# An Interlaboratory Test of pH Measurements in Rainwater

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#### Accepted: October 23, 1985

An interlaboratory test of pH measurements in rainwater has been conducted. Various types of electrodes and junction materials were used in this test. The results of this exercise verify that there are significant differences in the pH values of low ionic strength solutions reported by various laboratories. Other work suggests that these differences are due to residual liquid junction potentials. Furthermore, this test confirms the efficacy of using dilute solutions of a strong acid as working standards for pH measurements in acid deposition studies.

Key words: acid rain; electrodes; interlaboratory; liquid junction potential; measurements; pH; rainwater; round-robin; standards.

## Introduction

The accurate measurement of pH in rainwater samples is an essential and critically important component in the monitoring of wet deposition for trends in the acidity of rainfall. Our laboratory has shown that serious biases may affect the accuracy, intercomparability, and reliability of these measurements [1]<sup>1</sup>. To verify this situation and to seek a remedy, an interlaboratory test was conducted.

About the Authors: William F. Koch and George Marinenko are chemists in NBS' Inorganic Analytical Research Division, while Robert C. Paule is a physical scientist with the Bureau's National Measurement Laboratory. The work they describe was funded in part by the U.S. Environmental Protection Agency (National Acid Precipitation Assessment Program). In November 1983, sets of samples were sent to 12 laboratories which voluntarily agreed to participate in this interlaboratory test of pH measurements in rainwater. (Appendix A lists the participants.) In addition, five sets of samples were tested independently by three scientists at the National Bureau of Standards (NBS). The purpose of this exercise was to gain information as to the utility of using dilute solutions of a strong acid as working standards for pH measurements in acid deposition studies.

### Background

It has been proven that residual liquid junction potentials at the reference electrode can seriously bias pH readings, especially if the ionic strengths of the buffer standards and the test solutions are vastly different [1,2]. In an effort to correct for these biases, the Electroanalytical Chemistry Group (within the Inorganic Analytical Research Division in the NBS Center for Analytical Chemistry), has been conducting research to test the feasibility of providing matrix specific pH standards

<sup>&</sup>lt;sup>1</sup> Figures in brackets indicate literature references.

for selected applications. It is imperative that such working standards be consistent with the National pH scale, as maintained through the NBS Standard Reference Materials pH buffers, in order that measurements of pH be as thermodynamically meaningful as possible and to avoid confusion caused by multiple pH scales. This interlaboratory test is a critical step in the evaluation and implementation of this approach.

#### Experimental

Each set of samples consisted of eight solutions in 60 mL polyethylene bottles labeled A through H. Participants were asked to measure the pH of each sample according to explicit instructions (Appendix B) and to record the values on a data sheet (Appendix C). Additional information was also requested (Appendix D). The composition of the eight solutions is shown in table 1. The participants were not informed of the identity of these solutions.

Table 1. Composition of test solutions.

Solution	Composition
А	0.05 molal potassium acid phthalate (SRM 185f, pH(S) 4.006 at 25 °C)
В	Hydrochloric acid, pH 3.68 at 25 °C
С	Hydrochloric acid, approx. pH 4.3
D	Simulated acid precipitation, approx. pH 4.1
E	Simulated acid precipitation, approx. pH 3.7
F	Identical to B
G	Identical to C
Н	Identical to A

The rationale behind the sample selection and the sequence of measurements was as follows: Solution A was intended as a check on the calibration of each participant's pH measurement system, since the composition of this solution was nearly identical to the one provided for calibration.

Solution B was prepared by dilution of high-purity hydrochloric acid. The pH of the solution was determined using hydrogen gas electrodes in cells without liquid junction. The apparatus and calculations were identical to those used in the certification of NBS buffers [3,4]. The pH value was confirmed through calculations based on independent measurements using highprecision coulometry and ion chromatography. Solution B served as the reference or normalizing solution for this test. Solution C also was prepared by dilution of hydrochloric acid and was intended as a low ionic strength acidic solution in a simple matrix. Solutions D and E were more complex acidic matrices composed of several anions and cations simulating the composition of rainwater. Solution F was a repeat of Solution B to check for instrument drift, and possible hysteresis of the

liquid junction. Solution G was a repeat of C to check instrument drift. Solution H was a repeat of A to check calibration drift and hysteresis. Participants were asked to repeat the sequence in order to establish the precision of the measurements. Participants were also asked to supply information as to types of electrodes and standards used.

