Certification of Standard Reference Material® 2193b

Calcium Carbonate [used as saturated Ca(OH)₂ solution]

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Abstract

This publication documents the production, analytical methods, and statistical evaluations involved in production of this SRM.

Keywords

Calcium carbonate, $CaCO_3$
Calcium hydroxide, $Ca(OH)_2$
pH
Standard Reference Material (SRM)

Technical Information Contact for this SRM

Please address technical questions about this SRM to srms@nist.gov where they will be assigned to the appropriate Technical Project Leader responsible for support of this material. For sales and customer service inquiries, please contact srminfo@nist.gov.

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Purpose and Description

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. SRM 2193b Calcium Carbonate ($CaCO_3$) was selected for its low level of alkali metal impurities and prepared to ensure high purity and uniformity. However, this SRM is certified **ONLY** as a pH standard [pH(S)], not as a pure substance. A unit of SRM 2193b consists of 30 g of calcium carbonate.

Storage

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 and Use

The water used for preparation of the SRM 2193b buffer solution should be protected from atmospheric carbon dioxide. This water must be prepared either by (1) boiling of distilled water (conductivity < 2 μS cm^{-1}) 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 $M\Omega$ cm, conductivity < 0.06 μS cm^{-1}). Prepared solutions must be protected against evaporation and contamination.

Put 7.5 g SRM 2193b 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 hour at this temperature. Immediately transfer the product (CaO) to a desiccator and allow to cool. After cooling, gently crush any lumps and add slowly to 100 cm^3 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 dm^3 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.

By this procedure, approximately 1 week is required to obtain a truly saturated solution (0.0203 mol kg^{-1} [5]). 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 two 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 saturated $Ca(OH)_2$ solution 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 h, it is preferable to use a fresh filtered solution for each measurement. Provided that excess $Ca(OH)_2$ is present, the stock saturated solution maintains its pH value when stored in the thermostated water bath.

For the pH measurement of highly alkaline solutions (> 11), a 2-point calibration is suggested. Prepare and use 0.01 mol kg^{-1} borax (SRM 187f 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.

Notice: 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) 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.

History and Background

SRM 2193b is the third member of the SRM 2193 Calcium Carbonate series. The supply of the previous material, SRM 2293a, was exhausted in 2016. Figure 1 displays the sales history of the previous members of the series.
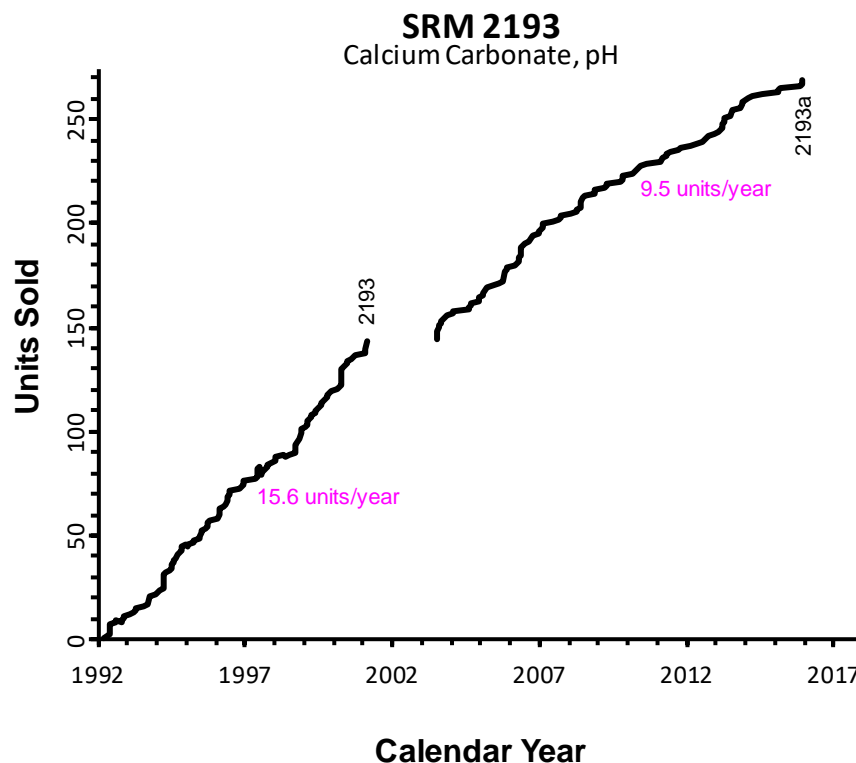
Figure 1: Sales History of SRM 2193 and 2193a

The lines trace the sale of the SRM 2193 and SRM 2193a units over time. The magenta labels state the average yearly sales rate for these materials.

SRM 2193b is supplied in solid form as calcium carbonate, $CaCO_3$. To prepare the buffer, the SRM material is converted first to calcium oxide, CaO, and then to calcium hydroxide,$Ca(OH)_2$. The buffer comprises an aqueous solution saturated at 25 °C with $Ca(OH)_2$.

Samples from 12 stratified-random-selected bottles of candidate SRM 2193b were checked for homogeneity using glass electrode measurements. The certification value was then assigned based on primary pH measurements in Harned cells, using a composite sample from the same bottles. The assigned uncertainty incorporates the results of both sets of measurements.

Certification pH(S) values presented in this report are valid only for renewal SRM 2193b and do *not* apply to other renewals (e.g., SRM 2193a).

<div align="center">

Solution and Electrode Preparation

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Homogeneity buffer solution preparation
The homogeneity assessment was performed prior to certification, using buffers independently prepared from each of the 12 individual bottles of the candidate SRM 2193b and one bottle of SRM 2193a (previous issue used as the calibrant for the homogeneity assessment). Preparation of the $Ca(OH)_2$ buffer solution followed the procedure given in the certificate for SRM 2193a [1]. Ultrapure reagent grade (resistivity > 18 MΩ cm), filtered (0.22 µm) water was used to prepare all solutions. A nominal mass of 7.5 g was taken from each bottle. Samples of SRM 2193a and SRM 2193b were ignited in Vycor crucibles for 1 h at 950 °C to 1000 °C in a muffle furnace. Each CaO sample was slowly added to 100 cm^3 water and the suspension was boiled on a hot plate for 15 min. After the suspension cooled, it was filtered on a medium-porosity glass filter, and the collected solid $Ca(OH)_2$ was dried in an oven for 2 h at 110 °C and ground in a mortar and pestle to a fine powder. The powdered $Ca(OH)_2$ (4.38 to 6.34 g recovered) was added to 400 cm^3 (nominal) water and was saturated at 25 °C in a Techne S1500 Orbital Incubator/Shaker for at least one week with constant shaking.

Harned cell buffer solution preparation
The SRM 2193b buffer solution for the certification was prepared from a composite sample consisting of nominally equal masses from each individual bottle (7.1 g to 7.5 g) to yield 63.39 g of solid $Ca(OH)_2$. The composite buffer was prepared in a single carboy and saturated in a temperature bath at 25 °C in 9.438 kg water for at least a week with periodic (nominally every 24 h) shaking. From this stock solution, 12 buffer solutions containing added sodium chloride (NaCl) were prepared in four sets by adding filtered $Ca(OH)_2$ solution to weighed amounts of NaCl. Each set contained one solution at each molality (b_{NaCl}): (0.005, 0.01, or 0.015) mol kg^{-1}. The NaCl (Merck Suprapur, stated Br level <10 µg g^{-1}) was dried for 4 h at 110 °C and stored in a desiccator before use. The exact value of b_{NaCl} was calculated from the measured masses of buffer and NaCl used to prepare each solution. Each buffer solution was designated by a code giving the chloride molality in mmol kg^{-1} and stock buffer solution (e.g., 10B represents the solution with $b_{NaCl} = 0.010$ mol kg^{-1} prepared from

stock solution B). Solutions were stored in sealed Mylar bags until use. Certification measurements were performed within 10 days of the buffer preparation.

Hydrochloric acid solution preparation
Analytical reagent-grade hydrochloric acid (HCl) (Mallinckrodt AR, stated Br level <0.005 %) was used for the measurements of the standard redox potential, E°, of the Ag|AgCl electrodes. A 19 L batch of HCl with a nominal molality of 0.01 mol kg^{-1} was previously prepared and stored in a glass bottle fitted with a trap to minimize evaporation of the solution on storage. The molality of HCl was assayed by coulometric acidimetry using a 1 mol kg^{-1} potassium chloride (KCl) supporting electrolyte [2,3]. The mean of twelve coulometric titrations, performed prior to, concurrent with, and after the Harned cell measurements, was used in the pH(S) calculations. The coulometrically-determined value of the HCl molality (determined as H$^+$) was 0.010 009 50 mol kg^{-1}; its uncertainty is discussed below (see: Calculation of Uncertainties).

Electrode preparation
The Pt electrodes consisted of Pt black on a Pt substrate (platinized Pt) and are referred to hereafter as Pt electrodes (Pt|H$_2$ in Harned cells). The electrodes were replatinized in 2004 for the certification of SRM 187e (borax pH SRM) [4]. Pt flags approximately 0.5 cm by 1.5 cm in size were spot-welded to Pt wire. Prior to platinization, the Pt flags were cleaned of Pt black by immersion in heated 4 mol L^{-1} HCl + 2 mol L^{-1} HNO$_3$ ("50 % aqua regia"). Each was platinized for 5 min at a constant current of 100 mA in a U-tube filled with 2 % Pt(II) in 2 mol L^{-1} HCl with 0.005 % Pb(C$_2$H$_3$O$_2$) added. During the deposition, the solution in the U-tube was agitated, yielding electrodes that were uniform black in color. A Pt wire was the anode. Following platinization, the Pt electrodes were rinsed in a stream of water and stored in deionized water between uses. Individual Pt electrodes were "paired" with specified Ag|AgCl electrodes for all measurements.

The thermal electrolytic Ag|AgCl electrodes ("Batch F") were previously prepared using high-purity 1 mm Ag wire (Puratronic, 99.999 %) and Ag$_2$O [5] and were stored in 0.01 mol kg^{-1} HCl since their preparation. The Ag|AgCl electrodes were equilibrated overnight (14 h) in the respective solution for the next day's Harned cell measurement. The Ag|AgCl electrodes were stored in 0.01 mol·kg^{-1} HCl if the time to the next analysis was more than a day.

