PROTOCOL FOR COLLECTING, PROCESSING, AND SHIPPING PRECIPITATION SAMPLES

Manual for Task Group G Site Operators, National Atmospheric Precipitation Assessment Program

By Michael M. Reddy, Randolph B. See, and Timothy D. Liebermann

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CONVERSION FACTOR

Multiply	By	To obtain
micrometer (μm)	$3.937X10^{-5}$	inch
milliliter (mL)	0.03382	ounce, fluid
millimeter (mm)	25.4	inch

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ABSTRACT

This report documents the protocol for collecting, processing, and shipping precipitation samples as part of an investigation of the effects of acid rain on carbonate-rock building materials. These effects are being investigated at four sites in the eastern United States--Washington, D.C.; Chester, New Jersey; Newcomb, New York; and Research Triangle Park, North Carolina. At each site, precipitation-runoff samples are collected from glass sheets, limestone and marble slabs, and blanks. Precipitation samples also are collected in a wet-only precipitation collector modified for continuous pH measurement. All samples are processed and shipped in the same manner.

INTRODUCTION

Precipitation samples are being collected and analyzed as part of the National Atmospheric Precipitation Assessment Program (NAPAP), Task Group G study regarding the effects of acid rain on carbonate-rock building materials. These effects are being investigated at four sites in the eastern United States--Washington, D.C.; Chester, New Jersey; Newcomb, New York; and Research Triangle Park, North Carolina (see cover). At each site, precipitation-runoff samples are collected from glass sheets, limestone and marble slabs, and blanks. Precipitation samples also are collected in a wet-only precipitation collector modified for continuous pH measurement. All samples are processed and shipped in the same manner.

This report, which is chapter A of an operations manual for the site operators, documents the protocol for collecting, processing, and shipping precipitation samples from all collectors. Operational protocol for the wet-only precipitation collector is documented in chapter B of the manual.

SITE CHARACTERISTICS

As currently developed (1986), each monitoring site has four racks. Each of the four racks is placed on three plywood boxes or bases. Sample bottles, supplies, and other equipment are located inside the bases. Each rack has two, 12 by 24 inch slots for glass sheets, stone slabs, or blanks providing a maximum of eight slots per site. Four slots are available for precipitation-runoff sample collection, and four slots are used for other purposes. Racks are numbered 1 through 4. Slots used for collecting samples are numbered A1 through A4; the other slots are numbered B1 through B4. Racks are side by side, in sequential order. Slots may be arranged in any workable order. Each set of racks, A and B, contains at least one glass sheet, one limestone slab, one marble slab, and one blank slot. Plexiglass splash guards are placed between the slots to avoid contamination between slots.

Some sites also have a wet-only precipitation collector modified for continuous pH measurement. Samples from this continuous precipitation monitor are processed and shipped in the same manner as the precipitation-runoff samples.

SITE MAINTENANCE

Visual inspection of the racks needs to be made immediately after arrival

at the site. If maintenance is required, it needs to be done after the water sample is removed and before the replacement bottle is installed. Debris deposited by natural causes on a rack should be left as is. Other debris (for example, leaves jamming the drain outlet of the rack) needs to be gently removed and such removal is noted on the Inspection Log. After removing debris, rinse the area previously covered by the debris with distilled water, making certain that water drains freely.

Minor repairs needs to be made immediately after the water sample is removed. For serious problems, call Michael M. Reddy, Randolph B. See, or Marilyn G. Werner at (303) 236-3617 or FTS 776-3617. Submit a copy of the Stone Slab Yearly Report or the Inspection Log when appropriate. Follow the Site Protocol in Section VII of the Site Management Plan.

Maintenance of the wet-only precipitation collector is discussed in chapter B of this manual. Copies of both chapters need to be stored at the site.

SAMPLE COLLECTION

The protocol for sample collection is designed for the collection of a sample after every storm. The protocol is as follows:

1. Check apparatus for normal operation.
2. If a collection bottle contains any water, remove, cap, and label the bottle with a unique sample number and the date and time of removal. Make other notes, as necessary.
3. Perform and make a note of any maintenance.
4. Replace original collection bottle with a clean, pre-labeled collection bottle. (Collection bottles need to be rinsed well with distilled water three times and air dried.)
5. Check the in-line, fiber-glass filter and replace the filter if debris has accumulated.
6. Insert the sample-collection line into the replaced collection bottle.