## **Results and Discussion**

Because the samples were to be sent to participants via the U.S. Postal System during the winter months, it seemed advisable to test whether freezing and thawing the solutions would affect the pH values. A set of samples was frozen in a laboratory freezer for 24 hours and then thawed. No significant differences in pH values were observed with this set versus a control set which had not been frozen. Even after several freeze-thaw cycles, there were no significant differences noted.

Full cooperation was obtained from all participants with regard to quality, completeness, and timeliness of response. All of the measured pH values are shown in table 2, including the buffer standards used by the participants (STD 1 and STD 2). The average pH values for measurement trials 1 and 2 for each solution by each participant are shown in table 3. The laboratory number does not correspond to the alphabetical listing of laboratories in Appendix A. The data and general results will first be presented graphically since this is easier to assimilate, and will then be described in a more quantitative fashion through the use of statistical analyses of variance. As a general rule in routine pH measurements using combination electrodes, an uncertainty of  $\pm 0.02$ pH units is to be expected. This permissable variability will be applied in the following discussion of the data.

With the exception of laboratory 3, all participants reproduced the value for solution A, the standard buffer solution of potassium acid phthalate. Subsequent to the test, laboratory 3 discovered that the commercial buffer that they were using was biased. They have since corrected this problem. This indicates that good calibration practices were in effect and that the instruments were in a state of control. It also suggests that if accurate results are required, then standardization should be done using quality reference buffers, such as Standard Reference Materials supplied by the National Bureau of Standards. The values for solution H (which is identical to A) scatter a little more, with three labs (7, 8, and 17) being out of compliance. However, this is most likely due to hysteresis at the liquid junction. When comparing the values for A and H, and C with G, no trends in instrument drift are apparent. Furthermore, hysteresis of the electrodes, when subjected to buffers and low ionic strength solutions, should not be a major problem if, as for this

