate analyses recorded and reported to the QA officer and program manager in the Report of Duplicate Analyses (Section 9.4). Analytical precision is commonly defined and reported as the standard deviation of duplicate analyses. An additional factor of 2 is included in the denominator to take into account the random error associated with both measurements. Thus, for precipitation measurements analytical precision for the ith analyte is defined as

$$S_i = \left(\sum_{i=1}^{N_i} d_i^2 / 2N_i \right)^{\frac{1}{2}} \qquad 9\text{-}13$$

where d_i denotes the difference for the duplicate analysis of the ith analyte, and N_i is the number of sample pairs for the ith analyte in the reporting period.

9.2.2 <u>Accuracy of Chemical Analysis</u> - Accuracy of chemical analyses should be determined monthly from results of the analyses of blind samples submitted to the laboratory by randomly selected field sites. These samples, prepared by diluting various precipitation standards (NBS or EPA), should be shipped in sealed plastic bottles to the field sites. Each sample should be identified and accompanied by two postcards. On arrival at the field site, the sample should be refrigerated at 4°C until it is forwarded to the laboratory. At the end of the first week in which no event has occurred, the sample should be transferred to a clean weighed container generally used for shipment (plastic bottle, plastic bag or sampling bucket). The sample should be weighed, and an aliquot should be measured at the site for pH and for specific conductance. A field data form should be filled out with the measured values and the other required data. To do this, a simulation of a normal precipitation record will have to be used. Sample and site identification, sampling date(s), pH, conductivity and weight should be recorded on postcards. The sample and the data form should be sent to the laboratory (as for an event sample), and the postcards mailed to the QA officers for both the monitoring network and for the blind sample preparation laboratory; thus, if one card is lost, the information will be available from the second. Once received at the laboratory, such a sample is treated as a routine sample and is analyzed in the normal manner for all constituents of interest.

At regularly scheduled intervals, when the analytical laboratory sends a printout of sample results to the QA officer, he should identify the blind field samples and transfer their data to the QA data file. He should also notify the analytical laboratory to delete these results from the precipitation data file. The laboratory is then informed on its performance analyzing the QA samples. Data should be summarized by the same computational procedure indicated by Equations 9-1 through 9-7. The QA officer should also obtain QA samples from EPA's EMSL Quality Assurance Division and/or from the U.S. Geological Survey semiannually as an external check on analytical accuracy.

9.3 Data Quality Reporting

The QA officer should provide the following reports to the program manager on a routinely scheduled basis:

1. Measurement System Precision -- Quarterly reports, summarizing all data on collocated samples and duplicate analyses performed during the three months, should include differences in analytical results for the split samples and the average difference for each analyte. The report should compare average differences with the QC ranges typical for the laboratory and the measurement method.

2. Analytical Accuracy -- Quarterly reports, summarizing data on at least three blind QA samples analyzed by the laboratory in the three months, should include the different constituent concentrations and an average difference and standard deviation computed for each. Data for the comparison obtained by the QA officer should include also a summary of all spike recovery data for the reporting period.

3. Field Measurements Accuracy -- Quarterly reports should give the accuracy of the measurements performed by the field operator using audit or test samples sent from the laboratory on a monthly basis. Audit results should include the laboratory analyses of the sample before it was sent to the field and the field analysis. The data summary should give the mean and standard deviation for each station and for the network as a whole. Typical acceptance criteria for pH and conductivity are presented in Table 9-2. These data should be used to indicate when a bad pH electrode or conductivity standard needs replacing.

4. Site Evaluations -- Semiannual reports should be made providing a qualitative evaluation of the site and operational procedures. The auditor visiting the field sites summarizes his observations and provides recommendations for corrective action, if appropriate. The auditor observes and documents the operator's performance in the analysis of unknown performance evaluation samples for pH and conductivity. The report should also summarize instrument performance checks conducted on the precipitation sampler and the rain gauge and any recalibration that has been performed on the latter.

9.4 Data Forms

Blank data forms on the following pages were taken or adapted from EPA forms and from other references. The titles are at the top of the figures as is customary. The two forms included here are:

1. Monthly Field Audit Report

2. Report of Duplicate Analyses

9.5 References

1. L. Topol, "Precision of Precipitation Chemistry Measurements", Proceedings APCA Specialty Conference on Atmospheric Deposition, SP-49, pp. 197-209, November 1982.

2. R.J. Schwall, M. Lev-On and L. Topol, "Guide for Collocation Planning" Final Technical Report to Work Assignment No. 51, EPA Contract No. 68-02-3767, Rockwell International Environmental Monitoring and Services Center (EMSC8391. FR), in preparation.

3. Electric Power Research Institute, "Acid Precipitation in the Eastern United States (1978-1980)", Contract Nos. RP 1376-1 and RP 1630-2, Rockwell International Environmental Monitoring and Services Center, Final Report.

MONTHLY FIELD AUDIT REPORT

Sample #: ____________________

Date of Preparation of Field Audit Sample: ____________________

____
(Analyst Signature)

LABORATORY ANALYSIS BEFORE SHIPMENT[a] TO THE FIELD			LABORATORY ANALYSIS AFTER RETURN[a] FROM THE FIELD		
Date: ________			Date: ________		
	Conductivity	pH		Conductivity	pH
1.	________	________	1.	________	________
2.	________	________	2.	________	________
3.	________	________	3.	________	________
±Average Std. Dev.	______	______	±Average Std. Dev.	______	______

LABORATORY ANALYSIS OF AUDIT SAMPLES VS. FIELD ANALYSIS

		Conductivity (mho/cm)			pH		
Site	Field Date	Field Analysis	Lab[b] Analysis	Diff.[c]	Field Analysis	Lab[b] Analysis	Diff.[c]

a) These data are for three laboratory aliquots which are analyzed before shipment of samples, are then refrigerated, and are reanalyzed with the samples returned from the field.
b) Values after return from the field.
c) Diff. = Field-Lab

REPORT OF DUPLICATE ANALYSIS

Analyte	Analysis Technique	Routine[a] (ID_____) Date	Routine[a] (ID_____) Result	Duplicate[b] (ID_____) Date	Duplicate[b] (ID_____) Result	Diff.[c]
pH						
Conductivity						
Sulfate						
Nitrate						
Chloride						
Phosphate						
Carbonate						
Bicarbonate						
Acidity						
Strong Acid						
Ammonium						
Sodium						
Potassium						
Magnesium						
Calcium						

---

a. Value reported as routine sample

b. Duplicate sample, might have different ID

c. Diff. = Duplicate - Routine

10.0 ACID PRECIPITATION MONITORING PROGRAM EVALUATION

Establishing a schedule for audits and independent checks to evaluate the quality of data provided by the total measurement system is an important part of an overall Quality Assurance Program. A complete audit for a precipitation chemistry network should include both qualitative and quantitative evaluations. The quantitative evaluation, derivation of estimates of precision and accuracy, has been discussed in Section 9.0. Overall program audits, site evaluations, laboratory system audits and performance audits will be discussed here.

10.1 Program Audits Guidance

A program audit is a qualitative on-site inspection and appraisal of the QA efforts used for the program. The topics that should be reviewed by audits and the sections of this manual pertaining to them are as follows:

1. Overall Program Operation (Management):
   Background material - Sections 2.0 and 3.0
   Review questionnaire - Section 10.2, items A through E;

2. QA Project Plan and Its Implementation:
   Background material - Sections 2.2 and 2.3
   Review questionnaire - Section 10.2, item F;

3. Site Documentation:
   Background material - Sections 4.0 and 5.0
   Review questionnaire - Section 10.3;

4. Site and/or Field Operation:
   Background material - Section 6.0
   Review questionnaire - Section 10.2, item G;

5. Support/Analytical Laboratory Operation:
   Background material - Section 7.0
   Review questionnaire - Section 10.4;

6. Performance Audits:
   Background material - Sections 6.0, 7.0 and 9.0
   Specific guidance - Section 10.5;

7. Data Handling, Analysis, Validation and Reporting:
   Background material - Section 8.0
   Specific guidance - Section 10.6.

For each monitoring network, a program audit should be conducted as soon as possible after the start of monitoring; subsequent audits should be conducted at least once each year thereafter. In order to conduct a program audit effectively, the auditor or audit team should:

(a) Decide on the audit scope - this should depend on the size of the program and the use of the data derived from the program.

(b) Select appropriate questionnaires and have organization personnel complete and return them prior to the on-site visit. Several questionnaires and checklists suggested for this application have been prepared and included in this manual.

(c) Review the completed questionnaires and supporting documentation prior to the on-site visit in order to become as familiar as possible with Program Operations and to discover potential problem areas ahead of time.

(d) Set-up and carry out on-site evaluation and interviews - the auditor should, at a minimum, visit the program operations headquarters, a field site, and field laboratory. If the support analytical laboratory operations are to be evaluated, then the auditor should visit the laboratory also. He should interview responsible individuals and members of the technical staff with respect to the material presented in the completed questionnaire.

(e) Conduct an exit briefing with program personnel to give a preliminary report of audit findings and to set some expected time frame in which the organization can expect to receive the audit report.

(f) Prepare, edit and deliver a written report of audit results and program assessment in DRAFT form; receive and incorporate comments made by the organization and issue as a completed document.

10.1.1 Support Material - For a program audit the following material should be used:

1. Overall Program Operation; Field and Field/Lab Operations Questions - The auditor should use questionnaires similar to or identical with the two questionnaires given in Section 10.2. The first of these questionnaires is intended to cover management and organizational activities while the second addresses site operation and field measurement activities.

2. QA Project Plan - This document should be checked for completeness against the material found in Section 2.0 and throughout this manual.

3. Site Documentation - A completed checklist/form such as that given in Section 5.0 should be obtained for at least one site in the monitoring network. The auditor should visit that site and verify the accuracy of the information written on the form. The questionnaire given in Section 10.3 of this chapter may be used for this purpose.

4. Analytical Laboratory Operations - The auditors should use a questionnaire based on or identical to that contained in Section 10.4.

10.1.2. Reporting - At the conclusion of any program/laboratory/site audit assignment the auditor should prepare a complete evaluation report. A possible format for such a report would include, as appropriate:

1. General Background - This section identifies who was interviewed and who was present for the audits and their affiliation. A general overview of audit procedures should also be given.

2. Field Laboratory - This may be included where such a laboratory is maintained within, or is supported by, the central analytical laboratory. The field laboratory and site operation may be evaluated as a separate entity or during an audit of overall operations.

3. Analytical Laboratory - This section should describe current ongoing operations in sufficient detail as to present a complete understanding of the level to which both QC and QA have been implemented. Since this is the major portion of the report, this section will necessarily include examples of documentation which the auditor feels are critical to an understanding of operations. Since support to a precipitation monitoring program requires many different types of analyses, the auditor may choose to describe in detail two or three analyses which he considers representative of laboratory operations.

4. Data Management - This section should describe data management practices and the levels of data screening, QC checks and independent data processing audits employed.

5. Conclusions and Recommendations - In this section the auditor should discuss the audit findings with a view to potential data impact, and where possible, indicate potential courses of corrective action.

The report should be prepared in DRAFT format and submitted to both the audit requestor and the audited organization. This allows for the early clearing of potential misunderstandings and points of contention and offers a mechanism for the inclusion of additional information necessary to complete the report. Once the comments to the DRAFT report have been received, they should be reviewed and incorporated. The report can then be issued in final form and copies sent to responsible parties for appropriate distribution.

10.2 Overall Program Operation Questionnaire

GENERAL INFORMATION

Questionnaire Completion Date: ______________

On-Site Visit Date: ________________________

Organization Name and Address:

____

____

____

Telephone No. FTS: ________________ Commercial: ( ) ______________

Person Completing Questionnaire ____________________________________

Position: ____

Telephone No. ( ) ____

Organization Director: ____

Monitoring Supervisor: ____

Quality Assurance Officer: ____

On-Site Audit Conducted By: ____

Affiliation of Auditor(s): ____

____

Persons Present During Entrance Interview:

____

____

Persons Present During Exit Interview:

____

A. GENERAL

1. How long has the program been operational?

Number of Sites ____________

Operating Since ____________

2. What is the objective of the monitoring program?

Baseline ____________

Trends ____________

Other ____________

3. Provide a current organizational chart indicating each person's participation in the current program.

4. Have the following been prepared, approved, issued, revised?

QA Project Plan ________ Date________

Documentation on Sites and Network ________ Date________

Standard Operating Procedures for Field Sampling ________ Date________

Standard Operating Procedures for Analytical Lab ________ Date________

5. Does the program operate in compliance with

EPA Protocol? Yes_____ No_____ Comments ____________

NADP Protocol? Yes_____ No_____ Comments ____________

NTN Protocol? Yes_____ No_____ Comments ____________

Other Protocol? Yes_____ No_____ Comments ____________

____

____

6. Was the operating protocol derived from any of the above and modified to meet network needs?

Explain ____________________________________

____

____

____

7. Indicate number of sites currently operational as part of network?

8. How many of these sites have collocated instrumentation for precipitation measurements?

B. STAFFING

1. Please include a list of educational background, experience and training for each responsible person identified in the program organization chart.

2. Are the following adequate to current and proposed program operation?

Staff Site? Yes___ No___ Comment________________________
Organization? Yes___ No___ Comment________________________
Staff Qualifications? Yes___ No___ Comment________________________
Staff Utilization Yes___ No___ Comment________________________

3. Do staff members receive regular and periodic training to maintain and upgrade job skills? Please indicate examples of each responsible individual's training including period and training method (course?, on-the-job?, etc.)

____
____
____
____

4. Are staff members adequately conversant with appropriate standard operating procedures to carry out job duties?

Yes _______ No_______ Comment____

5. Has a staff member been identified as a Quality Assurance Officer?

Yes _______ No_______ Comment____
If not, who handles this responsibility?____________________________
(Name)
Who does he report to?____
(Name and Title)

6. Which of the following references are available to staff members?

(a) Atmospheric Environment ______________________________
(b) Journal of the Air Pollution Control Association ______________
(c) Environmental Science and Technology ____________________
(d) (Other) ____

C. NETWORK DESIGN

1. Are all sites documented according to specified criteria?

   Yes ______ No ______ Comment ____________________

   (Please attach an example of the documentation for one site)

2. Has the network been designed in accordance with stated program objectives? Include a brief description of any siting compromises.

   Yes ______ No ______ Comment ______________________________

3. Is there a written plan describing the overall network?

   Yes ______ Title ____________________________ Date __________
   No ______

4. Does the organization have records identifying the status and history of each site? Does it include

   (a) Some site identification?

   Yes _____ No _____ Comment ______________________________

   (b) Site coordinates and elevation?

   Yes _____ No _____ Comment ______________________________

   (c) Photos or slides, taken to adequately show siting?

   Yes _____ No _____ Comment ______________________________

   (d) Date monitoring initiated? ______________________________

   (e) Model, manufacturer and serial numbers of equipment at the site and sampling schedule? ______________________________

   (f) Reason for periods of missing data? ______________________________

5. Is equipment installed at site in accordance with

   (a) Manufacturer's specifications? Yes ___ No ___ Comment __________

   (b) Network guidelines? Yes ___ No ___ Comment __________________

   (c) Sound scientific principles? Yes ___ No ___ Comment __________

6. Does the network design consider

(a) Access? Yes ___ No ___ Comment ______________________________

(b) Power availability? Yes ___ No ___ Comment ______________________

(c) Potential localized interferences such as closely located sources?

Yes ___ No ___ Comment ____

____

____

7. How often are sites visited? ______________________________________

8. How often are samples removed? ___________________________________

D. NETWORK OPERATION

1. Is equipment in the network operated in accordance with organization's standard operating procedures (where such exist)?

Yes___ No___ Comment ______________________________

2. Are the operating procedures compatible with

(a) Agency QA plan? Yes___ No___ Comment ______________________________
(b) EPA guidelines? Yes ___ No___ Comment ______________________________
(c) Manufacturer's recommendations? Yes___ No____ Comment ____________
____

3. Is equipment operated on a (documented) schedule? (Please attach a copy for one site.) Yes___ No___ Comment ______________________________

4. Are an adequate supply of spare parts and expendables maintained at the site by the network to minimize downtime?

Yes___ No___ Comment______________________________

5. Are all sites operated year round? Yes_____ No_______

Explain Schedule ______________________________
____

6. Is a bound logbook maintained at the site? Yes_____ No______

containing records of site visits? ______________________________
problems? ______________________________
data? ______________________________

7. Is routine minor maintenance performed regularly at the site?

Yes_______ No_______ Comment ______________________________

By Whom: ______________________________
(Name - Position)

8. Does the person performing such maintenance possess (or have access to):
   (a) Standard troubleshooting/maintenance procedures? Yes ___ No ___
   Comment ______________________________
   (b) Instrument manuals? Yes ___ No ___ Comment ______________
   (c) Other guidance? Explain ______________________

9. Indicate which tasks (if any) are included as part of site operation duties:

Task	Frequency

10. Are any measurements made on samples at sites? Yes_____ No_____

Comment ______________________________

	At Site (Yes/No)	Freq. (Times per wk)	Measurement Device
Cond.			
pH			
Precip. depth			
Wt/Vol.			
Other			

(Attach pages as necessary.)

11. How are samples shipped to analytical lab? (Please circle appropriate response.)

in buckets
in bottles
other*

without field measurements
with field measurements

by truck
hand delivered
by mail
other*

*Explain ____

____

____

____

____

E. DATA AND RECORDKEEPING

1. Please indicate data sources and, as necessary, attach examples of, or briefly describe, the data format?

   (a) field site/field lab data include:
   rain gauge charts ______________________
   copies of data sheets ______________________
   copies of logbooks ______________________
   other ______________________

   (b) analytical lab data include:
   analytical results ______________________
   calibration data ______________________
   separate QC data ______________________

   (c) other data source used in conjunction with acid precipitation:
   meteorological data ______________________
   aerometric data ______________________
   source emission data ______________________

2. Are field data checked for reasonableness?

   Yes ______ No ______ Indicate what is checked ______________

   ____

   ____

   ____

   ____

   ____

   ____

3. Are analytical lab data checked for reasonableness?

Yes ______ No ______ Indicate what is checked ____________________

____

____

____

____

____

4. Are a portion of data from field reverified by lab (such as duplicate pH, conductivity or weight measurements)?

Yes ______ No ______ Specify ____________________________________

5. Are such crosschecks used to validate or flag data? ______________

Yes ______ No ______ Indicate any cutoff points ___________________

____

6. How are data finally reported? How often? _____________________

____

____

____

____

7. Where and how are data archived? For how long? ________________

____

____

____

____

F. QUALITY ASSURANCE

1. Is there a defined QA function ongoing within the network?

   Yes ______ No ______ Comment ____

   ____

2. Is this function independent of all routine operations?

   Yes ______ No ______ Comment ____

   ____

3. Does the individual responsible for this function regularly evaluate or audit the following operations?

   (a) Site operations (Performance Audits)? Yes ___ No ___

   Comment on Frequency ________________________________

   (b) Site data? Yes ___ No ___

   Indicate % of data recalculated ________________________

   (c) Analytical laboratory operations? Yes ___ No ___

   Indicate dates of last audits of lab____________________

   (d) Analytical laboratory data? Yes ___ No ___

   Indicate % data recalculated __________________________

4. Does QA maintain (and/or prepare) independent check solutions or standards specifically used to monitor accuracy?

   Yes ____ No ____ Comment on types, concentrations and uses

   ____

   ____

   ____

5. Does the QA function include the use of EPA supplied check samples such as from interlaboratory surveys?

   Yes ____ No ____ Comment on frequency and analytes checked

   ____

   ____

   ____

6. Does the analytical support lab participate in EPA, USGS and other interlaboratory round robin test programs?

Yes ___ No ___ Comment on frequency and attach last results summary

____

____

____

G. FIELD SITE EVALUATION

This portion of the questionnaire concerns measurements made by field or support personnel independent of any measurements made by the analytical support laboratory. If measurements are made only by the analytical lab, please mark only those applicable.

This part of the questionnaire is to be repeated for each site visited during a program audit.

1. Site address ______________________________________
   Designation (no./identifier) ______________________________

2. Does the agency have the necessary hand tools, electrical testing and calibration equipment to operate and maintain equipment, calibrate rain gauges and repair samplers at the site?
   Yes_____ No_____ Comment ______________________________

3. For precipitation collection are the following types of equipment used?
   (a) Automatic precipitation collectors? ____________________
   (b) Bucket manual-type collectors? ______________________
   (c) Recording rain gauges (sensitive to ±0.01 in. (0.25mm)? _______
   (d) Event pen markers on rain gauges? ____________________

4. Are buckets cleaned at site? Yes _______ No________
   Identify responsible person ________________________

5. Does site have adequate supply of deionized water? Yes___ No___
   (indicate source) and average conductivity (µS/cm) ______________
   ____

6. Please indicate the types, make and model of field measurement equipment (attach pages as necessary - not necessary if site documentation has been attached).

