pH MEASUREMENT OF LOW-CONDUCTIVITY WATERS

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ABSTRACT

pH is an important and commonly measured parameter of precipitation and other natural waters. This report analyzes the various sources of errors in pH measurement, and suggests procedures for improving the accuracy and precision of pH measurements in natural waters with conductivities of less than 100 microsiemens per centimeter at 25° Celcius. Detailed procedures are given for the preparation of dilute sulfuric-acid standards to evaluate the performance of pH electrodes in low-conductivity waters. A daily check of the pH of dilute sulfuric-acid standards and deionized water saturated with a gas mixture of low carbon-dioxide partial pressure (air) prior to the measurement of the pH of low-conductivity waters is suggested.

INTRODUCTION

pH is an important and commonly measured parameter of precipitation and other natural waters. Interlaboratory studies have shown that significant problems exist in the accurate measurement of pH of waters with conductivities of less than 100 μS/cm (microsiemens per centimeter at 25° Celcius), such as meteoric precipitation encountered in studies of watersheds (Tyree, 1981; Mason, 1984; Koch and others, 1986). The suggestions presented in this report are aimed at improving the accuracy and precision of pH measurement of meteoric precipitation and other low conductivity waters, and are based on extensive laboratory and field experience.

Accurate measurement of pH in low-conductivity waters is difficult, but possible, if proper procedures are followed. Proper calibration of electrodes with buffers does not guarantee accurate pH measurement in low-conductivity waters (Covington and others, 1983; Davison and Woof, 1985). Electrodes should be calibrated in buffers and their performance checked daily in standard sulfuric-acid solutions with conductivities of less than 20 μS/cm.

The performance of the electrodes should be further checked with deionized water saturated with an analyzed N_2-CO_2 (nitrogen-carbon dioxide) gas mixture with a CO_2 mole fraction of less than 0.5 percent. Recently, the National Bureau of Standards (NBS) developed a standard reference material for rainwater pH and acidity measurement. It consists of four 50-mL (milliliter) bottles at two acidity levels. These solutions were prepared from high purity salts and acids and have a pH of 4.30, acidity of 0.050 meq/L (milliequivalents per liter) and specific conductance of 26 μS/cm for SRM 2694-I at 25°C, and a pH of 3.59, acidity of 0.284 meq/L, and specific conductance of 130 μS/cm for SRM 2694-II at 25.0°C. Problems have been reported with these standards mainly due to the very dilute and unbuffered nature of the solutions. NBS makes no assurance as to the composition and stability of the solutions after the bottles are removed from their sealed aluminized bags or after the bottles are opened (Koch and others, 1986). Further details on the preparation, use and certification of these standards can be found in six articles of Volume 91, Number 1 of the 1986 issue of the Journal of Research (National Bureau of Standards, 1986). The high cost ($158.00) for a total of 200 mL of solution makes these standards impractical for daily electrode performance evaluation. Our experience indicates that electrodes that operate properly in very dilute acid solutions will perform well in low-conductivity natural waters. Well behaved electrodes will measure pH of dilute H_2SO_4 (sulfuric-acid) solutions with theoretical pH values of 4.5 or more (table 1) to within ± 0.03 pH units. Many commercial electrodes are unsuitable for pH measurement in low-conductivity waters (Brezinski, 1983; Covington and others, 1983, 1985; Davison and Woof, 1985). We have found that almost 50 percent of new "research grade" electrodes from one manufacturer were unsuitable for accurate pH measurement in very low conductivity natural waters.

The problems associated with the pH measurement of low conductivity waters have been extensively investigated. Supplementary information on these problems can be found in the works of Ives and Janz (1961), Bates (1973), Seymour and others (1978), Westcott (1978), Gallaway and others (1979), Covington (1981), Brezinski (1983), Covington and others (1983, 1985), Sisterson and Wurfel (1984), Koch and others (1986).

This paper presents some theoretical aspects and the suggested procedures for the measurement of pH in low-conductivity waters and the preparation of low-ionic-strength sulfuric-acid solutions.

Table 1. Concentration, pH, and specific conductance of dilute sulfuric-acid solutions

Normality 1	Molarity	γ_{H^+}	Theoretical pH 2	Theoretical specific conductance 3	Stability of the solutions 4	ML of sulfuric-acid required to prepare 2 liters of solution [5] (mL)		
						0.200N [6]	0.0200N [7]	0.00200N [8]
1×10^{-6}	5.0×10^{-7}	0.999	6.00	0.429	A			1
2×10^{-6}	1×10^{-6}	.998	5.70	.857				2
3×10^{-6}	1.5×10^{-6}	.998	5.52	1.28	B			3
4×10^{-6}	2×10^{-6}	.997	5.40	1.71				4
5×10^{-6}	2.5×10^{-6}	.997	5.30	2.14				5
6×10^{-6}	3×10^{-6}	.997	5.22	2.56				6
7×10^{-6}	3.5×10^{-6}	.996	5.16	2.99				7
8×10^{-6}	4×10^{-6}	.996	5.10	3.42				8
9×10^{-6}	4.5×10^{-6}	.996	5.05	3.84				9
1×10^{-5}	5×10^{-6}	.996	5.00	4.27	C		1	10
2×10^{-5}	1×10^{-5}	.994	4.70	8.51			2	
3×10^{-5}	1.5×10^{-5}	.992	4.53	12.74	C		3	
4×10^{-5}	2×10^{-5}	.991	4.40	16.95			4	
5×10^{-5}	2.5×10^{-5}	.990	4.31	21.15			5	
6×10^{-5}	3×10^{-5}	.989	4.23	25.34			6	
7×10^{-5}	3.5×10^{-5}	.988	4.16	29.53			7	
8×10^{-5}	4×10^{-5}	.988	4.10	33.70			8	
9×10^{-5}	4.5×10^{-5}	.987	4.05	37.87			9	
1×10^{-4}	5×10^{-5}	.986	4.01	42.03	D	1	10	
2×10^{-4}	1×10^{-4}	.981	3.71	83.28		2		
3×10^{-4}	1.5×10^{-4}	.977	3.53	124.0	D	3		
4×10^{-4}	2×10^{-4}	.974	3.41	164.0		4		
5×10^{-4}	2.5×10^{-4}	.971	3.31	204.4		5		
6×10^{-4}	3×10^{-4}	.968	3.24	244.0		6		
7×10^{-4}	3.5×10^{-4}	.966	3.17	283.4		7		
8×10^{-4}	4×10^{-4}	.964	3.11	322.6		8		
9×10^{-4}	4.5×10^{-4}	.962	3.06	361.4		9		
1×10^{-3}	5×10^{-4}	.960	3.02	400.1	E	10		

