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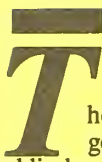
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U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

Standard Reference Materials:

Standardization of pH Measurements

Yung Chi Wu, William F. Koch, and Richard A. Durst



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Preface

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The 260 Series is dedicated to the dissemination of information on different phases of the preparation, measurement, certification, and use of NBS SRM's. In general, much more detail will be found in these papers than is generally allowed, or desirable, in scientific journal articles. This enables the user to assess the validity and accuracy of the measurement processes employed, to judge the statistical analysis, and to learn details of techniques and methods utilized for work entailing greatest care and accuracy. These papers also should provide sufficient additional information not found on the certificate so that new applications in diverse fields not foreseen at the time the SRM was originally issued will be sought and found.

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Abstract

One of the most widely performed analytical measurements in chemical laboratories is that of pH using the glass electrode. In order to ensure the consistency of these measurements, the National Bureau of Standards has recommended an operational scale of pH, maintained in terms of the pH(S) of a series of standard solutions. Certified samples of buffer materials, from which the standard reference solutions of reproducible pH can be prepared, as well as solutions in the case of rainwater, are issued by the National Bureau of Standards as Standard Reference Materials. This report is concerned primarily with a discussion of the method used at NBS for the assignment of pH(S) values to these standard solutions, a description of the NBS measurement facilities for pH, and a summary of the characteristics of the buffer materials. A brief discussion of the types of electrodes used and the calibration of pH instrumentation is also presented.

Key words: activity; activity coefficients; buffers; buffer solutions; certification; glass electrode; hydrogen electrode; hydrogen ion; measurement; pH; Standard Reference Materials; standards; thermodynamics;

Foreword to the First Edition
December 1975

The certification of samples of buffer materials which define points on the National pH scale has evolved over a period of several decades primarily under the direction of Roger G. Bates. While this process is still not complete and the future will likely see pH standards developed for specialized purposes, e.g., pH in sea water and biological fluids such as blood, we have currently reached a point where the primary standards available and the certification techniques involved are relatively well established and few changes are anticipated in terms of the basic technology and philosophy of the NBS pH scale. Consequently, the time seemed opportune to prepare this addition to the "260 Series" of NBS Special Publications which was established for the purpose of reporting technical work done at NBS in the area of Standard Reference Materials.

This report is concerned primarily with a description of the concept of pH, its definition, and the method and facilities used at NBS for the assignment of pH values to the standard buffer solutions. A brief discussion is also included of pH instrumentation and some of the potential pit-falls associated with the measurement of pH and the use of these standards. One additional point is worth noting. The pH certificates reproduced in the appendix of this publication refer to specific stocks of the Standard Reference Materials and, since batch-to-batch pH variability exists, the use of these values for other sources of these buffer materials is not recommended. It is anticipated that in the near future the International Union of Pure and Applied Chemistry will recommend a revised pH scale defined by these standards but of sufficiently reduced precision that analytically pure reagents may be used for routine pH calibration.

Finally, certain commercial materials and equipment are identified in this report in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

Richard A. Durst
Analytical Chemistry Division

Foreword to the Second Edition

Since the first edition of this document was published in December, 1975, several changes have occurred that affect the applicability of the original document, both technically and practically. For instance, we have added the certifications of SRM 2185, the pD standard of potassium hydrogen phthalate, and of SRM 2694, the pH standards for acidic rainwater. We are no longer recommending the use of SRM's 922 and 923, [tris(hydroxymethyl)-aminomethane and tris(hydroxymethyl)aminomethane hydrochloride, respectively] as a pH standard, because of the large residual liquid junction potentials associated with this buffer system when used in an operational cell, even though it is possible to assign an exact pH value to this buffer system in a cell without liquid junction. However, the Tris system is still an excellent buffer in the physiological range; the difficulty is assigning an exact pH value in an operational cell. Moreover, most of the pH SRM's listed in the first edition have been recertified. The new pH values for these new lots of materials differ, albeit slightly, from those of the previous lots. In addition, the apparatus and instrumentation have been modified to improve the accuracy of the measurements. All these changes and improvements necessitate that the document be revised in order to fulfill its intended purpose.

The purpose of this document is to provide the user with a description of the concept of pH, its definition, and the methods and facilities used at NBS for the assignment of pH values to the buffer materials and solutions issued by NBS as Standard Reference Materials. A brief discussion of some of the pitfalls associated with the measurement of pH and the use of these standards is also included. It should be noted that the pH certificates reproduced in the appendix of this publication refer to specific stocks of the Standard Reference Materials and, since batch-to-batch variability exists, the use of the certified values for other sources of materials is not recommended.

Finally, certain commercial materials and equipment may be identified in this document to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

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1. Introduction

Measurement and control of acidity and alkalinity are frequently essential in both industrial processes and research work. Commercial pH meters with electrodes of the glass type, some of which it is claimed can measure pH values with a reproducibility of 0.001 unit, are used in nearly every laboratory where chemical analyses or control tests are performed. These instruments, in effect, compare the pH values of the test or sample solutions with those of standard solutions of known pH. These standard solutions are used to calibrate the readings of the electrode measurement system. It is very important to have universal agreement on a standard scale of pH, and to adopt standard reference solutions of known pH to maintain and to describe this scale, to ensure measurement comparability and compatibility.

The National Bureau of Standards is actively engaged in research to advance and maintain standards for pH measurements. It advocates the adoption of an operational pH scale based on thermodynamic principles and rational conventions, and described in terms of the pH(S) of a series of standard solutions whose assigned pH values are related to the negative of the common logarithm of the hydrogen ion activity, $-\log a_{\text{H}}$, in the respective solutions. Certified samples of buffer materials, from which standard reference solutions of reproducible pH can be prepared, or in some cases, certified solutions of known pH, are issued by the National Bureau of Standards as Standard Reference Materials (SRM's).

This report is concerned primarily with a description of the method used at the National Bureau of Standards to assign pH values to the standard reference solutions. The characteristics of these solutions are summarized and the theory, definitions, and conventions used to arrive at the assigned values are discussed. A brief review of types of electrodes and methods of calibration of pH assemblies is given, but for more details on these subjects, specific monographs (see references) and the technical literature of the equipment manufacturer should be consulted. Finally, some of the limitations and pitfalls of pH measurements and subsequent interpretation of data are discussed.

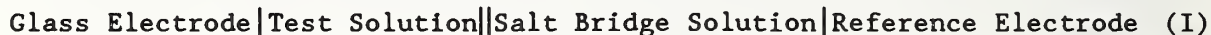
2. Definition of pH

The negative logarithm of the hydrogen ion activity has been given the symbol pH [1]¹. It should be noted here that the original definition was in terms of hydrogen ion concentration [2]. The present definition of pH is associated with the "effective" concentration of hydrogen ion. The importance of this quantity lies in the fact that it is the measure of the chemical reactivity of the acid and alkali in aqueous solutions. It is used extensively in biomedical studies and in monitoring agricultural and industrial processes. Functionally, pH lies at the base of many chemical synthetic processes and is

¹Numbers in brackets indicate literature references at the end of this paper.

essential in many analytical measurements. In biological and biochemical research, pH is important because it is fundamental to natural processes.

The determination of pH is based on physicochemical principles and can be performed by various techniques such as colorimetry, conductivity, and potentiometry. Of these, the potentiometric or the electromotive force (emf) method is the simplest, the most accurate, and hence the most widely used. This is particularly true since the invention and commercialization of the hydrogen ion sensitive glass electrode. The employment of the glass electrode for determining pH generally requires the following arrangement:



where the single vertical bar is the electrode-solution interface and the double vertical bar is a liquid junction denoting an interface between the test solution and the salt bridge solution, the latter having an ion in common with the reference electrode.

From the measured electromotive force of cell (I), the pH can be computed via the following equation:

$$\text{pH} \equiv -\log a_{\text{H}} = \frac{E - (E_{\text{pH}}^{\circ} + E_j)}{RT \ln 10/F} = \frac{E - E_{\text{pH}}^{\circ'}}{k} \quad (1)$$

where a_{H} = the hydrogen ion activity (the charge, +, is dropped for convenience)

- E = the observed emf of the cell
- E_{pH}° = a constant, dependent on temperature and pressure and the types of electrodes used
- E_j = the liquid junction potential of a given cell
- R = the gas constant, $8.314510 \text{ J mol}^{-1} \text{ K}^{-1}$
- T = the kelvin temperature, $273.15 + ^{\circ}\text{C}$
- F = the Faraday constant, $96485.309 \text{ C mol}^{-1}$
- k = $(RT \ln 10)/F$
- $E_{\text{pH}}^{\circ'} = E_{\text{pH}}^{\circ} + E_j$

The last quantity, $E_{\text{pH}}^{\circ'}$, cannot be accurately evaluated. However, if $E_{\text{pH}}^{\circ'}$ is assumed to be constant for a given system [3], and if a solution of known pH [pH(S)] is available, then the pH of an unknown solution [pH(X)] can be determined by using cell (I) twice: first with solution S, then with solution X and calculating the pH(X) from the difference in the respectively measured emf's as follows:

$$\text{pH(X)} = \text{pH(S)} + \frac{E_x - E_s}{k} \quad (2)$$

If pH(X) differs significantly from pH(S) or if the emf response of the system differs from the ideal Nernstian response of 1 pH unit per volt $(RT \ln 10/F)$,

then two pH standards (S1 and S2) should be used. The value of pH(X) can be computed according to eq (3), assuming linearity between the standards:

$$\text{pH}(X) = \text{pH}(S1) + \frac{E_X - E_{S1}}{E_{S2} - E_{S1}} [\text{pH}(S2) - \text{pH}(S1)] \quad (3)$$

The choice of the two buffers S1 and S2 should be such that pH(X) falls between the values pH(S1) and pH(S2). Such is the practical determination of pH today.

Therefore, the availability of standard pH solutions is a necessary condition for the application of eq (2) or eq (3). Moreover, according to the application of Henderson's or Planck's equation for the approximation of the liquid junction potential [4-6], the standard pH solution should be made as similar to the test solution as possible with respect to pH and composition. Under such conditions the assumption regarding the constancy of E_{pH}° is sound. Since in practice the conventional pH scale spans 14 pH units, several pH standards are required for establishing calibration points over the entire pH range.

In the United States, pH standards are developed and maintained by the National Bureau of Standards (NBS). Many foreign countries have also adopted the NBS approach to pH standardization. The early research in pH standards began at NBS in the late 1930s [7], and is manifest today through the issuance of Standard Reference Materials. This approach, as well as the materials and values for the NBS pH buffer standards, have been accepted internationally. The theory and practices which are at the base of the certification process undergo periodic critical examination at NBS to remain current with new developments and technology and to be responsive to changing and expanding national needs. A detailed discussion of the theory, the process, and the refinement of the evaluation and certification of pH standards at the NBS follows.

