NBSIR 82-2581

Simulated Precipitation Reference Materials, IV

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Inorganic Analytical Research Division
Washington, DC 20234

June 1982

Issued October 1982

Prepared for
U.S. Environmental Protection Agency
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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, ***Secretary***
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Director***

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This report describes work performed at the National Bureau of Standards under the sponsorship of the United States Environmental Protection Agency to establish the composition of a fourth series of reference materials intended to be used for the intercalibration of precipitation measurement stations, to evaluate the stability of the first three series of reference materials, to evaluate current methodologies for pH and acidity measurements, and to make recommendations to improve future reference materials and measurement protocols.

Key words: acidity, acid rain; chemical analysis; conductance; pH; precipitation; rain; reference materials; trace elements.

1. Introduction

The analysis of the composition of rainfall and other forms of precipitation is an excellent means to monitor global atmospheric pollution. Such measurements must necessarily be made at widely spaced geographical locations, over extended periods of time, and by many independent investigators. It is imperative that the measuring stations be intercalibrated if the data obtained are to be correlated and combined for environmental interpretation. The measurment of a series of substantially identical samples by stations in a measurement system is an accepted method of evaluating laboratory performance for intercalibration purposes.

This report describes work done at the National Bureau of Standards under the sponsorship of EPA[1] to establish the composition of a fourth series of reference materials intended to be used for the intercalibration of precipitation measurement stations, to evaluate the stability of the first three series of reference materials, to evaluate current methodologies for pH and acidity measurements, and to make recommendations to improve future reference materials and measurement protocols.

This is the fourth series of solutions prepared for EPA and is designated Simulated Precipitation Reference Materials IV (SPRM IV). The details of the first three series are contained in: NBSIR 75-958, "Simulated Precipitation Reference Materials," October 1975 [1]; NBSIR 77-1315, "Simulated Precipitation Reference Materials II," September 1979 [2]; NBSIR 79-1953, "Simulated Precipitation Reference Materials III," April 1980 [3].

SPRM IV is similar in concept to those prepared previously at the National Bureau of Standards. It was prepared in May of 1981 by a contract laboratory under the direct supervision of the Environmental Protection Agency and the guidance of the National Bureau of Standards. Two reference solutions, low concentrations (Level 1)

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[1] This work was performed at the National Bureau of Standards for the United States Environmental Protection Agency under Interagency Agreement, EPA IAG#: AD-13-F-2-535-0, Subagreement 5.

and high concentrations (Level 2), were prepared of specified components at levels similar to those expected in natural samples. In addition, two reference solutions (Levels 3 and 4) containing approximately 2 microequivalents (μeq) and 5 μeq of sulfuric acid per ampoule, respectively, were prepared specifically for the measurement of acidity, conductance, and pH. The four sets of solutions were prepared in bulk and then transferred to 20 milliliter (mL) glass ampoules using an automatic dispensing and sealing machine.

2. Instructions for Use

2.1 Levels 1 and 2

The sample solutions for Levels 1 and 2 are contained in 20 mL glass ampoules which have been pre-scored to facilitate opening. When these samples are accurately diluted 1 to 50 with high-quality distilled water (such as ASTM Type II or better), the resultant solutions simulate natural rainwater with regard to the concentrations of major components and trace elements. The recommended procedure for preparation of a sample for analysis is as follows:

1. Rinse the outside of the ampoule with distilled water to remove dust, and dry in clean air or with a clean, lint-free cloth.

2. Hold ampoule in a vertical position, tip over and back, and gently tap to transfer any liquid from the top to the body of the ampoule.

3. Hold ampoule with a paper towel (a precaution to prevent injury to hand), and snap off the top at the scored constriction.

4. Accurately pipet 10.0 mL of the concentrate from the ampoule into a clean 500 mL volumetric flask. Use Class A volumetric glassware.

5. Add distilled water to the flask to dilute to the calibrated volume, and mix contents thoroughly.

6. Treat the resulting solution with the same care and in the same manner as a sample of natural rainwater.

2.2 Levels 3 and 4

The sample solutions for Levels 3 and 4 are contained in 20 mL glass ampoules which have been pre-scored to facilitate opening. These solutions are intended for use without additional dilution.

2.2.1 Acidity Measurement

Transfer the contents of <u>two</u> ampoules into a suitable titration vessel. Open the ampoules according to the recommended method outlined in Section 2.1(1-3). Hold the inverted ampoules over the titration vessel until the solution has drained as much as possible. Check for visible inclusions of solution in the ampoule and tap gently if required. Do <u>not</u> rinse the ampoules. Any film of solution remaining in the ampoules will not cause significant error.