Table 1 - Continued
FOOTNOTES:

[1] For sulfuric-acid, normality equals 2 times molarity.

[2] Theoretical pH is accurate to within ± 0.02 pH units. Temperature is 25.00°C.

[3] Values calculated for specific conductance are within ± 0.2 percent of literature values. Literature data for sulfuric-acid at these concentrations are of poor quality. Measurements should be made near 25°C because the temperature coefficient of sulfuric-acid is significantly different from that of KCl. The automatic temperature compensation of the meters are those of KCl and, therefore, can introduce a significant error in conductivity if the temperature of the sulfuric-acid is significantly different from 25°C. Saturation with atmospheric CO_2 can add up to 1.0 μS/cm to the above values. In addition, the background conductivity of the distilled or deionized water should be added. The background should be less than 1.0 μS/cm. Deionized water is essentially CO_2 free, and remains so if stored in glass.

[4] The stability of solutions are as follows:
A. Very unstable, can only be prepared with extreme difficulty from CO_2-free, ultrapure distilled water. Must be protected from atmospheric CO_2. Not recommended.
B. Must be prepared from very high purity distilled water. Stable for 4-8 hours. Not recommended.
C. Must be prepared from high purity distilled water, should be replaced every 24 hours.
D. Stable for about 1 week.
E. Stable for about a month.

[5] Sulfuric-acid solutions are prepared by adding the indicated volumes to a 2-L volumetric flask and filling to the mark with distilled water. See text for details. The necessary equipment needed to prepare solutions with pH values of 5.5, 5.0, 4.5, 4.0, 3.5 and 3.0 are:
a) One 2-L volumetric flask,
b) pipets 1 mL, 3 mL, 10 mL and 20 mL (one each),
c) commercially available standard solutions of sulfuric-acid (0.0200 and 0.200 N solutions),
d) deionized water.

[6] Fisher Scientific Company [a]0.200 Normal sulfuric-acid solution Cat. No. SO-A-218. Other commercial standard sulfuric-acid solutions of the same concentration can be used.

[7] Fisher Scientific Company 0.0200 Normal sulfuric-acid solution, Cat. No. SO-A-226. Other commercial standard sulfuric-acid solutions of the same concentration can be used.

[8] The 0.00200N solution can be prepared by adding 20 mL of 0.200N sulfuric-acid (Fisher Scientific Co. Cat. #SO-A-218) to a 2-L volumetric flask and filling to volume with distilled water. Solution is stable for at least one month.

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[a] The use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

pH MEASUREMENT OF LOW-CONCUCTIVITY WATERS

Electrode Performance

The glass electrode-reference electrode pair can perform poorly in dilute solutions such as rain (Gallaway and others, 1979). Measurement of pH is difficult because the readings are often erratic and unstable. Streaming potentials and junction potentials may be large at the reference electrolyte-sample interface (Brezinski, 1983), and the glass electrode is subject to drift, asymmetry potential (Bates, 1973), and long times to reach "stable" readings. Considerable care must be taken to avoid trace contamination of solutions. Stirring potential errors are generated by the reference electrode and are a problem with low-ionic-strength solutions (Brezinski, 1983). Stirring potentials greater than 0.5 pH units have been reported in rainwater (Gallaway and others, 1979). Accurate pH measurements can only be obtained in unstirred quiescent solutions and buffers after the samples have been thoroughly homogenized by stirring (Gallaway and others, 1979; Brezinski, 1983; Davison and Woof, 1985). Junction potentials are real and cannot be eliminated in practice (Bates, 1973). Calculations given below suggest, however, the error in the measurement of pH of rain due to liquid junction is not much greater than 0.06 pH units.

Correctly working glass-electrode/reference-electrode pairs generally give 98.5 to 99.5 percent the response of that expected from the theoretical Nernst relation, which is

$$E = E^\circ - \frac{RT}{nF} \ln a_{H^+} \qquad (1)$$

where E is the potential of glass-reference pair in mv (millivolts); E° is the standard potential of this electrode pair; R, n and F are constants; T is the temperature in Kelvins; and a_{H^+} is the activity of the hydrogen ions. (Note: pH = $-\log a_{H^+}$)

Making appropriate substitutions for the constants at 25°C, (1) becomes

$$E = E^\circ + 59.16 \text{ pH}.$$

From the measured potential (E, in mv) of an electrode pair in solutions of known pH (such as NBS buffer solutions), and the theoretical Nernst response (59.16 mv/pH at 25°C), the percent theoretical slope should be calculated. The theoretical slopes as a function of temperature are given on table 2.

Before measurements begin on a routine basis, the electrodes to be used should be carefully checked. Slope and E° should be determined daily for about a week with new electrodes before the electrodes can be considered reliable for use, and checked again with each new calibration. The slope is never the theoretical value and is given by equation (2).

$$E = E^\circ + S \text{ pH}, \qquad (2)$$

where S is the slope.