3. Thermodynamic Foundation of pH

The use of pH in the expression $\text{pH} = -\log a_H$ is purely a formalism because a_H , a single (hydrogen) ion activity, is indeterminate. The ultimate definition of pH should be made in terms of determinable quantities. One way of determining the pH of a weak acid (HA) may be from the dissociation constant, K_a , of the acid, assuming K_a is known or can be independently determined. Activity coefficients still enter into the expression, but in this case, as ratios. Therefore, uncertainties involving exact knowledge of activity coefficients tend to be minimized to insignificance.

$$K_a = \frac{a_H a_A}{a_{HA}} = \frac{a_H m_A \gamma_A}{m_{HA} \gamma_{HA}} \quad (4)$$

and

$$\text{pH} = \text{p}K_a + \log \frac{m_A}{m_{HA}} + \log \frac{\gamma_A}{\gamma_{HA}}, \quad (5)$$

and with the aid of the Debye-Hückel equation [8,9],

$$\log \gamma_i = -Az_i^2\sqrt{I}/(1 + B\dot{a}_i\sqrt{I}) + bI \quad (6)$$

where m = molality of the constituents

γ_i = activity coefficient of the i th species

$I = \frac{1}{2}\sum m_i z_i^2$. (This is the definition of ionic strength only if the electrolyte is fully dissociated. Otherwise, the degree of dissociation, α , should be included. Thus $I = \frac{1}{2}\sum \alpha m_i z_i^2$; e.g., I for 0.05 m potassium hydrogen phthalate at 25 °C is not 0.05 but 0.0533, due to the partial dissociation of the biphthalate [10].)

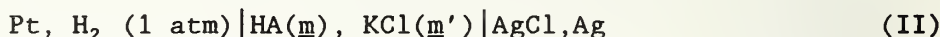
z_i = ionic charge of the i th ion

A and B = constants dependent on the temperature and dielectric constant of the solvent

\dot{a}_i = the ionic size parameter

b = an adjustable parameter.

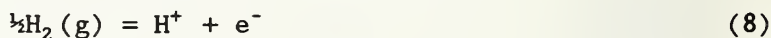
On the other hand, the pH of the same acid can be determined without the knowledge of K_a , using a galvanic cell without liquid junction, sometimes called the Harned cell:



The emf of this cell at 101.325 kPa (one atmosphere) of hydrogen pressure is given by:

$$E = E_{\text{Ag, AgCl}}^\circ - (RT/F) \ln m_H m_{\text{Cl}} \gamma_H \gamma_{\text{Cl}} \quad (7)$$

where m 's are molalities, γ 's the activity coefficients, R, T, F have their usual significance, and E is the measured emf. $E_{\text{Ag, AgCl}}^\circ$ is the potential of the silver/silver chloride electrode measured relative to the "standard hydrogen electrode," $[\text{Pt}, \text{H}_2 (1 \text{ atm}) | a_H=1]$, for which the reaction is:



and

$$E_H = E_H^\circ - (RT/F) \ln \frac{a_H}{\sqrt{p_{\text{H}_2}}} \quad (9)$$

where p_{H_2} is the pressure of the H_2 gas. When $p_{\text{H}_2} = p_{\text{H}_2}^\circ \equiv 1$ atmosphere, and $a_H \equiv 1$, then, $E_H = E_H^\circ$. Since half-cell potentials cannot be measured independently, it has been established by convention that $E_H^\circ = 0$ at all temperatures. All other half-cell potentials are computed in relation to $E_H^\circ = 0$.

By collecting all the known quantities on the right hand side, eq (7) may be rewritten as

$$-\log a_H \gamma_{C1} = [(E - E^\circ)/k] + \log \underline{m}_{C1} \quad (10)$$

Since, by definition, $\gamma_{C1} = 1$ as $\underline{m}_{C1} \rightarrow 0$, by plotting the right hand side of eq (10) vs \underline{m}_{C1} and extrapolating to $\underline{m}_{C1} = 0$, the limiting value of the acidity function can be expressed as $-\log (a_H \gamma)_I^\circ$ [10]. This value corresponds to the acidity function at the particular ionic strength, I, of the weak acid HA and

$$\text{pH} = -\log(a_H \gamma)^\circ + \log \gamma_{(at I)}. \quad (11)$$

The last term of eq (11) may be evaluated from eq (6). Therefore, all the quantities related to pH, either from the dissociation constant or from the emf of galvanic cells without liquid junction, can be determined or calculated. Hence, within this framework, the term pH is defined.

It should be noted that the application of eq (6) for the evaluation of the activity coefficients requires assumptions outside the domain of thermodynamics. However, it has been experimentally proven that this equation is a suitable approximation for the activity coefficients of strong electrolytes up to 1 molal concentration [11,12] and, therefore, the use of this equation is justified for the determination of pH at ionic strength lower than 1 molal.

As the ionic strength decreases, the last term in eq (6) becomes insignificant, and the influence of λ also decreases. By selecting a value for $B\lambda_1$ (for example 1.5, as recommended by the Bates-Guggenheim convention [13,14] at the ionic strength of around 0.1 molal), the resultant uncertainty in pH is less than 0.005 pH unit, even if $B\lambda_1$ is varied by as much as 10%. The ionic strength of the standard pH solutions certified by NBS is less than 0.1 molal. Thus the Bates-Guggenheim convention,

$$\log \gamma_1 = -Az_1^2 \sqrt{I} / (1 + 1.5\sqrt{I}) \quad (12)$$

is justified within the present experimental uncertainty (see table 1), and is applicable to the certification of the NBS primary buffer standards.

With the adoption of the Bates-Guggenheim convention, it has become possible to assign pH(S) values to the primary standard solutions with an uncertainty of ± 0.005 pH units. The assigned values of pH(S) for the standard solutions at temperatures from 0 to 50 °C, and even to 95 °C for certain buffers, are smoothed values calculated by the equation:

$$\text{pH}(S) = (A/T) + B + CT + DT^2 \quad (13)$$

where T is the temperature in kelvin. Inasmuch as each lot of material is individually certified, the pH(S) values of different lots may differ slightly in the third decimal place.

New demands for pH standards of ionic strength greater than 0.1 molal, such as that for seawater, render the use of Bates-Guggenheim convention inapplicable. In these cases, one is faced with two choices, both equally

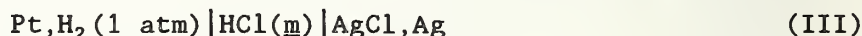
difficult. The first is to evaluate the single ion activity coefficient; the other is to minimize and fully characterize the liquid junction potential. Both of these are classical problems; their solutions are long overdue. We are currently working on a conventional procedure and will test it experimentally. At present, in solutions with ionic strengths between 0.1 and 1.0 molal, the certainty of a pH standard is limited to ± 0.02 pH unit.

4. NBS Standardization of pH Solutions

The standardization of pH solutions was initiated at NBS in the late 1930's when Hamer [15] suggested the use of a galvanic cell without a liquid junction, similar to cell II, for the purpose. Later Hamer and Acree [7] proved experimentally the applicability of cell II for the determination of pH. Early in the 1940's, Bates et al. [16] published a list of provisional pH values for standard buffers. In the following years the experimental setup and the treatment of data were significantly refined as the state of the art of the measurement advanced.

The principle of the determination of pH and the thermodynamics of the establishment of a pH scale have been discussed in section 3. Because of the complexity of ionic interactions in electrolyte solutions, the knowledge of ionic activity coefficients has been advanced little in recent years. The only improvements that have occurred in the determination of pH have been in the methods of measurement. Among various methods for determining pH, Hamer et al. [7,15] and later Bates [13,17,18] have ably demonstrated that a galvanic cell without a liquid junction, such as cell II, is best suited for the purpose.

Since eq (7) is used for the determination of pH, it is necessary to know $E_{\text{Ag,AgCl}}^{\circ}$. The value of $E_{\text{Ag,AgCl}}^{\circ}$ is determined using the following cell [11],



and the equation,

$$E_{\text{Ag,AgCl}}^{\circ} = E_{\text{cell}} - E_{\text{H}}^{\circ} \quad (14)$$

where $E_{\text{H}}^{\circ} \equiv 0$, under the conditions described in the previous section. However, the best values of E° reported for this cell disagree by 0.2 mV or more [19,20]. This indicates that not all silver-silver chloride electrodes behave identically. Therefore, for the most accurate pH work, the E° value of each individual Ag,AgCl electrode must be determined in cell III and the stability of each electrode firmly established before it may be used in cell II.

Using cell II, relying on thermodynamic principles, and adopting the Bates-Guggenheim convention, the NBS has certified six primary and two secondary pH standards. They are listed in table 1. The uncertainty associated with each of the primary standards is 0.005 pH and the uncertainty of the secondary standards is 0.01 pH.

The widespread use of cell I for practical pH measurements necessitates the use of pH standards that are traceable to the primary standards for

calibration purposes. The work at NBS satisfies this need by providing definitively calibrated and certified pH standards. The advantages and shortcomings of cell I have been discussed in section 2. Nevertheless, it is of interest to evaluate the data obtained with cell I by using a combination glass electrode to test the internal consistency of the NBS pH standards. The reference junction was a ceramic frit. Measurements of emf were made in five of the NBS pH standard solutions under an argon atmosphere. The emf values were plotted versus the certified pH values and fitted by a least squares procedure. The results are shown in table 2. The maximum deviation among all pH(S) listed in table 2 is 0.002 pH units. These results were corroborated with another set of experiments using a glass electrode and a saturated calomel reference electrode with a fine flowing liquid junction. In this set, the electrode system was calibrated with one buffer solution, and then all others measured, assuming Nernstian response. Thus, it is concluded that the NBS pH scale is internally consistent to at least 0.003 pH unit, confirming the usefulness of the approximations and conventions described earlier in this report.

5. The Operational Determination of pH and the Problem of Liquid Junction

The operational definition of pH entails the measurement of pH with cell I and the comparison of the pH of the unknown solution with that of the standard as shown in eq (2). Such comparison assumes the constancy of the liquid junction potential, E_j , in eq (1). This assumption has only limited validity. In some instances significant errors in the pH determination may be introduced by this assumption.

The problem of liquid junction potential has been the subject of numerous studies [3,15,21,22] which indicate that the liquid junction potential is not a thermodynamic quantity, i.e., that the liquid junction potential cannot be specifically defined. For example, E_j depends on the concentration of the salt bridge and on the temperature, but no functional correlation has been found. E_j also varies with specific electrolytes, such as strong and weak acids. Furthermore, it changes with the geometrical structure and the manner in which the junction of the salt bridge is formed [15,21]. Therefore, E_j cannot be determined exactly and eq (2) cannot be considered a rigorous thermodynamic definition of pH.

For the reasons outlined above, one cannot in general assume E_j to be constant when determining pH in solutions of unknown nature. It has been reported that the uncertainty in determining pH in acid rain [22,23] and in biological fluids [24], using a combination glass electrode in cell I, is significant, often as large as 0.5 pH.

Table 1. NBS pH Standards

<u>Solution composition (molality)</u>	<u>pH(S) at 25 °C</u>	<u>Temperature range (°C)</u>	<u>SRM</u>
Primary Standards:*			
potassium hydrogen tartrate ($\text{KHC}_4\text{H}_4\text{O}_6$, sat'd. at 25 °C)	3.557	25 to 95	188
($\text{KHC}_4\text{H}_4\text{O}_6$, 0.01 <u>m</u>)	3.639	0 to 60	188
potassium dihydrogen citrate ($\text{KH}_2\text{C}_6\text{H}_5\text{O}_7$, 0.05 <u>m</u>)	3.776	0 to 50	---
potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$, 0.05 <u>m</u>)	4.006	0 to 50	185f
potassium dihydrogen phosphate/ disodium hydrogen phosphate (KH_2PO_4 , 0.025 <u>m</u> + Na_2HPO_4 , 0.025 <u>m</u>)	6.863	0 to 50	186Id/186IId
(KH_2PO_4 , 0.0087 <u>m</u> + Na_2HPO_4 , 0.0304 <u>m</u>)	7.410	0 to 50	186Id/186IId
sodium tetraborate decahydrate, (borax) ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 0.01 <u>m</u>)	9.180	0 to 50	187c
sodium bicarbonate/sodium carbonate (NaHCO_3 , 0.025 <u>m</u> + Na_2CO_3 , 0.025 <u>m</u>)	10.010	0 to 50	191a/192a
Secondary Standards:**			
potassium tetroxalate ($\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, 0.05 <u>m</u>)	1.679	0 to 50	189
calcium hydroxide ($\text{Ca}(\text{OH})_2$, sat'd. at 25 °C)	12.454	0 to 60	in prep.

