DEPARTMENT OF COMMERCE UNITED STATES OF AMERICA

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2193a

Calcium Carbonate pH Standard
[used as saturated $Ca(OH)_2$ solution]

This Standard Reference Material (SRM) is intended for use in preparing solutions for calibrating electrodes for pH measuring systems at pH values above 11.0. This lot of calcium carbonate ($CaCO_3$) was selected for its low level of alkali metal impurities. However, this SRM is certified **ONLY** as a pH standard, **NOT** as a pure substance. A unit of SRM 2193a consists of 30 g of $CaCO_3$.

Certified Values and Uncertainties: The certified standard pH, pH(S), values provided in Table 1 correspond to $\log(1/a_{\mathrm{H}})$, where a_{H} is the conventional activity of the hydrogen (hydronium) ion referred to the standard state ($p° = 1\ \mathrm{atm} = 1.013\,25 \times 10^5\ \mathrm{Pa}$) 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 2193a. Minor variations of pH(S) values (of the order of 0.01 units) may be expected to occur between different lots of this SRM.

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 and NIST Guides [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: curve-fit; standard electrode potentials, E^{o}; material homogeneity; molality of HCl, b_{HCl}, used for determining E^{o}; 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 uncertainty [4,5] of the conventional calculation of $\log \gamma_{\mathrm{C1}}$ (Bates-Guggenheim convention [6]). The value of $u_c(y)$ has been multiplied by 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 taken into account [7]. The measurand is the certified pH, pH(S), values listed in Table 1 as a function of temperature. The certified value is traceable to NIST's primary measurement of pH.

Expiration of Certification: The certification of **SRM 2193a** is valid, within the measurement uncertainties specified, until **01 July 2020**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise.

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.

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

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Certificate Issue Date: 30 September 2015
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Table l. Certified pH(S) Values and Expanded Uncertainties as a Function of Temperature

Before use for pH calibrations, a freshly filtered, saturated (at 25 °C) solution of $Ca(OH)_2$ must be prepared from SRM 2193a as described in the "Instructions for Use" section of this certificate. The certified pH(S) and U of this solution as a function of temperature are given below.

t/°C	pH(S)	u_c(measurement)(a)	$u_c(y)$(b)	k	U(b)
5	13.232	0.0030	0.0058	2.0	0.011
10	13.026	0.0025	0.0056	2.0	0.011
15	12.830	0.0025	0.0056	2.0	0.011
20	12.645	0.0024	0.0056	2.0	0.011
25	12.469	0.0024	0.0055	2.0	0.011
30	12.303	0.0071	0.0087	2.0	0.017
35	12.145	0.0071	0.0087	2.0	0.017
37	12.084	0.0071	0.0087	2.0	0.017
40	11.995	0.0071	0.0087	2.0	0.017
45	11.853	0.0072	0.0087	2.0	0.017
50	11.717	0.0074	0.0089	2.0	0.017

(a) u_c(measurement) includes components associated with the measurement method and material homogeneity, but does not include the uncertainty of the Bates-Guggenheim convention (0.0050) [4,5].

(b) $u_c(y)$ includes u_c(measurement) combined with u(Bates-Guggenheim convention) = 0.0050 [4,5].

Reference Values: To attain traceability to the NIST reference pH(S) values for SRM 2193a 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 Table 1 and its corresponding expanded uncertainty, U_R:

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

where k_R is the coverage factor for U_R. The value of $k_R = 2.0$ at all temperatures. A NIST reference value is a noncertified value that is 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].

NOTICE AND WARNINGS TO USERS(1)

Source of Material: The calcium carbonate ($CaCO_3$) was obtained from a commercial company. This material conforms to the specifications of the American Chemical Society for "calcium carbonate, low in alkalies" [8].

Storage: SRM 2193a is stable when stored in its original container, with the cap tightly closed, in a dry environment, and under normal laboratory temperatures. The saturated solution of $Ca(OH)_2$, prepared as described below, should be freshly filtered before use in pH calibrations.

INSTRUCTIONS FOR USE

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 µS/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 MΩ·cm).

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(1) Certain commercial instruments, materials, or processes are identified in this report 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 instruments, materials, or processes identified are necessarily the best available for the purpose.

Preparation and Use of the Saturated $Ca(OH)_2$ Solution: Put 7.5 g SRM 2193a into a platinum or fused silica (Vycor®) crucible or dish, heat slowly in a muffle furnace to 950 °C to 1000 °C and ignite for 1 h at this temperature. Immediately transfer the product (CaO) to a dessicator and allow to cool. After cooling, gently crush any lumps and add slowly to 100 mL carbon dioxide-free water while stirring. Heat the resulting $Ca(OH)_2$ suspension to boiling for 15 minutes, cool, and filter on a sintered-glass funnel of medium porosity. Dry the resulting solid $Ca(OH)_2$ in an oven for 2 h at 110 °C and crush in a mortar and pestle to a fine powder. Put the obtained $Ca(OH)_2$ (approximately 5 g) into a 1 L plastic bottle, add approximately 1 kg carbon dioxide-free water and shake the bottle periodically (nominally every 2 h, four times per day). Between periods of shaking, maintain the bottle at 25 °C in a thermostated water bath.

To obtain a truly saturated solution ($0.0202\ mol{\cdot}kg^{-1}$) by this procedure, approximately 1 week is required. However, after 1 day of mixing the excess $Ca(OH)_2$ with water, the pH is lower by only 0.02 pH units than that of the saturated solution. After 2 days, the difference is only 0.01 pH units.

Filter a portion of the saturated $Ca(OH)_2$ solution immediately before use (a syringe feeding a 0.45 µm in-line filter works well). Use the fresh filtrate as the pH standard.

Stability of Prepared Solution: The filtered solution (see above) will develop a $CaCO_3$ film on its surface in a few minutes. Although the pH of this filtered solution changes only slightly in 1 hour, it is preferable to use a fresh filtered solution for each measurement. The stock saturated solution maintains its pH value if stored in the thermostated water bath, provided that excess $Ca(OH)_2$ remains present.

Calibration of pH Electrode-Meter Systems for High-Alkalinity Measurements (pH > 11): For the pH measurement of highly alkaline solutions, a 2-point calibration is suggested. Prepare and use $0.01\ mol{\cdot}kg^{-1}$ borax (SRM 187d or current renewal) as the first standard and adjust the pH meter accordingly. Then use the freshly filtered, saturated $Ca(OH)_2$ solution prepared from SRM 2193a as the second standard and adjust the temperature compensation to set the pH reading to the certified value.

Notice to User: For pH measurements in highly alkaline solutions using commercial glass-reference electrode systems, larger uncertainties are to be expected. The sources of this uncertainty are: (1) changing liquid junction potential with increasing concentration of the highly mobile OH^- ions; (2) nonideal performance of glass electrodes, including poorer reproducibility, sluggish response, and “sodium error”; and (3) higher sensitivity of pH to temperature changes. An uncertainty of 0.05 pH is not uncommon and is reasonable for pH measurements in highly alkaline solutions.

REFERENCES

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Certificate Revision History: 30 September 2015 (Change of expiration date; editorial changes); 13 December 2007 (Update of certification period); 19 June 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; or via the Internet at http://www.nist.gov/srm.