2.2.2 Conductance and pH Measurements

Transfer the contents of one ampoule into a clean beaker of the proper size to facilitate the measurement of conductivity and pH. Open the ampoule according to the method outlined in Section 2.1(1-3). Remove substantially all the contents by shaking. However, these measurements being intensive by nature are not influenced by the quantity of sample used and hence quantitative delivery is not required. It is recommended to measure conductivity of the sample first, followed by measurement of pH. This will prevent leakage from the reference electrode from affecting the measured value of the conductivity of the solution.

3. Analysis of SPRM IV

In most cases, solutions from six ampoules at each level were analyzed for each specific component. From a practical standpoint, all determinations were not made from a single set of ampoules but rather, each technique analyzed a separate set. There is no reason to believe that at the time of filling of the ampoules, the solutions were anything other than homogeneous. The recommended values of the components of SPRM IV are given in Tables 1 and 2. The methods used for the analytical measurements are summarized in the following sub-sections.

Table 1. Simulated Precipitation Reference Materials IV, Levels 1 and 2

(diluted 10 mL to 500 mL)

	Level 1	Level 2
pH	4.36(0.10)[a]	4.03(0.10)[a]
Specific Conductance, μS/cm	20.4(1.0)	49.0(1.0)
Acidity, μeq/500 mL	27.8(0.2)	73.4(0.5)
Fluoride, μg/mL	0.17(0.1)	0.23(0.1)
Chloride, μg/mL	0.80(0.1)	3.08(0.04)
Nitrate, μg/mL	0.91(0.1)	2.26(0.02)
Sulfate, μg/mL	1.49(0.1)	3.12(0.04)
Ammonium, μg/mL	0.220(0.002)	0.562(0.006)
Sodium, μg/mL	0.314(0.005)	0.596(0.006)
Potassium, μg/mL	0.140(0.001)	0.538(0.006)
Magnesium, μg/mL	0.061(0.001)	0.172(0.002)
Calcium, μg/mL	0.197(0.004)	0.63(0.02)
Manganese, μg/mL	0.034(0.002)	0.178(0.001)
Iron, μg/mL	0.032(0.001)	0.056(0.001)
Copper, μg/mL	0.086(0.003)	0.302(0.012)
Lead, μg/mL	0.044(0.015)	0.12(0.05)
Cadmium, μg/mL	0.044(0.001)	0.260(0.012)
Nickel, μg/mL	0.072(0.006)	0.16(0.02)
Zinc, μg/mL	0.081(0.005)	0.421(0.015)

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[a] The values in parentheses represent uncertainties based on an evaluation of the combined effects of method imprecision, possible systematic errors, and material variability.

Table 2. Simulated Precipitation Reference Materials IV, Levels 3 and 4 (undiluted)

	Level 3	Level 4
pH	4.12(0.10)[a]	3.71(0.10)[a]
Specific Conductance, μS/cm	36.0(1.0)	87.0(2.0)
Acidity, μeq/2 ampoules	4.01(0.08)	9.40(0.33)

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[a] The values in parentheses represent uncertainties based on an evaluation of the combined effects of method imprecision, possible systematic errors, and material variability.

3.1 Measurement of pH

Six samples of each of the four levels were analyzed for pH. Levels 1 and 2 were diluted 10 mL to 500 mL; Levels 3 and 4 were analyzed without dilution. The pH was measured with a combination glass electrode and digital pH meter which had been calibrated with NBS Standard Reference Material (SRM) pH buffers (pH 4.01, SRM 185e and pH 6.86, SRM 186-Ic/186-IIc). A detailed recommended procedure for measuring pH in low ionic strength solutions is given in a later section of this report. The limitations of the measurement are also discussed. Because of these limitations, the accuracy of the pH measurement in these samples can be no better than 0.1 pH number.

3.2 Measurement of Specific Conductance

Six samples of each of the four levels were analyzed for specific conductance. Levels 1 and 2 were diluted 10 mL to 500 mL; Levels 3 and 4 were analyzed without dilution. Conductance was measured with a platinum dip-cell having a cell constant of 0.09975 cm^{-1} determined through use of a 0.001 demal KCl solution at a frequency of 1000 Hz. The values reported were determined at 23 ± 1 °C.

3.3 Measurement of Acidity

The acidity content of each level was determined by coulometric titration of hydrogen ion to an endpoint as indicated by the inflection-point in the sigmoidal titration plot. Titration to a fixed-pH-endpoint can seriously bias the results. This matter is discussed in detail in a later section of this report.