7. Are there an adequate number of clean buckets kept at the site?
   Yes ______ No______ Indicate number usually on hand ____________

8. Is the collector sensor cleaned periodically with deionized water?
   Yes _____ No_____ How often?______________________________

9. For wet/dry collectors, is the rim of the dryfall bucket wiped clean regularly?
Yes_____ No_____ How Often?______________________________

10. Is the rain sensor tested regularly?
Yes_____ No_____ Each Site Visit? ________________________
How Often? ______________________________________
By what method? __________________________________

11. Is the dryfall bucket inspected for moisture at each site visit?
Yes_____ No_____ How Often?______________________________

12. Are rain gauge pens (weight trace and event) checked for ink?
Yes_____ No______ How Often?_____________________________

13. Is the rain gauge clock wound at prescribed intervals?
Yes_______ No_______ Indicate Interval?___________________

14. Is the clock accurate to ±1/2hr per week?
Yes_______ No_______ Comment___________________________

15. Indicate the frequency of calibrations for
(a) Rain gauge ______________per_________________
(b) pH meter ______________per_________________
(c) Conductivity meter ______________per_____________
(d) Balance for precipitation weighing ___________per___________

16. Are rain gauges calibrated
(a) upon installation? Yes________ No________
(b) at least semi-annually? Yes________ No________
(c) after major maintenance? Yes________ No________
(d) when performance audits indicate the need? Yes_____ No_____

17. Is a conductivity standard solution kept at site?
Yes ________ No________ Indicate Source ________________________
Indicate conc. ________ μmho/cm. Kept for how long?______________

18. Are the shelf life and accuracy of conductivity standards documented?
Yes ________ No________ Comment_____________________________

19. Is the conductivity meter calibrated under the same conditions as used for the samples?
Yes ________ No________ Indicate Discrepancies ________________

20. Are standard pH buffers kept at site? Yes________ No________

pH 4 __________ (source) __________
pH 7__________ (source) __________
pH 8__________ (source) __________
Other__________ (source) __________

21. Is the pH meter calibrated with simulated precipitation reference solutions in addition to standard buffers?
Yes________ No________ Frequency ________________________________
Source of reference solutions ________________________________
Briefly outline procedure used ________________________________
____
____
____

22. Is conductivity standard kept refrigerated when not in use?
Yes________ No________ Comment________________________________

23. Are pH and conductivity meter calibrations checked at least at one point immediately prior to sample measurement?
Yes ________ No________ Briefly outline procedure ________________
____
____

24. Are measurements made at known temperature?
Yes________ No________ Indicate Temp. °C____________

25. Where are measurement data recorded?
(a) Site Logbook? ________________________________
(b) Data Sheet? ________________________________
(c) Other? ________________________________

26. Are other check solutions maintained at site?

Conductivity

level	source	frequency of use	replacement interval

pH

level	source	use	shelf life

27. Is a check on the rain gauge calibration made regularly?
Yes______ No__________ Indicate Frequency ______________

28. Is the outside of wet bucket wiped dry before weighing?
Yes_______ No_________ Comment ____________________

29. Is precipitation measured by weight? Yes______ No______
by volume? Yes ________ No_________

30. Has the balance used to weigh precipitation been calibrated?
Yes______ No__________ Frequency ___________

31. Has the balance calibration been performed with traceable weights?
Yes _______ No_______ Indicate traceability of weights_____

32. Is balance zeroed before each use?
Yes _______ No________ Comment______________________

33. How are pH and conductivity cells/electrodes stored between use?

pH	Conductivity
buffer (indicate pH) ____________	conductivity standard ____________
deionized water ____________	deionized water ____________
other ____________	other ____________

34. Are samples allowed to come to room temp. before measurements are made? Yes ________ No ________ Comment ____________

35. Are separate sample aliquots used for pH and conductivity?
Yes ________ No ________ If no, indicate which measurement is made first ____________

36. Are aliquots discarded after use?
Yes ________ No ________ Comment ____________

37. How are samples shipped to laboratory? (Circle appropriate response)
In buckets/In bottles/In plastic bags
By air/By surface mail/By truck
With cold-packs/At ambient temperature
Comments ____________
____

38. Are samples shipped within 24 hours of collection?
Yes ________ No ________ Briefly describe sample storage and treatment prior to shipment. ____________
____
____

39. Do copies of field measurements accompany sample? Yes ________
No ________ Are any additional copies made? How many ____________
Purpose ____________
____

40. Do these records indicate (please attach an example data sheet if possible)

date of event Yes____ No____

beginning and ending dates for cumulative sampling period Yes____ No____

amount of precipitation Yes____ No____

temperature Yes____ No____

pH Yes____ No____

conductivity Yes____ No____

signature Yes____ No____

additional comments Yes____ No____

10.3 Site Documentation Evaluation

10.3.1 General Guidance - During the initial phase of network installation, each site should be documented using a site documentation form such as that included in Section 5.0 or that used by the NADP. This form should be completed by organization personnel to record station location, site classification, station instrumentation, topography and important pollutant sources. This documentation should be repeated at least annually thereafter.

It is important that the information contained on such site documentation be verified as accurate. While it does not fall within the scope of the quality assurance function to prepare these site documents, the Quality Assurance officer should verify, for a small number of sites, that the information contained in such documents is accurate and complete. He should note any changes which may affect data quality and notify organization management of such problems. Of particular importance in this regard are sites where collocated instrumentation has been placed; such data may be used to estimate measurement or data precision.

The suggested questions in 10.3.3 should only be used as guidance and should be modified as necessary to fit the exact documentation used in the Site Description Report. In general, the site evaluation auditor will perform the following tasks:

(a) obtain from organization management completed copies of site description documentation;

(b) schedule on-site visits for all or a representative number of sites;

(c) evaluate site and seek information to answer those questions given in the questionnaire (10.3.3 or Appendix B); and

(d) prepare a site evaluation report.

This site documentation evaluation may be performed concurrently with the site visitations required for program audits.

10.3.2 Site Evaluation Reporting - At the conclusion of a site evaluation or evaluation of a group of sites for a single organization, the auditor should prepare a brief written report. This report should include at least a discussion of observations made during the site visit as noted in the questionnaire and a copy of the site documentation used for the evaluation. Where major discrepancies are noted, additional information needs to be included. If further documentation has been provided by the auditor, a newly completed accurate site description document should be attached. Recommendations to improve siting and thus the data quality obtained from the respective sites should be included.

10.3.3 Site Documentation Review - to be completed for each site reviewed

1. Site Address ____________________

   Designation (Number/Identifier) ____________________

2. Has the data acquisition objective changed?
   Yes_______ No_______ Comment ____________________

   ____

3. Verify the longitude and latitude by independently obtaining maps of the area. OK ______ Problem ____________________

4. Are the names, addresses and identification of responsible individuals still valid? If not, note changes. ____________________

   ____

   ____

5. Verify that all instrumentation is present and note any that are not operational. Give reason for non-operation and estimate of down-time. Is this a potential data impactor? Comment ____________________

   ____

   ____

6. Has additional equipment been added since the site documentation was prepared or equipment removed or changed? Add any changes to the equipment list.

   ____

   ____

   ____

   ____

7. If measurements are made at the site (or closely located site laboratory), verify the indicated information on type, model, description, etc., of pH and conductivity meters, balance, etc.
   OK ____________________ Problem ____________________

8. Is there a map indicating location and distances to the major sources which may affect data gathered at the site?
   Yes ______ No ______

9. Is it still valid? Yes _____ No _____ Or have the number and/or location of sources changed? ______________________________
Note problem areas ______________________________________

10. Review sketch of map. Is it complete with respect to indication of roadways, parking areas, buildings (including number of stories), tree lines, power lines, bodies of water, and fences?
Complete _____________ Incomplete (note problem areas) ___________

____

____

11. Verify all distances using a tape measure or rule? Indicate significant discrepancies. _______________________________________

____

____

12. Walk around the site and compare view in the four cardinal directions with that as given in the site photos. If photos have not been included with the site documentation, the auditor should take at least one in each of the four cardinal directions (N,S,E&W) looking outward from the main sampler.

13. Are there any obstacles with a height that subtends an angle of 30° with the ground horizontal?

____

____

14. Are the precipitation collectors and/or rain gauges at least 7 feet (2 meters) apart and no further than 15 meters apart?

____

____

15. Are rain gauge and precipitation collector placed in a line perpendicular or parallel to the prevailing wind, or in the direction specified for network sites? If parallel, is the wet bucket end upwind of the rest of the collector?

____

____

16. Is the rain gauge level? Yes _____ No _____ Comment ____________

17. Is the access door to the rain gauge on the leeward side of the wind path? Yes ______ No ______ Comment ______________________________

18. Is the rain gauge capable of measuring 0.01" (.025cm) of precipitation? Yes ______ No ______ Comment ____________________________________

19. Is the precipitation fall to the sites unobstructed? (The auditor should comment on vegetative obstructions such as trees which do not now pose any problem but which may impact precipitation within the next few years.) ____________________________________

____

____

____

20. For collocated precipitation collectors is the distance between them 7-45 ft (2-15 meters)? Yes ______ No ______ Comment ____________________________________

____

21. Will there be any changes made to the site or site equipment in the near future? Note the intended changes and schedule, and estimate any potential data impact. (Attach sheets as necessary.)

10.4 Laboratory Operations Evaluation

Each analytical support laboratory should be evaluated at least once each year to qualitatively assess the laboratory's ability to produce analytical data of high quality. Such an evaluation is commonly referred to as a systems audit and is performed in a manner very similar to that described in Section 10.2 for systems audits of overall operations.

10.4.1 Procedure - A laboratory systems audit is normally conducted in three steps. First, a questionnaire, such as that included in Section 10.4.2, is sent to the analytical laboratory prior to the audit visit. The laboratory should then fill out the questionnaire as completely as possible and return it with sufficient documentation through the use of attachments. Second, the questionnaire is reviewed by the auditor to become familiar with the system operations and to determine any weaknesses and potential problem areas. Third, after the questionnaire has been reviewed, the onsite interviews are scheduled. The preliminary review of the questionnaire serves the purpose of allowing a greater amount of time to be spent onsite examining potential problem areas.

The auditor should interview the laboratory manager, any person who has direct analytical responsibility for precipitation sample analysis, personnel associated with data validation, analysis and reporting, and the person identified by the laboratory manager who has responsibility for quality assurance. The information gathered from these interviews should be complete and up to date and should present an adequate picture of the current and proposed levels of implementation of all quality assurance activities, including internal quality control.

At the conclusion of the series of interviews, the auditor should inform the laboratory manager of the audit interview results and discuss any potential data impacting problems uncovered. This is commonly referred to as an exit interview. During this activity, the auditor also explains the reporting procedures and schedule.

10.4.2 Analytical Laboratory Questionnaire

GENERAL INFORMATION

Questionnaire Completion Date ____________________

On-Site Visit Date ______________________________

Laboratory: ____

____

Street Address: ____

City: ____________________ State: ____________________ Zip: _______________

Laboratory Phone No. (Area Code)(______)________________________________

Organization Director: ____

Laboratory Director: ____

Quality Assurance Officer: ____
(Quality Control Chemist)

Questionnaire completed by (if more than one, please indicate which section(s) of the questionnaire completed):

____

____

On-Site Audit Conducted by: _______________________________________

____

Affiliation of Auditor(s): ____

____

Persons Present During Entrance Interview: ____________________________

____

Persons Present During Exit Interview: ________________________________

____

A. GENERAL

1. Please use a simple block diagram to show the organization structure and how the laboratory functions within it.

2. Standard Operating Procedures (SOP)

   a. Has the organization written and implemented official Standard Operating Procedures?

   Yes_____ No_____ Comment_____________
   Implementation Date: ____________________________

   b. Is the SOP Manual followed in detail?

   Yes_____ No_____ Comment_____________

   c. Does it contain all quality control steps practiced?

   Yes_____ No_____ Comment_____________

   d. Does each analyst have a copy at his/her disposal?

   Yes_____ No_____ Comment_____________

   e. Has an instrument performance study been completed for each analysis?

   Yes_____ No_____ Comment_____________

3. Please provide a complete list of laboratory personnel, their educational background, analytical experience in general and specific experience in precipitation sample analysis.

4. Laboratory Staff Training

a. Is a formal training program used? Yes_____ No_____

If yes, is it:

Organization wide Yes_____ No_____

In-house Yes_____ No_____

On-the-job training Yes_____ No_____

b. Training ouside local organization (courses attended).

Course description or title	Who attended	Course length	Course type*	Year of attendance

*State, Federal, College, University or other

c. Publications routinely received and used by the organization.

5. Laboratory Facilities

Item	Available		Comments
	Yes	No	(adequacy of facility and/or space)
1. Support Gas			
2. Lighting			
3. Compressed Air			
4. Vacuum Systems			
5. Electrical Services			
6. Hot and Cold Water			
7. Laboratory Sink			
8. Ventilation System			
9. Hood Space			
10. Cabinet Space			
11. Bench-top Area			
12. Lab Space			
13. Lab Space Utilized for Offices			
14. Office Space			
15. Storage Space			

6. Laboratory Equipment

Item	# of units	Equipment Make Model	Condition/Age Good-Fair-Poor	Ownership Air Water	% of time used in Rainwater Programs
Balance analytical					
Vacuum Filtration apparatus					
NBS traceable calibrated thermometer					
Desiccator					
Ion Chromatograph					
Technicon					
Atomic Absorption					
Balance, top loader					
Class "S" weights					
Balance table					
Distilled water or deionized water					
Conductivity meter					
Glassware					
pH meter					
Drying oven					
Hot plates					
Refrigerator					

B. SAMPLE LOGISTICS

Receiving Clerk ______________________ Initials __________
(Name)

		Yes	No
1.	Are all chemicals dated on receipt and discarded when shelf life is exceeded?		
2.	Are all samples received by the laboratory logged into a bound notebook?		
3.	Are all samples filtered before analysis?		
4.	Are all samples stored in the refrigerator between analyses?		
5.	Are all containers washed before they are sent to the field?		
6.	Is the conductivity of the last rinse water measured for 10% of the washed containers?		
7.	If the conductivity of the rinse is greater than 2 µmhos/cm, is the container rinsed further?		
8.	After the containers and lids are dried are the containers capped immediately?		
9.	Are precautions taken not to touch the inside of the containers and lids?		
10.	Are all samples stored in a refrigerator when not being analyzed?		
11.	Are precautions taken not to breathe on the sample?		
12.	After completion of the analyses, are the samples stored in a refrigerator for at least six months?		

C. GRAVIMETRIC MEASUREMENTS

1. Is the analytical balance calibrated daily with weights traceable to NBS? ____ ____

2. Is a Balance Calibration Log kept up to date? ____ ____

3. Is routine factory service scheduled? ____ ____

   Date next service is due: ____________________

D. pH MEASUREMENT

Analyst ______________________________ Initials __________
(Name)

		Yes	No
1.	Does the analyst have his/her own copy of the standard operating procedures?	____	____
2.	Does the analyst have his/her own copy of instrument performance data?	____	____
3.	Does the analyst have his/her own copy of safety instructions?	____	____
4.	Does the analyst have his/her own copy of the latest monthly QC plots?	____	____
5.	Is the analyst aware of the most recent control limits?	____	____
6.	Does the analyst have a copy of the most recent list of samples in-house to be analyzed?	____	____
	Date of list ______________________		
7.	Are all solutions properly labelled?	____	____
8.	Has a pH Meter/Electrode Acceptance Test been completed and documented for the meter and electrode currently in use?	____	____
9.	Is the pH electrode rinsed well before and after buffer and sample measurements?	____	____
10.	Before and after samples are analyzed, is the pH meter and electrode calibration checked with simulated precipitation reference samples (low ionic strength)?	____	____
11.	Is the pH meter recalibrated after every set of twenty samples with simulated precipitation reference samples (low ionic strength)?	____	____

12. After the initial calibration of the day, when the meter is recalibrated after a series of measurements, is the old calibration information written down before the meter settings are changed? ____ ____

13. Is the pH electrode reference solution analyzed first and are the results compared to the pre-established control or warming limits? ____ ____

14. Are the following control samples analyzed with each run?

Distilled Water Blanks ____ ____

Old Samples ____ ____

QC Spike ____ ____

15. Are electrodes stored as recommended by the manufacturer? ____ ____

16. Are electrodes checked and filled, if necessary, before each analysis? ____ ____

E. TOTAL ACIDITY ANALYSIS

Analyst - ______________________________ Initials__________
(Name)

	Yes	No
1. Does the analyst have his/her own copy of the standard operating procedures?	_____	_____
2. Does the analyst have his/her own copy of instrument performance data?	_____	_____
3. Does the analyst have his/her own copy of safety instructions?	_____	_____
4. Does the analyst have his/her own copy of the latest monthly QC plots?	_____	_____
5. Is the analyst aware of the most recent control limits?	_____	_____
6. Does the analyst have a copy of the most recent list of samples in-house to be analyzed?	_____	_____
7. Are all solutions properly labelled?	_____	_____
8. Has a pH Meter/Electrode Acceptance Test been completed and documented for the meter and electrode currently in use?	_____	_____
9. Are micropipets calibrated on at least a quarterly basis or whenever the tip breaks?	_____	_____
10. Are repipets calibrated on a quarterly basis?	_____	_____
11. Is the stock 1.0 N NaOH standardized each month against potassium acid phthalate and protected from CO_2 absorptions?	_____	_____
12. Is solution temperature carefully monitored during analysis to see that it changes by less than 0.1°C?	_____	_____

13. Are conditioning solution data and analyst spike data calculated and plotted real time? _____ _____

14. Are the ψ function correlation coefficients of these data examined to ensure that they are greater than 0.9990? _____ _____

15. Are the following analyzed each day?

    Three conditioning solutions and an analyst spike initially. _____ _____

    An analyst spike and a conditioning solution at the end of the analysis. _____ _____

    A QC spike. _____ _____

16. Are electrodes stored as recommended by the manufacturer? _____ _____

17. Are electrodes checked and filled if necessary before each analysis? _____ _____

F. AUTOMATED COLORIMETRY MEASUREMENTS

Analyst ______________________________ Initials __________
(Name)

		Yes	No
1.	Does the analyst have his/her own copy of the standard operating procedures?	____	____
2.	Does the analyst have his/her own copy of instrument performance data?	____	____
3.	Does the analyst have his/her own copy of safety instructions?	____	____
4.	Does the analyst have his/her own copy of the latest monthly QC plots?	____	____
5.	Is the analyst aware of the most recent control limits?	____	____
6.	Does the analyst have a copy of the most recent list of samples in-house to be analyzed?	____	____
7.	Are all solutions properly labelled?	____	____
8.	Is a Standard Preparation Form completed when new stock standards are prepared?	____	____
9.	Are dilute calibration standards prepared fresh daily?	____	____
10.	Is the analyst spike prepared fresh daily from an independent stock?	____	____
11.	Is the calibration curve at least a five point curve?	____	____
12.	Is the first calibration curve of the day checked for detection limit and linearity?	____	____
13.	Are the analyst spike data calculated and plotted real time?	____	____

14. Is each new calibration curve checked to see that instrumental response changed less than 5%? ____ ____

15. Are the following control samples analyzed with each run?

Blanks ____ ____

Old Samples ____ ____

Analyst Spikes ____ ____

QC Spike ____ ____

16. Is water pumped through all lines daily before and after analysis? ____ ____

17. Are pump tubes changed at least once per month? ____ ____

18. Is the pump cleaned when the pump tubes are changed? ____ ____

19. Is soap solution pumped through all lines once per week? ____ ____

20. Is the flowcell cleaned with a sulfuric acid-potassium dichromate solution once per month? ____ ____

21. Is the pump oiled once per three months? ____ ____

Date of last service ________________

22. Is the colorimeter mirror assembly and color filter cleaned and the alignment optimized once per three months? ____ ____

Date of last service ________________

G. ION CHROMATOGRAPHY ANALYSIS

Analyst ______________________________ Initials __________
(Name)

	Yes	No
1. Does the analyst have his/her own copy of the standard operating procedures?	_____	_____
2. Does the analyst have his/her own copy of instrument performance data?	_____	_____
3. Does the analyst have his/her own copy of safety instructions?	_____	_____
4. Does the analyst have his/her own copy of the latest monthly QC plots?	_____	_____
5. Is the analyst aware of the most recent control limits?	_____	_____
6. Does the analyst have a copy of the most recent list of samples in-house to be analyzed?	_____	_____
Date of list ___________________________		
7. Are all solutions properly labelled?	_____	_____
8. Is a Standard Preparation Form completed when new stock standards are prepared?	_____	_____
9. Are dilute calibration standards prepared fresh weekly?	_____	_____
10. If manual techniques are used, are samples and eluent prepared fresh daily from the same concentrated stock buffer?	_____	_____
11. Is the analyst spike prepared from an independent stock?	_____	_____
12. Is the calibration curve at least a four point curve for each analytical range?	_____	_____

13. Is the first calibration curve of the day checked for detection limit and linearity? _____ _____

14. Are the percent recoveries for the analyst spike data calculated in real time and compared to pre-established warming and control limits? _____ _____