By using two buffers (1, 2) of known pH

$$E_1 = E° + S\ pH_1$$

and $$E_2 = E° + S\ pH_2,$$

which gives $$S = \frac{E_1 - E_2}{pH_1 - pH_2} \tag{3}$$

and $$E° = E_2 - S\ pH_2. \tag{4}$$

After soaking a new electrode pair overnight, the slopes are typically low (~98.5%) and improve steadily within the first week (to ~99.5%). It's important to keep a daily log of electrode slopes and E° because they can signal problems in the electrode operation.

Electrodes that give slopes outside of the 98.5- to 99.8-percent interval are suspect. Slopes outside this interval can be caused by:

- Failure to obtain correct E value in a buffer, for example due to asymmetry potential.
- Errors in the buffers used.
- Slow but continuous electrode drift caused by partially clogged junction in the reference electrode.
- Contamination of the reference electrode element due to aging and possibly precipitation of AgBr from contaminants in the KCl filling solution.

Table 2. A tabulation of the log K_H and log K_1 of carbon dioxide and the theoretical slope of pH electrodes as a function of temperature [K_H = Henry's law constant for CO_2, and K_1 = first dissociation constant of carbonic acid]

°C	log K_H[1]	log K_1[1]	Theoretical slope [2]
0	-1.108	-6.579	54.197
1	-1.126	-6.565	54.396
2	-1.147	-6.552	54.594
3	-1.159	-6.540	54.792
4	-1.176	-6.528	54.991
5	-1.192	-6.516	55.189
6	-1.208	-6.505	55.388
7	-1.224	-6.494	55.586
8	-1.239	-6.483	55.784
9	-1.254	-6.473	55.983
10	-1.294	-6.463	56.181
11	-1.284	-6.454	56.380
12	-1.299	-6.445	56.578
13	-1.313	-6.436	56.777
14	-1.327	-6.427	56.975
15	-1.341	-6.419	57.173
16	-1.354	-6.411	57.372
17	-1.368	-6.403	57.570
18	-1.381	-6.396	57.769
19	-1.394	-6.389	57.967
20	-1.407	-6.382	58.165
22	-1.432	-6.369	58.562
23	-1.444	-6.363	58.761
24	-1.456	-6.357	58.959
25	-1.468	-6.352	59.157
26	-1.480	-6.347	59.356
27	-1.491	-6.342	59.554
28	-1.502	-6.337	59.753
29	-1.513	-6.332	59.951
30	-1.524	-6.328	60.149
31	-1.535	-6.324	60.348
32	-1.546	-6.320	60.546
33	-1.556	-6.317	60.745
34	-1.567	-6.313	60.943
35	-1.577	-6.310	61.141
36	-1.587	-6.307	61.340
37	-1.596	-6.304	61.538
38	-1.606	-6.302	61.737
39	-1.616	-6.300	61.935
40	-1.625	-6.297	62.133

[1] Calculated from the equations of Plummer and Busenberg (1981).

[2] Theoretical slope equals (RT log 10)/F where R is the gas constant, F is Faraday's constant and T is the temperature in kelvins.

The asymmetry potential results from the fact that glasses "remember" where they have been (Metcalf, 1984). Ions in the buffers and test solutions actually exchange with the glass surface and change its composition. When radical changes in solution composition are made (such as between buffers and test solutions), one often observes a slow "drift" in pH measurements to the true value (± .005 pH) over a period of as much as 30 minutes.

It is difficult to say how long it is necessary to wait before taking a reading because different changes are occurring simultaneously. Normally electrodes drift from day to day in an oscillating manner. E° typically varies by ± 2 mv. The slope generally remains fairly constant (to within ± 0.2 percent Nernst slope) once the new electrode has been in solutions for about a week. Good working electrodes almost always drift about 0.1 to 0.2 mv/hr. Electrodes are usually calibrated before and after use and can be adjusted with assumed linear-drift corrections for E° and slope. pH is then calculated from the drift-corrected E° and slope ($E°_t$, S_t which are functions of time) and the observed mv reading (E_t) at the time of measurement.

$$pH = \frac{E_t - E°_t}{S_t} . \qquad (5)$$

While the electrode is going through its normal drift behavior, there are superimposed on the observed potential, real changes due to (for example) equilibration of the glass surface with the test solutions, establishment of steady flowing junctions at the reference and attainment of thermal stability. Only experience with a particular electrode pair will indicate how long to wait for a steady reading. In a recent study of the pH of calcium bicarbonate solutions (Plummer and Busenberg, 1982), 15 minutes were often required to reach steady readings within ± 0.2 mv. But these times may be much longer in rain samples. Fortunately precision within ± 0.005 pH is not required, but there is no general rule for how long to wait. A good laboratory practice is to monitor E (or pH) on a chart recorder as a function of time to indicate when the readings have reached the background drift rate.

A recent advance in pH measurement is the Orion Research Inc. Ross electrode which eliminates the temperature dependence of the reference-electrode and thus minimizes measurement time. Readings steady to ± 0.01 pH are easily obtained within one minute with properly working Ross electrodes, but longer times are required in very dilute solutions and at low temperatures.

Buffer Characteristics

pH measurements are as accurate as the buffers used for calibration. Therefore, the following precautions should be taken to maximize the accuracy of pH measurement:

1. Do not use buffers after their expiration dates. The pH of the buffers may have been changed substantially by absorption of carbon dioxide, mold growth, or evaporation.

2. Always cap the buffer bottles to prevent evaporation and contamination with atmospheric carbon dioxide.

3. Never pour used buffer back into the bottles.

Some characteristics of the three NBS buffers used for the calibration of pH are:

1. Of all NBS buffers, the pH 4.01 buffer is the least resistant to contamination and is subject to mold growth. (Many commercial preparations of this buffer contain mold inhibitors.) This buffer is relatively unaffected by dilution and not affected by atmospheric carbon dioxide contamination.

2. The pH 6.86 buffer is moderately affected by dilution and is fairly resistant to contamination. This buffer is not affected by atmospheric carbon dioxide for the short time needed for pH electrode calibration. This buffer should not be left exposed to atmospheric carbon dioxide in open beakers over long periods of time.

