PRECISION OF THE MEASUREMENT OF pH AND

SPECIFIC CONDUCTANCE AT NATIONAL ATMOSPHERIC

DEPOSITION PROGRAM MONITORING SITES,

OCTOBER 1981-NOVEMBER 1983

By LeRoy J. Schroder and June O. Brennan

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 84-4325

CONTENTS

TABLES

METRIC CONVERSION TABLE

For the reader who may prefer to use inch-pound units, conversion factors for terms used in this report are listed below:

Multiply SI units	By	To obtain inch-pound units
liter (L)	1.057	quart (qt)
milliliter (mL)	.03382	ounce, fluid (oz)
millisiemens	1.000	millimho
microsiemens per centimeter at 25° Celsius (µS/cm at 25°C)	1.000	micromho per centimeter at 25° Celsius (µmho/cm at 25°C)

PRECISION OF MEASUREMENT OF pH AND SPECIFIC CONDUCTANCE AT NATIONAL
ATMOSPHERIC DEPOSITION PROGRAM MONITORING SITES,
OCTOBER 1981-NOVEMBER 1983

By LeRoy J. Schroder and June O. Brennan

ABSTRACT

Five intersite comparison studies for the determination of pH and
specific conductance, using simulated-precipitation samples, were managed by
the U.S. Geological Survey for the National Atmospheric Deposition Program.
These five intersite comparisons were performed to estimate the precision of
determinations made by sampling-site operators. Simulated-precipitation
samples were prepared from nitric acid and deionized water. It was determined
that the pH and specific conductance were stable for at least 10 weeks when
stored in 125-milliliter, high-density polyethylene bottles. Pooled variances
for pH and specific conductance were calculated for determinations made by the
sampling-site operators. The estimated variance for site-operator deter-
mination of pH was 0.25 for pH values ranging from 3.79 to 4.62; estimated
variance for specific conductance was 4.6 microsiemens per centimeter at $25°$
Celsius for specific-conductance values ranging from 10.4 to 59.0 microsiemens
per centimeter at $25°$ Celsius. These estimated variances were for deter-
minations made from October 1981 to November 1983.

INTRODUCTION

The National Atmospheric Deposition Program (NADP) was organized by the
North Central Region of the State Agricultural Experiment Stations to
investigate problems of atmospheric deposition and its effects on the
environment. The NADP has established a nationwide atmospheric-deposition
monitoring network supported by the U.S. Departments of Agriculture, Commerce,
Energy, and the Interior, U.S. Environmental Protection Agency, State
agencies, public utilities, and private industry. About 140 atmospheric-
deposition monitoring sites currently (1984) are being operated for the
NADP.

Each sampling-site operator determines the pH and specific conductance of
each weekly precipitation sample collected at the site. The sample and
results of the pH and specific-conductance determinations are sent to the
NADP Central Analytical Laboratory (CAL) in Champaign, Illinois. The data
have not been published by the NADP; however, beginning in 1984, the site-
operator determinations for pH and specific conductance will be published
by the NADP. The U.S. Geological Survey is managing an intersite comparison
for the determination of pH and specific conductance for the NADP. Simulated-
precipitation samples were mailed to NADP site operators in October 1981,
April and November 1982, and May and November 1983.

1

This paper describes the preparation, stability, analytical protocol, and handling and data analysis for the simulated-precipitation samples, NADP site-operator results, and the estimated precision of pH and specific-conductance results obtained by the site-operators for October 1981 through November 1983.

SIMULATED-PRECIPITATION SAMPLES

Sample Preparation

Dilute nitric-acid solutions (simulated-precipitation samples) were prepared by adding reagent-grade concentrated nitric acid to 20.0 L of 1.5 megohm (MΩ) deionized water. The required volume of concentrated nitric acid to prepare the simulated-precipitation sample was calculated as follows (Dean, 1978):

1. Target pH of the simulated-precipitation sample was chosen.
2. Hydrogen-ion concentration was calculated from the equation pH=-log[H+].
3. Molarity of the solution was calculated from the hydrogen-ion concentration.
4. Volume of concentrated nitric acid required was calculated.

The equation for required acid volume is:

$$V = \frac{100wM}{pd} \times 20 \qquad (1)$$

where
- V is the volume of concentrated nitric acid, in milliliters;
- w is the molecular weight of nitric acid, in grams per mole;
- M is the desired molarity;
- p is the weight percent of concentrated nitric acid; and
- d is the density of concentrated nitric acid, in grams per milliliter.

