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Douglas L. Sisterson^a; Brent E. Wurfel^b

^a Atmospheric Physics Program, Environmental Research Division, Argonne National Laboratory, Argonne, IL, U.S.A. ^b Guest Research Participant at Argonne National Laboratory from Beloit College, Beloit, WI

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Methods for Reliable pH Measurements of Precipitation Samples

DOUGLAS L. SISTERSON and BRENT E. WURFEL†
*Atmospheric Physics Program, Environmental Research Division,
Argonne National Laboratory, Argonne, IL 60439, U.S.A.*

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Significant errors in precipitation acidity determinations can result from improper use of pH electrodes. Conventional electrodes measure free hydrogen ion activity instead of hydrogen ion concentration or free acidity. Correction from activity to concentration is a function of ionic strength and can be large for the low ionic strengths typical of precipitation samples. Also, differences between sample and standard calibration buffer solution ionic strengths can result in liquid-junction potentials that affect electrode readings. Streaming potentials due to the stirring of precipitation samples can cause the single, largest error in pH. Certain procedures can be employed to reduce individual types of errors. These and methods to assess pH electrode performance are discussed.

KEY WORDS: pH electrode operation and measurements, Gran's titrations, precipitation acidity determinations.

1. INTRODUCTION

The current interest in acid precipitation has placed great emphasis on the ability to accurately measure the pH of solutions of low ionic strengths, such as precipitation samples. In studies of precipitation chemistry and acidity, researchers often must evaluate the statistical significance of small pH differences reported by different investigators, or perhaps even perform the demanding measurements

†Guest Research Participant at Argonne National Laboratory from Beloit College, Beloit, WI.

themselves. The conventional laboratory pH measurement techniques, using pH electrodes, were developed for laboratory solutions generally having ionic concentrations much higher than typical precipitation samples. Therefore, the use of pH electrodes and titration for analyzing precipitation acidity is often abused. Almost every laboratory measuring pH has its own methods, some based on erroneous or outdated information. Unfortunately, no standard method for pH measurements of precipitation exists. Most of the pertinent information, however, is widely scattered throughout the literature and has not been previously compiled.

Electrodes do not measure hydrogen ion concentration (i.e., acidity) directly, but rather an emf which can be related to the hydrogen ion activity. Conversion from activity to concentration depends upon the ionic strength of precipitation and may be complex. Without the correction, the measured pH can be different from the actual acidity or true pH. Differences between sample and standard calibration buffer solution ionic strengths result in liquid-junction potentials that can also affect electrode readings. Streaming potentials due to the stirring of precipitation samples during pH measurement can cause the single, largest error in pH. Each of these errors may be individually small¹ but they are additive and may cause uncertainties in typical measurements to be 0.10 pH units,² and even as large as 0.50 pH units.³

Due to uncertainties in pH measurements, either the absolute calibration of the pH electrode must be verified directly by a low ionic strength solution of known pH or the free acidity must be determined independently and used to verify the pH electrode determination of the sample's free acidity. For the later case, data from simple titrations of precipitation samples can, in many cases, be used for pH verification by a method developed by Gran.^{4,5} This paper reviews the procedures for effective use of pH electrodes in acidity determinations of precipitation and the means to verify those determinations.

2. pH ELECTRODE OPERATION

The most commonly used electrometric measurement of pH is provided by an electrode reversible to the hydrogen ion, a salt bridge, and a reference electrode. Discussion and limitations of

various pH electrodes may be found elsewhere.⁶ Of the several electrodes reversible to hydrogen ion, the glass electrode with a ceramic-type junction is by far the most convenient and versatile.² Silver-silver chloride is frequently used as an inner reference in glass electrodes and is used for example in the following discussion of pH electrode operation.

a. Configuration of glass electrodes

There are two main configurations of glass pH electrodes, but they operate in the same manner. The combination electrode (Figure 1) combines the indicating and reference electrodes into one unit while the other type has separate units (Figure 2). The indicating or glass electrode consists of an internal sealed tube containing a chloride salt solution and silver-silver chloride half-cell. The immersion tip of this tube is a special hydrogen-ion activity-sensitivity glass bulb. The measurement of pH is accomplished by determining the electrical potential that is developed across the glass bulb between the sample

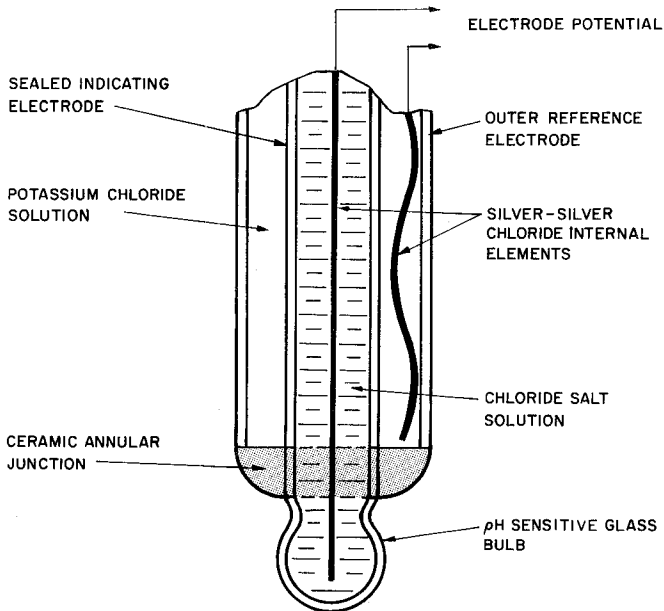


FIGURE 1 Combination electrode.

