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Standard Reference Material® 2193b
Calcium Carbonate
(used as saturated calcium hydroxide solution)
(pH Standard)
CERTIFICATE OF ANALYSIS

Purpose: 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.

Description: A unit of SRM 2193b consists of 30 g of calcium carbonate.

Certified Values: Certified pH standard, pH(S), values for solutions prepared from SRM 2193b are provided in Table 1. The pH(S) values correspond to $\lg(1/a_H)$, where a_H is the conventional activity of the hydrogen (hydronium) ion referred to the standard state (p = 1 atm = 1.013 25 ´ 10^5 Pa) on the scale of molality. When the saturated $Ca(OH)_2$ buffer solution is prepared and evaluated in the manner described below, the pH(S) certified values, standard uncertainties, u[pH(S)], and expanded uncertainties, U_{95}[pH(S)], are metrologically traceable to the International System of Units (SI) through temperature, amount-of-substance, mass, and to the Bates-Guggenheim convention used to define ionic activity. These values include all known sources of variability and bias. Provided measurement uncertainties, u[pH(*meas*)], are metrologically traceable to the International System of Units (SI) through temperature, amount-of-substance, and mass. These values, u[pH(*meas*)], include all known sources of variability and bias ***except*** for the intrinsic uncertainty of the Bates-Guggenheim convention.

Table 1. Certified pH(S) Values for a Saturated $Ca(OH)_2$ Solution Prepared from SRM 2193b[(a)]

Temperature °C	pH(S)	Measurement Uncertainty u[pH(*meas*)][(b)]	Standard Uncertainty u[pH(S)][(b)]	Expanded Uncertainty U_{95}[pH(S)]
5	13.218	0.0027	0.0057	0.011
10	13.011	0.0024	0.0056	0.011
15	12.815	0.0024	0.0055	0.011
20	12.629	0.0024	0.0055	0.011
25	12.453	0.0024	0.0055	0.011
30	12.286	0.0061	0.0079	0.016
35	12.129	0.0061	0.0079	0.016
37	12.068	0.0061	0.0079	0.016
40	11.980	0.0061	0.0079	0.016
45	11.840	0.0061	0.0079	0.016
50	11.709	0.0062	0.0080	0.016

(a) These certified values apply ONLY to a saturated $Ca(OH)_2$ solution prepared from SRM 2193b using the procedure defined below.
(b) These values are associated with 60 degrees of freedom.

Period of Validity: The certification of **SRM 2193b** is valid, within the stated uncertainty, until **30 April 2022**, provided the SRM is handled and stored in accordance with the instructions given in this certificate. The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of Certified Values: NIST will monitor this SRM to the end of the period of validity. 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.

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

Preparation of the Saturated $Ca(OH)_2$ Solution: The water used to prepare a saturated $Ca(OH)_2$ buffer solution from the SRM 2193b material should be protected from atmospheric carbon dioxide. This water must be prepared either by (1) boiling 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, conductivity < 0.06 µS/cm). Prepared solutions must be protected against evaporation and contamination.

Prepare the saturated solution by putting 7.5 g of SRM 2193b into a platinum or fused silica 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 calcium oxide (CaO) to a desiccator 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 hours, four times per day). Between periods of shaking, maintain the bottle at 25 °C in a thermostated water bath.

By this procedure, approximately 1 week is required to obtain a truly saturated solution (0.0203 mol kg^{-1}). After 1 day of mixing the excess $Ca(OH)_2$ with water, the solution pH is lower than that of the saturated solution by approximately 0.02 pH units. After 2 days, the difference decreases to approximately 0.01 pH units.

Immediately before use filter a portion of the saturated $Ca(OH)_2$ solution – a syringe feeding a 0.45 µm in-line filter works well. Use the fresh filtrate as the pH standard. The filtered solution will develop a calcium carbonate ($CaCO_3$) film on its surface in a few minutes. Although the pH of this filtered solution changes only slightly in 1 h, it is preferable to use a freshly filtered solution for each measurement. Provided that excess $Ca(OH)_2$ is present, the stock saturated solution maintains its pH value when stored at 25 °C with periodic shaking.

Calibration of pH Electrode-Meter Systems for High-Alkalinity Measurements (pH > 11): A 2-point calibration is suggested for the pH measurement of highly alkaline solutions. Prepare and use 0.01 mol kg^{-1} borax (SRM 187f *Sodium Tetraborate Decahydrate (Borax) pH Standard* 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 2193b as the second standard and adjust the temperature compensation to set the pH reading to the certified value.

For pH measurements in highly alkaline solutions using commercial glass-reference electrode systems, expect larger uncertainties than those listed in Table 1. The sources of this uncertainty are: (1) changing liquid junction potential with increasing concentration of the highly mobile OH^- ions; (2) non-ideal 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.

Additional Information: Full details on the production and evaluation of SRM 2193b are provided in NIST Special Publication 260-197.

If you use this SRM in published work, please reference

Easley RA, Waters JF, Guthrie WF (2019) Certification of Standard Reference Material® 2193b Calcium Carbonate [used as saturated $Ca(OH)_2$ solution]. (National Institute of Standards and Technology, Gaithersburg, MD), NIST Special Publication (SP) 260-197. https://doi.org/10.6028/NIST.SP.260-197

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, Maryland 20899-2300; telephone (301) 975-2200; e-mail srminfo@nist.gov; or the Internet at https://www.nist.gov/srm.

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