At the start and conclusion of the certification measurements, the potentials of each of the six Ag|AgCl electrodes were compared in the 0.01 mol kg^{-1} HCl storage solution against a single reference Ag|AgCl electrode from a previous electrode batch which was not exposed to the alkaline buffer. The maximum deviation among the six electrodes used in the Harned cells prior to the certification was 50 µV and post certification was 32 µV. The average offset electrode potential, as compared to the single reference Ag|AgCl electrode, prior to certification was 327 µV and the average post certification (after exposure to the alkaline buffer) was 126 µV. The average shift in electrode potential over the duration of the measurements of -200.8 µV was intrinsically factored into the overall uncertainty budget of the E° determination, $u_A(E^\circ)$.

Homogeneity Assessment

Measurement of pH was performed with a Keithley model 6514 electrometer connected to a Thermo Scientific Orion micro combination pH electrode (glass electrode + Ag|AgCl internal reference electrode). Samples were stored at 25 °C in a Techne S1500 Orbital Incubator/Shaker until use and were then thermostated in a GeneMate digital dry bath, the temperature of which remained within a ±0.05 °C range for all runs. The meter/electrode assembly was calibrated with standard buffers of SRM 187e prepared according to certification instructions [9] and SRM 2193a. The SRM 2193b test samples were prepared as stated above.

The pH electrode response (slope factor) was determined with two, freshly prepared standard buffers (SRM 187e and SRM 2193a). The pH electrode was equilibrated for approximately 30 min in the SRM 2193a solution prior to the start of the homogeneity assessment. For each measurement, the pH electrode was placed in the sample (contained in 2 cm^3 microcentrifuge tubes) and the solution was stirred with the electrode for 30 s. The glass electrode potential (vs. the Ag|AgCl reference electrode) was measured in the quiescent solution after an additional 30 s. The SRM 187e borate buffer was measured at the start and end of each run to determine the practical pH electrode response (slope) factor, k', while minimizing any memory effects on the liquid junction potential within the set of calcium hydroxide measurements. Before and after each sample measurement, an aliquot of the SRM 2193a calibrant was measured using this same protocol. Each potential reading was recorded to 0.01 mV (corresponding to roughly 0.0002 pH units). The protocol corrected for small drifts in the pH electrode response by measuring the difference in pH (ΔpH) obtained from the mean of the two bracketing aliquots of the SRM 2193a calibrant measured immediately preceding and following the SRM 2193b sample. The ΔpH between the SRM 2193a calibrant and each sample for the ith sample, ΔpH$_i$, was calculated by Eq. 1 where E_A and $E_{A'}$ are the potentials recorded for the bracketing SRM 2193a calibrant aliquots A and A′, and E_i is the potential recorded for the SRM 2193b sample:

$$\Delta\text{pH}_i = \left(E_i - \frac{E_A + E_{A'}}{2}\right)/k' \tag{1}$$

Following each measurement of $E_{A'}$, the difference $E_A - E_{A'}$ was calculated. If $E_A - E_{A'}$ was greater than 0.25 mV (corresponding to roughly 0.004 pH units), the preceding three measurements (E_A, E_i, and $E_{A'}$) were repeated. This protocol eliminated bias in cases where sudden shifts or high drift rates were present, while preserving the experimental design.

The homogeneity assessment used a nested experimental design, based on a hierarchical variance components model. The design yielded two ΔpH$_i$ values for three SRM units in each run; the set of 12 SRM units was measured in the four runs over two days. Values are reported as ΔpH$_i$ to emphasize that they are used for homogeneity assessment only and not for assignment of the pH(S) value of the SRM. Values of ΔpH$_i$ were analyzed using a random effects statistical model based on the experimental design. The model was fit using Bayesian methods to determine a probability distribution for the value of the bottle-to-bottle standard deviation. The bottle-to-bottle standard deviation was shown to not depend heavily on assumed prior probability distributions incorporated in the fit of ΔpH$_i$ to the model. See Appendix A for details of this analysis.

Table 1 details the bottle numbers of the SRM 2193b units used the homogeneity assessment.
Table 2 summarizes the results of the homogeneity assessment.

Table 1. Bottles Used in the Homogeneity Assessment

Set 1	Set 2	Set 3	Set 4
36	68	1	107
27	162	126	5
116	42	60	48
36	68	60	5
27	162	126	108
116	42	1	48

Table 2. Results of Homogeneity Assessment for SRM 2193b

SRM unit	ΔpH_1	ΔpH_2
1	-0.0006	-0.0016
5	0.0004	0.0013
27	-0.0008	-0.0008
36	0.0014	0.0008
42	-0.0018	-0.0020
48	-0.0003	-0.0019
60	-0.0005	-0.0008
68	0.0014	0.0000
107	0.0006	-0.0005
116	0.0013	0.0003
126	-0.0019	-0.0009
162	0.0020	0.0007
Mean	-0.0002	
Standard Deviation of the Mean	0.0011	
v_{eff}	27.37	

[a] Provided by NIST Statistical Engineering Division analysis.

Based on the results of the homogeneity assessment, a minimum of 7.5 g of SRM 2193b
should be used to prepare pH(S) buffer solutions as described above, yielding ca. 130 g of
solution. Use of smaller mass of SRM 2193b may increase the uncertainty of pH(S) of the
prepared solution, if the material is heterogeneous at that level.

Certification of pH(S)

The following subsections present the procedure for the primary measurements for certification of pH(S).

Randomization Protocol
The certification procedure for pH SRMs entails measurements in six Harned cells filled either with buffer solution or with 0.01 mol kg^{-1} HCl according to the randomization protocol outlined in Table 3. Cells containing buffer yield corrected cell potentials, E_I. Cells containing HCl yield corrected cell potentials, E_{II}. The E_{II} values are used in the determination of the $E°$ values of the respective Ag|AgCl electrodes.

Table 3. Solution Randomization Protocol for Certification Measurements

Run 1A/1B	Run 2A/2B	Run 3A/3B	Cell
HCl	15A	15B	1
HCl	5A	5C	2
15D	HCl	5D	3
10C	HCl	10D	4
10A	10B	HCl	5
5B	15C	HCl	6

Subsets of each run are denoted by the A and B following the run number.

Twelve buffer solutions were randomized among three measurement sets, subject to the following conditions:
1. Four buffer solutions and two 0.01 mol kg^{-1} HCl solutions were measured in each run.
2. Each of the 12 buffer solutions was measured once at each temperature.
3. In each run, E_I values were measured for solutions with each value of b_{NaCl}.
4. In each run, E_I values were measured for one pair of solutions having the same nominal value of b_{NaCl}, but from separate source buffers as described in *Harned cell buffer solution preparation*, above.
5. In the whole set of measurements, each Harned cell was used for E_I measurements with two different values of b_{NaCl}, plus its E_{II} (HCl) measurement.

Each measurement set (designated 1, 2, and 3) was composed of two subsets, designated by A or B following the set number (1A, 1B, . . ., 3A, 3B). Each set took two successive workdays. Subset A of each set consisted of measurements performed at (25, 5, 10, 15, 20, and 25) °C and were performed on the first day for sets 2 and 3 and second day for set 1. Subset B consisted of measurements performed at (25, 30, 35, 37, 40, 45, 50, and 25) °C and were performed on the first day for set 1 and on the second day for sets 2 and 3. In each subset, the concluding measurement at 25 °C, denoted by "recheck", was performed to evaluate the uncertainty component associated with the given series of measurements. The ordering of the solutions in subsets A and B of each run (with respect to the cell and electrode numbers) was identical. The order of the measurement temperatures in the "staircase" was selected to expedite the measurements and to minimize the use of ice,

required for the 25 °C to 5 °C transition in subset A and 50 °C to 25 °C transition in subset B. The entire series of measurements (subsets 1A through 3B) was performed in six workdays.

This randomization protocol permits direct, simultaneous comparisons of two pairs of cells containing identical solutions (two buffer, two HCl) at all times within every run, yet it preserves the overall randomization of the set of measurements yielding a given pH(S) value. These features are significant in providing quality assurance to the primary pH measurement.

Harned Cells and Measurement Preparations
The six Harned cells used in this work each consisted of a single glass unit comprised of three humidification tubes in series connected to a two-compartment electrochemical cell of ca. 30 cm^{-3} volume. No frit was used in any of the humidification tubes, nor at the H$_2$ inlet to the electrochemical cell. The cells were thermostated in a water bath (Fluke Corporation, Model 7009) to a precision of ±0.002 °C for all measurements. Temperature of the water bath was measured with a platinum resistance thermometer (Hart Scientific, Model 5628) and digital temperature readout (Hart Scientific, Model 1502a).

Each Ag|AgCl electrode was pre-equilibrated overnight (> 14 h) in a test tube containing a separate aliquot of the solution to be measured on the following day. After each Ag|AgCl electrode was transferred to its scheduled Harned cell, the remaining aliquot in the test tube was used to rinse the corresponding Pt|H$_2$ electrode before insertion into the given Harned cell.

Measurement of Cell Potentials
Measured cell potentials, E_{meas}, were obtained at atmospheric pressure, p_{atm}. Each E_{meas} value was corrected to the standard pressure for the H$_2$ gas, $p° = 101\ 325$ Pa, yielding the corrected cell potential, E_{cell}:

$$E_{cell} = E_{meas} - 0.5 \frac{RT \ln 10}{F} \log \frac{p_{atm} - p_{H_2O}}{p°}$$

(2)

where R is the gas constant (8.314 4598 J mol^{-1} K^{-1} [6]), T is the thermodynamic temperature of the bath (and cells), F is the Faraday constant (96 485.332 89 C mol^{-1}[6]), and p_{H_2O} is the vapor pressure [7] of water at T. The term $RT \ln 10/F$ is designated as k, which has dimensions of V. Values of T and p_{atm} used in Equation 2 were noted at the specific time that the E_{meas} values were recorded for each sample. The input to the digital voltmeter was nulled to zero immediately before recording each set of E_{meas} values to correct for thermal contact offsets.

At each temperature, E_{meas} for each cell was recorded at 5 min intervals until all six values were stable [drift rate less than 1 µV min^{-1} (10 µV in 10 min)]. Typically, a period of 40 min at the given temperature was required to meet this condition. A minimum of 120 min was used before the initial 25°C measurements in each run to ensure quantitative purging of O$_2$ from the Harned cells and saturation of Pt electrode surface with H$_2$.