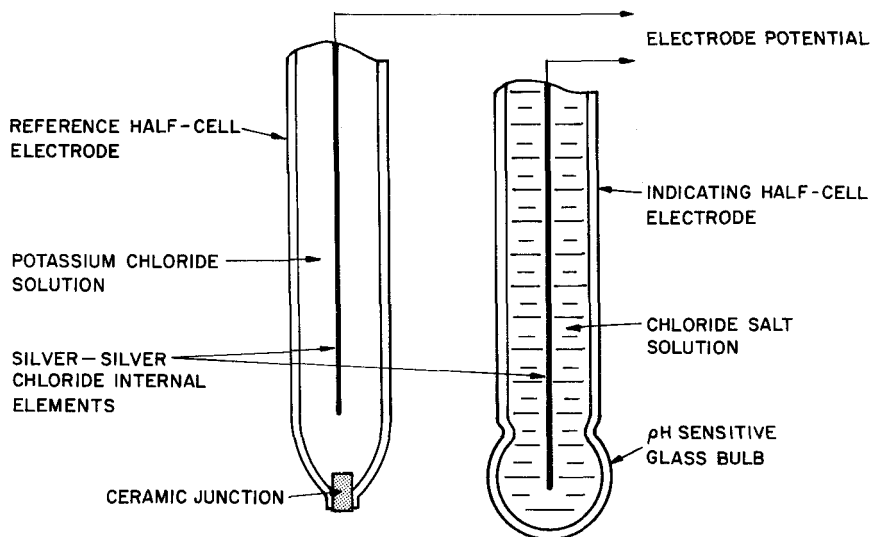


FIGURE 2 Separate indicating and reference electrodes.

and the chloride salt solution in the glass electrode. The reference electrode permits the measurement of this potential by providing a stable reference potential and completion of the circuit. The reference electrode consists of a silver-silver chloride internal element enveloped in a 4 molar potassium chloride solution saturated with silver chloride. A ceramic layer at the immersion tip forms a liquid junction that allows flow of ions from the potassium chloride electrolyte solution from the reference electrode to establish a "salt bridge" for electrical contact with the sample. The pH electrode is calibrated routinely in standard buffer solutions.

b. Conversion from activity to concentration

The acidity or true pH of a solution is defined in terms of the negative log of the hydrogen ion concentration $[H^+]$. Although the hydrogen ion concentration is the desired parameter to measure, pH electrodes measure a potential which is a function of the hydrogen ion activity a_{H^+} rather than $[H^+]$. Although the a_{H^+} and $[H^+]$ are usually assumed to be equal, there are many instances when the pH determined by an electrode must be corrected for an accurate acidity determination.

Unlike the true pH, the pH determined by an electrode is

$$\text{pH} = -\log a_{\text{H}^+}. \quad (1)$$

This is related to $[\text{H}^+]$ by the equation

$$[\text{H}^+] = a_{\text{H}^+}/\gamma_{\text{H}^+}, \quad (2)$$

where γ_{H^+} is the hydrogen ion activity coefficient and is a function of the ionic strength μ ,

$$\mu = \frac{1}{2} \sum c_i z_i^2, \quad (3)$$

where c is the concentration of individual ions and z is the charge of those ions. For values of $\mu \leq 10^{-2}$ M, a range characteristic of precipitation samples, the extended Debye-Huckel expression is appropriate for the determination of γ_{H^+} and can be expressed in the form:

$$\log \gamma_{\text{H}^+} = (Az^2 \mu^{1/2}) / (1 + aB\mu^{1/2}), \quad (4)$$

where $A=0.51$ and $B=0.33$ are constants for aqueous solutions at 25°C ⁷ and a is the ion size parameter (Ångström units). With $\alpha \equiv \log \gamma_{\text{H}^+}$, Eqs. (1-2) can be combined and expressed as

$$[\text{H}^+] = 10^{-(\text{pH} + \alpha)}. \quad (5)$$

Because the determination of γ_{H^+} usually requires a chemical analysis of the precipitation sample in order to calculate μ , γ_{H^+} is often assumed to be unity. The resulting error in $[\text{H}^+]$ can be examined by considering precipitation samples with extreme high and low ionic strengths chosen for example from the National Atmospheric Deposition Program (NADP) rain chemistry network.⁸ Table I shows the chemistry of the two samples chosen for example from the National Atmospheric Deposition Program (NADP) rain chemistry network.⁸ Table I shows the chemistry of the two samples chosen for discussion. The Coweeta sample considered (measured $\text{pH}=4.83$) had a relatively low ionic strength, $\mu=1.89 \times 10^{-5}$ M. From Eq. (4), γ_{H^+} is equal to 0.99, corresponding to a -0.002 pH correction, which is insignificant. The Wooster sample (measured

TABLE I

Relatively high and low ionic strength precipitation samples chosen from the 1979 National Atmospheric Deposition Program Quarterly Reports.