15. Are the following control samples analyzed with each run?

    Blanks _____ _____

    Old Samples _____ _____

    Analyst Spikes _____ _____

    QC Spike _____ _____

16. Is the drip tray examined daily for reagent spills, and are spills cleaned up daily? _____ _____

17. Are pumps oiled once per week? _____ _____

18. Is the anion precolumn cleaned once per month with 0.1 M Na_2CO_3? _____ _____

19. Is the Br^-, NO_3^- resolution checked once a month and documented? _____ _____

H. ATOMIC ABSORPTION ANALYSIS

Analyst ______________________ Initials ________
(Name)

	Yes	No
1. Does the analyst have his/her own copy of the standard operating procedures?	____	____
2. Does the analyst have his/her own copy of instrument performance data?	____	____
3. Does the analyst have his/her own copy of safety instructions?	____	____
4. Does the analyst have his/her own copy of the latest monthly QC plots?	____	____
5. Is the analyst aware of the most recent control limits?	____	____
6. Does the analyst have a copy of the most recent list of samples in-house to be analyzed?	____	____
Date of list ______________________		
7. Are all solutions properly labelled?	____	____
8. Is a Standard Preparation Form completed when new stock standards are prepared?	____	____
9. Are dilute calibration standards prepared fresh monthly?	____	____
10. Is the analyst spike prepared from an independent stock?	____	____
11. Is the instrument allowed to warm up at least 15 minutes with the flame on before the final wavelength adjustment is made?	____	____
12. Is the calibration curve at least a five point curve?	____	____

13. Is the first calibration curve of the day checked for detection limit and linearity? _____ _____

14. Are the analyst spike data calculated and plotted real time? _____ _____

15. Is each new calibration curve checked to see that instrumental response changed less than 5%? _____ _____

16. Are the following control samples analyzed with each run?

Blanks _____ _____

Old Samples _____ _____

Analyst Spikes _____ _____

QC Spike _____ _____

I. DATA MANAGEMENT

Data Clerk ______________________________ Initials __________
(Name)

		Yes	No
1.	Are field data sheets filled in an organized manner?	____	____
2.	Does the data clerk do a 100% QC check for accuracy of data input to the computer?	____	____
3.	Is output from computer checked with input data?	____	____
4.	Does strip chart reduction by on-line electronic digitization receive at least 5% manual spot checking?	____	____
5.	Are control charts or equivalent checks (e.g., computer calculated range limits or regression charts) current and available for inspection?	____	____
6.	Do laboratory records include the following information?		
	a. Sample identification number	____	____
	b. Station identification	____	____
	c. Sample type	____	____
	d. Date sample received in laboratory	____	____
	e. Time, date and volume of collection	____	____
	f. Date of analysis	____	____
	g. Analyst	____	____
	h. Results of analysis (including raw analytical data)	____	____
	i. Recipient of the analytical data	____	____

7. Are rain gauge chart data for event times and amount checked? ____ ____

8. Does laboratory follow chain-of-custody procedures from sample receipt to discard? ____ ____

9. Does the data clerk routinely repot quality control data sheet information to the analyst? ____ ____

10. Does the data clerk submit quality control data sheet information to the lab manager along with the analytical data to be reported? ____ ____

11. Are computer printouts and reports routinely spotchecked against laboratory records before data are released? ____ ____

12. Are manually interpreted strip chart data spotchecked after initial entry? ____ ____

13. Are minimum detection limits calculated by an approved method or baseline standard deviation? ____ ____

14. Are calibration curve coefficients tabulated and regularly reviewed as evidence for instrumental control? (An alternative is to use Regression-Hypothesis testing in lieu of control charting.) ____ ____

15. Are control charts, regression charts or computer QC data bases up to date and accessible? ____ ____

J. LABORATORY QUALITY CONTROL

Quality Control Chemist ______________________________ Initials __________
(Name)

	Yes	No
1. Does the QC chemist have his/her own copy of the standard operating procedures?	____	____
2. Does the QC chemist have his/her own copy of instrument performance data?	____	____
3. Does the QC chemist have his/her own copy of safety instructions?	____	____
4. Does the QC chemist have his/her own copy of the latest monthly QC plots?	____	____
5. Is the QC chemist aware of the most recent control limits for each analytical method?	____	____
6. Does the QC chemist prepare and submit a blind QC spike once per month for each analytical method?	____	____
7. Does the QC chemist routinely review and report blind QC spike data to the laboratory manager?	____	____
8. Does the QC chemist update control limits and obtain new control chart plots once per month?	____	____
9. Does the QC chemist review the quality control data sheet provided by the data clerk, and then decide whether or not to release data for reporting?	____	____
10. Does the QC chemist prepare monthly check samples for the field sites?	____	____
11. Does the QC chemist compare the laboratory and field data to the monthly check sample's value and report this to the laboratory manager?	____	____

K. LABORATORY MANAGEMENT

Laboratory Manager ______________________________ Initials __________
(Name)

	Yes	No
1. Does the laboratory manager have his/her own copy of the standard operating procedures?	_____	_____
2. Does the laboratory manager have his/her own copy of instrument performance data?	_____	_____
3. Does the laboratory manager have his/her own copy of safety instructions?	_____	_____
4. Does the laboratory manager have his/her own copy of the latest monthly QC plots?	_____	_____
5. Is the laboratory manager aware of the most recent control limits?	_____	_____
6. Does the laboratory manager review the following before reporting data?		
a. The data itself	_____	_____
b. The quality control data sheet with analyst notes	_____	_____
c. The quality control chemist QC reports	_____	_____
d. The ion summation ratios for the data	_____	_____
e. The calculated vs. measured sample conductivity	_____	_____
7. Does the laboratory manager ensure that at least 5% of the data have been checked indepedently by the QA officer? (p. 1 of 6, Section 3)	_____	_____
8. Does the laboratory manager ensure that all the necessary corrections have been implemented in the data base before release?	_____	_____

10.5 Performance Audits

10.5.1 Network Performance Audits - A performance audit for a precipitation monitoring network should be made at least once per year on all sites. The purpose of the audit is to quantitatively assess site operations which are usually performed during the site and/or field laboratory audit visit. This on-site visit may be combined with a site evaluation or other types of audits such as program systems audits or laboratory systems audits.

Detailed and complete protocols for performance audits of an organization's precipitation network should be developed by the organization operating the network. A complete performance audit should be designed to include, as a minimum, the following activities:

1. Check Sample Analysis -- The auditor takes to the site a 150-ml check sample of known pH and conductivity. Such samples are prepared by the auditor's support laboratory to closely resemble that site's ambient samples in terms of pH and conductivity. The sample can then be used as follows:

   (a) The station operator is requested to provide a precleaned bucket.

   (b) The auditor adds the sample to the clean bucket.

   (c) The station operator is asked to treat this sample as though it were a routine precipitation sample.

   (d) The auditor observes, asks questions, and takes notes on sample treatment and field measurements (usually sample volume or weight, pH and conductivity).

   (e) The auditor records the results of the pH, conductivity and volume (wt) measurements and, based on a comparison of the support laboratory value with that obtained by the station operator, an assessment of the accuracy of site measurements is obtained.

2. Calibration of Weighing Bucket Rain Gauge -- The auditor brings to the site a set of calibrated weights. Such weights may be obtained directly from the rain gauge manufacturer but should be certified at the auditor's

support lab prior to the audit. At the site the auditor proceeds as follows:

(a) The rain gauge stripchart in use is marked, checked for the correct time setting, removed and a new chart put in place. The new chart is used for the audit.

(b) The gauge funnel and collection bucket are removed.

(c) The weight-handle assembly is placed on the platform normally occupied by the collection bucket and the gauge is zeroed.

(d) Weight plates representing 1" depths (approximately 825 grams each for the Belfort gauge) are then stacked onto this assembly and the indicated inches of precipitation are read from the stripchart recorder.

(e) If the gauge is properly calibrated, each weight should cause the stripchart to indicate 1" of rain. Since added weights are known, the found (read from the stripchart) and audit (calculated from known weight) precipitation amounts may be compared.

(f) The gauge is calibrated to at least twice the maximum precipitation expected for that site or to 8", whichever is greater. If the gauge is out of calibration by more than 0.05 in. at any depth, it must be adjusted according to the manufacturer's directions.

(g) The stripchart is removed and the original chart replaced and the pen set to the correct time. The audit chart is annotated and kept with the records of the audit.

3. Operation of Wet/Dry Automatic Sampler (e.g. Aerochem Metrics) -- This is performed to check proper sampler operation and to make certain that the sampler would collect an entire precipitation event if one occurred. To check this, the auditor should add 1-2 drops of distilled or deionized water to the precipitation sampler sensor. The sampler is judged to be operating normally if, within a few seconds, the lid covering the wet bucket moves to cover the dry bucket.

After the wet bucket has been open for several minutes, the auditor should touch the sensor plate to check that it is heating. If so, the moisture is removed from the sensor plate by blowing. The sensor plate then dries more quickly and the lid should cover the wet bucket again.

Lid opening and closing cycles may occur during an event. Where the rain gauge at the site has been interfaced with the sampler and equipped with an event pen, the auditor should check if marks, indicating a lid cycle, are recorded on the rain gauge strip chart.

4. Review of Site Procedures and Data Documentation -- The auditor should observe site personnel performing all the routine site operation duties. This should include handling of samples and sampling containers, checks on instrumentation and data recording. If a check sample has been analyzed, as described above, part of this check has already been performed.

   If an analysis check sample has not been used, the auditor should ask site personnel to describe in detail how samples, buckets and measurements are handled. After determining (or observing) sample handling, the auditor should then interview site personnel to gather detailed information on standards (pH and conductivity), sample treatment after analysis, water supply and data recording. This interview is used to assess operator training and performance and to establish sample and data integrity up to the point where both leave the site.

10.5.2 Performance Audit Reporting - At the conclusion of the audit, a short report should be prepared summarizing audit results and recommendations. The audit report should serve to establish that a precipitation sample from the audited site is collected, handled, measured, and shipped to a support laboratory for further analysis in a proper manner, and that all data are properly documented. A format for this report is suggested below together with material to be included under each topic.

1. Introduction - summary of data, time, place of audit, site and organization identification; and identification of people present during the audit.

2. Audit procedures - summary of audit procedures employed together with notation of any deviations from previous accepted procedures. Included are references to traceability to establish credibility of all standards used for the audit.

3. Site operations and audit results - summary of data obtained both from observations and interviews of site personnel; included in this section should be copies of data forms used at the site and/or other pertinent documentation; included at the end of this section are summary tables of the audit results themselves.

4. Discussion of audit results and recommendations - brief discussion and interpretation of the results together with a discussion of any problem's impact on data integrity and quality. Recommendations should also be included to remedy such problems.

10.5.3 Laboratory Performance Audits - As a part of the independent checks to evaluate the quality of data provided by the total measurement system, performance audits of the central analytical laboratory provide an assessment of measurement accuracy. These audits are carried out by having the laboratory analyze well-characterized, independently-prepared simulated precipitation solutions.

Performance audits should be conducted at least quarterly by analyzing rain-type solutions for all the observables reported in precipitation samples. It is acceptable to send the samples to the laboratory and request that they be processed as "blind" samples. Performance audits of field pH and conductivity should be performed during an on-site program audit.

Samples useful for performance assessment are available from at least four organizations - Environmental Protection Agency/Environmental Monitoring Support Laboratory (Cincinnati), United States Geological Survey, Environmental Protection Agency/Environmental Monitoring Systems Laboratory (Research Triangle Park), and the Canadian National Water Research Institute. The first three organizations conduct interlaboratory surveys every six months; the Canadian tests are more frequent. Each analytical laboratory supporting an acid precipitation monitoring program is encouraged to participate in these round-robin surveys.

1. EPA Cincinnati - (Quality Assurance Branch, EMSL - Cincinnati, EPA, Cincinnati, Ohio 45268, 513/684-7327). QC water/wastewater samples are available without cost. All samples are prepared from ACS reagent grade chemicals and are sent as concentrates in sealed glass ampoules. When diluted to the indicated volume, values obtained by the laboratory should agree with those given by the EPA. Samples are available for:

Minerals/Physical Analyses - Na^+, K^+, Ca^{+2}, Mg^{+2}, SO_4^{-2}, Cl^-, F^-, pH, alkalinity/acidity, total hardness, total dissolved solids, and specific conductance (available in two concentrations).

Nutrients - Nitrate-N ammonium,-N, Kjeldahl-N, orthophosphate and total phosphorus (available in two concentrations).

2. United States Geological Survey - (Leroy Schroder, Water Resources Division, USGS National Water Quality Laboratory, 5293 Ward Road, Arvada, CO 80002). These samples approximate precipitation samples. They are available in a limited supply and may be requested only by government laboratories.

3. EPA Research Triangle Park - (Performance Evaluation Branch - MD77B EMSL-RTP, EPA, Research Triangle Park, NC 27711, 919/541-4531). These are commercially prepared, reference, concentrated synthetic rain samples of well-characterized composition. They are prepared from reagent grade salts, following a procedure developed by the National Bureau of Standards. Samples are characterized by analysis by EPA and three (3) independent laboratories. Dilution instructions are supplied with the samples, together with appropriate reporting forms. They are available free of charge to both private and governmental organizations.

4. Canadian National Water Research Institute - (Mr. K.I. Aspila or Ms. Susan Todd, National Water Research Institute, P.O. Box 5050, 867 Lakeshore Rd., Burlington, Ontario L7R4A6, 416/637-4638 or 637-4653). Samples consist of soft water, precipitation and synthetic rain and have all the constituents present in precipitation. Samples available only during test periods.

For ongoing accuracy assessment during those quarters when interlaboratory or round-robin surveys are not available, the laboratory is encouraged to obtain and use additional samples from the suppliers given above. It is important that all samples used for such accuracy assessment be submitted "blind" in order to obtain a representative picture of ongoing operations.

For performance audits, it is not recommended that the laboratory prepare its own independent standards since no easy means exists to characterize them well before use. In all cases the known integrity of the purchased standards is higher than that which can easily be achieved by a single laboratory, and the turnaround time on results for such samples should be sufficiently short to prove useful.

10.6 Data Processing Audits

10.6.1 General Guidance - Data processing may involve reading a strip chart or other instrument output tape, calculating the concentrations and transcribing these results to a data form. In a data processing audit a certain percentage of results is recalculated. In a system which has a large proportion of manual data processing activity, the audit should be regularly performed by an individual other than the one who originally reduced the data. In a computerized data acquisition environment the difference in personnel may not be as critical but, in general, the audit should be performed as independently and objectively as possible.

The data processing audit should be performed on each of the groups of data as they are reported. Thus if an agency is reporting summaries by quarter, each quarter's data should be checked. Similar strategies should be employed for semiannual or annual reporting.

The auditor should obtain the complete data base for that period. At least 5% of the total number of events in the audit data base should be selected at random for checking. Since calculation of data is critical for a proper derivation of precision summaries for collocated sites in the network, at least one site with collocated samples should be included in the audited data. For each site, at least two analytes other than pH or conductivity should be recalculated. Note that the same two analytes may be used for all sites.

If the recalculated results do not agree to within rounding errors with the reported values, the entire data base should be rejected and returned to the laboratory supervisor for further quality control measures and data validation before being released.

10.6.2 Estimating the Percent Error in a Data Base - The following can be applied to estimate the percent error in data bases. Each organization will differ in the total number of values in its data base and the acceptable error level. For large data bases ($N \geq 3000$) and for the simple case where no errors are found in n values tested, the following table gives the approximate n

values required to be checked to yield the listed error probability p at the significance level x:

x	0.05	0.05	0.05	0.05	0.10	0.10
p	0.01	0.02	0.05	0.10	0.01	0.10
n	298	148	58	28	229	22

Thus for a large data base, if 148 values are checked and no errors found, the probability of errors in the base is less than 2% at the 5% significance level (95% probability).

For small to moderate size data bases ($N \leq 3000$), the above binomial approximation is inadequate. Therefore, an approximation to a non-replacement sampling model is used. For testing that the data base has less than 2% errors (at the 5% significance level), the following table yields the number of test values n needed, for N values in the data base:

N	100	1000	3000
n	78	140	146

If errors are found in the tests, the upper and lower confidence bounds b of the error fraction (f) of a data base of size n can be estimated from Equation 10-1.

$$f = nb \pm 1.96[n(1-b)]^{1/2} \quad \text{10-1}$$

where the test is applied to $n \simeq 300$ measurements ($n \simeq 0.1N$) and f failures (errors) are found. The larger the parent base N, the more accurate the estimate. Thus if a random check of 706 values in a data base of over 7200 values yields 14 errors, the error bounds are approximately 3.3 to 1.2%.

APPENDIX A

Operation and Maintenance Procedures for Precepitation Measurement Systems

(Originally Volume Vb of the Quality Assurance Handbook,
EPA 600/4-82-042b, Revised 1986)

CONTENTS OF APPENDIX A

Section

CONTENTS (Continued)

Section

CONTENTS (Continued)

Section

1.0 INTRODUCTION

The increasing national awareness of the harmful effects of acid deposition on the ecology and materials has led to a significant increase in the number of deposition monitoring networks and related effects studies. It has become necessary to provide uniform, systematic and approved precipitation monitoring procedures so that the acquired data are accurate and comparable among all monitoring networks. The purpose of this operations and maintenance (O & M) manual is to describe in detail the currently recommended procedures for conducting precipitation monitoring. However, it is essential that these procedures be supplemented by the quality assurance tasks which are presented in the Quality Assurance Manual for Precipitation Measurement Systems (1). While these two manuals contain the procedures recommended by the Environmental Protection Agency, it must be emphasized that network protocols take precedence if conflicts occur.

The basic goals of this manual are to instruct how to collect representative samples without contamination and to preserve sample integrity for analysis. The possibility of sample contamination, degradation, or reaction must be minimized. The sample collector, the first object that contacts the sample, must meet these basic goals and must be reliable. The Department of Energy (DOE) Health and Safety Laboratory (HASL) type automatic, wet/dry collector (2), (3), (4) has been tested and accepted by most U.S. monitoring networks. Discussion is limited to this type of collector. A reliable rain gauge, pH and conductivity meter, a balance, and other accoutrements are also needed in a monitoring station.

The material in this manual is based primarily on the procedures used in the Electric Power Research Institute (EPRI) precipitation network and the Utility Acid Precipitation Study Program (UAPSP) in the Eastern United States, in the National Atmospheric Deposition Program (NADP), and in the Multi-State Atmospheric Power Production Pollution Study (MAP3S).

The EPA handbooks for air pollution measurements (5,6) and for water measurements (7) were used as guides for format and content. The analytical procedures are based on those in the manual: Development of Standard Methods for the Collection and Analysis of Precipitation (March, 1986) (7). To have this O & M manual stand alone without requiring referrals to the other EPA handbooks, some duplication of material was required; this material is referenced.

1.1 COLLECTION SITES

Collection sites must be located to meet the objectives of the monitoring program--for example, baseline, regional or urban, and siting criteria is given in Section 5.0 of the quality assurance manual (1). The quality assurance manual also contains the general rules for the placement of precipitation collectors, and the appropriate siting documentation. In addition, siting characteristics may be quantified (8) if desired. In essence, the site must yield representative samples--thus must not have obstructions which may affect the results.

1.2 PARAMETERS AND ANALYTES GENERALLY MEASURED

The constituents and/or indicators commonly measured are listed below. All are measured in the laboratory; items 8, 9, and 10 are also measured in the field.

1. Sulfate ($SO_4^{=}$) - Concentrations above the baseline values are caused mainly by human activities, principally by the release of SO_2 during the burning of fossil fuels and during refining processes; the SO_2 is oxidized to sulfate in the atmosphere.

2. Nitrogen Compounds (NO_3^-, NH_4^+ and - NO_x - essentially $NO + NO_2$) concentrations above the baseline values are caused primarily by the burning of fossil fuels, such as for transportation purposes; NH_3 occurs chiefly from biochemical reactions.

3. Chloride Ion (Cl^-) - Originates chiefly from sea salt aerosols.

4. Phosphate (orthotribasic PO_4^{-3}) - Source is soil, rock, and fertilizers; an important nutrient.

5. Metal Ions (Na^+, K^+, Ca^{++}, Mg^{++}) - Na^+ originates mainly from sea salt aerosols, but all of these ions can originate from soil dust in desert, semiarid and intensively cultivated areas.

6. Acidity - both SO_2 and NO_2 form the strong acids found in precipitation; organic acids are frequently also present.

7. Alkalinity - Calcareous material (e.g., soil carbonate ($CO_3^=$)), can make precipitation alkaline, and can neutralize the effects of acids.

8. pH - A quantitative measure of precipitation acidity or alkalinity. In a theoretically clean atmosphere, a water sample in equilibrium with atmospheric CO_2 would measure pH 5.6; the acidity increases as the pH decreases from 5.6 to zero. Alkaline samples have pH 7 to 14.

9. Specific Conductance - The reciprocal of the resistance of a solution; its magnitude depends on the concentrations and types of dissolved salts.

10. Precipitation Amount - Value required both to calculate the weighted mean values of the constituents and to derive the total amount of materials deposited over a time period.

