



National Institute of Standards & Technology

# Certificate of Analysis

Standard Reference Material<sup>®</sup> 191d

pH Standard

Sodium Bicarbonate (191d-I)

Sodium Carbonate (191d-II)

This Standard Reference Material (SRM) is intended for use in preparing solutions for calibrating electrodes for pH measuring systems. SRM 191d consists of two components, each prepared to ensure high purity and uniformity: Sodium Bicarbonate, NaHCO<sub>3</sub> (191d-I); and Sodium Carbonate, Na<sub>2</sub>CO<sub>3</sub> (191d-II). However, neither SRM component is certified for purity of substance. A unit of SRM 191d consists of 25 g of sodium bicarbonate (191d-I) and 30 g of sodium carbonate (191d-II), each contained in its respective clear glass bottle.

**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 ( $p^{\circ} = 1 \text{ atm} = 101\,325 \text{ Pa}$ ) on the scale of molality. The values were derived from emf measurements of cells without liquid junction by the primary measurement (Harned cell) method [1]. **NOTE:** These certified values apply only when both SRM 191d components are used together. Minor variations of pH(S) values (on the order of a few thousandths of a unit) may be expected to occur between SRM renewals.

The expanded 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/JCGM Guide [2]. 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: the standard deviation of the pH(S) values after smoothing with respect to temperature as described in reference 3; standard electrode potentials,  $E^{\circ}$ ; molality of HCl,  $b_{\text{HCl}}$ , used for determining  $E^{\circ}$ ; measured cell potentials; correction to the standard pressure for H<sub>2</sub> gas; mean activity coefficient of HCl at  $b_{\text{HCl}}$ ; gas constant; temperature; Faraday constant; the molality of added NaCl; the stability of the primary measurement; material homogeneity for each component; and the uncertainty of the conventional calculation of  $\log \gamma_{\text{Cl}}$  (Bates-Guggenheim convention [4]). Current expert opinion [1,5] has assessed the uncertainty attributable to the Bates-Guggenheim convention as 0.010 pH (95 % confidence level). 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. The certified pH(S) values and their expanded uncertainties are stated in Table 1. 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 taken into account [6].

**Expiration of Certification:** The certification of **SRM 191d** is valid, within the measurement uncertainty specified, until **30 June 2018**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Storage and 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 Chemical Sciences Division.

Carlos A. Gonzalez, Chief  
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Gaithersburg, MD 20899  
Certificate Issue Date: 05 September 2013  
*Certificate Revision History on Last Page*

Robert L. Watters, Jr., Director  
Office of Reference Materials

Coordination of the technical measurements leading to the certification of SRM 191d was provided by T.W. Vetter of the NIST Chemical Sciences Division.

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

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

A solution of molality 0.025 mol/kg with respect to both NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> 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. Values of *U* are given at the approximate 95 % level of confidence. The coverage factor, *k*, at each temperature is 1.96. The corresponding degrees of freedom, *v*<sub>eff</sub>, of *u*<sub>c</sub>(*y*) at each temperature is >1000.

Table 1. Certified pH(S) Values, Combined Standard Uncertainties, and Expanded Uncertainties for SRM 191d.

Temperature (°C)	pH(S)	<i>u</i> <sub>c</sub> ( <i>y</i> ) <sup>(a)</sup>	<i>U</i>
10	10.179	0.0052	0.010
15	10.118	0.0052	0.010
20	10.063	0.0052	0.010
25	10.014	0.0052	0.010
30	9.968	0.0052	0.010
35	9.926	0.0052	0.010

<sup>(a)</sup> *u*<sub>c</sub>(*y*) is the combined standard uncertainty, which includes *u*<sub>c</sub> for the measurement (see Table 2, below) and the standard uncertainty of the Bates-Guggenheim Convention (0.0050) [1,5].

**Reference Values:** To attain traceability to the NIST reference pH(S) values for SRM 191d 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 they are listed to the number of decimal places corresponding to two significant figures for the corresponding expanded uncertainty, *U*<sub>R</sub>:

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

where *k*<sub>R</sub> is the coverage factor corresponding to a level of confidence of 95 % for *U*<sub>R</sub>. Table 2 also lists the reference *v*<sub>eff</sub> values at each temperature. 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].

Table 2. Reference pH(S) Values and Reference Uncertainties<sup>(a)</sup> for SRM 191d.

Temperature (°C)	pH(S)	<i>u</i> <sub>c</sub> (measurement)	<i>k</i> <sub>R</sub>	<i>v</i> <sub>eff</sub>	<i>U</i> <sub>R</sub>
10	10.1786	0.0015	2.02	44.3	0.0031
15	10.1179	0.0015	2.01	49.9	0.0030
20	10.0632	0.0014	2.01	49.0	0.0029
25	10.0137	0.0015	2.01	49.6	0.0029
30	9.9683	0.0015	2.01	48.7	0.0029
35	9.9264	0.0015	2.01	45.1	0.0031

<sup>(a)</sup> *u*<sub>c</sub>(measurement) and *U*<sub>R</sub> 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) [1,5].