*Uncertainty: ± 0.005 pH**Uncertainty: ± 0.01 pH

Table 2. Internal consistency of the NBS pH scale

<u>Standard Solution</u>	<u>SRM</u>	<u>@ 25 °C</u>	<u>ΔpH</u>
Tartrate (0.01 M)	188		
pH(S)		3.639	
pH(meas)		3.638	+0.001
Phthalate	185e		
pH(S)		4.004	
pH(meas)		4.006	-0.002
1:1 Phosphate	186Ic/186IIc		
pH(S)		6.863	
pH(meas)		6.861	+0.002
Borax	187b		
pH(S)		9.183	
pH(meas)		9.184	-0.001
Carbonate	191/192		
pH(S)		10.014	
pH(meas)		10.014	+0.000

6. NBS Facilities for pH Certification Measurements

The NBS emf measurement system has gone through several modifications during the last three decades. The current setup is essentially the same as it was in the 1930s, but the instrumentation has advanced to the state of the art, which is more precise, more accurate and more convenient. The system is described as follows:

A. Apparatus

1. Constant Temperature Bath

A double-walled, thermally insulated with rock wool, stainless steel rectangular enclosure, with an open top and 200 liter (50 gallon) capacity, (operating volume of 150 liters of water) constitutes the bath. A quartz thermometer (Hewlett-Packard Co., Palo Alto, CA) with a frequency meter (Data Precision, Inc, Danvers, MA) calibrated with the NBS temperature standard to 0.001 °C was used for sensing the temperature in the bath. The bath temperature was controlled with a dial setting temperature control unit (Yellow Springs Instrument Co., Yellow Springs, OH), which was connected to a 1200 watt quartz heater (Corning Co., Corning, NY). The unit consists of a thermistor and a Wheatstone-type bridge. A cooling system is required to offset the heating. Coiled copper tubing connected to a chilled water (12 °C) source was satisfactory for bath temperatures above 15 °C. For bath temperatures at or below 15 °C, a refrigeration unit was used in the bath. The high cooling capacity of the refrigeration unit was balanced by three auxiliary 1200 watt quartz heaters which were controlled by variable transformers. For rapid heating or cooling, hot water or ice was used, respectively, to bring the bath temperature close to the dial setting

at which the control unit operated effectively. Four submersion circulating pumps with nozzles set at different directions were used for uniform stirring. The bath temperature was controlled to within ± 0.005 °C between 10 and 40 °C; at 0, 5, 45, and 50 °C the temperature control was limited to ± 0.01 °C.

2. Measuring Instruments

A digital barometer (Setra Systems, Acton, MA) calibrated against the NBS standard barometer was used to record the atmospheric pressure. A digital multimeter (Model 3500, Data Precision, Danvers, MA) with 10 Mohm input impedance, calibrated by the NBS Electricity Division, was used to determine emf. Temperature was measured as described above.

3. Electrodes

The platinized platinum electrodes were made with platinum foils (1/2 x 2 1/2 cm) attached to 22 gauge platinum wires which were sealed into soft glass tubes which in turn were joined to standard-taper glass joints. Each electrode was platinized at a current density of 100 mA/cm² for three min, in a 2% chloroplatinic acid (H₂PtCl₆) solution to which a small amount of lead acetate (10 mg Pb(C₂H₃O₂)₂ · 3H₂O per liter) was added to improve the plating characteristics. The plating was uniformly black and firmly adhered to the electrode. The electrode served as the hydrogen electrode and was stable and reproducible (± 0.02 mV).

The silver/silver chloride electrode was prepared on two different supporting wires, viz, silver (99.999% pure) or platinum, by the thermal electrolytic method (19). A thoroughly washed Ag₂O paste was coated onto the wires. These were heated at 500 °C for 3 to 4 h to convert the silver oxide to a spongy, porous silver metal and then were cooled under an inert, argon atmosphere. They were anodized in 1 molal HCl solution which was purged with argon gas, at 10 mA for the time required to convert 15% of the spongy silver to AgCl. The electrodes were washed with distilled water and were stored in 0.05 M HCl solution (also purged with argon). The E° of each electrode was determined in 0.05 M HCl solution [$\gamma = 0.8304$ (10)]. The E° values of platinum wire supported and silver wire supported electrodes were statistically identical. The average E° for a set of electrodes produced at NBS was determined to be 0.22244 V with a standard deviation of 0.00003 V. Another set of electrodes was provided by Radiometer A/S (Copenhagen, Denmark). The E° value provided with the electrodes was 0.22240 V (Std. dev. 0.00002 V) and was confirmed in our laboratory. This set of electrodes appeared to be more stable than those produced at NBS after two months of use and storage. Further details of the preparation of the platinized (or pallidized) platinum and the silver/silver chloride electrodes can be found in references [13], [19], and [25].

4. Galvanic Cell without Liquid Junction

The specially designed emf measurement cell shown in figure 1 consists of a hydrogen gas electrode compartment, a silver/silver chloride electrode compartment, and a series of gas-dispersion compartments for humidifying the incoming hydrogen gas by passage through the buffer solution. Six measurement cells, containing each of the three levels of added chloride in duplicate, are placed in the controlled temperature water bath as shown in figure 2. Also shown in this figure are the coiled copper tubing hydrogen gas inlets.

B. Materials

The materials used in the production of Standard Reference Material pH standards are of high quality as specified on the pH certificates (see Appendix). In performing a pH certification, the first requirement is to prepare the solutions and measurement cells with utmost care. In the case of the buffer salts and as specified in the pH certificates, the carefully dried and weighed salts are dissolved in high-purity, distilled/deionized water having a conductivity of less than $2 \mu\text{S}/\text{cm}$ at 25°C . For buffers in the neutral and basic regions, carbon dioxide must also be removed from the water prior to dissolution of the buffer salts. The hydrogen gas must be free of oxygen and may be purified of oxygen by passage through a catalytic reduction tube or through a palladium purifier.

C. Calculation of pH(S)

The data reduction consists of a series of operations (vide supra) including correcting the experimental emf values to the standard partial pressure of hydrogen, calculating the acidity functions, extrapolating to $m_{\text{Cl}^-} = 0$ to obtain the limiting acidity functions, evaluating the chloride ion activity coefficient using the Bates-Guggenheim convention, and finally calculating the $\text{p}a_{\text{H}^+}$ values. These experimental values are then smoothed with respect to temperature (eq 13) by the method of least squares to give the certified pH(S).

7. Recommended Standards

The pH scale recommended by the National Bureau of Standards is maintained in terms of the pH(S) assigned to the six primary and two secondary reference solutions listed in table 1. The composition and properties of the standard solutions are given in table 3. The phthalate, phosphate, borax, carbonate, and tetroxalate buffer solutions are prepared by dissolving the indicated weights of the pure reference materials in water and diluting to 1 dm^3 (1 liter). The directions for the preparation of the molal solutions are given on a volume basis, i.e., grams per liter of solution, to simplify the preparation of the buffer solutions. However, the weights of the salts indicated in table 3, and in the NBS certificates for these pH standards are corrected for solution density and air buoyancy and thus correspond to the nominal

Table 3. Composition and Properties of Standard Solutions

<u>Solution</u>	<u>Buffer Material</u>	<u>Mass (g) in air/dm³</u>	<u>Dilution Value¹</u>	<u>Buffer Value²</u>	<u>Temp. Coeff.³</u>
Tetroxalate, 0.05m	$\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	12.61	+0.186	0.070	+0.001
Tartrate, sat'd	$\text{KHC}_4\text{H}_4\text{O}_6$	>7	+0.049	0.027	-0.0014
Citrate, 0.05m	$\text{KH}_2\text{C}_6\text{H}_5\text{O}_7$	11.41	+0.024	0.034	-0.0022
Phthalate, 0.05m	$\text{KHC}_8\text{H}_4\text{O}_4$	10.12	+0.052	0.016	+0.0012
Phosphate, 1:1			+0.080	0.029	-0.0028
0.025m	KH_2PO_4	3.387			
0.025m	Na_2HPO_4	3.533			
Phosphate, 1:3.5			+0.07	0.016	-0.0028
0.008695m	KH_2PO_4	1.179			
0.03043m	Na_2HPO_4	4.303			
Borax, 0.01m	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	3.80	+0.01	0.020	-0.0082
Carbonate, 1:1			+0.079	0.029	-0.0096
0.025m	NaHCO_3	2.092			
0.025m	Na_2CO_3	2.640			
Calcium hydroxide, sat'd	$\text{Ca}(\text{OH})_2$	>2	-0.28	0.09	-0.033

¹Dilution value is the change in pH observed when a buffer solution is diluted with an equal volume of water [1]; $\Delta\text{pH}_x = \text{pH}(C/2) - \text{pH}(C)$.

²Buffer value, β , is a differential ratio $db/d\text{pH}$ where db is an increment of strong base expressed in moles of hydroxide ion per liter [1].

³Temperature coefficient is the change in pH with temperature, $\delta\text{pH}/\delta T$, expressed as pH/K .

concentration on the molal scale. The NBS certificates also give the weights of the pure reference materials needed to make the indicated molal solutions by dilution with 1.000 kilogram of pure water. The tartrate and calcium hydroxide solutions are made by shaking an excess of the pure material with water in a glass-stoppered bottle. The excess, insoluble material should be removed by filtration or decantation [13]. The calcium hydroxide standard solution is best stored in a polyethylene bottle and made fresh daily from CaO . The tartrate solution is about 0.034 mol/kg, and the calcium hydroxide solution about 0.021 mol/kg.