3.4 Determination of Anions

Six samples from each of Levels 1 and 2 were analyzed by ion chromatography for fluoride, chloride, nitrate, and sulfate. For convenience, Level 1 was diluted 1:3 with the same carbonate buffer solution as used as the eluent for the chromatography. Similarly, Level 2 was diluted 1:13. All four anions in each sample were determined sequentially with a single injection. The ion chromatograph was calibrated before every sample with three multi-component standards which bracketed the levels in the sample. A linear plot, peak height versus concentration, was used for quantitation. Each sample was analyzed twice. The results summarized in Table 1 have been adjusted to reflect a dilution of 10 mL to 500 mL.

3.5 Determination of Ammonium Ion

The chosen technique consisted of chemical measurement according to the procedure given in the following reference: C. O. Willits, and C. L. Ogg, "1949 Report of Standardization of Microchemical Methods, Micro Kjeldahl Nitrogen Determinations," USDA Eastern Regional Research Laboratory, Philadelphia, PA. A micro-Kjeldahl steam distillation apparatus was used to separate the ammonia (released by sodium hydroxide) which was trapped in boric acid. The ammonia was titrated with standardized 0.01 mol/L hydrochloric acid using methyl purple indicator.

3.6 Determination of Metals

Several techniques were employed for the determination of the metals in Levels 1 and 2. These are described in the following sub-sections. When more than one technique was used for the determination of any single element, an average value was calculated and reported in Table 1.

3.6.1 Polarography

Six samples at each level were analyzed for copper, lead, cadmium, nickel, and zinc by cathode-ray polarography. Nickel and zinc were determined in a supporting electrolyte of dilute sulfuric acid and pyridine. Copper, lead, and cadmium were measured in an ammonium acetate buffer solution. A multi-point calibration curve was used for quantitation.

3.6.2 Atomic Absorption and Flame Emission Spectrometry

Sodium, potassium, and calcium were determined by flame emission spectrometry. Flame atomic absorption spectrometry was used to determine magnesium, manganese, iron, copper, cadmium, zinc, nickel, and lead. Calibration standards were prepared by dissolution of pure salts or pure metals.

3.6.3 Inductively Coupled Plasma Spectrometry

The inductively coupled plasma technique was used to determine zinc, lead, cadmium, iron, manganese, nickel, magnesium, and copper. Three multi-element standards were prepared to establish calibration curves for these elements. Two separate calibration runs were used for each sample.

3.7 Discussion of Analytical Results

The results of the analyses are summarized in Tables 1 and 2. The values in parentheses represent uncertainties based on an evaluation of the combined effects of method imprecision, possible systematic errors, and material variability. The rather high degree of uncertainty in some of the values, notably copper, lead, nickel, and zinc is a matter of great concern. It is believed that the major cause of the problem is adsorption of the metals on the glass, with hydrolysis of the metals being a further complication. The addition of citrate ion to counter these effects has proved to be unsatisfactory and has created the further problem of the growth of algae in the long term. Recommendations to produce more stable solutions will be discussed in a later section of this report.

4. Stability of Simulated Precipitation Reference Materials

The stability of these reference materials is an integral factor in the evaluation of laboratory performance for intercalibration purposes. To this end, periodic checks have been made on SPRM I through III with respect to pH and conductance. This stability monitoring program is continuing with SPRM IV. In addition, two projects have been instituted to evaluate the use of polyethylene bottles rather than glass ampoules as storage containers in an effort to improve the long-term stability. As previously stated (Section 3.7), glass is not an appropriate storage container for the transition elements or the heavy metals. There is mounting evidence that glass is equally inappropriate for the alkali metals and hydrogen ion due to exchange reactions, which adversely affect the concentration of the alkalis, the pH, and the conductance of the solutions.

4.1 SPRM I through SPRM III

The results of the long-term stability check on SPRM I through SPRM III are summarized in Tables 3-5. In general, there is a decrease in conductance with time, most markedly in those solutions containing only dilute sulfuric acid (Series 740000, 930000, and 940000). The pH of these samples also indicate considerable instability and variability. Algae were apparent in some of the ampoules which contained citrate.

4.2 SPRM IV

The stability of SPRM IV in glass ampoules with respect to pH, conductance, and acidity over a nine-month period is summarized in Table 6. Again, in those solutions composed of dilute sulfuric acid (Levels 3 and 4) there is a sharp drop in conductance with a concomitant increase in pH. This is most likely due to an exchange of sodium ion in the glass with hydrogen ion in the solution.