Location	pH	Ca	Mg	K	mg/l				
					Na	NH ₄	NO ₃	Cl	SO ₄
Coweeta, NC 2/13/79-2/20/79	4.83	0.03	0.007	0.004	0.072	<0.02	0.20	0.05	0.30
Wooster, OH 4/17/79-4/24/79	3.94	6.00	1.344	0.357	3.383	2.36	16.01	2.02	26.12

pH = 3.94) had a relatively high ionic strength, $\mu = 1.53 \times 10^{-3}$ M, which results in $\gamma_{H^+} = 0.96$ and a pH correction of -0.02 , or about a $+5\%$ correction for $[H^+]$ in Eq. (5). Each multiple increase of -0.02 pH units requires the square of that multiple times the ionic strength. For example, a four-fold increase in the ionic strength of the Wooster sample would double the pH error to -0.04 (about a $+10\%$ difference in $[H^+]$). Since the Wooster sample chosen was one of the highest ionic strength samples encountered, a $+5\%$ error in $[H^+]$ or -0.02 pH units may result by neglecting the Debye-Huckel correction for the typical range of precipitation ionic strength. This error can be expressed as a bias of -0.01 ± 0.01 pH units where the uncertainty in the bias is assumed to be ± 2 standard deviations (2σ).

c. Liquid-junction and streaming potentials

Electrodes approximate the pH of a solution by the Nernst equation which relates the potential measured by the pH electrode in a standard buffer solution to the precipitation sample. The Nernst equation is

$$\text{pH} = \text{pH}_b + \{(E - E_b) F\} / (2.303 RT), \quad (6)$$

where pH_b refers to the pH of the buffer solution, E is the measured potential of the precipitation sample, E_b is the measured potential of the buffer solution, F is Faraday's constant, R is the gas constant, and T is absolute temperature.

In practice, the flow of the potassium chloride electrolyte solution through the ceramic junction also creates a potential—the liquid

junction potential E_j . This term represents the difference between junction potentials of the precipitation sample and the calibrating buffer solutions as a result of their potentially large differences in ionic strength and ionic mobility. Table II shows ionic strength values for typical buffer solutions used in the calibration of pH electrodes. Differences between junction potentials can lead to errors as large as ± 0.02 pH units.⁹ This error is assumed to be 2σ and can be reduced by calibrating the pH electrode in dilute unbuffered solutions of an inorganic strong acid (e.g. H_2SO_4 , HNO_3) of known pH which approximate the range of acidity of typical precipitation samples. The dilute strong acid solution should be titrated at least weekly with NaOH to verify the pH. The preparation and maintenance of the dilute strong acid and base titrant is not an easy task and will be discussed later in more detail. Another alternative to the reduction of the liquid junction potential is to add an inert salt (i.e.; the salt of a strong acid with a strong base) such as potassium chloride, to increase the ionic strength of the precipitation sample. Of course the absence of acidic or basic contaminants in the salt must be established (by titration preferably). The addition of 1 or 2 drops of 0.1 N KCl to a 40 ml precipitation sample of pH 4.0 does not significantly affect the a_{H^+} of the sample according to the extended Debye-Huckle expression in Eqs. (2-4) and does reduce, but not eliminate, the liquid junction potential error. To completely eliminate the liquid junction potential, the sample would have to be brought to the same ionic strength as the calibration buffers (Table II); but this will significantly affect the a_{H^+} of the sample. Again, trace contaminants can introduce a significant source of error unless ultra-pure potassium chloride is used. Furthermore, the effects of KCl or any inert salt on the species present in solution must be understood.² Because of these uncertainties, the addition of KCl or an inert salt is least favorable for reducing the liquid junction potential.

TABLE II
National Bureau of Standard buffer ionic strengths.

Buffer	pH	Ionic strength
Potassium hydrogen phthalate	4.008 at 25°C	0.05 M
Disodium hydrogen phosphate	6.865 at 25°C	0.025 M
Borax	9.180 at 25°C	0.01 M

Stirring the precipitation sample during pH measurement assures uniform concentration of the sample and fast pH electrode response. However, stirring also produces a streaming potential E_s that can result in a serious difference between the stirred and unstirred pH of a sample. E_s is proportional to the pressure drop in the vortex due to the stirring rate and inversely proportional to conductivity.⁹ A comparison of stirred and unstirred pH measurement differences for 67 precipitation samples collected at Argonne has been made. The pH of the samples used ranged from 3.5 to 5.0 (median pH was 4.21) and the conductivity ranged from 10–86 $\mu\text{S cm}^{-1}$ (median conductivity was 31.6 $\mu\text{S cm}^{-1}$). The mean difference (or bias) was -0.04 pH units (standard error of 0.006 pH units) with individual differences ranging from $+0.09$ to -0.12 pH units. A stirring rate of 2 ± 1 revolutions per second produced very little vortex formation; but, even this small variation probably produces the large departures from the mean difference. At faster rates, the pH differences can be greater than 0.50 pH units due to E_s .³ Therefore, to eliminate the large errors associated with the streaming potential, the precipitation sample should be thoroughly agitated and allowed to come to rest before taking a pH reading which may take several minutes or longer to stabilize.

d. Summary of pH electrode errors

Table III summarizes the individual errors associated with a properly operating pH electrode. These errors represent the range of uncertainty expected for typical precipitation samples, not necessarily the error of any one particular measurement. These range of

TABLE III
Summary of individual pH errors for a properly functioning electrode.

