

**Tisch Environmental, Inc.**  
**OPERATIONS MANUAL**

**TE-78-100**  
**APS Acid Rain Sampler**

## Acknowledgement

This manual was revised under the guidelines of the Methods Development and Quality Assurance Technical Committee of the National Atmospheric Deposition Program.

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## FOREWORD

This manual is intended as a guide to operators of NADP collection sites. In addition to the sample collection procedures and maintenance functions, additional details describing the NADP program have been included so that those collecting the samples can understand the rationale for the care required in executing the procedures requested.

As experience is gained in field operations, it is expected that problems will arise which were not anticipated and that procedures may need to be modified in the future. Please forward comments and suggestions to the Program Coordinator's Office.

## 1.0. INTRODUCTION

### 1.1. Deposition: A Background

Because precipitation is a very good scavenging agent for many substances (both solid and gaseous) in the atmosphere, changes in the chemical composition of precipitation are good indicators of change in atmospheric composition. The nutrient status, growth, and development of plants on land and in surface waters are influenced by the availability of beneficial nutrients and injurious substances dispersed in the atmosphere. Similarly, the health and reproductive capacity of domestic and wild animals and fish populations are influenced by atmospheric trace constituents. It is now recognized that substances deposited as precipitation, aerosols, and gases significantly augment the supply of both essential elements and potentially injurious substances.

The amount of substances dispersed in the atmosphere and deposited in precipitation, aerosols, and gases is projected to increase still further. Thus, there is an increasing need for careful measurement of the amounts, nature, and biological effects of these substances. Such measurements are essential for responsible management of the agricultural, forest, and aquatic ecosystems of the United States.

### 1.2. NADP Program Objectives

The NADP was created by the Association of State Agricultural Experiment Stations (North Central Regional Project NC-141) to conduct research on atmospheric deposition and its effects on surface waters and agricultural and forest lands in cooperation with federal, state, and private research agencies by:

1. Discovering and characterizing biologically important geographical and temporal trends in the chemical climate of North America through the continued development and maintenance of the NADP/NC-141 atmospheric chemical deposition monitoring network. The network data will make possible the determination

of trends in the supply of both beneficial and potentially injurious substances in precipitation and dry particulate matter deposited in various regions of the United States.

2. Organizing and coordinating research on the effects of chemical changes in atmospheric deposition. These include: (a) the productivity of agricultural crops, forests, rangelands, wet lands, soils, and surface and ground waters; (b) the health and productivity of domestic food animals, wildlife and fish; (c) atmospheric visibility and the corrosion of metals, masonry and stone, paints and other protective coatings and other materials in machinery or structures.

## 2.0. THE NADP MONITORING AND RESEARCH PROGRAM

### 2.1. Site Selection: General Considerations

Collection sites for the Network are selected to give accurate and representative information concerning spatial, as well as seasonal, yearly, and other temporal variations in the chemistry of wet and dry deposition falling within major physiographic, agricultural, aquatic, and forested areas within each cooperating state and region. The sites are selected on the basis of available knowledge of sources of substances in the atmosphere, prevalent forms of deposition, frequency of precipitation events and other meteorological and atmospheric processes that influence the deposition of substances in each state or region. Wherever possible, collection sites include locations where watershed, marine, freshwater, or other hydrological research is already underway, or where research is being conducted on nutrient cycling, air pollution, or atmospheric chemistry. This permits the Network data to be compared with past records of precipitation chemistry maintained at some of these research installations.

### 2.2. NADP Sampling Strategy

In establishing the Network the NADP has sought to ensure a uniformity of commitment, a uniformity of sampling protocol, and a uniformity of analytical techniques and procedures. We believe these are the ingredients essential to a successful network design and operation. To this end the NADP has designated specific precipitation collection equipment to be used throughout the network which allows precipitation to be recorded, collected and verified (Appendix 1). A strict weekly sampling protocol and a clear definition of sample types further makes comparisons between sites possible. The sample types and definition of the sampling periods are discussed in the following sections.

Additionally, every sample is analyzed at a single laboratory, the Central Analytical Laboratory (CAL) operated by the Illinois State Water Survey, Champaign, Illinois, for the following constituents: sulfate



( $\text{SO}_4^{--}$ ), nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), chloride ( $\text{Cl}^-$ ), orthophosphate ( $\text{PO}_4^{--}$ ), sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), calcium ( $\text{Ca}^{++}$ ) and magnesium ( $\text{Mg}^{++}$ ). These constituents have been shown to be the major inorganic ions characterizing wet deposition. As overall indicators of precipitation quality, pH and specific conductance are measured at both field sites and at CAL. Finally, the entire program is monitored by a Quality Assurance Program administered by U.S. Geological Survey.

#### 2.2.1. Sample Types

Atmospheric deposition has two components, wet and dry. Wet deposition includes wetfall, or precipitation, in whatever form it strikes the earth and can best be characterized as a mixture of dissolved particles and gases and undissolved particles in water. These substances are present at the parts per million level, or even lower. Dry deposition includes all other matter which has been scattered in the winds and deposited on the surface.

To separate the wet from the dry deposition components, scientists have for years employed samplers which automatically exposed either a wetfall container during the occasion of precipitation or a dryfall container during all other times. This notion of a wet/dry collector is a compromise, since in no way does such a device exclude the dryfall that occurs during the course of a rainstorm. Fortunately, this compromise is generally not considered to be too serious, because the total, or bulk deposition during a storm is dominated in most circumstances by the wet portion. As a matter of practice, then, the wetfall samples collected with a wet/dry collector are considered to be *wet-deposition-only*.

Two 3½ gallon buckets designated Wet and Dry on the instrument base serve as the receptacles for wet and dry deposition in the

Wet/Dry Collector. In the discussion that follows, *samples* will be referred to as *WET-SIDE* or *DRY-SIDE*, rather than Wet or Dry. This nomenclature avoids the confusion which follows when a wet bucket contains no precipitation and is dry or a dry bucket contains water.

The NADP has placed the highest priority on the collection of *wet-deposition-only samples* collected from the *WET-SIDE* of the

Wet/Dry Collector. In the ideal case this sample type would

contain 100% of the precipitation that occurred during a *sampling period* (See Section 2.2.2). During normal operation of the collector, however, small amounts of precipitation occasionally appear in the *DRY-SIDE* bucket due to the collectors inability to sample some types of light dry snow, dew and other trace precipitation events. In other instances an interruption of electrical power or other malfunctions may prevent the sampler from covering the *DRY-SIDE* bucket during precipitation. If the *WET-SIDE* bucket has only been uncovered during periods of precipitation and has *never been exposed to dry deposition (periods of no precipitation)* the term *wet-deposition-only* is still used to describe the sample type. The collection efficiency of the sampler, however, is said to be less than 100% and is determined by comparing the volume collected in the *WET-SIDE* bucket to the volume collected in the standard rain gage (see also Section 3.3.2).

A *dry-deposition-only sample* is collected from the *DRY-SIDE* of the Wet/Dry Collector on those occasions when 100% of the precipitation events were collected by the *WET-SIDE* bucket. In practice the *DRY-SIDE* bucket usually contains small amounts of water and hence is not truly a *dry-deposition-only sample*.

