National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 185h

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 185h, Potassium Hydrogen Phthalate ($KHC_8H_4O_4$), was prepared to ensure high purity and uniformity. However, this SRM is certified **ONLY** as a pH standard [pH(S)] not as a pure substance. A unit of SRM 185h consists of 60 g of potassium hydrogen phthalate.

Certified Values and Uncertainties: The certified pH(S) values provided in Table 1 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 = 1.013 25 $\times$ 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 SRM 185h. 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: extrapolation to obtain the acidity function, $p(a_H\gamma_{Cl})^\circ$; standard electrode potentials, E°; material homogeneity; molality of HCl, b_{HCl}, used for determining E°; 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 [4,5] of the conventional calculation of log γ_{Cl} (Bates-Guggenheim convention [6]). Current expert opinion [4,5] 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 [7]. The certified pH(S) values and their expanded uncertainties, U, are stated in Table 1.

Expiration of Certification: The certification of this SRM is valid until **31 October 2013**, 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 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.

Willie E. May, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 11 November 2003

John Rumble, Jr., Chief
Measurement Services Division

A solution of molality 0.05 mol/kg 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.

Table 1. Certified pH(S) Values and Expanded Uncertainties (95 % Confidence)[a,b]

t/°C	pH(S)	u_c(measurement)[a]	$u_c(y)$[b]	k_{cov}	U[b]
5	4.004	0.0007	0.0050	1.96	0.010
10	4.001	0.0007	0.0050	1.96	0.010
15	4.001	0.0006	0.0050	1.96	0.010
20	4.003	0.0007	0.0050	1.96	0.010
25	4.008	0.0006	0.0050	1.96	0.010
30	4.015	0.0011	0.0051	1.96	0.010
35	4.023	0.0011	0.0051	1.96	0.010
37	4.027	0.0011	0.0051	1.96	0.010
40	4.034	0.0011	0.0051	1.96	0.010
45	4.046	0.0011	0.0051	1.96	0.010
50	4.060	0.0011	0.0051	1.96	0.010

[a] u_c(measurement) includes all components associated with the measurement method and assessment of material homogeneity, but **DOES NOT** include the standard uncertainty of the Bates-Guggenheim Convention (0.0050) [4,5].

[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) [4,5].

Reference Values: To attain traceability to the NIST reference pH(S) values for SRM 185h when traceability to the SI is not necessary, the uncertainty of the Bates-Guggenheim convention is excluded from the uncertainty calculation. The respective pH(S) values in Table 2 are identical to those in Table 1 but are listed to the number of decimal places corresponding to 2 significant figures for the corresponding expanded uncertainty, U_R:

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

where k_R is the coverage factor for U_R. NIST reference values are non-certified 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 [7].

Table 2. Reference pH(S) Values and Expanded Reference Uncertainties (95 % Confidence)[a]

t/°C	pH(S)[a]	u_c(measurement)	k_R	U_R
5	4.0042	0.0007	2.06	0.0014
10	4.0011	0.0007	2.06	0.0013
15	4.0008	0.0006	2.06	0.0013
20	4.0031	0.0007	2.06	0.0014
25	4.0077	0.0006	2.07	0.0013
30	4.0146	0.0011	1.97	0.0022
35	4.0234	0.0011	1.97	0.0022
37	4.0274	0.0011	1.97	0.0023
40	4.0340	0.0011	1.97	0.0023
45	4.0463	0.0011	1.97	0.0022
50	4.0601	0.0011	1.97	0.0022

[a] u_c(measurement) and U_R each include all components associated with the measurement method and assessment of material homogeneity, but **DO NOT** include the uncertainty of the Bates-Guggenheim Convention (0.0050) [4,5].

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: The potassium hydrogen phthalate ($KHC_8H_4O_4$) was obtained from a commercial company. This material conforms to the specifications of the American Chemical Society for primary standard chemicals [8].

Storage: SRM 185h is stable when stored in its original container, with the cap tightly closed, in a dry environment, and under normal laboratory temperatures.

INSTRUCTIONS FOR USE

Drying Instructions: SRM 185h should be dried for 2 h at 110 °C and stored in a desiccator over anhydrous $Mg(ClO_4)_2$ before use.

Source Water for Solution Preparation: The water used in the preparation of the SRM 185h buffer solution need not be protected from atmospheric carbon dioxide, and elaborate precautions for the exclusion of air from the solution are not necessary. Distilled water with an electrolytic conductivity not greater than 2 μS/cm or water directly obtained from a point-of-use, deionization-based system, of electrolytic conductivity less than 1 μS/cm, may be used, without boiling. The solution should, however, be protected against evaporation and contamination by molds. SRM 185h buffer solutions should be replaced at least every month, or whenever mold is detected.

Preparation of the 0.05 mol/kg Solution: Quantities denoted by m_W and associated numerical factors in this paragraph include the effect of air buoyancy, i.e., they correspond to the balance indication in units of mass obtained in the laboratory (the *balance reading*). Weigh by difference, approximately 9.8 g of SRM 185h, $m_{W,185h}$, to an accuracy of 1 mg, into a clean, dry, 1 L polyethylene bottle. Add a quantity of CO_2-free water, equal to 97.887 multiplied by $m_{W,185h}$, to an accuracy of 0.1 g. Shake until the solid has totally dissolved. Gravimetric preparation in this manner eliminates the need to weigh exactly predetermined masses of solid samples. Proportionately smaller quantities of each SRM may be used in this preparation, provided that $m_{W,185h}$ exceeds 4.0 g.

Stability of Prepared Solution: Solutions should be discarded after one month or sooner if mold or sediment appears.

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] Baucke, F.G.K.; *Anal. Bioanal. Chem*.; Vol. 734, p. 772 (2002).

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

[7] 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).

[8] *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.