## NOTICE AND WARNINGS TO USERS

**Source of Material<sup>(1)</sup>:** The sodium bicarbonate ( $\text{NaHCO}_3$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) were obtained from a commercial company. The homogeneity of each material was assessed in the course of the certification of this SRM. These materials conform to the respective specifications of the American Chemical Society [7].

## INSTRUCTIONS FOR STORAGE AND USE

**Storage:** Each component of SRM 191d is stable when stored in its original container, with the cap tightly closed, in a dry environment, and at normal laboratory temperatures. SRM 191d-II (sodium carbonate) is hygroscopic, and the material may form a cake on extended storage. This absorption of moisture and caking is not a problem in the preparation of the SRM buffer if the SRM 191d-II sample is dried as specified below.

**Drying Instructions:** Dry the sodium bicarbonate (191d-I) for 24 h at 20 °C to 25 °C over anhydrous magnesium perchlorate before use. Break up any caked SRM 191d-II material before drying. Dry the sodium carbonate (191d-II) for 2 h at 275 °C in a platinum or fused silica crucible and then cool the dried material to room temperature in a desiccator over anhydrous magnesium perchlorate. Store both materials in a desiccator over anhydrous magnesium perchlorate between the drying and weighing.

**Preparation of Carbon Dioxide-Free Water:**  $\text{CO}_2$ -free water must be used for making the solutions. Prepare  $\text{CO}_2$ -free water either by (1) dispensing water directly from a deionization-based point-of-use system (resistivity greater than 17  $\text{M}\Omega\cdot\text{cm}$  at delivery) into the vessel used to prepare the buffer solutions, or (2) boiling distilled water (conductivity less than 0.5  $\text{M}\Omega\cdot\text{cm}$ ) for 10 min and guarding it with a soda-lime tube while cooling.

**Preparation of the 0.025 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 2.05 g  $\pm$  0.05 g of SRM 191d-I,  $m_{W,191d-I}$ , to an accuracy of 0.2 mg, into a clean, dry, 1 L polyethylene bottle<sup>(2)</sup>. Add a quantity of  $\text{CO}_2$ -free water, equal to 475.845 multiplied by  $m_{W,191d-I}$ , to an accuracy of 0.1 g. Shake until the solid has totally dissolved. Weigh by difference 2.45 g  $\pm$  0.05 g of SRM 191d-II,  $m_{W,191d-II}$ , 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 SRM 191d-I solution, equal to 377.917 multiplied by  $m_{W,191d-II}$ , to an accuracy of 0.1 g. Shake until the solid has totally dissolved. Discard any remaining SRM 191d-I solution not transferred to the second bottle. Gravimetric preparation in this manner reduces the possibility of  $\text{CO}_2$  absorption by the buffer and eliminates the need to weigh exactly predetermined masses of solid samples.

The amounts in the preceding paragraph may be scaled to different-sized bottles, provided that  $m_{W,191d-I}$  exceeds 0.50 g and  $m_{W,191d-II}$  exceeds 0.65 g. In addition, the SRM 191d-I solution should occupy between 85 % and 95 % of the total internal volume of the first bottle in the preparation of the SRM 191d buffer solution.

The corresponding  $m_W$  values yielding a molality of each component equal to 0.025 000  $\text{mol}\cdot\text{kg}^{-1}$  are 2.1015 g  $\text{NaHCO}_3$  and 2.6516 g  $\text{Na}_2\text{CO}_3$  per 1000.0 g  $\text{H}_2\text{O}$ .

**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.

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<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.

<sup>(2)</sup> The specified target mass of SRM 191d-I is calculated for a 1 L (nominal volume) bottle with a total internal volume of 1.050 L.

## REFERENCES

- [1] Buck, R.P.; Rondinini, S.; Covington, A.K.; Baucke, F.G.K.; Brett, C.M.A.; Camões, M.F.; Milton, M.J.T.; Mussini, T.; Naumann, R.; Pratt, K.W.; Spitzer, P.; Wilson, G.S.; *Measurement of pH. Definition, Standards, and Procedures*; IUPAC Recommendation 2002; Pure Appl. Chem., Vol. 74, pp. 2169–2200 (2002); available at <http://www.iupac.org/publications/pac/2002/pdf/7411x2169.pdf> (accessed Sep 2013).
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- [7] *Reagent Chemicals*, 9th ed.; American Chemical Society: Washington, DC (1999).

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*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 <http://www.nist.gov/srm>.*