Error type	Bias	2σ
No Debye-Huckel correction	-0.01	± 0.01
Liquid-junction potential	0.00	± 0.02
Streaming potential (2 ± 1 revolutions per second at Argonne)	-0.04	± 0.10
Total error (at rest after stirring)	-0.01	± 0.02
Total error (stirred)	-0.05	± 0.10

uncertainties arise from errors in the determination of the hydrogen ion concentration. Although all our calculations were done in terms of the hydrogen ion concentration, the errors are reported in terms of pH units for convenience since electrodes yield pH values. While the individual errors are small, they are additive (total errors are determined from twice the square root of the sum of the squares of individual standard deviations). The total error (at rest after stirring) appears quite small; yet, there is still uncertainty in electrode performance that could significantly affect the measured pH. For example, extensive use of electrodes particularly for low pH samples depletes ions from the reference electrode electrolyte solution (e.g., Figures 1 and 2). While the pH electrode will properly calibrate in the high ionic strength buffer solutions, it may not be able to establish sufficient electrical contact in a low ionic strength precipitation sample resulting in an improper value of E in the determination of pH in Eq. (6).

A quick test to check the proper operation of a pH electrode involves calibrating the electrode in the appropriate buffers (best are those which bracket the typical pH of rainfall of the area) with the pH and corresponding millivolt readings for the buffers recorded. The procedure is repeated for dilute strong acid solutions of known pH. The difference in the millivolt readings divided by the difference in pH readings should be 59.15 ± 2 at 25°C . This value results from the evaluation of constants in the Nernst equation, Eq. (6). This test should be done just before precipitation sample measurements to ensure the electrode Nernstian expression is valid. If the value is different, the electrode or meter is not functioning properly; usually the pH electrode is at fault. Some procedures for troubleshooting pH electrode problems are given in the Appendix.

3. VERIFICATION OF pH MEASUREMENTS

Measured pH values may be verified in one of two manners. Either the absolute calibration of the pH electrode is verified directly by a low ionic solution of known pH or the free acidity of the sample is determined independently and used to verify the pH electrode determination of the sample's free acidity.

A single dilute strong acid solution may be prepared⁶ and used to verify absolute pH after routine calibration of the electrode. The

preparation of this solution is not a trivial task because it involves successive dilutions of concentrated standard strong acid reagents. Although the pH of the solution is theoretically calculated, the actual value should be verified, as by titration with a standard base, since there are potential errors due to trace contaminants found in standard strong acid reagents and inexact dilutions. This low ionic strength dilute strong acid solution is prone to contamination since it is not buffered and requires special storage, such as being kept sealed and refrigerated when not in use. The pH of this solution should be determined by titration or a new solution prepared before each verification of the electrode, particularly if such determinations are made infrequently (once a week).

The free acidity of the sample can be verified by a relatively simple acid/base titration. The accuracy of this or any titration, however, depends upon the preparation and maintenance of good titrant which is not a simple task and is discussed in more detail later. Titration of precipitation samples, in general, allows a good deal of information to be learned about the acidity of the sample. Gran^{4,5} developed a procedure for the analysis of titration data that allows the determination of the strong, total, and weak (by difference) acid concentrations of a sample. While beyond the scope of this paper, Gran's method for potentiometric acid/base titrations of precipitation is highly recommended and discussions of its use are presented elsewhere.¹⁰⁻¹⁵ Furthermore, specific acids present in precipitation can be inferred from simulations of detailed titration curves.¹⁶ Here, we only use Gran's method for the free acidity determination of a sample and compare those results to the pH electrode's determination of the free acidity.

Either method of pH electrode measurement verification can be successfully employed, but with some difficulty. We have found the titration method to be most useful (because we titrated our samples for strong, total, and weak acidity by Gran's method) and discuss titration procedures for verification of free acidity here in detail.

a. Gran's function and strong acid determinations

To increase confidence in measured pH, the free acidity of a precipitation sample can be determined from a simple titration. Our discussion is limited to only the determination of the strong acid concentration by Gran's method. The important assumptions in

Gran's method for the determinations of strong acids are that there is sufficient free hydrogen ion for determination and only strong acids contribute to the free acidity of a solution. These limit the application of Gran's method to pH electrode verification in precipitation samples of pH less than 5.0. Precipitation is naturally acidic due to carbonic acid, a weak acid formed by the dissolving of ambient CO_2 in "unpolluted" water, resulting in a solution pH of ~ 5.6 . Dissolution of a variety of natural substances (including carbonates) can produce pH values substantially different from 5.6. Strong acids, however, are dominant below pH 5.0 and are responsible for the increased acidity of precipitation.

Gran's function can be expressed as:

$$\psi_i = (V_i + V_s) 10^{-(E_i - E)[F/(2.303 RT)]}, \quad (7)$$

where E_i and Ψ_i are the measured potential and Gran's function value, respectively, corresponding to successive additions of base titrant of volume V_i , E is an arbitrary constant usually taken to be the measured potential of the precipitation sample prior to titration, and V_s is the volume of the precipitation sample being titrated. With Eq. (6), Eq. (7) may be rewritten as:

$$\psi_i = (V_i + V_s) 10^{-(\text{pH}_i - \text{pH}_s)}, \quad (8)$$

where pH_i is the pH corresponding to successive additions of base titrant and pH_s is the initial pH of the precipitation sample while stirred. Stirring during a titration ensures complete mixing of the titrant and sample, and decreases the response time of the pH electrode. Because Gran's function uses only the differences in measured pH, streaming potentials, activity coefficient changes, ionic strength differences, liquid-junction potential effects, etc., are eliminated as long as the temperature and the stirring rate during the titration remain constant.

