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

Standard Reference Materials:

Standardization of pH Measurements

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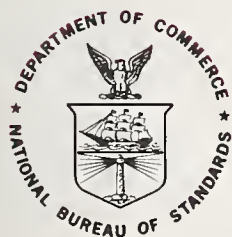
Standard Reference Materials:

Standardization of pH Measurements

Special Publication, no. 262-53.

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PREFACE

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Inquiries concerning the technical content of this paper should be directed to the author(s). Other questions concerned with the availability, delivery, price, and so forth will receive prompt attention from:

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FOREWORD

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 pitfalls 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, not does it imply that the material or equipment identified is necessarily the best available for the purpose.

Richard A. Durst
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STANDARD REFERENCE MATERIALS:
STANDARDIZATION OF pH MEASUREMENTS

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One of the most widely performed analytical measurements in chemical laboratories is that of pH using the glass electrode. In order to insure the consistency of these measurements, the National Bureau of Standards has adopted an operational scale of pH defined in terms of the pH(S) of a series of standard buffer solutions. Certified samples of buffer materials, from which the standard reference solutions of reproducible pH can be prepared, are issued by the NBS. At present, the operational scale is defined by the pH of seven primary and three secondary standard solutions.

This report is concerned primarily with a discussion of the method used at the NBS for the assignment of pH values to the standard buffer solutions, a description of the NBS measurement facilities, and a summary of the characteristics of these standards. A brief discussion of the types of electrodes used and the calibration of pH instrumentation is also presented.

Key words: Buffers; buffer solutions; glass electrode; pH; pH buffers; pH electrode; pH measurement; pH standards.

1. Introduction

Measurement and control of acidity and alkalinity are frequently essential in both industrial and research work. Commercial pH meters with electrodes of the glass type, some of which are claimed to 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 are used to compare the pH of unknowns and standard buffer solutions with which the electrode systems are periodically calibrated. It is therefore very important to have universal agreement on a standard scale of pH and to adopt standard reference buffers to define fixed points on this scale.

The National Bureau of Standards proposes the adoption of an operational pH scale defined in terms of the pH(S) of a series of standard buffer solutions whose assigned pH values correspond 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, are issued by the National Bureau of Standards. At present, the operational scale is defined by the pH of seven primary and three secondary standard solutions.

This report is concerned primarily with a description of the method used at the National Bureau of Standards for the assignment of pH values to the standard buffer solutions and a summary of the characteristics of these standards. The types of electrodes and calibration of pH assemblies are discussed briefly, but for more details on these subjects, specific monographs (see references) and the technical literature of the equipment manufacturer should be consulted.

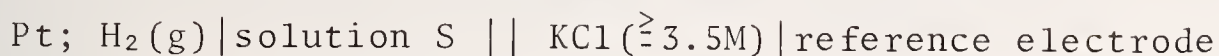
2. Definition of pH

The operational definition of the pH value is given by equation 1 [1]¹:

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

$$\text{pH}(X) = \text{pH}(S) + \frac{(E_x - E_s)F}{RT \ln 10} \quad (1)$$

where E_s is the electromotive force of the cell:



and E_x is the electromotive force of the same cell when the standard buffer solution S [$\text{p}a_{\text{H}} = \text{pH}(S)$] is replaced by the sample solution X; F is the faraday, $96,487 \text{ C}\cdot\text{mol}^{-1}$; R is the gas constant, $8.3143 \text{ JK}^{-1}\text{mol}^{-1}$; and T is the absolute temperature in kelvins, $T = t(^{\circ}\text{C}) + 273.15$. The double vertical line indicates a liquid junction between two different solutions and a single vertical line represents a phase boundary.

Although the hydrogen gas electrode is the primary indicator for hydrogen ions, the glass electrode is much more convenient and versatile and is usually used for practical pH determinations. However, corrections must be applied to measurements made in strongly acid and strongly alkaline solutions where the response of the glass electrode no longer parallels that of the standard hydrogen electrode.

The interpretation of the pH values computed by equation 1 obviously depends to a large extent upon the significance of the number assigned to the standard solution. If imperfections in this method of comparison could be ignored, the pH unit would derive its character exclusively from that of $\text{pH}(S)$. A consideration of various possible standard scales reveals that none can be thermodynamically exact if the pH is to be a measured quantity.

The choice of a unit for expressing the degree of acidity of the standard solutions is most properly made in the light of (1) the nature of the response of physicochemical phenomena to changes of acidity and (2) the techniques and methods of measurement. The term pH was originally proposed by Sørensen [2] and defined as:

$$\text{pH} = -\log c_{\text{H}}, \quad (2)$$

where c_{H} is the concentration of the hydrogen ion. Later, as modern theories of electrolytic solutions developed, it became clear that, except in special cases, it is not possible to ascertain the concentration of hydrogen ions in buffer solutions by direct electrode measurement and the numerical values of acidity determined by the experimental procedure of Sørensen bear no simple direct relation to chemical equilibria formulated in terms of activities.

Inasmuch as the effective concentration or activity, a_H , is fundamental in chemical equilibria, a definition of pH on the activity basis has much to recommend it. Furthermore, the well-established electrometric method of pH measurement furnishes a number related more closely to a_H than to c_H . For these reasons pH(S) is defined in terms of activity:

$$\text{pH(S)} \equiv -\log a_H = -\log (m_H \gamma_H) \quad (3)$$

where m is molality and γ is the activity coefficient on the molal scale. The fact that the activity of a single ionic species is a concept lacking unique physical significance does not preclude the establishment of a reasonable scale of $\text{p}a_H$, but this scale must be a conventional one. In other words, the values of a_H , although not unique hydrogen ion activities, will nevertheless be numbers which, when inserted into equations involving a_H , will furnish equilibrium data consistent with those obtained by rigorous thermodynamic methods [1].

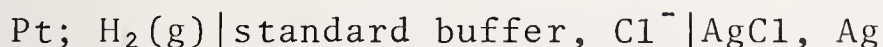
Under ideal experimental conditions, the measured pH is regarded as approaching the true $-\log a_H$ in the sample solution. These conditions are realized most closely for buffer solutions of concentrations between 0.01 and 0.1 molar and pH between 3 and 11. Concentrated solutions, particularly those containing strong acids and bases, display larger deviations. Measurements in mixed solvents or nonaqueous media must be treated as numbers only, since the interpretation of pH in solvents other than pure water is difficult and a single pH scale encompassing all solvents, referred to the aqueous standard state, cannot be realized at the present time. However, significant advances have been made in recent years in extending the pH concept and measurement methods to mixed solvents of which water is the second component [3]. By a procedure analogous to that by which aqueous pH standards have been established, $\text{pH}^*(\text{S})$ values can be assigned to buffer solutions in both nonaqueous and binary mixed solvents [3, 10].

The pH concept has been extended one more step by the assignment of $\text{pD}(\text{S})$ values to the citrate, phosphate and carbonate buffers in heavy water, deuterium oxide. The one fundamental difference between the pH and pD scales is the use of the deuterium gas electrode as the ultimate reference basis for the deuterium ion activity scale. Otherwise, the procedure used for assigning the standard reference values is exactly analogous to the pH procedure [3]. The NBS has certified reference materials for the preparation of the phosphate and carbonate buffers (see table 3 and the appendix).