Table 2.	pH readings f	for both	measurement	trials 1	and 2.
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Lab. No.	STD 1	STD 2	Α	в	С	D	Е	F	G	Н	STD 1	STD 2
	_											
1	3.997	6.860	4.016	3.716	4.401	4.265	3.787	3.727	4.415	3.998	4.014	6.860
	4.014	6.863	4.014	3.719	4.402	4.270	3.786	3.727	4.414	3.996	4.016	6.862
2	4.000	7.020	4.000	3.710	4.380	4.160	3.770	3.720	4.370	4.010	4.000	7.020
	4.000	7.010	4.010	3.700	4.370	4.150	3.760	3.710	4.370	4.010	3.990	7.010
3	4.010	6.870	3.960	3.530	4.190	4.010	3.660	3.590	4.210	3.990	4.030	6.880
3	4.010	6.850	3.960	3.540	4.210	4.010	3.680	3.620	4.230	4.000	4.020	6.860
		6.051	1.000		( 202			2.516	4 205	4 000	4.005	6.040
4	4.005 4.008	6.851 6.859	4.006 4.007	3.720 3.728	4.393 4.392	4.203 4.208	3.772 3.780	3.716 3.730	4.385 4.384	4.002 4.009	4.005 4.010	6.849 6.859
	4.000	0.859	4.007	3.720	4.372	4.208	5.780	3.750	4.504	4.007	4.010	0.007
5	4.000	6.830	4.000	3.720	4.370	4.140	3.760	3.700	4.360	3.990	3.990	6.820
	4.000	6.840	4.000	3.720	4.370	4.160	3.770	3.710	4.360	4.000	4.000	6.840
6	4.010	7.000	4.006	3.734	4.417	4.187	3.787	3.727	4.404	4.020	4.010	7.003
	4.010	6.973	4.005	3.711	4.365	4.160	3.770	3.710	4.370	4.006	4.022	6.97
7	4.004	6.871	4.024	3.583	4.218	4.047	3.860	3.602	4.088	4.082	4.063	6.914
·	4.004	6.863	3.995	3.545	4.171	4.049	3.848	3.630	4.159	4.007	3.991	6.85
8	4.000	7.010	4.010	3.460	4.130	3.970	3.610	3.570	4.210	4.060	4.030	7.030
0	4.000	7.000	4.000	3.430	4.070	3.910	3.560	3.520	4.150	4.040	4.030	7.02
9	4.000	7.410	4.020	3.720	4.340	4.140	3.780	3.730	4.320	4.020	4.000	7.39
	4.000	7.410	4.010	3.720	4.320	4.140	3.770	3.720	4.320	4.010	4.010	7.40
10	4.000	7.000	4.000	3.710	4.390	4.170	3.770	3.700	4.380	4.000	4.000	7.00
	4.000	7.000	3.990	3.710	4.390	4.160	3.760	3.700	4.380	4.000	3.990	6.99
11	4.010	6.990	4.010	3.740	4.400	4.170	3.800	3.740	4.400	4.020	4.010	6.97
	4.000	6.990	4.020	3.760	4.450	4.200	3.810	3.760	4.410	4.030	4.030	7.00
12	4.000 3.997	6.863 6.862	4.000 4.001	3.668 3.667	4.324 4.331	4.121 4.124	3.732 3.734	3.682 3.676	4.344 4.338	4.010 4.008	4.003 4.003	6.86 6.85
	3.337	0.802	4.001	5.007	4.551	4.124	5.754	5.070	4.558	4.000	4.005	0.05
13	4.004	6.885	4.006	3.705	4.394	4.165	3.751	3.692	4.390	3.990	3.992	6.87
	4.002	6.866	4.003	3.709	4.399	4.171	3.762	3.704	4.397	4.000	4.001	6.86
14 ,	4.003	6.878	4.005	3.735	4.393	4.181	3.790	3.735	4.400	4.005	4.007	6.86
	4.003	6.873	4.006	3.720	4.392	4.178	3.783	3.720	4.394	4.007	4.005	6.85
15	4.002	6.830	4 002	3.743	4.371	4.161	3.775	3.748	4.383	4.002	4.000	6.80
15	4.002	6.879	4.002 3.997	3.743	4.368	4.158	3.761	3.748	4.383	3.996	4.000	6.88
16	4.010	6.840	4.000	3.610	4.300	4.090	3.700	3.640	4.290	4.010	4.000	6.84 6.85
	4.000	6.840	4.030	3.630	4.290	4.070	3.700	3.640	4.280	4.000	4.010	0,8;
1 <b>7</b>	4.000	6.980	3.990	3.720	4.410	4.190	3.820	3.740	4.440	3.980	4.000	7.0
	4.000	6.990	3.990	3.730	4.450	4.190	3.780	3.720	4.430	3.980	3.990	6.9

Solution Lab. No.	Α	В	С	D	E	F	G	Н
1	4.02	3.72	4.40	4.27	3.79	3.73	4.42	4.00
2	4.00	3.70	4.38	4.16	3.77	3.72	4.37	4.01
3	3.96	3.54	4.20	4.02	3.67	3.60	4.22	4.00
4	4.01	3.72	4.39	4.21	3.78	3.72	4.38	4.00
5	4.00	3.72	4.37	4.15	3.77	3.70	4.36	4.00
6	4.01	3.72	4.39	4.17	3.78	3.72	4.39	4.01
7	4.01	3.56	4.19	4.05	3.85	3.62	4.12	4.04
8	4.00	3.44	4.10	3.94	3.58	3.54	4.18	4.05
9	4.02	3.72	4.33	4.14	3.78	3.72	4.32	4.02
10	4.00	3.71	4.39	4.16	3.76	3.70	4.38	4.00
11	4.02	3.75	4.42	4.18	3.80	3.75	4.40	4.02
12	4.00	3.67	4.33	4.12	3.73	3.68	4.34	4.01
13	4.00	3.71	4.40	4.17	3.76	3.70	4,39	4.00
14	4.01	3.73	4.39	4.18	3.79	3.73	4.40	4.01
15	4.00	3.72	4.37	4.16	3.77	3.73	4.38	4.00
16	4.02	3.62	4.30	4.08	3.70	3.64	4.28	4.00
17	3.99	3.72	4.43	4.19	3.80	3.73	4.44	3.98