In an experiment to confirm this suspected "glass effect" a second set of SPRM IV samples was placed in 60 mL polyethylene (CPE) bottles from the same bulk solutions and at the same time as the samples in glass ampoules. The improvement in stability in all four levels over the same period of time is shown in Table 7. However, the growth of algae in Levels 1 and 2 (which contain citrate) contained in plastic bottles was quite apparent. There has been no evidence of algae growth in any of the sample solutions which do not contain citrate.

4.3 Long-term Stability in Polyethylene Bottles

To evalute the stability of dilute acid solutions with respect to pH and conductance over a long period of time, a solution of sulfuric acid was prepared on July 24, 1980 and subsequently placed in several 60 mL polyethylene (CPE) bottles. On a periodic basis, individual bottles are opened and the solutions analyzed for pH and conductance. The results to date of this ongoing experiment are shown in Table 8. The first date, 7/24/80, represents measurements made on the bulk solution before bottling. There appears to be a slight upward trend in the conductance of the solution. However, relative to storage in glass ampoules, this small change is insignificant. No detectable change in the pH of the solution is apparent.

Table 3. Stability of SPRM I

Series 1975A

	pH	Specific Conductance ($\mu S \cdot cm^{-1}$)
1975	6.18	5.8
1979	--	5.1
June 1980	5.94	5.3
July 1980	5.74	5.2
August 1980	5.66	5.3

Series 1975B

	pH	Specific Conductance ($\mu S \cdot cm^{-1}$)
1975	6.15	18.3
1979	--	17.1
June 1980	5.70	17.2
July 1980	5.76	17.1
August 1980	5.66	17.0

Series 1975C

	pH	Specific Conductance ($\mu S \cdot cm^{-1}$)
1975	6.20	59.8
1979	5.75	57.0
June 1980	5.67	53.0
July 1980	5.63	56.2
August 1980	5.62	55.9

Series 1975D

	pH	Specific Conductance ($\mu S \cdot cm^{-1}$)
1975	6.07	117.0
1979	5.78	112.0
June 1980	5.59	113.4
July 1980	5.59	111.2
August 1980	5.64	111.4

Table 4. Stability of SPRM II

Series 710000

	pH	Specific Conductance (μS·cm^{-1})
1977	4.48	28.8
1979	4.25	30.8
June 1980	4.24	29.5
July 1980	4.17	29.7
August 1980	4.14	33.4
October 1980	4.04	30.0

Series 720000

	pH	Specific Conductance (μS·cm^{-1})
1977	4.08	77.9
1979	4.07	84.4
June 1980	4.06	80.3
July 1980	3.97	82.3
August 1980	3.97	82.0
October 1980	3.90	82.6

Series 730000

	pH	Specific Conductance (μS·cm^{-1})
1977	5.98	190.5
1979	5.86	205.2
June 1980	5.61	200.2
July 1980	5.60	199.2
August 1980	5.66	198.7
October 1980	5.55	200.8

Series 740000

	pH	Specific Conductance (μS·cm^{-1})
1977	3.81	80.0
1979	4.02	--
June 1980	4.00	60.4
July 1980	3.95	60.0
August 1980	3.91	59.0
October 1980	3.83	59.1

Table 5. Stability of SPRM III

Series 910000

	pH	Specific Conductance ($\mu S \cdot cm^{-1}$)
1979	5.03	13.2
June 1980	4.87	12.8
July 1980	4.78	12.6
August 1980	4.83	11.8
October 1980	5.18	8.9
June 1981	5.46	8.7

Series 920000

	pH	Specific Conductance ($\mu S \cdot cm^{-1}$)
1979	4.35	43.4
June 1980	4.27	41.3
July 1980	4.25	41.8
August 1980	4.22	40.9
October 1980	4.15	38.3
June 1981	4.35	36.5

Series 930000

	pH	Specific Conductance ($\mu S \cdot cm^{-1}$)
1979	3.91	69.1
June 1980	4.05	48.2
July 1980	3.97	46.0
August 1980	3.95	47.9
October 1980	3.89	46.6
February 1981	4.18	44.2
June 1981	4.04	41.8

Series 940000

	pH	Specific Conductance ($\mu S \cdot cm^{-1}$)
1979	3.62	121.4
June 1980	3.72	91.6
July 1980	3.62	99.8
August 1980	3.59	97.3
October 1980	3.53	94.3
February 1981	3.78	91.4
June 1981	3.66	92.6

Table 6. Stability of SPRM IV in Glass Ampoules

Level	pH		Specific Conductance (µS/cm)		Acidity (µeq)	
	6/81	3/82	6/81	3/82	6/81	3/82
1	4.36	4.50	20.4	18.6	27.8	27.3
2	4.03	4.13	49.0	46.4	73.4	73.2
3 (per 2 ampoules)	4.12	4.30	36.0	29.3	4.01	3.97
4 (per 2 ampoules)	3.71	3.80	87.0	76.1	9.40	9.91