1.3 SAMPLING PERIODS, DEFINITION OF EVENT

Precipitation sampling schedules that are commonly used include weekly, daily, event, and subevent (sequential). An event can be defined as a storm separated from a second storm by a dry interval, commonly at least six hours in the winter or at least three hours in the summer. The sampling schedule depends on the objectives of the program and on the available funds. Aerometric and/or meteorological studies such as transport modeling often require daily or hourly sampling. Studies of long-term trends, and spatial and temporal variability generally use longer sampling intervals. Sampling periods longer than one week are not advisable because significant changes may occur to the sample while it remains in the collector.

1.4 REFERENCES

1. Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. V - Manual for Precipitation Measurement Systems, Part I - Quality Assurance Manual. U.S. Environmental Protection Agency, Research Triangle Park, NC. EPA-600/4-82-042a (January 1985).

2. Volchok, H.L., and R.T. Graveson, Proc. Second Fed. Conf. on Great Lakes, pp. 259-264 (1976).

3. Galloway, J., Water, Air and Soil Pollution 6, p. 241 (1976).

4. Bogen, D.C., Water, Air and Soil Pollution 13, p. 453 (1980).

5. Quality Assurance Handbook for Air Pollution Measurement Systems - Vol. I - Principles, U.S. Environmental Protection Agency, Research Triangle Park, N.C., EPA-600/9-76-005 (December 1984).

6. Quality Assurance Handbook for Air Pollution Measurement Systems - Vol. II - Ambient Air Specific Methods, U.S. Environmental Protection Agency, Research Triangle Park, N.C., EPA-600/4-77-027a (May 1977).

7. Development of Standard Methods for the Collection and Analysis of Precipitation, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH (March 1986).

8. Eaton, W.C. and E.L. Tew, "Site Evaluation Assistance to New and Existing Acid Precipitation Collection Sites in the State-Operated Network," Research Triangle Institute, RTP, NC, under EPA Contract 68-02-4125 (August 1985).

2.0 FIELD OPERATIONS

Precipitation collection field operations are covered in the following major areas:

1. Equipment operation and maintenance;
2. Sample collection, handling, measurement, preservation, storage, and shipment;
3. Documentation of field activities;
4. Quality control procedures.

Precipitation samples are very dilute, thus large measurement errors can occur due to contamination or degradation. Field procedures must be accomplished in a way that ensures measurement accuracy.

2.1 EQUIPMENT AND SUPPLIES

This section contains a list of the field equipment required for typical precipitation collection stations, followed by a list of spare parts for support of these stations. The section concludes with detailed descriptions of the precipitation collectors and rain gauges most commonly in use. The rain gauge measures the amount of precipitation, and the precipitation collector collects the sample for chemical analysis. The two devices are not interchangeable.

2.1.1 Station Supplies

The equipment and supplies required depend upon sampling objectives. Equipment and supplies for a weekly precipitation sampling station are listed in Table 2-1. If plastic bag bucket liners are used, the number

TABLE 2-1. FIELD EQUIPMENT LIST FOR EACH STATION

Equipment/Material	Min. Quantity/Site
Automatic precipitation collector	1
Collection buckets (3.5 gal) for sampler and lids	5
Fuses for sampler	2
Recording rain gauge with event marker	1
Rain gauge mount	1
pH meter, electrode	1
Buffer, pH 4.0, and 7.0 (1 liter)	1
Conductivity meter and cell	1
Standard KCl solution, 74 µS/cm (500 mL)	1
Temperature probe	1
Pipette, syringe (20 mL capacity)	1
Tips, disposable (pkg. of 100)	1
Balance (20 kg capacity) or graduated cylinder (2 liter)	1
Set attachment weights for balance (1,2,2,5,10 kg)	1
Mailing cartons	3
Wash bottle	1
Test tubes, plastic (17x100 mm) disposable, or vials (35 mL)	375
Test tube rack	1
Rain gauge charts (package of 100)	1
Self-adhesive labels	300
Envelopes	300
Logbook (bound with perforated pages)	1
Data forms	300
Kimwipes or other tissues (boxes)	15
Shipping tape (rolls)	3
Mallet, rubber	1
Deionized water	
Saran wrap (roll)	1
Bucket tie down	1

TABLE 2-1. FIELD EQUIPMENT LIST FOR EACH STATION (cont.)

Equipment/Material	Min. Quantity/Site
Additional Requirements for Bags:	
Bucket modified for use with bags	2
Bucket lids	2
Plastic bucket liners (bags)	50
Strap with Velcro fasteners	2
Polyethylene gloves (box of 100)	1
500 mL polyethylene bottles	50
Indelible marking pen (black)	2
Scissors	1
Plastic cable ties (pkg. of 100)	1

of wet buckets required are reduced from five to two and a supply of bucket liners, plastic gloves, plastic bottles, cable ties, two retaining straps, and scissors would be added to the list. Equipment required for event or daily precipitation sampling is similar. Similar supplies as listed in the table are also recommended for event or daily sampling. For sequential sampling, the list in Table 2-1 should include a different type of collector, a lower capacity (2.6 kg) more sensitive balance, polyethylene bottles with caps, and possibly a means for storing and shipping the sample in a cold state (insulated containers and freeze-gel packs), and few, if any, buckets. If meteorological and/or aerometric measurements are made, the appropriate instruments must be included in the list; however, these instruments are not discussed in this manual.

All sites require deionized or distilled water. If this cannot be produced at the site, it can be purchased locally. It is advisable to use only water which has the analysis (or conductivity) printed on the label. The specific conductance of the water should be 3 µS/cm or less and should be measured before the water is used.

2.1.2 Spare Parts

Precipitation collector fuses should be kept at each station along with spare parts and supplies. For larger networks, these items are more conveniently supplied through the field manager or the central laboratory when needed. Supplies for a network of 10 to 12 stations are listed in Table 2-2. The polyethylene bottles are for special sampling studies and/or for sample storage in the laboratory.

Electrodes in contact with solution have a limited life because the wet glass membrane ages. Only electrodes that can be stored in a dry state have a long shelf life. However, electrodes should not be emptied, cleaned and filled with electrolyte solution by the station operators. When an electrode breaks or becomes suspect (Section 2.5.3.3), it should

TABLE 2-2. SUPPLIES LIST FOR A NETWORK OF 10 TO 12 STATIONS

EQUIPMENT/MATERIAL	NO.
Precipitation collector fuses (12)	1
Precipitation collector sensor and motor box	2
Rain gauge clock	2
Rain gauge chart clip	3
Rain gauge chart paper (package of 100)	3
Rain gauge pens and ink (set)	1
pH meter	1
pH electrode	3
Buffer, pH 3.0, 4.0, 6.0, and 7.0 (1 gal)	2
Conductivity meter	1
Conductivity cell (cell constant ~1)	2
Standard KCl solution, 74 μS/cm	(a)
Syringe (20 mL)	20
Pipette, disposable tips	100
Shipping cartons and collection containers	36
Polyethylene sample bottles	
16 oz (500 mL)	600
8 oz (250 mL)	600
4 oz (100 mL)	600
2 oz (50 mL)	200
Wash bottle	12
Temperature probe	3
Test tubes, plastic (17x100 mm) disposable, 35 mL vials	1000
Test tube racks	12
Self-adhesive labels	1000
Envelopes	1000
Logbooks	12
Data forms	300
Kimwipes or other tissues (boxes)	36
Shipping tape (rolls)	12
Plastic bucket liners (bags)	500
Polyethylene gloves (pkg. of 100)	12
Bucket modified (for use with plastic bucket liners if network uses bags)	24
Collection buckets and lids (3.5 gal)	24
Saran wrap (roll)	12
Strap with fastener	24
Marking pen (black)	24
Scissors	12
Plastic cable ties (pkg. of 100)	12
Bucket tie down	24

(a) Make up as needed

be replaced with a new tested electrode from the central laboratory. Regardless whether the electrode is used or stored, it has a finite useful life.

2.1.3 Precipitation Collector Description

The HASL-type precipitation collector (see Figure 2-1 and Appendix A) has two containers and a common lid. 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. Two polyethylene buckets (1,2) are generally used to collect wet and dry deposition, respectively, for inorganic species. For organic constituents, glass or stainless steel containers should be used. 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 goes on when the temperature falls below approximately 4°C to melt snow or ice on the sensor plate, and the second goes on when the lid lifts off the sample bucket to heat the sensor to about 55°C. Heating increases the rate of water evaporation from the sensor, and hastens the closing of the wet bucket by the lid after precipitation ceases to minimize the exposure time 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. A bucket tie-down is useful in windy weather.

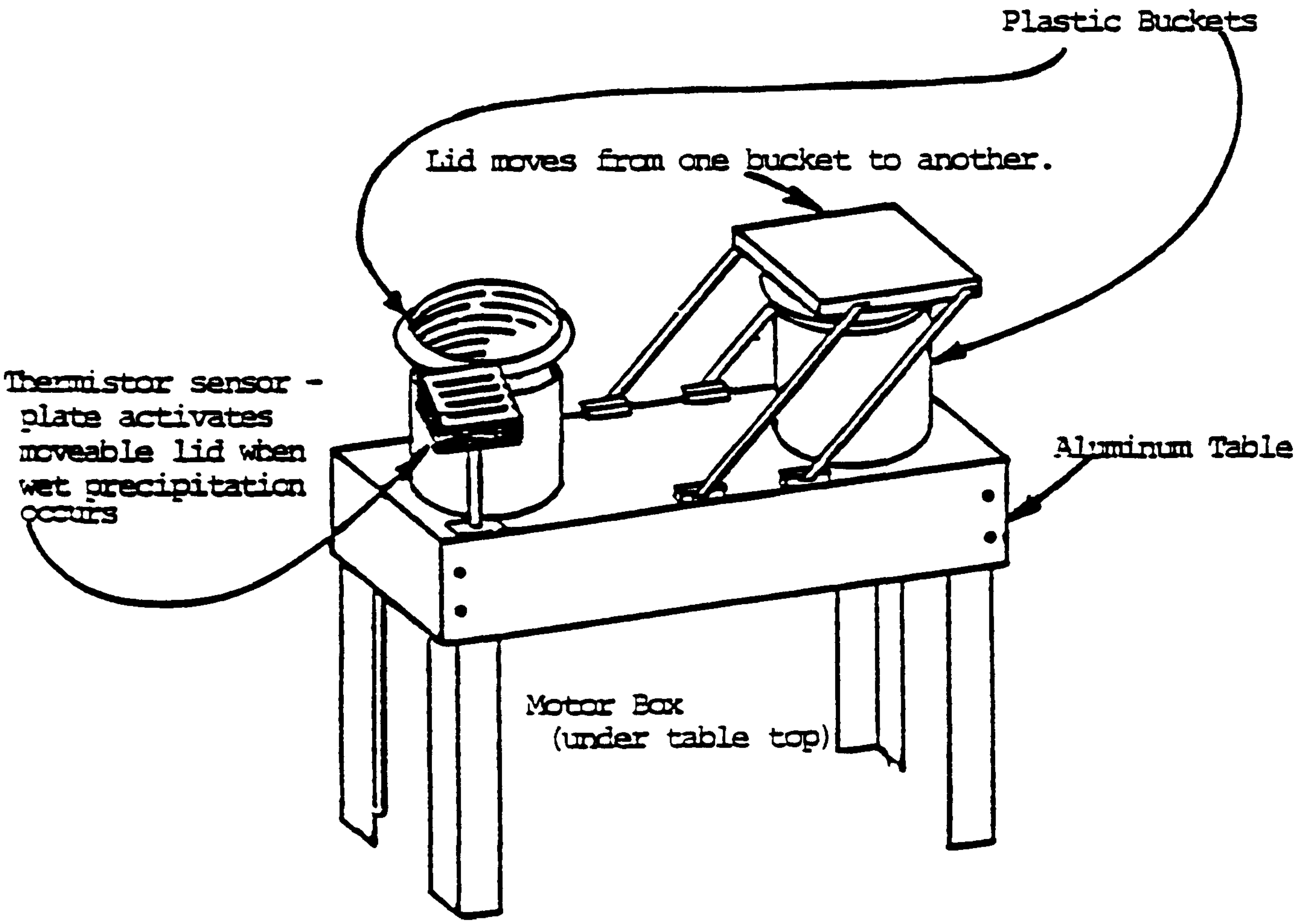

Figure 2-1. Wet/Dry Precipitation Collector

2.1.4 Rain Gauge Description

To reference all the precipitation amounts against a standard, a recording rain gauge is used to measure the quantity of precipitation. Recording rain gauges are of two basic designs (identified by the principle on which they operate)--the weighing-type gauge and the tipping bucket-type gauge. Recording rain gauges should be capable of measuring precipitation to approximately 0.25 mm (0.01 in.), and be accurate to a few percent. For the weighing gauges, the sensitivity is a few hundredths of an inch (less than 1 mm), and the accuracy is independent of precipitation rate and is about 1% of full scale. For the tipping bucket gauges, the generally accepted accuracy is 1% for precipitation rates of 25 mm/h (1 in./h) or less, 4% for rates of 75 mm/h (3 in./h), and 6% for rates up to 150 mm/h (6 in./h). The precipitation rates are either measured directly or derived from the cumulative precipitation data. The weighing gauges generally have 8-day clocks and charts, and a 0 to 30 cm (0 to 12 in.) dual traverse weighing range. See Appendix B for a typical weighing rain gauge manual.

The recording rain gauge should have an event marker pen to indicate when the wet-side collector bucket is open or closed. The times can be read off the 8-day chart. The Aerochem Metrics collector will interface with the Belfort 5-780 series rain gauge. The event pen typically is actuated, rising from its baseline, when the collector lid opens; and remains actuated until the lid closes, whereupon the pen falls to its baseline position again. To prevent the event marker pen from interfering with the sample trace pen on the weighing gauge, the two are offset on the time axis. Thus only one pen can be set at the correct time. Care must be taken to use the correct event beginning or ending time. Since the operator is seldom present to observe the collector behavior during an event, the event marker pen is invaluable for indicating a collector malfunction. For precipitation collector assembly, operation, installation, and servicing, see the manufacturer's instructions.

2.2 INSTALLATION AND ACCEPTANCE TESTS

After a suitable site location is chosen, the precipitation collector and rain gauge must be properly installed and system acceptance tests performed before actual precipitation data can be collected.

2.2.1 Precipitation Collector

2.2.1.1 Installation--

The precipitation collector should be mounted on the ground so that the rims of the buckets are level and at least 1 m above the ground. The collector should be properly anchored against strong winds, and the bucket should be secured to the precipitation collector by means of a spring or elastic cord (bungee cord) hooked to the bucket handle and collector table edge. The precipitation collector may be shielded from the wind, but it should not be put in an area where excessive turbulence will be caused by the shield or where there are obstructions such as trees and buildings (Reference 3, Section 5). For the placement of any neighboring collectors and rain gauges of equal or smaller height, the distance between rain gauge and collector, or between collector and collector, should be at least equal to the height of the taller object. Correct spacing should minimize interference as well as splash effects. To ensure that the collector dry bucket does not act as an obstruction for the wet bucket (or precipitation sample), the collector should be aligned either perpendicularly to the prevailing winds or with the dry bucket downwind of the wet bucket. The ground surface around the collector and rain gauge should consist of natural vegetation or gravel. It should not be paved because a hard surface may cause contamination from dust settling and water splashing into the collector or gauge.

2.2.1.2 Acceptance Tests--

Precipitation collector acceptance tests should be carried out before the collector is used in the field. These tests include: (1) sensor heating and actuating the lid when the sensor is shorted with water drops, (2) sensor cooling and return of the lid to the wet-side bucket upon removal of the shorting material (water may be wiped dry), (3) sensor temperature attainment (50°-60°C) when the lid is off the wet bucket, (4) sensor temperature (1°-2°C) when ambient temperature falls below freezing and (5) lid cycling and sealing observation. 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 wet 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 neither is the problem, the sensor or motor box is probably faulty and should be replaced. To remove the box, see the manufacturer's instructions.

b) Affix a temperature probe (thermistor, thermometer, or thermocouple) to the sensor plate near the screw head in the plate. Make sure good contact occurs, and cover the probe with an insulating material. Short the grid and plate together with a paper clip or coin. The temperature should start to climb in a few minutes, 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 manufacturer's instructions, reprinted in Appendix A.

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 if the plastic foam gasket is secured in the correct position. To remove the seal, see the manufacturer's instructions and Section 2.3.1, step 5. If this is not the problem, contact 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 (1/32 in.)) 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 temperatures. 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, either the problem must be remedied or the apparatus returned to the manufacturer. In general, the problem can be rectified by the operator replacing the sensor or the motor box. Do not replace any switches.

2.2.2 Rain Gauge

2.2.2.1 Installation--

The rain gauge should be mounted on a firmly anchored support or base so that its funnel rim is level and at about the same height as the collector rim to enable comparisons of collection amounts between the two. The Belfort gauge can be mounted with three bolts to a level platform of 30.5 x 30.5 x 0.48 cm (12 x 12 x 3/16 in.) hot-rolled steel, welded to a 5.1 cm (2 in.) diameter 1.0 m (3.5 ft.) pipe. The pipe is sunk in cement for stability, and it should extend above ground about 0.53 m (21 in.) to bring the gauge to the same height as the precipitation collector. Alternatively, the gauge can be mounted (bolted) to cinder blocks. Holes can be drilled in the cinder block with a masonry bit. The level of the gauge can be adjusted by the addition of washers to the bolts. The gauge level can be checked with a carpenter's level placed at two intersecting positions. The gauge mouth should be high enough so that it will not be covered by snow.

In open, windy areas, a wind shield (e.g., swingleaf wind shields such as the Alter used by the U.S. Weather Service) should be used with the rain gauge.

For rain gauges which contain a clock (recorder), the access door to the chart drive should be on the leeward side of the gauge and should be kept closed to minimize dirt and moisture affecting the chart and the clock mechanism. Never oil any part of the gauge except for the chart drive, and oil this only when necessary with a light machine oil.

2.2.2.2 Acceptance Tests--

Rain gauge 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 gauge level and zeroed, add water equivalent to several inches. For the Belfort rain gauge 5-780 series, 1 in. = 824 g.

b) If the rain gauge does not read correctly, adjust it according to the manufacturer's instructions (Appendix B, Instruction Book for Universal Recording Rain Gauge).

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 in.), and measure the response. (For the Belfort recording rain gauge 5-780 series, 0.51 mm = 16.4 g (0.02 in.). If there is no response or if the response is more than 1.0 mm (0.04 in.), contact the manufacturer. Check the turnover point on dual traverse gauges. For tipping bucket gauges, add water in 0.25 mm (0.01 in.) increments, and note when the bucket empties.

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 h, and check the pen traces and the clock time. The time should be correct to within 0.5 h/24 h of running. If the clock does not meet this specification, it should be replaced. If any other problems are evident but are not addressed in the manufacturer's instructions, call the manufacturer.

e) Note that the event and weight trace pens are offset about 4 h so that they cannot interfere with each other. Set the weight pen for the correct time. Make sure that the pens (weight and event) are writing. If contact between the pen tips and the chart paper is made but writing does not occur, draw some ink with a toothpick down the pen tip to form a small pool at the contact point.

f) Connect the wires to the proper terminals on the collector and the rain gauge. Short the collector rain sensor, and observe if the event pen moves up about 3 mm (1/8 in.) from its baseline. Remove the short, and note if the event pen falls back to its baseline position. If problems with the event pen occur, notify the manufacturer.

2.3 EQUIPMENT CHECKS, MAINTENANCE AND TROUBLESHOOTING

This section contains the checks or maintenance that should be conducted on a routine basis on the precipitation collector and rain gauge. In addition, equipment problems that commonly occur are discussed, and troubleshooting remedies are presented. Records of all equipment checks and maintenance should be clearly documented in the station logbook. If malfunctions occur, attempt to diagnose and correct the problem as soon as possible. If the problem cannot be corrected, ask the field manager and/or the equipment manufacturer for advice and direction. Record the diagnosis and corrective action taken in the logbook.

2.3.1 Precipitation Collector

The precipitation collector does not require calibration, but to ensure proper functioning of the collector the following checks and maintenance should be conducted. The tasks are divided into routine checks, special calibration/maintenance and winter maintenance.

2.3.1.1 Routine Checks--

These checks should be performed at daily or weekly intervals in accordance with network procedures.

1. Collector Sensor Test - Short the sensor with a piece of metal or some water to check the lid opening and the sensor heating functions. When the sensor short is removed, the lid should close within a few seconds, and the sensor should cool. If an event pen is used, mark its traces on the rain gauge chart for these tests. Clean the sensor at monthly intervals or as needed.

2. Inspection of Dry Collector Bucket - If the collector has a dry bucket (as the wet/dry collector has), check the bucket after an event or a time period in which an event depositing more than 0.25 mm (0.01 in.)

of precipitation has occurred. Ascertain if the dry bucket contains or did contain any precipitation. Precipitation in the dry bucket is possible evidence of a collector malfunction. Possible causes of such a malfunction are (1) a dirty or faulty sensor, (2) a too high sensor heating temperature and/or a low precipitation rate, (3) a defective magnetic mercury switch in the motor box, or (4) the lid arm too far out from the magnetic switch to actuate it. All of the above reasons, except for the dirty or faulty sensor, can cause lid cycling.