3. The pH 9.18 buffer is not appreciably affected by dilution and is moderately resistant to contamination. The pH value of this buffer can change substantially if exposed to atmospheric carbon dioxide in an open beaker for a long period of time. However, the buffer is highly stable in an open beaker for the time needed for pH electrode calibration.

Contamination of buffers occurs when improperly washed electrodes are placed in the buffer solution. Dilution occurs when very wet but clean electrodes are placed in the buffer solution. Dilution is not a serious problem; however, contamination of one buffer with another can result in very serious errors.

Measurement of pH in Low-Conductivity Sulfuric-Acid

Low-conductivity waters (<100 μS/cm) have very low buffering capacities and are easily contaminated. The following procedure is recommended.

1. Wash the electrodes at least 3 times with distilled water.

2. When checking calibration with dilute sulfuric-acid standards, wash electrodes or electrode assembly 2 times with the dilute sulfuric-acid solution before measuring the pH.

3. At 25°C, wait at least 5 minutes before recording the pH to allow for thermal and pH equilibration. At lower temperatures, longer equilibration times are required. With the Orion Ross electrode, one minute should be sufficient to obtain stable readings at most field temperatures. Longer times are required at low temperatures and with sulfuric-acid solutions of less than 20 μS/cm conductivities.

4. The conductivity of the dilute sulfuric-acid solutions should be checked to assure that the acid was not contaminated and was properly prepared. The pH 5.00 sulfuric-acid solution should have a conductivity of between 4 and 5 μS/cm. The pH 4.53 sulfuric-acid solution should have a conductivity of between 12 and 14 μS/cm. The theoretical values for pH and conductivity of sulfuric-acid solutions are given in table 1. Actual values measured for these solutions agreed remarkably well with the calculated theoretical values.

5. Make all readings on unstirred quiescent solutions after the solution has been homogenized by stirring.

Thorough washing of the electrodes is essential for accurate pH measurement in the field. Wash the electrodes well with the low-conductivity water before measuring its pH.

The Practice of Adding Potassium Chloride to Test Solutions

Addition of KCl to the test solution increases the conductivity of the solution which decreases the response time of the electrode and gives generally more stable readings. Although addition of KCl (or KBr) may be useful in acidimetric titrations, there are some potential problems in its use for routine pH measurements.

1. Addition of KCl changes the ionic strength of the test solution which results in a change in pH. This effect is most important in dilute (high pH) rain. Typically, one might add 3 drops of saturated KCl solution to a 100 ml sample of rain. The total KCl concentration is about 0.01 molal. The calculations below show the expected change in pH of dilute sulfuric-acid solutions initially at pH 5.00, 4.00, 3.00, and 2.00 upon addition of KCl to 0.01 m.

mH_2SO_4	Calculated pH for Varying Concentrations of KCl					
	0.0	.002	.004	.006	.008	.010 (mKCl)
5.024×10^{-6}	5.00	5.02	5.03	5.03	5.03	5.04
5.093×10^{-5}	4.00	4.01	4.02	4.03	4.03	4.03
5.424×10^{-4}	3.00	3.01	3.01	3.01	3.02	3.02
6.969×10^{-3}	2.00	2.00	2.00	2.00	2.00	2.00

The changes are (theoretically) small but vary with the amount of H_2SO_4 in the solution and amount of KCl added.

2. More serious problems with KCl addition probably result from impurities in the salt. A check of labels on KCl bottles from separate lots from the same supplier gave the pH of 5-percent KCl solutions as 5.6, 7.9, and 8.5. So, in practice, depending on the particular sample of KCl used and the particular test solutions, large changes in pH could result upon addition of the salt, unless considerable care is exercised to purify the salt before use. If it is absolutely necessary to add KCl, use KCl available from NBS (SRM 999) or another material with similar high purity.

Junction-Potential Errors

There are small differences in pH between measured and calculated values of dilute sulfuric-acid solutions. The differences result from a potential generated by the contact between the reference-electrode filling solution and the test solution (or standard solution) (Illingsworth, 1981; Brezinski, 1983). Junction potentials cannot be measured directly. Work on the differences in junction potential between two solutions indicates that, at least for dilute solutions (such as acid rain), pH errors due to liquid junction can be calculated and appropriate corrections made. The magnitude of the junction error depends on the chemical composition and concentration of the filling solution in the reference electrode and chemical composition and ionic strength of the standards and test solutions.

Calculations of junction potentials were made using the Henderson equation (Bates, 1973; Plummer and Busenberg, 1982). The results indicated that measured pH will always be higher than the true (thermodynamic) pH. The error does not depend significantly on the concentration of the KCl filling solution between 3M and saturated KCl but may differ significantly if other solutions such as the Orion 90-01 filling solution are used. If NBS buffers (pH 4.01, 6.86, 7.41) are used with the electrodes, the measured pH will be too high by about 0.06 pH at pH 5.70 varying approximately linearly with pH to about 0.01 pH too high at pH 2 in dilute sulfuric-acid solutions. If, however, the calibration is made with dilute sulfuric-acid standards, the junction potentials cancel somewhat leading to possibly lower errors. Theoretical calculation procedures are available for correcting measured pH for liquid junction potentials. The use of sulfuric-acid standards for calibration rather than true buffers is not recommended because of the instability of dilute sulfuric-acid solutions. Covington and others (1983) recommend the use of very dilute "buffer" solutions to minimize junction potentials. Four "buffers" with pH values at 25°C of 4.12, 7.07, 7.61 and 9.20 are available. The pH values of these solutions have been measured in cells without liquid junctions for the temperatures of 5, 10, 15, 10, 25 and 30°C (Covington and others, 1983). These solutions have very low buffering capacity and are very easily contaminated. Low ionic strength "buffers" are available from Orion Research, Inc.