3. Assignment of pH Values to Standards

The practical importance of the electrometric pH determination, together with the fact that the pH value lacks a unique fundamental definition, have led to the adoption of an operational pH scale, defined by equation 1. Accordingly, pH is defined in terms of the pH(S) of one or more selected standard buffer solutions together with the observed change in emf when the standard is replaced by the sample in a suitable cell. In order to endow the measured pH with as much significance as possible, three measures have been adopted [1]: first is the selection of a conventional p_{a_H} scale for the numerical values of pH(S); second is the selection of reference solutions with ionic strengths less than 0.1; and third is the restriction of primary standards to the pH range between the approximate limits 2.5 and 11.5.

The National Bureau of Standards issues certified samples of buffer materials from which standard reference solutions of reproducible pH can be prepared. In the National Bureau of Standards' method of assignment of pH(S) values, the acidity function, $p(a_{H^+} \gamma_{Cl^-})$, is first determined for a series of suitable buffer solutions containing added small concentrations of a soluble chloride salt. The emf of hydrogen - silver chloride cells of the type:



is measured for each solution under carefully controlled conditions. This cell is well suited for this type of measurement because: (1) the hydrogen electrode is the fundamental indicator of hydrogen ion activity, (2) the hydrogen and silver-silver chloride electrodes are well-characterized and highly reproducible, and (3) this cell avoids the uncertainties of the liquid-junction potential [3]. From the known values of the chloride ion concentration and the standard emf, E° , the acidity function $p(a_{H^+} \gamma_{Cl^-})$ is readily obtained from the measured emf, E , by the equation:

$$p(a_{H^+} \gamma_{Cl^-}) = \frac{(E - E^\circ) F}{RT \ln 10} + \log m_{Cl^-} \quad (4)$$

The limiting value of this acidity function $p(a_{H^+} \gamma_{Cl^-})^\circ$ with respect to the buffer solution without added chloride, i.e., the limit approached by $p(a_{H^+} \gamma_{Cl^-})$ as the concentration of added chloride approaches zero, can be obtained by extrapolation. The p_{a_H} of the buffer is then computed from $p(a_{H^+} \gamma_{Cl^-})^\circ$ by the introduction of a conventional individual ionic activity coefficient for chloride:

$$p a_H = p(a_H \gamma_{C_1})^\circ + \log \gamma_{C_1} \quad (5)$$

Inasmuch as this quantity, γ_{C_1} , has no independent thermodynamic definition, the Bates-Guggenheim convention [4] has been adopted for the evaluation of $\log \gamma_{C_1}$:

$$\log \gamma_{C_1} = \frac{-AI^{1/2}}{1 + 1.5 I^{1/2}} \quad (6)$$

where A is the Debye-Hückel slope and I is the ionic strength. This equation is intended to apply to aqueous solutions at ionic strengths not exceeding 0.1, and the coefficient 1.5 in the denominator is to be used over the temperature range 0 to 95 °C.

The final step in the assignment of pH values is the identification of the $p a_H$ of certain selected reference solutions with pH(S). The primary standards have pH values in the range 3 to 11 and are chosen for their reproducibility, stability, buffer capacity and ease of preparation [1]. For these primary standard buffer solutions:

$$pH(S) = p a_H \quad (7)$$

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

$$pH(S) = \frac{A}{T} + B + CT + DT^2 \quad (8)$$

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

Originally, it was attempted to certify primary standards suitable for calibrating any portion of the entire pH scale from 0 to 14. However, it was soon recognized that the liquid-junction potential of the common pH cell displays considerably greater variability outside of the intermediate pH range from 2.5 to 11.5. In spite of these liquid-junction potential uncertainties, which could result in differences of several hundredths of a pH unit, it is nevertheless desirable to

affirm the proper functioning of the glass electrode outside of this intermediate pH region. For this purpose, additional secondary pH standards have been designated: potassium tetroxalate of $\text{pH}(S) = 1.68$ at 25°C and a saturated solution of calcium hydroxide of $\text{pH}(S) = 12.45$ at 25°C .

Even within the intermediate pH range, secondary standards may have certain advantages over the primary standards. For example, the secondary standard may be more easily prepared, more stable or chosen to match the composition and pH of a type of sample on which repeated measurements are to be made [1]. Recently, NBS certified a buffer solution of tris(hydroxymethyl)aminomethane ("tris") and tris·hydrochloride. This buffer was selected as a physiological pH standard because of its freedom from undesirable side reactions in biological fluids and the similarity of its pH temperature coefficient to that of blood [5]. Although intended as a primary standard, the tris buffer should be regarded as a secondary standard for pH until consistency with the primary standard scale is demonstrated.

Variations in the liquid-junction potential are never entirely absent, even in the intermediate pH range. For this reason, some inconsistency in pH exists among the primary standards when these are used to standardize cells in which a liquid junction is involved [3]. The differences may not be large, but they are such as to make it unrealistic under normal conditions of measurement, to consider the experimental $\text{pH}(X)$ to have an uncertainty of much less than 0.01 unit. The actual magnitude of the inconsistency depends on the structure of the liquid junction and the temperature. The third decimal place assigned to the pH of standard solutions is therefore of limited significance for measurements made with ordinary pH assemblies.

4. NBS Facilities for pH Certification Measurements

In 1972, the NBS emf measurement system was automated in order to increase the reliability of the data acquisition and to reduce the time required for a pH certification run from about five 8-hour days to two 24-hour days with minimal operator attention. The primary purpose of this system is to cause a constant temperature water bath to cycle through a preprogrammed set of temperatures and to record the data when the bath temperature and potentials read from the measurement cells pass certain stability and control requirements.

The temperature-controlled emf measurement system is diagrammed in figure 1. A centrally located computer, a Univac Series 60, model 6135, is time-shared with about