3. Test of Wet-Side Bucket or Plastic Liner - At weekly intervals, if no event has occurred, test the wet-side bucket for cleanliness. Add 250 mL of deionized or distilled water, swirl the bucket so that its interior is washed, and measure the specific conductance of the solution. If the conductance is over 3 µS/cm, rinse the bucket until the rinse water conductance is less than 3 µS/cm. Conductivities greater than 3 µS/cm indicate that the bucket is contaminated due to poor initial cleaning, dry deposition and/or handling. If high conductivities are frequent at a site, poor collector sealing and/or an operator handling problem are probably present and must be corrected.

4. Examination of the Event Pen Marker Trace - At weekly intervals, inspect the event marker trace to see if the lid cycled. The event trace openings and closings should correspond to the beginning and end of the event as indicated by the slopes of the sample weight trace. Numerous up and down markings in short time intervals indicate lid cycling. Some cycling traces may occur when no event is apparent; this can occur during short, light rain events. Cycling during a heavy rainfall is symptomatic of a collector problem. No lid movement traces when the sample weight trace shows that an event occurred indicates either a collector or sensor malfunction.

2.3.1.2 Special Calibration/Maintenance--

These special maintenance and troubleshooting tasks should be undertaken as needed. Any other maintenance advised by the equipment manufacturer should be carried out at the recommended time periods.

1. Minimizing Lid Lifting by Strong Winds - Where strong winds are common, check the lid to be sure it does not wobble or is not lifted off the bucket by the wind. If either is a common occurrence, replace the springs on the collector with stronger ones, and readjust the lid arm and the counterweight balance.

2. Lid Cycling - As a common occurrence, lid cycling can be due to several causes. First, cycling during low rainfall can take place if the hot sensor plate dries the sensor rapidly. If this is a frequent occurrence, lower the temperature by turning the potentiometer screw (see manufacturer's instructions). Second, the lid arm can be loose or too far out from the magnetic switch in the motor box. Third, the switch may be defective. (For the last two, see Section 2.1.2.2, step 6).

3. Lid Malfunctioning - Another common source of collector problems is a faulty sensor. The lid may remain open, not open or open intermittently. The lid staying open indicates a shorted rain sensor. A short can be verified by unscrewing the sensor cannon connector at the motor box. The lid should then close over the wet bucket; if the lid does close, check if dirt is shorting the sensor plate and grid. If so, clean with a toothbrush or by passing a card between the grid and plate. For the other problems, the simplest remedy is to replace the sensor.

4. Replacement of Collector Lid Seal - Replace the plastic foam underseal on the lid annually or as soon as needed. It will deteriorate with time, especially in hot, dry climates. The collector lid seal is removed using the following procedure:

   a) With the collector power disconnected, place the collector lid in the middle position.

   b) Remove the two (2) screws on the edge of the lid.

   c) Remove the two (2) L-brackets into which the screws were threaded.

   d) Remove the lid pad by prying it gently along its edge with a coin or a screwdriver.

5. Cleaning Techniques and Schedule - Wash the collector rain sensor monthly with deionized water to remove dirt, salt, and film buildup. If a film persists, clean the sensor grid and plate with detergent and a toothbrush. Wipe the rim of the dry bucket weekly with clean tissues (e.g., Kimwipes) to prevent carryover of dustfall to the sealing gasket and then to the wet bucket.

6. Site Maintenance and Inspection for Obstacles - Periodically mow the grass and inspect the site area for new obstacles (e.g., a growing bush or tree) that may become an obstacle even though not one initially.

2.3.1.3 Winter Maintenance--

Check the sensor temperature if the ambient temperature falls below freezing to ensure that the heater is working. This may be done by adding snow to the sensor and observing if the snow melts (the lid will open). If necessary, the following may be conducted to prevent the freezing of equipment:

1. Prevention of Lid Freezing--To prevent the lid from freezing to the bucket, the following is recommended (4):

   a) Attach a peaked roof (available from Aerochem Metrics) to the lid to prevent buildup of snow on the lid and to help insulate the lid.

   b) Cut a small notch in one corner of the roof to insert a power cord.

   c) Attach the power cord inside the roof to an air thermostat (Honeywell or WRAP-ON) set for about 2°C (36°F); tape the cord to the roof arms.

   d) Use a 60-W or 75-W light bulb as a heater; set the bulb on a piece of 9 mm (3/8 in.) Styrofoam on the lid top to prevent a hot spot.

   e) Install a piece of 18 mm (3/4 in.) Styrofoam under the slope of the roof to minimize heat loss.

   f) To compensate for the additional weight on the lid, add two large U-bolts to the counterweight shaft (approximately 200 gms).

2. Prevention of Lid Arms Freezing to Table--To prevent freezing of the lid arms to the table, insulate one from the other.

   a) Wrap and tape a plastic sheet around each lid arm to make a boot.

   b) Tape one end of the boot to the table and the other end to the arm.

   c) Check to see that the boot is secure and does not tear loose when the lid arms move between the closed and the open bucket positions.

2.3.2 Weighing Bucket Rain Gauge

The weighing bucket rain gauge must be calibrated upon installation and at least at annual intervals thereafter. To ensure proper functioning of the gauge, the following routine checks, calibrations and maintenance should be conducted. Any other maintenance recommended by the manufacturer should be carried out.

2.3.2.1 Routine Checks--

These checks should be performed at daily, weekly or monthly intervals as appropriate.

1. Adjusting the Zero Setting - At daily or weekly intervals with no precipitation in the rain gauge, adjust the zero setting if necessary with the (red) fine adjust screw. The zero setting will fluctuate with temperature, but generally not more than ±0.75 mm (0.03 in.).

2. Checking the Pail Level - When the rain gauge pail is removed, be sure it is replaced correctly so that it is level.

3. Adjusting and Winding the Clock - Weekly, for an eight day clock, wind the clock (or chart drum) on the weighing gauge, and correct the time setting if necessary. Be sure to correct for backlash and to set the time correctly with respect to a.m. and p.m. Note the event pen times are offset from the weighing pen by about 4 h; set the weighing pen to the correct time.

4. Inspection of Pens and Ink - Weekly, inspect the pens to see if they have ink and are writing. If they are not writing, clean the pens, refill them, and be sure they are working. To help start the pens writing, use a flat toothpick to make the ink from the pen reservoir form a small pool at the point of contact between the pen and the chart.

5. Chart Replacement - At the prescribed interval, generally weekly, remove the old chart and replace it with a new one. Close the access door to the chart.

6. Level Check - At bimonthly intervals, measure the gauge level to ensure that it is still horizontal.

2.3.2.2 Calibrations--

Two types of calibrations are recommended. A single point check to be performed monthly and a multi-point calibration to be conducted at least annually.

1. Rain Gauge Check - Once a month, add several known weights of tap water to the rain gauge to see that it is measuring correctly. For the Belfort weighing gauge, 25.4 mm = 1 in. = 824 g.

2. Rain Gauge Calibration - At 12-month intervals (unless test 1 shows it is necessary sooner), calibrate and adjust the weighing bucket rain gauge at each 25 mm (1 in.) level according to the manufacturer's instructions. A set of weights and a linearity tool can be obtained from the manufacturer for the calibration. Alternatively, weighed quantities of tap water can be used. For the Belfort gauge, 25.4 mm = 1 in. = 824 g. With a dual traverse pen recorder such as the Belfort (0 to 6 in. and 6 to 12 in. traverses), the range 127 to 178 mm (5 to 7 in.) has been found difficult to calibrate and to keep calibrated. To minimize use of this range interval, the rain gauge bucket can be emptied after each event or week of events. In the winter, antifreeze must be added to the weighing gauge bucket to help melt the captured snow. Thus a severe or prolonged storm can bring the gauge to the 127 to 178 mm (5 to 7 in.) level. If it is found that a calibration problem exists in the 127 to 178 mm (5 to 7 in.) range, it is recommended that the bucket be emptied whenever the 127 mm (5 in.) range is approached and that new antifreeze be added. If a tipping bucket gauge is used, it can be calibrated by adding a measured volume of water, using a slow drip technique, as specified in the manufacturer's instructions.

2.3.2.3 Winter Maintenance--

In the winter, rain gauge problems can be caused by (1) snow filling or drifting out of the gauge, (2) freezing of the collected precipitation which can damage the gauge bucket, and (3) the cold affecting the clock and/or ink.

Therefore, the following actions should be taken:

a) Remove the funnel in the inlet mouth.

b) Add approximately 1600 g (2 in.) of an ethylene glycol-methyl alcohol (40:60) antifreeze mixture (Belfort manual, Section 4.3). To retard evaporation, add 180 mL (6 oz) of a 10W motor oil. Do not adjust the gauge reading after adding the antifreeze. The gauge will indicate rainfall of approximately 50 mm (2 in.). The ethylene glycol-methanol with precipitation added to yield 150 mm (6 in.) of solution will freeze below -40°C (-40°F). For less severe conditions, use approximately 50 mm (2 in.) of ethylene glycol antifreeze alone. When enough precipitation has been collected to yield 127 mm (5 in.), the mixture will be liquid at -24°C (-12°F). Since the weighing gauge is most difficult to keep in calibration in the 127 to 178 mm (5 to 7 in.) range, empty the gauge when the 127 mm (5 in.) level is reached, and add new antifreeze. The antifreeze will not only aid in melting the snow, but will prevent freezing of collected precipitation and resulting damage to the container.

c) In extremely cold periods, the clock (if not new) may run slowly, and/or the ink may not flow. Low-temperature ink is available from the rain gauge manufacturer. Use of a low-temperature lubricant may be helpful if the clock runs too slowly.

2.4 SAMPLE COLLECTION AND HANDLING

2.4.1 Avoiding Contamination

Careful handling of equipment and samples to prevent contamination is extremely important. The dissolved substances have very low concentrations, so any contamination will result in large errors. Thus all articles that contact the samples must be clean. All the buckets and containers have been cleaned at the central laboratory. Only the materials (e.g., sample buckets, electrodes, cells, and probes) that are used and not returned to the laboratory must be rinsed. All rinses should be done with deionized or distilled water.

2.4.2 Sampling Schedules

Sampling schedules generally used include weekly, daily, event, and subevent. Daily and weekly samples should be removed at the same time of day for each sampling period unless precipitation is occurring at that time; then a delay of up to 12 h for daily sampling and 24 h for weekly is permissible. For event schedules, remove the sample immediately after the event or at a set time daily.

For sequential schedules, treat the samples similarly to the event samples. Since one event may produce several samples, it is important to identify each sample in the chronological order of occurrence. For sequential sampling it is important that the time corresponding to each subevent specimen be known so that correlations with other data can be made.

The samples are identified and measured for amount, pH, and conductivity. They are then sealed in plastic bottles, if event or daily samples, and stored in a refrigerator until shipment (Sections 2.5 and 2.6).

2.4.3 Collection and Handling Procedures

Precipitation samples are collected in wet buckets, plastic bag bucket liners, or plastic bottles. The methodology for each is given below.

The containers for the wet samples should have been cleaned prior to shipment to the field and do not require rinsing in the field before use. Never substitute a precipitation collector dry bucket for a wet bucket. At all times, take care not to contact the inside wall of a container, a lid or a cap with any object--especially one's finger which can leave a deposit of salt and oil. The container should be capped until immediately before use, and must be resealed immediately after use. Since human breath contains ammonia, do not exhale into a container.

2.4.3.1 Wet Buckets--

Immediately before use, label the new precipitation collector wet bucket (or for sequential sampling, the capture bottles). Weigh the bucket after the label is affixed. The label should contain the station identification, the date placed in use, and the bucket weight (without lid). After the sampling period, the final weight is added. Use a pencil or ball point pen to inscribe the labels. Below are standard operational procedures to be adopted when handling precipitation collection buckets.

a) Do not remove a clean bucket from the plastic bag in which it is shipped until it is to be placed in the collector.

b) Check the collector bucket for precipitation at the scheduled times. Move the lid from the wet bucket by contacting a coin or metal object to the sensor grid-plate to activate the motor and move the lid to the dry sample bucket. The lid will remain open until the metal object bridging the sensor is removed. NEVER TRY TO FORCE THE LID OPEN BY HAND.

c) Remove the bucket from the collector at the scheduled time, and replace it with a clean, weighed, labeled bucket.

d) Remove the lid from the new bucket after it has been placed in the precipitation collector, and cover the removed sample bucket with the new lid to minimize the chance of contamination. Fasten lid on old bucket with masking tape.

e) If no sample is present, seal the empty bucket and return it to the laboratory, or, depending on the protocol, rinse it at the field station for reuse (see Section 2.6.3).

f) Remove and replace the rain gauge chart. Record readings (times of start and end of precipitation) on data form. For the final amount of precipitation reading, use the maximum value on the rain chart at end of event because loss of water by evaporation will occur on standing.

g) If there is no antifreeze in the rain gauge, empty its bucket. If there is antifreeze, do not empty the bucket until the reading is 127 mm (5.0 ± 0.3 in.); then empty the bucket and add new antifreeze.

h) Weigh bucket and sample (see Section 2.5.1).

2.4.3.2 Plastic Bag Liners--

When plastic bags are used for bucket liners, the buckets are modified by drilling a vent hole near the bucket rim to allow air to escape (5). A new bag is inserted in the bucket each week and removed at the end of the weekly collection period. Avoid touching the inside of the bucket or bag below its top except when wearing polyethylene gloves.

a) To insert the plastic bag (5), use a clean pair of plastic disposable gloves. Open the bag to fill it with air.

b) About 4 to 5 in. down from the opening, squeeze the bag closed to capture the air in the bag.

c) Push the inflated bag into the bucket until it touches the bottom.

d) Fold the upper 4 or 5 in. of the bag over the bucket rim and adjust to minimize creases on the rim.

e) Secure the bag flap to the outside of the bucket just above the first ridge (and above the handle) with a retaining strap (see Figure 2-2).

f) The bag can be opened more fully inside the bucket by smoothing the bag against the inside wall. Always wear clean gloves while doing this.

g) Weigh the bucket + bag assembly and record the weight.

h) Cover bucket with its lid until it is to be placed in the precipitation collector.

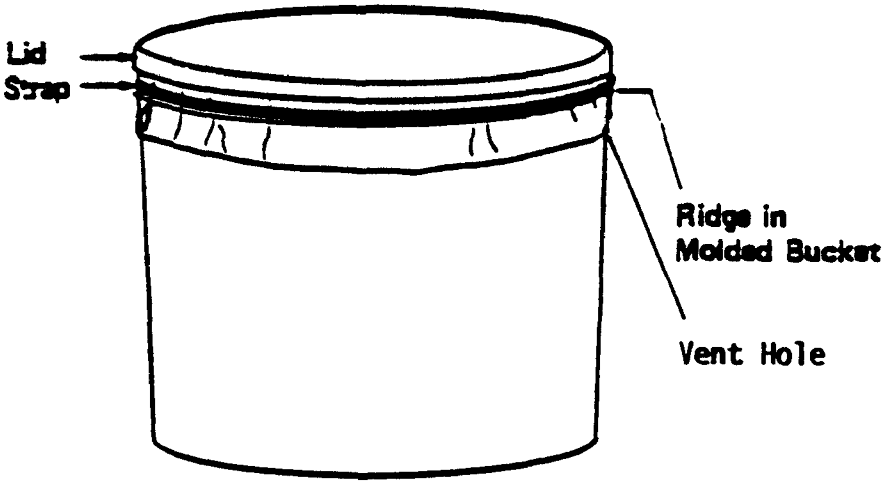

Figure 2-2. Plastic Bag Liner Assembly

To remove the sample (e), carry the covered bucket containing the liner with or without a sample to the site laboratory.

a) After the bucket containing the liner, retaining strap, and sample is weighed, remove the retaining strap without passing it over the open bucket (to avoid any contamination falling in).

b) Push up some of the liner flap outside the bucket to enable the top of the liner to be grasped.

c) Lift the bag up out of the bucket several inches.

d) Holding the bag with one hand, squeeze the bag shut about one in. below the bucket rim and close the bag with a cable tie. If sample is frozen, allow it to melt completely before closing the bag with the cable tie.

e) Remove the bag from the bucket, swirl to mix contents, and wash one of its bottom corners with deionized water.

f) Elevate the cleaned, dried corner so that it is not in contact with solution and cut off about 1/2 in. using cleaned scissors.

g) Lower the cut corner, carefully pouring an aliquot of the sample into a clean, 500-mL, wide mouth plastic bottle. Label the bottle with an indelible marking pen. Discard any collected sample remaining in the bag.

2.4.3.3 Bottles--

For event or daily sampling, the number of buckets required, as well as storage and shipment space, are minimized by transferring the sample from the bucket after it is weighed (Section 2.5.1.2) to a 500-mL labeled, wide-mouth polyethylene bottle. If frozen, the sample must be completely melted and mixed before transferring. If sufficient sample is present (e.g., more than 300 mL), use 50 mL to rinse the shipping bottle. One 500-mL bottle per event is a sufficient sample for all measurements; the rest of the sample may be discarded.

For sequential samples, which are collected through a funnel directly into prenumbered, prelabeled polyethylene bottles, seal the bottles immediately after the samples are collected.

Wash the sample bucket or, for sequential precipitation collectors, the funnel and tubing with deionized water until the rinse water has a specific conductance below 2 µS/cm (step 3, Section 2.3.1).

The samples are now ready for field measurement; check that the containers are correctly labeled.

2.5 FIELD MEASUREMENTS

The field measurement procedures for weighing, conductivity, pH, and temperature should be identical to those used by the central laboratory. Each bucket is weighed both before and after sampling. If sufficient sample (more than 70 g) is available, its pH and conductivity are measured both in the field laboratory and at the central laboratory. These measurements are used as a check to detect sample changes. If less than 70 g of sample are collected, the sample is sent to the central laboratory without measuring conductivity and pH.

2.5.1 Weighing Sample Containers

2.5.1.1 Balance Specifications--

The balance should have a capacity of 20 kg and a precision of at least ±10 g. The mass of precipitation collected by the precipitation collector is measured to determine the rain collector efficiency compared to the rain gauge.

2.5.1.2 Procedure--

a) Before each weighing, brush off the balance pan with a soft brush.

b) With the balance level, adjust to zero (see manufacturer's instructions).

c) Before sampling, place a new bucket, or a bucket containing a new plastic bag liner, without its lid (and/or bottle with its lid) on the balance, and weigh to the nearest gram. Do not allow the bucket lid's inner surface to contact any object. Record the weight on the data form and on the container label (Section 2.7.3).

d) Before weighing the bucket containing a sample, tap the covered bucket to knock any water drops off the inside lid surface into the bucket, wipe off the outside of the bucket, remove the tape and the lid from the bucket, and place lid with its outer surface on the table.

e) After the balance has been zeroed, place the bucket without its lid on the balance pan, cover the open bucket with Saran Wrap, and weigh to the nearest gram.

f) Record the weight on the bucket label and on the field data form.

g) Subtract the initial weight of the empty container from the final weight of container plus sample to obtain the sample weight. Record on field data form.

h) Avoid breathing onto the sample to prevent ammonia contamination.

i) If sample is more than 70 g, remove an aliquot of about 20 g for conductance and pH measurements. For this, a disposable syringe can be used. If sample is frozen, allow it to melt completely in its closed container, and swirl the container to assure homogeneity before removing the aliquot. Reweigh sample plus container to obtain aliquot weight by difference.

j) Seal container with lid; obtain and record total weight to be shipped to the central laboratory. If sample is shipped in its bucket, secure the lid with a rubber mallet.

2.5.2 Specific Conductance Measurement

2.5.2.1 Apparatus Requirements--

The conductivity meter should permit selection of several different measurement ranges between 0 to 10 and 0 to 1000 µS/cm, and have a precision of ±0.5% of range and an accuracy of at least ±1.0% full scale. The range most frequently used is 0 to 100 µS/cm. A temperature-compensated cell with a cell constant of 1.0/cm is preferred.

For calibration, use a KCl solution of known specific conductance and be sure the temperature of the KCl standard and the sample are the same. For rain samples, a 0.0005M KCl solution which has a specific conductance of 74 µS/cm at 25°C is appropriate.

The specific conductance of the sample can be measured on the same aliquot as used for pH. If this is to be done, measure the specific conductance before measuring the pH to avoid any possible error due to electrolyte contamination from the pH electrode.

2.5.2.2 Procedure--

Measure the specific conductance for all samples over 70 g, using the procedure in Method 120.1 (Specific conductance) (6).

1. Summary of Method

   a) Measure the specific conductance of a sample by using a self-contained conductivity meter, Wheatstone bridge-type or equivalent.

   b) Analyze samples preferably at 25°C. If not and if the meter does not have automatic temperature compensation, measure at 20° to 28°C, and correct to 25°C.

2. Sample Handling and Preservation

   a) Perform analyses in the field laboratory and/or the central laboratory.

   b) If analysis is not completed within 24 h of sample collection, store sample at 4°C for preservation. Wash the apparatus with high quality distilled/deionized water, and prerinse with sample before use.

   c) Remove sample aliquot for measurement, and seal the bulk sample. Allow sample aliquot to come to ambient temperature before proceeding with conductance measurement.