Measurement of Acidity

It is strongly recommended that the Gran titration method discussed by Seymour and others (1978), Gallaway and others (1979), McQuaker and others (1983), Sisterson and Wurfel (1984), and Marinenko and Kock (1985) be endorsed. This method is frequently used in precision determination of alkalinity. The method could be automated with an automatic titrator and microprocessor for routine determination of strong and weak acids present. Effects of the addition of KCl or KBr to improve the electrode stability and response can be corrected for by running a blank. The method has the further advantage of depending on differences in E rather than absolute E so that uncertainties in electrode calibration are not important. Measurement of acidity is one of the most reliable determinations that can be made of acid rain. It should be checked by charge balance with chemical analyses of the sample.

Preparation of Dilute Sulfuric-Acid Solutions

The following is the minimum equipment needed for the preparation of the sulfuric-acid solutions. Class-A glassware should be used.

1. One 1-mL pipet.
2. One 3-mL pipet.
3. One 2000-mL (2 liter), class-A volumetric flask (two flasks are preferable).
4. A commercial 0.0200 N (0.0100 molar) sulfuric-acid solution (Fisher Scientific Co. Cat. No. SO-A-226 or a similar commercial standard).
5. Freshly distilled or deionized water with a conductivity of preferably less than 1 µS/cm. This quality of deionized water is obtained by passing water through a research-grade commercial mixed-bed ion-exchange column.

The commercial standard sulfuric-acid solution used in this procedure is dilute and safe. Mouth pipeting is not recommended because this solution contains formaldehyde as a mold inhibitor. When good laboratory facilities are not available, a 1-mL Eppendorff pipet can be used instead of the 1-mL and 3-mL pipets.

Preparation of pH 5.00 Sulfuric-Acid Solution

I. Reagents

1. Commercial 0.0200 N sulfuric-acid solution.
2. Freshly distilled or preferably freshly deionized water with a conductivity of less than 1 µS/cm

II. Supplies

1. A 1-mL class A pipet. A 1000-µL (1-mL) Eppendorff pipet is satisfactory.
2. A 2-L class-A volumetric flask.

III. Procedure

1. Wash your pipet with distilled or deionized water. Allow the pipet to dry. If you are using an Eppendorff pipet, draw in 1 mL of distilled water, then discard it. Repeat this procedure 2 more times. The inside of the pipet tips should be water repellent. If water sticks to them, discard the tip. Wipe the outside of the pipets, preferably with a filter paper. Use paper wipes if necessary, but do not use brown paper towels.

2. Draw 1-mL of 0.0200 N sulfuric-acid in the pipet, then discard it.

3. Add 1-mL of 0.0200 N sulfuric-acid to the 2000-ml clean volumetric flask. (The flask should be cleaned by washing at least 5 times with distilled or deionized water just before use.).

4. Fill the flask to the mark on the neck with deionized or distilled water.

5. Mix the solution in the volumetric flask by inverting the stoppered flask at least 10 times.

6. The conductivity of this solution should be 4 µS/cm plus the background conductivity of the water used for the preparation of the solution.

7. This solution should not be kept for more than 24 hours. Avoid transferring this solution into another container, since this increases the risk of contamination.

Preparation of pH 4.53 Sulfuric-Acid Solution

I. Reagents

1. Same as in the previous section.
2. Same as in the previous section.

II. Supplies

1. 3-mL class-A pipet. A 1000-µL (1-mL) Eppendorff or similar pipet is satisfactory.

III. Procedure

1. Same as the previous section.
2. Draw 3-mL of 0.0200 N sulfuric-acid and discard.
3. Add 3-mL of 0.0200 N sulfuric-acid to the 2000-mL (2-L) clean volumetric flask.
4. Same as in the previous section.

5. Same as in the previous section.
6. The conductivity of the solution should be 13 µS/cm plus the background conductivity of the water used to prepare the solution.
7. Same as in the previous section.

Preparation of Other Sulfuric-Acid Solutions

Other dilute sulfuric-acid solutions can be prepared by the procedures given in the previous sections. The amount and concentration of the commercial standard sulfuric-acid solutions to be added to a 2000-mL volumetric flask are given in table 1.

Evaluation of the pH and Conductivity of Dilute Sulfuric-Acid Solutions

The equivalent conductance of sulfuric-acid at infinite dilution (Λ_0) was calculated from the ionic conductance of H^+ and SO_4^{2-} from the data given by Robinson and Stokes (1970) and Kohlrausch's law of the independent migration of ions. The conductance values were converted to SI (Systeme International d'Unites) units. (Old International ohm = 1.0005 absolute ohm.) The variation of the equivalent conductance (Λ) with concentrations from 0.005 molar to infinite dilutions were calculated from the best fit of the actual experimental data in the literature to the equation of Kohlrausch (Robinson and Stokes, 1970),

$$\Lambda = \Lambda_0 - bc^{1/2} \qquad (6)$$

where b is a constant and c is the concentration in equivalents of solute per liter of solution (normality of the acid). The calculated values are always within ± 0.2 percent of the literature values. Similar values are obtained by the Onsager equation; however, calculations are very involved and results are slightly less accurate because sulfuric-acid is an unsymmetric electrolyte.

The specific conductance of sulfuric-acid at 25.00°C between pH 3 and 4 is given on figure 1, and between pH 4 and 5 is given on figure 2. To the values obtained from these graphs should be added the background specific conductance of the water used to prepare these solutions. The pH effects of atmospheric CO_2 contamination can be calculated and are insignificant for these solutions (pH 3-5). The effects of CO_2 on conductivity can be significant at values greater than pH 5. Best results are obtained by using freshly deionized water and storing the solutions in glass.

pH of Deionized or Distilled Water Saturated With Air or a N_2-CO_2 Gas Mixture

Even if dilute sulfuric-acid standards are used ($pH \leq 4.5$), it is desirable to measure the pH of distilled water equilibrated with outdoor air or preferably with a N_2-CO_2 gas mixture of known composition before making any pH measurements in low-conductivity waters (Reddy and others, 1985). These precautions assure that the pH electrodes are operating properly in low-conductivity waters and that the measurements are reliable.