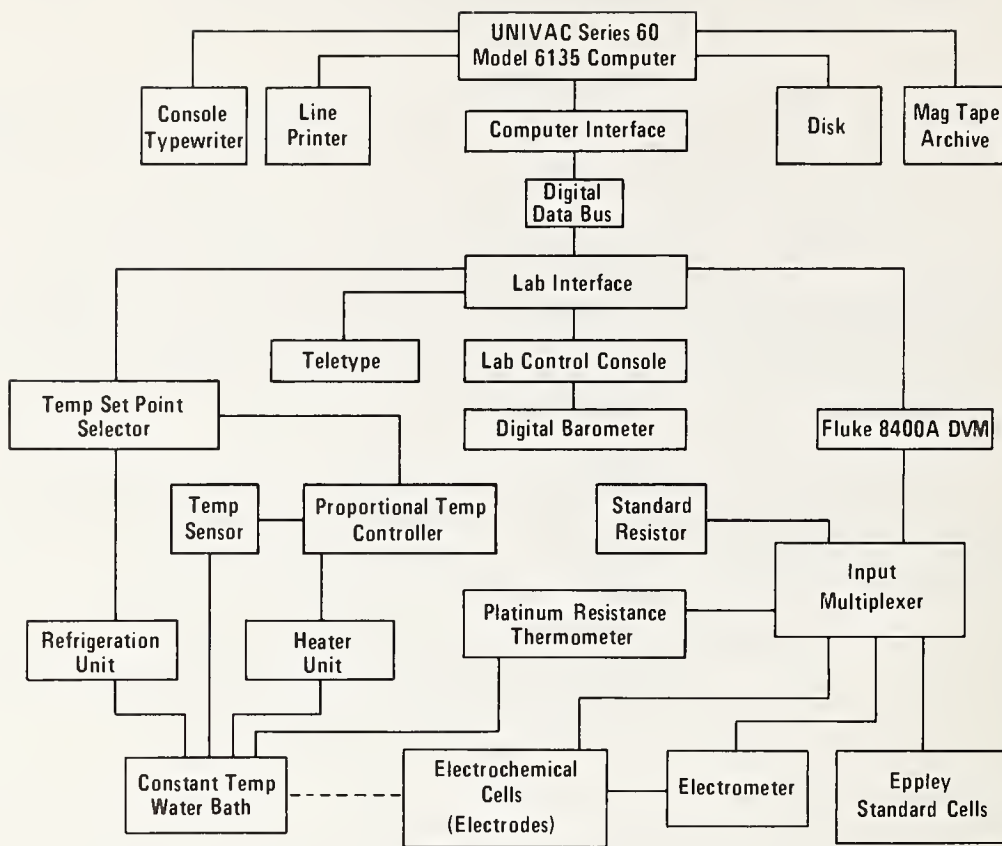


Figure 1. Diagram of the temperature-controlled emf measurement system.

a dozen other systems in the Analytical Chemistry Division. The data communications system consists of four main parts: (1) the digital data bus, (2) the computer interface, (3) the laboratory logic box interface, and (4) the laboratory control console. The computer interface connects the computer to the laboratory via the digital data bus and laboratory interface. The laboratory instrument console provides control and the capability of entering auxiliary data for use by the computer to service and/or control the interfaced system. Two-party line digital data busses have been installed in the Chemistry Building with outlets for each laboratory. The communication between the laboratory and the computer interfaces is accomplished by a multilevel time-sharing scheme. The laboratory interface contains the logic circuitry necessary to connect as many as four experimental systems to the digital data bus. Data that are routinely collected by the system are stored on a random-access disc for a period of several days. If space on the disc becomes scarce, the data files are read onto a master archive magnetic tape for storage.

In performing a pH certification, the first requirement is to prepare the buffer solutions and measurement cells with utmost care. As specified in the pH certificates (see Appendix), the carefully dried and weighed salts are dissolved in distilled water of sufficient purity to give a conductivity of less than $2 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ ($\text{ohm}^{-1}\cdot\text{cm}^{-1}$) 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 is purified of oxygen by passage through a catalytic reduction tube or through a palladium purifier.

The specially designed emf measurement cell shown in figure 2 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. Details of the preparation of the platinized (or palladized) platinum and the silver/silver chloride electrodes can be found in references [1] and [8].

The prepared measurement cells, usually consisting of two cells containing each of the three levels of added chloride, are placed in the controlled temperature water bath as shown in figure 3. Also shown in this figure are the coiled copper tubing hydrogen gas inlets and the two platinum resistance thermometers.

The complete measurement system, with the laboratory logic box interface (open) on the rear wall, is shown in

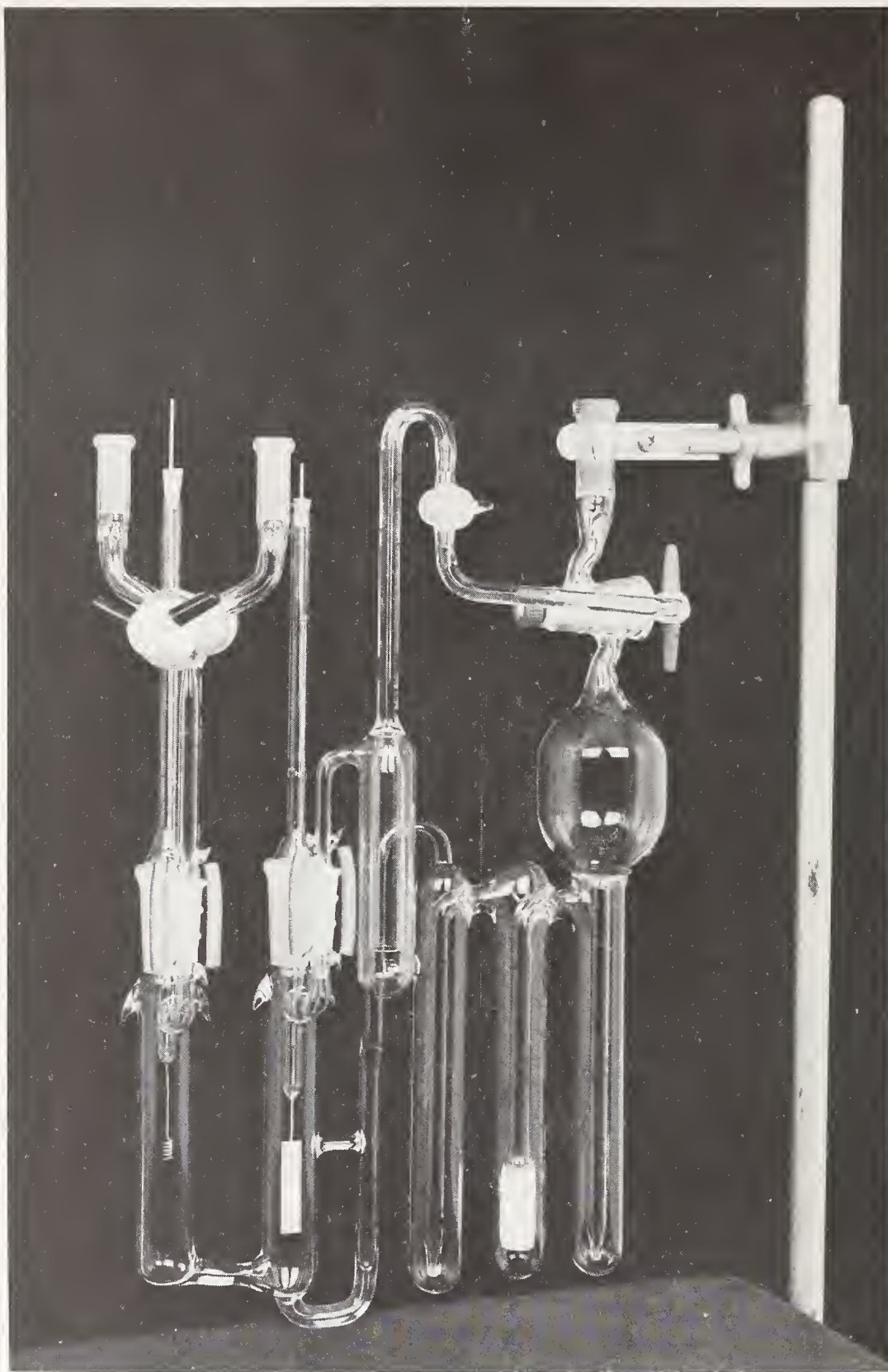


Figure 2. Emf measurement cell used for the certification of pH buffer solutions.