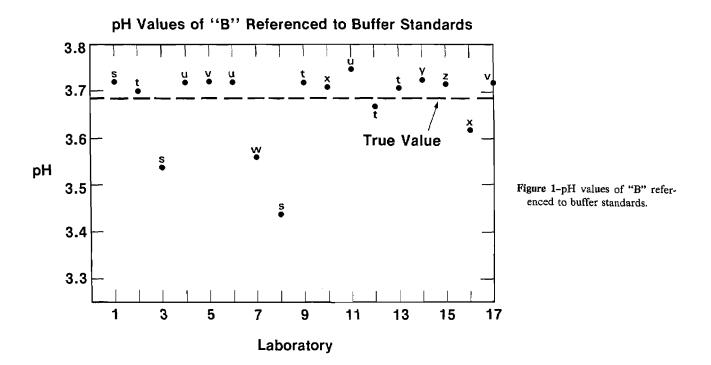
exercise, a strict measurement protocol is established and followed. In fact, with the exceptions of laboratories 3, 7, and 8, excellent repeatability was observed for the duplicate solutions (A/H, B/F, and D/G). It can be concluded that, with few exceptions, the precision of pH measurements made by a single operator, using a single set of electrodes, is within the permissable variability of  $\pm 0.02$  pH, and is not a matter of great concern. The data reported in table 2 for the duplicate measurements also shows good within-laboratory precision. However, this conclusion can be misleading because of the constraints of a single laboratory, a single operator, and a single set of electrodes, and because of the inattention to the matter of accuracy. Figure 1 shows the wide range of pH values obtained by the participants for solution B and their relationship to the true pH of this solution. The lower case letters, s through z, above each data point serve to categorize the electrodes used by the participants according to type and manufacturer. The range of values spans more than 0.3 pH units. Only two laboratories are within the permissable variability of 0.02 pH. Most laboratories are biased several hundredths of a unit high. A few laboratories are biased low and once again laboratories 3, 7, and 8 stand out in this regard. It is clear, that in spite of excellent withinlaboratory precision, between-laboratory precision is very poor, and the measurements show a great deal of systematic bias. The high degree of scatter is confirmed by the values reported for solutions C, D, and E, as shown in figure 2. The solid line is the mean value of the 17 measurements and should be viewed as a point of reference only, not as the true value. Unlike B, the true pH values for these solutions have not been determined.

Exhibited in figure 3 are the results of normalizing the pH values of C, D, and E, with respect to B. In essence,

solution B is used as the calibration standard rather than the customary buffer solution. The vast improvement in terms of decreased scatter is obvious. Most values are now within  $\pm 0.02$  pH units of the mean. (The extremely high value for E by laboratory 7 must be considered an outlier and is discussed in more detail below.)

As noted, the participants included in their reports the make, model, and type of electrodes used in their measurements. Eight distinct types of electrodes were used in the study. These have been identified in code on figures 1-3 with the lower case letters s through z. An association of the type of electrode with deviations from either the true value or the mean is exhibited by only two of the eight types, namely, "s" and "w." Type "s" is a combination electrode in which the liquid junction of the reference electrode is somewhat larger in area than the other electrodes used in the test. This apparently results in a larger variability in residual liquid junction potential. However, when normalized with solution B, the values obtained by electrode "s" conform quite well. Type "w", used by laboratory 7, is a combination electrode which incorporates a gel-filled reference electrode. During this test, this electrode behaved quite erratically in low ionic strength solutions, as evidenced by its non-conformity even after the normalization process.

Electrode types "y" and "z" had open-junction reference electrodes; that is, the junction between the filling solution of the reference electrode and the sample solution was formed at a capillary tip, rather than across a ceramic or fiber frit as is customary in combination electrodes. In the low ionic strength solutions tested in this exercise there was no apparent advantage to this type of junction, although it has proven its worth in other types of solutions. Correlations with the other requested information (Appendix D) were not readily apparent.



pH Values of "C", "D", and "E" Referenced to Buffer Standards

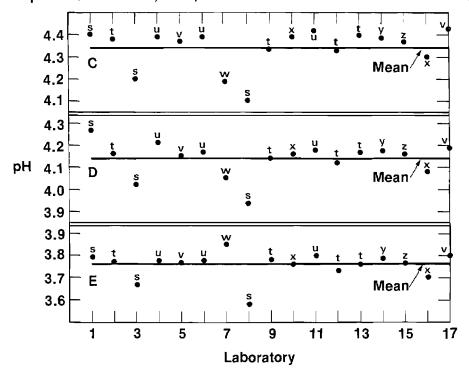


Figure 2-pH values of "C," "D," and "E" referenced to buffer standards.