SAMPLE PROCESSING

Samples are to be processed immediately after collection, preferably indoors under controlled conditions, using reliable equipment. All glassware is to be scrupulously clean. If possible, perform all measurements at a room temperature of 25 ^{o}C (degree Celsius). The pH and specific conductance of several standard solutions at 25 ^{o}C are presented in Attachment I. Record all sample measurements on Attachment II, the site observer's record sheet.

Cleaning Glassware

Collection bottles and glassware (both new and used) needs to be rinsed three times with distilled water, then rinsed with dilute nitric acid, then rinsed three times with distilled water, and then allowed to air dry. Dilute nitric acid is prepared by mixing 1 part of acid with 20 parts of water.

Filtration Procedure

1. Wear rubber gloves. Do not touch the inside of the filtration equipment.
2. Use a 0.45-µm sealed filter attached to a 50-mL syringe to provide pressure. Use of a pump filtration assembly with 50-mm diameter, 0.45-µm filter is an acceptable alternative to the filtration syringe.
3. Rinse the filter by passing 25 mL of distilled water through filter, followed by 10 mL of sample. Discard this filtrate.

4. Rinse a clean shipping bottle with 25 mL of distilled water. Filter one-half (as much as 250 mL) of the sample through the filter and into the shipping bottle. If the filter clogs completely before 250 mL have been filtered, rinse the syringe and use a new rinsed filter.
5. Cap and label the shipping bottle; specify "FILTERED."
6. Discard filters. The syringe can be reused if it is still operating well. Use separate syringes and filters for filtering the limestone, marble, and blank samples, or rinse well with distilled water between samples.

Volume Measurment and Processing Options

1. Pour sample into a clean graduated cylinder with a volume of 1000 mL (millimeters); record volume to nearest 10 mL.
2. If volume is less than 200 mL:
   a. Measure pH and specific conductance of unfiltered sample.
   b. Pour any remaining sample, without filtering, into a clean shipping bottle with a volume of 250 mL.
3. If the volume is more than 200 mL:
   a. Measure pH and specific conductance of unfiltered sample.
   b. Filter one-half of remaining sample into a clean shipping bottle with a volume of 250 mL.
   c. Pour remaining one-half of sample, without filtering, into another clean shipping bottle with a volume of 250 mL.

pH Measurements

About 20 mL of sample are needed for these measurements. General procedures applying to all measurements during calibration of the instrument and measuring of sample pH are:

1. Before first measurement and between measurements, rinse the glass pH electrode three times with distilled water, then rinse with the next solution to be measured.
2. Carefully adjust the temperature compensation for every measurement.
3. Allow all measurments to stabilize before recording them; this may take as much as 15 minutes for dilute solutions.

Before sample pH is measured, the instrument is to calibrated as follows:

1. Measure pH of distilled water and standard dilute acid.
2. Calibrate the zero adjustment using the pH 7.00 buffer.
3. Adjust the slope control using the pH 4.00 buffer.
4. Repeat steps 2 and 3 until measurements for each buffer are within 0.01 pH unit of known value.
5. Measure the pH of distilled water and standard dilute acid as checks of proper operation.
6. Record all measurements associated with calibration on Attachment III, the instrument calibration record sheet.

Measure sample pH as follows:

1. If sample volume is less than 200 mL, make 1 measurement.
2. If sample volume is more than 200 mL, make 2 measurements.
3. Record measurements on Attachment II.
4. After all samples are measured, or after every 10 samples are measured, check for calibration drift by measuring pH 7.00 and 4.00 buffers. If calibration has drifted more than 0.05 pH units, recalibrate the pH meter.