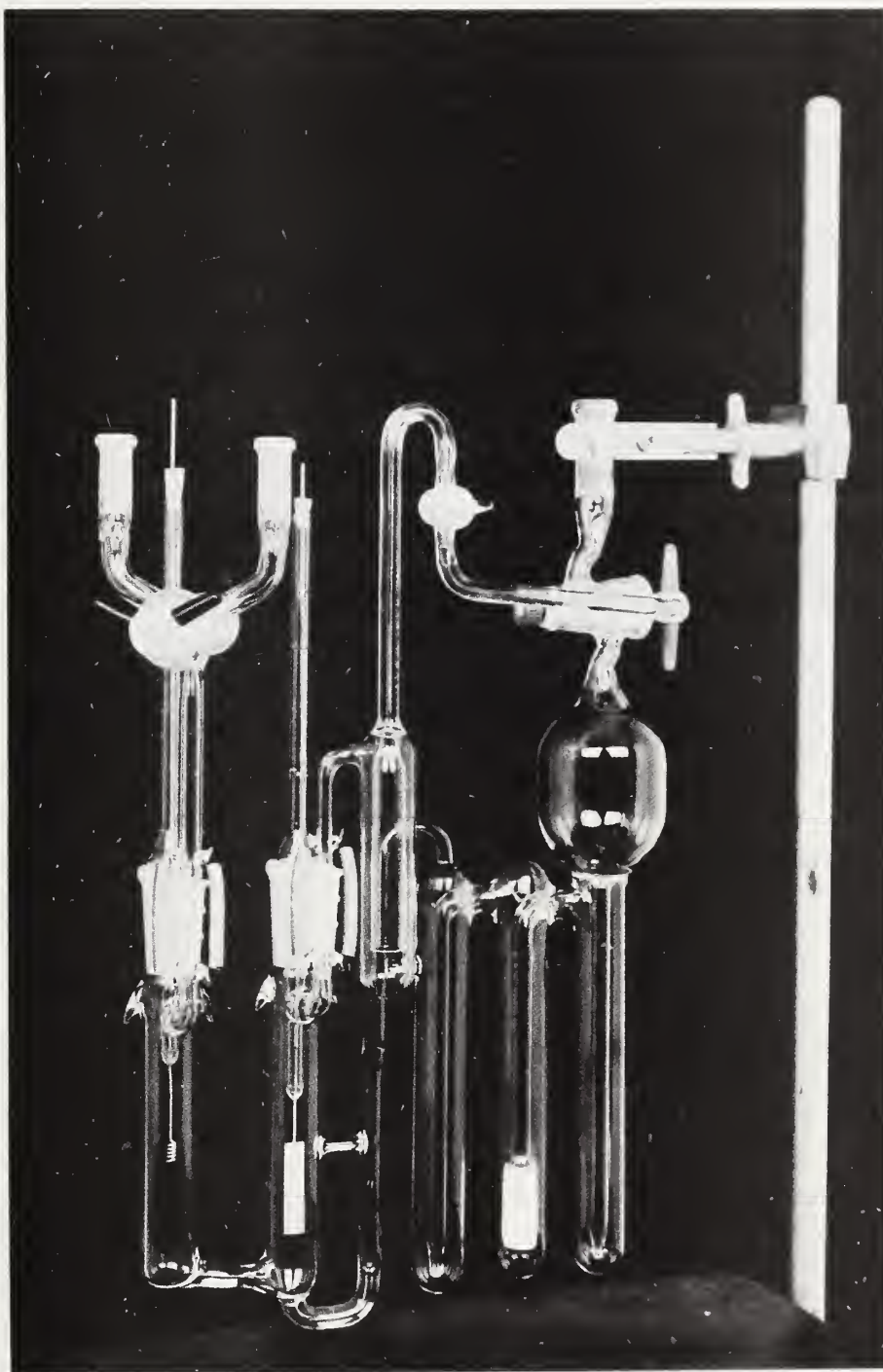


Figure 1. Emf measurement cell used for the certification of pH buffer solutions.

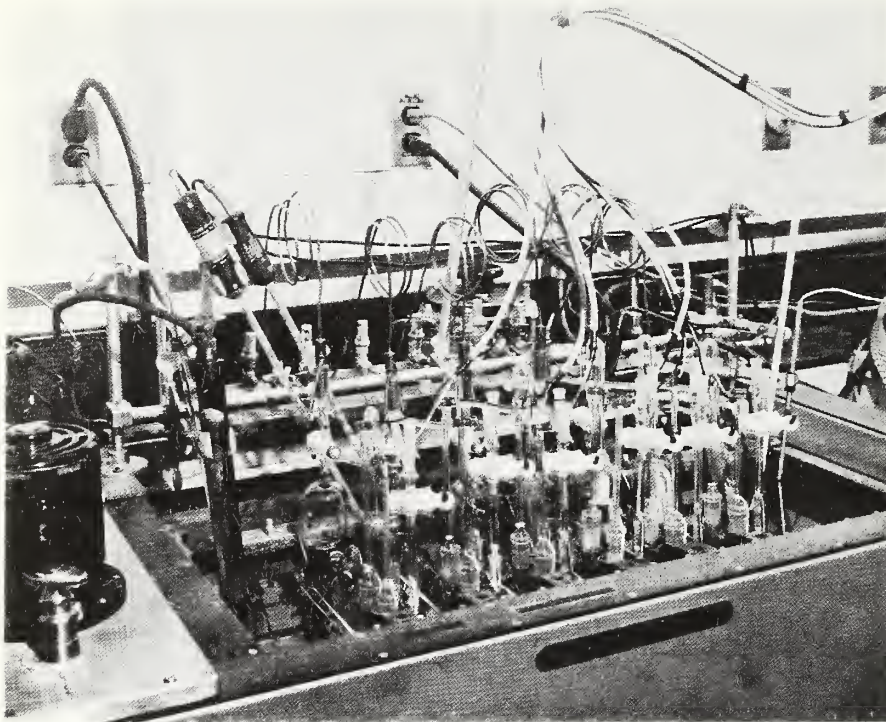


Figure 2. Emf measurement cells in position in the controlled-temperature water bath.

Prior to weighing, a few of the reference materials should be oven-dried for two hours: potassium hydrogen phthalate at 110 °C, potassium dihydrogen phosphate and disodium hydrogen phosphate at 110-130 °C, and the sodium carbonate at 275 °C. The other materials do not require oven drying but should not be exposed to excessively high humidity. Storing in a desiccator is recommended. When drying the salts, only a sufficient quantity for the preparation of the buffer solution should be sampled and dried in a weighing bottle. It is not recommended to dry the entire bottle of salt at once. Depending on user preference, the weighed samples of reference materials should be diluted either to the appropriate weight or volume, as specified on the certificates, with distilled or deionized water at 25 °C. The distilled water should have a conductivity no greater than 2 $\mu\text{S}/\text{cm}$. In addition, the phosphate, borax and carbonate buffers should be prepared using water purged with carbon dioxide-free nitrogen or argon, or using freshly boiled water of pH 6.7 to 7.3. Boiled water should be protected from contamination by atmospheric carbon dioxide by cooling and storing in a bottle fitted with a tube of carbon dioxide absorbent, e.g., soda lime. Exposure of the prepared buffer solutions to the atmosphere should also be minimized. The more acidic buffers as well as the saturated calcium hydroxide solution may be prepared from air-equilibrated water, pH 5.6 to 6.0. It is recommended that the buffer solutions be replaced about once a month, and sooner if mold, particulate, or other evidence of contamination is observed. The tartrate buffer is particularly subject to mold growth, accompanied by an increase in pH. The addition of a small amount of thymol has been found to be an effective preservative, although this treatment should be avoided for measurements of the highest accuracy [13].

In addition to the primary and secondary buffer materials, a new class of pH Standard Reference Materials is now available, intended to simulate the matrices of select solutions. The purpose of these new standards is to improve the accuracy and comparability of pH measurements in solutions in which the residual liquid junction potential between the customary buffer standards and the sample solution is suspected to be significant, variable, and/or unpredictable. The first set of such standards was developed for acid rain studies, SRM 2694, Simulated Rainwater. A detailed description of the production, analysis, and uses of this SRM is given in NBS Special Publication 260-106 [26]. As needs develop, additional matrix-specific pH SRM's will be issued. In the research stage at present is the development of pH standards for seawater and for biological fluid applications.

A unique class of matrix specific pH standards are those intended for use in heavy water, D_2O . These standards are called pD standards. At present, there are three recommended pD standards issued as SRM's, including the new standard in the acidic region, potassium hydrogen phthalate, SRM 2185 [27].

A complete list of the pH and pD Standard Reference Materials presently available from the National Bureau of Standards is given in table 4, and their certificates are given in the Appendix. Although considerable work has gone into the determination of pH values for the citrate and calcium hydroxide solutions, reference materials have not yet been certified.

Table 4. NBS pH and pD Standard Reference Materials*

<u>Material</u>	<u>SRM Designation</u>
Potassium hydrogen phthalate	185f
Potassium dihydrogen phosphate	186-I-d
Disodium hydrogen phosphate	186-II-d
Sodium tetraborate decahydrate	187c
Potassium hydrogen tartrate	188
Potassium tetroxalate	189a
Sodium bicarbonate	191a
Sodium carbonate	192a
Simulated Rainwater	2694
Potassium hydrogen phthalate (pD)	2185
Potassium dihydrogen phosphate (pD)	2186-I
Disodium hydrogen phosphate (pD)	2186-II
Sodium bicarbonate (pD)	2191a
Sodium carbonate (pD)	2192a

*Available from the Office of Standard Reference Materials, National Bureau of Standards, Gaithersburg, Maryland 20899. Request NBS Special Publication 260 for price list and ordering information.

8. pH Instrumentation and Electrodes

A comprehensive discussion of pH instrumentation and electrodes is beyond the scope of this report, and for more details, the referenced monographs and the equipment manufacturers' literature should be consulted. However, we present a brief discussion to give general information to the practitioner about the type of instrumentation and electrodes available.

In recent years, many excellent pH meters capable of providing pH values with a reproducibility of a few thousandths of a pH unit have become readily available. However, while modern digital pH meters can be read to the nearest 0.001 pH unit, the fundamental meaning of these measured values is considerably less certain than the precision of the measurement. In making pH

measurements, it is important to remember that the pH assembly is designed to indicate the difference between a standard buffer and a test solution, both of which should be at the same temperature. To affirm the proper functioning of the glass electrode and the accuracy of the instrument over the pH range of the test solutions, the assembly should be calibrated with two standards which bracket the pH of the samples. With this procedure, it is assumed that the emf of the cell varies linearly with the pH within the range of the standards but that the pH electrode response slope is not necessarily exactly Nernstian, i.e., $(RT \ln 10)/F$ volts per pH unit. The pH of the test solution is given by eq (3). In actual practice, with most modern direct-reading instruments, the above calibration is made by adjusting the standardization and sensitivity (slope) controls on the instrument. Errors caused by fluctuations in the residual liquid-junction potential and temperature are minimized by standardizing the assembly at a pH close to that of the test solution.

There are four principal types of pH indicator electrodes:

1. the hydrogen (gas) electrode,
2. the glass electrode,
3. the metal-oxide electrodes, and
4. the quinhydrone electrode.

The hydrogen electrode is the ultimate standard for the determination of pH, but special precautions must be taken to ensure obtaining the most reliable and theoretically correct results. Its use, therefore, is limited, owing to experimental difficulties. The other pH electrodes, in particular the glass electrode, are commonly used for routine measurements.

The glass electrode is the most widely used pH-indicator electrode. It is applicable over a wide pH range and exhibits high stability, reliability and reproducibility. It is the only one of the four types of pH electrodes that is completely free of oxidation-reduction interferences. The construction and response of this electrode has been discussed in detail elsewhere [13]. Suffice it to say that the pH-responsive surface consists of a thin membrane formed from a special glass, which after suitable conditioning, develops a surface potential that is an accurate indicator of the hydrogen ion activity of the test solution. The glass membrane is usually made as thin as is consistent with adequate mechanical strength. Even so, its electrical resistance is very high, usually in the range from tens to hundreds of megohms, which is the reason that electronic amplifiers must be used to obtain adequate measurement accuracy. The exact mechanism of operation of the glass electrode is still a matter of some conjecture. However, there seems to be no doubt that during the conditioning process of the glass membrane, there is an exchange between alkali metal ions, such as sodium or lithium, in the interstices of the glass matrix with hydrogen ions (protons) from the solution. The exchange of labile protons between the stable sites in the conditioned glass surface (gel layer) and the solution phase appears to be the mechanism by which the surface phase-boundary potential mirrors changes in hydrogen ion activity in the solution. The fact that this process is one of proton transfer rather than electron transfer is the reason for the freedom from redox perturbations.