3. Specific Conductance Meter Standardization

   a) Follow the manufacturer's instructions for the operation of the instrument.

   b) Allow sample aliquot to come to room temperature (23°-27°C), if possible.

   c) Use 74 µS/cm standard. For dip tube cell, rinse and shake test tube or vial three times with deionized or distilled water.

   d) Add 1.3 cm (0.5 in.) of 74 µS/cm solution to test tube; swirl to coat walls; drain. Add 20 mL of solution or enough to cover electrodes; insert rinsed conductivity cell. Remove and shake; repeat two times.

   e) Insert cell; set meter to conductivity, and control knob to read 74. Readjust after 1 min. Move cell up and down to remove bubbles, readjust to 74 if required.

   f) Discard solution; shake cell and tube dry. Put a second aliquot of 74 µS/cm solution in same tube; check reading. Readjust meter if necessary. Discard solution.

   g) For closed bottom type cell, use above instructions omitting the test tube, and add sufficient water or solution to cover electrodes.

h) Determine the temperature of the sample to ±0.5°C. If the temperature of the sample is not 25°C, make the correction (as shown below) to convert reading to 25°C. After measurement, either discard the solution or save it for pH measurement; never pour the solution back into its container. Record the data in logbook.

The following temperature corrections are based on the standard KCl solution, and are used with instruments with no automatic temperature compensation.

(1) If the temperature of the sample is below 25°C, add 2% of the reading per degree.

(2) If the temperature is above 25°C, subtract 2% of the reading per degree.

Report results as conductivity (μS/cm) at 25°C on the data form.

4. Conductance Test

a) For dip tube cell, rinse and shake a new test tube or vial five times with deionized or distilled water. Rinse and shake conductivity cell three times.

b) Pour deionized or distilled water into test tube or vial. Dip and shake cell three times before reading. Let solution stand until quiescent. If the conductance exceeds that of the deionized water, repeat rinses until it is equal to that of the water. Record latter of two readings on the field data form for conductivity of distilled water.

c) Drain and shake tube; shake cell dry.

d) Rinse test tube or vial with sample. Pour sample into tube to cover electrodes. Reseal bulk sample container. Dip and shake cell three times, then, after solution has come to rest, measure conductance and record.

e) For closed bottom type cell, use similar procedure, and add sufficient deionized water or sample to cover electrodes.

f) Save this sample for pH test.

g) Rinse cell with deionized water; drain, shake, blot and store.

2.5.2.3 Conductivity Measurement Problems and Tests--

The conductivity cell generally has few problems; store the cells as recommended by the manufacturer. The working conductivity standard is 0.0005M KCl, which will slowly degrade and is easily contaminated. To minimize errors due to changes in the calibration standard, replace the 74 μS/cm working solution at approximately quarterly intervals.

When a new working standard is received, correlate it against the old working standard. Report the measured value of the old working standard to the central laboratory, and always return enough of the old standard to the central laboratory so that it can be remeasured. Never return the old working standard before checking it against the new solution.

Store the conductance standards in a refrigerator to minimize changes but always bring them to room temperature before use. Changes of less than 3% may be ignored. If the change is more than 3%, order a new standard from the central laboratory.

If the conductance meter has an internal standardization circuit, use it to check the KCl standard by following the manufacturer's instructions. If the KCl standard has changed from its original value by more than 5%, inform the central laboratory immediately. Since the internal meter calibration is not a traceable standard, it must not be substituted for the KCl solution.

Another means of evaluating the working conductance standard is to compare it against the Q.A. samples received periodically from the central laboratory. Return the test samples to the central laboratory with the next sample shipment for remeasurement. If the laboratory finds that the field conductance differs from the laboratory value by more than 10%, the central laboratory will replace the old conductance standard. Store the cells as recommended by the manufacturer.

2.5.3 pH Measurement

2.5.3.1 Apparatus and Equipment (7)--

LABORATORY pH METER -- The meter may have either an analog or digital display with a readability of 0.01 pH unit. A meter that has separate calibration and slope adjustment features (8) and is electrically shielded to avoid interferences from stray currents or static charge is necessary. It may be powered by battery or 110 V AC line; if battery powered, the meter must have a battery check feature. A temperature compensator control to allow accurate measurements at temperatures other than 25°C is desirable.

SENSING ELECTRODE -- Select a sensing electrode constructed of general-purpose glass. This electrode generates lower resistance, faster response, and has a reliable range of 0-14 pH units. Refer to the manual accompanying the probe for the manufacturer's recommendations on electrode storage.

REFERENCE ELECTRODE -- The reference electrode recommended for wet deposition analysis is one equipped with a ceramic junction. The ceramic construction minimizes differences in potential between high ionic strength buffers and low ionic strength samples thus reducing errors from residual junction potentials. A reference probe equipped with a ceramic junction in an annular ring configuration generates a more stable potential in less time due to a higher flow of internal electrolyte into the solution. Single pore ceramic frit junctions also provide adequate electrolyte flow.

COMBINATION ELECTRODE -- The combination electrode combines the indicating and reference elements in a single unit. Since sample volume requirements are a consideration when analyzing wet deposition samples, combination electrodes are more convenient than separate glass and reference electrodes.

Before use, the electrode should be equilibrated in 1×10^{-4} mol/L hydrochloric acid (7) and stored in the same solution. Refer also to Appendix C.

THERMOMETER -- The thermometer should be readable to 0.5°C in the ambient range.

Stations may receive the required calibration buffer and storage solutions from the central laboratory, according to network protocol. The stations should notify the laboratory when the buffers need to be replaced.

2.5.3.2 Procedure--

The pH is measured for all samples weighing over 70 g. If the measurement is made on the same aliquot as that used for conductivity, the pH must be measured after the conductivity (6). An alternate procedure using dilute buffers is presented in Appendix C.

1. Scope and Application--This method is applicable to precipitation samples.

2. Summary of Method--The pH of a sample is determined electrometrically by using a glass electrode with a reference electrode.

3. Sample Handling and Preservation--

   a) Perform the analyses on site immediately after sample collection.

   b) After removal of a sample aliquot, seal the bulk sample container; if the container is a bucket use a rubber mallet to secure the lid.

4. Reagents--Standard buffer solutions may be available from the central laboratory, according to network protocol. Store buffer solutions at room temperature.

5. pH Measurement--Always determine the conductance first. Rinse water should be the best grade of deionized or distilled water available. A combination electrode is recommended. Rinse the pH electrode prior to each measurement. Report the pH to the nearest 0.01 unit and the temperature to the nearest 1.0°C on the data form.

CALIBRATION FUNCTION:

a) Adjust the temperature control on the meter to room temperature. Rinse the electrode(s) with three changes of water or with a flowing stream from a wash bottle. Dispense two aliquots of the buffer with the higher pH into separate, clean sample cups. Insert the electrode(s) into one aliquot for 30 seconds.

b) Remove the electrode(s) from the first aliquot and insert directly into the second. Allow either two minutes for equilibration or allow sufficient time for the reading to remain steady within ±0.01 pH unit for 30 seconds.

c) Adjust the calibration control until the reading corresponds to the temperature corrected value of the reference buffer solution.

SLOPE FUNCTION:

a) Rinse the electrode(s) with three changes of water or with a flowing stream from a wash bottle. Dispense two aliquots of the second reference buffer solution into separate, clean sample cups. Insert the electrode(s) into one aliquot for 30 seconds.

b) Remove the electrode(s) from the first aliquot and insert directly into the second. Allow the system to equilibrate.

c) Adjust the slope function until the reading corresponds to the temperature corrected value of the reference buffer solution.

CALIBRATION CHECK:

a) Remove the electrode(s), rinse thoroughly, and place into the first reference buffer solution. If the pH does not read within ±0.01 unit of the temperature corrected value, repeat the calibration procedure until the buffers agree.

SAMPLE MEASUREMENT:

a) Again, remove the electrodes from the buffer and rinse them thoroughly, using multiple rinsings (wash bottles are recommended). Use 30 mL of water and be sure to rinse the tip. Gently blot the electrode tip dry. Determine the pH of the pH CHECK SAMPLE. Allow the electrode to equilibrate without stirring for 2-4 minutes, or allow sufficient time for the reading to remain steady within ±0.01 pH unit for 30 seconds, and read and record the pH to the nearest 0.01 pH unit.

b) Repeat above step only using the same 20 mL aliquot used to measure conductivity. Record the pH of the PRECIPITATION SAMPLE to the nearest 0.01 pH unit.

c) Discard the 20 mL aliquot used for conductivity and pH measurements (do not return the aliquot to the bucket) and rinse the electrodes one last time. Store the pH electrode in the KCl-HCl solution (see Section 2.5.3.1). Change the storage solution weekly.

2.5.3.3 Electrode Problems and Tests--

Two diagnostic tests which indicate the aging of the electrode are presented here.

The first test uses periodic test samples sent out to the field stations by the central laboratory. The samples should have pH and specific conductance values typical of precipitation. They should be unknown to the site operator, and are measured for both variables. These are measures of the station's accuracy if the laboratory value is assumed to be correct and if no solution change occurs in shipment.

The test solution is poured into five test tubes and the conductivity and then pH of each tube are measured as if they were five different samples. That is, the conductivity cell and pH electrode are rinsed before and after each tube is measured. The readings are tabulated and the average value and standard deviation calculated. From these results and from the time required to attain stable readings, electrode performance and precision can be evaluated. The standard deviation(s) is calculated from the relation:

$$s = \left[\sum_{i=1}^{5} (x_i - \bar{x})2/n \right]^{1/2} \qquad 2\text{-}2$$

where x_i and $\bar{x}$ are the measured and the average pH readings of the series and where n is the number of sample aliquots measured.

If the average of five field pH measurements differs from the laboratory by more than ±0.15 unit, or the standard deviation is greater than 0.05 pH unit, the pH electrode may need replacing. The samples are returned to the laboratory with the results for recheck and evaluation. Consultation with the station operator on the technique may identify the source of the problem.

The second test uses a reference solution, which has a known pH and a conductivity similar to those of rain samples, to check the pH electrode at the station at weekly intervals. The measurement procedure is identical to that used for the rain sample. Store the solution in a refrigerator, and replace it when needed or when the solution pH or conductivity appears to have changed. For the reference solution, the pH value should agree with the value assigned by the central laboratory to better than ±0.10 unit.

If the first measurement differs by more than ±0.1 pH unit from the others for the same solution, this value should be excluded. Thus, for the test sample, a sixth sample tube should be measured. If this poor first reading behavior is exhibited by an electrode, and if sufficient precipitation sample exists, two tubes of each precipitation sample should be measured for pH, and the second value entered on the data form. The time to attain a stable reading, i.e., when pH is constant to ±0.01 unit for 30 sec., should be no more than 2 minutes for a properly working electrode. Results of these tests serve as guides for both the measurement technique and the equilibration time to be used for precipitation sample measurements. If an electrode consistently shows behavior poorer than that given by the above time and pH difference criteria, the electrode should be replaced. If the reference solution pH measurement has changed from the previous month's value by more than 0.10 unit, check the solution's conductivity. If the conductivity has changed by more than 10% from its original value, the solution and not the electrode has probably degraded and should be replaced. Always return enough of the solution so that it can be checked by the central laboratory.

2.5.4 Temperature

2.5.4.1 Requirements --

The temperature probe must display at least 0.5°C increments. A thermistor, thermocouple, or thermometer can be used. The probe should be calibrated by the central laboratory.

2.5.4.2 Procedure--

a) Before measuring a solution, rinse the temperature probe with deionized water, and shake it dry.

b) To minimize contamination, do not insert the probe into any solution until after the other measurements, i.e., conductivity and pH, have been made.

c) Read and record the temperature to the nearest 0.5°C.

2.6 SAMPLE IDENTIFICATION, PRESERVATION, STORAGE, AND SHIPMENT

2.6.1 Background

Samples must be adequately identified so that they can be readily and correctly matched up with their data forms. The sample label should contain station identification, sampling date, and sample weight. Use a pencil or a ball-point pen to mark the label so that it is still legible if it gets wet.

Sample degradation can be caused by chemical interactions--for example, with particles or gases, or biochemical reactions. Preservation of sample integrity after removal from the collector can be improved by filtration, sealing the sample, and storage in the dark. Freezing is not recommended. Refrigeration is typically used for daily or event samples but not for weekly samples. To minimize contamination, sample filtration is performed in the central laboratory.

In the case of duplicate (collocated) or sequential collectors, treat each sample container as a separate sample. For duplicate collectors, distinguish the samples by adding a -1 and -2 beside the station identification space on the data form. For sequential samples, add -11, -12, -13, and so forth to denote the chronological order of collection for each event.

Sample shipments are made weekly to the central laboratory for economic reasons for weekly, daily, event, or sequential samples. Generally, the shipment should be made early in the week (preferably on Mondays or Tuesdays) and shipped to the central lab by the U.S. Postal Service first class mail, or by other carriers that will guarantee delivery within three days. The method used should be prescribed by the network protocol. All samples must be well-identified, and should be accompanied by the appropriate data forms.

The central laboratory, upon receipt of the shipment, will replace the used sample buckets or containers with clean ones by return mail or other delivery mode.

2.6.2 Procedure

Label each sample with station identification, date of sampling period, and sample weight (Section 2.4.3.1).

2.6.2.1 Weekly Cumulative Samples--

a) Be sure the sample is sealed, identified, and accompanied by its data form.

b) Pack the weekly sample collection bucket or plastic bottle (if a liner is used) into a cardboard carton or other protective box.

c) Seal the carton, and ship it to the central laboratory by first class mail or other method if prescribed in the program protocol.

2.6.2.2 Daily, Event or Sequential Samples--

Refrigerate event and sequential samples until they are shipped, and keep them cold during shipment. Ship by first class mail or other method if prescribed in the program protocol.

a) Be sure the samples are sealed, properly identified, and accompanied by their data forms.

b) Pack the samples in cardboard-enclosed Styrofoam boxes with gel freeze-packs. Keep the freeze-packs in the freezer compartment of the refrigerator for about 24 h before shipping to ensure that they are completely frozen. The gel packs are preferred because they are less likely to leak when thawed. Generally, four packs per box is sufficient to keep the samples cold for 4 or 5 days. Seal the cartons, and ship to the central laboratory.

2.6.3 Field Blanks

Field blanks are used to determine the contamination of the sample bucket or plastic bag bucket liner when there has been no measurable precipitation for a week. The blanks levels are measured from a thorough rinse of the bucket or its plastic liner and yield information on the previous bucket cleaning, operator handling, contamination while in the collector, and so forth.

2.6.3.1 Buckets--

For weekly samples, when there has been no precipitation, the empty wet-side bucket is removed from the precipitation collector. Depending on network protocol, the bucket is either sealed and shipped to the central laboratory or treated at the field lab as follows. At the field lab, 100 mL of deionized water is poured into the bucket, and the bucket is swirled and tipped for the water to reach as much of the interior surface as possible. Allow the water to stand for about 5 minutes and then measure the conductance as in Section 2.9. Also measure the conductance of the deionized water. Record both values in the site logbook and on the field report form. Record under "Remarks" that the report is for a field blank. Mail the field report form to the central laboratory.

Rinse out the bucket several more times using sufficient deionized water (approximately 100 mL) to reach all the surfaces. Collect the third rinse and measure the conductance. Continue the rinses until there is no difference between the conductance of the deionized water and the rinse sample. Cap the empty bucket securely and save for reuse on the precipitation collector.

2.6.3.2 Bottles--

For daily or event samples which are shipped to the central laboratory in plastic bottles, if no precipitation has been collected in a week, prepare a field blank following the procedure described in 2.6.3.1. Perform the rinses that are required for buckets and record the conductances on the field report form and note under "Remarks" that the report is for a field blank. If the protocol calls for analysis of the blank, the first rinse is shipped to the central laboratory in a labeled, sealed plastic bottle using a similar procedure as for a sample.

2.7 DOCUMENTATION

All data, observations, and changes or modifications must be documented with dates on the proper data forms and/or in logbooks. The data forms should be in duplicate (NCR paper) with one copy kept in the station records and one shipped with the sample. The logbook entries are made out in duplicate. One copy of the logbook entry is kept at the station and the other is mailed with the data form and the rain chart to the central laboratory.

2.7.1 Logbook

Use a bound logbook with perforated pages that can be torn out easily. Record all problems and actions; dates and times of visits; equipment changes; procedural changes or modifications; standard solution changes; electrode replacement; operator changes, and so forth, in the logbook. Submit one copy to the central laboratory and keep the other at the station.

2.7.2 Rain Gauge Charts

Mark the rain gauge chart with station identification, dates and notations for tests, and any problems encountered, and submit weekly to the central laboratory.

2.7.3 Field Data Forms

The field data form must contain all of the following information: station, operator, date, sample weight, sampling times, field values of pH and conductance, and any problems encountered.

Start a new form when a clean bucket is installed in the collector. (For daily, event or sequential sampling use a new form for each sample collected.) Complete the form when the sample is removed from the collector. An example of a data form used by the State-Operated Network for weekly sampling is in Figure 2-3. The items below refer to Figure 2-3.

- **STATION NAME** and **ID** supplied by the project coordinator.
- **OBSERVER'S** signature and printed initials; person completing the form even if substituting for regular observer.
- Enter **DATE ON** and **OFF** (mo/day/yr) and the local **TIME** when sample buckets are installed and removed; specify 24-h time.
- Check appropriate boxes for the three **SITE OPERATIONS**. Diagnose items 1 and 3 from the event pen trace on the rain chart. Add evidence for item 1, for example, the lack or presence of moisture in the dry bucket and the reasonableness between the collector and rain gauge amounts in the **PRECIPITATION RECORD** below. Be sure the weight trace is complete for the sampling time period.
- **SAMPLE CONDITION** is a qualitative observation of precipitation quality. Note any comment on obvious causes of the condition under **REMARKS**.
- Complete the form for **SAMPLE WEIGHT** by entering weight of SAMPLE BUCKET with BAG (if one is used). Include total weight of sealed bucket, bag, and sample, beneath **SAMPLE WEIGHT** designation. Start a new form for newly installed bucket by entering <u>BUCKET WEIGHT</u> of bucket with a bag. Obtain the weight of precipitation in exposed bucket by subtracting BUCKET WEIGHT + BAG from BUCKET + BAG + SAMPLE WEIGHT, and entering it as **SAMPLE WEIGHT**.
- The **PRECIPITATION RECORD** gives daily **TYPE** (if known) and the **AMOUNT** (in.). Circle proper type (R,S,M, or U) under each day. The M denotes a mixture of rain plus snow/sleet/hail. Obtain the daily AMOUNT from recording rain gauge, and record it in the squares. Trace (T) indicates precipitation of 0.25mm (0.01 in.) or less. If rain gauge, chart, or pen malfunctioned and if no amount can be observed, circle **MM**. For cumulative weekly

ACID PRECIPITATION FIELD REPORT

Send Completed Form With Each Bottle To. CENTRAL LABORATORY

STATION **Name**________________

ID ☐☐☐☐

OBSERVER ________________________

	DATE MO	DATE DAY	DATE YR	TIME 0000-2400
BUCKET ON				
BUCKET OFF				

SITE OPERATIONS CHECK YES OR NO FOR EACH ITEM FOR WET-SIDE SAMPLES ONLY (If NO, Explain in Remarks)

YES	NO	
		1 Collector appears to have operated properly and sampled all precipitation events during entire sampling period
		2 Rain gauge appears to have operated properly during the week
		3 Collector opened and closed at least once during the week

SAMPLE CONDITION COMPLETE FOR ALL SAMPLES CONTAINING PRECIPITATION

YES	NO	
		1 Bird droppings
		2 Cloudy or discolored
		3 Soot or dirt
		4 Insect(s) in sample

(Describe All Else in Remarks)

SAMPLE WEIGHT - Grams

☐☐☐☐☐•☐ Bucket + Bag + Sample

− ☐☐☐☐☐•☐ Bucket + Bag

= ☐☐☐☐☐•☐ Sample Weight

PRECIPITATION RECORD

R - Rain Only S - Snow Only M - Mixture U - Unknown
Z - Zero T - Trace MM - Missing

TYPE Circle One For Each Day of Precipitation

AMOUNT In Inches or Circle One

← BUCKET ON TO BUCKET OFF →

TUES	WED	THURS	FRI	SAT	SUN	MON	TUES
R S M U	R S M U	R S M U	R S M U	R S M U	R S M U	R S M U	R S M U
☐•☐☐	☐•☐☐	☐•☐☐	☐•☐☐	☐•☐☐	☐•☐☐	☐•☐☐	☐•☐☐
Z T MM	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM

Total Sampling Period Precipitation From Rain Gauge ☐☐•☐☐ Inches (gauge)
Total Precipitation From Sampler = Sample Weight x 0.00058 inches gram ☐☐•☐☐ Inches (wt)

SAMPLE CHEMISTRY
Only for Wet-Side Buckets with Precipitation

MO	DAY

☐☐☐ Aliquot Removed

Conductance ☐☐•☐ µS/cm Distilled Water

☐☐•☐ Standard Certified ÷ ☐☐☐☐•☐ Standard Measured = ☐•☐☐ Correction Factor

☐•☐☐ Correction Factor × ☐☐☐☐•☐ Sample Measured = ☐☐☐☐•☐ Sample Corrected

pH

☐☐•☐☐ CALIBRATION SOLUTION

☐☐•☐☐ SAMPLE

REFERENCE SOLUTIONS

pH ☐☐•☐☐

CONDUCTIVITY ☐☐☐☐•☐ CORRECTED

REMARKS For Example Contamination By Operator, Equipment Malfunction, Harvesting in Area

SUPPLIES
Circle if Needed

- Field Forms
- Bags
- Bottles
- pH Reference Solution
- Conductivity Reference Solution
- Indicate other needed supplies in remarks

ENCLOSE WHITE COPY WITH SAMPLE

samples, add all daily rain gauge amounts, and record TOTAL SAMPLING PERIOD PRECIPITATION (in.). Do not merely subtract initial reading for week from final reading because errors occur due to evaporation. Convert TOTAL COLLECTOR PRECIPITATION amount collected from grams to inches by multiplying **SAMPLE WEIGHT** by 0.00058 in./g, and record in appropriate boxes.

