National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Materials®

Potassium Dihydrogen Phosphate (186-I-g)

Disodium Hydrogen Phosphate (186-II-g)

pH Standards

These Standard Reference Materials (SRMs) are intended for use in preparing solutions for calibrating electrodes for pH measuring systems. SRMs 186-I-g, Potassium Dihydrogen Phosphate (KH_2PO_4) and 186-II-g, Disodium Hydrogen Phosphate (Na_2HPO_4) were prepared to ensure high purity and uniformity. However, these SRMs are certified **ONLY** as a pH standard, pH(S), not as pure substances. A unit of each SRM consists of its respective salt contained in a clear glass bottle. A unit of SRM 186-I-g contains 30 g of potassium dihydrogen phosphate. A unit of SRM 186-II-g contains 45 g of disodium hydrogen phosphate.

Certified Values and Uncertainties: The certified pH(S) values provided in Tables 1 and 2 correspond to $\log (1/a_H)$, where a_H is the conventional activity of the hydrogen (hydronium) ion referred to the standard state (p° = 1 atm = 1.01325×10^5 Pa) on the scale of molality. The values were derived from emf measurements of cells without liquid junction by the primary measurement method [1, 2]. **NOTE:** These certified values apply **ONLY** to SRMs 186-I-g and 186-II-g. Minor variations of pH(S) values (of the order of a few thousandths of a unit) may be expected to occur between SRM lots.

The uncertainty in the certified value, U, is calculated as $U = ku_c(y)$, where $u_c(y)$ is the "combined standard uncertainty" calculated according to the *ISO Guide* [3]. The value of $u_c(y)$ is intended to represent the combined effect of the following uncertainty components associated with the primary measurement method and material homogeneity: curve-fit; standard electrode potentials, E^o; material homogeneity; molality of HCl, b_{HCl}, used for determining E^o; measured cell potentials; correction to the standard pressure for H_2 gas; mean activity coefficient of HCl at b_{HCl}; gas constant; temperature; Faraday constant; the molality of NaCl; and the uncertainty [4] of the conventional calculation of $\log \gamma_{Cl}$ (Bates-Guggenheim convention [5]). Current expert opinion [5,6] has assessed the uncertainty attributable to the Bates-Guggenheim convention as 0.010 pH (95 % confidence interval). The value of $u_c(y)$ has been multiplied by a coverage factor, k, obtained by the Student's t-distribution for effective degrees of freedom at the given temperature and a 95 % confidence level. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST [6]. The certified pH(S) values and their expanded uncertainties, U, are stated in Tables 1 and 2.

Expiration of Certification: The certification of this SRM is valid until **31 December 2007**, within the measurement uncertainties specified, provided the SRM is handled and stored in accordance with the instructions given in this certificate. However, the certification is invalid if the SRM is damaged, contaminated, or modified.

The experimental work leading to the certification of this material was performed by R.H. Shreiner and K.W. Pratt of the NIST Analytical Chemistry Division.

Statistical consultation was provided by W.F. Guthrie of the NIST Statistical Engineering Division.

The support aspects involved in the certification of this SRM were coordinated through the Standard Reference Materials Program by B.S. MacDonald of the NIST Measurement Services Division.

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Table 1. Certified pH(S) Values and Expanded Uncertainties (95 % confidence) for the Equimolal Formulation[a,b]

A solution of molality of 0.025 mol/kg with respect to both KH_2PO_4 and Na_2HPO_4 (equimolal formulation) is recommended for the calibration of pH measuring systems. The pH(S) and the expanded uncertainty, *U*, of this solution as a function of temperature are given in Table 1.