Table 7. Stability of SPRM IV in Polyethylene Bottles

Level	pH		Specific Conductance (µS/cm)		Acidity (µeq)	
	6/81	3/82	6/81	3/82	6/81	3/82
1	4.34	4.41	22.4	21.0	---	32.8
2	4.03	4.08	50.9	48.4	---	74.8
3 (per 2 ampoules)	3.87	3.90	52.4	53.0	---	6.19
4 (per 2 ampoules)	3.59	3.59	105.9	104.1	---	11.58

Table 8. Stability of Dilute Sulfuric Acid in Polyethylene Bottles

Date	pH	Specific Conductance (µS/cm)
7/24/80	3.90	45.0
7/25/80	3.90	45.3
8/5/80	3.87	45.0
8/6/80	3.90	46.0
8/14/80	3.90	45.5
10/27/80	3.79	44.4
1/30/81	3.86	47.0
6/24/81	3.95	48.0
3/5/82	3.93	48.1

5. Evaluation of Current Methodologies for pH and Acidity Measurements

Research is being conducted at the National Bureau of Standards to improve the measurement of pH and acidity in low-conductivity, unbuffered solutions such as encountered in natural precipitation. A survey of the literature and experiments performed at NBS has shown that serious errors may affect the reliability and comparability of acid rain analyses in the important parameters of pH and acidity. Preliminary results of this research have been presented at the Symposium and Workshop on Sampling and Analysis of Rain, sponsored by ASTM Committee D-22 and held in Philadelphia, PA on October 7, 1981. The following sub-sections are excerpted from that presentation.

5.1 Definition of pH

In 1909, the Danish chemist, S. P. L. Sorensen, published two papers in which he distinguished between the degree of acidity (the intensity factor) and the total acidity (the capacity factor) of a solution [4]. Both the concept and the notation of pH grew from these publications. In pure terms, pH is intended to represent the negative logarithm of the hydrogen ion activity of a solution. The realization of this pure concept of pH is not attainable with present theory and technology. Hence, reliance on standards and conventions (i.e., an operational definition) is mandatory.

The history of and rationale behind the various pH scales used in the last 70 years is a story in itself. Roger G. Bates summarizes the major developments in his book "Determination of pH: Theory and Practice" [5] and updates them in a recent monograph [6]. Today, the most widely used convention is the NBS practical pH scale, the physical realization of which is embodied in the NBS pH buffers issued as Standard Reference Materials [7]. These seven primary and three secondary standard buffer materials cover the pH range from 1.68 to 12.45 and define the pH(S) scale.

It must be stressed that these buffers form the basis of an operational definition of pH as given by the equation [7]

$$\mathrm{pH(X)} = \mathrm{pH(S)} - \frac{(E_X - E_S)F}{RT \ln 10}$$

where: E_S is the electromotive force of the cell —

reference electrode $|\mathrm{KCl}(\geq 3.5\ \mathrm{mol/L})||$solution $S|\mathrm{H_2(g)}$; Pt;

E_X is the electromotive force of the same cell substituting sample solution X for the standard buffer solution S; F is the Faraday constant; R is the gas constant; and T is the thermodynamic temperature. This definition incorporates several assumptions, conventions, and compromises which have been discussed by Bates [5,6] and Durst [7]. As such, the NBS scale (and any other conventional scale) has imposed limitations as to its use and more importantly as to the interpretation of results obtained through it. According to Bates, quantitative interpretation of measured pH values should not be attempted unless the medium closely resembles the standard of reference, that is, aqueous solution of buffers and simple salts within the pH range of 3 to 11 and with ionic strengths between 0.01 and 0.1. Acid rain samples generally do not meet these constraints. Hence, pH measurements of such samples have limited accuracy even under favorable laboratory and field conditions. Furthermore, fundamental interpretation in terms of hydrogen ion activity is rendered impossible.

5.2 pH Experiments

The customary way of measuring pH is electrometrically with a glass electrode and a reference electrode, often combined into a single unit for convenience. The glass elctrode replaces the hydrogen electrode in the aforementioned electrochemical cell. Various configurations are commercially available tailored for specific applications as well as for general laboratory use. It is evident that such an arrangement measures not a single quantity (i.e., hydrogen ion activity), but rather a sum of potentials. These "unwanted" potentials include asymmetry potentials, liquid-junction potentials, streaming potentials, and several others related to the non-ideal behavior of the solution and of the electrodes [8]. Insofar as these potentials are constant between standard S and sample X, they can be electronically offset and the equation defining pH holds true. However, in solutions such as acid rain, which are unbuffered and low in ionic strength, there can be substantial changes in these potentials, particularly the liquid-junction potential. These residual potentials can easily bias the pH reading by 0.1 pH number. Several experiments were conducted to reveal and confirm these conclusions.