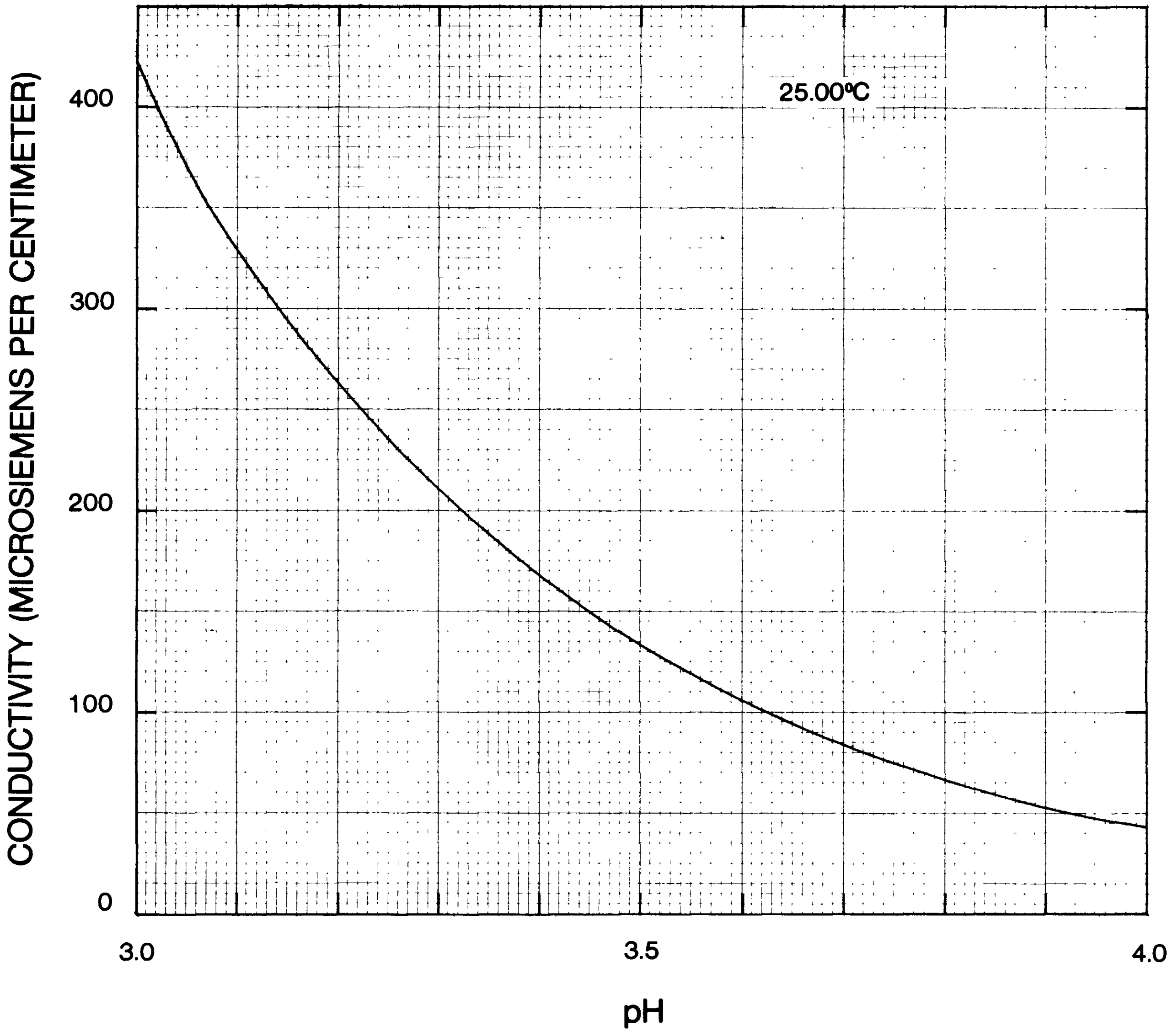

Figure 1. Relation of conductivity to pH of sulfuric-acid solutions in the pH range 3.0 to 4.0 at 25.00°C.