The only other sample type identified by the NADP as being definable is the *bulk sample*. A *bulk sample* occurs whenever a *WET-SIDE* or *DRY-SIDE* bucket is *exposed continuously to both wet and dry deposition for the duration of the sampling period*. A bulk sample has never been covered during any part of the sampling period. This type of sample occurs when a collector fails to operate for an entire sampling period but sample buckets are continually changed weekly according to the NADP guidelines outlined in Section 3.2.

All other samples, not described above, are considered to be *undefined sample types* and are excluded from the standard NADP data base. These samples usually occur when a collector fails during a sampling period, leaving the *WET-SIDE* bucket exposed to dry deposition; when non-standard or modified equipment is used to collect an NADP sample or when an operator fails to adequately document collector operation.

### 2.2.2. The Standard Sampling Period

The *sampling period* is the interval of time between bucket installation and bucket removal. In the absence of any operational failures of the collector, standard sampling periods are defined as follows:

*WET-SIDE* samples accumulate for one week. These buckets are removed from the collector and replaced at or about 9 AM (0900 local time) each Tuesday. If it is raining or snowing at collection time, buckets are changed, instead, after the precipitation stops, but in no case later than midnight on Tuesday. *WET-SIDE* buckets are replaced weekly and sent to the Central Analytical Laboratory (CAL) even if no precipitation was collected during the sampling period. Dry *WET-SIDE* buckets are checked for the same ions as *WET-SIDE* samples that contain precipitation to assess the quality of the cleaning and handling of the bucket at CAL and at the site, as well as to evaluate how well the collector seals the bucket from wind-blown dirt and debris.

*DRY-SIDE* samples accumulate for eight weeks. At the end of each eight week period both the *WET-SIDE* and *DRY-SIDE* buckets are removed and replaced at the same time.

Following this standard protocol results in 52 (or possibly 53) *WET-SIDE* and 6 or 7 *DRY-SIDE* buckets submitted for analysis per year, thus every NADP site contracts for the analysis of 58 or 59 samples per annum.

### 3.0. OBSERVERS INSTRUCTIONS FOR OPERATING AN NADP SITE

#### 3.1. Requirements for the Collection of Wet and Dry Deposition

Because the success of the NADP depends upon each site's continuing commitment to strictly follow the procedures outlined in this manual, the acceptance of a site into the NADP Network is based in part on the site's ability to implement these procedures. Acceptance also assumes a commitment by each site to adhere to the following general guidelines:

1. Each site is expected to operate continuously for a 5-10 year period.
2. Sites will use the precipitation collection equipment listed in Appendix 1 to gather wet and dry deposition samples for the NADP program.
3. Sites will maintain this equipment in good working order at the original location specified on the SITE DESCRIPTION QUESTIONNAIRE submitted to the NADP.
4. Changes or modifications in the site or to its equipment will be submitted to the Program Coordinator's Office prior to implementation and documented in the REMARKS block on the FIELD OBSERVER REPORT FORM. This includes moving the site, siting other equipment in close proximity to the existing NADP samplers (100 ft), installation of snow roofs or event recorders, etc. See also NADP Site Selection and Installation Instruction Manual.
5. Sites will adhere to the weekly Tuesday to Tuesday sample collection schedule following the procedures outlined in this manual and submit these samples with a completed FIELD OBSERVER REPORT FORM to CAL at the Illinois State Water Survey, Champaign, Illinois for analysis.

In some instances when these guidelines are not followed, data sets and sometimes entire sites must be excluded from the NADP data base in order to maintain the integrity and quality of the Network. We hope this manual and these guidelines will help to keep these occurrences to a minimum and prevent the waste of time and effort associated with excluded sample sets.

### 3.2. Field Procedures

#### 3.2.1. Standard Bucket Changing

At the end of the standard sampling period (See Section 2.2.2) the sample bucket is removed from the collector as follows:

1. Always approach the collector and work from the downwind side to minimize windblown contaminants from entering the buckets. Open one of the black shipping containers and remove the new lid from the plastic bag making sure you do not touch those surfaces which will come in contact with the precipitation sample. Place the lid on the bucket to be removed. With masking tape or a similar tape, temporarily fasten the lid on the bucket. Remove the bucket with lid from the collector and place it back into the plastic bag and into the shipping container. The tape and compression of the shipping container packing material on the bucket lid helps prevent the sample from leaking during transportation back to the field laboratory. This step (taping, bagging and boxing) also prevents packing material fibers from contaminating the sample and documents any leakage that might occur.
2. Place the new bucket on the collector after removing the plastic bag in which it was shipped. Buckets are not to be removed from plastic bags until they have been taken to the sampling site and are ready to be placed on the collector. This helps avoid dust and other contamination from finding its way into the bucket before it is installed.
3. Note the TIME of the bucket change. This TIME will be used to complete two different FIELD OBSERVER REPORT FORMS (See Section 3.3). On the previous week's FIELD OBSERVER REPORT FORM it is entered as the BUCKET OFF TIME. On the current FIELD OBSERVER REPORT FORM, it is used for the BUCKET ON TIME of the sample bucket just installed.

If replacing both a weekly *WET-SIDE* and an eight week *DRY-SIDE* bucket, be sure to label which bucket is removed from which side. This occurs on six or seven occasions during the year.

4. If both buckets are being removed, the polyethylene underside of the                      sampler lid should be cleaned with distilled or deionized water (if outside temperatures permit) and/or wiped with a clean laboratory tissue. This removes loose dirt on the cover and limits any excess buildup that would contaminate the samples.

Careful handling of equipment and samples to prevent contamination is extremely important because the dissolved substances naturally occurring in precipitation have a very low concentration and any additional contamination will cause erroneous results. For example, one drop of human perspiration will completely invalidate a sample for sodium, chloride, and possibly other ions. Even a fingerprint on the inside of a bucket or lid will contain more sodium than an entire sample.

#### 3.2.2. Non-Standard Bucket Changes

A non-standard sampling period occurs every time a bucket is installed on or removed from the collector on a day other than Tuesday or every time a *WET-SIDE* bucket is not left in place for one week or a *DRY-SIDE* bucket for eight weeks. Non-standard sampling periods might occur when a collector is undergoing repair or replacement of essential collector parts, when the site becomes inaccessible because of severe storms or weather, or when regular or substitute personnel are unavailable to replace the buckets and service the rain gage. *These occasions should be very infrequent and should be minimized whenever possible.*

Should a non-standard sampling period become necessary, the following priorities should be exercised to minimize the problems which will result from sampling over different periods:

*First*, if the sample bucket can be replaced on Monday (preferably late in the day) or Wednesday (preferably early in the day) instead of Tuesday, this should be done in lieu of any other day.

*Second*, the sample bucket can be allowed to accumulate for an additional week, until the following Tuesday. For *WET-SIDE* samples this allows the comparison, at least in principle, of two *standard* samples with one two-week sample.

No matter which of these two alternatives become necessary, a non-standard sampling period must be *specially* documented in the PRECIPITATION RECORD and REMARKS blocks on the field form. Section 3.3.2., Block 8 PRECIPITATION RECORD describes the special documentation required.

A special non-standard sampling period occurs when the *WET-SIDE* bucket is completely filled with snow or rain before the end of a standard sampling period.