- Space is provided for ONE measurement of sample conductivity and pH. Only one is necessary, but if the quality of the measurement is suspect and if over 70 g of sample remain, repeat the measurement, and record only the final value. Mention only problems in the remarks section. (Instructions in Sections 2.5.2 and 2.5.3.) Enter **DATE** of determination as well as volume in mL of sample **ALIQUOT REMOVED**. Record **CONDUCTANCE** of **DISTILLED** (or **DEIONIZED**) **WATER** used for rinses and **SAMPLE MEASURED** conductance corrected to 25°C. If resistance bridge cannot be adjusted, insert measured value of 74 µS/cm standard in **STANDARD MEASURED** to calculate **CORRECTION FACTOR**; then calculate and record the **SAMPLE CORRECTED** value. For conductivity meters adjusted to 74 µS/cm value using KCl standard, the correction factor is 1.0. The sample aliquot used for the conductance measurement can also be used for pH measurement. Never return any aliquot to the bulk sample. Avoid contaminating bulk sample or aliquot. Measure pH of **SAMPLE** aliquot (Section 2.5.3). After the measurement is completed, recheck the pH 4 buffer value, and enter it if it differs by less than ±0.03 from 4.00. If the difference is more than ±0.03, repeat calibration, and remeasure the pH of the sample aliquot and the pH 4 buffer.

- Obtain **SUPPLIES** by circling the appropriate material. If pH standards are needed, write it in this section. To avoid running out, request new material when about one-fourth of original supply remains.

- The **REMARKS** space is provided for the observer to record any unusual problems, weather, or other occurrences at the field site or in the laboratory. Unusual occurrences in site area may include contamination by the operator, moisture in the dry bucket, plowing, harvesting, burning, increased atmospheric pollution or dust, or power outage. The importance of the information requested in the remarks section cannot be overemphasized. Careful observation of the sample and occurrences in the surrounding environment can aid greatly in evaluating the validity of the sample and in the interpretation of the data collected.

2.8 QUALITY CONTROL

Quality control procedures are used on a routine basis to help assure the collection of high quality data. Complete documentation of all observations and measurements, the use of known test solutions for pH tests, and the recheck of the pH calibration after sample measurements are examples of quality controls. In addition, these types of audits are used to test the field operators and the central laboratory. The first type, performance audits, uses blind samples made up by the Network Quality Assurance Manager or central laboratory for pH and specific conductance measurements to test the measurement capability at the sites. The second type is field systems audits by an experienced observer. The third type requires the field personnel to forward a sample received from quality assurance personnel to the central laboratory disguised as a regular precipitation sample to test both field and laboratory sample handling and analysis.

2.8.1 Unknown or Quality Control Test Samples for the Field

To evaluate the quality of each station's pH and conductivity measurements as well as to detect problems with these measurements, test samples of rain-type composition should be received from the central laboratory on a regular (e.g., quarterly) basis.

1. Measure these samples for pH and conductance as soon as possible after receipt. Use the same procedure as for precipitation samples (Sections 2.5.2 and 2.5.3).

2. Fill out a data form; record the data and the results in SAMPLE CHEMISTRY, and identify the sample in REMARKS.

3. Return the results on a data form, and the remainder of the sample to the central laboratory.

At the central laboratory, the sample is remeasured to be sure it has not changed during shipment to and from the station. Comparisons between the site and laboratory results will assist in the validation of routine field data. If the comparison results are poor, the Network Coordinator should initiate troubleshooting with the field operator to determine the cause of the problem and take the appropriate corrective action.

2.8.2 Site Visits/Audits

To review the quality of the measurement system and to evaluate each station's performance firsthand, a site visit should be conducted once a year or at least once every two years by experienced personnel. The audit covers all aspects of site operation.

1. About 4 to 6 weeks before the audit, a questionnaire should be sent from the Network Coordinator's office to the field personnel. They fill in the questionnaire (Section 10.0, quality assurance handbook (3)) and return it prior to the auditor's visit so that the auditor can assess the operator's overall capabilities and prepare pertinent questions.

2. The auditor will either add a test sample to a clean bucket at the station, or give the sample to the operator for measurement. The operator will weigh the sample, measure its pH and conductivity, and record the data on a data form.

3. The auditor will inspect all equipment, check the calibration of the rain gauge, offer advice, and ask questions while the operator goes through the rounds and tests.

4. If there are any problems, the auditor attempts to correct them; and failing to do so, the auditor will bring them to the attention of the site supervisor.

5. The site personnel will be informed of the results at the end of the audit. A written audit report will be submitted to the site supervisor, site sponsor, network coordinator and other officials who are concerned with operation of the site. A follow-up on corrective action will be made in 60 days. The follow-up can be by letter, telephone or revisit.

2.8.3 Blind Samples for the Laboratory

Blind samples will be sent to each station at various times for testing and forwarding to the central laboratory for analysis as part of the quality assurance program. The following are instructions and guidelines to be followed:

1. A reference sample can be shipped in a 500-mL polyethylene bottle with two preaddressed postcards, a mailing label, and a set of data.

2. Refrigerate the sample at 4°C until it can be submitted to the central laboratory during a week in which your site had no wet deposition.

3. If your precipitation samples are submitted in buckets, pour the contents of the bottle into a clean sample bucket (one which has not been used in the field) when you are ready to submit the reference sample; weigh, and record as usual on a data form.

   If your precipitation samples are sent in bottles, transfer the sample to one of your bottles, weigh, and record as usual on a data form.

4. Remove your normal aliquot and measure its pH and specific conductance; record these values as usual on the data form.

5. Fill out the rest of the regular field report form, and ship it with the sample to the central laboratory as a normal precipitation sample. Make up the information for PRECIPITATION RECORD, and so forth, on the data form.

6. Furnish the information requested on the two postcards which accompanied the sample and mail the self-addressed cards.

7. Place a clean bucket in the collector, and proceed as usual.

2.9 FIELD PROCEDURE SUMMARY

To serve as an outline, an operating procedure summary is given below. It includes the basic steps, but it is not complete. The conductivity and pH procedures are those applicable to most of the current instruments, but they may not pertain to a specific instrument being used. Check the manufacturer's instructions, and adapt this summary to your network as necessary.

Site Visits

a) Daily: check rain gauge for event occurrence. If an event occurred, record its date and time, number of lid openings, and amount of precipitation from gauge. Note the weather. Weekly: change chart, fill pens, and wind clock. Monthly: check rain gauge calibration, and clean collector sensor. Check the condition of the lid pad.

b) Check dry side buckets for moisture and other unusual occurrences. If not interested in the dry bucket analysis, wipe off the rim and leave the dry bucket in place. The dry side buckets should be cleaned weekly and replaced semi-annually.

c) If event occurred, replace wet bucket with a newly weighed one. Put new weighed lid firmly on removed sample bucket. Record observations on data form and in logbook.

d) Check collector, sensor, and rain gauge for problems.

Sample Handling

a) Wipe outside of bucket dry; tap lid to knock off drops; remove, weigh bucket (to nearest 1.0 g). Record on sample data form.

b) If sample is frozen, allow it to melt completely.

c) If sample is sent to the laboratory in a bottle rather than bucket, pour the sample into a 125, 250 or 500 mL sample bottle. Discard any sample over bottle capacity. Mark total sample weight on bottle.

d) Rinse sample bucket with deionized or distilled water, shake, and drain.

e) For sample in sealed bucket or bottle, allow at least 1 h for sample to reach room temperature before performing measurements.

2.10 REFERENCES

1. Galloway, J.N., and G.E. Likens, Water, Air and Soil Pollut. 6, 241 (1976).

2. Galloway, J.N., and G.E. Likens, Tellus 30, 71 (1978).

3. Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. V - Manual for Precipitation Measurement Systems, Part I - Quality Assurance Manual. U.S. Environmental Protection Agency, Research Triangle Park, NC. EPA-600/4-82-042a (January 1981). October 1984 Revision in print.

4. Martin, C.W. NADP Winter Operation of Sampler, Hubbard Brook Experimental Forest, West Thornton, NH; letter to V.C. Bowersox, March 25, 1980.

5. Eaton, W.C., and E.D. Estes, "Use of Plastic Bags as Bucket Liners For the Aerochem Metrics Precipitation Collector", Research Triangle Institute, Research Triangle Park, NC, RTI-2474-86 (May 1984).

6. Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, Cincinnati, OH, EPA-600/4-79-020 (March 1979).

7. Koch, W.F., and G. Marinenko, Guidelines for the Measurement of pH in Acidic Rainwater. National Bureau of Standards, for EPA.

8. Galloway, J.N., B.J. Cosby, G.E. Likens, and J. Limnol. Oceanogr. 24, 1161 (1979).

3.0 CENTRAL LABORATORY SUPPORT OPERATIONS FOR THE FIELD

The central laboratory will supply clean containers to the field sites, prepare reference standards to be used to calibrate field instruments, and furnish quality control samples for use in the field. This section discusses the care of glass and plasticware, the preparation of reference solutions, and the evaluation of field equipment by the central laboratory. The referred data forms are in Section 3.7.

The central laboratory will serve as a focal point for solving field operational problems involving equipment malfunctions. It will serve as a central distributor of replacement parts for the collector, rain gauge, pH meter, conductivity meter, balance, thermometers or thermistor probes, and ancillary supplies. The central laboratory will provide consultation service to field personnel on any technical question involving siting, sample collection, analysis, data quality and transport of the collected sample. The central laboratory will work with site personnel as intensively as necessary to assure that data quality meets standards set by the monitoring program.

3.1 CLEANING AND SUPPLYING OF GLASSWARE AND PLASTICWARE

3.1.1 Cleaning of New or Used Plasticware

a) Rinse with deionized water 6 to 10 times. NOTE: If the plastic needs to be rubbed to remove a film, use a natural sponge.

b) Let stand, filled with deionized or distilled water for 48 h. Empty and dry in an oven at 70°C.

c) After initial cleaning (steps 1 and 2), check a portion (~10%) of the containers to ensure that rinsing has been adequate. To do this, add 50 mL of deionized water to the cleaned container, seal the container with a cap or with Parafilm, and slowly rotate it so that the water touches all inner surfaces. DO NOT SHAKE. Check the conductivity of the water (Section 4.3); it should be less than 2.0 µS/cm. If any of the containers fail the check, rerinse all of the containers cleaned for the checked samples and retest 10%.

d) After the plasticware is clean and dry, cap the containers and place them in a plastic bag to be sealed for shipment or storage.

3.1.2 Cleaning of Glassware

3.1.2.1 Glassware Used for Metal Analyses--

a) Rinse with deionized water twice and with 10% HNO_3 once.

b) Rinse 6 to 10 times with deionized water.

3.1.2.2 Glassware Used for Anions and NH_4^+--

a) Rinse with deionized water twice and with 10% KOH solution once.

b) Rinse 6 to 10 times with deionized water.

c) If water beads on the inner surface, the glassware needs to be cleaned more thoroughly. Wash with detergent, and then clean with 10% KOH solution. If water still beads, soak the glassware overnight in 10% KOH, and rinse 6 to 10 times with deionized water.

3.1.3 Supplying Containers to the Field

After a sample shipment has been logged in at the central laboratory, replace the bucket or other sample container with a clean one. The clean, sealed containers are shipped to the field site in plastic bags and shipping cartons on an as-needed basis to maintain their supply. If cold packs and insulated containers are used, these are returned also. Check that the Styrofoam boxes are intact and not cracked; if cracked, replace with a new one. The shipment can be made by ground transport since each site should have a 3-week supply of these materials on hand.

3.2 PREPARATION OF STANDARDS FOR THE FIELD

3.2.1 Preparation and Measurement of Conductivity Standards

a) Weigh out 7.456 g of predried (2 h at 105°C) KCl and dissolve it in 1 liter of deionized water (0.10M KCl).

b) Dilute 20 mL of the 0.1M KCl to 4 liters with deionized water (0.0005M KCl).

c) Fill washed 0.5-liter plastic bottles with the 0.0005M KCl solution to be sent to the field. Label the bottles with the preparation date and keep the solutions refrigerated.

d) Measure the conductivity of the solution in each bottle (Section 4.3).

e) Fill out the Field Conductivity Standard form and label the bottle with the measured conductivity.

f) Send new standards to the field monthly. When old standards are returned to the laboratory, remeasure the conductivity. Complete the Field Conductivity Standard form.

3.2.2 Preparation and Measurement of pH Reference Solution

a) Prepare 4 liters of a 10^{-4} to 10^{-5}N H_2SO_4 solution for the pH reference solution by diluting 4 mL or 0.4 mL of commercially available 0.100N sulfuric acid stock solution.

b) Fill washed 500-mL bottles with the pH reference solution. Label the bottles with the preparation date. Keep the solutions refrigerated.

c) Measure the pH of the solution in each bottle (Sections 4.2).

d) Fill out the Field pH Test Solution form, and label the bottle with the measured pH.

e) Remeasure the pH of these solutions after they are returned from the field. Complete the Field pH Test Solution form.

3.2.3 Preparation of Quality Control Samples

a) Monthly, prepare a mixed solution of 10^{-3} to 10^{-6}N H_2SO_4 from commercially available 0.100N solution and 0.0001M to 0.0003M KCl to be used as a quality control sample. A 0.10M KCl stock solution is prepared by dissolving 7.456 g of predried (2 h at 105°C) KCl in 1 L of deionized water at 25°C. For 0.0001N KCl, dilute 1 mL of the 0.10 M stock solution to 1000 mL with deionized water.

b) Fill clean 60-mL polyethylene bottles with the mixed audit sample, and send each site one sample. Three bottles should be retained by the laboratory.

c) Immediately measure the three samples kept by the laboratory for pH (Section 4.2) and conductivity (Section 4.3). Check the laboratory electrode against another backup electrode for one sample. Fill out the appropriate section of the Field Quality Control Audit Sample Report (Section 3.6.). Refrigerate the laboratory samples.

d) When the field quality control audit samples from all sites have been returned to the laboratory, reanalyze the samples along with the laboratory's three aliquots. Check the laboratory electrode against another backup electrode for one sample. Complete the Summary Field Quality Control Audit Sample Report.

3.3 INITIAL EVALUATION OF FIELD EQUIPMENT

All meters and electrodes should be tested before they are shipped to the field. The meters have a serial number affixed, but the electrodes do not. A unique identification number should therefore be taped to each electrode.

3.3.1 Evaluation of Conductance Meters and Cells

3.3.1.1 Evaluation of Accuracy and Precision of Meter--

a) Prepare a 0.0003M KCl Test Solution--Dilute 3 mL of the stock 0.10M KCl solution (Section 3.2) to 1 liter with deionized water. (Prepare daily.)

b) Calibrate the Field Conductance Meter--Calibrate as indicated by the manufacturer or as described in Section 4.3.

c) Fill 11 Vials or Plastic (17x100 mm) Tubes--Fill to a depth of 3 cm (or to cover the electrode) with the 0.0003M KCl. The first tube is to be used as a rinse tube.

d) Measure the Conductance of the 10 Solutions--Between each measurement, rinse the conductivity cell thoroughly with distilled water, carefully shake it dry, and dip it in the rinse solution three times.

e) Calculate an Average Value and the Standard Deviation--Use the following relationships. Programmed calculators make this a simple operation.

$$\bar{x} = \frac{\sum_{i=1}^{10} x_i}{n} \qquad 3\text{-}1$$

and

$$s = \left[\sum_{i=1}^{10} (x_i - \bar{x})^2/(n-1) \right]^{1/2} \qquad 3\text{-}2$$

where

x_i = the measured value (in μS/cm or pH units),

$\bar{x}$ = the average value,

s = standard deviation, and

n = the number of values.

f) Record the Results--Record results on the Conductance Meter/Cell Acceptance Test form and the Conductance Acceptance Test Summary Form. The conductivity meter and cell are acceptable if the average value is within 2% of the theoretical value of 44.6 μS/cm (25°C) and if the relative standard deviation is less than 2%.

3.3.1.2 Evaluation of Linearity of Meter--

a) Prepare three of the following standards so that each range of the meter has at least one standard

Standard	Preparation	Normality KCl
147.0 µS/cm	Dilute 1 mL of 0.1N KCl to 100 mL	0.001
75.0 µS/cm	Dilute 500 µL of 0.1N KCl to 100 mL	0.0005
44.6 µS/cm	Dilute 300 µL of 0.1N KCl to 100 mL	0.0003
14.9 µS/cm	Dilute 100 µL of 0.1N KCl to 100 mL	0.0001
7.5 µS/cm	Dilute 50 µL of 0.1N KCl to 100 mL	0.00005

b) Calibrate the field conductivity meter as indicated by the manufacturer.

c) Measure the conductivity of each standard as described in Section 4.3.1.5.

d) Determine the linearity of the meter by performing a linear least squares fit on the data. Record the results on the Conductance Meter/Cell Acceptance Test Form and the Conductance Acceptance Test Summary Form. The coefficient of correlation should be 0.999 or better. If it is less than 0.999, the meter should be adjusted. Some manufacturers provide procedures for these adjustments. Otherwise, the meter should be returned to the manufacturer for calibration.

3.3.2 Evaluation of pH Meters

a) Calibrate the Field pH Meter--Calibrate as indicated by the manufacturer or as described in Section 4.2.4. A laboratory pH electrode of documented performance should be used.

b) Fill 11 Vials or Plastic (17x100 mm) Tubes--Fill to a depth of 3 cm with fresh pH electrode reference solution (Section 3.2.2). The first tube is to be used as a rinse tube.

c) Measure the pH of the 10 Solutions--Between each measurement, rinse the pH electrode thoroughly with deionized or distilled water, carefully drain or shake it dry, and dip it in the rinse solution three times.

d) Calculate an Average Value and the Standard Deviation--See Section 3.3.1.1, (e).

e) Record the Results--Record on the pH Meter/Electrode Acceptance Test Form and the pH Acceptance Test Summary Form. The pH meter is acceptable if the average pH is within 0.1 pH unit of the calculated value and the standard deviation is less than 0.03 units. (Calculated pH = -log (Normality H_2SO_4).

3.3.3 Evaluation of pH Electrodes

a) Assign Each New pH Electrode an Identification Number--Allow it to equilibrate overnight in 1×10^{-4} mol/L HCl.

b) Rinse the Electrode Carefully with Deionized Water--Prior to testing, and then place it successively in deionized water in different test tubes until a constant pH reading is achieved.

c) Calibrate the Laboratory pH Meter--Calibrate as indicated by the manufacturer or as described in Section 4.2.

d) Measure the pH of 10 Tubes--Measure pH reference solution as described in Section 3.3.2 and note drift, noise and response time.

e) Calculate an Average Value and the Standard Deviation--See Section 3.3.1.1, (e).

f) Record the Results--Record on the pH Meter/Electrode Acceptance Test Form and the pH Acceptance Test Summary Form. The pH electrode is acceptable if the average pH is within 0.1 pH unit of the calculated value and if the standard deviation is less than 0.03 pH unit.

3.3.4 Evaluation of Field Balance and Thermometers

Reference weights traceable to NBS are necessary for balance calibration. Each laboratory should purchase a set of NBS-traceable weights to be used to certify a set of working weights used in the field and laboratory. Semi-annual calibration checks are recommended. The procedure used to certify weights is as follows:

a) zero the balance according to manufacturer's recommendations,

b) weigh the working certified 1.0 and 5.0 Kg weights,

c) weigh reference 1.0 and 5.0 Kg weights,

d) repeat this procedure five times, and

e) complete the Certification of Working Weights to NBS form.

Working reference weights should be certified by this procedure once a year. The NBS-traceable weights are kept as primary standards. All working reference weights should weigh within 0.1% of the NBS-traceable weights.

Each laboratory should have an NBS-traceable thermometer. One thermometer in the laboratory should be certified against the NBS-traceable standard. Keep the NBS-traceable thermometer as a primary standard. Assign all laboratory and field thermometers (or temperature probes) identification numbers, and then calibrate them against the (secondary) certified thermometer. Calibrate the temperature probes in a circulating water bath in the 0° to 25°C range against the certified thermometer, and complete the Thermometer Calibration Log Form. File one copy in the laboratory, and send another to the field with the temperature probe. If the water bath does not have a cooling coil, an ice-water mixture can be used to achieve the low-temperature reading. Calibration at two temperatures, near 0° and 25°C, is sufficient and a linear temperature behavior may be assumed. Temperature differences between the certified thermometer and the test thermometer should be no greater than 0.5 degree.