	pH(S)	u_c(measurement)[a]	$u_c(y)$[b]	*k*	*U*
5	6.951 5	0.000 76	0.0051	2.0	0.010
10	6.922 9	0.000 73	0.0051	2.0	0.010
15	6.898 9	0.000 76	0.0051	2.0	0.010
20	6.879 6	0.000 74	0.0051	2.0	0.010
25	6.864 0	0.000 80	0.0051	2.0	0.010
30	6.852 6	0.001 2	0.0051	2.0	0.010
35	6.843 5	0.001 1	0.0051	2.0	0.010
37	6.840 8	0.001 0	0.0051	2.0	0.010
40	6.837 2	0.001 0	0.0051	2.0	0.010
45	6.834 6	0.001 0	0.0051	2.0	0.010
50	6.833 1	0.001 2	0.0051	2.0	0.010

[a] u_c(measurement) includes components associated with the measurement method and material homogeneity, but does not include the uncertainty of the Bates-Guggenheim Convention (0.0050) [4].

[b] $u_c(y)$ is the combined standard uncertainty, which includes u_c(measurement) and the standard uncertainty of the Bates-Guggenheim Convention (0.0050) [4].

Table 2. Certified pH(S) Values and Expanded Uncertainties (95 % confidence) for the Physiological Formulation[a,b]

A solution of molality of 0.008 695 mol/kg with respect to KH_2PO_4 and 0.030 43 mol/kg with respect to Na_2HPO_4 (physiological formulation) is recommended for pH measurements in the physiologically important range pH 7 to 8. The pH(S) and *U* of this solution as a function of temperature is given in Table 2.

t/°C	pH(S)	u_c(measurement)[a]	$u_c(y)$[b]	*k*	*U*
5	7.5026	0.0011	0.0051	2.0	0.010
10	7.4747	0.0010	0.0051	2.0	0.010
15	7.4511	0.0010	0.0051	2.0	0.010
20	7.4323	0.0010	0.0051	2.0	0.010
25	7.4157	0.0011	0.0051	2.0	0.010
30	7.4044	0.0012	0.0051	2.0	0.010
35	7.3956	0.0012	0.0051	2.0	0.010
37	7.3940	0.0012	0.0051	2.0	0.010
40	7.3897	0.0012	0.0051	2.0	0.010
45	7.3870	0.0012	0.0051	2.0	0.010
50	7.3848	0.0013	0.0052	2.0	0.010

[a] u_c(measurement) includes components associated with the measurement method and material homogeneity, but does not include the uncertainty of the Bates-Guggenheim Convention (0.0050) [4].

[b] $u_c(y)$ is the combined standard uncertainty, which includes u_c(measurement) and the standard uncertainty of the Bates-Guggenheim Convention (0.0050) [4].

Reference Values: To attain traceability to the NIST reference pH(S) values for the 2 formulations of SRM 186-I-g/SRM 186-II-g when traceability to the SI is not necessary, the uncertainty of the Bates-Guggenheim convention is excluded from the uncertainty calculation. Each reference value includes the respective pH(S) value in Tables 1 and 2 and its corresponding expanded uncertainty, U_R:

$$U_R = k_R u_c(\text{measurement})$$

where k_R is the coverage factor for U_R. For both formulations, $k_R = 2.0$ at all temperatures except for the equimolal formulation at 30 °C, where $k_R = 2.1$. NIST Reference values are noncertified values that are the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty [6].

NOTICE AND WARNINGS TO USERS

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

Source of Material:[1] The potassium dihydrogen phosphate (KH_2PO_4) and the disodium hydrogen phosphate (Na_2HPO_4) were obtained from a commercial company. These materials conform to the specifications of the American Chemical Society for reagent grade chemicals [7].

Storage: SRMs 186-I-g and 186-II-g are stable when stored in their original container, with the caps tightly closed, in a dry environment, and under normal laboratory temperatures.

INSTRUCTIONS FOR USE

Drying Instructions: The two salts should be dried for two hours at 110 °C before use and stored in a desiccator over anhydrous $Mg(ClO_4)_2$.