*With heavy snow* the bucket should be changed when snow first fills the bucket even if it is still snowing. The filled bucket should be allowed to thaw and at the end of the standard sampling period the two *WET-SIDE* samples should poured together and treated as one sample. If a third bucket becomes necessary the original bucket should be reinstalled in the collector. (Usually after the snow has melted, there will be sufficient room in this bucket for additional sample collection.) Note this special case in block 11 REMARKS of the FIELD OBSERVER REPORT FORM. Ship both buckets to CAL, one containing the composite sample and the other empty bucket for cleaning.

*With heavy rain* the bucket should be changed just before it becomes full (about a 9 inch rainfall) especially if it is still raining. Each bucket is then treated as if it were a separate weekly sample and is documented accordingly. (See Section 3.2.1, Standard Bucket Changing).

### 3.2.3. Resetting the Belfort Recording Rain Gage and Event Recorder

(See also Appendix 4)

1. Open the sliding access door on the rain gage and lift the pens off of the chart by moving the pen shifter outward. Remove the catch bucket and empty it except during winter operation when it will be filled with antifreeze solution (See Section 4.3.1.). Replace the bucket, change the chart and return the pen shifter to its normal position.
2. If appropriate, rezero the rain amount pen. Rezeroing is usually not required and should only be done when the rain gage catch bucket is dry. Rezeroing of the pen after emptying a wet catch bucket usually results in the pen drifting below the zero line on the chart.

3. The ink level of each pen should be checked and refilled if necessary. Ink frequently adsorbs water vapor in humid weather and can double its original volume. If the lines on the chart record are very light, the pen ink has possibly become diluted with water. Replace the diluted ink with fresh ink. Tissue paper can be used to absorb the ink out of the pen nibs.

### 3.3. Completing the FIELD OBSERVER REPORT FORM

#### 3.3.1. Preliminary Observations

The FIELD OBSERVER REPORT FORM provided to each site by CAL, is used to record essential information for the interpretation of chemical analysis and precipitation data. The form may be completed with either ball point pen or a medium hardness sharp pencil. Be certain recorded notations appear on all copies and that it is completely filled out and legible. Incomplete or illegible forms require additional time to process and expensive phone inquiries by CAL to the site observer or site supervisor.

Blocks 1-4 should be completed for all *WET*- and *DRY-SIDE* samples. Other blocks are completed only for those buckets indicated by the general block instructions.

#### STATION Block 1:

Fill in the STATION NAME and STATION I.D. as assigned by the Program Coordinators office. The STATION I.D. is a six digit number also known as a SAROAD code for Aerometric Sampling Networks. The code, developed by EPA's Office of Air Quality Planning and Standards, uniquely identifies your site location by region, state and county, and/or town.

#### OBSERVER Block 2:

The OBSERVER SIGNATURE and INITIALS reported should be those of the person who fills out the form and performs the weekly sampling and field laboratory analysis even if he is only substituting for the regular observer. If more than one person is involved in these tasks the signature and initials should be those of the person to whom communications concerning this sample and this week's site operations should be directed.





NATIONAL ATMOSPHERIC DEPOSITION PROGRAM  
A cooperative program of the U.S. Environmental Protection Agency and the National Science Foundation  
U.S. Environmental Protection Agency, Washington, D.C. 20460  
National Science Foundation, Washington, D.C. 20540

# NADP FIELD OBSERVER REPORT FORM

Send Completed Form With Each Bucket To  
The Central Analytical Laboratory

CAL/NHEL Use Only

BUICK	LD
DA	ND
QA	NN
NS/Exclude	S

1. STATION	Name	2. OBSERVER	Initials
4. BUCKET ON	ID	Signature	Check One Wet-Side Dry-Side

5. SITE OPERATIONS	Check Yes or No for each item for Wet-Side samples only
1. Collector appears to have operated properly and sampled all precipitation events during entire sampling period	YES NO
2. Rain gage appears to have operated properly during the week	YES NO
3. Collector opened and closed at least once during the week, other than for testing	YES NO

6. SAMPLE CONDITION	Check Yes or No for all samples containing precipitation
1. Bird Droppings	YES NO
2. Cloudy or Discolored	YES NO
3. Unusual amounts of soot or dirt for this site	YES NO

7. SAMPLE WEIGHT	For all buckets containing precipitation
8. PRECIPITATION RECORD	For Wet-Side Samples Only

9. SAMPLE CHEMISTRY	Only for Wet-Side buckets with Precipitation
10. SUPPLIES	Circle if needed

11. REMARKS	For example: Insect contamination, contamination by operator, equipment malfunction, harvesting in area, etc.
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### SAMPLE BUCKET Block 3:

Check the box indicating the side of the sampler from which the bucket was removed. If the bucket is from the side marked Wet, check *WET-SIDE*, even if no precipitation has occurred and the bucket is dry. Similarly a check in the *DRY-SIDE* box does not require that the bucket be dry.

Very small amounts of water or snow in the *DRY-SIDE* bucket can be expected. Dew, light drizzles and/or snow flurries at times are not "heavy" enough to trigger the operation of the collector. Large amounts of water in the *DRY-SIDE* bucket, however, indicate the collector has malfunctioned, perhaps because of a power failure or perhaps due to more serious electrical/mechanical difficulties. This type of malfunction should be noted in Block 5, SITE OPERATIONS and in Block 11, REMARKS.

### BUCKET ON/OFF Block 4:

The DATE ON (month/day/year) and local TIME should be entered when the sample bucket(s) is installed (BUCKET ON) and then again when it is removed (BUCKET OFF) (See Section 3.2.1, number 3). In both cases 24-hour TIME should be specified. 24-hour time runs from midnight to midnight (0000 hrs-2400 hrs) where noon is 1200 hrs. Therefore 9:00 AM would be 0900 hrs and 5:00 PM would be 1700 hrs.

Whether or not your site is on STANDARD or DAYLIGHT-SAVINGS time is indicated by checking the appropriate box at the bottom of the block. Only one box should be checked except during those sampling periods when your site changes to or from STANDARD time. During these periods both boxes should be checked. If during these unique sampling periods data verification indicates an inconsistency in these times, the BUCKET ON time will be assumed to be correct.

The information in this block is essential to calculate Greenwich Mean Time (GMT) sometimes called 'Zulu Time'.

### SITE OPERATIONS Block 5:

Complete for all *WET-SIDE* samples.

Check YES or NO for each question. The answer to these questions and the comments provided in the REMARKS block are used to decide whether the sample has a definable type as outlined in section 2.2.1. and whether the general sampling requirements outlined in section 3.1. have been met. Since the operator is the one who observes the operation of the equipment in the field it is important to obtain his assessment of the site's performance over the sampling period. For Questions 1 and 2 a YES response indicates correct site operation while a NO response indicates problems which must be documented in the REMARKS block.

A NO response to Question 3 should only be indicated if your station is equipped with an event recorder. The NO answer identifies samples which can be used as NADP site-specific blanks. These dry *WET-SIDE* samples are analyzed for all of the normal parameters and serve as contamination checks on such steps as human handling at CAL and at the site, bucket washing at CAL, and the adequacy of the "

Wet/Dry Collector cover to seal the bucket at the site. Without the event marker information, however, blank samples cannot be distinguished from those exposed to dry deposition or light rain during the sampling period. Hopefully several of these samples will be available from each site each year. Test or servicing events should not be used to indicate a YES response.