Typically sodium hydroxide (NaOH) is used to titrate acidity. The preparation and maintenance of CO_2 -free titrant requires strict precautions. Deionized water must be extensively boiled (~ 30 minutes) to remove CO_2 . A saturated solution of NaOH is prepared with the CO_2 -free water. A small amount of the saturated NaOH is diluted with CO_2 -free water to the appropriate molarity of NaOH to

be used for the titration. The titrant must be sealed in a flask with a CO_2 trap to protect the titrant from ambient CO_2 . Exact procedures are discussed in analytical chemistry texts.¹⁷ We recommend that the molarity of the NaOH titrant be verified after initial preparation and once a week thereafter. This can most easily be done by titration with potassium biphthalate (KHP), using phenolphthalein as an indicator. The addition of NaOH to the precipitation sample during titration has a negligible effect on ionic strength of the sample since Na^+ replaces H^+ in the ratio of 1:1; i.e., there is no increase to the total number of ions in solution during the titration and therefore no effect on the measured pH.

Depending on the initial pH of the sample, the molarity of the base and the amount of titrant added may be adjusted to produce detailed titration data for analysis. For most samples, ~ 0.02 M NaOH is appropriate. The titration is carried out in a CO_2 -free atmosphere, provided by flushing an enclosure containing the sample with an inert gas such as N_2 . At equilibrium, the amount of CO_2 dissolved in precipitation is strictly a function of the pH of the sample. The CO_2 -free enclosure prevents additional CO_2 from dissolving during the course of the titration. More will be said about dissolved CO_2 later.

The titration is carried out to a +1.0 pH unit increase from pH_s . From these data, a plot of ψ_i versus V_i determines a line which becomes asymptotic to the abscissa, as shown in Figure 3. The intersection of the extrapolated linear portion of this plot with the abscissa corresponds to the amount of titrant needed to neutralize the strong acid component of the precipitation sample. Therefore the $[\text{H}^+]$ of the strong acid component can be determined and related to a true pH (i.e. $-\log[\text{H}^+]$) by

$$\text{pH}_c = -\log \{(V_{\text{int}} \times M_b)/(V_b + V_s)\}, \quad (9)$$

where V_{int} is the volume (in liters) of base resulting from the intercept value of the extrapolated extended linear portion of the ψ_i versus V_i plot, V_b is the total amount of titrant used over the course of the titration, M_b is the molarity of the base, and pH_c is the pH calculated from the strong acid concentration.

b. Effects of CO_2 on titrations and Gran's function

Precipitation may equilibrate or even become supersaturated with

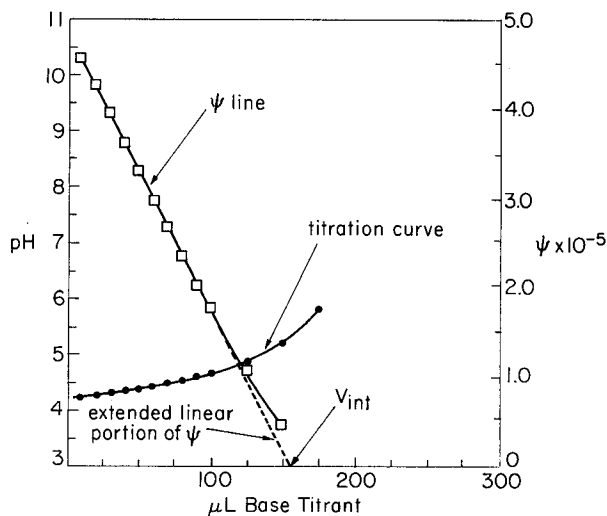


FIGURE 3 Plot of the base titration curve and Gran's function (Ψ). See text for discussion.

CO_2 as it falls through the atmosphere. The latter is due to raindrops partially evaporating as they fall through atmosphere. Usually, by the time the sample is removed from the collector, CO_2 is in equilibrium with the sample. As mentioned earlier, CO_2 dissolves in water to form carbonic acid, a weak acid with a dissociation constant pK_a of 5.6. Although 50% of the carbonic acid is dissociated at pH 5.6, the contribution of H^+ to the pH causes a 0.01 pH unit change at \sim pH 5.0. Since the sensitivity suggested by most manufactures of glass electrodes is $\sim \pm 0.01$ pH units (and since most commercial buffers are accurate to only ± 0.01 pH units at 25°C), the effects of CO_2 on the pH of a solution may only be first detectable by the electrode at \sim pH 5.0. Below this value, strong acids dominate the free acidity of a solution and the contribution of CO_2 to the free hydrogen ion concentration or free acidity is insignificant⁷ even in the laboratory environments where CO_2 concentrations may be several times greater than ambient concentrations.