A flow rate of 0.35 cm^3 s^{-1} to 0.53 cm^3 s^{-1} of H$_2$ was used depending on the given cell. Three series-connected humidification chambers of total volume ca. 50 cm^3 (when totally filled) supplied H$_2$ saturated with H$_2$O vapor to the H$_2$ nozzle of the chamber of the electrochemical cell containing the Pt|H$_2$ electrode.

Table 4 reports the temperature-dependent parameters used to determine pH(S). Values for $E°$, $u_A(E°)$, the standard potential of the Ag|AgCl electrodes and the Type A uncertainty [8] of the extrapolation, $u_A[p(a_H\gamma_{Cl})°]$ are listed in Table 5 for each temperature.

Table 4. Temperature-Dependent Parameters Used in the Determination of pH(S)

$T/°C$	p_{H2O}/kPa [7]	$\gamma_{\pm HCl}$ [9]	I_{buffer} [10]	A_D [10,11]
5	0.8726	0.9074	0.053	0.4952
10	1.2281	0.9067	0.051	0.4988
15	1.7056	0.9060	0.050	0.5026
20	2.3388	0.9051	0.050	0.5066
25	3.1690	0.9042	0.049	0.5108
30	4.2455	0.9033	0.049	0.5150
35	5.6267	0.9024	0.048	0.5196
37	6.2795	0.9020	0.048	0.5215
40	7.3814	0.9014	0.048	0.5242
45	9.5898	0.9003	0.048	0.5291
50	12.344	0.8992	0.047	0.5341

Table 5. $E°$, $u_A(E°)$, and $u_A[p(a_H\gamma_{Cl})°]$ Values as a Function of Temperature

$T/°C$	$E°$/V	$u_A(E°)/\mu V$	$u_A[p(a_H\gamma_{Cl})°]^a$
5	0.234018	22	0.01563
10	0.231369	33	0.01268
15	0.228564	23	0.01081
20	0.225591	18	0.00938
25	0.222406	22	0.00425
25 (down recheck)	0.222457	17	0.00821
25 (up recheck)	0.222168	64	0.00396
30	0.219161	22	0.00624
35	0.215726	39	0.00605
37	0.214256	44	0.00574
40	0.212104	52	0.00532
45	0.208302	51	0.00437
50	0.204369	80	0.00377

^{a} Type A uncertainty for a single extrapolation to p($a_H\gamma_{Cl}$)°.

Calculation of pH(S)

Values of E_{cell} for cells I and II below are referred to hereafter as E_I and E_{II}. The term "measurement" incorporates the recording of p_{atm} and subsequent correction to yield E_{cell} at the standard pressure, $p° = 101\ 325$ Pa.

Measurements of E_I for cell I,

$$Pt|H_2(g, p°)|Ca(OH)_2 \text{ buffer, NaCl}(b_{NaCl})|AgCl|Ag \tag{I}$$
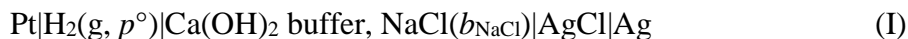
were obtained for the 12 buffer solutions. Measurements of E_{II} for cell II,

$$Pt|H_2(g, p°)|HCl(b_{HCl})|AgCl|Ag \tag{II}$$

were simultaneously performed using the coulometrically-standardized HCl to determine the $E°$ values of the Ag|AgCl reference electrodes.

Values of $E°$ were calculated from each E_{II} according to Equation 3:

$$E° = E_{II} - 2k \log \frac{b_{HCl} \gamma_{\pm HCl}}{b°} \tag{3}$$

where $\gamma_{\pm HCl}$ is the mean activity coefficient of HCl at molality b_{HCl} and $b° = 1\ mol \cdot kg^{-1}$. Values for $\gamma_{\pm HCl}$ are taken from [12] for each temperature. Measurement of E_{II} and subsequent calculation of $E°$ is referred to below as the "determination of $E°$."

Values for the acidity function, $p(a_H \gamma_{Cl})$, were calculated for each measured E_I value using Equation 4, where the operator p represents $-\log_{10}$:

$$p(a_H \gamma_{Cl}) = \frac{(E_I - E°)}{k} + \log \frac{b_{NaCl}}{b°} \tag{4}$$

The value of $E°$ used in Equation 4 was the mean of the set of six determinations of $E°$ performed at the given temperature. The least-squares line of the 12 values for $p(a_H \gamma_{Cl})$ was then extrapolated to $b_{NaCl} = 0$ to yield $p(a_H \gamma_{Cl})°$ at the given temperature.

The value for the pH, pa_H, was calculated from this $p(a_H \gamma_{Cl})°$ value using Equation 5:

$$pa_H = p(a_H \gamma_{Cl})° + \log \gamma_{Cl}° \tag{5}$$

where $\log \gamma_{Cl}°$ is the trace activity coefficient of the Cl⁻ ion at the ionic strength, I (SI unit: mol kg⁻¹), of the buffer. The value of $\log \gamma_{Cl}°$ was obtained from the Debye-Hückel function using the Bates-Guggenheim convention [11]:

$$\log \gamma_{Cl}° = -\left(A_D \sqrt{I}\right) / \left(1 + 1.5\sqrt{I}\right) . \tag{6}$$

Values for the Debye-Hückel constant A_D were taken from [5,12] for each temperature. Values for I include the effect of the dissociation of the buffer [10].

Following the calculation of pa_H at each temperature, the final recommended standard pH value at each temperature, pH(S), was obtained by performing a polynomial curve fit [5] of the entire set of 12 experimental pa_H values using Equation 7, where A, B, C, and D are the parameters of the curve fit; numeric values of the curve fit parameters are given in the

footnote of Table 6. The pa_H value determined at 25 °C ("25 °C down" and "25 °C up") was entered as one point in the curve fit

$$\text{pH(S)} = A + B\frac{\text{K}}{T} - C\frac{T}{\text{K}} + D\frac{T^2}{\text{K}^2}. \tag{7}$$

Certification Values

Table 6 lists the certification pH(S) values for SRM 2193b from $T = 5$ °C to $T = 50$ °C at 5 °C intervals, plus at $T = 37$ °C along with summary of the combined standard uncertainties, u_c(cert), and the certified 95 % expanded uncertainties, U(cert). The equation for the polynomial curve fit is listed as a footnote.

Table 6. NIST Certification Result

t/°C	pH(S)[a]	u_c(cert)[b]	k_{cert}[c]	U(cert)[d]
5	13.218	0.0057	1.99	0.011
10	13.011	0.0056	1.99	0.011
15	12.815	0.0055	1.99	0.011
20	12.629	0.0055	1.99	0.011
25	12.453	0.0055	1.99	0.011
30	12.286	0.0079	1.98	0.016
35	12.129	0.0079	1.98	0.016
37	12.068	0.0079	1.98	0.016
40	11.980	0.0079	1.98	0.016
45	11.840	0.0079	1.98	0.016
50	11.709	0.0080	1.98	0.016

[a] Equation for determining pH(S): pH(S) = $2.64915 + 3664.76\frac{\text{K}}{T} - 0.023670\frac{T}{\text{K}} + 5.14012\text{x}10^{-5}\frac{T^2}{\text{K}^2}$

[b] Combined standard uncertainties, including $u_{B\text{-}G}$, for the certified pH(S) values

[c] Coverage factors for the certified pH(S) values

[d] Approximate 95 % expanded uncertainties for the certified pH(S) values

Table 7 lists u_c(meas), the combined standard uncertainty of the measurement; k_{meas}, the coverage factor of the measurement; and U(meas), the expanded uncertainty of the measurement proper. Values of u_c(meas) and U(meas) include all known instrumental factors pertaining to this primary pH measurement [8] but *exclude* the contribution from the inherent uncertainty of the Bates-Guggenheim convention [11].

Table 7. Certification Results Excluding u_{B-G}.

$t/°C$	pH(S)[a]	u_c(meas)[b]	k_{meas}	U(meas)
5	13.2176	0.0027	2.00	0.0054
10	13.0109	0.0024	1.98	0.0048
15	12.8148	0.0024	1.98	0.0048
20	12.6289	0.0024	1.98	0.0047
25	12.4529	0.0024	1.98	0.0047
30	12.2863	0.0061	2.00	0.0121
35	12.1289	0.0061	2.00	0.0121
37	12.0684	0.0061	2.00	0.0122
40	11.9804	0.0061	1.99	0.0122
45	11.8403	0.0061	1.99	0.0122
50	11.7086	0.0062	1.99	0.0123

a   Values of pH(S) are the same as in Table 6, but are reported to the number of decimal places corresponding to two significant figures for u_c(meas).

b   Includes all components of the pH(S) measurement and homogeneity assessment but excludes the estimated uncertainty of the Bates-Guggenheim convention.

Calculation of Uncertainties

The basis for each source of uncertainty is summarized in Table 8. Detailed values for each certification temperature are given in Appendix B.

Table 8. Summary of Uncertainty Components

Component	Type	Basis for $u(x_i)^a$
pH(S) curve fit	A	Standard deviation, at certification temperature, of polynomial curve fit obtained from set of experimental pa_H values (see Eq 8).
u_A, for Ag|AgCl electrode standard potential, $E°$	A	Standard deviation of mean of 6 $E°$ determinations performed concurrently with buffer measurements.
SRM homogeneity	A	Fit using Bayesian methods implemented via Markov Chain Monte Carlo simulation using a random effects statistical model based on the experimental design.
HCl molality, $[u_c(b_{HCl})]$	A+B	Combined standard uncertainty, u_c, of coulometric determination. Includes Type A and Type B components (see text below).
Measured cell potential, E_{meas}, in E_I measurements (digital voltmeter, DVM)	B	Calibration [28], 21.4 µV V^{-1} relative. DVM verified each day by check of Weston cell and zeroed before each measurement.
Activity coefficient, $\gamma_{\pm HCl}$	B	0.0002 (uniform distribution) by evaluation of literature sources.
E_{meas} for $E°$ (E_{II}) measurements (DVM)	B	Calibration, verified as above.
NaCl molality, $u_c(b_{NaCl})$	B	Combined standard uncertainties of weighings and of molar mass [13]
Temperature, T (combined for E_I and E_{II} cells, assumed correlated)	B	u_c of Pt resistance thermometer (0.005 K, 95 % confidence interval), bridge display (0.005 K, 95 % confidence interval), and observed stability of bath (0.008 K).
Gas constant, R	B	CODATA u_c [6].
Pressure, p_{atm}	B	0.01% of digital barometer reading.
Faraday constant, F	B	CODATA u_c [6].
Temperature cycling, $u(T$ cycling)	B	Absolute value of difference in p($a_H\gamma_{Cl}$)° values for "25 °C" and "25 °C recheck" sets (as applicable), taken as uniform distribution.

a Except as noted, numerical uncertainties, a_i, or relative half-widths, a_i/x_i, of a rectangular (uniform) distribution of possible values of the input quantity, x_i. See Tables 3a through 3k for the corresponding normalized $u(x_i)$.