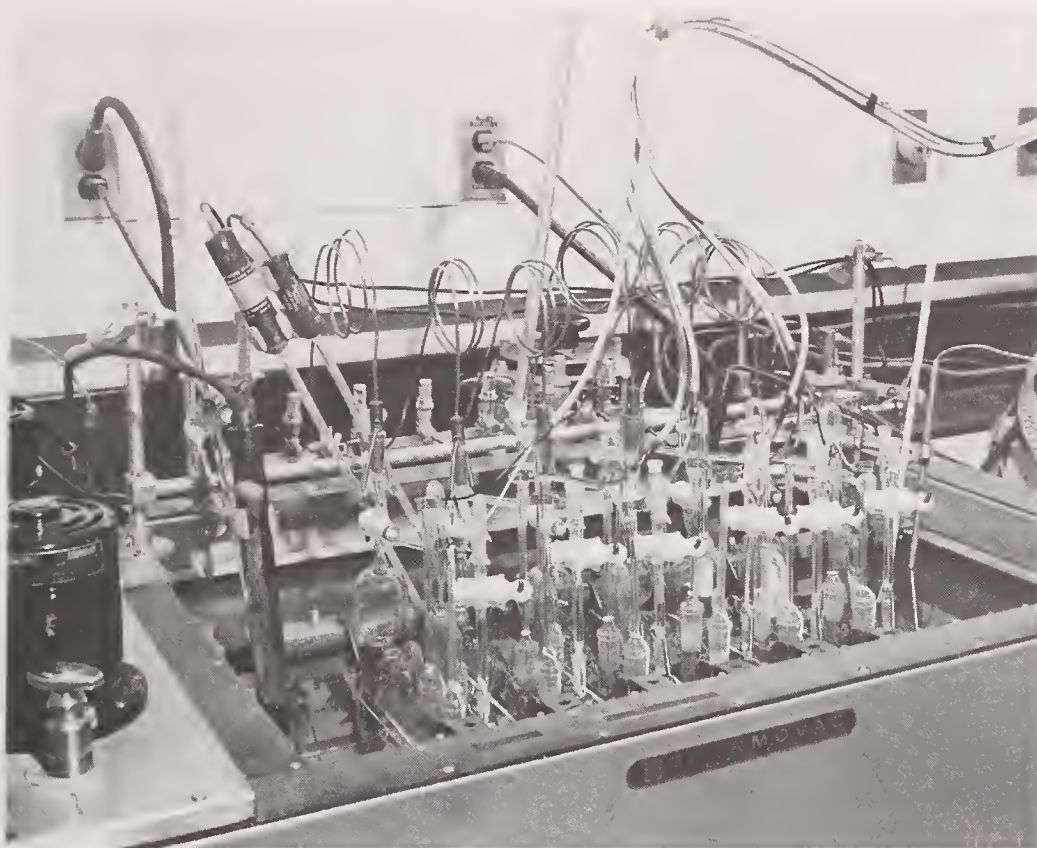


Figure 3. Emf measurement cells in position in the controlled-temperature water bath.

figure 4. Another view, figure 5, shows the entire electronics rack and the thermostated standard cells on the laboratory bench top. Briefly, the equipment in the electronics rack consists of (from the top): a digital barometer which is automatically monitored during the certification measurements is used to correct the partial pressure of hydrogen for variations in the atmospheric pressure; the autoranging and autofunctioning digital voltmeter which serves as the analog-to-digital converter for both resistance and emf measurements; the proportional temperature controller which, in conjunction with the temperature set point selector (next panel down) and the bath refrigeration unit, maintains preset bath temperatures to better than ± 0.01 °C by means of immersion heaters; and the DVM input multiplexer which, under computer control, switches the various measurement parameters into the DVM for A-to-D conversion prior to transmission to the computer for acquisition and storage. The functions multiplexed include: temperature (platinum resistance), standard resistor (calibration), standard emf cells (calibration), and up to ten measurement cells. The control console permits communication with the computer via a series of thumbwheel switches which enter all of the required input parameters, e.g., temperature sequence, number of cells, time delays, and program identification numbers. The control console also includes a set of pushbuttons which are used to set-up, start (send), and terminate the experiment as well as indicator lights which signal operations (data acquisition, operate, auto, etc.) or problems (error, reject). A vibrating-reed electrometer is located below the control console and, in conjunction with the three-position pH switch, provides a high-impedance input to the DVM for measurements with glass and high-resistance ion-selective electrodes. The remainder of the equipment in the rack constitutes the Mueller bridge system for manual checking of the water bath temperature via the second platinum resistance thermometer shown in figure 3.

In operation, computer control begins by automatically positioning the temperature set point selector at the starting sequence number. When the bath temperature achieves the nominal value, within certain preset control limits as indicated by the platinum resistance thermometer, the input multiplexer automatically switches through the readout positions. After a programmed time delay, the multiplexer recycles through the positions and compares the values to the previous sets of data. After three cycles, if the data agree within the requisite control limits, the computer sets the temperature control to the next sequence value and the operation is repeated. If any of the values exceed the control limits, an out-of-range message is printed next to the incorrect value and, following two more cycles, the computer

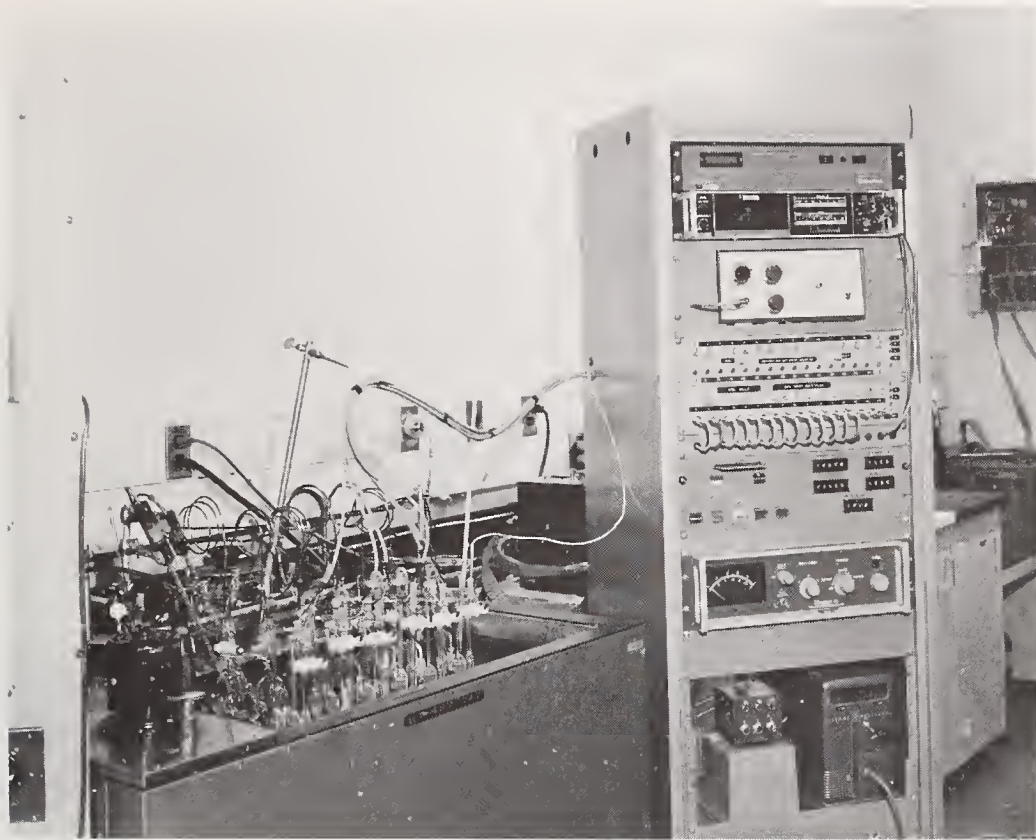


Figure 4. View of the measurement facility including the water bath, instrument rack and laboratory logic box interface (open on rear wall).