Although the glass electrode exhibits remarkable specificity for hydrogen ion, it is by no means perfect. Departures from ideal behavior can be found in alkaline solutions containing high concentrations of alkali metal ions and also in solutions of strong acids. By modifying the composition of pH glasses, electrodes have been developed which show a reduction in both the alkaline and acid errors. This should be considered when selecting glass electrodes; that is, the type of electrode chosen should be substantially error-free under the conditions of measurement. The glass electrode has been fabricated into a wide variety of designs for special applications. The most common type is the immersion electrode, but capillary and microelectrodes are also used rather widely, particularly in biological studies [28, 29].

The metal-oxide electrodes, e.g., antimony, bismuth, iridium, and tungsten, develop a potential by a redox reaction involving the metal and a thin layer of oxide present on the surface of the metal. In practice, their pH response is variable and non-linear. Careful calibration is critical. The electrode response is sensitive to dissolved oxygen concentration, the composition of the buffer and test solutions, and to stirring rate. It is also affected by oxidizing and reducing agents, certain complexing anions, and traces of some cations. The main advantages of the metallic pH electrodes are rapid response and rugged construction. They can be used under extreme pressure and/or temperature conditions. They are also relatively inexpensive, and exhibit low impedance, thus requiring less sophisticated (and less expensive) read-out devices.

The quinhydrone electrode is also a redox electrode that produces an emf dependent upon the pH. It is subject to a variety of limitations which greatly restricts its use. For example, it is subject to an alkaline error that limits its application to solutions of pH less than 8. Of less importance is the salt error resulting from unequal changes in the activity coefficients of hydroquinone and quinone. However, this error becomes important only at high ionic strengths. Finally, this electrode is poisoned by proteins, and cannot be used in the presence of strong oxidizing or reducing agents. The use of the quinhydrone electrode has all but been abandoned. Its inclusion in this report is primarily for completeness and for historical reasons.

The electrical circuit of the pH cell is usually completed via a salt bridge and reference electrode. The three main requirements for a satisfactory reference electrode are reversibility, reproducibility and stability [19]. The four principal reference electrodes are the mercury/mercury(I) chloride (calomel), the silver/silver chloride, the mercury/mercury(I) sulfate, and the thallium amalgam/thallium(I) chloride electrodes. The most widely used reference electrode is probably the calomel electrode which is highly reproducible but suffers from instability at elevated temperatures (>80 °C) caused by disproportionation of the mercury(I) chloride. The silver/silver chloride and thallium amalgam/thallium(I) chloride are less sensitive to temperature effects and are recommended for measurements above 80 °C.

Probably the greatest source of difficulty in a pH cell is the liquid junction which is formed at the area of contact between the salt bridge and the test solution. The magnitude of the liquid-junction potential depends on the design and characteristics of the liquid junction, e.g., the composition and

concentration of the salt-bridge solution, and the type of junction (capillary, porous plug, cracked bead, sleeve, membrane, flowing). Unfortunately, measurements made with the best reference electrodes and the most reproducible liquid junctions are still subject to a residual liquid-junction potential error. This error results from a difference in the liquid-junction potentials at the boundaries between the salt bridge and the test and standard buffer solutions. In general, the residual liquid-junction potential can be minimized by correct design of the liquid junction, properly selected salt-bridge solution, ionic strengths of the test and standard solutions approximately equal or less than 0.1, the pH between 3 and 11, the proper choice of standards, and the exclusion of other phases such as colloids and suspensions. A more detailed discussion of these and other sources of error in potentiometric measurements can be found in reference 30.

The most commonly used salt-bridge solution is potassium chloride saturated at room temperature. It has been demonstrated experimentally, and can also be shown by calculations using the Henderson equation for liquid-junction potentials [13], that the higher the concentration of KCl in the salt-bridge solution, the more effective it is in reducing the liquid-junction potential. The saturated KCl salt bridge is not without its disadvantages, however. The most serious problem is the blockage of flow at the liquid junction by crystals of KCl which form upon lowering of the temperature or, over longer periods, caused by evaporation of water from the salt-bridge solution. The blockage raises the resistance of the cell and impairs the reproducibility of the liquid-junction potential. For this reason, a slightly unsaturated solution, but not less than 3.5 mol/L, is recommended.

9. Conclusion

The definition and measurement of pH, as we know it today, is the result of eight decades of research and evolutionary development. This process is continuing as the feasibility of providing matrix-specific pH standards for selected applications is being tested. The first application of such standards is embodied in SRM 2694, Simulated Rainwater. The effort at NBS will be expanded to include matrices such as seawater, biological fluids, and eventually non-aqueous media. This new generation of pH standards will be consistent with the current NBS pH scale and will be as thermodynamically meaningful as possible. This should avoid the confusion that would be caused by several inconsistent pH scales. This work will necessarily involve a re-evaluation of the presently accepted definitions and conventions incorporated in the pH values of the SRMs issued by NBS and of the recommended standards of organizations such as the International Union of Pure and Applied Chemistry [31].

The ultimate goal of the NBS research program on pH is to develop and maintain a unified pH scale based on clearly stated thermodynamic criteria, with a wide range of applicability to practical pH measurements. The present projects form the foundations for this goal and will lead to intensive investigations into liquid junction potentials, activity coefficients, and the concept of single ion activities.

10. Acknowledgement

The authors wish to acknowledge the contributions of Dr. Roger G. Bates and Dr. Walter J. Hamer, whose efforts over many years at NBS resulted in the basis for the national pH scale described in this report.

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National Bureau of Standards

Certificate

Standard Reference Material 185f

Potassium Hydrogen Phthalate

pH Standard

This Standard Reference Material (SRM) is intended for use in preparing solutions for calibrating electrodes for pH measuring systems. SRM 185f, Potassium Hydrogen Phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$), was prepared to insure high purity and uniformity.

The pH value of the standard pH(S), corresponds to $\log(1/a_{\text{H}})$ where a_{H} is a conventional activity of the hydrogen (hydronium) ion referred to the standard state on the molal scale. The certified values listed below were derived from emf measurements of cells without liquid junction by the method of calculation described in the Journal of Research of the National Bureau of Standards 66A, 179 (1962). The uncertainty of the pH(S) of SRM 185f is estimated not to exceed ± 0.005 unit for the temperature range 0 to 50 °C.

The 0.05-molal solution is recommended for the standardization of pH equipment. The pH(S) of this solution as a function of temperature is given below: These certified values apply only to SRM 185f.

<u>°C</u>	<u>pH(S)</u>	<u>°C</u>	<u>pH(S)</u>
0.0	4.006	30.0	4.012
5.0	4.001	35.0	4.021
10.0	3.999	37.0	4.025
15.0	3.999	40.0	4.031
20.0	4.001	45.0	4.043
25.0	4.006	50.0	4.057

The values of pH(S) of SRM 185f were not measured above 50 °C. For pH(S) values for the temperature range 55-95 °C for potassium hydrogen phthalate, refer to National Bureau of Standards Special Publication 260-53, "Standardization of pH Measurements," December 1975, pp 25-26. The estimated uncertainty of these values as applied to SRM 185f is ± 0.01 unit for the temperature range 55-95 °C.

The potassium hydrogen phthalate was obtained from Mallinckrodt, Inc. It meets the specifications of the American Chemical Society for reagent-grade material, but may not be entirely free of impurities such as traces of occluded water, free acid or alkali, chlorides, sulfur compounds, or heavy metals.

The analytical measurements were performed by Yung-Chi Wu and William F. Koch of the Inorganic Analytical Research Division.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of E.L. Garner, Chief, Inorganic Analytical Research Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W.P. Reed.

Directions for Use

Preparation of the 0.05-molal solution: The salt should be dried for 2 hours at 110 °C before use. Add 10.21g of SRM 185f to 1000.0g of distilled water and mix thoroughly. The distilled water should have a conductivity not greater than 2×10^{-6} siemens/cm. If volumetric apparatus is to be used, transfer 10.12g of SRM 185f to a 1-liter volumetric flask. Add distilled water to dissolve the salt, fill to the mark with distilled water at 25 °C, and mix thoroughly by shaking.

The water used in the preparation of this pH buffer solution need not be protected from atmospheric carbon dioxide, and elaborate precautions for the exclusion of air from the solution are not necessary. The solution should, however, be protected against evaporation and contamination by molds. This buffer solution should be replaced, at least every month or whenever mold is detected, if the highest accuracy is required.

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

Certificate

Standard Reference Materials

Potassium Dihydrogen Phosphate (186-I-c)

Disodium Hydrogen Phosphate (186-II-c)

These standard reference materials are intended for use in defining the pH(S) scale. The lots of potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4) were prepared to ensure high purity and uniformity. They meet the specifications of the American Chemical Society for reagent-grade materials, but should not be considered as entirely free from impurities such as traces of water, free acid or alkali, carbon dioxide, chlorides, sulfur compounds and heavy metals.

The pH(S) values listed below correspond to $\log(1/a_{\text{H}})$, where a_{H} is a *conventional* activity of the hydrogen (hydronium) ion referred to the standard state on the scale of molality. The values were derived from the emf of cells without liquid junction by the method of calculation described in the Journal of Research of the National Bureau of Standards, 66A, 179 (1962). The uncertainty of the assigned values of pH(S) is estimated not to exceed ± 0.005 unit from 0 to 50 °C. The values listed below apply only to the lots here certified. Minor variation of pH(S) (of the order of a few thousandths of a unit) may be expected to occur between different lots.

The solution 0.025 molal with respect to both KH_2PO_4 and Na_2HPO_4 is recommended for the calibration of pH equipment. The pH(S) of this solution as a function of temperature is given below:

°C	pH(S)	°C	pH(S)	°C	pH(S)
0	6.982	20	6.878	37	6.839
5	6.949	25	6.863	40	6.836
10	6.921	30	6.851	45	6.832
15	6.898	35	6.842	50	6.831

For pH measurements in the physiologically important range pH 7 to 8 a solution 0.008695 molal in KH_2PO_4 and 0.03043 molal in Na_2HPO_4 is also useful. The pH(S) values for this solution as a function of a temperature follow: [See Journal of Research of the National Bureau of Standards, 65A, 267 (1961).]

°C	pH(S)	°C	pH(S)	°C	pH(S)
0	7.534	20	7.430	37	7.392
5	7.501	25	7.415	40	7.388
10	7.472	30	7.403	45	7.385
15	7.449	35	7.394	50	7.384

The potassium dihydrogen phosphate was obtained from the Mallinkrodt Chemical Works of St. Louis, Missouri; the disodium hydrogen phosphate from the J. T. Baker Chemical Co., of Phillipsburg, New Jersey. The experimental work leading to the certification of this material was carried out by M. Paabo and B. R. Staples.

The overall direction and coordination of technical measurements leading to the certification were performed under the chairmanship of R. A. Durst.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T. W. Mears.

Washington, D. C. 20234
September 1, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

(over)

PREPARATION OF THE 0.025-MOLAL SOLUTION

Transfer 3.387 g of the potassium dihydrogen phosphate (186-I-c) and 3.533 g of the disodium hydrogen phosphate (186-II-c) to a 1-liter volumetric flask. Dissolve and fill to the mark with distilled water at 25 °C. The distilled water should not contain dissolved carbon dioxide and should have a conductivity no greater than 2×10^{-6} ohm⁻¹ cm⁻¹. Carbon dioxide-free water can be prepared by boiling a good grade of distilled water for 10 minutes and guarding it with a soda-lime tube while cooling. The salts should be dried for 2 hours at 110 °C to 130 °C before use. Although elaborate precautions to prevent contamination of the buffer solution with atmospheric carbon dioxide are usually unnecessary, the container should be kept tightly stoppered at all times when a sample is not actually being removed. (The figures given are weights in air.)