SAMPLE CONDITION Block 6:

Complete for all samples that contain precipitation.

The SAMPLE CONDITION boxes provide qualitative information about the sample that might not otherwise be obtained if not completed by the observer. These observations should be made at the time the *WET-SIDE* bucket (or in some cases when liquid is present in the *DRY-SIDE* bucket) is changed, ideally before the bucket is agitated, and before the lid is placed on the removed bucket.

Checking the appropriate box YES or NO and providing additional comments in Block 11, REMARKS will help determine the degree of particulate matter and contamination in the sample at the time of collection. Contamination of the sample reported by the site operator may indicate the sample no longer represents a precipitation event and therefore should be excluded from other NADP samples in the NADP data base. Bird droppings, for example, are a gross contaminant that become homogenized in transit and are sometimes not visible in the sample when it arrives at CAL. Other gross contaminants especially insects should be documented in the REMARKS, Block 11.

*Never attempt to remove any contaminant, no matter how large, from a bucket.*

3.3.2. Reporting Precipitation

The NADP uses precipitation information from both the

Wet/Dry Collector and the Belfort Recording Rain Gage to determine the amount of precipitation and deposition that fell during a given sampling period. The amount of the precipitation contained in the *WET-SIDE* bucket (SAMPLE WEIGHT) is used as the basis for determining chemical analysis concentrations. However, this amount value represents only what fell in the bucket. At times when trace amounts of precipitation occur that do not trigger the collector sensor, when power outages occur or when the sampler malfunctions, this amount value will not represent the true precipitation amount for the sampling period. The rain gage then is used to determine the true amount of precipitation that fell during a sampling period and together with the chemical analysis concentrations is used to determine deposition.

SAMPLE WEIGHTS Block 7:

Wet/Dry Collector. The field sample weight is compared with the CAL sample weight to quantify the magnitude of any sample leakage.

In the field laboratory, remove the bucket from the shipping container and plastic bag. Carefully wipe any liquid or debris from the exterior of the sample bucket. Remove the tape used to secure the lid and weigh the sample *including the lid* to the nearest gram. The balance used for weighing the sample containers should have a 20 kg capacity and a sensitivity of 1 g, (see Appendix 1). Record this weight as BUCKET + LID + SAMPLE in grams on the data form.

PRECIPITATION RECORD Block 8:

First, the type of precipitation should be circled for each day precipitation occurred. Circle R if only rain occurred, S if only snow occurred, and M for any combination of the above including sleet and freezing rain. Use U for unknown, for those instances when you do not know the precipitation type. Hail should be considered as rain (TYPE R) but additionally documented in the REMARKS block.

Next, record the amount of precipitation from the rain gage chart for each day to the nearest one hundredth of an inch (two decimal places) (See Section 4.3.3.). On the first Tuesday (or day) of the sampling period, report only the precipitation that occurred after the bucket was installed. If no precipitation occurred circle Z in the box immediately below the amount for that day. Likewise if you do not know the amount of precipitation circle MM to indicate that it is missing or unknown. *It is just as important that you indicate when precipitation did not occur as it is to indicate that precipitation did occur.* The T is circled in those instances where a trace amount of precipitation occurred (less than .01 inches).

The bottom of the Precipitation Record block contains a place to record the TOTAL SAMPLING PERIOD PRECIPITATION FROM THE RAIN GAGE. This should be the sum of the daily precipitation amounts. The second line records the amount of precipitation in inches that fell in the sampler (TOTAL PRECIPITATION FROM THE SAMPLER). This value is obtained by multiplying the SAMPLE WEIGHT in grams (from block 7) x 0.00058. If the collector and rain gage are operating properly and more than 0.50 inches of precipitation occurred during the sampling period the two values should agree to within 15%. If they do not agree CAL may be consulted for assistance.

### 3.3.3. Field Laboratory Analysis

*All samples and standards should be kept covered and allowed to come to room temperature before any aliquots or measurements are taken. If the sample is frozen, allow it to melt and come to room temperature before proceeding.*

Space on the FIELD OBSERVER REPORT FORM is provided for one value of conductivity and pH. If the quality of the measurement is suspect, and the determination is repeated using the same aliquot, only the final value is recorded. Appendix 2 provides additional information helpful in resolving pH and conductivity measurement problems. Problems should be mentioned in REMARKS, block 11.

### SAMPLE CHEMISTRY Block 9:

If the SAMPLE WEIGHT measured in block 7 is less than 70 grams, omit the SAMPLE CHEMISTRY section and proceed to section 3.3.4., REMARKS, block 11.

If the SAMPLE WEIGHT measured in block 7 is 70 grams or more remove a single 20 ml aliquot of wet sample using the clean, disposable calibrated syringe supplied with each sample collection bucket. *In order to avoid contamination, be careful not to touch the inner surface of the bucket when removing the aliquot (the tip of the syringe will not cause a contamination problem).*

Record the DATE and TIME of the laboratory analysis on the FIELD OBSERVER REPORT FORM as well as the milliliters (mls) of the aliquot removed.

### Conductance Measurement

*Always determine specific conductance first. All water used to rinse glassware and conductance electrode must be of the best grade of distilled or deionized water available.*

1. If your conductance meter has a calibration control, standardize your instrument according to the instruction manual using the 75  $\mu$ S/cm standard solution supplied by the CAL, otherwise proceed directly to step 2.

2. Measure the conductance of the 75  $\mu\text{S}/\text{cm}$  standard using your meter.
3. This value, obtained to the nearest 0.1  $\mu\text{S}/\text{cm}$  is recorded in the space marked STANDARD MEASURED. Discard the used portion of the standard after completing the measurement.
4. Rinse the cell three times with deionized or distilled water, discarding each rinse. Determine the specific conductance of your distilled or deionized water and record the value as DISTILLED WATER on the data form to the nearest 0.1  $\mu\text{S}/\text{cm}$ . The value should not exceed 10. (This value should be the lowest reading you are able to obtain after repeated rinsings. Usually three rinsings are sufficient).
5. Without rerinsing the cell, but shaking off the excess water, determine the specific conductance of the 20 ml aliquot of WET-SIDE sample. Record this value as the SAMPLE MEASURED.
6. The SAMPLE CORRECTED conductivity is calculated using a ratio technique which incorporates the necessary cell constant, temperature and calibration adjustments. Proceed as follows: Divide the STANDARD CERTIFIED value (75.0) by the value you recorded as STANDARD MEASURED. This is the CORRECTION FACTOR. Multiply the SAMPLE MEASURED value by the CORRECTION FACTOR to obtain the SAMPLE CORRECTED value, i.e.,  
$$\text{SAMPLE CORRECTED} = (75 \div \text{STANDARD MEASURED}) \times \text{SAMPLE MEASURED}$$
7. Retain the sample in a clean beaker for the pH measurement.
8. Rinse and then store the conductance electrode in deionized or distilled water when not in use. Change storage water weekly.