Specific-Conductance Measurements

About 20 mL of sample are needed for these measurements. General procedures applying to all measurements during calibration of the instrument and measuring of sample specific conductance are:

1. Between measurements, rinse the measuring cell three times with distilled water, then rinse with the next solution to be measured.
2. If possible, adjust the meter to the appropriate cell constant. Also adjust for temperature with every measurement.
3. Allow readings to stabilize. Record all specific conductances, temperatures, and the cell constant.
4. Measure the specific conductance of low and high standard solutions and of distilled water.
5. If your meter does not have adjustments for temperature or cell constant, you may use the following formulae to compute the specific conductance of your standard solutions at 25°C:

$$C_2 = \frac{C_m K}{1 + 0.02 (T-25)}$$

where

C_2 = actual specific conductance (µS/cm);
C_m = measured specific conductance (µS/cm);
K = cell constant; and
T = temperature (°C).

6. Measure specific conductance of distilled water and standard dilute acid solutions and KCL solutions as checks.
7. Measure specific conductance of sample and repeat if sample volume exceeds 200 ml.
8. After all samples are processed, measure specific conductance of distilled water and standard solutions.

Quality Control

To determine if any loss or contamination is occurring in the sample processing, a filtered standard reference sample and filtered distilled-water blank sample are to be submitted each month. The operator is to process these samples exactly as the precipitation sample. It is not necessary to send an unfiltered sample for either the standard reference or distilled-water samples. Because of the expense of the standard reference sample, waste is to be avoided. The standard reference sample needs to be kept tightly capped, refrigerated, and away from light.

As a check on analytical variation, the operator is to submit a set of duplicate samples each month for the first storm that has volume larger than 1,000 mL. Duplicate samples are to be processed in the same manner as all other precipitation samples. A filtered and unfiltered sample are to be provided for each duplicate sample. Sample bottles are to be labeled and log-in sheets are to be annoted to identify one set of samples as duplicates.

SAMPLE SHIPPING

Pre-Shipping Instructions

1. Pour remaining sample into a rinsed, clean, 250-mL shipping bottle; cap and label the bottle. Specify "UNFILTERED." Only one unfiltered bottle is needed; any remaining sample may be discarded.
2. Tape (preferably with black electrical tape) the caps of all shipping bottles, make sure all bottles are labeled properly, and pack securely

inside a shipping box.
3. Enclose log-in sheet and any other records in the box.
4. Refrigerate box until shipping if such a facility is available. If refrigeration is not available, keep samples in a cool, dark location.
5. Clean and pre-label the used collection bottles for future use.

Shipping Instructions

1. Ship as soon as possible after processing.
2. Make sure box is sturdy, well taped, and that mailing label is complete and firmly attached.
3. Send via U.S. Postal Service; write "Priority Mail" on box.
4. Using shipping labels provided, send box to:

Michael Reddy
U.S. Geological Survey
National Water Quality Laboratory
5293 Ward Road
Arvada, Colorado 80002

LABELING, RECORD KEEPING, AND NOMENCLATURE

This section contains a brief description of the record-keeping system and of specific terms. Attachment IV contains the format to be used for recording all required information on bottle labels. It is advisable to keep a copy of all records sent to the U.S. Geological Survey.

1. Sample bottles are used to collect runoff onsite and transport it to the laboratory. The bottles are to be labeled with the following codes:
   a. Sample # -- The unique number associated with a storm. For example, the 17th storm of 1984 would have the sample #1984-17.
   b. Sample Type -- G = Glass
      L = Limestone
      M = Marble
      B = Blank
      P = Continuous Precipitation Monitor
      D = Distilled Water
      S = Standard Reference
   c. Site -- DC = Washington, D.C.
      NJ = New Jersey
      NY = New York
      NC = North Carolina
   d. Side -- was the sample collected from the Left (L) or Right (R) side of the rack?
   e. If bottle overflowed, write, "OVERFLOWED."
   f. Comments -- for example: intense storm; snowmelt; bird droppings in bottle; everything frozen.
   g. Precipitation will be assumed to be rain unless otherwise specified.
2. Shipping bottles hold filtered and unfiltered samples during shipping. They are to be labeled either "FILTERED" or "UNFILTERED."
3. The site observer's record sheet is a complete record for each storm and accompanies the samples during shipment. Fill out sheets as carefully and as completely as possible.
4. The monthly record of water samples (Attachment V) is a summary and is to be compiled and mailed every month.
5. An inspection log is to be sent monthly if maintenance was performed.
6. A stone-slab yearly report (Attachment VI) contains information about the slabs themselves. Fill it out yearly or when a slab is installed, moved, or dismantled.