Preparation of Carbon Dioxide-Free Water: Carbon-dioxide free water must be used for making the solutions. This water must be prepared either by (1) boiling a good grade of distilled water (conductivity < 2 μS/cm) for 10 min and guarding it with a soda-lime tube while cooling or (2) dispensing water directly from a deionization-based point-of-use system into the vessel used to prepare the buffer solutions (resistivity > 17 MΩ^{g}cm).

Preparation of the Equimolal (0.025 mol/kg) Solution: Measure 3.40 g of KH_2PO_4, $m_{186\text{-I-f}}$, to an accuracy of 1 mg into a clean, dry, 1 L polyethylene bottle. Add a mass of carbon dioxide-free water equal to 293.730 multiplied by $m_{186\text{-I-f}}$. Shake until the solid has totally dissolved. Measure 3.36 g of Na_2HPO_4, $m_{186\text{-II-f}}$, to an accuracy of 1 mg into a separate clean, dry, 1 L polyethylene bottle. Add to the second bottle containing $m_{186\text{-II-f}}$ a mass of the KH_2PO_4 (186-I-f) solution equal to 282.561 multiplied by $m_{186\text{-II-f}}$. Shake until the solid has totally dissolved. Preparation in this manner reduces the possibility of CO_2 absorption by the buffer and also eliminates the need for measurement of exact masses of solid samples.

Preparation of the Physiological Buffer Solution: Measure 1.18 g of KH_2PO_4, $m_{186\text{-I-f}}$, to an accuracy of 1 mg into a clean, dry, 1 L polyethylene bottle. Add a mass of carbon dioxide-free water equal to 844.537 multiplied by $m_{186\text{-I-f}}$. Shake until the solid has totally dissolved. Measure 4.10 g of Na_2HPO_4, $m_{186\text{-II-f}}$, to an accuracy of 1 mg into a separate clean, dry, 1 L polyethylene bottle. Add to the second bottle containing $m_{186\text{-II-f}}$ a mass of KH_2PO_4 (186-I-f) solution equal to 487.586 multiplied by $m_{186\text{-II-f}}$. Shake until the solid has totally dissolved. Preparation in this manner reduces the possibility of CO_2 absorption by the buffer and also eliminates the need for exact measurement of masses of solid samples.

Stability of Prepared Solution: Solutions are stable for one month. For the highest accuracy, prepare fresh solutions on a weekly basis.

[1] Certain commercial equipment, instruments, or materials are identified in this certificate in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Although elaborate precautions to prevent contamination of these buffer solutions with atmospheric CO_2 are usually unnecessary, the container should be kept tightly capped at all times when a sample is not actually being removed. The solution should be replaced after two weeks or sooner if molds or sediment appear, or if it has been exposed repeatedly to air containing carbon dioxide.

REFERENCES

[1] Wu, Y.C.; Koch, W.F.; Marinenko, G.; *A Report on the National Bureau of Standards pH Standards*; J. Res. Natl. Bur. Stand.: Vol. 89, p. 395 (1984).

[2] Wu, Y.C.; Koch, W.F.; Durst, R.A.; *Standard Reference Materials: Standardization of pH Measurements*; NBS Spec. Publ. 260-53 (February 1988).

[3] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed. ISO, Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/.

[4] Buck, R.P.; et. al.; *Measurement of pH. Definition, Standards, and Procedures*; IUPAC Recommendation 2002, *Pure Appl. Chem*, Vol. 74, p. 2169 (2002); also available on-line at http://www.iupac.org/publications/pac/2002/pdf/7411x2169.pdf.

[5] Bates, R.G.; Guggenheim, E.A.; *A Report on the Standardization of pH and Related Terminology*; *Pure Appl. Chem.*; Vol. 1, p. 163 (1960).

[6] May, W.; et. al.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136, U.S. Government Printing Office: Washington, DC (2000).

[7] *Reagent Chemicals*; 8th Ed., American Chemical Society: Washington, DC (1993).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.