#### pH Measurement

*Always determine the conductivity first. Rinse water should be of the best grade of deionized or distilled water available. A combination electrode is recommended (but not required) (See Appendix 1). Always rinse the pH electrode(s) prior to each measurement.*

1. Adjust the temperature control on the meter to room temperature. Rinse the electrode thoroughly using multiple rinsing with deionized or distilled water (be sure to rinse the tip) and gently blot the electrode tip dry with a clean absorbent laboratory wipe such as a Kimwipe<sup>R</sup>. Determine the pH of the certified pH 7.00 standard furnished by CAL. If it does not read 7.00, use the intercept or standardize control to reset the pH to 7.00.
2. Repeat the rinsing and blotting of the electrode and next determine the pH of the 4.01 pH standard furnished by CAL. If it does not read 4.01 use the slope control to set the pH to 4.01.
3. Repeat step 1 to check the pH 7 buffer. If you obtain the same value, go on to step 4. Otherwise, repeat steps 1-3. If you can not obtain the same value, check Appendix 2 for a possible solution to the problem. CAL will also be pleased to help you diagnose the problem.

4. Again, remove the electrodes from the buffer and rinse them thoroughly, using *multiple rinsings* (wash bottles are recommended). Use at least 100 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 for 4 minutes without stirring and read and record the pH to the nearest .01 pH unit.
5. Repeat step 4 only using the same 20 ml aliquot used to measure conductance. Record the pH of the PRECIPITATION SAMPLE to the nearest .01 pH unit.
6. Discard the 20 ml aliquot used for conductance and pH measurements (*Do not return the aliquot to the bucket*) and rinse the electrodes one last time. Store the pH electrode in a pH 7 buffer. Change the storage solution weekly.

#### 3.3.4. Remarks/Supplies

##### SUPPLIES Block 10:

CAL will supply upon request only those items listed in block 10. The supplies will be sent with one of the clean buckets being returned to the site. Other supplies as well as instrument maintenance and replacement are the responsibility of each individual site.

##### REMARKS Block 11:

The REMARKS space is used to record any equipment failures, repairs or calibration, unusual problems, events, weather, contamination or other occurrences at the field site or field laboratory. Unusual occurrences in the site area could include plowing, harvesting, burning, increased atmospheric pollution or dust, power outage, etc. *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.*

#### 3.3.5. Mailing Instructions

The lid can now be securely fastened on the bucket(s) by hammering in place with a rubber mallet. Sample leakage during shipment has been a common problem, so make certain the lid is hammered firmly in place. Place the sample container into a plastic bag removed from the new bucket or lid and seal tightly.

Enclose the *original and one copy* of the completed FIELD OBSERVER REPORT FORM in the shipping box along with the sample bucket and ship to the Central Analytical Laboratory. The additional copy is for your site records. When shipping the bucket be sure the pre-addressed mailing card on the shipping box has the correct address showing.

#### 4.0. ROUTINE MAINTENANCE, CALIBRATION AND TROUBLESHOOTING OF EQUIPMENT

##### 4.1. Wet/Dry Precipitation Sampler (see also Appendix 3)

###### 4.1.1. Maintenance

*Weekly* test the precipitation sensor immediately after installing the rain gage chart by placing two or three drops of water on the sensor grid. The top should then expose the *WET-SIDE* container and the event recorder should indicate the sampler has opened. Within several minutes the top should return to its original position exposing the *DRY-SIDE* container and the event recorder should indicate the sampler has closed. This response can be speeded by blotting the sensor with absorbent material. Faulty sensors should be returned for repair or exchange.

*Periodically* wash the rain sensor grid with clean water to remove any accumulation of minerals, bird droppings, etc., that could close the circuit and present a false event signal. Such a short leaves the wet bucket open during dry periods. A shorted rain sensor can be verified by unscrewing the sensor cannon connector at the motor box. With the rain sensor disconnected, the cover should always position itself over the *WET-SIDE* bucket (i.e., in the dry collection status). To clean the space between the sensor grid and the plate, cut a strip of cardboard from a time card or a manila folder to a width of about 1.8 inches (4.5 cm); this can be passed under the grid and between the teflon washers which fix the separation of the grid and plate.

*Every eight weeks* when both *WET-SIDE* and *DRY-SIDE* buckets are removed from the collector the polyethylene underside of the

sampler lid is cleaned with distilled or deionized water (if outside temperatures permit) and/or it is wiped with a clean laboratory tissue. This removes loose dirt on the cover and limits any excess buildup that would contaminate the samples.



#### 4.1.2. Winter Operation

Depending on the geographic location of the site, winter operation may or may not pose a serious problem for collecting wet and dry deposition. The two most common problems encountered during winter operation of the \_\_\_\_\_ sampler are the freezing of the collector lid to one of the buckets and the immobilization of the lid due to heavy snow or ice accumulation. If either of these problems is a regular occurrence at your site then the investment in a peaked or heated snow roof should be made.

Typical symptoms of the above problems include: rain gage indicates more precipitation than is accountable in the bucket and event recorder does not indicate the correct number of events; event recorder indicates bucket stayed open for unusually long periods after precipitation event; snow and ice in the *DRY-SIDE* bucket; constantly blown fuses; worn thrust collars and burned out motor.

#### 4.1.3. Sensor Calibration

### 4.2. Event Recorder

#### 4.2.1. Weekly Maintenance

Each Tuesday when the precipitation sensor is tested (see Section 4.1.1.) the event recorder should also be tested. The test is identical to the weekly maintenance test performed on the \_\_\_\_\_ Collector Sensor. When water activates the sensor and the *WET-SIDE* container is being exposed, the event recorder should rise above its baseline position on the rain gage chart. When the sensor dries and the collector returns to its original position, the event recorder should return to its baseline position. See Figure 4-1.

#### 4.2.2. Chart Interpretation

(see Section 4.3.3.)

#### 4.3. Belfort 5-780 Recording Rain Gage

(see also Appendix 4)

##### 4.3.1. Winter Operations

Blowing snow poses the biggest problem in the winter operation of the rain gage. Besides the inaccurate measurement of precipitation caused by snow blowing out of the gage, the dashpot may be damaged if snow finds its way into the weighing mechanism. Both problems may be prevented by the following procedure:

- A. Remove the funnel that is fixed to the bottom of the collector by rotating the funnel until its bead clears the pins in the collector tube. Then lift it off.
- B. Empty the catch bucket, replace it in the gage, and add to it an antifreeze solution composed of two pints of ethylene glycol and three pints of methyl alcohol (methanol). Add six ounces of 10W motor oil to the solution to retard evaporation.
- C. Do not make any zeroing adjustment to the gage after adding the antifreeze and oil to the bucket: the gage will indicate a rainfall level of approximately 2 3/4".
- D. The antifreeze solution and oil are self-mixing with respect to the snow and ice added to it. Table 4-1 gives the approximate freezing temperatures of the antifreeze solution when diluted by additional water-content to the gage levels indicated. The catch bucket should be emptied and recharged with fresh antifreeze and oil whenever the gage level and the prevailing temperatures indicate that freezing of catch is probable.