After addition of the required volume of concentrated nitric acid to 20.0 L of deionized water, the solution was mechanically stirred for at least 24 hours in a sealed container. About 150 subsamples were transferred into 125-mL, high-density polyethylene bottles. Measurements of pH were made on four of the subsamples. Hydrogen-ion concentration was calculated using the average pH from the four subsample measurements. Nitrate concentration (equivalents per liter) of the solution was assumed to be the same as the hydrogen-ion concentration. Conductivity of the solution was calculated using the equation (Castellan, 1971):

$$K = k(1/1000)\Sigma_i C_i \lambda_i \qquad (2)$$

where   K is the conductivity in millisiemens;
         k is the constant of proportionality (reciprocal ohms, centimeter,
           and equivalents per liter);
         C is the concentration of ions in the solution (equivalents
           per liter); and
         λ is the equivalent conductivity of the ion (H^+=349.8, NO_3^-=71.44).

The conductivity measured for the same four subsamples used to measure the pH
was compared to the calculated conductivity using the equation:

$$E = \frac{\text{measured conductivity-calculated conductivity}}{\text{calculated conductivity}} \times 100 \qquad (3)$$

where

     E is the percent error.

The percent error for conductivity was less than 5 percent for all five audit
samples.

Sample Stability

     Dilute nitric-acid solutions have stable pH and specific conductance for
at least 10 weeks, when they are stored at ambient temperature in high-
density polyethylene bottles. Ten subsamples of the nitric acid solutions,
prepared for the April 1982 and November 1982 intersite comparisons, were
analyzed for pH and specific conductance at a rate of 1 per week for the
10 weeks after solution preparation. The stability experiments were con-
current with the two intersite comparisons. Both pH and specific conductance
were measured by one individual using the same instruments on each sample.
Three additional samples from the April 1982 solution were analyzed for pH
and specific conductance 22 weeks after preparation.

     The solution prepared for the April 1982 intersite comparison had a
calculated pH of 4.52. The mean of pH determinations made on 10 subsamples by
the U.S. Geological Survey was 4.53±0.02. The mean of 10 pH determinations
made during 10 weeks, using a different subsample each week, was 4.55±0.03.
The solution prepared for the November 1982 intersite comparison had a
calculated pH of 3.95. Ten replicate determinations by the U.S. Geological
Survey had a mean pH of 3.90±0.03. Ten different subsamples were analyzed
at a rate of 1 per week for 10 weeks. The mean of the 10 determinations
for pH was 3.92±0.05.

3

Specific conductance was measured by the U.S. Geological Survey for both the April and November 1982 solutions. The April 1982 solution had a calculated specific conductance of 12.7 µS/cm. The mean of 10 replicate determinations for specific conductance by the U.S. Geological Survey was 11.5±0.4 µS/cm. Mean specific conductance was 11.4±0.9 µS/cm for 10 sub-samples analyzed at a rate of 1 per week for 10 weeks. The nitric-acid solution prepared for the November 1982 intercomparison had a calculated specific conductance of 47.2 µS/cm. Ten replicate analyses of the solution for specific conductance gave a mean of 37.2±0.7 µS/cm. Mean specific conductance of 10 subsamples analyzed during the 10 weeks was 37.0±0.8 µS/cm.

Subsamples of the April 1982 nitric-acid solution were analyzed 22 weeks after preparation and storage. Results from 2 of the 3 samples were nearly identical to the mean obtained from the 10-week study for both pH and specific conductance. However, results from one sample were different. The measured pH of this sample was 4.26, and the specific conductance was 13.5 µS/cm; the reason for the different pH and specific conductance is unknown.

A visual inspection of the pH and specific-conductance results from the two 10-week studies did not indicate any time dependency. Results obtained from the 3 samples analyzed 22 weeks after preparation indicated that for 1 subsample the pH and specific conductance had changed. Therefore, the dilute nitric-acid solutions were stable for at least 10 weeks and may have been stable for longer periods.