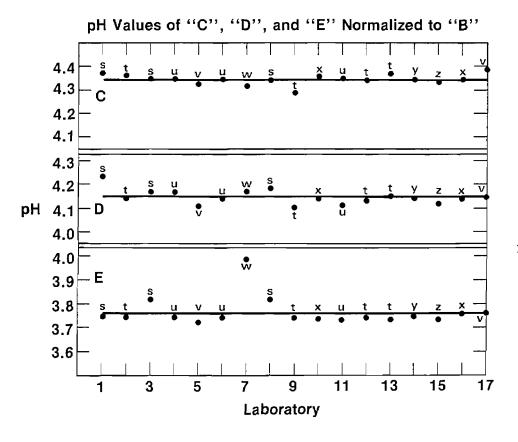


Figure 3-pH values of "C," "D," and "E" normalized to "B."

## Statistical Analysis

The original pH data from the laboratories, as well as the result obtained by mathematically recalibrating the original data with the individual laboratory's solution B measurements, have been quantitatively evaluated. Table 2 gives the original data and table 4 the recalibrated data. One-way analyses of variance were run on the original and the recalibrated data for non-buffer solutions C through G. The analyses of variance calculations gives within- and between-laboratory components of variance. The square roots of these quantities are called the within- and between-laboratory components of standard deviation, and are reported in table 5.

Examination of table 5 results shows the withinlaboratory components of standard deviation to be about 0.015 pH units, and to be approximately equal for the original and the recalibrated data sets. The betweenlaboratory components of standard deviation, however, are markedly different between the original and the recalibrated data sets. As expected, the recalibrations with solution B have resulted in greatly improved betweenlaboratory precisions. The component of betweenlaboratory standard deviation is about 0.07 pH units for the original data, and is about 0.03 for the recalibrated data. The reader may evaluate the stability of the precision estimates by comparing the results from the identical solutions C and G.

#### Conclusion

The results of this interlaboratory test show that the use of dilute strong acid solutions of known and independently verifiable pH (e.g., solution B) to standardize pH instrumentation greatly improves betweenlaboratory precision in the measurement of pH in low ionic strength solutions, such as acidic rainwater. Thus, the use of such solutions by all those involved in network monitoring of wet deposition is recommended to improve the intercomparability of the measurements as a function of time and location. To aid in this endeavor, Standard Reference Material, SRM 2694, "Simulated Rainwater" has been prepared and analyzed by our laboratory and is available through the Office of Standard Reference Materials of NBS. SRM 2694 consists of a set of two 50 mL solutions in polyethylene bottles. The nominal pH of Level I is 4.3 and that of Level II is 3.6. The acidity and the specific conductance have also been determined, as well as several of the major cations and anions commonly found in rainwater. Guidelines for the measurement of pH in rainwater with the use of these materials are included with the Certificate of Analysis.