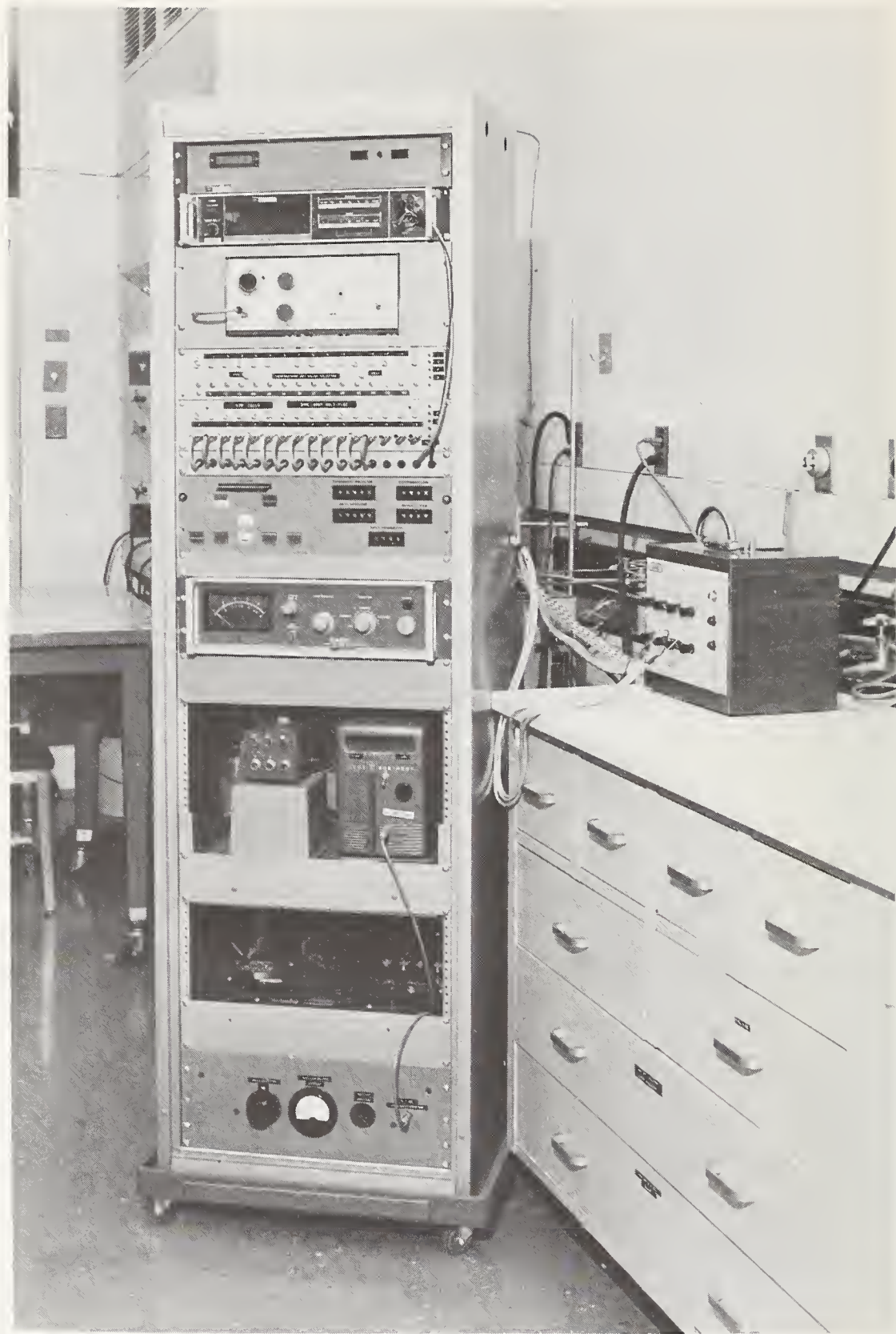


Figure 5. Close-up view of the instrument rack with thermostated standard cells on the laboratory bench to the right.

proceeds to the next sequence temperature after again flagging the out-of-range value. Depending on the temperature value or the direction of the temperature change, the computer turns on the refrigeration unit or an auxiliary heater. After the temperature sequence is completed, the routine is automatically terminated. Reduction of the acquired data is performed by batch operation on the NBS central computer, a Univac 1108. The data reduction consists of a series of operations including correcting the experimental emf values to the standard partial pressure of hydrogen, calculating the acidity functions, extrapolating to no added chloride to obtain the limiting acidity functions, evaluating the chloride ion activity coefficient using the Bates-Guggenheim convention, and finally calculating the p_{aH} values. These experimental values are then smoothed with respect to temperature (equation 8) by the method of least squares to give the certified pH(S) values.

5. Recommended Standards

The National Bureau of Standards pH scale is defined in terms of the pH(S) assigned to the seven primary and three secondary reference solutions, listed in table 1. The composition and properties of the standard solutions are given in table 2. The citrate, phthalate, phosphate, borax, carbonate, tetroxalate, and tris buffer solutions are prepared by dissolving the indicated weights of the pure reference materials in pure water and diluting to 1 dm³ (1 liter). The directions for the preparation of the molal solutions are given on a volume basis, i.e., grams per liter of solution, in order to simplify the preparation of the buffer solutions. However, the weights of the salts indicated in table 2 and in the NBS certificates for these pH standards are corrected for solution density and air buoyancy and thus correspond exactly to the nominal concentration on the molal scale. 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 material should be removed by filtration or decantation [1]. The calcium hydroxide standard solution is best stored in a polyethylene bottle. The tartrate solution is about 0.034m and the calcium hydroxide solution about 0.021m.

Prior to weighing out the reference materials, several should be oven dried: phthalate at 110 °C, phosphates (both) at 110-130 °C, and the sodium carbonate at 275 °C; each salt for two hours. The other materials do not require oven drying but should not be exposed to excessively high humidity.

The weighed samples of reference materials should be placed in a 1-liter volumetric flask, dissolved, and filled to the mark with distilled water at 25 °C. The distilled water should have a conductivity no greater than 2×10^{-6} S·cm⁻¹. The phosphate, tris, borax and carbonate buffers should also be prepared using water purged with a carbon dioxide free gas or freshly boiled water of pH 6.7 to 7.3. Boiled water should be protected from contamination by atmospheric carbon dioxide with a tube of carbon dioxide absorbant, e.g., soda lime, during cooling. 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-equilibrium water, pH 5.6 to 6.0.