3.4 MONITORING OF FIELD OPERATION

It is the function of the central laboratory to monitor field results to determine if a site is operating properly. The laboratory receives a copy of the site log book and sample data sheets weekly. From these and the results of the monthly Quality Control Sample (Section 3.2.3) the central laboratory can determine if the site is functioning properly.

3.4.1 Evaluation of Field Conductivity and pH Measurement Systems

As needed, the central laboratory sends Quality Control (QC) samples (Section 3.2.3) to each field site. After all samples have been measured for conductivity and pH by the site operators, returned to the central laboratory and remeasured by the central laboratory, the results are recorded on the Monthly Field Audit Report (Section 9.1.2, QA Manual (1)). Accuracy is estimated and the acceptance criteria are applied.

If a site's QC sample result is outside the pH acceptance criteria, the pH reference solution (Section 3.2.2) values recorded by the site operator on recent field sample data sheets are checked. If these results are also questionable, a new pH electrode which has been checked by the central laboratory (Section 3.3.3) is sent to the field with a new QC sample. If the pH system still does not function properly, the pH meter is replaced.

If a QC conductance value measured by the site operator is outside the conductivity acceptance criteria, a new conductance standard is sent to the site. If this does not solve the problem, the conductivity meter and cell are replaced. In all cases the central laboratory personnel communicate with the site operator to determine if there is an outside cause of malfunctioning.

3.4.2 Evaluation of Field Precipitation Collector, Rain Gauge and Balance

All measurements in the field, including sample weight and rain gauge reading, are recorded by the site operator on field data forms and all observations are noted in a bound log book with perforated second copies that can be torn out easily. These pages are sent to the central laboratory for review along with the data forms. Central laboratory personnel evaluate the performance of the precipitation collector, rain gauge, and balance from these sources, the weekly telephone call, and the precipitation collector collection efficiency. In addition, the performance of the rain gauge and balance are evaluated by reviewing the field records when the site operators check the rain gauge and balance with known weights. During field audits, the auditor evaluates all site equipment.

3.5 REPORT FORMS

Blank data forms are included in this section for the convenience of the manual user. Use of the forms is discussed throughout Section 3. The forms included are listed below:

Title

Field Conductivity Standard Report

Field pH Reference Solution

Field Quality Control Audit Sample Report - Laboratory Data

Conductivity Meter/Cell Acceptance Test Report

Conductivity Acceptance Test Summary

pH Meter/Electrode Acceptance Test Report

pH Acceptance Test Summary

Certification of Working Weights to NBS-Traceable Standards

Thermometer Calibration Log

3.6 REFERENCES

1. Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. V - Manual for Precipitation measurement Systems, Part I - Quality Assurance Manual. U.S. Environmental Protection Agency, Research Triangle Park, NC. EPA-600/4-82-042a (January 1981). Revised January 1985.

FIELD CONDUCTIVITY STANDARD REPORT

DATE OF PREPARATION OF
0.1M KCl STOCK SOLUTION: ________

DATE OF PREPARATION OF
DILUTE FIELD STANDARD: ________

(Analyst's Signature)

LABORATORY ANALYSIS BEFORE SHIPMENT TO THE FIELD (μS/cm)

$\bar{x}$ = ______________ s = ______________

Laboratory Values After Use In The Field:

Field Site #	Lab Value (μS/cm)	Date of Lab Analysis	Analyst's Initials

FIELD pH REFERENCE SOLUTION

DATE OF PREPARATION OF 0.1N H_2SO_4 STOCK SOLUTION ____________

____________ (Analyst's Signature)

VOLUME OF STOCK TAKEN ____________

FINAL DILUTION VOLUME OF FIELD pH ELECTRODE TEST SOLUTION ____________

DATE OF PREPARATION OF TEST SOLUTION ____________

LABORATORY ANALYSIS BEFORE SHIPMENT TO THE FIELD (pH)

$\overline{pH}$ = ____________   s = ____________

LABORATORY ANALYSIS OF ALIQUOTS RETURNED FROM THE FIELD

Field Site #	Lab Values After Return		
	Date of Analysis	pH	Anal. Init.

FIELD QUALITY CONTROL AUDIT SAMPLE REPORT

SAMPLE # ____________

Date of Preparation of Field Audit Sample: ____________

Vol. of H_2SO_4 Stock Used: _____mL; Normality of H_2SO_4 Stock: ____________

Date of H_2SO_4 Stock Preparation: ______

Vol. of KCl Stock Used: _____mL; Normality of KCl Stock: ____________

Date of KCl Stock Preparation: ________

Final Dilution Volume of
Field Audit Samples: _____mL;

____
(Analyst's Signature)

LABORATORY ANALYSIS BEFORE SHIPMENT* TO THE FIELD

	Conductivity	pH
Average and Std. Dev.		

LABORATORY ANALYSIS OF ALIQUOTS RETURNED FROM THE FIELD

SITE #	DATE OF LAB ANALYSIS	CONDUCTIVITY VALUE	pH VALUE	ANALYST'S INITIALS

---

* These data are for three laboratory aliquots which are analyzed before shipment of samples, are then refrigerated, and are reanalyzed with the samples returned from the field.

CONDUCTIVITY METER/CELL ACCEPTANCE TEST REPORT

DATE OF TEST: ______________

____
(Analyst's Signature)

PREPARATION DATE OF
KCl REFERENCE SOLUTIONS: ______________

METER TYPE/SERIAL NO. ________/________

CONDUCTIVITY CELL TYPE/SERIAL NO. ________/________

INDICATE WHETHER TEST OF _____METER OR _____CELL

CONDUCTIVITY VALUES OBTAINED FOR PRECISION TEST (0.0003M KCl SOLUTION) (Section 3.5.1.1)

Aliquot 1: ______________
Aliquot 2: ______________
Aliquot 3: ______________
Aliquot 4: ______________
Aliquot 5: ______________
Aliquot 6: ______________
Aliquot 7: ______________
Aliquot 8: ______________
Aliquot 9: ______________
Aliquot 10: ______________

Average conductivity and
standard deviation: ______________________

CONDUCTIVITY VALUES OBTAINED FOR LINEARITY TEST (Section 3.5.1.2)

Normality KCl	Expected Conductivity (μS/cm)	Found Conductivity (μS/cm)

Slope _________

Intercept _______

Linearity _______

Accepted ________________ Rejected ________________

CONDUCTIVITY ACCEPTANCE TEST SUMMARY

Meter Type/ Serial #	Cell Type/ Serial #	Date of Check	Linearity	Conductivity Value Average and Standard Deviation(μS/cm)	Number of Values	Anal. Initials

pH METER/ELECTRODE ACCEPTANCE TEST REPORT

DATE OF TEST: ________________

____
(Analyst's Signature)

PREPARATION DATE OF
pH ELECTRODE REFERENCE SOLUTION: ______________

NORMALITY OF pH ELECTRODE REFERENCE SOLUTION: ___________

Meter Type/Serial No. _________/__________

pH Electrode Type/Serial No. ________/________

Indicate whether test of _____meter or _____electrode

pH VALUES OBTAINED:

4.0(3.0) Buffer before: _____________
7.0(6.0) Buffer before: _____________
Aliquot 1: _____________
Aliquot 2: _____________
Aliquot 3: _____________
Aliquot 4: _____________
Aliquot 5: _____________
Aliquot 6: _____________
Aliquot 7: _____________
Aliquot 8: _____________
Aliquot 9: _____________
Aliquot 10: _____________
4.0(3.0) Buffer after: _____________
7.0(6.0) Buffer after: _____________

---

pH ELECTRODE REFERENCE SOLUTION: (Section 3.5.2)

Calculated pH of reference solution: _________________

Average pH and standard deviation: ___________________

Check One: Accepted ____________ Rejected ___________

pH ACCEPTANCE TEST SUMMARY

Meter Type/ Serial #	Electrode Type/ Serial#	Date of Ref Soln. Prep.	Date of Check	pH Value Average and Standard Deviation	Number of Values	Anal. Initials

CERTIFICATION OF WORKING WEIGHTS TO NBS-TRACEABLE STANDARDS

DATE OF CERTIFICATION: ____________________

WEIGHT SET SERIAL #: ____________________ (Analyst's Signature)

BALANCE 0	__________	BALANCE 0	__________
NBS 1kg	__________	NBS 1kg	__________
NBS 5kg	__________	NBS 5kg	__________
TEST 1kg	__________	TEST 1kg	__________
TEST 5kg	__________	TEST 5kg	__________
* * *		* * *	
BALANCE 0	__________	BALANCE 0	__________
NBS 1kg	__________	NBS 1kg	__________
NBS 5kg	__________	NBS 5kg	__________
TEST 1kg	__________	TEST 1kg	__________
TEST 5kg	__________	TEST 5kg	__________
* * *		* * *	
BALANCE 0	__________	BALANCE 0	__________
NBS 1kg	__________	NBS 1kg	__________
NBS 5kg	__________	NBS 5kg	__________
TEST 1kg	__________	TEST 1kg	__________
TEST 5kg	__________	TEST 5kg	__________

SUMMARY: (Section 3.5.4)

Average and Standard Deviation

BALANCE 0	__________	TEST 1kg	__________
NBS 1kg	__________	TEST 5kg	__________
NBS 5kg	__________		

Check One: Accepted ________ Rejected __________

THERMOMETER CALIBRATION REPORT

DATE OF CALIBRATION: ____________

IDENTIFICATION NUMBER: ___________

____
(Analyst's Signature)

Certified Thermometer (°C)	Test Thermometer (°C)	Correction (°C) (Section 3.3.4)
___________	___________	___________
___________	___________	___________
___________	___________	___________

Check one: Accepted _________ Rejected _________

4.0 LABORATORY PROCEDURES

The laboratory procedures herein are for chemical measurements and analyses of precipitation samples. Methods include analyses for pH, specific conductance, acidity, NH_4^+, PO_4^{-3}, SO_4^{-2}, NO_3^-, Cl^-, F^-, Na^+, K^+, Ca^{++}, Mg^{++}, and dissolved Al, Cd, Cu, Fe, Pb, Mn and Zn. Detection limits for these procedures will vary with instruments and conditions, but representative detection limits, concentration ranges, precision and bias are presented in each method. Brief discussions of the methods are presented in this section with the full text of the procedures in the appendices.

4.1 GRAVIMETRIC MEASUREMENTS

In both the field and the central laboratory the volume of rainwater is determined by measuring the mass of the rain and multiplying the mass by 1 g/cm^3 to obtain the volume. The mass of rain is measured in the field to determine the rain collector efficiency (compared to that of the rain gauge), and the mass of the sample sent to the central laboratory is measured as a check to determine if leakage occurred in shipment. The sample should be sent to the central laboratory in plastic buckets or plastic bottles. If sent in the bucket, the sample is weighed at the field station and by the central laboratory. If transferred to polyethylene bottles, the sample is weighed in the bucket at the field station and the weight entered on the Field Data Form. The volume received is estimated by the central laboratory. If collected in bottles, the sample is weighed by both the field station and the central laboratory.

4.1.1 Apparatus

The balance should have a capacity of 20 kg and a precision of at least ±10 g (for bucket weighing) or 1 kg with a precision of ±0.5 g (for bottle weighing).

4.1.2 Calibration

Calibrate the balance monthly, using weights traceable to NBS-traceable weights. Store the NBS-traceable weights (primary references) in the laboratory, certify the working calibration weights against these, and complete the Certification of Working Weights to NBS report (Section 3.4). Recertify all working calibration weights against the NBS-traceable weights every six months. The procedure for weight certification is the same as for field balances (Section 3.3.4). Calibrate each balance using weights close to those actually measured. Calibrate high-capacity balances, using 1.0 and 5.0 kg weights.

4.1.3 Procedure

To obtain the weight of the sample received in the laboratory, use the following procedure. During the procedure, avoid breathing on the sample to avoid NH_3 contamination.

a) Be sure that the balance is level, and then adjust its zero knob so that the balance zeroes (see manufacturer's instructions).

b) Place the bucket without its lid or the plastic bottle on the balance pan, and weigh it to the nearest 10 grams or place the bottle on the balance and weigh it to the nearest gram.

c) Record the weight on the bucket or bottle label and on a data sheet.

d) Subtract the initial weight of the empty container (recorded on the Field Data form) from the final weight of container plus the sample to obtain the sample weight shipped.

4.2 pH MEASUREMENT

pH is measured in precipitation samples electrometrically by using either a pH half cell with a reference electrode or a combination electrode. The pH meter/electrode(s) measurement system is calibrated with two reference buffer solutions that bracket the expected sample pH. The acceptable method for the measurement of pH is presented in Appendix C.

4.3 CONDUCTANCE MEASUREMENT

Specific conductance is measured in precipitation samples electrolytically using a conductance cell. The conductance meter/cell system is calibrated using potassium chloride solutions of known specific conductances in the range of precipitation samples. The acceptable method for the measurement of specific conductance can be found in Appendix D.

4.4 SAMPLE FILTRATION

After measuring the pH and specific conductance, but before measuring the other analytes, filter the rainwater sample. Use vacuum or pressure filtration to minimize exposure of the sample to laboratory air. The vacuum apparatus can be a bell jar (ground-glass plate) of sufficient size to contain a 250-mL (8-oz) bottle, or it can be the apparatus used by the Illinois State Water Survey for the National Atmospheric Deposition Program (NADP). The recommended filter material is a 0.45- m membrane filter (Millipore HA); the filter funnel should be plastic. Before each filtration, thoroughly rinse the apparatus, including the filter, with 200 mL deionized water and a portion of sample if there is a sufficient amount. Filter the sample as quickly as possible, and cap the labeled sample bottle containing the filtrate to minimize contact with laboratory air. If the filtered particulates are to be analyzed, they should be oven-dried at 60°C for one hour and stored in glass vials.

4.5 ACIDITY MEASUREMENTS

Two methods for measuring acidity are acceptable. The first method measures both strong and total acidity, while the second method only measures total acidity.

In the first method, strong and total acidity are measured in the precipitation samples by titrating the sample with dilute sodium hydroxide solution and following the titration electrometrically with a pH half cell and reference electrode or a combination electrode. The titration is continued until a pH of 10.4 is reached. A method first introduced by Gran (1) is used to calculate the strong and total acidity. The Gran functions are plotted versus the volume of titrant added. The total and strong acidity are obtained by extrapolating the linear portions of the curve to zero. Weak acidity is obtained by subtracting the strong acidity from the total acidity. This method can be found in Appendix E.

In the second method, total acidity is measured by titrating the sample electrometrically with a combination pH electrode to a pH of 8.3. The total acidity is calculated from the volume and concentraiton of titrant. This method is included with the above method in Appendix E.

4.6 DETERMINATION OF SULFATE

Sulfate is measured in the precipitation samples by one of two methods; ion chromatography or automated colorimetry using barium-methylthymol blue. The ion chromatographic method utilizes ion exchange resins for separation and conductivity for detection. After a sample is injected onto the separator column containing the ion exchange resin, an eluent is used to pump the sample through the column. The anions are separated depending on their radius and valence. After eluting from the separator column, the ions are converted to the corresponding acids which are detected in the conductance cell against a background of neutralized eluent.

The automated colormetric method of analysis for sulfate uses the blue colored barium-methylthymol blue complex to determine the concentration of sulfate in the sample. After interfering cations are removed by an ion exchange column, the sulfate in the sample reacts with barium chloride to form barium sulfate. Excess barium ions react with the methylthymol blue to form the chelate. Thus, the concentration of the sulfate in the sample is inversely proportional to the intensity of the blue-colored chelate which is measured colorimetrically at 460 nm.

The ion chromatographic method is presented in Appendix F, while the colorimetric method can be found in Appendix G.

4.7 DETERMINATION OF NITRATE

Nitrate is measured in the precipitation samples either by ion chromatography or automated colorimetry using cadmium reduction. The ion chromatographic method is identical to the method described in Section 4.6. It can be found in Appendix F.

The colorimetric method uses a color reagent made from NEDA (n-(1-naphthyl)-ethylene-diamine dihydrochloride), phosphoric acid and sulfanilamide to develop a color that can be used to measure the nitrate present in a sample. After mixing with ammonium chloride, the nitrate in the sample is reduced in a copper-cadmium column to nitrite. The nitrite is mixed with the color reagent and forms a reddish-purple complex which is measured colorimetrically at a wavelength of 520 nm. The concentration of the original nitrate in the sample is directly proportional to the intensity of the color complex formed by the nitrite. This method can be found in Appendix H.

4.8 DETERMINATION OF CHLORIDE

Chloride is measured in precipitation samples by chemically suppressed ion chromatography or automated colorimetry using thiocyanate. The ion chromatographic method is identical to the method described in Section 4.6. It can be found in Appendix F.

The colorimetric method of analysis for chloride uses a colored ferric thiocyanate complex to determine the concentration of chloride in the sample. The chloride ions react with mercuric thiocyanate liberating thiocyanate ions which reacts with ferric ions. The concentration of the original chloride ions in the sample is directly proportional to the intensity of the colored ferric thiocyanate complex. This method is included with this manual as Appendix I.

4.9 DETERMINATION OF ORTHOPHOSPHATE

Orthophosphate is measured in the precipitation samples either by ion chromatography or automated colorimetry using the phosphomolybdenum blue complex. The ion chromatographic method is identical to the method discussed in Section 4.6. It can be found in Appendix F.

The colorimetric method involves developing the phosphomolybdenum blue complex by mixing the sample with an acidified solution of ammonium molybdate, ascorbic acid and antimony potassium tartrate, and passing the mixture through a 37°C temperature bath. The concentration of orthophosphate is proportional to the intensity of the phosphomolybdenum blue complex measured colorimetrically at 880 nm. This method is presented in Appendix J.

4.10 DETERMINATION OF FLUORIDE

Fluoride is determined in the precipitation samples using an ion-selective electrode with a reference electrode. The meter/electrode system is calibrated with fluoride solutions of known concentrations. The specified method is presented in Appendix K.

4.11 DETERMINATION OF AMMONIUM

Ammonium is determined in the precipitation samples by one of three methods; ion chromatography, ion-selective electrode or automated colorimetry using the indophenol blue complex.

The ion chromatographic method utilizes ion exchange resins for separation and conductance for detection. After a sample is injected onto the separator column containing the ion exchange resin, an eluent is used to pump the sample through the column. The cations are separated depending on their radius and valence. After eluting from the separator column, the ions are converted to the corresponding bases which are detected in a conductance cell against a background of neutralized eluent. This method can be found in Appendix F.

The second acceptable method for determining ammonium is to use a gas sensing ion-selective electrode with a reference electrode. Ammonium ion is converted to ammonia gas when the pH of the sample is adjusted to pH 11-14. An electrode potential develops across the sensing membrane in proportion to the ammonia concentration in solution. The meter/electrode system is calibrated with ammonium solutions of known concentrations. This method is included as Appendix L of this document.

The third method for determining ammonium in precipitation samples is the automated colorimetric method using the indophenol blue complex. After removing cations that could form hydroxide complexes, the sample is mixed with alkaline phenol and hypochlorite to form the indophenol blue complex. Sodium nitroprusside is added to precipitation samples to intensify the color. The concentration of the ammonium is proportional to the intensity of the indophenol blue complex measured colorimetrically at 630 nm. This method can be found in Appendix L with the second method described above.

4.12 DETERMINATION OF SODIUM, POTASSIUM, MAGNESIUM AND CALCIUM

Sodium, potassium, magnesium and calcium are measured in precipitation samples either by chemically suppressed ion chromatography or flame atomic absorption spectrophotometry. The ion chromatographic procedure is identical to the one described in Section 4.11 for ammonium. It can be found in Appendix F of this document.

The flame atomic absorption spectrophotometric method of analysis for these metals involves aspirating the sample into a flame where the cations are converted to ground state atoms. A light beam from a hollow cathode lamp which emits light specific to the metal of interest is passed through the flame, isolated by a monochromator and measured by a photodetector. The ground state atoms of the metal of interest absorb the light. The concentration of the metal in the sample is proportional to the amount of light absorbed in the flame. This method is presented in Appendix M.

4.13 DETERMINATION OF ALUMINUM, CADMIUM, COPPER, IRON, LEAD, MANGANESE AND ZINC

Aluminum, cadmium, copper, iron, lead, manganese and zinc are measured in precipitation samples by graphite furnace atomic absorption spectrophotometry. Microliter quantities of sample are deposited into a graphite tube where it is electrothermally dried, pyrolyzed and atomized.

A light beam from a hollow cathode lamp which emits a spectrally pure line source of light specific to the metal of interest is passed through the atoms which are at ground state. The atmos of the specific metal absorb the light. The concentration of the metal is proportinal to the amount of light absorbed in the flame. This method can be found in Appendix N.

4.14 REFERENCE

1. Gran, G., "Determination of the Equivalent Point in Potentiometric Titrations," Acta Chemica Scandinavica, 4, 1950, p. 559.