For samples with pH values greater than 5.0, the dissociation of carbonic acid causes a buffering effect on the acid side of the titration and Gran's method for the determination of the strong

acids is no longer valid. Precipitation samples can be purged of CO_2 and other volatile weak acids by bubbling ultra-pure N_2 through the sample for ~ 30 minutes before titration. However, above pH 5.0, the contribution of strong acids to the total acidity of a solution is negligible and there is little strong acid left to titrate. For precipitation with values above pH 5.0, independent checks on the pH may be done by comparison with dilute strong acid solutions of known pH or by inference from simulations of detailed titration curves, mentioned previously.

c. Error analysis of titrations

While pH electrode errors do not influence the titrimetric determination of pH_c , there are other potential difficulties associated with the titration. The molarity of the base, the volume of the sample, and the amount of titrant added by each injection must be carefully evaluated against the sensitivity of the pH electrode and the pH of the sample. For example, if the sensitivity of the electrode is ± 0.01 pH unit and the addition of titrant only causes a 0.005 increase in pH, it is difficult to determine the linear portion of the ψ_i versus V_i plot in Figure 3. This problem results in some scatter of data points during the course of the titration. Extrapolation of the line to the intercept is extremely sensitive to the scatter of points, more so that the absolute placement of the points. On the other hand, large additions of titrant can cause large increases in pH_i resulting in too few points in the linear portion of the plot and thus uncertainty in the determination of the intercept value. This problem can be greatly reduced by increasing the number of data points in the linear portion of the plot, and by using linear regression in determining V_{int} .

There is much room for error with such small volumes of titrant, depending upon the method used for titrant delivery. Typically the use of microliter pipetter and microliter burettes is standard practice in titrations, the latter being the more accurate. We used microliter pipettors and found it necessary to take precautions against incomplete delivery of the titrant. Toluene can be used to efficiently scavenge the titrant from pipettors.¹⁶ This is accomplished by depressing the plunger past the first detente, immersing the tip in toluene and drawing the toluene until the first detente is again reached, placing the tip in the titrant, and allowing the plunger to

fully withdraw. The toluene forces complete delivery of the titrant when injected into the precipitation sample during titration. Toluene is immiscible and has no effect on the volumetric relationships of the titration. Although there is potential trace contamination error with the addition of toluene, the incomplete delivery of the titrant is a greater error.

Error analysis of pH_c extremes can be made based on each component of Eq. (9). If the molarity is known within ± 0.0005 M, V_i within $\pm 2\%$ (using a $10\ \mu\text{l}$ pipetter calibration), and the volume of the sample within ± 1.0 ml, (variations in V_b are usually insignificant), then the maximum difference in pH_c is ± 0.02 pH units for the typical range of V_{int} (50 – $500\ \mu\text{l}$) observed at Argonne. This error is assumed to be $\pm 2\sigma$ and assumes a constant stirring rate; however, we later discovered some variation in the rate at which the samples were stirred (i.e., 2 ± 1 revolutions per second.) As discussed earlier, small variations in stirring probably produce the large departures from the mean difference between individual stirred and unstirred samples (± 0.10 from Table III). Fifty percent of this variation is estimated to be due to stirring rate inconsistencies which would result in an error of ± 0.05 pH units (2σ). The total error (2σ) in pH_c at Argonne including E_s is ± 0.07 pH units ($2 \times [(0.03)^2 + (0.01)^2]^{1/2}$). Since Gran's function uses differences in pH and since the stirring rate is not constant, the error due to E_s has been doubled.

It is extremely important to stir and completely mix the solution during titration to ensure equilibrium has been reached. The streaming potential error can be eliminated by first stirring the solution after the injection of the titrant, then making the pH measurement in the quiescent solution.³ However, we found it took 3–10 minutes for a stable pH reading in the quiescent solution as opposed to 30–60 sec in the stirred solution. We attributed the increase in response time to a small static charge that may have built up on the electrode bulb during stirring. The charge dissipated slowly in the quiescent solution. This problem, however, may be electrode specific, since response times and sensitivity of glass electrodes vary. At best, the advantages of either method are unclear. We recommend stirring during the pH measurement during titrations to ensure complete mixing of titrant and sample, to reduce the time necessary to complete a titration, and caution against potentially large errors associated with non-constant stirring rates.

The overall performance of the pH electrode can be evaluated by comparing estimated and observed pH_c and pH errors. The error (2σ) between pH_c and pH was estimated for the Argonne samples to be -0.01 ± 0.08 pH units ($2 \times [(0.04)^2 + (0.01)^2]^{1/2}$). The actual error (2σ) based on 48 precipitation sample analyses at Argonne was determined to be -0.03 ± 0.10 pH units. The agreement between estimated and observed errors appears reasonable with most of the error due to stirring rate inconsistencies. Table IV summarizes the differences in pH_c and pH for estimated and observed results.

TABLE IV
Summary of the errors associated with pH_c and pH determinations.

	Bias	2σ
Individual estimated errors		
pH_c (constant stirring)	0.0	± 0.02
pH_c (non-constant stirring for 2 ± 1 revolutions per second at Argonne)	0.0	± 0.07
pH (Table III, unstirred)	-0.01	± 0.02
Total estimated error		
pH + pH_c (constant stirring)	-0.01	± 0.03
pH + pH_c (non-constant stirring)	-0.01	± 0.08
Actual observed error		
pH + pH_c (non-constant stirring)	-0.03	± 0.10

d. Acid back-titrations

If the difference between pH and pH_c is larger than the total accountable error, either a gross error occurred during titration or, most likely, partially dissociated hydrogen ions from weak acids might be contributing to the free acidity of the precipitation sample so that Eqs. (7) and (8) would no longer be valid. Acid back-titrations would easily resolve the uncertainty in titration error as well as indicate the presence of weak acids. Furthermore, there are methods to identify the weak acids present from back-titrations. While there have not been any reports of weak inorganic acids interfering with acidity below pH 5.0, some evidence of weak acids (probably organic) has been found in some precipitation samples.¹⁸