Table 4-1 Gage Catch Freezing Temperature  
(glycol-methanol-water mixture)

Gage Level, Inches	6	7	8	10	12
Freezing Temperature, °C	-40	-30	-23	-13	-4

Reprinted from: Belfort Instrument Company Instruction Book

#### 4.3.2. Calibration

Without a "linearity tool" and a set of calibration weights available through Belfort Instrument Co., only rough checks on calibration may be made. Calibration of the gage is based on the assumption that 622.7 gms of water in the 5-780 series gage equals 1" of precipitation and that the check is best made at mid-range, which is at 3" with the 5-780 series gage. To check calibration, zero the gage with a dry rain gage catch bucket in place and then add 2468 gms of water to the dry bucket. The chart should indicate 2.90-3.10" of precipitation if calibration is correct.

Calibration should be checked at least twice per year and any time consistent disagreement between the rain gage and Aerochem Metrics sampler cannot be explained. Be sure to report the results of this check in the REMARKS block on the FIELD OBSERVER REPORT FORM.

Should recalibration become necessary a properly equipped, qualified person should be contacted to recalibrate the instrument. Factory recalibration is available through Belfort Instruments.

#### 4.3.3. Rain Gage and Event Recorder Chart Interpretation

The NADP sampling protocol requires that weekly precipitation be recorded in daily amounts on the FIELD OBSERVER REPORT FORM and, that the sum of these daily amounts correspond to the volume of liquid present in the Wet/Dry Collector. When differences in the amount of precipitation between the Rain Gage and the Wet/Dry Collector are identified, an event record is used to determine where the discrepancy occurs and the significance of the difference. Discrepancies are reported in data block 11, REMARKS on the FIELD OBSERVER REPORT FORM.

Figure 4.1. represents a sample rain gage chart with an event recorder tracing. Like most weekly charts used in the NADP network it covers an eight day period. Scaling of the chart is in inches and is represented by the numbers printed along the major divisions of the chart; 1-11, 2-10, 3-9, etc. Since this chart is designed for a dual traverse rain gage the number printed before the dash represents the precipitation amount as the pen swings upward recording 0-6 inches of precipitation. The number after the dash represents additional precipitation as the pen swings downward recording 6-12 inches of precipitation. Each chart division then represents 0.05 inches of precipitation.

In general accumulating precipitation is recorded on the lower portion of the chart and the number and duration of precipitation "events" is recorded on the upper portion of the chart. For the purposes of interpreting the precipitation record (bottom line) numbers have been added corresponding to the precipitation events (top line). Note - As designed the event recorder trace (top line) lags behind the precipitation record by ~4 hrs. This offset allows the rain gage pen to swing freely full scale 0-12" without interference from the event recorder pen.

Starting at Tuesday's 0 event, note that the baseline of the chart drifts. Up to 0.05 inches on the chart is normal and usually a result of the sensitive mechanical linkage connected to the pen arm, responding to daily temperature oscillations. The chart paper also expands and contracts due to changes in humidity. If a precipitation event had occurred, the event recorder would have shown a deflection from baseline.

Event 1 demonstrated how the event recorder works in relation to the precipitation amount. The event marker (top line) deflects at the start of the precipitation event and stays deflected until the event is over at which time the tracing returns to its baseline position. The precipitation amount is measured from the start of the rise in the rain gage tracing (bottom line) to the end of the rise. This event then started about 8 a.m. on Wednesday and lasted until midnight, leaving 0.40" of precipitation. This is confirmed by the event recorder which also shows the event starting at 8 a.m. and stopping at midnight.

Event 2 precipitation is measured again from the start of the rise of the event to the end of the rise. It does not include the rise of event 1 and ignores the fact that the pen tracing dropped about 0.03" between the finish of Event 1 and the start of Event 2. This difference may be due to drift or evaporation but in any case is not important to Event 2 or to Event 1. Remember, we are trying to determine the amount of rain that *fell* in the rain gage bucket, not the amount that is *still* in the rain gage bucket. Again, the event recorder confirms the event.

Event 3 is like Event 2 and also is confirmed by the event recorder. Note, however, how the event recorder more accurately indicates the start of the event.

The interpretation of Event 4 requires that you understand exactly what the event recorder does. It records the time the wet bucket is

exposed to deposition. It does not actually record the start/stop and duration of precipitation events. We only assume it records precipitation events based on the assumption the wet/dry collector opens for precipitation events. The event marker on Event 4 shows the \_\_\_\_\_ sampler did open, however, the rain gage tracing (bottom line) is inconclusive as to whether precipitation did occur. Unless you have reason to believe otherwise, this should be recorded as a trace amount of precipitation. In this case the fact that the \_\_\_\_\_ Collector opened is just as important as determining the amount of precipitation falling in the rain gage (See block 5, SITE OPERATIONS on the FIELD OBSERVER REPORT FORM).

Event 5 is similar to Events 2 and 3. This event better illustrates the sometimes dramatic fall of the rain gage tracing and its irrelevance to the determination of precipitation in Event 5 or 4 or 3. During Event 5, 0.23" of precipitation occurred.

Events 6 and 7 are similar to Event 4 and reflect the type of tracing that might occur during periods of intermittent drizzle or heavy fog. The collector opens frequently or stays open while no appreciable precipitation occurs. Event 8 is not a precipitation event but rather a "Test" event which occurs when the \_\_\_\_\_ sensor is activated by the operator to change the buckets. This event will occur either at the end of the sampling period or at the beginning of the sampling period depending on when the rain gage chart is changed in relation to the WET-SIDE sample buckets.

Table 4.2 indicates the amount of precipitation for each event and the total for the week. *The correct weekly total amount of precipitation can only be determined by determining the amount of precipitation in each event and adding the amounts.*

To complete the PRECIPITATION RECORD block on the FIELD OBSERVER REPORT FORM, Table 4.2 event data must be rearranged into daily precipitation amounts. This is accomplished by adding events, as in Events 6 and 7, or splitting events, as in Event 2, to get the proper amounts of precipitation for each day. The correct daily amounts of precipitation are listed in Table 4.3.

## 5.0 ON SITE QUALITY ASSURANCE SAMPLES

Occasionally you may be asked to participate in one or both of the NADP Quality Assurance Programs. These programs are administered by the U.S. Geological Survey (USGS) and are designed to evaluate the quality of work performed at CAL and at each field laboratory.

### 5.1. The NADP Intersite Comparison Study

In this program a standard solution aliquot is sent to each site to be evaluated for pH and specific conductance. Procedures for analysis are described on information submitted with the sample. The results are tabulated and compared to the calculated and determined values as measured by the U.S. Geological Survey.

### 5.2. The NADP "Blind" Sample Program

This program provides a basis for overall NADP program Quality Assurance by submitting a standard sample to each site and allowing them to submit the sample to CAL in lieu of a normal precipitation sample. The results indicate not only how effective the CAL is in determining chemical constituents but also the magnitude of contamination inherent to the NADP protocol. The program works as follows.

Field Site Operators transfer the QA sample to a clean, unused sample bucket, and transmit it to CAL as a precipitation sample. QA samples are only submitted to CAL in a week during which no precipitation was recorded; so that the record of wet deposition at the cooperating site is not interrupted.

#### MATERIALS PROVIDED

- 1 - 500 ml polyethylene bottle containing QA sample
- 2 - pre-addressed postcards to be completed and sent to Gibson and Schroder.
- 1 - mailing label to send used *WET-SIDE* bucket and remaining QA sample to USGS.