Calculation of u_c(meas), k_{meas}, and U(meas)

The values of c_i (sensitivity factor), $u(x_i)$ (standard uncertainty), $u_i(y)$ (component of the combined standard uncertainty), and v_i (degrees of freedom of $u(x_i)$) are calculated for the ith component. Unless otherwise noted, the $u(x_i)$ for each Type B component to the uncertainty was treated as having a uniform probability distribution. All values of $u_i(y)$ associated with the pH(S) measurement are summed in quadrature to obtain the combined standard uncertainty of the measurement, u_c(meas), which has v_{eff}(meas) degrees of freedom. For the determination of $E°$, the combined Type A uncertainty components, $u_A(E°)$; and the combined Type B uncertainty components, $u_B(E°)$, are tabulated separately. The value of U(meas) of the pH(S) measurement is calculated by multiplying u_c(meas) by k_{meas}. The value of k_{meas} corresponds to approximately 95 % confidence, based on the value of v_{eff} (meas) calculated from the Welch-Satterthwaite equation [14,15]. The values of c_i, $u(x_i)$, $u_i(y)$, v_i, u_c(meas), v_{eff} (meas), k_{meas}, and U(meas) are calculated following ISO guidelines [8].

The Type A uncertainty of the measurement was obtained by combining the uncertainties of the curve fit to obtain pH(S), the Type A uncertainty of $E°$, the homogeneity assessment of the SRM 2193b source material, and the coulometric determination of b_{HCl}.

The Type A uncertainty of the curve fit to obtain pH(S) from the pa_H values includes the Type A component, $u_A[p(a_H\gamma_{Cl})°]$, associated with the extrapolation of the p($a_H\gamma_{Cl}$) values at different b_{NaCl} to obtain p($a_H\gamma_{Cl}$). The u_A (curve fit) values (see Appendix B) are somewhat smaller than the $u_A[p(a_H\gamma_{Cl})°]$ values calculated using solely the extrapolation at the corresponding temperature. In effect, the curve fit "leverages" the entire set of measurements at all temperatures to obtain a lower uncertainty at each component temperature.

The Type A uncertainty of the $E°$ determination, $u_A(E°)$, is estimated from the standard deviation of the mean of all six determinations of $E°$ at the given temperature. The uncertainty of the Ag|AgCl electrode drift due to the high alkaline environment was inherently included in the $u_A(E°)$. For the measurements at 25 °C, the values of $u_A[p(a_H\gamma_{Cl})°]$ and $u_A(E°)$ used to calculate u_c(meas) were determined using the set of respective measurements obtained in the "25 °C" data, not including the recheck measurements. Table 7 reports values of $u_A(E°)$ for each set of measurements (including the "25 °C recheck" runs).

The uncertainty associated with the homogeneity of the SRM material was obtained from the statistical analysis of the measured ΔpH_i values and was used as the Type A uncertainty. This estimate includes the inherent resolution of the measurement of ΔpH_i and allows for different levels of random variation between runs, bottles and measurements. All random errors were assumed to be mutually independent and normally distributed. No unit-to-unit differences were apparent.

The combined standard uncertainty in the molality of the HCl [$u_c(b_{HCl}) = 1.83 \times 10^{-6}$ mol kg^{-1} with $v_{eff} = 70.88$] is calculated using the model developed from knowledge gained in CCQM-K73 [16]. Additional details on the calculations used in estimation of the HCl assay uncertainty are provided in Appendix C.

The Type B uncertainty of the acidity function was obtained by combining the uncertainty components for E_{meas} for the buffer and $E°$ measurements, $\gamma_{\pm HCl}$, b_{NaCl}, T, R, p_{atm}, F, and the uncertainty for T cycling. Values not referred to NIST calibrations below were taken from the instruction manuals for the respective instruments. The "manual values" were taken as uniform uncertainty intervals and have been treated as described above.

A Solartron 7071 voltmeter was used to determine E_{meas}. The Type B uncertainty was treated as a uniform uncertainty interval $[u(E_{meas}) = 0.0012 \% E_{meas}/\sqrt{3}]$. Verification checks performed daily against a saturated Weston cell were in accordance with this uncertainty. Separate sources are listed for the determination of E_{meas} for the Harned cells containing buffer (E_I) and those containing 0.01 mol kg^{-1} HCl.

The uncertainty of $\gamma_{\pm HCl}$ was an assumed value [17], treated as a uniform uncertainty $[u(\gamma_{\pm HCl}) = 0.0002/\sqrt{3}]$, as the literature [27] gives no estimate of uncertainty. The value of $\gamma_{\pm HCl}$ was taken as the value at $b_{HCl} = 0.01$ mol kg^{-1}. The correction for $\gamma_{\pm HCl}$ (since b_{HCl} was not exactly 0.01 mol kg^{-1}) and the uncertainty of this correction are each negligible.

The platinum thermometer was calibrated by the manufacturer. The calibration at the other temperatures of interest was obtained by a polynomial curve fit from these points. The uncertainty in temperature $[u(T) = 0.0055$ K] was obtained from the Type B calibration uncertainty and the observed drift in bath temperature during the certification measurements.

The uncertainty in b_{NaCl}, $u(b_{NaCl})$, is based on the uncertainties in the mass (m) measurements associated with the addition of NaCl to the buffer solution. The uncertainty in the mass measurements are based on the uncertainties given in the balance manuals and are treated as uniform probability distributions. The microbalance calibration certificate, used for the NaCl additions, verified the performance agreed with the manufacturer specifications. The uncertainty in m_{NaCl}, $u(m_{NaCl})$, is calculated using an uncertainty of 2.9 µg for the tare mass of the Pt weighing boat and for the mass of the boat containing the NaCl. The uncertainty in the mass of the buffer solution, m_{buffer}, $u(m_{buffer})$, is calculated using an uncertainty of 2.9 mg for the tare mass of the bottle and for the weighing of the bottle containing the buffer solution.

The Type B uncertainty associated with the cycling of temperature T, $u(T$ cycling), is obtained from the deviation between the respective 25 °C pa_H value and the corresponding "25 °C recheck" pa_H value obtained for the measurements performed at 25 °C at the end of the given run. The deviation in pa_H for the "25 °C up" and 25 °C up recheck" runs is treated as a uniform probability distribution and divided by $\sqrt{3}$ to obtain the $u(x_i)$ attributable to temperature cycling in the "25 °C up" measurements. The value of $u(T$ cycling) is included as an uncertainty component in u_c(meas) for $T \leq 25$ °C. This component is included in u_c(meas) for $T = 25$ °C to cover any possible change between the filling of the cell and the initial 25 °C measurements.

The $u(T$ cycling) values incorporate several factors. Small changes in E_{cell} result from changes in b_{HCl} (or b_{NaCl} in the buffer solutions) associated with two separate physical effects. First, incomplete equilibration of H$_2$ with p_{H2O} in the humidification tubes increases b_{HCl} (and b_{NaCl} in the buffer solutions) via evaporation, decreasing E_{cell}. Evaporation occurs to some

extent at all temperatures, but it is negligible below 25 °C. Second, reflux of condensate H_2O from the H_2 outlet back into the Harned cells decreases b_{HCl} (or b_{NaCl}), thus increasing E_{cell}. Reflux only occurs at bath temperatures well above the laboratory ambient temperature, where condensation occurs in the H_2 exit tubes, i.e., above 35 °C in the "25 °C up" subsets. In addition to these physical processes, slow re-equilibration with the Ag|AgCl electrodes [presumably of the solubility equilibrium $AgCl(s) = Ag^+(aq) + Cl^-(aq)$] can also occur during temperature cycling. These three effects combine to yield net apparent changes in E_{II} [hence, $E°$] and E_I [hence, p($a_H\gamma_{Cl}$)] in the respective Harned cells.

For all temperatures, the major sources of uncertainty for the primary pH(S) measurements, $u_c(y)$, which excludes the uncertainty contributed by the material heterogeneity and the uncertainty of the Bates-Guggenheim convention, are $u(T\ cycling)$, $u_A(curve\ fit)$, and $u_A(E°)$.

1. For measurements at temperatures > 25 °C, the estimated variance of T cycling, $u^2(T\ cycling)$, contributes 93 % to 98 % of the total combined variance for the primary pH(S) determination, $u_c^2(y)$.
2. For measurements at temperatures ≤ 25 °C, $u^2(T\ cycling)$ represents 52 % to 75 % of $u_c^2(y)$. The $u_A^2(curve\ fit)$ contributes 17 % to 43 % to $u_c^2(y)$ and $u_A^2(E°)$ contributes 2 % to 7 % to $u_c^2(y)$. The remaining component uncertainty sources contribute less than 1 % to $u_c^2(y)$.

The $u_c(meas)$, k_{meas}, and U_{meas} values reported in Table 7 include all known instrumental and batch-related (homogeneity) factors pertaining to SRM 2193b but do *not* include the contribution from the inherent uncertainty of the Bates-Guggenheim convention (U_{B-G}). These respective values thus may be used as a basis for traceability to the measurement of this renewal, SRM 2193b. Any bias resulting from the deviation of the Bates-Guggenheim convention from the "true" (but immeasurable) value of log γ_{Cl} will be identical for all renewals of a given SRM buffer [or corresponding certified reference material (CRM) from another national metrological institute (NMI)], since the ionic composition of each solution is nominally identical. Hence, traceability from one SRM renewal to another or between NMI's is reflected by the uncertainties reported in Table 7 and the uncertainty of the SRM or CRM.