The solution should be replaced after a few weeks or sooner if molds or sediment appear, or if it has been exposed repeatedly to air containing carbon dioxide.

PREPARATION OF THE PHYSIOLOGICAL STANDARD SOLUTION

The physiological standard solution pH(S) = 7.415 at 25 °C, is prepared by transferring 1.179 g of potassium dihydrogen phosphate (186-I-c) and 4.303 g of disodium hydrogen phosphate (186-II-c) to a 1-liter volumetric flask, dissolving, and filling to the mark with water of the quality described above. (The figures given are weights in air.)

This buffer solution is more sensitive to contamination with carbon dioxide than is the 0.025-molal solution. If the solution is to maintain the assigned pH(S) for a few weeks, exclusion of carbon dioxide may be essential.



National Bureau of Standards

Certificate

Standard Reference Material 187c

Sodium Tetraborate Decahydrate

(Borax)

This Standard Reference Material (SRM) is intended for use in preparing solutions for calibrating electrodes for pH measuring systems. SRM 187c, Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) meets the specifications of the American Chemical Society for reagent grade material. The water content of this salt, stored under ordinary conditions, is less than theoretical. This does not affect the use of this salt as a pH standard, but could lead to erroneous results if the partially desiccated salt is used as a boron or acidimetric standard.

The pH(S) values listed below correspond to $\log(1a_{\text{H}})$, where a_{H} is a conventional activity of the hydrogen (hydronium) ion referred to the standard state ($p^\circ = 1$ atmosphere) on the scale of molality. The values were derived from emf measurements of cells without liquid junction by the method of calculation described in the *Journal of Research of the National Bureau of Standards*, 66A, 179 (1962). The uncertainty of the pH(S) of Standard Reference Material 187c is estimated not to exceed ± 0.005 unit from 0 to 50 °C.

The 0.01-molal solution is recommended for the calibration of pH equipment. The pH(S) of this solution as a function of temperature is as follows: These certified values apply only to SRM 187c.

<u>°C</u>	<u>pH(S)</u>	<u>°C</u>	<u>pH(S)</u>	<u>°C</u>	<u>pH(S)</u>
0.0	9.463	20.0	9.226	40.0	9.070
5.0	9.395	25.0	9.180	45.0	9.042
10.0	9.333	30.0	9.139	50.0	9.018
15.0	9.277	35.0	9.102		

The borax was obtained from Mallinckrodt, Inc. The experimental work leading to the certification of this material was carried out by W.E. Koch, and Yung-Chi Wu of the Inorganic Analytical Research Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W.P. Reed.

Washington, DC 20234
March 22, 1984

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(Over)

Directions for Use

Preparation of the 0.01-molal solution: Crush gently any large lumps of salt. The salt must not be dried in an oven before use. Transfer 3.81 g of the borax to a flask and dissolve in 1.000 kg of distilled carbon dioxide-free water. Alternatively, if volumetric apparatus is to be used, transfer 3.80 g to a 1-liter volumetric flask, dissolve in distilled carbon dioxide-free water, and fill to the mark with water at 25 °C. Water, sufficiently carbon dioxide-free, can be prepared by boiling for 10 min. and cooling in a vessel guarded by a soda-lime tube. The water should have a conductance less than $2 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. To avoid contamination of the buffer solution with atmospheric carbon dioxide, keep the stopper in place except when removing a portion of the solution. If desired, the solution may be protected with a soda-lime tube. Prepare fresh solutions at least once a month. For the highest accuracy, prepare fresh solutions on a weekly basis.

National Bureau of Standards

Certificate

Standard Reference Material 188

Potassium Hydrogen Tartrate (pH Standard)

This Standard Reference Material (SRM) is intended for use in preparing solutions for calibrating electrodes for pH measuring systems. SRM 188, potassium hydrogen tartrate ($\text{KHC}_4\text{H}_4\text{O}_6$), is a material of high purity and uniformity; however, it should not be considered entirely free from impurities such as traces of free acid or alkali, occluded water, chlorides, sulfur compounds, and heavy metals.

The certified values listed in the table below are the assigned pH(S) numbers for solutions of Standard Reference Material 188 as functions of temperature. These values correspond to $\log(1/a_{\text{H}})$, where a_{H} is the conventional activity of the hydrogen ion referred to the standard state on the scale of molality. They were derived from emf measurements of cells without liquid junction by the method of calculation described in the Journal of Research of the National Bureau of Standards 66A, 179(1962). The uncertainty in the pH(S) values listed is estimated not to exceed ± 0.005 unit from 0 to 60 °C and ± 0.01 unit from 70 to 95 °C. The certified values apply only to SRM 188.

A solution saturated with potassium hydrogen tartrate at 25 °C \pm 1 °C is recommended as a standard for the calibration of pH equipment between 25 and 95 °C.

Table 1

°C	pH(S)	°C	pH(S)	°C	pH(S)
25	3.557	45	3.547	70	3.580
30	3.552	50	3.549	80	3.609
35	3.549	55	3.554	90	3.650
38	3.548	60	3.560	95	3.674
40	3.547				

The 0.01 molal solution is recommended as a standard for the range 0 to 60 °C.

Table 2

°C	pH(S)	°C	pH(S)	°C	pH(S)
0	3.711	20	3.647	40	3.632
5	3.689	25	3.639	45	3.635
10	3.671	30	3.635	50	3.639
15	3.657	35	3.632	55	3.644
		38	3.631	60	3.651

Gaithersburg, MD 20899
 May 18, 1987
 (Revision of certificate
 dated 1-10-64)

Stanley D. Rasberry, Chief
 Office of Standard Reference Materials

Directions for Use

Preparation of the saturated solution: Add an excess of undried SRM 188 to distilled water in a glass-stoppered bottle or flask and shake vigorously. With 100 percent excess of the salt, a few minutes of shaking is sufficient for saturation. (Note: 100 mL of water at 25 °C will dissolve about 0.7 g of potassium hydrogen tartrate.) Allow the solid to settle and decant the clear solution, or filter if necessary. Store the solution in a glass-stoppered borosilicate glass bottle.

Preparation of the 0.01 -molal solution: Add 1.883 g (air weight) of undried SRM 188 to 1000.0 g of distilled water and mix thoroughly. If volumetric apparatus is to be used, transfer 1.878 g (air weight) of Standard Reference Material 188 to a 1-liter volumetric flask. Fill to the mark with distilled water and shake until all of the salt is dissolved and the solution thoroughly mixed.

Solutions of tartrate are very susceptible to mold growth, which is usually accompanied by an increase of a few hundredths in pH. For accurate results, tartrate standards should be prepared fresh each day. The distilled water used in preparation of these solutions should have a conductivity not greater than $2 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25 °C, but dissolved carbon dioxide need not be removed.

National Bureau of Standards

Certificate

Standard Reference Material 189a

Potassium Tetroxalate

pH Standard

This Standard Reference Material (SRM) is intended for use in calibrating pH measuring systems. SRM 189a, Potassium Tetroxalate Dihydrate ($\text{KHC}_2\text{O}_4 \cdot 2\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), is a highly pure and uniform material and its assay is close to 100 percent.

The pH value of this SRM, pH(S), corresponds to $\log(1/a\text{H})$ where aH is a conventional activity of the hydrogen ion referred to the standard state on the molal scale. The certified values listed below were derived from emf measurements of cells without liquid junction by the method of calculation described in the Journal of Research of the National Bureau of Standards 89, 395 (1984). The uncertainty of the pH(S) of SRM 189a is estimated not to exceed ± 0.005 unit for the temperature range 5 to 50 °C.

The liquid-junction potential of the common pH cell displays a considerably greater variability in solutions of pH less than 2.5 than in solutions of pH between 2.5 and 11.5. For this reason, solutions of potassium tetroxalate are not recommended as primary standards of pH. They are useful, however, as secondary standards and for confirmatory purposes, with the expectation that the experimental pH may differ by 0.02 to 0.05 unit from the values of pH(S) given below. They are also recommended when standards of pH are needed and a liquid junction is not involved.

The 0.05-molal solution is recommended for the standardization of pH equipment. The pH(S) of this solution as a function of temperature is given below. These certified values apply only to SRM 189a.

<u>°C</u>	<u>pH</u>	<u>°C</u>	<u>pH</u>
5	1.669	30	1.686
10	1.671	35	1.692
15	1.673	40	1.697
20	1.677	45	1.706
25	1.681	50	1.714

The values of pH(S) of SRM 189a were not measured above 50 °C for potassium tetroxalate, refer to the National Bureau of Standards Special Publication 260-53, "Standardization of pH Measurements," December 1975, pp 25-26. (The estimated uncertainty of these values as applied to SRM 189a is ± 0.01 for the temperature range 55-95 °C.)

The potassium tetroxalate was obtained from Fluka Chemical Corp. It meets the specifications of the American Chemical Society for reagent-grade material, but may not be entirely free of impurities such as traces of occluded water, free acid or alkali, chlorides, sulfur compounds, or heavy metals.

The analytical measurements were performed by Yung-Chi Wu and W.F. Koch of the Inorganic Analytical Research Division.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of J.R. DeVoe, Chief, Inorganic Analytical Research Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R.W. Seward.

Gaithersburg, MD 20899
April 21, 1986

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(over)

Directions for Use

Preparation of the 0.05-molal solution: Add 12.70 g of SRM 189a to 1000.0 g of distilled water and mix thoroughly. The distilled water should have a conductivity not greater than 2×10^{-6} siemens/cm. If volumetric apparatus is to be used, transfer 12.61 of SRM 189a to a 1-liter volumetric flask. Add distilled water to dissolve the salt, fill to the mark with distilled water at 25 °C, and mix thoroughly by shaking.

The water used in the preparation of this pH buffer solution need not be protected from atmospheric carbon dioxide, and elaborate precautions for the exclusion of air from the solution are not necessary. The solution should, however, be protected against evaporation and contamination by molds. This buffer solution should be replaced, at least every month or whenever mold is detected, if the highest accuracy is required.

National Bureau of Standards

Certificate

Standard Reference Materials

191a Sodium Bicarbonate

192a Sodium Carbonate

These Standard Reference Materials are intended for use in preparing buffer solutions to calibrate electrodes for pH measuring systems. The lots of sodium bicarbonate (NaHCO_3) and sodium carbonate (Na_2CO_3) were prepared to ensure high purity and uniformity. They meet the specifications of the American Chemical Society for reagent-grade materials, but should not be considered entirely free from impurities such as traces of water, free alkali, silica, chlorides, sulfur compounds and heavy metals.

pH(S) Values

The pH(S) values listed below correspond to $\log(1/a_{\text{H}})$, where a_{H} is a conventional activity of the hydrogen ion referred to the standard state on the scale of molality. The values were derived from the emf of cells without liquid junction by the method of calculation described in the Journal of Research of the National Bureau of Standards, 66A, 179 (1962). The uncertainty of the assigned values of pH(S) is estimated not to exceed ± 0.005 unit from 0 to 50 °C. The certified values listed below apply *only* to these lots.

A solution 0.025 molal with respect to both NaHCO_3 and Na_2CO_3 is recommended for the calibration of the glass electrode and pH meter used for pH measurements. The pH(S) of this solution as a function of temperature is given below.