### CONDITIONS

- (1) Only submit QA sample to CAL after a week when NO water has accumulated in the WET-SIDE bucket (NO wet-deposition at the site). QA samples should be kept refrigerated, not frozen if possible until this condition is met.
- (2) Do Not send QA sample to CAL in WET-SIDE buckets removed from the wet/dry collector; DOING SO WILL INVALIDATE THE SAMPLE.
- (3) Do Not notify CAL or indicate in any manner to CAL that a QA sample is being sent.

### PROCEDURES

- (1) When NO wet-deposition has been collected, change the WET-SIDE bucket on Tuesday according to the normal procedures.
- (2) Send the dry WET-SIDE bucket removed from the collector to USGS, by affixing the USGS mailing label to a black mailer. This bucket will be cleaned by USGS and returned for future use.
- (3) Pour approximately 75% of the QA sample from USGS into a clean, unused bucket from CAL. "Eyeball it," it is not necessary to get exactly 75%. This sample, now, is the "blind QA" sample to be sent to CAL. Treat it as (carefully as) a rain sample. The sample remaining in the bottle from USGS is to be returned to USGS along with "dirty" bucket (2 above). Simply place the capped bottle in the mailer with the bucket.
- (4) Following standard procedures for a precipitation sample (3.3.2), prepare a FIELD OBSERVER REPORT FORM for the "blind QA" sample (keep in mind CONDITION 3, above). Use dates and times for the week during which no precipitation had occurred (step 1). Check WET-SIDE for sample type and determine the SAMPLE WEIGHT as usual. Remove the normal aliquot and measure pH and conductance and record these values as usual. Create a PRECIPITATION RECORD: make the Total Sampling Period Precipitation from Rain Gage to total between .20 inches and .25 inches, then "make up" a daily precipitation record such that the sum of the daily amounts equals exactly the weekly total. Be clever! If it is winter and cold outside, record snow, for example. For SITE OPERATIONS, answer Yes to all questions and for SAMPLE CONDITION, answer No to all questions. Seal, bag, and ship the bucket to CAL, along with the "phoney" field sheet.
- (5) Complete the information requested on the 2 postcards from USGS and mail to the pre-addressees.

### CONDITIONS

- (1) Only submit QA sample to CAL after a week when *NO* water has accumulated in the *WET-SIDE* bucket (*NO* wet-deposition at the site). QA samples should be kept refrigerated, not frozen if possible until this condition is met.
- (2) Do Not send QA sample to CAL in *WET-SIDE* buckets removed from the wet/dry collector; *DOING SO WILL INVALIDATE THE SAMPLE*.
- (3) Do Not notify CAL or indicate in any manner to CAL that a QA sample is being sent.

### PROCEDURES

- (1) When *NO* wet-deposition has been collected, change the *WET-SIDE* bucket on Tuesday according to the normal procedures.
- (2) Send the dry *WET-SIDE* bucket removed from the collector to USGS; by affixing the USGS mailing label to a black mailer. This bucket will be cleaned by USGS and returned for future use.
- (3) Pour approximately 75% of the QA sample from USGS into a clean, unused bucket from CAL. "Eyeball it," it is not necessary to get exactly 75%. This sample, now, is the "blind QA" sample to be sent to CAL. Treat it as (carefully as) a rain sample. The sample remaining in the bottle from USGS is to be returned to USGS along with "dirty" bucket (2 above). Simply place the capped bottle in the mailer with the bucket..
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- (5) Complete the information requested on the 2 postcards from USGS and mail to the pre-addressees.



## 6.0 DIRECTORY

### 6.1. National Atmospheric Deposition Program

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Sheri Uber, (217)333-3936  
Shipping problems  
Supplies  
Field Measurements (pH,  
conductivity, weights)

Scott Dossett, (217)333-0249  
Data on computer printouts  
Wet/Dry sampler and rain gage  
questions

Mark Peden, (217)333-8325  
General questions about analyt-  
ical procedures and equipment  
in use at CAL. Also, call Mark  
if you can not reach Sheri Uber

## APPENDIX 1

## APPENDIX 1 NADP Equipment Requirements

### Wet/Dry Precipitation Collector

#### Recording Rain Gage Equipped with an Event Recorder

Requirements:

Must meet National Weather Service specifications #450.2201 and #450.2203 have 0.5% full scale accuracy,  $-40^{\circ}$  -  $+125^{\circ}\text{F}$ , and 0.01" precipitation sensitivity, have an 8.00" collector opening and chart timing  $\pm 14$  minutes/week.

Recommended:

Belfort Universal Rain Gage, 5-780 series equipped with an event recorder

The event recorder may be purchased separately  
or installed with a Belfort Universal Rain Gage.

NOTE: Products listed below are examples of equipment meeting the requirements of the project. Listing of these products does not constitute endorsement by the project staff.

### Balances

Requirements:

20 kg capacity and 1 g sensitivity

Example:

1. Ohaus Model 11190

### Specific Conductance Meters

Requirements:

0.1-1,000 umho range(s) and readability to 0.1 umho

Examples:

1. Lab-Line Lectro Mho meter, Mark V
2. Barnstead Model PH-70 CB
3. Yellow Springs Instrument, Model 31
4. Beckman RC-16C

### Specific Conductance Electrodes

#### Requirements:

Cell constant of 1.0 and a sample volume requirement of  $\leq 10$  ml.

#### Examples:

1. Barnstead Model E3416 (dip)
2. Lab-Line Model 11201 (beaker)
3. Yellow Springs Instrument Model 3403 (dip)

### pH Meters

#### Requirements:

Read 0-14 pH units, digital display with readability to .01 pH units, 115 VAC power supply, and separate calibration, slope, and temperature controls.

#### Examples:

- |                 |               |
|-----------------|---------------|
| 1. Beckman 3500 | 5. Fisher 630 |
| 2. Beckman 3560 | 6. Orion 601  |
| 3. Brinkman 103 | 7. Orion 701  |
| 4. Corning 125  |               |

### pH Electrodes

#### Requirements:

Refillable glass combination electrode with an annular ceramic junction

#### Examples:

1. Beckman Futura, 34105-190 with combination Cable #34105-382, or -360 or -350
2. Beckman Futura, 34105-189
3. Beckman Futura, 34105-101
4. Orion, 9162

### Suggested Labware

5 100 ml plastic beakers

1 250 ml wash bottle

Laboratory wipes such as Kimwipes<sup>R</sup>

Distilled or deionized water, conductivity below 10  $\mu\text{S}/\text{cm}$

APPENDIX 2

## APPENDIX 2 Troubleshooting pH and Conductivity Measurements

### Introduction

This Appendix assists field personnel in diagnosing problems with pH meters and electrodes, and conductivity meters and cells. There are far too many makes and models of equipment to discuss them individually, but the basic principal of operation is similar. A discussion of the theory of pH measurements, and the operation of pH electrodes and conductivity cells is presented at the end of this Appendix. It is strongly recommended that all field personnel have an owner's manual and become familiar with the operation and maintenance of their own particular meter, electrode, and cell. Manuals can be obtained from the appropriate manufacturer. Spare pH electrodes should be available at each field site.