1. Several combination pH electrodes of various configurations, sizes, and manufacturers were calibrated simultaneously in a single solution of NBS buffer potassium hydrogen phthalate, SRM 185e [pH(S) at 23.0 °C, 4.002]. After copious rinsing with distilled water, the electrodes were all dipped into a solution of 10^{-4} mol/L hydrochloric acid. The solution was stirred initially to ensure homogeneity, then allowed to settle to a quiescent state. Stable pH numbers were recorded after five minutes. Readings were then taken with the solution stirred. These data are summarized in Table 9.

Table 9. Response of Combination pH Electrodes in 10^{-4} mol/L HCl

	Recorded pH Number		
Electrode	Quiescent	Stirred	Δ(Q-S)
1	3.944	3.816	0.128
2	3.864	3.661	0.203
3	3.908	3.741	0.167
4	3.899	3.841	0.058
5	3.875	3.755	0.120
Range	0.080	0.180	

2. The above experiment was repeated using the glass sensors of the combination electrodes but using a single silver/silver chloride electrode as the reference for all. These data are summarized in Table 10.

Table 10. Response of pH Electrodes with a Common Reference Electrode in 10^{-4} mol/L HCl

	Recorded pH Number		
Electrode	Quiescent	Stirred	Δ(Q-S)
1	3.942	3.889	0.053
2	3.943	3.883	0.060
3	3.944	3.877	0.067
4	3.942	3.888	0.054
5	3.956	3.878	0.078
Range	0.014	0.012	

3. Several reference electrodes (both saturated calomel and silver/silver chloride types) with various kinds of junctions (fiber, ceramic, annular, frit, sleeve, and double) were tested in three solutions: 1 mol/L potassium chloride; 0.05 molal potassium hydrogen phthalate; and 10^{-4} mol/L hydrochloric acid. Potentials were measured versus a saturated calomel electrode with a ceramic junction in quiescent and stirred solutions. These data are tabulated in Table 11.

Table 11. Response of Reference Electrodes Versus a Common Reference Electrode in Various Aqueous Media

		Potential (mV)		
Electrode		1 mol/L KCl	KHP Buffer	10^{-4} mol/L HCl
A(fiber)	Q	-48.7	-46.7	-43.6
	S	-48.7	-47.4	-47.2
B(frit)	Q	-3.3	-0.4	+1.6
	S	-3.3	+0.7	+6.7
C(double)	Q	-3.8	-1.4	+7.9
	S	-3.8	-0.6	+10.5
D(sleeve)	Q	-2.9	+0.7	+4.7
	S	-2.9	+2.0	+10.0
E(micro)	Q	-35.7	-33.8	-31.9
	S	-35.6	-32.5	-26.8
F(ceramic)	Q	-49.8	-48.5	-47.6
	S	-49.7	-47.6	-45.5
G(annular, double)	Q	-32.1	-19.2	-6.3
	S	-31.9	-17.9	-3.5

Q = quiescent   S = stirred

5.3 Discussion of pH Experiments

The data in Table 9 clearly demonstrate that five randomly selected electrodes calibrated in identical fashion yield five different pH numbers with a range of 0.08 when used to test a solution that approximates the pH and ionic strength of acid rain. Even larger deviations have been noticed with other electrodes. Also illustrated is the dramatic effect (sometimes referred to as streaming potentials) that stirring the solution has on the pH number. It should be noted that stirring has negligible effect (less than 0.01 pH number) in the standard buffer solutions.

The fact that the liquid junction of the reference electrode is the major source of the problem is indicated by comparison of Table 10 with Table 9. Using a single reference electrode, all glass electrodes read virtually identically. Again the effect of stirring is obvious.

Experiment 3 confirms the serious nature of residual liquid-junction potentials and further illustrates the effect of stirring. The change in potential between two reference electrodes in going from standard buffer to a solution similar to acid rain is typically 3 mV (which will bias the pH reading by 0.05) and in the case of a double-junction electrode is almost 13 mV. It must be noted that this observed change in potential is somewhat muted by the fact that the liquid potential of the common reference electrode, against which all others are being measured, is also shifting.