<u>°C</u>	<u>pH(S)</u>	<u>°C</u>	<u>pH(S)</u>	<u>°C</u>	<u>pH(S)</u>
0.0	10.316	20.0	10.062	40.0	9.884
5.0	10.244	25.0	10.011	45.0	9.850
10.0	10.178	30.0	9.965	50.0	9.819
15.0	10.118	35.0	9.922		

The sodium bicarbonate and sodium carbonate were obtained from the Mallickrodt, Inc., St. Louis, Mo. The experimental work leading to the certification of this material was carried out by Y.C. Wu, G. Marinenko and W.F. Koch, NBS Inorganic Analytical Research Division.

The overall direction and coordination of technical measurements leading to the certification were performed under the chairmanship of E.L. Garner, Chief, NBS Inorganic Analytical Research Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W.P. Reed and L.J. Powell.

Gaithersburg, MD 20899
November 21, 1984
(Revision of Certificate
dated 5-11-83)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(over)

Directions for Use

Preparation of the 0.025-molal solution: Transfer 2.092 g of sodium bicarbonate (SRM 191a) and 2.640 g of Na_2CO_3 (SRM 192a) (weights in air) to a 1-liter volumetric flask. Dissolve and fill to the mark with distilled water at 25 °C. The distilled water should contain no dissolved carbon dioxide and should have a conductivity no greater than 2×10^{-6} siemens/cm. Carbon dioxide-free water can be prepared by boiling a good grade of distilled water for 10 min. and guarding it with a soda lime tube while cooling. The sodium bicarbonate should not be dried by heating; the sodium carbonate should be dried for 2 hr. at 275 °C before use. Although elaborate precautions to prevent contamination of the buffer solution with atmospheric carbon dioxide are usually unnecessary, the container should be kept tightly stoppered at all times when a sample is not actually being removed.

The solution should be replaced after a few weeks or sooner if sediment appears or if it has been exposed repeatedly to air containing carbon dioxide.

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 2694

Simulated Rainwater

This Standard Reference Material (SRM) has been developed to aid in the analysis of acidic rainwater by providing homogeneous materials as control standards at each of two levels of acidity. SRM 2694 consists of four 50 mL solutions, two at each level, in polyethylene bottles. It was prepared by the dissolution of high-purity salts and acids in high-purity distilled/deionized water. Certified values and method(s) used for certification are given in Table 1. Values in parentheses are *not* certified, but are included for information only. Transition and heavy metals are not included in SRM 2694 as they are not stable in solutions at this pH level. Analysts are referred to SRM 1643b "Trace Elements in Water" for applications involving trace metal determinations.

Table 1

Simulated Rainwater

Constituent Elements/ Parameters	Methods	2694-I	2694-II
pH @ 25 °C	c	4.27 ± 0.03	3.59 ± 0.02
Specific Conductance (μS/cm @ 25.0 °C)	b	26 ± 2	130 ± 2
Acidity, meq/L	d	0.050 ± 0.002	0.284 ± 0.005
Fluoride, mg/L	a,c	0.054 ± 0.002	0.098 ± 0.007
Chloride, mg/L	a,c	(0.24)	(1.0)
Nitrate, mg/L	a,f	—	7.06 ± 0.15
Sulfate, mg/L	a,e	2.75 ± 0.05	10.9 ± .2
Sodium, mg/L	a,g,h	0.205 ± 0.009	0.419 ± 0.015
Potassium, mg/L	a,g,h	0.052 ± 0.007	0.106 ± 0.008
Ammonium, mg/L	a,c	—	(1.0)
Calcium, mg/L	g,i,k	0.014 ± 0.003	0.049 ± 0.011
Magnesium, mg/L	g,j	0.024 ± 0.002	0.051 ± 0.003

The certified values are based on proven reliable methods of analysis. The estimated uncertainties are 2 standard deviations of the certified values, except for uncertainties associated with SO₄, acidity, pH, and specific conductance which are based on scientific judgment and are roughly equivalent to 2 standard deviations of the certified value.

Note: The nitrate value for 2694-I is not certified because of instability. It is believed that bacterial or fungal activity contributes to that instability.

Techniques:

- | | |
|--|--|
| a. Ion Chromatography | f. Spectrophotometry |
| b. Conductimetry | g. Laser Enhanced Ionization Spectrometry |
| c. Potentiometry/Ion Selective Electrodes | h. Flame Emission Spectrometry |
| d. Coulometry | i. Inductively Coupled Plasma Spectrometry |
| e. Isotope Dilution Thermal Ionization Mass Spectrometry | j. Flame Atomic Absorption Spectrometry |
| | k. Direct Current Plasma Spectrometry |

The overall direction and coordination of the technical measurements leading to this certificate were performed under the direction of J.R. DeVoe, Chief, NBS Inorganic Analytical Research Division.

The technical and support aspects involved in the preparation, analysis, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T.E. Gills and L.J. Powell.

Gaithersburg, MD 20899
 April 23, 1986
 (Revision of Certificate
 dated 9-19-85)

Stanley D. Rasberry, Chief
 Office of Standard Reference Materials

(Over)

The preparation and analyses of these solutions were performed by W.F. Koch, G. Marinenko, T.C. Rains, R. W. Burke, M. Knoerdel, W.R. Kelly, G.C. Turk, Mo De-Ming, M.S. Epstein, T.A. Rush, T.A. Butler, K. Han and M.V. Smith in the NBS Inorganic Analytical Research Division.

The statistical analysis of the certification data was performed by R.C. Paule of the National Measurement Laboratory.

Notice and Warnings to Users:

Expiration of Certification: The data included in this Certificate of Analysis are valid for 6 months from the shipping date.

Precautions: The solutions of SRM 2694 are very dilute, unbuffered, and as such are very susceptible to contamination. Therefore, the solutions should be used immediately upon opening. No assurances can be made as to the composition or stability of the solutions after being opened and recapped. SRM 2694 should be stored in an area free from acid and/or ammonia fumes or vapors. Refrigeration of the solutions is not necessary; however, they should not be exposed to extreme heat.

Additional Information: If conductance and pH are to be measured on the same sample, then conductance must be measured first to prevent leakage from the pH reference electrode filling solution from affecting the conductance. The measurement of pH should be performed according to the guidelines set forth in the attachment to this document to minimize the bias caused by residual liquid junction potentials. Acidimetric titrations should be performed on samples that have been purged of dissolved carbon dioxide to prevent drifting endpoints and high results. Care must be exercised in the determination of chloride and fluoride by ion chromatography to avoid possible errors associated with the negative water-dip in the baseline.

Ammonium ion is not certified in these solutions because of the instability of ammonium ion, particularly in 2694-I. The concentration of ammonium ion in 2694-I was originally 0.1 $\mu\text{g/L}$, but is gradually decreasing. Thus no value is given for ammonium in this solution. The concentration of ammonium in 2694-II appears to be more stable than in 2694-I. Thus a value of 1.0 mg/L is given *for information only*. However the user should be aware of the possible unreliability of this value. The cause of the instability is not known at this time. It does not appear to affect significantly any other component in the solutions.

The temperature coefficient for the specific conductance of both solutions in SRM 2694 has been determined experimentally to be 1.5 percent per degree Celsius at 25 °C. The density of the solutions is 0.997 g/mL at 23 °C.

SRM 2694

Page 2

GUIDELINES FOR THE MEASUREMENT OF pH IN ACIDIC RAINWATER

This report presents a recommended procedure for the measurement of pH in acidic rainwater. The intent of this guideline is to improve the accuracy and precision of the pH measurement with special emphasis on reducing the effect of the residual liquid junction potential. It consists of three major parts: Calibration Sequence, Control Sequence, and Rainwater Measurement Sequence. The purposes of the Calibration Sequence are to accurately calibrate the pH measurement system with robust buffer solutions, to accurately set the slope, and to verify that the measurement system is functioning properly. The purpose of the Control Sequence is to quantitatively determine the magnitude of the residual liquid junction potential bias for a particular set of electrodes which must be applied in the rainwater measurement sequence to obtain more reliable and intercomparable results. Each sequence should be executed in stepwise order with strict adherence to detail.

Note: This guideline is applicable only to the measurement of pH in acidic rainwater and acidic low ionic strength aqueous solutions. It should not be used for other applications as inaccuracies may ensue.

General Directions

Record the solution temperature to within 1 °C. Record all pH values to at least 0.01 pH unit. Make all measurements in a quiescent solution. Fully document all calibration and control standards.

Calibration Sequence

- 1) Standardize the pH electrodes and meter using SRM 185F, Potassium Hydrogen Phthalate [pH(S) 4.006 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. Rinse the electrodes with distilled water (ASTM Type II or better).
- 2) With the slope adjustment of the meter set at 100 percent, and the temperature adjustment set at the temperature of the buffer solution, check the Nernstian 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.^A 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.^B DO NOT CONTINUE until the conditions for calibration and Nernstian response have been satisfied. If the reading for the second buffer is within 0.03 pH units of the prescribed value, record the value and continue.

Control Sequence

- 3) 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.
- 4) Insert the electrodes into a clean beaker (10-20 mL capacity) containing a portion (10-20 mL) of the rainwater control standard (e.g., SRM 2694-I^C). Be certain that the reference junction and glass bulb are completely immersed. Do not insert the electrodes directly into the polyethylene bottles.
- 5) Stir or swirl the solution to ensure homogeneity and contact with the electrodes.
- 6) Allow the solution to settle to a quiescent state (approx. 30 seconds). Record the pH after the reading has stabilized.^D
- 7) Discard this portion of the control standard. Do not use for subsequent control checks or for other analytical determinations such as specific conductance, anions, cations, and acidity.
- 8) Repeat steps 3 through 7 with a second rainwater control standard (e.g., SRM 2694-II).^C
- 9) Calculate the differences between the true pH values of the rainwater control standard and the values as determined by the pH measurement system.^E Average the differences and apply this bias correction to subsequent rainwater measurements. (For example, if the pH measurement system displays the pH of the control 0.13 pH units lower than the true value, add 0.13 pH units to the subsequent pH measurements of rainwater.)

Rainwater Measurement Sequence

- 10) 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.
- 11) Insert the electrodes into a clean beaker containing a portion (10-20 mL) of the rainwater sample. Be certain that the reference junction and glass bulb are completely immersed.
- 12) Stir or swirl the solution to ensure homogeneity and contact with the electrodes.
- 13) Allow the solution to settle to a quiescent state (approx. 30 seconds). Record the pH after the reading has stabilized.
- 14) Apply the bias correction as determined in step 9 and report this corrected value as the pH of the rainwater sample.
- 15) Discard this portion of the rainwater sample. Do not use it in other analytical tests.
- 16) Repeat steps 10 through 15 for subsequent rainwater samples.
- 17) Repeat the Control Sequence at regular intervals, based upon quality control guidelines, performance history of the measurement system, frequency of measurements, and required accuracy.

Storage of Electrodes

- 18) When not in use, soak the electrodes in a solution which is 0.1 mol/L potassium chloride and 1×10^{-4} mol/L hydrochloric acid. Do not store the electrodes in buffers, concentrated acids, concentrated potassium chloride, basic solutions, or distilled water. Do not allow the electrodes to dry out.
- 19) Use these electrodes exclusively for rainwater measurements.

