

Standard Reference Material[®] 191d

Sodium Bicarbonate (191d-I) Sodium Carbonate (191d-II)

(pH Standard)

CERTIFICATE OF ANALYSIS

Purpose: The certified values delivered by this Standard Reference Material (SRM) are intended for use in preparing solutions for calibrating electrodes for pH measuring systems.

Description: A unit of SRM 191d consists of 25 g of Sodium Bicarbonate, NaHCO₃ (191d-I) and 30 g of Sodium Carbonate, Na₂CO₃ (191d-II), each contained in its respective clear glass bottle. Each component is prepared to ensure high purity and uniformity. However, neither SRM component is certified for purity of substance.

Certified Values: 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 [1]. The certified pH(S) values provided in Table 1 correspond to $\log(1/a_{\text{H}})$, where a_{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 by potentiometric measurements of cells without liquid junction by the primary measurement (Harned cell) method [2]. **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 [3].

The measurand is the pH of the specified buffer solution. The certified values are metrologically traceable to the International System of Units (SI) of amount-of-substance and mass and to the convention [4] used to define ionic activity, including its uncertainty [2, 5].

A solution of molality 0.025 mol/kg with respect to both NaHCO₃ and Na₂CO₃ is prepared 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, ν_{eff} , of u_c at each temperature is >1000.

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

Temperature (°C)	pH(S)	$u_c^{(a)}$	U
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

^(a) The combined standard uncertainty, u_c , includes u_c for the measurement (see Table A1, below) and the standard uncertainty of the Bates-Guggenheim Convention (0.0050) [2, 5].

Non-Certified Values: Non-certified values are provided in Appendix A.

Period of Validity: The certified values delivered by SRM 191d are valid within the measurement uncertainty specified until **30 November 2032**. The certified values are nullified if the material is stored or used improperly, damaged, contaminated, or otherwise modified.

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Maintenance of Certified Values: NIST will monitor this SRM over the period of its validity. If substantive technical changes occur that affect the certification, NIST will issue an amended certificate through the NIST SRM website (<https://www.nist.gov/srm>) and notify registered users. SRM users can register online from a link available on the NIST SRM website or fill out the user registration form that is supplied with the SRM. Registration will facilitate notification. Before making use of any of the values delivered by this material, users should verify they have the most recent version of this documentation, available through the NIST SRM website (<https://www.nist.gov/srm>).

Uncertainties: The expanded uncertainty in the certified value, U , is calculated as $U = ku_c$, where u_c is the *combined standard uncertainty* calculated according to the ISO/JCGM Guide [6]. The value of u_c 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 4; standard electrode potentials, E° ; 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 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 [2, 5] has assessed the uncertainty attributable to the Bates-Guggenheim convention as 0.010 pH (95 % confidence level). The value of u_c 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.

Safety: Consult the Safety Data Sheet (SDS) for hazard information.

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.

Source of Material: The sodium bicarbonate (NaHCO_3) and sodium carbonate (Na_2CO_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].

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. Sodium carbonate should be used within two weeks of heating at 275 °C.

Preparation of Carbon Dioxide-Free Water: CO_2 -free water must be used for making the solutions. Prepare 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, $m_{\text{W},191\text{d-I}}$, to an accuracy of 0.2 mg, into a clean, dry, 1 L polyethylene bottle. 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. Add a quantity of CO_2 -free water, equal to 475.845 multiplied by $m_{\text{W},191\text{d-I}}$, 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, $m_{\text{W},191\text{d-II}}$, 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 $m_{\text{W},191\text{d-II}}$, 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 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 $m_{\text{W},191\text{d-I}}$ exceeds 0.50 g and $m_{\text{W},191\text{d-II}}$ 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 NaHCO_3 and 2.6516 g Na_2CO_3 per 1000.0 g H_2O .

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

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- [3] Pratt, K.W.; *Longitudinal meta-analysis of NIST pH Standard Reference Materials: a complement to pH key comparisons*; Anal. Bioanal. Chem., Vol. 407, pp. 3193–3203 (2015).
- [4] Bates, R.G.; Guggenheim, E.A.; *A Report on the Standardization of pH and Related Terminology*; Pure Appl. Chem., Vol. 1, pp. 163–168 (1960).
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- [7] *Reagent Chemicals*, 9th ed.; American Chemical Society: Washington, DC (1999).

Certificate Revision History: 05 February 2025 (Editorial changes; updated format); 09 December 2024 (Change of expiration date; editorial changes); 01 October 2020 (Updated title, editorial changes); 19 July 2018 (Change of expiration date; editorial changes); 05 September 2013 (Editorial changes); 01 December 2009 (Original certificate date).

Certain commercial equipment, instruments, or materials may be identified in this Certificate of Analysis 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.

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the Office of Reference Materials 100 Bureau Drive, Stop 2300, Gaithersburg, MD 20899-2300; telephone (301) 975-2200; e-mail srminfo@nist.gov; or the Internet at <https://www.nist.gov/srm>.

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APPENDIX A

Non-certified Values: To attain traceability to the NIST non-certified 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 A1 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_R :

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

where k_R is the coverage factor corresponding to a level of confidence of 95 % for U_R . Table A1 also lists the non-certified v_{eff} values at each temperature. NIST non-certified values 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 [1]. The non-certified values are traceable to the SI units for amount-of-substance and mass and to this defining convention [4], taken as an exact value with no uncertainty (the uncertainty of the Bates-Guggenheim convention is excluded from the uncertainty calculation).

Table A1. Non-certified pH(S) Values and Non-certified Uncertainties^(a) for SRM 191d.

Temperature (°C)	pH(S)	$u_c(\text{measurement})$	k_R	v_{eff}	U_R
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

^(a) The uncertainty for measurement, $u_c(\text{measurement})$, and expanded uncertainty, 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) [2, 5].

Period of Validity: The non-certified values are valid within the measurement uncertainty specified until **30 November 2032**. The value assignments are nullified if the material is stored or used improperly, damaged, contaminated, or otherwise modified.

Maintenance of Non-Certified Values: NIST will monitor this material to the end of its period of validity. If substantive technical changes occur that affect the non-certified values during this period, NIST will update this Certificate of Analysis and notify registered users. SRM users can register online from a link available on the NIST SRM website or fill out the user registration form that is supplied with the SRM. Registration will facilitate notification. Before making use of any of the values delivered by this material, users should verify they have the most recent version of this documentation, available through the NIST SRM website (<https://www.nist.gov/srm>).

***** End of Appendix A *****