National Institute of Standards & Technology

Certificate

Standard Reference Material 2193

Calcium Carbonate pH Standard

This Standard Reference Material (SRM) is intended primarily for use in preparing solutions for calibrating pH measuring systems in pH ranges above 11.0. Calcium carbonate ($CaCO_3$), is a commercially available material and the lot was selected for its extremely low level of metal impurities. It is certified only with respect to pH(S) values, not as a pure substance. SRM 2193 is supplied in the form of a white powdered material in a 30 g unit.

The certified pH(S) values listed below were derived from EMF measurements of cells without liquid junction using hydrogen gas and AgCl/Ag electrodes (where the pressure of hydrogen gas was 101 325 Pa (1 atm) by the method described in reference [1].) The pH(S) value corresponds to log $(1/a_H)$ where a_H is the conventional activity of the hydrogen ion referred to the standard state on the molal scale.

A freshly filtered saturated solution (0.0202 molal) of calcium hydroxide (see directions for use on reverse side), prepared from calcium carbonate, is recommended for the standardization of pH measuring systems. The certified pH(S) values of this solution as a function of temperature are given below. These values apply only to this SRM lot.

°C	pH(S)	°C	pH(S)
0.0	13.42	30.0	12.30
5.0	13.21	35.0	12.14
10.0	13.01	37.0	12.08
15.0	12.82	40.0	11.99
20.0	12.64	45.0	11.84
25.0	12.46	50.0	11.71

Uncertainty: A 95%, 95% tolerance interval for the assigned values of pH(S) is estimated not to exceed ± 0.02 pH units for the temperature range 0 to 50 °C.

Stability: SRM 2193 is stable when stored in its original container, with the cap tightly closed under normal laboratory conditions of temperature and humidity.

The certification measurements were performed by Y.C. Wu and D. Feng of the Inorganic Analytical Research Division. Corroborating measurements were made by H.B. Kristensen at Radiometer A/S, Copenhagen, Denmark.

Statistical analysis was provided by S.B. Schiller of the NIST Statistical Engineering Division.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W.F. Koch, Deputy Chief, Inorganic Analytical Research Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Standard Reference Materials Program by J.C. Colbert.

Gaithersburg, MD 20899
October 22, 1991

William P. Reed, Chief
Standard Reference Materials Program

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Directions for Use

Preparation of Saturated (at 25 °C) Calcium Hydroxide Solution: Put 7.5 g calcium carbonate (SRM 2193) into a platinum crucible or dish, heat it slowly in a muffle furnace to 1000 °C and ignite for 1 hour. Immediately transfer to a dessicator and allow to cool. After cooling, add it slowly to 100 mL water while stirring. Heat the suspension to boiling, cool, and filter on a sintered-glass funnel of medium porosity. Dry the solid calcium hydroxide in an oven at 110 °C and crush to powder. Put the obtained calcium hydroxide (approximately 5 g) into a 1-L polyethylene bottle, add 1 kg carbon dioxide-free water, prepared by boiling distilled/deionized water (ASTM Type 1) for 10 minutes and guarding it with a soda-lime tube while cooling. Shake it every two hours. Between periods of shaking, maintain the bottle at 25 °C in a thermostated water bath[1].

Filter a portion of the saturated calcium hydroxide solution on a sintered-glass funnel of medium porosity. Use the fresh filtrate solution as a pH standard. The filtered solution will be turbid on the surface in a few minutes. Although the pH of this solution changes only slightly in 1 hour, it is preferable to use a fresh filtered solution for each measurement.

To obtain a truly saturated solution (0.0202 molal) by this procedure, approximately 1 week is required. However, after 1 day of mixing the excess calcium hydroxide 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.

Calibration of pH electrode-meter systems for high alkalinity measurements: For the pH measurement of highly alkaline solutions, a two point calibration is suggested. Prepare, and use 0.01 molal borax (SRM 187) as the first standard and adjust the pH meter accordingly. Then use the freshly filtered saturated calcium hydroxide solution prepared from SRM 2193 as the second standard and adjust the "Temperature Compensator" of the pH meter to set the reading to the certified value.

Notice to user: For pH measurements in highly alkaline solutions using commercial glass-reference electrode systems, larger errors are to be expected. The reasons for this lie in: 1) changing liquid junction potential with alteration of the concentration of highly mobile hydroxide ions; 2) higher sensitivity of pH to temperature changes; 3) poorer performance of glass electrodes, including poorer reproducibility, sluggish response and "sodium error". Therefore, an uncertainty of 0.05 pH unit is not uncommon and is reasonable for pH measurements of highly alkaline solutions.

REFERENCE

[1] R.G. Bates, V.E. Bower, and E.R. Smith, J. Res. Nat. Bur. Stand. (U.S.), 56(6), 305 (1956).

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1 If it is not convenient to put the bottle in a water bath, the saturated calcium hydroxide solution may be made at room temperature. However, a correction must be made due to the change of solubility with temperature:

$$\Delta pH = 0.003\ (25\text{-}t)$$

where t is the approximate room temperature.