Sample-Analysis Protocol

NADP sampling-site operators received the simulated-precipitation samples through the mail. Operators were instructed to determine the pH and specific conductance of each sample, using the NADP guidelines (Bigelow, 1982). The pH-determination protocol required that the sampling-site operators use the following procedure: (1) Standarize their pH meter using a 7.00 pH standard supplied by CAL; (2) rinse the pH electrode; (3) determine the pH of a 4.01 pH standard supplied by CAL; (4) adjust the pH-meter slope control to obtain a pH reading of 4.01; (5) rinse the pH electrode; (6) determine the pH of the simulated-precipitation sample; and (7) report the value obtained from the simulated-precipitation sample to the nearest 0.01 pH unit.

The specific-conductance-measurement protocol required that sampling-site operators use the following procedure: (1) Standarize their conductance meter, using a potassium chloride solution (specific conductance 75 µS/cm) supplied by CAL; (2) remeasure the specific conductance of the potassium chloride solution; (3) rinse the conductivity cell three times with deionized water; (4) measure the conductivity of the simulated-precipitation sample; and (5) report the specific conductance of the simulated-precipitation in microsiemens per centimeter using the formula:

$$\text{Specific conductance} = (75 \div \text{measured standard conductivity}) \times \text{measured simulated-precipitation sample conductivity.} \qquad (4)$$

Sample Handling and Data Analysis

Sampling-site operators measured the pH and specific conductance using the protocols listed in the previous section. Measurements by these operators usually required less than 40 mL of the 125-mL sample. The remainder of the sample and operator's analytical results were returned to the U.S. Geological Survey. The U.S. Geological Survey analyzed all returned samples for pH or specific conductance or both when: (1) Reported pH was more than ±0.4 units from the calculated pH; or (2) reported specific conductance was more than ±20 percent from the calculated specific conductance. These limits were chosen arbitrarily for the October 1981 study; they were used for all subsequent studies.

The U.S. Geological Survey analysis of the returned audit samples was used to determine if either the pH or specific conductance had changed in the samples. If the pH measured by the U.S. Geological Survey was within ±0.15 pH unit, or if the specific conductance was within ±10 percent of the calculated values, the sample was considered unchanged. If U.S. Geological Survey analytical results were outside these limits, the sample was declared "different," and the site-operator results were flagged in the data sets.

Means and standard deviations for pH and specific conductance were calculated for each intersite comparison, using all unflagged results obtained from the site operators. Reported pH values were converted to hydrogen-ion concentrations before calculation of the means and standard deviations. All site-operator results that were greater than 1.5 standard deviations from the intersite comparison means were noted. Each sample for which the pH or specific-conductance results were greater than 1.5 standard deviations from the mean also were analyzed by the U.S. Geological Survey. Each NADP sampling-site manager and operator were sent the results for each intersite comparison. The information sent included: (1) Frequency distribution of pH and specific-conductance results; (2) mean and standard deviation for both parameters; (3) U.S. Geological Survey analytical results if applicable; and (4) a notice that the sampling-site operator's results were greater than 1.5 standard deviations from the mean, if applicable.

RESULTS OF INTERSITE COMPARISON STUDIES

Summaries of data for the five separate NADP intersite comparisons for pH and specific conductance are given in table 1. Standard deviations for pH determinations from these studies ranged from 0.19 to 0.30; and the relative standard deviations ranged from 4.7 to 6.9 percent. Pooled standard deviation (Dixon and Massey, 1969) for pH from the five studies was 0.25. Standard deviations for specific-conductance determinations ranged from 2.2 to 7.4 μS/cm. The relative standard deviation ranged from 12.2 to 21.2 percent. The pooled standard deviation for specific conductance was 4.6 μS/cm.

5

Table 1.--*Results of pH and specific-conductance determinations from five intersite comparison studies*

[μS/cm=microsiemens per centimeter at 25° Celsius]

| Study date | pH | | Specific conductance (μS/cm) | | Range | | Number of site-operators reporting |
	Mean	Standard deviation	Mean	Standard deviation	pH	Specific conductance (μS/cm)	
October 1981	4.27	0.26	20.6	3.1	3.3-5.4	14 -26	73
April 1982	4.54	.24	12.2	2.2	3.7-5.9	6.0-56	98
November 1982	4.02	.19	37.9	5.3	3.3-4.5	3.2-52	93
May 1983	3.79	.26	59.0	7.4	3.3-4.4	6.0-90	100
November 1983	4.62	.30	10.4	2.2	3.5-5.9	2.4-21	108

The American Society for Testing and Materials, 1984, recommends a test for bias. Percent bias between the calculated pH and specific-conductance values and intersite-comparison means for each study are given in table 2. The mean pH value for each intersite comparison is higher than the calculated pH value, indicating a positive bias for site-operator determinations of pH. However, the magnitude of the pH bias is small. There is no consistent pattern for bias when comparing the specific-conductance means and calculated values.