These experiments indicate that the imprecision of pH measurements of acid rain-like solutions using different glass/reference electrodes is at least 0.1 pH number and further that the measurement can be biased by a minimum of 0.05 pH number. Much larger deviations are sometimes observed and are not unexpected. The use of double-junction reference electrodes does not remedy the situation and may compound the problem. It is often suggested to add potassium chloride to a low ionic strength solution to obviate residual liquid junction potentials. Indeed, this will reduce the residual potential but will not eliminate it. Furthermore, the addition of salt may cause new problems. Of course, the absence of acidic or basic contaminants in the salt must be established. More importantly the effects of the salt on the species present in solution must be understood. These effects are opposite in sign and varying in magnitude between strong acids and weak acids. It is, therefore, not recommended to add potassium chloride to acid rain solutions. Alternate pH scales have also been proposed [9]. Although these scales can prove helpful in specific situations, they are generally not recommended because of the confusion they may cause. This confusion could result from the lack of universal acceptance of these alternates, the lack of standards, the failure to properly identify these scales as alternates, and the absence of a unifying link to the national pH(S) scale.

5.4 Recommended Procedure for Measurement of pH

Therefore, until further research improves the situation, the following protocol is recommended for the routine measurement of pH in acid rain. Obtain a suitable glass/reference electrode pair or combination pH electrode. (Glass electrodes with the standard-sized sensor appear to give a fast and stable response. The junction in the reference electrode which gives the least change in potential in different solutions appears to be of the ceramic type). Standardize the electrodes and meter using SRM 185e, potassium hydrogen phthalate [pH(S) 4.004 at 25.0 °C, 0.05 molal]. Ascertain the Nernstian response of the electrodes with a second buffer, either SRMs 186 Ic and IIc [pH(S) 6.863 at 25.0 °C] or SRM 189 [pH(S) 1.679 at 25.0 °C]. Re-establish calibration of the pH measuring system at regular intervals with the phthalate buffer. Rinse the electrodes thoroughly with distilled water and then dip them into a clean beaker containing a portion of the acid rain. After stirring, allow the solution to settle to a quiescent state. Most electrodes reach a reasonable degree of stability after five minutes. Record the pH number and repeat the measurement with a fresh portion of the acid rain. The two readings should agree to within 0.1 pH number. Non-compliance generally indicates that the electrodes were not rinsed adequately after standardization with the buffers. Report the pH of the rain sample to the nearest 0.1 pH number. Exercise caution in deriving thermodynamic significance from the value. Rather, view the pH measurement as a screening procedure to indicate whether additional study of the sample in terms of acidity is warranted.

5.5 Measurement of Acidity

In a related way, the measurement of total acidity, while a simple matter in solutions of moderate and high acid content, is beset with potentially serious errors in solutions of extremely low acidity. The consequences of such errors are perhaps more important than errors in pH measurements in that the capacity factor rather than the intensity factor is the more meaningful term in acid-base chemistry.

Procedures that depend on titration to a fixed pH endpoint are particularly prone to error. To illustrate this point, two solutions of hydrochloric acid (nominally 10.4 and 0.16 μeq/g) were titrated by three procedures. All three procedures involved controlled-current coulometric titration with electrogenerated hydroxyl ion but differed in the manner in which the endpoint was determined. In method A, the endpoint was determined by location of the inflection point in the sigmoidal plot of pH versus microequivalents of base added. Method B used a closed-loop procedure in which sodium citrate was added to the supporting electrolyte and pre-titrated to pH 8.3 (the neutrality point for citrate). Then the sample of acid was added, and the solution was titrated back to pH 8.3. Method C involved addition of the acid sample to neutral supporting electrolyte (about pH 7) and titration to pH 8.3. The data are summarized in Table 12. Agreement between method A and method B was excellent. However, method C gave consistently high results with the relative error increasing as the amount of acidity decreased. Furthermore, it has been observed that method C exhibits a sample size dependency on the acidity titer, which is not apparent in either of the other methods.

Table 12. Dependence of "Total Acidity" on Titration Procedure

	Total Acidity (μeq/g)		
Sample	Method A	Method B	Method C
1	10.38	10.36	10.53
2	0.161	0.165	0.222

It must be concluded that procedures which require titration to a fixed-pH endpoint should not be used for acid rain analyses. Closed loop procedures are satisfactory but with concomitant loss in sensitivity at endpoints of higher pH. Titration to a inflection point (or multiple inflection points for mixed acid systems) is the preferred technique. The method of Gran [10] is equally acceptable, since it differs from inflection-point titrations only in the way the endpoint data are manipulated.