Calculation of Values for k_{cert} and $U(cert)$
To attain traceability to the SI (rather than to the measurement of the renewal of this pH SRM), it is necessary to include the contribution attributable to the inherent uncertainty of the Bates-Guggenheim convention [11] . Current expert opinion [18,19] has assessed U_{B-G} as 0.010 pH (95 % confidence interval). Dividing this value by 2 yields $u_{B-G} = 0.005$. The value of v_i for u_{B-G} is taken as 60, which is the approximate number of degrees of freedom for $k = 2$ at 95 % confidence. This contribution must be included if traceability to the SI is required. Values of the certification combined standard uncertainty, $u_c(cert)$, are obtained at each temperature by summing the corresponding $u_c(meas)$ value and u_{B-G} in quadrature. A new coverage factor, k_{cert}, is calculated by reapplication of the Welch-Satterthwaite equation using $u_c(meas)$, $v_{eff}(meas)$, and $u_c(cert)$. The certification expanded uncertainty, $U(cert)$, is obtained by Equation 8:

$$U(cert) = k_{cert}\ u_c(cert) \tag{8}$$

Certificate of Analysis

In accordance with ISO Guide 31: 2000, a NIST SRM certificate is a document containing the name, description, and intended purpose of the material, the logo of the U.S. Department of Commerce, the name of NIST as a certifying body, instructions for proper use and storage of the material, certified property value(s) with associated uncertainty(ies), method(s) used to obtain property values, the period of validity, if appropriate, and any other technical information deemed necessary for its proper use. A Certificate is issued for an SRM certified for one or more specific physical or engineering performance properties and may contain NIST reference, information, or both values in addition to certified values. A Certificate of Analysis is issued for an SRM certified for one or more specific chemical properties. Note: ISO Guide 31 is updated periodically; check with ISO for the latest version. [https://www.nist.gov/srm/srm-definitions]

For the most current version of the Certificate of Analysis for NIST SRM 2193b Calcium Carbonate [used as saturated $Ca(OH)_2$ solution], please visit:
https://www-s.nist.gov/srmors/view_cert.cfm?srm=2193b

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Appendix A: Heterogeneity Analysis of SRM 2193b

This report summarizes the analysis of bottle-to-bottle heterogeneity for SRM 2193b. The data used for this analysis were collected using a nested design with measurements made in five measurement runs, with two bottles of the candidate SRM measured in some runs and three bottles measured in others. Twelve bottles of the material were measured in all. Two measurements were made on material drawn from each of the bottles measured in each run. The bottles were randomly sampled from the population of bottles of prepared materials, bottles were randomly assigned to measurement runs, and the run order of the measurements each day was randomized. With this design a hierarchical variance components model can be fit to the data to assess random variability associated with runs, bottles, and measurements.

Results derived from the raw data were recorded for one quantity, ΔpH, the measured difference in pH for the candidate material versus the previous generation of this material, SRM 2193a. This quantity is measured using a secondary method for pH because the primary method, used for most of the certification measurements, is too time consuming to use for heterogeneity assessment. The secondary method is calibrated using the previous generation of each pH SRM to correct for instrument drift within each run. This should also correct for drift between runs, though the variance component analysis alone could also do that when there is no drift within runs. Because the purpose of these measurements it to assess material heterogeneity, the mean of these measurements is not important to this analysis. The primary requirement of this measurement is that it allow variability in the true pH between bottles to be assessed on the pH scale. The data used in this analysis are shown in Table A-1.

Table A-1: Data for Analysis of Variability from Different Sources in SRM 2193b

Day	Bottle	Measurement Order	rBottle	ΔpH
3	1	11	1	-0.00059295879956728
3	1	16	1	-0.00160945959882382
4	5	17	2	0.00042631182851566
4	5	19	2	0.00127893548554504
5	27	22	3	-0.00084512295503672
5	27	23	3	-0.00076061065953314
1	36	1	4	0.00143670902356175
1	36	3	4	0.00076061065953314
2	42	7	5	-0.00177503215847632
2	42	10	5	-0.00202860818111662
4	48	18	6	-0.00034104946281175
4	48	20	6	-0.00187577204546657
3	60	13	7	-0.00050825039962827
3	60	14	7	-0.00084708399938141
2	68	5	8	0.00143693079495817
2	68	8	8	0.00000000000000000
5	107	21	9	0.00059158606852503
5	107	24	9	-0.00050707377302146
1	116	2	10	0.00126768443255460
1	116	4	10	0.00033804918201430
3	126	12	11	-0.00186358479863892
3	126	15	11	-0.00093179239931946
2	162	6	12	0.00202860818111662
2	162	9	12	0.00067620272703919

The first step in the analysis of the data was an exploratory analysis. In this analysis plots of the data were examined for evidence of uncorrected measurement drift, outliers, factor effects, and any other features that might impact further analysis for certification. These plots are shown in Figure A-1; they were made using the software package R [A1]. None of the exploratory plots suggested anything unexpected or unusual, so all data were used in subsequent analyses, as originally planned.
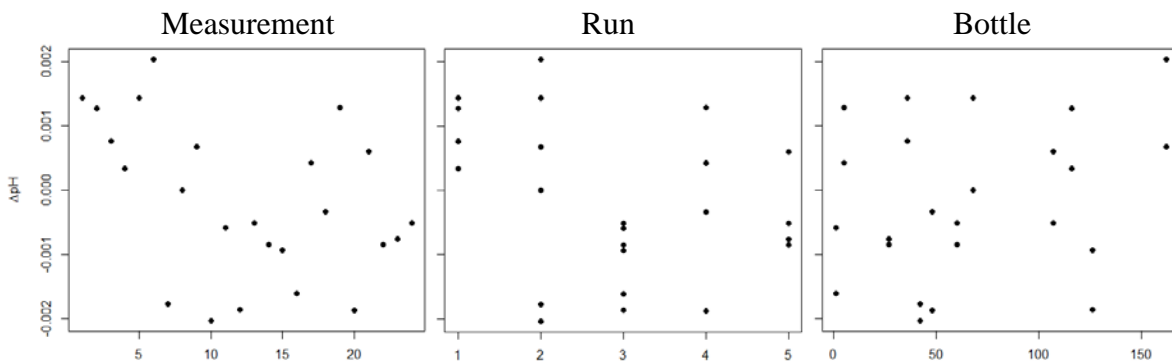
Figure A-1: ΔpH values plotted in measurement, run, and bottle order

Based on the experiment design and the exploratory plots, a hierarchical variance components model was then fit to the data. This model assumes a single, unknown mean, μ, for each observation, y_{ijk}, but allows for different levels of random variation between runs, bottles, and measurements. The random errors associated with each run are denoted by ρ_i, the random errors associated with each bottle are denoted by $\beta_{(i)j}$, and the random errors associated with each measurement are denoted by $\varepsilon_{(ij)k}$. The variances associated with each source of random error, run, bottle, and measurement, are denoted σ_R^2, σ_B^2, and σ_M^2, respectively. All random errors are assumed to be mutually independent of one another and normally distributed. The statistical model in mathematical notation is:

$$y_{ijk} = \mu + \rho_i + \beta_{(i)j} + \varepsilon_{(ij)k}; \ i = 1,\ldots,5; j = 1,2 \text{ or } j = 1,2,3; k = 1,2;$$

$$\rho_i = \mathrm{N}\left(0,\sigma_R^2\right); \beta_{(i)j} = \mathrm{N}\left(0,\sigma_B^2\right); \varepsilon_{(ij)k} = \mathrm{N}\left(0,\sigma_M^2\right)$$

The model was fit using Bayesian modeling methods via Markov Chain Monte Carlo simulation as implemented in the software package OpenBUGS [A2, A3]. A Bayesian model was used because it provides uncertainty estimates that have a clear statistical interpretation, are not based asymptotic theory or other approximations, and are always positive.

To fit the Bayesian model, prior assessments of the values of each parameter in the model must be provided. The prior assessment for each parameter is specified as probability distribution for the parameter's unknown value. These distributions are called prior distributions because they are specified independently of the data (i.e., before the data are observed or used). For this analysis, essentially non-informative prior distributions were used. Such distributions are relatively flat and have relatively large variances so that they will not provide much quantitative information about the values of the parameters. In this case shifted and scaled beta distributions with hyper-parameters $\alpha_H = 1$ and $\beta_H = 1$ were used (i.e. shifted and scaled uniform

distributions). The ranges and locations of the prior distributions for each parameter were set so that they greatly exceeded all practical parameter values possible.

Fitting the model with a range of different prior distributions confirmed that the results were insensitive to the parameters chosen for the prior distributions. The check on prior sensitivity also was carried out using shifted and scaled beta distributions, but for different combinations of the hyper-parameters, with $\alpha_{H_i} \in \{0.8, 1.2\}$ and $\beta_{H_i} \in \{0.8, 1.2\}$. The same shifting and scaling values used in the original model fit with uniform priors were used throughout the prior sensitivity check. The two hyper-parameter values used for each of the four primary parameters in the model, $\{\mu, \sigma_R, \sigma_{\boldsymbol{R}}, \sigma_M\}$, were assigned using a supersaturated $UE(s^2)$ optimal experiment design [A4] to study the combined effects of eight factors in four runs. The alternative prior specifications and the associated results from the fit of each model are shown in Table A-2.

Table A-2: Output from Models with Different Priors

Model	Parameter	Prior	Posterior Mean	Posterior Standard Deviation
1	mu	4*Beta(1.0,1.0)	-0.07390	0.3126
	sigma.R	4*Beta(1.0,1.0)	0.4066	0.3954
	sigma.B	4*Beta(1.0,1.0)	0.5154	0.2047
	sigma.M	4*Beta(1.0,1.0)	0.3993	0.09724
	mu.nb	NA	0.0000	0.001108
2	mu	4*Beta(1.2,1.2)	-0.07368	0.3488
	sigma.R	4*Beta(1.2,0.8)	0.4927	0.4680
	sigma.B	4*Beta(0.8,0.8)	0.5016	0.2110
	sigma.M	4*Beta(0.8,1.2)	0.3985	0.09779
	mu.nb	NA	0.0000	0.001081
3	mu	4*Beta(1.2,0.8)	-0.0679	0.2862
	sigma.R	4*Beta(0.8,0.8)	0.3496	0.3682
	sigma.B	4*Beta(0.8,1.2)	0.4924	0.2037
	sigma.M	4*Beta(1.2,0.8)	0.4091	0.1029
	mu.nb	NA	0.0000	0.001070
4	mu	4*Beta(0.8,1.2)	-0.08369	0.2769
	sigma.R	4*Beta(0.8,1.2)	0.3345	0.3418
	sigma.B	4*Beta(0.8,1.2)	0.5013	0.2012
	sigma.M	4*Beta(0.8,1.2)	0.3978	0.09764
	mu.nb	NA	0.0000	0.001081
5	mu	4*Beta(0.8,0.8)	-0.07211	0.3348
	sigma.R	4*Beta(1.2,1.2)	0.4623	0.4191
	sigma.B	4*Beta(0.8,0.8)	0.4957	0.2105
	sigma.M	4*Beta(1.2,0.8)	0.4084	0.1021
	mu.nb	NA	0.0000	0.001073

The results for the four primary parameters are relative as the data were rescaled for the computations. The data transformation is $\Delta pH_S = \Delta pH \cdot 500$. Besides the primary parameters with individual priors, results for prediction of ΔpH for a new bottle, mu.nb, are also shown. The posterior standard deviation of mu.nb from Model 1 is the heterogeneity uncertainty to be combined with results from the primary pH measurement method. Values of mu.nb are assumed to be normally distributed.