7. Records of pH and specific conductance measurements and notes are to accompany each shipment for which pH and specific-conductance was measured.
   a. Heading -- for example: samples collected on 7-14-84 after intense thunderstorm.
   b. Remarks -- for example: 25 ^{o}C, unstirred, temperature compensation not possible with this meter.
8. Specific-conductance measurement -- for 'Cell Constant?' and 'Temperature?,' answer Yes or No, depending on whether the reported reading was already adjusted for that factor.
9. Alkalinity measurement -- It is not necessary to make an onsite alkalinity calculation.

SUMMARY

Interpretation of dilute precipitation samples requires that a representative, uncontaminated sample be obtained. Great care needs to be taken in collecting, processing, and shipping these samples to provide accurate data for evaluation. If problems cannot be avoided, detailed documentation is to be provided so that the validity of samples can be determined. If the procedures outlined in this report are followed, the validity and quality of the data obtained should be reliable.

REFERENCE

U.S. National Park Service, Acid Rain Site Management Plan for Dimension Stone, Washington, D.C..

Reddy, Michael M.; See, Randolph B.; and Liebermann, Timothy D., 1986, Operational Protocol for a Recording Precipitation Monitor, U.S. Geological Survey Open-File Report 86-405-B.

Attachment I -- Approximate Values of Standard Solutions

Sulfuric-Acid Solutions

Normality	pH at 25 °C	Specific-conductance at 25 °C
0.1	1.27	-----
0.01	2.11	-----
0.001	3.03	415
0.0001	4.01	42.7

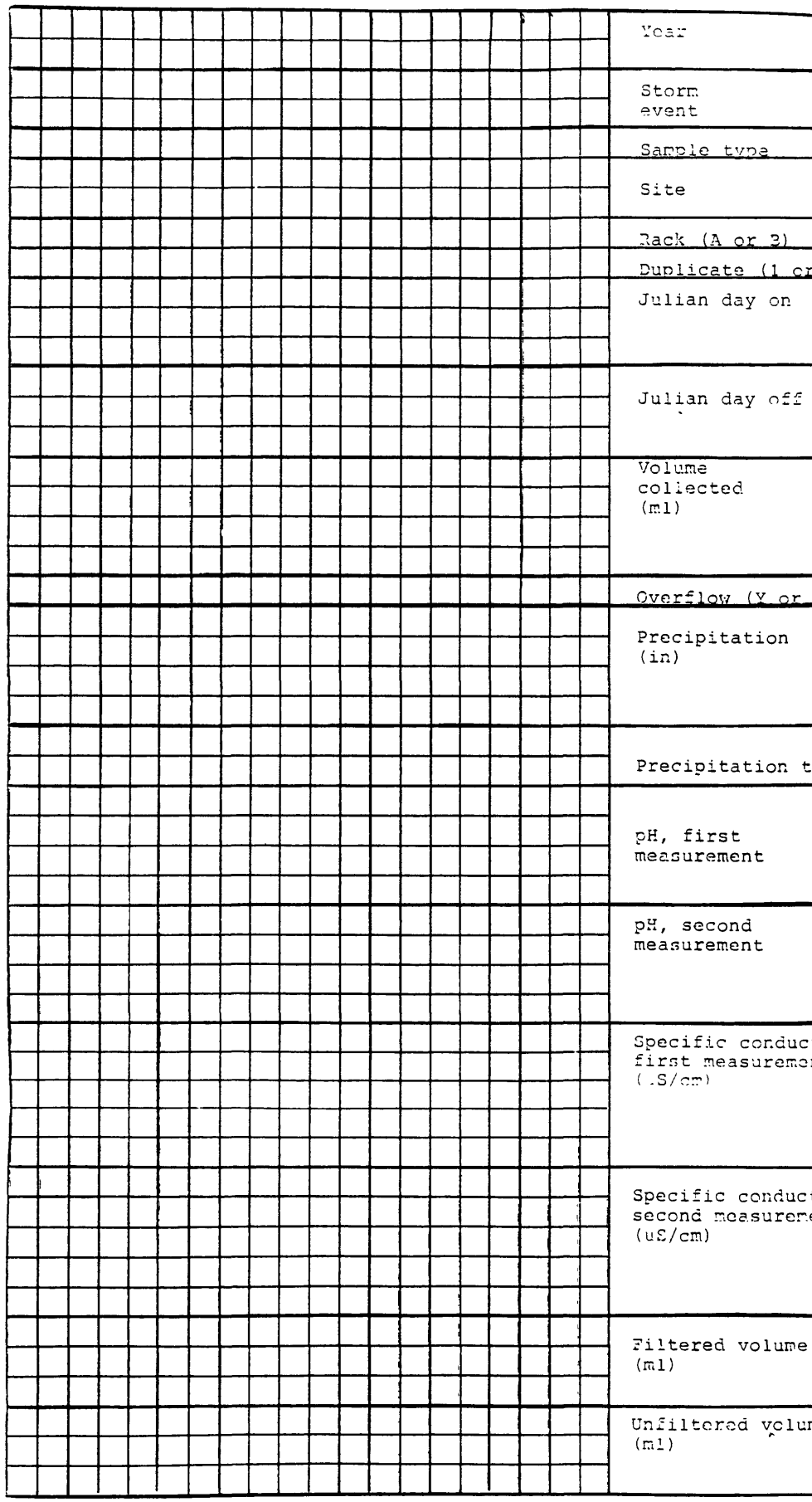
The actual pH of H_2SO_4 changes very little with temperature. However, to compensate for the effects of temperature on the measuring system, a significant correction may be required. The magnitude of the correction increases linearly as the temperature differs from 25 °C and as the actual pH differs from pH 7. A temperature compensation error that is slight at pH 6 will cause an error 3 times as great at pH 4. Thus, it is important to measure and compensate for temperature as accurately as possible. To minimize potential errors, make all measurements at 25 °C.

