



# Certificate of Analysis

## Standard Reference Material® 186g

### pH Standards

#### Potassium Dihydrogen Phosphate (186-I-g)

#### Disodium Hydrogen Phosphate (186-II-g)

This Standard Reference Material (SRM) is intended for use in preparing solutions for calibrating electrodes for pH measuring systems. SRM 186g consists of two components, each prepared to ensure high purity and uniformity:  $\text{KH}_2\text{PO}_4$ , Potassium Dihydrogen Phosphate (186-I-g) and  $\text{Na}_2\text{HPO}_4$ , Disodium Hydrogen Phosphate (186-II-g). However, neither SRM component is certified for purity of substance. A unit of SRM 186g consists of 30 g of potassium dihydrogen phosphate (186-I-g) and 45 g of disodium hydrogen phosphate (186-II-g), each contained in its respective clear glass bottle.

**Certified Values and Uncertainties:** The certified pH(S) values provided in Tables 1 and 2 correspond to  $\log(1/a_{\text{H}})$ , where  $a_{\text{H}}$  is the conventional activity of the hydrogen (hydronium) ion referred to the standard state ( $p^\circ = 1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$ ) 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 results obtained using 186-I-g and 186-II-g together. Minor variations of pH(S) values (of the order of a few thousandths of a unit) may be expected to occur if either 186-I-g or 186-II-g is used with pH standards from previously issued lots of SRM 186.

The uncertainty in the certified value,  $U$ , is calculated as  $U = k u_{\text{c}}(y)$ , where  $u_{\text{c}}(y)$  is the *combined standard uncertainty* calculated according to the ISO Guide [3]. The value of  $u_{\text{c}}(y)$  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,  $E^\circ$ ; material homogeneity; molality of  $\text{HCl}$ ,  $b_{\text{HCl}}$ , used for determining  $E^\circ$ ; measured cell potentials; correction to the standard pressure for  $\text{H}_2$  gas; mean activity coefficient of  $\text{HCl}$  at  $b_{\text{HCl}}$ ; gas constant; temperature; Faraday constant; the molality of  $\text{NaCl}$ ; and the uncertainty [4] of the conventional calculation of  $\log \gamma_{\text{Cl}}$  (Bates-Guggenheim convention [5]). Current expert opinion [4] has assessed the uncertainty attributable to the Bates-Guggenheim convention as 0.010 pH (95 % confidence interval). The value of  $u_{\text{c}}(y)$  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 **SRM 186g** is valid, within the measurement uncertainty specified, until **30 April 2023**, provided the SRM is handled in accordance with instructions given in this certificate (see "Instructions for Use and Storage"). This certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

**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. Registration (see attached sheet or register online) will facilitate notification.

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

Carlos A. Gonzalez, Chief  
Chemical Sciences Division

Gaithersburg, MD 20899  
Certificate Issue Date: 14 August 2018  
*Certificate Revision History on Last Page*

Steven J. Choquette, Director  
Office of Reference Materials

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

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

**Traceability:** The measurand is the pH of the specified buffer solution. The certified values in Tables 1 and 2 are metrologically traceable to the International System of Units (SI) of amount-of-substance and mass and to the definition of single ionic activity.

A solution of molality 0.025 mol/kg with respect to both  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  (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.

Table 1. Certified pH(S) Values and Expanded Uncertainties (95 % Confidence) for the Equimolal Formulation<sup>(a,b)</sup>

$t/^{\circ}\text{C}$	pH(S)	$u_c(\text{measurement})^{(a)}$	$u_c(y)^{(b)}$	$k$	$U$
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

<sup>(a)</sup>  $u_c(\text{measurement})$  includes components associated with the measurement method and material homogeneity, but does not include the uncertainty of the Bates-Guggenheim Convention (0.0050) [4].

<sup>(b)</sup>  $u_c(y)$  is the combined standard uncertainty, which includes  $u_c(\text{measurement})$  and the standard uncertainty of the Bates-Guggenheim Convention (0.0050) [4].

A solution of molality 0.008 695 mol/kg with respect to  $\text{KH}_2\text{PO}_4$  and 0.030 43 mol/kg with respect to  $\text{Na}_2\text{HPO}_4$  (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 are given in Table 2.

Table 2. Certified pH(S) Values and Expanded Uncertainties (95 % Confidence) for the Physiological Formulation<sup>(a,b)</sup>

$t/^{\circ}\text{C}$	pH(S)	$u_{\text{c}}(\text{measurement})^{(a)}$	$u_{\text{c}}(y)^{(b)}$	$k$	$U$
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

<sup>(a)</sup>  $u_{\text{c}}(\text{measurement})$  includes components associated with the measurement method and material homogeneity, but does not include the uncertainty of the Bates-Guggenheim Convention (0.0050) [4].

<sup>(b)</sup>  $u_{\text{c}}(y)$  is the combined standard uncertainty, which includes  $u_{\text{c}}(\text{measurement})$  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 186g (186-I-g and 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,  $U_{\text{R}}$ :

$$U_{\text{R}} = k_{\text{R}} u_{\text{c}}(\text{measurement})$$

where  $k_{\text{R}}$  is the coverage factor for  $U_{\text{R}}$ . For both formulations,  $k_{\text{R}} = 2.0$  at all temperatures except for the equimolal formulation at 30  $^{\circ}\text{C}$ , where  $k_{\text{R}} = 2.1$ . 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].