A probability distribution for each measurement, conditional on the values of the parameters in the model, is also specified. In this case the random errors associated with each factor were modeled as following normal distributions. Then, based on the model and the observed data, the prior distributions for each parameter are updated using Bayes' Theorem to obtain new distributions for each parameter given the information in the data. These new distributions, called posterior distributions, are then used to obtain uncertainty intervals about each quantity of interest.

Diagnostic plots showed that the Markov Chains had converged by the 10000th iteration of the simulation. Then 10000 additional iterations were run for each of six parallel Markov chains for model validation and to estimate the parameter values. Box plots of the posterior predictive residuals from the model for each data point indicated that the models fit the data reasonably well.

Assuming the hierarchical model provides an adequate description of the measurement process, a proposed value of the heterogeneity standard uncertainty in SRM 2193 pH was determined from the predictive ΔpH distribution for a randomly selected unit of this material. The predictive distribution is used because the uncertainty obtained accounts for both the inherent variability between ΔpH values from different units and the uncertainty arising from the different levels of sampling variation that impacts our knowledge of the heterogeneity standard deviation. Proposed values for the heterogeneity standard uncertainty for SRM 2193b and associated effective degrees of freedom are given in Table A-3.

Table A-3: Summary Statistics for a New Bottle of SRM 2193b

ΔpH	Standard Uncertainty	Effective Degrees of Freedom
0.0000	0.001108	27.37

The effective degrees of freedom are provided for use in any further uncertainty computations carried out using the methods of the GUM and were approximated by computing an average coverage factor from the 95 % expanded uncertainty interval from the Bayesian analysis and then numerically solving for degrees of freedom as if the coverage factor was obtained from a Student's t distribution.

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Appendix B: Uncertainty Component Details, 5 °C to 50 °C

Table B-1. Detail of Uncertainty Components for SRM 2193b, 5 °C

Component	Type	Estimate x_i	$u(x_i)$	units	Distribution	$\|c_i\|$	units	u_i(meas)/1	v_i
pH(S) curve fit	A	13.2176	1.6E-03	1	Gaussian	1	1	1.6E-03	10
u_A for $E°$	A	0.234018	2.2E-05	V	Gaussian	18.1	V^{-1}	4.1E-04	5
SRM homogeneity	A	1	1.1E-03	1	Uniform	1.0	1	1.1E-03	27.37
HCl molality [$u_c(b_{HCl})$]	A + B	0.01000950	7.8E-07	mol·kg^{-1}	Combined std.	86.78	kg·mol^{-1}	6.8E-05	71
E_{meas} (DVM)	B	1.083361	1.3E-05	V	Uniform	18.1	V^{-1}	2.4E-04	60
$\gamma_\pm$(HCl)	B	0.9074	1.2E-04	1	Uniform	0.957	1	1.1E-04	60
E_{meas} for $E°$ (DVM)	B	0.459394	5.7E-06	V	Uniform	18.1	V^{-1}	1.0E-04	60
NaCl molality [$u_c(b_{NaCl})$]	B	0.005000	3.0E-07	mol·kg^{-1}	Uniform	86.9	kg·mol^{-1}	2.6E-05	60
T	B	278.150	5.5E-03	K	Combined std.	4.22E-02	K^{-1}	2.3E-04	60
R	B	8.314460	4.8E-06	J·mol^{-1}·K^{-1}	Combined std.	1.41E+00	mol·K·J^{-1}	6.8E-06	60
p_{atm}	B	100532	5.8E+00	Pa	Uniform	4.88E-09	Pa^{-1}	2.8E-08	60
F	B	96485.3329	5.9E-04	C·mol^{-1}	Combined std.	1.22E-04	mol·C^{-1}	7.2E-08	60
T cycling	B	---	1.8E-03	1	Uniform	1	1	1.8E-03	60
Combined standard uncertainty of the measurement, u_c(meas); v_{eff} shown in right column								2.7E-03	58.63

Table B-2. Detail of Uncertainty Components for SRM 2193b, 10 °C

Component	Type	Estimate x_i	$u(x_i)$	units	Distribution	$\|c_i\|$	units	u_i(meas)/1	v_i
pH(S) curve fit	A	13.0109	9.8E-04	1	Gaussian	1	1	9.8E-04	10
u_A for $E°$	A	0.231369	3.3E-05	V	Gaussian	17.8	V^{-1}	5.8E-04	5
SRM homogeneity	A	1	1.1E-03	1	Uniform	1.0	1	1.1E-03	27.37
HCl molality [$u_c(b_{HCl})$]	A + B	0.01000950	7.8E-07	mol·kg^{-1}	Combined std.	86.78	kg·mol^{-1}	6.8E-05	71
E_{meas} (DVM)	B	1.084529	1.3E-05	V	Uniform	17.8	V^{-1}	2.4E-04	60
$\gamma_\pm$(HCl)	B	0.9067	1.2E-04	1	Uniform	0.958	1	1.1E-04	60
E_{meas} for $E°$ (DVM)	B	0.460834	5.7E-06	V	Uniform	17.8	V^{-1}	1.0E-04	60
NaCl molality [$u_c(b_{NaCl})$]	B	0.005000	3.0E-07	mol·kg^{-1}	Uniform	86.9	kg·mol^{-1}	2.6E-05	60
T	B	283.150	5.5E-03	K	Combined std.	4.07E-02	K^{-1}	2.3E-04	60
R	B	8.314460	4.8E-06	J·mol^{-1}·K^{-1}	Combined std.	1.39E+00	mol·K·J^{-1}	6.7E-06	60
p_{atm}	B	100485	5.8E+00	Pa	Uniform	4.75E-09	Pa^{-1}	2.8E-08	60
F	B	96485.3329	5.9E-04	C·mol^{-1}	Combined std.	1.19E-04	mol·C^{-1}	7.0E-08	60
T cycling	B	---	1.8E-03	1	Uniform	1	1	1.8E-03	60
Combined standard uncertainty of the measurement, u_c(meas); v_{eff} shown in right column								2.4E-03	100.83

Table B-3. Detail of Uncertainty Components for SRM 2193b, 15 °C

Component	Type	Estimate x_i	$u(x_i)$	units	Distribution	$|c_i|$	units	u_i(meas)/1	v_i
pH(S) curve fit	A	12.8148	1.0E-03	1	Gaussian	1	1	1.0E-03	10
u_A for $E°$	A	0.228564	2.3E-05	V	Gaussian	17.5	V^{-1}	3.9E-04	5
SRM homogeneity	A	1	1.1E-03	1	Uniform	1.0	1	1.1E-03	27.37
HCl molality [$u_c(b_{HCl})$]	A + B	0.01000950	7.8E-07	$mol·kg^{-1}$	Combined std.	86.78	$kg·mol^{-1}$	6.8E-05	71
E_{meas} (DVM)	B	1.085809	1.3E-05	V	Uniform	17.5	V^{-1}	2.3E-04	60
$\gamma_\pm$(HCl)	B	0.906	1.2E-04	1	Uniform	0.959	1	1.1E-04	60
E_{meas} for $E°$ (DVM)	B	0.462119	5.7E-06	V	Uniform	17.5	V^{-1}	1.0E-04	60
NaCl molality [$u_c(b_{NaCl})$]	B	0.005000	3.0E-07	$mol·kg^{-1}$	Uniform	86.9	$kg·mol^{-1}$	2.6E-05	60
T	B	288.150	5.5E-03	K	Combined std.	3.93E-02	K^{-1}	2.2E-04	60
R	B	8.314460	4.8E-06	$J·mol^{-1}·K^{-1}$	Combined std.	1.36E+00	$mol·K·J^{-1}$	6.5E-06	60
p_{atm}	B	100458	5.8E+00	Pa	Uniform	4.65E-09	Pa^{-1}	2.7E-08	60
F	B	96485.3329	5.9E-04	$C·mol^{-1}$	Combined std.	1.17E-04	$mol·C^{-1}$	6.9E-08	60
T cycling	B	---	1.8E-03	1	Uniform	1	1	1.8E-03	60
Combined standard uncertainty of the measurement, u_c(meas); v_{eff} shown in right column								2.4E-03	97.56

Table B-4. Detail of Uncertainty Components for SRM 2193b, 20 °C

Component	Type	Estimate x_i	$u(x_i)$	units	Distribution	$|c_i|$	units	u_i(meas)/1	v_i
pH(S) curve fit	A	12.6289	9.8E-04	1	Gaussian	1	1	9.8E-04	10
u_A for $E°$	A	0.225591	1.8E-05	V	Gaussian	17.2	V^{-1}	3.1E-04	5
SRM homogeneity	A	1	1.1E-03	1	Uniform	1.0	1	1.1E-03	27.37
HCl molality [$u_c(b_{HCl})$]	A + B	0.01000950	7.8E-07	$mol·kg^{-1}$	Combined std.	86.78	$kg·mol^{-1}$	6.8E-05	71
E_{meas} (DVM)	B	1.087170	1.3E-05	V	Uniform	17.2	V^{-1}	2.3E-04	60
$\gamma_\pm$(HCl)	B	0.9051	1.2E-04	1	Uniform	0.960	1	1.1E-04	60
E_{meas} for $E°$ (DVM)	B	0.463249	5.7E-06	V	Uniform	17.2	V^{-1}	9.8E-05	60
NaCl molality [$u_c(b_{NaCl})$]	B	0.005000	3.0E-07	$mol·kg^{-1}$	Uniform	86.9	$kg·mol^{-1}$	2.6E-05	60
T	B	293.150	5.5E-03	K	Combined std.	3.80E-02	K^{-1}	2.1E-04	60
R	B	8.314460	4.8E-06	$J·mol^{-1}·K^{-1}$	Combined std.	1.34E+00	$mol·K·J^{-1}$	6.4E-06	60
p_{atm}	B	100407	5.8E+00	Pa	Uniform	4.43E-09	Pa^{-1}	2.6E-08	60
F	B	96485.3329	5.9E-04	$C·mol^{-1}$	Combined std.	1.16E-04	$mol·C^{-1}$	6.8E-08	60
T cycling	B	---	1.8E-03	1	Uniform	1	1	1.8E-03	60
Combined standard uncertainty of the measurement, u_c(meas); v_{eff} shown in right column								2.4E-03	98.09