6. Summary and Recommendations

The fourth series of Simulated Precipitation Reference Materials (SPRM IV) has been characterized with respect to chemical composition. A program to monitor the stability of SPRM IV, stored in glass and in polyethylene, has been initiated. The program to monitor the stability of SPRM I through SPRM III over the long term has been completed. Experiments are in progress to assess the long-term stability of dilute acid solutions in polyethylene.

Results of the stability projects indicate that the simulated precipitation reference materials as made to date and as stored in glass ampoules are not stable with respect to pH, conductance, acidity, alkali metals, and several of the transition elements. It is recommended to make the following changes in future SPRMs:

1. Prepare solutions of two levels simulating the major components of precipitation, composed only of dilute mineral acids, alkali salts, and alkaline earth salts. These solutions would be analyzed for pH, conductance, acidity, sodium, potassium, magnesium, calcium, fluoride, chloride, phosphate, nitrate, and sulfate. Store in clean polyethylene (CPE) bottles.

2. Prepare solutions of two levels simulating the trace element composition of precipitation, stabilized with 0.5 mol/L nitric acid and stored in clean polyethylene (CPE) bottles.

Serious errors may affect the reliability and comparability of acid rain analyses in the important parameters of pH and acidity. Additional research is needed to gain a better understanding of this complex analytical problem, to establish practical and theoretically sound protocols for the measurement of pH and acidity in unbuffered, low ionic strength solutions, and to develop stable reference standards.

7. Acknowledgment

The participation of the following members of the staff of the Inorganic Analytical Research Division in the analysis of SPRM IV is gratefully acknowledged: E. R. Deardorff, E. J. Maienthal, T. C. Rains, T. A. Rush, T. A. Butler, and R. L. Watters, Jr.

The work was performed for the United States Environmental Protection Agency under Interagency Agreement, EPA IAG#: AD-13-F-2-535-0, Subagreement 5.

8. References

[1] Taylor, J. K., E. R. Deardorff, R. A. Durst, E. J. Maienthal, T. C. Rains, E. P. Schiede. "Simulated Precipitation Reference Materials," National Bureau of Standards (U.S.), NBSIR 75-958, October 1975, p. 21.

[2] Taylor, J. K., E. R. Deardorff, T. C. Rains. "Simulated Precipitation Reference Materials II," National Bureau of Standards (U.S.), NBSIR 77-1315, September 1977, p. 21.

[3] Deardorff, E. R., Rains, T. C., Koch, W. F. "Simulated Precipitation Reference Materials III," National Bureau of Standards (U.S.), NBSIR 79-1953, April 1980, p. 21.

[4] Sorensen, S. P. L., "Enzymstudien, II Über die Messung und die Bedeutung der Wasserstoffionenkonzentration bei enzymatischen Prozessen," Biochem. Z. 1909, 21, 131, Continuation Biochem. Z. 1909, 21, 201.

[5] Bates, R. G. "Determination of pH: Theory and Practice," 2nd ed., John Wiley & Sons, New York, 1973.

[6] Bates, R. G. "The Modern Meaning of pH," CRC Critical Reviews in Analytical Chemistry 1981, 10 (3), 247.

[7] Durst, R. A. "Standard Reference Materials: Standardization of pH Measurements," National Bureau of Standards (U.S.), Spec. Pub. 260-53, December 1975, p. 39.

[8] Durst, R. A. "Sources of Error in Ion-Selective Electrode Potentiometry," Chapter 5 in Ion-Selective Electrodes in Analytical Chemistry, Vol. 1, H. Freiser, ed., New York, NY: Plenum Publishing Corporation, 1978, p. 311-338.

[9] Galloway, J. N., B. J. Crosby, Jr. "Acid Precipitation Measurement of pH and Acidity," Limnol. Oceanogr. 1979, 24, 1161.

[10] Gran, G. "Determination of the Equivalence Point in Potentiometric Titrations," Acta Chem. Scan. 1950, 4, 559.

NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR 82-2581	2. Performing Organ. Report No.	3. Publication Date November 1982

4. TITLE AND SUBTITLE

Simulated Precipitation Reference Materials, IV

5. AUTHOR(S)

W. F. Koch, G. Marinenko, and J. W. Stolz

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

8. Type of Report & Period Covered

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

This report describes work performed at the National Bureau of Standards under the sponsorship of the United States Environmental Protection Agency to establish the composition of a fourth series of reference materials intended to be used for the intercalibration of precipitation measurement stations, to evaluate the stability of the first three series of reference materials, to evaluate current methodologies for pH and acidity measurements, and to make recommendations to improve future reference materials and measurement protocols.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

acidity; acid rain; chemical analysis; conductance; pH; precipitation; rain; reference materials; trace elements

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USCOMM-DC 6043-P80