Each NADP sampling-site operator was mailed a sample for each intersite comparison study. However, the U.S. Geological Survey did not receive results or the remainder of the sample from all sampling-site operators. About 3 percent of the sampling-site operators would report that they had instrument problems at the time of sample receipt. These operators normally were told to retain the intersite comparison sample and to determine the pH and specific conductance when their instruments were repaired. They also were requested to compare their results with the reported study results mailed to them by the U.S. Geological Survey. Several operators from each study reported results weeks or even months after the scheduled final date to return samples and results to the U.S. Geological Survey. Nonreporting site-operators, that is, operators that did not return results or explanations, usually constituted less than 4 percent of the sampling-site operators. However, for the November 1983 intersite comparison, 20 sampling-site operators, nearly 15 percent of the operators, did not report results. The reason for this large number of unreported results is unknown.

A portion of the simulated-precipitation sample was returned to the U.S. Geological Survey, with the analytical results. All returned samples, with results greater than 1.5 standard deviations from the pH or specific-conductance means, were analyzed by the U.S. Geological Survey. A total of 472 samples were returned to the U.S. Geological Survey. Less than 2 percent of these samples was found to have changed. These results were removed from the intersite-comparison data sets, before calculation of the means and standard deviations. All results reported to the U.S. Geological Survey, except results from the changed samples, were used to calculate the means and standard deviations of pH and specific conductance.

Table 2.--Comparison of calculated and determined pH and specific
conductance from five intersite comparison studies

[μS/cm=microsiemens per centimeter at 25° Celsius]

Study date	pH				Specific conductance (μS/cm)			
	Calculated	Intersite mean	± Percent bias	Statistically significant (95-percent confidence level)	Calculated	Intersite mean	± Percent bias	Statistically significant (95-percent confidence level)
October 1981	4.10	4.27	+4.1	yes	33.5	20.6	-38.5	yes
April 1982	4.52	4.54	+.4	no	12.7	12.2	-3.9	yes
November 1982	3.95	3.94	+1.8	no	47.2	37.9	-19.7	yes
May 1983	3.79	3.79	0.0	no	68.3	59.0	-13.6	yes
November 1983	4.51	4.62	+2.4	yes	13.0	10.4	-20.0	yes

CONCLUSIONS

Stable simulated-precipitation samples for pH and specific conductance can be prepared using nitric acid and deionized water. The resulting solutions have been found to be stable for at least 10 weeks for pH and specific conductance, when they are stored in 125-mL, high-density polyethylene bottles. Analysis of these samples 22 weeks after preparation indicated that the samples probably are stable for periods longer than 10 weeks but may not be stable for 22 weeks.

Results from the five intersite comparison studies for site-operator determination of pH and specific conductance were used to estimate the precision of the NADP monitoring-network site-operator analysis. The estimated standard deviation for site-operator determination of pH is 0.25 for samples with a pH range from 3.7 to 4.6. Estimated standard deviation for site-operator determination of specific conductance is 4.6 μS/cm for samples having a specific-conductance range from 10 to 59 μS/cm. The precision estimates are for sampling-site analytical results made from October 1981 through November 1983. These precision estimates may be valid for NADP sampling-site analytical results obtained during 1984.

Each intersite-comparison mean for pH and specific conductance was tested for bias at the 95-percent confidence level. The bias was significant for the October 1981 and May and November 1983 studies. The magnitude of the pH bias was small but always positive; specific-conductance bias was not consistent.

REFERENCES CITED

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section II, water: Philadelphia, p. 35-38.

Bigelow, D. S., 1982, NADP instruction manual--Site operation: Fort Collins, Colorado State University, National Resources Ecology Laboratory, 29 p.

Castellan, G. W., 1971, Physical chemistry (2d ed.): Reading, Mass., Addison-Wesley, p. 729-730.

Dean, J. A., 1978, Lange's handbook of chemistry (12th ed.): New York, McGraw-Hill, p. 11-25.

Dixon, W. J., and Massey, F. J., 1969, Introduction to statistical analysis (3d ed.): New York, McGraw-Hill, p. 112-114.