Notes

- A) For the highest accuracy and the most direct traceability to the National Bureau of Standards, it is recommended that freshly prepared solutions of Standard Reference Materials (SRM's) be used.
- B) 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, and
 - 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.
- C) Standard Reference Material 2694, Simulated Rainwater, is issued by the National Bureau of Standards, Office of Standard Reference Materials.
- D) Some systems may require five minutes or more to stabilize. If drifting persists, record the reading after 10 minutes and annotate the data accordingly. With such severe drift, it would be advisable to acquire a different type of pH electrodes which do not exhibit this adverse characteristic.
- E) The difference should agree to within 0.05 pH units. If not, repeat the Control Sequence.

A NOTE TO THE USER OF THIS SRM

Please take a moment to fill out and return this registration sheet. Frequently, we have difficulty contacting the actual users of SRMs, because the addresses to which we ship are often those of procurement agents. The information on this registration sheet will enable us to inform you, the user, directly of any changes in the Certificate, additions to the catalog, or other matters which may be of interest to you. Return of this sheet will also entitle you to a copy of a NBS Special Publication, describing the production, methods of analysis, and recommended uses of this SRM.

Thank you.

**PLEASE TAKE A MOMENT TO REGISTER YOUR NEW
SRM 2694, SIMULATED RAINWATER**

Date received: _____

Invoice No.: _____

Name: _____

Title: _____

Address: _____

Phone: _____

Comments: _____

**OFFICE OF STANDARD REFERENCE MATERIALS
ROOM B 316, CHEMISTRY BUILDING
NATIONAL BUREAU OF STANDARDS
GAITHERSBURG, MD 20899**

ATTN: T. E. GILLS

National Bureau of Standards

Certificate

Standard Reference Material 2185

Potassium Hydrogen Phthalate

pD Standard

This Standard Reference Material (SRM) is intended for use in preparing buffer solutions to calibrate electrodes for pD measuring systems. SRM 2185, Potassium Hydrogen Phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$), was prepared to ensure high-purity and uniformity. It meets the specifications of the American Chemical Society for reagent-grade material; however, it should not be considered to be entirely free of impurities such as traces of occluded water, free acid or alkali, chlorides, sulfur compounds, or heavy metals.

pD(S) Values

The certified pD(S) values listed below correspond to $\log(1/a_D)$, where a_D is a conventional activity of the deuterium ion referred to the standard state on the molal scale. The certified values were derived from emf measurements of cells without liquid junction by the method of calculation similar to that described in the Journal of Research of the National Bureau of Standards, 66A, 179 (1962). The uncertainty of the certified values of pD(S) is estimated not to exceed ± 0.005 unit from 5 to 50 °C. This uncertainty includes allowances for random error and all known sources of possible systematic error.

A 0.05-molal solution is recommended for the calibration of the glass electrode and pH meter used for pD measurement. The pD(S) of this solution as a function of temperature is given below:

<u>°C</u>	<u>pD(S)</u>	<u>°C</u>	<u>pD(S)</u>
5.0	4.542	30.0	4.518
10.0	4.532	35.0	4.521
15.0	4.524	40.0	4.527
20.0	4.520	45.0	4.534
25.0	4.518	50.0	4.543

The potassium hydrogen phthalate was obtained from Mallinckrodt, Inc., St. Louis, Mo.

The analytical measurements leading to the certification of the material were performed by Y.C. Wu and W.F. Koch, NBS Inorganic Analytical Research Division.

The overall direction and coordination of technical measurements leading to certification were performed under the chairmanship of J.R. DeVoe, Chief, NBS Inorganic Analytical Research Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W.P. Reed and L.J. Powell.

Gaithersburg, MD 20899
November 28, 1984

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(over)

Directions for Use

Preparation of the 0.05-molal solution: SRM 2185 should be dried for 2 hours at 110 °C before use. Add 10.218 g of the dried SRM to 1000.0 g of deuterium oxide (weights in air) and mix thoroughly. If volumetric apparatus is to be used, transfer 11.237 g of the dried SRM (weight in air) to a 1-liter volumetric flask. Dissolve and fill to the mark with deuterium oxide at 25 °C. Mix thoroughly by shaking. The deuterium oxide should have an isotopic composition of at least 99 mole percent D₂O and should have a conductivity no greater than 2×10^{-6} siemens/cm.

The buffer solution should be protected from air during storage and all transfers of the D₂O solution should be done in an inert atmosphere to avoid rapid isotope exchange. If the calibration process is completed within one hour, it is not necessary to exclude air from the working solution. The buffer solution should be discarded after a few weeks, or sooner, if mold is detected or if it has been exposed repeatedly to air.

U. S. Department of Commerce

C. R. Smith

Secretary

National Bureau of Standards

A. V. Astin, Director



Certificate of Analysis

Standard Reference Materials

Potassium Dihydrogen Phosphate (2186—I)

Disodium Hydrogen Phosphate (2186—II)

Purity

These lots of potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4) were prepared to ensure high purity and uniformity. They meet the specifications of the American Chemical Society for reagent-grade materials but should not be considered as entirely free from impurities such as traces of water, free acid or alkali, carbon dioxide, chlorides, sulfur compounds and heavy metals.

$pD(S)$ Values

The $pD(S)$ values listed below correspond to $\log(1/a_D)$, where a_D is the *conventional* activity of the deuterium ion referred to the standard state on the scale of molality. The values were derived from the emf of cells without liquid junction by a method of calculation analogous to that described for the assignment of $pH(S)$ values [Journal of Research of the National Bureau of Standards, 66A, 179 (1962)]. The uncertainty of the assigned values for $pD(S)$ is estimated not to exceed 0.01 unit. The values listed below apply only to the lots here certified. Minor variations of $pD(S)$ (of the order of a few thousandths of a unit) may be expected to occur between different lots.

The solution 0.025 molal with respect to both KD_2PO_4 and Na_2DPO_4 is recommended for the calibration of pH meters to be used for the measurement of pD in deuterium oxide. These compounds are prepared *in situ* by hydrogen-deuterium exchange between the protium salts, KH_2PO_4 and Na_2HPO_4 and the deuterium oxide solvent. The $pD(S)$ of this solution as a function of temperature is given below:

$t, ^\circ\text{C}$	$pD(S)$	$t, ^\circ\text{C}$	$pD(S)$	$t, ^\circ\text{C}$	$pD(S)$
5	7.539	25	7.428	40	7.387
10	7.504	30	7.411	45	7.381
15	7.475	35	7.397	50	7.377
20	7.449				

DIRECTIONS FOR USE

The preparation of the 0.025 molal solution should be carried out by the addition of weighed quantities of the salts to weighed quantities of deuterium oxide in the following proportions (weights in vacuo): 0.003402g KH_2PO_4 and 0.003549g Na_2HPO_4 per g of deuterium oxide. The deuterium oxide should have an isotopic composition of at least 99.5 mole percent D_2O . It should not contain dissolved carbon dioxide or other gases and should have a conductivity no greater than $2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. The salts should be dried for 2 hr at 100 to 130 $^\circ\text{C}$ before use. Although elaborate precautions to prevent contamination of the buffer solution with atmospheric carbon dioxide are usually unnecessary, the container should be kept tightly stoppered at all times when a sample is not actually being removed.

The development of the pD scale and the experimental work leading to the certification of these materials were performed by Maya Paabo and Roger G. Bates.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of Roger G. Bates.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T. W. Mears.

National Bureau of Standards

Certificate

Standard Reference Materials

2191a Sodium Bicarbonate

2192a Sodium Carbonate

These Standard Reference Materials (SRM's) are intended for use in preparing buffer solutions to calibrate electrodes for pD measuring systems. The lots of sodium bicarbonate (NaHCO_3) and sodium carbonate (Na_2CO_3) were prepared to ensure high-purity and uniformity. They meet the specifications of the American Chemical Society for reagent-grade materials; however, they should not be considered to be entirely free from impurities such as traces of water, free alkali, silica, chlorides, sulfur compounds, and heavy metals.

pD(S) Values

The pD(S) values listed below correspond to $\log(1/a_D)$, where a_D is a conventional activity of the deuterium ion referred to the standard state on the scale of molality. The values were derived from the emf of cells without liquid junction by the method of calculation similar to that described in the Journal of Research of the National Bureau of Standards, **66A**, 179 (1962). The uncertainty of the assigned values of pD(S) is estimated not to exceed ± 0.005 unit from 5 to 50 °C^a. The certified values listed below apply *only* to these lots.

A buffer solution which is 0.025 molal with respect to both NaHCO_3 and Na_2CO_3 is recommended for the calibration of the glass electrode and pH meter used for pD measurements. The pD(S) of this solution as a function of temperature is given below:

<u>°C</u>	<u>pD(S)</u>	<u>°C</u>	<u>pD(S)</u>	<u>°C</u>	<u>pD(S)</u>
5.0	10.993	25.0	10.732	40.0	10.60 ^a
10.0	10.917	30.0	10.684	45.0	10.57 ^a
15.0	10.849	35.0	10.641	50.0	10.54 ^a
20.0	10.787				

^aBecause of some uncertainty involved at high temperatures, the last three values are certified to only two decimal places. The estimated uncertainty is within ± 0.01 unit for these temperatures.

The sodium bicarbonate and sodium carbonate were obtained from Mallinckrodt, Inc., St. Louis, Mo.

The analytical measurements leading to the certification of these materials were performed by Y.C. Wu and W.F. Koch, NBS Inorganic Analytical Research Division.

The overall direction and coordination of technical measurements leading to the certification were performed under the chairmanship of J.R. DeVoe, Chief, NBS Inorganic Analytical Research Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W.P. Reed and L.J. Powell.

Gaithersburg, MD 20899
 November 15, 1984

Stanley D. Rasberry, Chief
 Office of Standard Reference Materials

(over)

Directions for Use

Preparation of the 0.025-molal solution: Add 2.101 g of sodium bicarbonate (SRM 2191a) and 2.651 g of sodium carbonate (SRM 2192a) to 1000.0 g of deuterium oxide (weights in air) and mix thoroughly. If volumetric apparatus is to be used, transfer 2.321 g of sodium bicarbonate and 2.928 g of sodium carbonate (weights in air) to a 1-liter volumetric flask. Dissolve and fill to the mark with deuterium oxide at 25 °C. Mix thoroughly by shaking. The deuterium oxide should have an isotopic composition of at least 99 mole percent D₂O. It should not contain dissolved carbon dioxide or other gases, and should have a conductivity no greater than 2×10^{-6} siemens/cm. Carbon dioxide-free deuterium oxide may be obtained by boiling while passing dry nitrogen or argon gas through the solution. The sodium bicarbonate should not be dried by heating; the sodium carbonate should be dried for 2 hours at 275 °C before use. The buffer solution should be protected from air during storage and all transfers of the D₂O solution should be done in an inert atmosphere to avoid rapid isotope exchange. If the calibration process is completed within one hour, it is not necessary to exclude air from the working solution.

The buffer solution should be discarded after a few weeks, or sooner, if sediment appears or if it has been exposed repeatedly to air.

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11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here) One of the most widely performed analytical measurements in chemical laboratories is that of pH using the glass electrode. In order to ensure the consistency of these measurements, the National Bureau of Standards has recommended an operational scale of pH, maintained in terms of the pH(S) of a series of standard solutions. Certified samples of buffer materials, from which the standard reference solutions of reproducible pH can be prepared, as well as solutions in the case of rainwater, are issued by the National Bureau of Standards as Standard Reference Materials. This report is concerned primarily with a discussion of the method used at NBS for the assignment of pH(S) values to these standard solutions, a description of the NBS measurement facilities for pH, and a summary of the characteristics of the buffer materials. A brief discussion of the types of electrodes used and the calibration of pH instrumentation is also presented.			
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