It is recommended that the buffer solutions be replaced about once a month, and sooner for the tartrate buffer which is 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 [1].

A complete list of the pH and pD Standard Reference Materials presently available from the National Bureau of Standards is given in table 3. Although considerable work has gone into the assignment of pH values to the citrate and calcium hydroxide solutions, reference materials have not yet been certified.

6. 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 manufacturer's literature should be consulted.

In general, the internal resistance of the pH cell will determine to a large extent the type of equipment required for the emf measurement. For low resistance cells, such as the hydrogen electrode/silver-silver chloride electrode cell used in the certification of pH buffers, the most accurate method of measuring the emf is by means of a potentiometer which "balances" or compares the unknown emf with the emf of a standard cell. However, because of the high resistance of the glass electrode, special high-impedance electrometers are required which do not draw an appreciable current. As a result of the great progress made

in electronic instrumentation in recent years, there are now many excellent pH meters capable of providing pH values with a reproducibility of a few thousandths of a pH unit. 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 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 X is then given by:

$$\text{pH}(X) = \text{pH}(S_1) + \frac{E_X - E_{S_1}}{E_{S_2} - E_{S_1}} [\text{pH}(S_2) - \text{pH}(S_1)] \quad (9)$$

In actual practice, with 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 quinhydrone electrode
3. the metal-oxide electrodes, and
4. the glass electrode.

The hydrogen electrode is the ultimate standard for the determination of pH values but special precautions must be taken to ensure the most reliable and theoretically correct pH response. Owing to the experimental difficulties associated with it, other pH electrodes are commonly used for routine measurements.

The quinhydrone electrode is a redox electrode which 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 which limits its application to neutral and acidic media of pH less than 8. Of less importance is the salt error resulting from unequal changes in the activity coefficients of hydroquinone and quinone, but this error only becomes important at high ionic strengths where the significance of pH is diminished. Finally, this electrode is poisoned by proteins and cannot be used in the presence of strong oxidizing or reducing agents.

The metallic electrodes, e.g., antimony, bismuth, 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 (non-linear) and 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, and they can be used under extreme pressure and/or temperature conditions.

The glass electrode is by far 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 [1,6]. 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 index 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. Then 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 mentioned above.

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 errorfree 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 [6,7].

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 [8]. The four principal reference electrodes are the mercury-mercurous chloride (calomel), the silver-silver chloride, the mercury-mercurous sulfate, and the thallium amalgam-thallic 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 mercurous chloride. The silver-silver chloride and thallium amalgam-thallic 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 buffer solutions approximately equal and less than 0.1,

the pH between 3 and 11, and the exclusion of other phases such as colloids and suspensions.

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 [1], 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 undersaturated solution, such as 3.5 molar, is recommended [1].

7. Conclusion

The definition and measurement of pH, as we now know it, is the result of a 65-year evolutionary process which was greatly influenced by two facts of modern technology. One is the very extensive, almost exclusive, use of commercial glass electrodes for the routine determination of the acidity of solutions. The other is the acknowledged fact that the majority of practical pH measurements need only be reproducible, since the fundamental interpretation of these numbers in terms of hydrogen ion activity would be sheer fantasy [3]. These facts led to the operational definition of pH (equation 1) which has now been adopted by the International Union of Pure and Applied Chemistry [9] and most of the world. In its broadest sense, this acceptance means that pH values can legitimately be assigned to a wide variety of media, e.g., D₂O and many nonaqueous solutions, in which a reproducible pH-related emf can be measured. The NBS pH Standard Reference Materials provide a means for tying the operational definition of pH to a consistent scale of pH values assigned with as much thermodynamic significance as is possible at the present state of this art.

The author especially wishes to acknowledge the contributions of Dr. Roger G. Bates whose efforts over many years at NBS resulted in the national pH scale and forms the basis of a large part of this report. Special thanks are also expressed to Mr. J. Paul Cali and the Office of Standard Reference Materials for their support of the pH certification program.

Table 1

NBS pH Standards		
<u>Solution composition (molality)</u>	<u>pH(S) at 25°C</u>	<u>Temperature range (°C)</u>
Primary Standards:		
KH tartrate (satd. at 25°C)	3.557	25 to 95
0.05m KH ₂ citrate	3.776	0 to 50
0.05m KH phthalate	4.004	0 to 95
0.025m KH ₂ PO ₄ + 0.025m Na ₂ HPO ₄	6.863	0 to 50
0.008695m KH ₂ PO ₄ + 0.03043m Na ₂ HPO ₄	7.415	0 to 50
0.01m Na ₂ B ₄ O ₇ • 10 H ₂ O	9.183	0 to 50
0.025m NaHCO ₃ + 0.025m Na ₂ CO ₃	10.014	0 to 50
Secondary Standards:		
0.05m K tetroxalate • 2H ₂ O	1.679	0 to 95
0.01667m tris + 0.05m tris • HCl	7.699	0 to 50
Ca(OH) ₂ (satd. at 25°C)	12.454	0 to 60

Table 2

Composition and Properties of Standard Solutions

<u>Solution</u>	<u>Buffer material</u>	<u>Weight in air (g)</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, satd.	$\text{KHC}_4\text{H}_4\text{O}_6$	>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			
Tris, 1:3			-0.03	0.020	-0.026
0.01667m	$(\text{CH}_2\text{OH})_3\text{CNH}_2$	2.005			
0.0500m	$(\text{CH}_2\text{OH})_3\text{CNH}_3\text{Cl}$	7.822			
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, satd.	$\text{Ca}(\text{OH})_2$	>2	-0.28	0.09	-0.033

¹Dilution value; 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/dpH 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 .

Table 3

NBS pH and pD Standard Reference Materials*

<u>Material</u>	<u>SRM designation</u>
Potassium hydrogen phthalate	185e
Potassium dihydrogen phosphate	186-I-c
Disodium hydrogen phosphate	186-II-c
Sodium tetraborate decahydrate	187b
Potassium hydrogen tartrate	188
Potassium tetroxalate	189
Sodium bicarbonate	191
Sodium carbonate	192
Tris(hydroxymethyl)aminomethane	922
Tris(hydroxymethyl)aminomethane hydrochloride	923
Potassium dihydrogen phosphate (pD)	2186-I
Disodium hydrogen phosphate (pD)	2186-II
Sodium bicarbonate (pD)	2191
Sodium carbonate (pD)	2192

*Available from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234. Request NBS Special Publication 260 for price list and ordering information.

8. References

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9. Appendix - Certificates for pH and pD Standard Reference Materials

U. S. Department of Commerce
Frederick B. Dent
Secretary

National Bureau of Standards
Richard W. Roberts, Director

National Bureau of Standards Certificate

Standard Reference Material 185e

Potassium Hydrogen Phthalate

pH Standard

E. S. Etz

This lot of potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) was prepared to insure high purity and uniformity. It meets the specifications of the American Chemical Society for reagent-grade material, but should not be considered to be entirely free of impurities such as traces of occluded water, free acid or alkali, 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 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 185e is estimated not to exceed ± 0.005 unit for the 0 to 60 °C temperature range and ± 0.01 unit from 70 to 95 °C. (The certified values listed below apply only to SRM 185c.)

