



National Institute of Standards & Technology

# Certificate of Analysis

Standard Reference Materials® 191c

pH Standards

Sodium Bicarbonate (191-I-c)

Sodium Carbonate (191-II-c)

This Standard Reference Material (SRM) is intended for use in preparing solutions for calibrating electrodes for pH measuring systems. SRM 191c consists of two components, each prepared to ensure high purity and uniformity: Sodium Bicarbonate,  $\text{NaHCO}_3$  (191-I-c) and Sodium Carbonate,  $\text{Na}_2\text{CO}_3$  (191-II-c). However, neither SRM component is certified for purity of substance. A unit of SRM 191c consists of 25 g of sodium bicarbonate (191-I-c) and 30 grams of sodium carbonate (191-II-c), each contained in its respective clear glass bottle.<sup>1</sup>

**Certified Values and Uncertainties:** The certified pH(S) values provided in Table 1 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 when both SRM 191c components are used together. 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,  $p(a_{\text{H}}\gamma_{\text{Cl}})^\circ$ ; standard electrode potentials,  $E^\circ$ ; material homogeneity; molality of 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 HCl at  $b_{\text{HCl}}$ ; gas constant; temperature; Faraday constant; the molality of NaCl; and the uncertainty [4,5] of the conventional calculation of  $\log \gamma_{\text{Cl}}$  (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 **SRM 191c** is valid, within the measurement uncertainties specified, until **31 October 2011**, provided the SRM is handled in accordance with instructions given in this certificate (see "Instructions for Use"). 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) will facilitate this notification.

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

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Certificate Issue Date: 20 July 2009  
See Certificate Revision History on Last Page

Robert L. Watters, Jr., Chief  
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<sup>1</sup>Previous renewals of SRM 191c designated the  $\text{Na}_2\text{CO}_3$  component (191-II-c), as SRM 192, 192a, and 192b. The new SRM numbering unifies SRM 191c nomenclature with that used with SRM 186g, which contains two phosphate buffers (186-I-g and 186-II-g).

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 Measurement Services Division.

A solution of molality 0.025 mol/kg with respect to both  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  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)<sup>(a,b)</sup>

$t/^{\circ}\text{C}$	pH(S)	$u_{\text{c}}(\text{measurement})^{(a)}$	$u_{\text{c}}(y)^{(b)}$	$k$	$U^b$
15	10.117	0.0016	0.0052	1.96	0.010
20	10.063	0.0018	0.0053	1.96	0.010
25	10.012	0.0016	0.0052	1.96	0.010
35	9.928	0.0020	0.0054	1.96	0.011

<sup>(a)</sup>  $u_{\text{c}}(\text{measurement})$  includes all components associated with the measurement method and assessment of material homogeneity, but **DO NOT** include the standard uncertainty of the Bates-Guggenheim Convention (0.0050) [4,5].

<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) [4,5].

**Reference Values:** To attain traceability to the NIST reference pH(S) values for SRM 191c (191-I-c and 191-II-c) 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,  $U_{\text{R}}$ :

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

where  $k_{\text{R}}$  is the coverage factor for  $U_{\text{R}}$ . 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)<sup>(a)</sup>

$t/^{\circ}\text{C}$	pH(S)	$u_{\text{c}}(\text{measurement})$	$k_{\text{R}}$	$U_{\text{R}}$
15	10.1172	0.0016	2.10	0.0033
20	10.0633	0.0018	2.08	0.0037
25	10.0123	0.0016	2.09	0.0033
35	9.9285	0.0020	2.09	0.0041

<sup>(a)</sup>  $u_{\text{c}}(\text{measurement})$  and  $U_{\text{R}}$  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

**Source of Material<sup>2</sup>:** The sodium bicarbonate ( $\text{NaHCO}_3$ ) and the sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) were obtained from a commercial company. These materials conform to the specifications of the American Chemical Society for reagent grade chemicals [8].

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<sup>2</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.

**Storage:** SRM 191c components are stable when stored in their original containers, with the caps tightly closed, in a dry environment, and under normal laboratory temperatures.

## INSTRUCTIONS FOR USE

**Drying Instructions:** The sodium bicarbonate (191-I-c) should be dried for 24 h at 20 °C to 25 °C in a vacuum desiccator ( $p < 30$  hPa) over anhydrous  $\text{Mg}(\text{ClO}_4)_2$  before use. The sodium carbonate (191-II-c) should be dried for 2 h at 275 °C in a Pt or fused silica crucible and then cooled to room temperature in a desiccator over anhydrous  $\text{Mg}(\text{ClO}_4)_2$ . Both materials should be stored in a desiccator over anhydrous  $\text{Mg}(\text{ClO}_4)_2$  between the drying and weighing.

**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 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 2.06 g of material 191-I-c,  $m_{\text{W},191\text{-I-c}}$  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 475.845 multiplied by  $m_{\text{W},191\text{-I-c}}$  to an accuracy of 0.1 g. Shake until the solid has totally dissolved. Weigh by difference approximately 2.52 g of material 192-II-c,  $m_{\text{W},191\text{-II-c}}$  to an accuracy of 0.2 mg, into a second clean, dry, 1 L polyethylene bottle. Add to this second bottle a quantity of 191-I-c solution, equal to 377.917 multiplied by  $m_{\text{W},191\text{-II-c}}$  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 material may be used in this preparation, provided that  $m_{\text{W},191\text{-I-c}}$  exceeds 0.62 g and  $m_{\text{W},191\text{-II-c}}$  exceeds 0.64 g.

**Stability of Prepared Solution:** Solutions should be discarded after two weeks or sooner if sediment appears 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 (1988).
- [3] ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st ed.; International Organization for Standardization: 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).
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- [8] *Reagent Chemicals*; 8th ed.; American Chemical Society; Washington, DC (1993).

Certificate Revision History: 20 July 2009 (Extension of certification period); 01 December 2003 (Original Certificate date).
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*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) 975-2200; fax (301) 926-4751; e-mail [srminfo@nist.gov](mailto:srminfo@nist.gov); or via the Internet at <http://www.nist.gov/srm>.*