## INSTRUCTIONS FOR USE AND STORAGE

**Drying Instructions:** The two salts should be dried for two hours at 110 °C before use and stored in a desiccator over anhydrous  $\text{Mg}(\text{ClO}_4)_2$ .

**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  $\mu\text{S}/\text{cm}$ ) 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  $\text{M}\Omega\cdot\text{cm}$ ).

**Preparation of the Equimolal (0.025 mol/kg) Solution:** Quantities denoted by  $m_{\text{W}}$  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 3.34 g of 186-I-g,  $m_{\text{W},186\text{-I-g}}$ , to an accuracy of 0.2 mg, into a clean, dry, 1 L polyethylene bottle. Add a quantity of  $\text{CO}_2$ -free water, equal to 293.730 multiplied by  $m_{\text{W},186\text{-I-g}}$ , to an accuracy of 0.1 g. Shake until the solid has totally dissolved. Weigh by difference approximately 3.37 g of 186-II-g,  $m_{\text{W},186\text{-II-g}}$ , to an accuracy of 0.2 mg, into a second clean, dry, 1 L polyethylene bottle. Add to this second bottle a quantity of the 186-I-g solution, equal to 282.561 multiplied by  $m_{\text{W},186\text{-II-g}}$ , to an accuracy of 0.1 g. Shake until the solid has totally dissolved. Gravimetric preparation in this manner reduces the possibility of  $\text{CO}_2$  absorption by the buffer and also eliminates the need to weigh exactly predetermined masses of solid samples. Proportionately smaller quantities of each may be used in this preparation, provided that  $m_{\text{W},186\text{-I-g}}$  exceeds 0.9 g and  $m_{\text{W},186\text{-II-g}}$  exceeds 0.8 g.

**Preparation of the Physiological Buffer Solution:** Quantities denoted by  $m_{\text{W}}$  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 1.16 g of 186-I-g,  $m_{\text{W},186\text{-I-g}}$ , to an accuracy of 0.2 mg into a clean, dry, 1 L polyethylene bottle. Add a quantity of  $\text{CO}_2$ -free water, equal to 844.537 multiplied by  $m_{\text{W},186\text{-I-g}}$ , to an accuracy of 0.1 g. Shake until the solid has totally dissolved. Weigh by difference, approximately 4.12 g of 186-II-g,  $m_{\text{W},186\text{-II-g}}$ , to an accuracy of 0.2 mg, into a second clean, dry, 1 L polyethylene bottle. Add to this second bottle a quantity of the 186-I-g solution, equal to 231.626 multiplied by  $m_{\text{W},186\text{-II-g}}$ , to an accuracy of 0.1 g. Shake until the solid has totally dissolved. Gravimetric preparation in this manner reduces the possibility of  $\text{CO}_2$  absorption by the buffer and also eliminates the need to weigh exactly predetermined masses of solid samples. Proportionately smaller masses of each may be used in this preparation, provided that  $m_{\text{W},186\text{-I-g}}$  exceeds 0.6 g and  $m_{\text{W},186\text{-II-g}}$  exceeds 2.1 g.

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

Although elaborate precautions to prevent contamination of these buffer solutions with atmospheric  $\text{CO}_2$  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 mold or sediment appears, or if it has been exposed repeatedly to air containing carbon dioxide.

**Storage:** Both components of SRM 186g (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.

**Source of Material<sup>(1)</sup>:** The potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) and the disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) were obtained from a commercial company. These materials conform to the specifications of the American Chemical Society for reagent grade chemicals [7].

---

<sup>(1)</sup> Certain commercial equipment, instruments or materials are identified in this certificate to adequately specify 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.

## 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 (1988).
- [3] JCGM 100:2008; Evaluation of Measurement Data Guide to the Expression of Uncertainty in Measurement (GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (JCGM) (2008); available at [https://www.bipm.org/utis/common/documents/jcgm/JCGM\\_100\\_2008\\_E.pdf](https://www.bipm.org/utis/common/documents/jcgm/JCGM_100_2008_E.pdf) (accessed Aug 2018); 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 <https://www.nist.gov/pml/nist-technical-note-1297> (accessed Aug 2018).
- [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.; Parris, R.; Beck II, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definition of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136 (2000); available at <https://www.nist.gov/sites/default/files/documents/srm/SP260-136.PDF> (accessed Aug 2018).
- [7] *Reagent Chemicals*; 8th ed., American Chemical Society: Washington, DC (1993).

**Certificate Revision History:** 14 August 2018 (Change of expiration date; editorial changes); 05 March 2013 (Extension of certification period); 06 March 2008 (Editorial change); 28 November 2007 (Extension of certification period); 07 November 2003 (This revision reflects (1) a correction in the "INSTRUCTIONS FOR USE" section, particularly the gravimetric factor by which  $m_{w,186-II-g}$  is multiplied and (2) editorial changes to reflect a single SRM number designation of SRM 186g); 23 May 2003 (Original certificate date).

*Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail [srminfo@nist.gov](mailto:srminfo@nist.gov); or via the Internet at <https://www.nist.gov/srm>.*