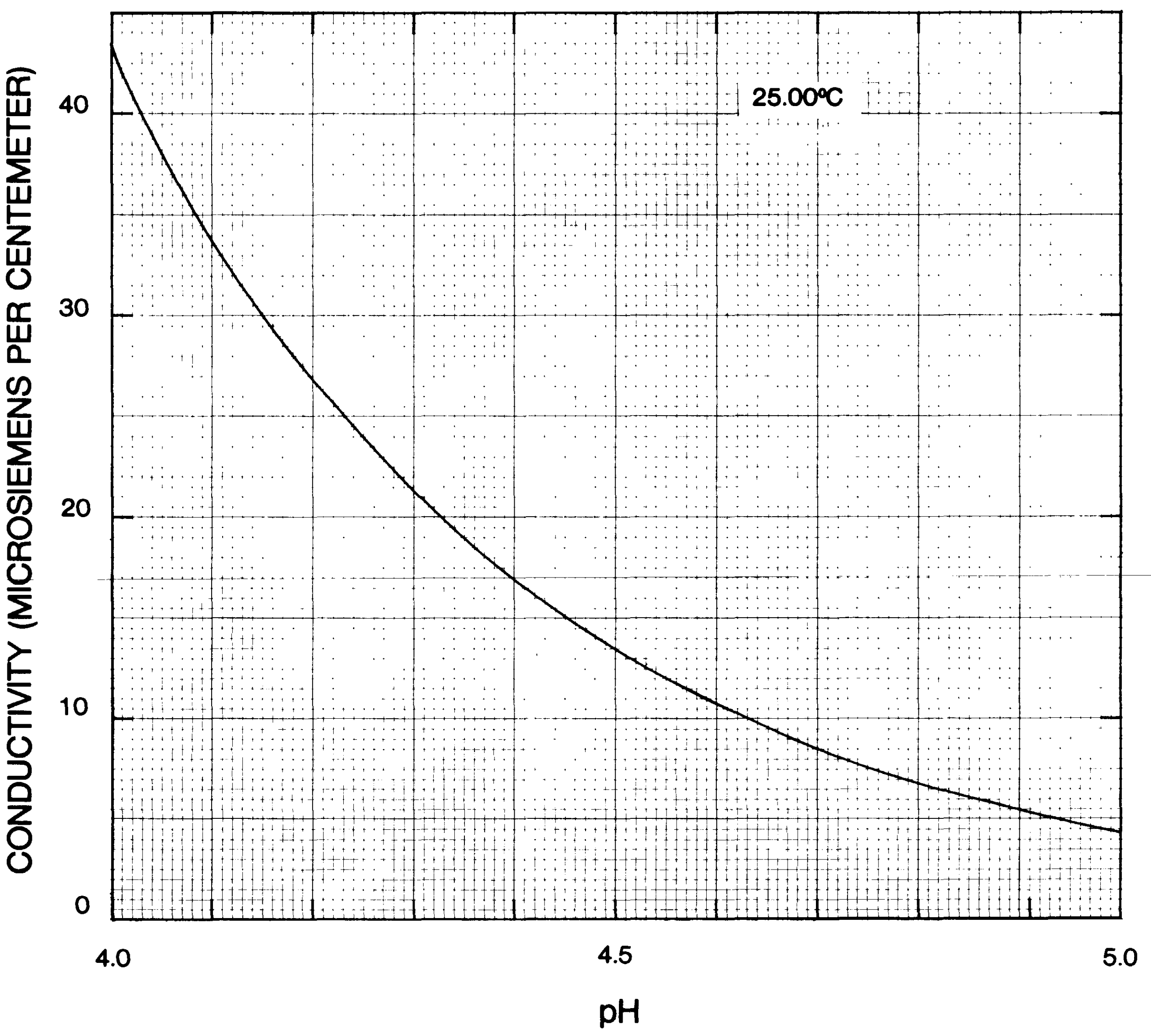

Figure 2. Relation of conductivity to pH of sulfuric-acid solutions in the pH range 4.0 to 5.0 at 25.00°C.

The pH of deionized or distilled water saturated with any N_2-CO_2 gas mixture or air can be easily calculated to within 0.01 pH units from the equation

$$pH = -0.5\ (\log K_H + \log K_1 + \log P_{CO_2}) \qquad (7)$$

where K_H, K_1 and P_{CO2} are the Henri's Law constant for CO_2, the first dissociation constant of carbonic acid and the CO_2 partial pressure in atmospheres. The log K_H and log K_1 values as a function of temperature are given in table 2. The P_{CO2} of air is $10^{-3.5}$ atmospheres at sea level. The P_{CO2} of any gas mixture including air can be calculated from the expression

$$P_{CO_2} = \frac{X_{CO_2} \cdot B}{760} \qquad (8)$$

where X_{CO2} is the mole fraction of CO_2 in the gas mixture and B is the true barometric pressure. U.S. Weather Service reports barometric pressure normalized to mean sea level elevation. This is not the true barometric pressure and should not be used in equation (8). If the barometric pressure is not known, 760 corrected for elevation can be used as an estimate. Elevation corrections of barometric pressure can be found in any handbook of physics and chemistry.

Maintenance and Care of pH Electrodes

Modern glass electrodes can give years of reliable service if a few simple rules are followed.

1. Recommended storage solutions of electrodes vary from manufacturer to manufacturer, and include pH 7.0 buffer to which has been added 10 g/L KCl, "slightly acidic" concentrated KCl, pH 4.0 buffer, etc. NBS recommends storage of electrodes to be used exclusively for rainwater measurement in a solution containing 0.1 and 0.0001 mol/L KCl and HCl, respectively, and to avoid storage of the electrodes in concentrated KCl, basic solutions or buffers (Koch and others, 1986). We believe that the NBS recommendations are most appropriate for the electrodes that will be used for measurement in low-conductivity waters. Caution--if the filling hole of the electrode is sealed, an increase in barometric pressure can force the storage solution into the porous junction, this causes several problems: (1) Precipitation of AgCl in the porous junction because AgCl is less soluble in dilute KCl; (2) even if no clogging occurs, the presence of dilute KCl in the junction can cause extremely large junction potentials (Brezinski, 1983). The problems can be avoided by uncapping the filling hole and waiting long enough for the porous junction to be flushed with the concentrated KCl filling solution. Never store the pH electrode in concentrated KCl solutions, because the absorbed potassium reduces the glass sensitivity to hydrogen ions. For very long-term storage, it is preferable to store the pH electrode dry.

2. Do not handle the glass bulb with fingers. Fingers leave a protein film on the glass that decreases the sensitivity of the electrode.

3. Never wipe the electrode with paper towels or paper wipes. Wiping the glass with paper creates a static charge that results in drifting pH readings. Wiping electrodes with paper towels can also scratch the very thin glass bulb. Gently touch the wet pH bulb with filter paper to wick away all excess water.

4. If contamination of the glass electrode is suspected, it can often be restored to normal operation by cycling the electrode between the 10.0 and 4.0 buffers several times. If this treatment does not work, leave the electrode in pH 10 buffer for 2 hours, then soak it overnight in the KCl-HCl solution.

5. If the glass electrode becomes contaminated with grease or oil, the organics can be removed by washing the glass electrode with acetone, methanol or both. DO NOT SOAK THE ENTIRE ELECTRODE ASSEMBLIES IN THE ORGANIC SOLVENT. Pour the solvent in a small plastic beaker, then immerse the glass bulb of the electrode in the organic solvent for about a minute. Soak the electrode in the NBS recommended KCl-HCl solution overnight before use.