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:

°C	pH(S)	°C	pH(S)	°C	pH(S)	°C	pH(S)
0	4.003	25	4.004	45	4.042	70	4.12
5	3.998	30	4.011	50	4.055	80	4.16
10	3.996	35	4.020	55	4.070	90	4.19
15	3.996	37	4.024	60	4.085	95	4.21
20	3.999	40	4.030				

The potassium hydrogen phthalate was obtained from the J. T. Baker Chemical Company of Phillipsburg, N. J.

The overall direction and coordination of the technical measurements leading to 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
May 21, 1973

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

Directions for Use

Preparation of the 0.05-molal solution: Transfer 10.12 grams of SRM 185e to a 1-liter volumetric flask. Add distilled water to dissolve the salt and fill to the mark with distilled water at 25 °C. The distilled water should have a conductivity not greater than 2×10^{-6} ohm⁻¹ cm⁻¹. Mix thoroughly by shaking. The salt should be dried for 2 hours at 110 °C before use.

The water used in the preparation of this pH buffer standard 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 standard buffer solution should be replaced at frequent intervals and when mold is apparent.

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

PREPARATION OF THE 0.025-MOLAL SOLUTION

Transfer 3.387 g of the potassium dihydrogen phosphate (186-I-e) and 3.533 g of the disodium hydrogen phosphate (186-II-e) 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-e) 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.

Certificate

Standard Reference Material 187b

Sodium Tetraborate Decahydrate

(Borax)

This standard reference material is intended for use in defining the pH(S) scale. This lot of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) was prepared to ensure high purity and uniformity. It 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 were the partially desiccated salt used as a boron or acidimetric standard.

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 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 187b 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:

°C	pH(S)	°C	pH(S)	°C	pH(S)
0	9.460	20	9.227	37	9.093
5	9.392	25	9.183	40	9.074
10	9.331	30	9.143	45	9.044
15	9.276	35	9.107	50	9.017

The borax was obtained from the J. T. Baker Chemical Company of Phillipsburg, N. J. The experimental work leading to the certification of this material was carried out by B. R. Staples.

The overall direction and coordination of the technical measurements leading to 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 9, 1970

J. Paul Cali, Acting 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 3.80 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.

National Bureau of Standards Certificate

Standard Sample 188

Potassium Hydrogen Tartrate
(pH Standard)

Purity

This lot of potassium hydrogen tartrate ($\text{KHC}_4\text{H}_4\text{O}_6$) was prepared to insure high purity and uniformity and to assay close to 100 percent. However, it should not be considered as entirely free from impurities such as traces of free acid or alkali, occluded water, chlorides, sulfur compounds, and heavy metals.

The values listed in this certificate are the assigned $\text{pH}(\text{S})$ numbers for solutions of Standard Sample 188. These values 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. 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 $\text{pH}(\text{S})$ listed is estimated not to exceed ± 0.005 unit from 0 to 60 °C and ± 0.01 unit from 70 to 95 °C.

A solution saturated with potassium hydrogen tartrate near 25 °C is recommended as a standard for the calibration of pH equipment between 25 and 95 °C. The $\text{pH}(\text{S})$ of this solution as a function of temperature is given below:

°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 also recommended as a standard for the range 0 to 60 °C. The $\text{pH}(\text{S})$ of this solution as a function of temperature is as follows:

°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

Directions for Use

Preparation of the saturated solution: Add an excess of Standard Sample 188 to distilled water contained 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. (One hundred 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 Pyrex bottle. For an accuracy of ± 0.001 unit the temperature of saturation must lie between 24 and 26 °C.

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

Preparation of the 0.01-molal solution: Transfer 1.878 g (air weight) of Standard Sample 188 to a 1-liter volumetric flask. The salt need not be dried before use. Fill to the mark with water of the quality described above and shake until all of the salt is dissolved and the solution thoroughly mixed. For most accurate results, prepare the solution fresh each day.

A. V. ASTIN, Director

WASHINGTON, D.C. 20234
January 10, 1964

718-028 GPO

National Bureau of Standards Certificate

Standard Sample 189

Potassium Tetroxalate
($p a_{\text{H}}$ Standard)

Purity

This lot of potassium tetroxalate dihydrate ($\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$) was prepared to insure high purity and uniformity and to assay close to 100 percent. However, it is certified only with respect to its $p a_{\text{H}}$ value, not as a pure substance.

$p a_{\text{H}}$ Values

The values listed in this certificate are the conventional $p a_{\text{H}}$ numbers for solutions of Standard Sample 189. The values given 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. 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 is estimated not to exceed ± 0.005 unit from 0 to 60 °C and ± 0.01 unit from 60 to 95 °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 $p a_{\text{H}}$ given above. They are also recommended when standards of $p a_{\text{H}}$ are needed and a liquid junction is not involved.

The 0.05-*m* solution is recommended for use as a standard for $p a_{\text{H}}$. The $p a_{\text{H}}$ values of this solution are given in the following table:

°C	$p a_{\text{H}}$	°C	$p a_{\text{H}}$	°C	$p a_{\text{H}}$
0	1.666	30	1.683	55	1.715
5	1.668	35	1.688	60	1.723
10	1.670	38	1.691	70	1.743
15	1.672	40	1.694	80	1.766
20	1.675	45	1.700	90	1.792
25	1.679	50	1.707	95	1.806

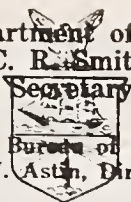
Directions for Use

Preparation of the 0.05-molal solution: Transfer 12.61 g (air weight) to a 1-liter volumetric flask. Dissolve the salt and fill to the mark with distilled water at 25 °C. It is not necessary to remove dissolved atmospheric carbon dioxide from the water and the salt should not be dried.

WASHINGTON, D.C. 20234
January 10, 1964

A. V. ASTIN, *Director*

718-628 GPO



Certificate of Analysis

Standard Reference Materials

Sodium Bicarbonate (191)

Sodium Carbonate (192)

PURITY

These lots of sodium bicarbonate (NaHCO_3) and sodium carbonate (Na_2CO_3) were prepared to insure 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 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 (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 variations 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 NaHCO_3 and Na_2CO_3 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	10.321	20	10.064	40	9.891
5	10.248	25	10.014	45	9.859
10	10.181	30	9.968	50	9.831
15	10.120	35	9.928		

The sodium bicarbonate and sodium carbonate were obtained from the Mallinckrodt Chemical Works of St. Louis, Mo. The experimental work leading to the certification of this material was carried out by Bert R. Staples and Roger G. Bates.

The overall direction and coordination of technical measurements leading to the 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 Thomas W. Mears.

Washington, D. C. 20234
July 15, 1968

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(over)

Directions for Use

Preparation of the 0.025-molal solution. Transfer 2.092 g of sodium bicarbonate (191) and 2.640 g of Na_2CO_3 (192)(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 $2 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$. 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.