F STD 1 STD 2 н STD 1 STD 2 Lab. No. Α В С D Ε G 4.379 1 3.961 6.824 3.980 3.680 4.365 4.229 3.962 3.978 6.824 3.751 3.691 3.975 6.824 3.975 3.680 4.363 4.231 3.747 3.688 4.375 3.957 3.977 6.823 3.970 6.990 2 3.970 3.680 4.350 4.130 3.740 3.690 4.340 3.980 3.970 6.990 3.980 6.990 3.990 3.680 3.740 3.690 3.990 3.970 6.990 4.350 4.130 4.350 3 4.160 7.020 4.110 3.680 7.030 4.340 4.160 3.810 3.740 4.360 4.140 4.180 4.150 6.990 4.100 3.680 4.350 4.170 3.820 3.760 4.370 4.140 4.160 7.000 4 3.965 6.811 3.966 3.680 4.353 4.163 3.732 3.676 4.345 3.962 3.965 6.809 3.960 6.811 3.959 3.680 4.344 4.160 3.732 3.682 4.336 3.961 3.962 6.811 5 6.790 3.960 3.960 3.680 4.330 4.100 3.720 3.660 4.320 3.950 3.950 6.780 3.960 6.800 3.960 3.680 4.330 4.120 3.730 3.670 4.320 3.960 3.960 6.800 3.956 6.946 3.952 6 3.680 4.363 4.133 3.733 3.673 4.350 3.966 3.956 6.949 3.979 6.942 3.974 3.680 4.334 4.129 3.739 3.679 4.339 3.975 3.991 6.942 7 4.101 6.986 4.121 3.680 4.315 3.957 3.699 4.185 7.011 4.144 4.179 4.160 4.139 6.998 4.130 3.680 4.306 4.184 3.983 3.765 4.294 4.142 4.126 6.991 4.220 8 7.230 4.230 3.680 4.350 4.190 3.830 3.790 4.430 4.280 4.250 7.250 4.250 7.250 4.250 3.680 4.320 4.160 3.810 3.770 4.400 4.290 4.280 7.270 9 3.960 7.370 3.980 3.680 4.300 4.100 3.740 3.690 4.280 3.980 3.960 7.350 3.960 3.970 7.370 3.680 4.280 4.100 3.730 3.680 4.280 3.970 3.970 7.360 10 3.970 6.970 3.970 3.680 4.360 4.140 3.740 4.350 3.970 6.970 3.670 3.970 3.970 6.970 3.960 3.680 4.360 4.130 3.730 3.670 4.350 3.970 3.960 6.960 6.930 11 3.950 3.950 3.680 4.340 4.110 3.740 3.680 4.340 3.960 3.950 6.910 3.920 6.910 3.940 3.680 4.370 4.120 3.730 3.680 4.330 3.950 3.950 6.920 12 4.012 6.875 4.012 3.680 3.694 4.336 4.133 3.744 4.356 4.022 4.015 6.877 4.010 6.875 4.014 3.680 4.344 4.137 3.747 3.689 4.351 4.021 4.016 6.872 13 3.979 6.860 3.981 3.680 4.369 4.140 3.726 3.667 4.365 3.965 3.967 6.850 3.973 6.837 3.974 3.680 4.142 4.370 3.733 3.675 4.368 3.971 3.972 6.836 14 3.948 6.823 3.950 3.680 4.338 4.126 3.735 3.680 4.345 3.950 3.952 6.811 3.963 6.833 3.966 3.680 4.352 4.138 3.743 3.680 4.354 3.967 3.965 6.816 15 3.939 6.767 3.939 3.680 4.308 4.098 3.712 3.685 4.320 3.939 3.937 6.738 3.979 6.855 3.973 3.680 4.344 3.680 4.359 3.972 3.980 4.134 3.737 6.856 16 4.080 6.910 4.070 3.680 4.370 4.160 3.770 3.710 4.360 4.080 4.070 6.910 4.050 6.890 4.080 3.680 4.340 4.120 3.750 3.690 4.330 4.050 4.060 6.900 17 3.960 6.940 3.950 3.680 4.370 4.150 3.780 3.700 4.400 3.940 3.960 6.960

Table 4. pH values after normalization.

4.140

3.730

3.670

4.380

3.930

3.940

6.940

4.400

3.950

6.940

3.940

3.680

Table 5. Summary of results from the analyses of variance.

Components of		1	Solutions		
Standard Deviation (S)	С	G	D	E*	Fb
	Using	, Origina	l pH Re	adings (	table 2)
S, within-lab	0.020	0.018	0.014	0.014	0.015
S, between-lab	0.091	0.087	0.077	0.056	0.055
	Using	, Normali	ized pH I	Reading (	(table 4)
S, within-lab	0.014	0.022	0.014	0.012	0.014
S, between-lab	0.021	0.036	0.029	0.027	0.029

<sup>a</sup> Laboratory 7 data for solution E were judged to be outliers and were not used in the analysis of variance.

<sup>b</sup> Results for solution B are essentially the same as F.

#### References

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## APPENDICES

## Appendix A

Participants in alphabetical order according to institution:

- Brookhaven National Laboratory, Long Island, NY
- Department of Energy, Environmental Measurements Laboratory, New York, NY
- Environmental Science and Engineering, Inc., Gainesville, FL
- Florida Southern College, Lakeland, FL
- · Global Geochemistry Corp., Canoga Park, CA
- Illinois State Water Survey, Champaign, IL
- Martin Marietta Corporation, Baltimore, MD
- National Bureau of Standards, Gaithersburg, MD
- Research Triangle Institute, Research Triangle Park, NC
- Rockwell International, Newbury Park, CA
- Russell Sage College, Troy, NY
- South Coast Air Quality Management District
- United States Geological Survey, Denver, CO