There are several ways to verify the presence of weak acids that may be contributing to the free acidity of a precipitation sample. If

the sample is being titrated for total acidity by Gran's method, the difference between the total and strong acid concentration allows the weak acid concentration to be determined. The total acid function must be linear and will intersect the strong acid function if no weak acids (below pH 7.0) are present.³ Unfortunately, the total acid function is not linear if appreciable amounts of ammonia are present in the precipitation sample since ammonia dissociates causing a buffering effect on the alkaline side of the titration. Argonne precipitation samples contained significant concentrations of ammonia which resulted in non-linear total acid functions in nearly half the samples titrated. Even if ammonia were not present in appreciable amounts in precipitation samples, not all weak acids determined from Gran's titration for total acidity contribute to the free acidity of the solution. From the analysis of all proton sources in precipitation in the northeastern United States, weak (and Bronstead) acids, except for small and irregular contributions from organic acids, contribute only to the total acidity, not the free acidity.¹³ While Gran's method is useful for the characterization of strong, total, and weak acids in precipitation, it may not be appropriate for determining weak acids which contribute to the free acidity of a precipitation sample.

To verify the presence of only weak acids that contribute to the free acidity of a precipitation sample, separate but universally applicable back titrations can be performed. Since our discussion only deals with precipitation samples of pH 5.0 or less, the samples need only to be brought to \sim pH 5.0 in a CO₂-free environment by the addition of strong base (\sim 0.02 M NaOH) and titrated to 1.0 pH unit below pH_s of the sample with a strong acid (\sim 0.02 M). A graph is constructed by plotting the pH_i (abscissa) of the sample with each successive injection of acid titrant Va_i versus the pH_{c_i} where pH_{c_i} is determined from the predicted [H⁺] for each injection of Va_i . It can be shown that pH_{c_i} is:

$$\text{pH}_{c_i} = -\log \left\{ (Va_i M_a c) / [Va_i + (V_s + Vb_a)] \right\} \quad (10)$$

where c is the number of replaceable hydrogen ions of the strong acid used (Eq. for HNO₃, $c=1$; for H₂SO₄, $c=2$), Vb_a is the volume of the base necessary to raise the pH of the precipitation sample to \sim pH 5.0, and M_a is the molarity of the acid. If no weak acids are present, $\text{pH}_{c_i} = (\text{pH}_i - \alpha)$, resulting in a linear plot. If weak acids are

present, pH_{c_i} will over-predict the change observed in $(\text{pH}_i - \alpha)$ due to the buffering effect of the weak acid. This results in a bow in the otherwise linear plot and the $\text{p}k_a$ of the weak acid can be inferred at the point of maximum departure from linearity, as shown in Figure 4. It is possible, however, that several weak acids with similar $\text{p}k_a$ values could cause overlapping of the "bows" which does not readily permit qualitative analysis of the weak acids involved.

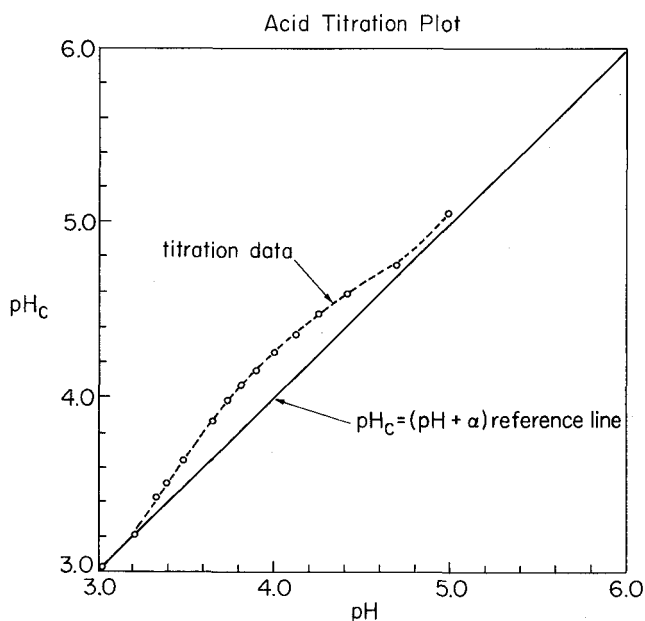


FIGURE 4 Plot of the acid titration curve. pH_c is $-\log[\text{H}^+]$ and $\text{pH} = -\log a_{\text{H}^+}$, where $[\text{H}^+]$ is the hydrogen ion concentration and a_{H^+} is the hydrogen ion activity. α is the correction for a_{H^+} to $[\text{H}^+]$.

Back titrations, however, can be excessively time consuming for analysis of many samples on a routine basis. To determine when a back titration is necessary, a straightforward analysis of the initial base titration data can be applied.¹⁹ The absolute value of the slope of the relevant linear part of the plot of ψ_i versus V_i is equal to the molarity of the base. The model detects any deviation in the slope from the molarity of the base (attributed to the buffering effect of weak acids) and indicates when a back titration is necessary.

4. CONCLUSION

Reliable free acidity measurements can be made using pH electrodes if appropriate care is exercised. However, the most important task in pH measurements is to first evaluate the performance of the electrode by calibrating it in the appropriate buffers with the pH and corresponding millivolt readings recorded. The difference in the millivolt readings divided by the difference in pH should be 59.15. If the value is significantly different, the pH electrode is probably at fault. Procedures for troubleshooting pH electrodes are given in the Appendix.