### Diagnosing pH Electrode Problems

New pH electrodes generally take longer to activate for the first time than indicated by the manufacturer. While the pH electrode will calibrate properly in buffer solutions, it is slow to respond to the pH of a rain sample. Therefore before field use, a new electrode should be stored in a pH 4 buffer for several days to insure proper activation and operation for pH measurements of rain samples.

To test the performance of the pH electrode, set the meter to the millivolt scale after following the procedure for calibration and record the millivolt readings in the pH 4 and pH 7 buffer solutions. The difference in the millivolt readings divided by the difference in pH readings should be 59.15 at 25°C. If this value is different than  $59.15 \pm 2$ , the electrode or meter is not functioning properly; usually, the pH electrode is at fault.

If the pH electrode does not calibrate properly in the buffer solutions, they may be contaminated. There is no simple way to determine if a buffer solution is contaminated other than by physical appearance, such as the presence of a surface film or debris. Buffer solutions usually last 3 months if infrequently used and tightly sealed, and should be dated and replaced after 3 months.

Wiping the electrode with tissue during calibration is not recommended as this may result in a static charge which affects measurements. Instead, gently blot the electrode dry with an absorbent wipe.

Make sure that the pH electrode cable is securely and properly connected to the meter and to the pH electrode, and that the contacts are clean. Check the cable for cuts. The electrode should be inspected for cracks or scratches on the special glass bulb (see Figure 1 of Appendix). Check the indicating and reference electrodes to see if they are broken. If any of these problems exist, the pH electrode must be replaced.

Errors can also result from a dirty electrode. Because the glass bulb is part of the measuring element of the electrode system, impurities can greatly affect its performance. One source of impurities is a contaminated buffer; also rain samples can be "dirty". Therefore, the pH electrode should be washed with a mild detergent diluted with de-ionized water several times a year. The special glass bulb can be gently rubbed with the fingertips and gently blotted dry with an absorbent wipe.

The reference electrode junction (see Figure 1 of Appendix) may be clogged or encrusted. To test for clogging, the electrode may be stored in a vertical position and allowed to dry overnight. If the junction is functioning properly, a light crusting will be present; if it remains clean, the junction is clogged and should be soaked in hot, deionized water for several minutes. Since the electrode is allowed to become dry during this procedure, it must be re-activated by storing it in a pH 4 buffer solution for several hours or as the owner's manual recommends.

The potassium chloride (KCl) electrolyte solution (see section on pH Electrode) may be depleted of ions. This is probably the most common and most serious problem, and is also the most difficult problem to detect. The pH electrode will calibrate properly in the buffer solutions but may not be accurately measuring the pH of the rain sample. An early indication of this problem is in the length of time it takes for the pH measurement to stabilize; a pH reading should only take 3 or 4 minutes. If the pH value takes 5 minutes or more to stabilize and even then tends to drift, the KCl filling solution may be depleted of ions. Calibrate a spare electrode and compare pH values as well as the time required to obtain a final pH value in the same rain sample. If the values differ by 0.10 pH unit, the original electrode should no longer be used. Another more direct method for testing the pH electrode for those field personnel who have access to a chemistry laboratory is outlined in the section on Preparation of a Test Solution.

Some pH electrodes are sealed so that the electrolyte solution cannot be replaced. These electrodes use a KCl gel and ions can only be replenished by regeneration. Other electrodes have an opening to replace the electrolyte solution. These electrodes use a liquid KCl solution and ions are replenished by simply replacing the KCl solution.

Regeneration procedures for sealed pH electrodes are outlined in the owner's manual or can be obtained from the appropriate manufacturer. Usually, the electrode can be regenerated by storing it in a vertical position and allowed to dry overnight, allowing gravitational settling of the more active gel at the top of the electrode. The reference electrode junction must then be cleaned as outlined earlier and re-activated by storing in a pH 4 buffer solution for several hours. Also, the pH electrode can be dipped into a boiling solution of 4 molar KCl (74.6 grams of KCl dissolved into a liter of deionized water) for 10 to 15 minutes. In any case, regeneration of the pH electrode is a last resort. Even after successful regeneration, it can only provide several good measurements. An electrode should not be regenerated more than once; use the spare electrode.

For other pH electrodes, the KCl solution can be replaced. Simply drain the electrode, and dissolve and rinse away any KCl crystals with hot deionized water. Refill it with the KCl solution obtained from the manufacturer, and soak it in a pH 4 buffer solution for several hours before use. The level of the KCl solution must not fall below the opening, and the fill hole must be opened when pH measurements are being made and closed when the pH electrode is being stored.

The presence of KCl crystals in the electrode does not affect its operation. Sometimes, brown particles in the refillable-type electrode are present; these are silver particles and result from the KCl solution being saturated with silver chloride. The presence of brown particles in the electrode is an indication that the electrolyte solution is properly saturated with silver chloride.

#### Diagnosing pH Meter Problems

The pH meter is rarely at fault. However, if the pH electrode is known to be functioning properly, yet does not calibrate in the buffer solutions, and the slope control or calibration dial seem to be ineffective, the problem may be with the meter. If the pH meter is battery operated, the batteries may be low or dead. Some older meters are AC operated but use a mercury battery for the reference potential. These batteries should be tested under load, that is with the meter turned on, and should be replaced when they have dropped to 10-15% below their rated voltages. If the batteries are not at fault, check the owner's manual for specific trouble-shooting tests before returning the pH meter to the manufacturer for repair.

The slope control or calibration dial provides a good indication of how the pH electrode and meter are functioning. Mark or record the position of the dial and note how far the dial has to be turned during calibration in the buffer solutions each time a calibration is performed. The fact that the dial has to be turned more and more each time, is an early indication of problems with the pH electrode or meter.

#### Diagnosing Conductivity Cell Problems

Most problems in conductivity measurements are due to measurement techniques or to the cell. All conductivity cells provide a chamber at the end of the two electrodes. The most common cell is bell-shaped (see Figure 2 of Appendix). The cell should be suspended in the rain sample such that both electrodes are submerged and free of trapped air. This can be accomplished by slightly tilting the cell and gently tapping the side, or it can be moved up and down in the rain sample in a plunging motion. The cell should never touch the sides or bottom of the beaker which contains the rain sample while a conductivity measurement is being made. If at all possible, the beaker containing the rain sample should be well insulated; i.e., not grounded. The presence of the electrical fields and stray currents caused by stirrer motors or heaters, etc., can cause problems in conductivity measurement. Equipment that is suspected of causing electrical fields should be disconnected during conductivity measurements.



The single-most important requirement for accurate and reproducible results in conductivity measurements is a clean cell. The cell can be soaked several times a year in a warm detergent diluted with deionized water and rinsed thoroughly with deionized water.

The two electrodes of the conductivity cell are either gold plated or are coated with platinum black. The gold-plated electrodes are virtually maintenance free, other than cleaning. Since the platinum-black coating is important to cell operation, electrodes require frequent inspection. If the coating appears thin or is flaking off. They must be cleaned and re-platinized. This relatively simple procedure is outlined in the owner's manual.

#### Concluding Remarks

Field personnel should be encouraged to become as familiar as possible with the equipment by reading and occasionally reviewing the owner's manual. In the long run, familiarity with the owner's manual will save time and improve the quality of the measurement.