6. The Lazaran reference-electrode which is being retrofitted on many Survey Hydrolab units needs no special care. It is highly reliable and provides years of continuous service. If the reference-electrode becomes coated with organic films, it can be restored to normal operation by wiping off the film with a paper wipe. No other maintenance is necessary. The Lazaran reference-electrode should always be placed in saturated KCl solution when not in use.

7. If the above fail to restore normal pH operation, you probably need a new glass electrode.

Suggestions

1. After calibration with the pH 4, 7, and 10 buffers, performance should be checked in an appropriate dilute sulfuric-acid standard with conductivities of less than 20 μS/cm. Procedures for preparation and handling are described above.

2. Sulfuric-acid standards should be checked for contamination before use through conductivity measurements as described above.

3. The electrode pair should be checked with deionized water saturated with an analyzed mixture of N_2-CO_2 containing less than 0.5 mole fraction percent CO_2. Use of air saturated deionized water could be used, this is less desirable because CO_2 concentrations can vary significantly in air (particularly indoors). The pH of deionized water can be very accurately calculated from the barometric pressure, the mole fraction of CO_2 in the gas, and the temperature using equation 7 or computer programs such as PHREEQE (Parkhurst and others, 1980).

4. The addition of KCl is not recommended because of potential for trace contamination and other complications.

5. Washing of the electrode at least three times, preferably with a portion of the sample to be measured, is recommended.

6. The Lazaran reference-electrode on retrofitted Hydrolab units should be capped with a saturated KCl solution when not in use.

7. Measurement and calibration should be made in quiescent (unstirred) solutions after the sample has been homogenized by stirring.

8. If the pH meter is capable of indicating percent Nernst slope or displaying millivolts, the performance of the electrode (slope) should be checked before use. Slopes less than 98 percent are unsatisfactory.

9. Other suggestions and recommendations are given in the preceeding pages.

REFERENCES

Bates, R. G., 1973, Determination of pH, theory and practice (2d ed.) : New York, John Wiley, 479 p.

Brezinski, P. D., 1983, Kinetic, static and stirring errors of liquid junction reference electrodes: Analyst, v. 108, p. 425-442.

Covington, A. K., 1981, Recent developments in pH standardization and measurement for dilute aqueous solutions: Analytica Chimica Acta, v. 127, p. 1-21.

Covington, A. K., Whalley, P. D., and Davison, W., 1983, Procedures for the measurement of pH in low ionic strength solutions including freshwater: Analyst, v. 108, p. 1528-1532.

Covington, A. K., Whalley, P. D., and Davison, W., 1985, Improvements in the precision of pH measurements - a laboratory reference electrode with renewable free-diffusion liquid junction: Analytica Chimica Acta, v. 169, p. 221-229.

Davison, W. and Woof, C., 1985, Performance tests for the measurement of pH with glass electrodes in low-ionic-strength solutions including natural waters: Analytical Chemistry, v. 57, p. 2567-2570.

Gallaway, J. N., Cosby, B. J., Jr., and Likens, G. E., 1979, Acid precipitation-measurement and pH and acidity: Limnology and Oceanography, v. 24, p. 1161-1165.

Illingsworth, J. A., 1981, A common source of error in pH measurement: Biochemistry Journal, v. 195, p. 259-261.

Ives, D. J. G., and Janz, G. J., 1961, Reference electrodes - theory and practice: New York, Academic Press, 651 p.

Koch, W. F., Marinenko, G., Paule, M. C., 1986, An interlaboratory test of pH measurements in rainwater: Journal Research National Bureau of Standards, v. 91, p. 23-32.

----------------- 1986, Development of a standard reference material for rainwater analysis: Journal Research National Bureau of Standards, v. 91, p. 33-41.

Marinenko, G. and Koch, W. F., 1985, Evaluation of methods used for the determination of acidity in acid rain samples: National Bureau of Standards Internal Report 85-3114, 16 pp.

Mason, B. J., 1984, The current status of research on acidification of surface waters: London, Royal Society Publication, 23 p.

McQuaker, N. R., Kluckner, P. D. and Sandberg, D. K., 1983, Chemical analysis of acid precipitation - pH and acidity determinations: Environmental Science and Technology, v. 17, p. 432-435.

Metcalf, R. C., 1984, Effect of storage solution composition on pH combination electrode times at low temperature: Analyst, v. 109, p. 1225-1226.

National Bureau of Standards, 1986, Journal of Research: v.91, no.1, 41p.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980, PHREEQE--A computer program for geochemical calculations: Water-Resources Investigations 80-96, 210 p.

Plummer, L. N. and Busenberg, E., 1982, The solubility of calcite, aragonite and vaterite in CO_2-H_2O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system $CaCO_3$-CO_2-H_2O: Geochimica et Cosmochimica Acta, v. 46, p. 1011-1040.

Reddy, M. M., Liebermann, T. D., Jelinski, J. C., Caine, N., 1985, Variation in pH during summer storms near the continental divide in Central Colorado, U.S.A.: Arctic and Alpine Research, v. 17, p. 79-88.

Robinson, R. A., and Stokes, R. H., 1970, Electrolyte solutions: London, Butherworths, 571 p.

Seymour, M. D.,, Schubert, S. A., Clayton, J. W., Jr., and Fernando, Q., 1978, Variations in the acid content of rain water in the course of a single precipitation: Water, Air, and Soil Pollution, v. 10, p. 147-161.

Sisterson, D. L., and Wurfel, B. E., 1984, Methods for reliable pH measurements of precipitation samples: International Journal of Environmental and Analytical Chemistry, v. 18, p. 143-165.

Tyree, S. Y., 1981, Rainwater acidity measurement problems: Atmospheric Environment, v. 5, p. 57-60.

Westcott, C. C., 1978, pH measurements: New York, Academic Press, 172 p.

Whewell, R. J., and Hughes, M. A., 1976, Interpretation of pH measurements in solutions containing sulfuric acid and copper sulfate: Journal Inorganic Nuclear Chemistry, v. 38, p. 180-181.