Table B-5. Detail of Uncertainty Components for SRM 2193b, 25 °C

Component	Type	Estimate x_i	$u(x_i)$	units	Distribution	$|c_i|$	units	u_i(meas)/1	v_i
pH(S) curve fit	A	12.4529	8.5E-04	1	Gaussian	1	1	8.5E-04	10
u_A for $E°$	A	0.222406	2.9E-05	V	Gaussian	16.9	V^{-1}	4.9E-04	5
SRM homogeneity	A	1	1.1E-03	1	Uniform	1.0	1	1.1E-03	27.37
HCl molality [$u_c(b_{HCl})$]	A + B	0.01000950	1.6E-06	mol·kg^{-1}	Combined std.	86.78	kg·mol^{-1}	1.4E-04	71
E_{meas} (DVM)	B	1.090238	1.3E-05	V	Uniform	16.9	V^{-1}	2.3E-04	60
$\gamma_\pm$(HCl)	B	0.9042	1.2E-04	1	Uniform	0.961	1	1.1E-04	60
E_{meas} for $E°$ (DVM)	B	0.464170	5.7E-06	V	Uniform	16.9	V^{-1}	9.7E-05	60
NaCl molality [$u_c(b_{NaCl})$]	B	0.005000	3.0E-07	mol·kg^{-1}	Uniform	86.9	kg·mol^{-1}	2.6E-05	60
T	B	298.150	5.5E-03	K	Combined std.	3.68E-02	K^{-1}	2.0E-04	60
R	B	8.314460	4.8E-06	J·mol^{-1}·K^{-1}	Combined std.	1.32E+00	mol·K·J^{-1}	6.3E-06	60
p_{atm}	B	100631	5.8E+00	Pa	Uniform	3.40E-09	Pa^{-1}	2.0E-08	60
F	B	96485.3329	5.9E-04	C·mol^{-1}	Combined std.	1.14E-04	mol·C^{-1}	6.7E-08	60
T cycling	B	---	1.8E-03	1	Uniform	1	1	1.8E-03	60
Combined standard uncertainty of the measurement, u_c(meas); v_{eff} shown in right column								2.4E-03	105.45

Table B-6. Detail of Uncertainty Components for SRM 2193b, 30 °C

Component	Type	Estimate x_i	$u(x_i)$	units	Distribution	$|c_i|$	units	u_i(meas)/1	v_i
pH(S) curve fit	A	12.2863	8.0E-04	1	Gaussian	1	1	8.0E-04	10
u_A for $E°$	A	0.219161	2.2E-05	V	Gaussian	16.6	V^{-1}	3.7E-04	5
SRM homogeneity	A	1	1.1E-03	1	Uniform	1.0	1	1.1E-03	27.37
HCl molality [$u_c(b_{HCl})$]	A + B	0.01000950	7.8E-07	mol·kg^{-1}	Combined std.	86.78	kg·mol^{-1}	6.8E-05	71
E_{meas} (DVM)	B	1.089973	1.3E-05	V	Uniform	16.6	V^{-1}	2.2E-04	60
$\gamma_\pm$(HCl)	B	0.9033	1.2E-04	1	Uniform	0.962	1	1.1E-04	60
E_{meas} for $E°$ (DVM)	B	0.465030	5.7E-06	V	Uniform	16.6	V^{-1}	9.6E-05	60
NaCl molality [$u_c(b_{NaCl})$]	B	0.005000	3.0E-07	mol·kg^{-1}	Uniform	86.9	kg·mol^{-1}	2.6E-05	60
T	B	303.150	5.5E-03	K	Combined std.	3.56E-02	K^{-1}	2.0E-04	60
R	B	8.314460	4.8E-06	J·mol^{-1}·K^{-1}	Combined std.	1.30E+00	mol·K·J^{-1}	6.2E-06	60
p_{atm}	B	100694	5.8E+00	Pa	Uniform	1.68E-10	Pa^{-1}	9.8E-10	60
F	B	96485.3329	5.9E-04	C·mol^{-1}	Combined std.	1.12E-04	mol·C^{-1}	6.6E-08	60
T cycling	B	---	5.9E-03	1	Uniform	1	1	5.9E-03	60
Combined standard uncertainty of the measurement, u_c(meas); v_{eff} shown in right column								6.1E-03	67.27

Table B-7. Detail of Uncertainty Components for SRM 2193b, 35 °C

Component	Type	Estimate x_i	$u(x_i)$	units	Distribution	$|c_i|$	units	u_i(meas)/1	v_i
pH(S) curve fit	A	12.1289	8.6E-04	1	Gaussian	1	1	8.6E-04	10
u_A for $E°$	A	0.215726	3.9E-05	V	Gaussian	16.4	V^{-1}	6.3E-04	5
SRM homogeneity	A	1	1.1E-03	1	Uniform	1.0	1	1.1E-03	27.37
HCl molality [$u_c(b_{HCl})$]	A + B	0.01000950	7.8E-07	mol·kg^{-1}	Combined std.	86.78	kg·mol^{-1}	6.8E-05	71
E_{meas} (DVM)	B	1.091323	1.3E-05	V	Uniform	16.4	V^{-1}	2.2E-04	60
$\gamma_\pm$(HCl)	B	0.9024	1.2E-04	1	Uniform	0.963	1	1.1E-04	60
E_{meas} for $E°$ (DVM)	B	0.465704	5.8E-06	V	Uniform	16.4	V^{-1}	9.4E-05	60
NaCl molality [$u_c(b_{NaCl})$]	B	0.005000	3.0E-07	mol·kg^{-1}	Uniform	86.9	kg·mol^{-1}	2.6E-05	60
T	B	308.150	5.5E-03	K	Combined std.	3.45E-02	K^{-1}	1.9E-04	60
R	B	8.314460	4.8E-06	J·mol^{-1}·K^{-1}	Combined std.	1.28E+00	mol·K·J^{-1}	6.1E-06	60
p_{atm}	B	100645	5.8E+00	Pa	Uniform	2.72E-10	Pa^{-1}	1.6E-09	60
F	B	96485.3329	5.9E-04	C·mol^{-1}	Combined std.	1.10E-04	mol·C^{-1}	6.5E-08	60
T cycling	B	---	5.9E-03	1	Uniform	1	1	5.9E-03	60
Combined standard uncertainty of the measurement, u_c(meas); v_{eff} shown in right column								6.1E-03	68.45

Table B-8. Detail of Uncertainty Components for SRM 2193b, 37 °C

Component	Type	Estimate x_i	$u(x_i)$	units	Distribution	$|c_i|$	units	u_i(meas)/1	v_i
pH(S) curve fit	A	12.0684	8.8E-04	1	Gaussian	1	1	8.8E-04	10
u_A for $E°$	A	0.214256	4.4E-05	V	Gaussian	16.2	V^{-1}	7.2E-04	5
SRM homogeneity	A	1	1.1E-03	1	Uniform	1.0	1	1.1E-03	27.37
HCl molality [$u_c(b_{HCl})$]	A + B	0.01000950	7.8E-07	mol·kg^{-1}	Combined std.	86.78	kg·mol^{-1}	6.8E-05	71
E_{meas} (DVM)	B	1.091866	1.3E-05	V	Uniform	16.2	V^{-1}	2.2E-04	60
$\gamma_\pm$(HCl)	B	0.902	1.2E-04	1	Uniform	0.963	1	1.1E-04	60
E_{meas} for $E°$ (DVM)	B	0.465880	5.8E-06	V	Uniform	16.2	V^{-1}	9.4E-05	60
NaCl molality [$u_c(b_{NaCl})$]	B	0.005000	3.0E-07	mol·kg^{-1}	Uniform	86.9	kg·mol^{-1}	2.6E-05	60
T	B	310.150	5.5E-03	K	Combined std.	3.41E-02	K^{-1}	1.9E-04	60
R	B	8.314460	4.8E-06	J·mol^{-1}·K^{-1}	Combined std.	1.27E+00	mol·K·J^{-1}	6.1E-06	60
p_{atm}	B	100586	5.8E+00	Pa	Uniform	1.59E-11	Pa^{-1}	9.3E-11	60
F	B	96485.3329	5.9E-04	C·mol^{-1}	Combined std.	1.10E-04	mol·C^{-1}	6.5E-08	60
T cycling	B	---	5.9E-03	1	Uniform	1	1	5.9E-03	60
Combined standard uncertainty of the measurement, u_c(meas); v_{eff} shown in right column								6.1E-03	68.89