There are several problems inherent to even properly operating electrodes which can lead to serious problems with pH measurements. The most critical problem is the streaming potential which can be reduced in theory to -0.01 ± 0.02 pH units. The sample should be agitated but then allowed to come to full rest; the pH is then made in the quiescent solution. If further accuracy is desired, the liquid-junction potential, resulting from the differences in ionic strength between standard buffers and samples, can be eliminated by calibrating the electrode in solutions of dilute strong acids of known pH. This is preferable to the addition of KCl to the sample which may be used to increase the ionic strength of the sample which in turn affects the measured pH of a sample. Furthermore, the Debye-Huckel correction for hydrogen ion activity to concentration can improve the measured pH.

The overall verification of the pH electrode performance or the free acidity of the sample, however, is critical in assessing the actual errors associated with pH measurements. A dilute strong acid solution may be used to verify absolute pH measurement after routine calibration of the electrode in standard buffers. Although the preparation, storage, and confirmation of dilute strong acid solution is tedious, verification of electrode absolute pH values is fast and straightforward.

Titration and the use of Gran's method to independently determine the hydrogen ion concentration of a solution may also be used to verify pH electrode determinations of free acidity for samples with values less than pH 5.0. Although the preparation and storage of good titrant requires extreme care, verification of the free acidity is straightforward and, in conjunction with Gran's titration method for the determination of strong, total, and weak acidity, allows a

great deal of information about of precipitation acidity to be determined.

Comparison of errors between hydrogen ion activity determined by electrode and hydrogen ion concentration by titration and Gran's function is estimated to be -0.01 ± 0.02 pH units (2σ). Even though titrations require stirring to ensure proper mixing of titrant and sample, streaming potentials are eliminated by constant stirring rates. However, stirring rate inconsistencies are the most significant contribution to error and may cause this difference to be much larger. For example, the difference between pH and free acidity was -0.03 ± 0.10 pH units (2σ) at Argonne for a stirring rate of 2 ± 1 revolutions per second.

For samples with pH values greater than 5.0, weak acids may significantly contribute to the free acidity and Gran's method is no longer applicable since it assumes only strong acids contribute to free acidity. Therefore, for such samples, the pH measurements can only be verified by dilute strong acid solutions of known pH or by inference from simulations of detailed titration curves.

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Appendix

TROUBLESHOOTING ERRORS AND MAINTENANCE OF pH ELECTRODES

Errors in pH measurements can result from a dirty electrode. Because the glass bulb is part of the measuring element of the electrode system, impurities can greatly affect its performance. One source of impurities is a contaminated buffer; also, the storage solution and precipitation sample can be “dirty”. The electrode should therefore be washed several times a year with a mild detergent diluted with deionized or distilled water. The special glass

bulb can be gently rubbed with the fingertips, rinsed with copious amounts of deionized or distilled water, and gently blotted dry with an absorbent wipe. Great care must be exercised when washing the glass bulb such that it does not become cracked or scratched.

There is no simple way to determine if a buffer solution is contaminated other than by physical appearance, such as the presence of a surface film or debris. The buffer solutions used for routine calibration will usually last 3 months if infrequently used and tightly sealed, and should be dated and routinely replaced after 3 months.

pH electrodes should be stored vertically and in a solution when not in use. The solution may be a pH 7 buffer, a 4 molar KCl solution, or a dilute pH 4 buffer; the last may deplete the reference solution more quickly but keeps the electrode "active" for fast response. The storage solution should be changed weekly.

The reference electrode junction may be clogged or encrusted. To test for clogging, the electrode may be stored dry in a vertical position overnight. If the junction is functioning properly, a light crusting at the liquid junction will be present; if it remains clean, the junction is clogged and should be soaked in hot, deionized or distilled water for several minutes. Since the electrode is allowed to dry during this procedure, it must be reactivated by storing it in a dilute pH 4 buffer after washing.

The reference electrolyte solution (KCl) may be depleted of ions; this is probably the most common and most serious problem, and is also the most difficult problem to detect. The pH electrode will calibrate properly in the buffer solutions (high ionic strength) but may not be accurately measuring the pH of the rain sample (low ionic strength). An early indication of this problem is in the length of time it takes for the pH measurement to stabilize; a pH reading should usually only take at most 3 or 4 minutes. If the pH value takes 5 minutes or more to stabilize and even then tends to drift, the KCl filling solution may be depleted of ions. Some pH electrodes are sealed so that the electrolyte solution cannot be replaced. These electrodes use a KCl gel and ions can only be replenished by regeneration. Other electrodes have an opening to replace the electrolyte solution. This opening should always be uncovered while measuring pH to allow free flow of the KCl through the junction. The opening should be closed when not in use to prevent

evaporation of the KCl solution. These electrodes use a liquid KCl solution and ions are replenished by simply replacing the KCl solution. Regeneration procedures for sealed pH electrodes are outlined in the owner's manual and should be used as appropriate.

Usually, the pH meter has a calibration dial, which is adjusted to get the electrode to read the proper value in the buffer. This provides a good indication that the pH electrode and meter are functioning. Mark or record the position of the dial and note how far it has to be turned during calibration in the buffer solutions each time a calibration is performed. The fact that the dial has to be turned more and more each time is an early indication of problems with the pH electrode or the meter. These and other possible problems are discussed in more detail elsewhere.²⁰