National Bureau of Standards Certificate

Standard Reference Materials

Tris(hydroxymethyl)aminomethane (922)

Tris(hydroxymethyl)aminomethane hydrochloride (923)

B. R. Staples

These Standard Reference Materials are intended primarily for use in preparing standard pH buffer solutions in the physiological range. Such systems are used in the clinical laboratory in cases where phosphate buffers would cause undesirable side reactions or do not adequately approximate the required variation of pH with temperature. Coulometric assay indicates the tris(hydroxymethyl)aminomethane to be 99.99 ± 0.02 mole percent after drying in a vacuum oven at 70°C for 24 hours. Coulometric assay of the tris(hydroxymethyl)aminomethane hydrochloride as received was 99.69 ± 0.05 mole percent.

The pH(S) values listed below correspond to $\log(1/\alpha_{\text{H}})$, where α_{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 by Bates [1]. The uncertainty of the assigned values of pH(S) is estimated not to exceed ± 0.005 unit. The values listed below apply only to the material herein certified.

The solution recommended for the calibration of pH equipment is 0.01667 molal with respect to tris(hydroxymethyl)aminomethane and 0.0500 molal with respect to tris(hydroxymethyl)aminomethane hydrochloride. The pH(S) of this solution as a function of temperature is as follows:

$^\circ\text{C}$	pH(S)	$^\circ\text{C}$	pH(S)	$^\circ\text{C}$	pH(S)
0	8.471	20	7.840	37	7.382
5	8.303	25	7.699	40	7.307
10	8.142	30	7.563	45	7.186
15	7.988	35	7.433	50	7.070

The tris(hydroxymethyl)aminomethane and tris(hydroxymethyl)aminomethane hydrochloride were obtained from the Sigma Chemical Company of St. Louis, Missouri.

The overall direction and coordination of technical measurements leading to the certification was 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
June 23, 1971
Revised December 13, 1973

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

The name "tris(hydroxymethyl)aminomethane" is used preferentially in this certificate since it is the name commonly used in clinical laboratories. Under the system of nomenclature recommended by the International Union of Pure and Applied Chemistry this material is named 2-amino-2-(hydroxymethyl)-1,3-propanediol. It is also known by several trivial and proprietary names, e.g., "tris", "THAM," "trizma," "tromethamine," "tromethane," etc. However, the certified values given herein apply only to the material supplied as an NBS-SRM.

These Standard Reference Materials (SRM's) are intended for "in vitro" diagnostic use only.

This material is for use in preparing standard buffer solutions for use in clinical chemistry. A buffer solution having the pH values certified on the face of this certificate is 0.01667 molal with respect to tris(hydroxymethyl)aminomethane and 0.0500 molal with respect to tris(hydroxymethyl)aminomethane hydrochloride. The preparation of this solution is described in the following paragraph.

Transfer 7.822 g of tris(hydroxymethyl)aminomethane hydrochloride (SRM 923) and 2.005 g of tris(hydroxymethyl)aminomethane (SRM 922) 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 tube of carbon dioxide absorbant. The certified pH(S) values apply for materials as received. No particular drying procedures are necessary. The tris(hydroxymethyl)aminomethane should not be heated above 80 °C and as a precaution the tris(hydroxymethyl)aminomethane hydrochloride should not be exposed to temperatures above 40 °C. (The figures given are weights in air.)

CAUTION: Reference electrodes containing linen-fiber junctions should not be used with this buffer. Such junctions produce large liquid-junction potentials, drift, and long equilibrium times.

Standard Reference Material 922 should be stored in a well-closed container at room temperature. Exposure to high temperatures (above 50 °C) and direct sunlight should be avoided. Experience has shown this compound to be stable in storage for at least 12 years [2]. If the material degrades such that the certified values are changed, the users will be notified by NBS. It is recommended that this material not be used after 5 years from the date of purchase.

Standard Reference Material 923 should be stored in a well-closed container at room temperature, preferably in a desiccator. Exposure to high temperatures (above 40 °C) and direct sunlight should be avoided. SRM 923, tris(hydroxymethyl)aminomethane hydrochloride is quite hygroscopic even at relative humidities of 30 to 50 percent [3]. Experience at NBS has indicated that properly stored this material is stable for at least 5 years. Weighing and other manipulations of SRM 923 should be avoided under conditions when the relative humidity exceeds 50 percent. If the material degrades such that the certified values are changed, the users will be notified by NBS. It is recommended that this material not be used after 5 years from the date of purchase.

This buffer solution is sensitive to contamination by carbon dioxide [4]. If the solution is to maintain the assigned pH(S) for a few weeks the exclusion of carbon dioxide is essential. The solution should be replaced after a few weeks, or sooner if mold or sediment appear, or if it is repeatedly exposed to air containing carbon dioxide.

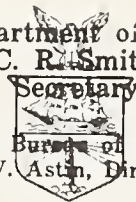
References:

- [1] R. G. Bates, Revised standard values for pH measurements from 0 to 95 °C, J. Research NBS **66A**, 179 (1962).
- [2] J. A. Riddick, Amine buffers as acidimetric standards, Ann. N.Y. Acad. Sci. **92**,357 (1961).
- [3] Sigma Tentative Technical Bulletin No. 106 B, Sigma Chemical Company, St. Louis, Mo., revised 1967.
- [4] R. G. Bates and H. B. Hetzer, Absorption of carbon dioxide by solutions of 2-amino-2-(hydroxymethyl)-1,3-propanediol, Anal. Chem. **33**,1285 (1961).

These Standard Reference Materials have been measured and certified at the laboratories of the National Bureau of Standards, Gaithersburg, Maryland. All inquiries should be addressed to:

Office of Standard Reference Materials
Room B311, Chemistry Building
National Bureau of Standards
Washington, D. C. 20234

The date of issuance and certification of these Standard Reference Materials was June 23, 1971.



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.

Washington, D. C.
May 28, 1968

W. Wayne Meinke, Chief
Office of Standard Reference Materials



Certificate of Analysis

Standard Reference Materials

Sodium Bicarbonate (2191)

Sodium Carbonate (2192)

Purity

These 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 as 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 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.

This solution, 0.025 molal with respect to both NaDCO_3 and Na_2CO_3 , is recommended for the calibration of pH meters to be used for the measurement of pD in deuterium oxide. The NaDCO_3 is prepared *in situ* by the hydrogen-deuterium exchange between the protium salt and the deuterium oxide solvent. The $pD(S)$ of these solutions 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	10.998	25	10.736	40	10.597
10	10.923	30	10.685	45	10.559
15	10.855	35	10.638	50	10.527
20	10.793				

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): 0.002100g NaHCO_3 and 0.002650g Na_2CO_3 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 sodium bicarbonate should not be dried by heating; the sodium carbonate should be dried for two hrs 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 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.

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16. 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 insure the consistency of these measurements, the National Bureau of Standards has adopted an operational scale of pH defined in terms of the pH(S) of a series of standard buffer solutions. Certified samples of buffer materials, from which the standard reference solutions of reproducible pH can be prepared, are issued by the NBS. At present, the operational scale is defined by the pH of seven primary and three secondary standard solutions. This report is concerned primarily with a discussion of the method used at the NBS for the assignment of pH values to the standard buffer solutions, a description of the NBS measurement facilities, and a summary of the characteristics of these standards. A brief discussion of the types of electrodes used and the calibration of pH instrumentation is also presented.				
17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons) Buffers; buffer solutions; glass electrode; pH; pH buffers; pH electrode; pH measurement; pH standards.				
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