Table B-9. Detail of Uncertainty Components for SRM 2193b, 40 °C

Component	Type	Estimate x_i	$u(x_i)$	units	Distribution	$|c_i|$	units	u_i(meas)/1	v_i
pH(S) curve fit	A	11.9804	8.0E-04	1	Gaussian	1	1	8.0E-04	10
u_A for $E°$	A	0.212104	5.2E-05	V	Gaussian	16.1	V^{-1}	8.4E-04	5
SRM homogeneity	A	1	1.1E-03	1	Uniform	1.0	1	1.1E-03	27.37
HCl molality [$u_c(b_{HCl})$]	A + B	0.01000950	7.8E-07	$mol \cdot kg^{-1}$	Combined std.	86.78	$kg \cdot mol^{-1}$	6.8E-05	71
E_{meas} (DVM)	B	1.092684	1.4E-05	V	Uniform	16.1	V^{-1}	2.2E-04	60
$\gamma_{\pm}$(HCl)	B	0.9014	1.2E-04	1	Uniform	0.964	1	1.1E-04	60
E_{meas} for $E°$ (DVM)	B	0.466198	5.8E-06	V	Uniform	16.1	V^{-1}	9.3E-05	60
NaCl molality [$u_c(b_{NaCl})$]	B	0.005000	3.0E-07	$mol \cdot kg^{-1}$	Uniform	86.9	$kg \cdot mol^{-1}$	2.6E-05	60
T	B	313.150	5.5E-03	K	Combined std.	3.35E-02	K^{-1}	1.9E-04	60
R	B	8.314460	4.8E-06	$J \cdot mol^{-1} \cdot K^{-1}$	Combined std.	1.26E+00	$mol \cdot K \cdot J^{-1}$	6.1E-06	60
p_{atm}	B	100558	5.8E+00	Pa	Uniform	1.16E-10	Pa^{-1}	6.7E-10	60
F	B	96485.3329	5.9E-04	$C \cdot mol^{-1}$	Combined std.	1.09E-04	$mol \cdot C^{-1}$	6.4E-08	60
T cycling	B	---	5.9E-03	1	Uniform	1	1	5.9E-03	60
Combined standard uncertainty of the measurement, u_c(meas); v_{eff} shown in right column								6.1E-03	69.00

Table B-10. Detail of Uncertainty Components for SRM 2193b, 45 °C

Component	Type	Estimate x_i	$u(x_i)$	units	Distribution	$|c_i|$	units	u_i(meas)/1	v_i
pH(S) curve fit	A	11.8403	8.6E-04	1	Gaussian	1	1	8.6E-04	10
u_A for $E°$	A	0.208302	5.1E-05	V	Gaussian	15.8	V^{-1}	8.1E-04	5
SRM homogeneity	A	1	1.1E-03	1	Uniform	1.0	1	1.1E-03	27.37
HCl molality [$u_c(b_{HCl})$]	A + B	0.01000950	7.8E-07	$mol \cdot kg^{-1}$	Combined std.	86.78	$kg \cdot mol^{-1}$	6.8E-05	71
E_{meas} (DVM)	B	1.094109	1.4E-05	V	Uniform	15.8	V^{-1}	2.1E-04	60
$\gamma_{\pm}$(HCl)	B	0.9003	1.2E-04	1	Uniform	0.965	1	1.1E-04	60
E_{meas} for $E°$ (DVM)	B	0.466520	5.8E-06	V	Uniform	15.8	V^{-1}	9.1E-05	60
NaCl molality [$u_c(b_{NaCl})$]	B	0.005000	3.0E-07	$mol \cdot kg^{-1}$	Uniform	86.9	$kg \cdot mol^{-1}$	2.6E-05	60
T	B	318.150	5.5E-03	K	Combined std.	3.25E-02	K^{-1}	1.8E-04	60
R	B	8.314460	4.8E-06	$J \cdot mol^{-1} \cdot K^{-1}$	Combined std.	1.25E+00	$mol \cdot K \cdot J^{-1}$	6.0E-06	60
p_{atm}	B	100492	5.8E+00	Pa	Uniform	2.88E-10	Pa^{-1}	1.7E-09	60
F	B	96485.3329	5.9E-04	$C \cdot mol^{-1}$	Combined std.	1.07E-04	$mol \cdot C^{-1}$	6.3E-08	60
T cycling	B	---	5.9E-03	1	Uniform	1	1	5.9E-03	60
Combined standard uncertainty of the measurement, u_c(meas); v_{eff} shown in right column								6.1E-03	69.19

Table B-11. Detail of Uncertainty Components for SRM 2193b, 50 °C

Component	Type	Estimate x_i	$u(x_i)$	units	Distribution	$|c_i|$	units	u_i(meas)/1	v_i
pH(S) curve fit	A	11.7086	8.8E-04	1	Gaussian	1	1	8.8E-04	10
u_A for $E°$	A	0.204369	8.0E-05	V	Gaussian	15.6	V^{-1}	1.2E-03	5
SRM homogeneity	A	1	1.1E-03	1	Uniform	1.0	1	1.1E-03	27.37
HCl molality [$u_c(b_{HCl})$]	A + B	0.01000950	7.8E-07	mol·kg^{-1}	Combined std.	86.78	kg·mol^{-1}	6.8E-05	71
E_{meas} (DVM)	B	1.095499	1.4E-05	V	Uniform	15.6	V^{-1}	2.1E-04	60
$\gamma_\pm$(HCl)	B	0.8992	1.2E-04	1	Uniform	0.966	1	1.1E-04	60
E_{meas} for $E°$ (DVM)	B	0.466713	5.8E-06	V	Uniform	15.6	V^{-1}	9.0E-05	60
NaCl molality [$u_c(b_{NaCl})$]	B	0.005000	3.0E-07	mol·kg^{-1}	Uniform	86.9	kg·mol^{-1}	2.6E-05	60
T	B	323.150	5.5E-03	K	Combined std.	3.16E-02	K^{-1}	1.8E-04	60
R	B	8.314460	4.8E-06	J·mol^{-1}·K^{-1}	Combined std.	1.23E+00	mol·K·J^{-1}	5.9E-06	60
p_{atm}	B	100499	5.8E+00	Pa	Uniform	1.41E-10	Pa^{-1}	8.2E-10	60
F	B	96485.3329	5.9E-04	C·mol^{-1}	Combined std.	1.06E-04	mol·C^{-1}	6.3E-08	60
T cycling	B	---	5.9E-03	1	Uniform	1	1	5.9E-03	60
Combined standard uncertainty of the measurement, u_c(meas); v_{eff} shown in right column								6.2E-03	71.24

Appendix C: Calculation of $u_c(b_{HCl})$

The uncertainty of the HCl assay includes the Type A standard deviation of the mean of 12 coulometric HCl titrations and Type B estimates connected with the interference from incompletely removed dissolved CO_2, the HCl weighing and air buoyancy correction, the electrical and time parameters associated with the coulometric titration, and the Faraday constant. The basis and detailed values for each source uncertainty considered in the calculation of $u_c(b_{HCl})$ are given in Table C-1.

The value of $u_c(b_{HCl})$ is somewhat larger than in previous renewals of SRM 2193b, owing to an increased value for the estimated Type B uncertainty associated with incomplete removal of CO_2. The uncertainty associated with the residual CO_2 is estimated by assuming the incomplete removal of CO_2 for an electrolyte solution saturated with ambient atmospheric CO_2. The Henry's law constant for CO_2 in 1 mol kg^{-1} sodium chloride (NaCl) [C1], $K_H(CO_2)$, was assumed for a solution of 1 mol kg^{-1} KCl. Neglecting a correction[1] for the increase in CO_2 solubility after dilution of the supporting electrolyte with the HCl sample, the relative molality of CO_2 with respect to the HCl sample, $r(CO_2)$, is

$$r(CO_2) = \frac{K_H(CO_2)\, p_{atm}\, x(CO_2)}{b_{HCl}} ,$$

where p_{atm} is ambient atmospheric pressure and $x(CO_2)$ is the fraction of CO_2 in air. Assuming a 75 % CO_2 removal efficiency, the estimated residual amount of CO_2 in solution is

$$\text{residual } CO_2 = r(CO_2)\, (1 - 0.75) .$$

No correction to the determined b_{HCl} is made for the estimated amount of CO_2 remaining after the N_2 aeration of the supporting electrolyte, but the residual CO_2 estimated uncertainty is included in calculation of $u_c(b_{HCl})$. The component uncertainty for CO_2 interference is modeled using a uniform distribution.

References

C1 Harned HS, Davis R. The ionization constant of carbonic acid in water and solubility of carbon dioxide in water and aqueous salt solutions from 0 to 50 °C. Journal of the American Chemical Society 1943; 60(10): 2030-2037.

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[1] Dilution of the supporting electrolyte (60 cm^3 of 1 mol kg^{-1} KCl) with the HCl sample (25 g of 0.01 mol kg^{-1} HCl) will lead to an increase in the solubility of CO_2 in the solution. However, on the short time scale (10 to 20 minutes) between the HCl sample addition and the N_2 aeration, it is not probable that a significant amount of ambient atmospheric CO_2 will diffuse into the coulometric cell headspace, which is continuously flushed with 99.999 % N_2, and become dissolved in the diluted electrolyte mixture.

Table C-1. Summary of Uncertainty Components in the Coulometric Assay of HCl

Source or input quantity	Type	Estimate, x_i	$u(x_i)$	units	distribution	$|c_i|$	units	$u_i(b_{HCl})$ / mol·kg^{-1}	v_i
CO_2 interference	B	0	1.65E-04	(mol kg^{-1}) / (mol kg^{-1})	Uniform	1.00E-02	mol·kg^{-1}	1.65E-06	60
Meas. replication of b_{HCl}	A	0.0100095	7.83E-07	mol·kg^{-1}	Gaussian	1	1	7.83E-07	11
m_{HCl}	B	0.0245	1.21E-07	kg	Uniform	4.09E-01	(mol·kg^{-1})/kg	4.95E-08	60
ρ_{air}	B	1.18108	6.82E-03	kg·m^{-3}	Uniform	8.77E-06	(mol·kg^{-1})/(kg·m^{-3})	5.98E-08	60
R_{std}	B	9.999602	3.50E-05	Ω	95% C.I.	1.00E-03	(mol·kg^{-1})/Ω	3.50E-08	60
I_{main} drift	B	0.1018250	1.18E-07	A	Uniform	9.83E-02	(mol·kg^{-1})/A	1.16E-08	60
E_{std}	B	1.0182097	1.00E-06	V	95% C.I.	9.83E-03	(mol·kg^{-1})/V	9.83E-09	60
ρ_{HCl}	B	998.0	5.76E-01	kg·m^{-3}	Uniform	1.19E-08	(mol·kg^{-1})/(kg·m^{-3})	6.83E-09	60
Cathode side-rxns	B	0	2.89E-07	(mol kg^{-1}) / (mol kg^{-1})	Uniform	1.00E-02	mol·kg^{-1}	2.89E-09	60
F	B	96485.3329	5.90E-04	C·mol^{-1}	u_c	1.04E-07	(mol kg^{-1})/(C mol^{-1})	6.12E-11	60
t	B	1009.61	1.01E-06	s	Uniform	4.31E-05	(mol·kg^{-1})/s	4.35E-11	60
Combined standard uncertainty, $u_c(b_{HCl})$, left column; effective degrees of freedom, v_{eff}, right column								1.83E-06	70.88