## Appendix B

## Directions for Measurement of pH for the Interlaboratory Test

- Make all pH measurements between 20 and 26 °C. Report the solution temperature to within 1 °C. Report all pH values to at least 0.01 pH unit. Make all measurements in a quiescent solution.
- Standardize the pH electrodes and meter using SRM 185e, potassium hydrogen phthalate [pH(S)

4.004 at 25.0 °C, 0.05 molal], or equivalent. Refer to ASTM D1293, "Standard Test Methods for pH of Water" for guidance. Record the value on the enclosed data sheet.

- 3) With the slope adjustment of the meter set at 100%, check the Nerstian response of the pH measurement system with a second buffer, SRM 186Ic/186IIc, potassium dihydrogen phosphate/ disodium hydrogen phosphate [pH(S) 6.863 at 25.0 °C] or equivalent. Refer to ASTM D1293 for guidance. If the reading for the second buffer is not within 0.03 pH units of the prescribed value, recheck the calibration of the system. DO NOT CONTINUE with the interlaboratory test until the conditions for calibration and Nernstian response have been satisfied. See Note A. If the reading for the second buffer is within 0.03 pH units of the prescribed value, record the value and continue.
- 4) Rinse the electrodes thoroughly with distilled water (ASTM Type II or better). Remove drops of water on the electrode by blotting gently (Do Not Rub!) with a clean lab tissue.
- 5) Insert the electrodes into a clean beaker (10-20 mL capacity) containing a portion (10-20 mL) of solution A (or subsequent solution). Be certain that the reference junction and glass bulb are completely immersed. Do not insert the electrodes directly into the polyethylene bottles.
- 6) Stir or swirl the solution to ensure homogeneity and contact with the electrodes.
- 7) Allow the solution to settle to a quiescent state (approx. 30 seconds). Record the pH value after the reading has stabilized. (Some systems may require five minutes or more to stabilize.) If drifting persists, record the value after 10 minutes in the quiescent state and note this fact in the

"Comments" column. Report only a single value for each solution per trial. Do not average several readings of the same solution.

- Repeat steps 4 through 7 for solutions B, C, D, E, F, G, and H in this assigned sequence. Do not change the order, and do not recalibrate with buffer standards within this sequence.
- 9) Remeasure buffer standards #1 and #2 (without adjusting the settings of the pH meter) and record the values.
- 10) Repeat steps 1-9 for Trial #2.

Note A: Possible causes for deviation from Nernstian response include:

- i) improper calibration
- ii) old or contaminated buffer solutions
- iii) insufficient rinsing of the electrodes between solutions
- iv) plugged reference junction
- v) defective electrodes
- vi) defective meter

It may be necessary to replace the electrodes with a new pair if the non-Nernstian behavior persists even with accurately and freshly prepared buffer standards.

# Appendix C

## DATA SHEET

## Interlaboratory Test NBS-AD-83

Laboratory/Scientists:

Date of Test: \_\_\_\_

Temperature of Test Solutions:

	pH	I Reading	
Sample	Trial #1	Trial #2	Comments
Standard Buffer #1 (Calibration)			
Standard Buffer #2			
Solution A			
Solution B			
Solution C			
Solution D			
Solution E			
Solution F			
Solution G			
Solution H			
Standard Buffer #1			
Standard Buffer #2			

# **INFORMATION SHEET**

## Interlaboratory Test NBS-AD-83

-pH Meter
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• Make/Model:
Readout: Digital; Analog;
• Sensitivity: 0.01 pH; 0.001 pH
-pH Electrodes
• Make/Model
- Combination Electrode:
- Glass Electrode:
- Reference Electrode:
• Size: micro; semi-micro;
other (specify)
• Range (in pH units): 0-10; 0-11; 0-14;
other (specify)
• Reference Electrode Filling Solution (specify, e.g., 4 M KCl)
<ul> <li>Reference Electrode Junction: ceramic; fiber; sleeve; double; other (specify)</li> </ul>
-Standard Buffers
• Nominal pH 4: SRM 185e; Commercial (specify brand and pH values)
Nominal pH 7: SRM 18Ic/186IIc; Commercial (specify brand and
pH value)
Other (specify brand and pH value)