Potassium Chloride Solutions

Normality	Specific-conductance at 25 °C
0.01	1413
0.001	147.0
0.0004	59.2
0.0001	14.9

To prepare 0.01 N KCl, heat anhydrous KCl at 180°C for 4 hours, then measure out 745.6 mg and add distilled water to make 1 L of solution at 20 °C. The pH of KCl solutions is the same as for distilled water, approximately 5.5-5.8.

ATTACHMENT II -- SITE OBSERVER'S RECORD SHEET



Attachment III -- Instrument Calibration Record Sheet

SITE NAME _____ OPERATOR NAME _____

STORM NUMBER _____

DATE ON _____ TIME ON _____

DATE OFF _____ TIME OFF _____

DATE SAMPLES PROCESSED _____

COMMENTS _____

CALIBRATION AND CHECK SOLUTIONS FOR SAMPLE PROCESSING

SOLUTION	pH	SPECIFIC CONDUCTANCE
PH 7 BUFFER		
PH 4 BUFFER		
10^{-3} N H_2SO_4		
10^{-4} N H_2SO_4		
10^{-3} N KCl		
10^{-4} N KCl		
M-82 STANDARD REFERENCE		
DISTILLED H_2O		

Attachment IV -- Formats for Bottle Labels

Examples of Labels

1. Collection bottles

   Sample - #1984-13-L (NY)

   On 7-15-84, (1412)

   Off 7-17-84 (1500)

   NOTE: Times are to be local military time, and time is to be recorded on the log-in sheet. Comments also are to be recorded on the log-in sheet, for example, OVERFLOWED, INTENSE STORM.

2. Shipping bottles

   #1984-13-L (NY)

   ON Date 7-15-84

   OFF Date 7-17-84

   UNFILTERED or FILTERED

Attachment V — Monthly Record of Water Samples

Month and year_____

Location_____

Operator_____

COLLECTION			MEASUREMENT			SHIPPING		
Date collected	Sample #	Stone type	pH	Conductance (µS/cm)	Alkalinity (mg/l $CaCO_3$)	Date sample shipped	Filt. Y/N	Unfilt. Y/N

Comments_____

Keep a copy of this report for your records.

Attachment VI -- Stone Slabs Yearly Report

Date_____

Location_____

Check one: Yearly report_____, Set up,_____Dismantle_____

Rack #	Slab #	Stone type	Condition of slab

Condition of racks and bases_____

Other comments_____

Recorded by_____

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