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Certification of Standard Reference Material® 915c Calcium Carbonate

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Abstract

Standard Reference Material® (SRM) 915c Calcium Carbonate is certified as a chemical substance of known purity. It is intended for use in the calibration and standardization of procedures for calcium (Ca) determinations employed in clinical analysis and for routine critical evaluation of the daily working standards used in these procedures. A unit of SRM 915c consists of a single glass bottle containing 20 g of the material. This publication documents the production, analytical methods, and computations involved in characterizing this product.

Keywords

Calcium; Calcium Carbonate; Carbonate; Coulometric acidimetry; Gravimetry;
Inductively Coupled Plasma Mass Spectrometry (ICP-MS);
Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES);
Standard Reference Material® (SRM).

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1. Introduction

Standard Reference Material® (SRM®) 915c Calcium Carbonate is an analytical standard of known purity. It is intended for use in the calibration and standardization of procedures for calcium (Ca) determinations employed in clinical analysis and for routine critical evaluation of the daily working standards used in these procedures. A unit of SRM 915c consists of a single glass bottle containing 20 g of the material.

SRM 915c has been assayed by gravimetry and coulometry with corrections based on known impurities. The certified values for SRM 915c are calculated from a combination of the results of assays by both techniques.

1.1. SRM 915 Sales History

The initial version of this material, SRM 915 Calcium Carbonate, was issued in 1969. SRM 915c is the third replacement material. Sales have been between 70 and 220 units per year.

The use of the SRM 915 series materials by country and/or geographic area for the periods 1990 through 1998, 1999 through 2007, and 2008 through 2017 is summarized in Fig. 1. The fraction of sales outside of the U.S.A. has increased slowly over time.

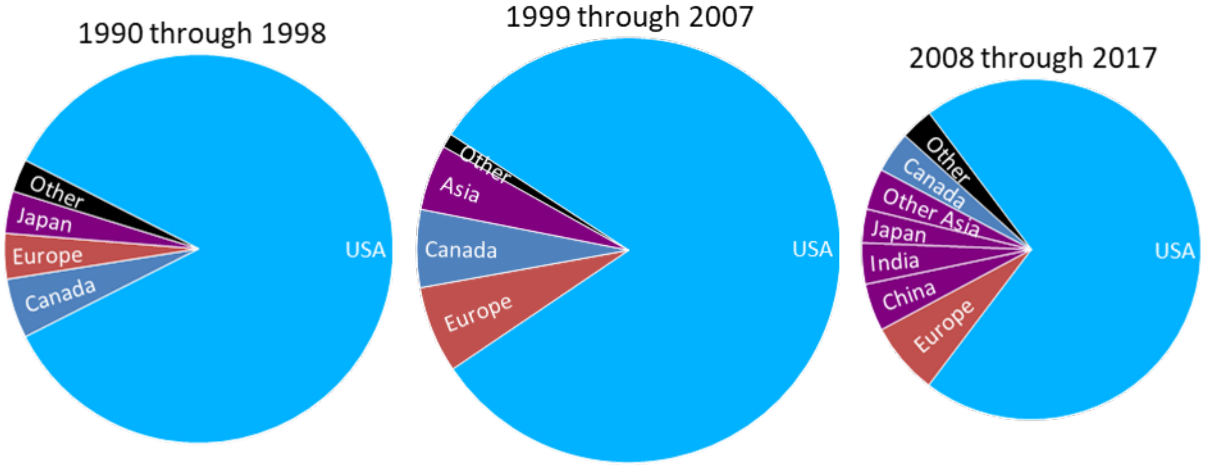

Fig. 1. Location of Customers for the SRM 915 Series Materials.

From left to tight, the three charts display the fraction of sales to various countries or geographic regions from the onset of currently accessible electronic records in 1990 to 12/31/1999, 1/1/2000 to 12/31/2009, and 1/1/2010 thru the date of the last unit sold in 2017. Slices are shown for individual countries only when they purchased at least 3 % of the units sold during that interval. The area of the circle is proportional to the number of units sold during the interval.

2. Material

2.1. Acquisition

After evaluating the Certificate of Analysis (COA) provided by GFS Chemicals, Inc. (GFS, Powell, Ohio, USA) for their Item 337 Calcium Carbonate, Chelometric Standard (ACS), Lot# C687441, 50 kg of this material was purchased as the source material for SRM 915c Calcium Carbonate.

2.2. Packaging

The bulk material was packaged by the National Institute of Standards and Technology (NIST) into 2456 glass bottles over seven days, with 350 packaged on each day except for 356 on the last day. Each bottle contains 20 g of the SRM 915c material.

For the analysis only, the bottles were identified by their packing order.

3. Impurities

Table 1 lists the impurity values reported to NIST by the manufacturer, GFS Chemicals, Inc. (GFS). The results for Ba, Mg, P (reported as PO_4^{3-}), K, Na, and Sr were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES). The ammonium ion limit is for the Nessler reagent method; the chloride limit is for a colorimetric method.

Table 1. Manufacturer's Values.

Impurity		µg/g
Ammonium	NH_4^+	< 30
Barium	Ba	1
Chloride	Cl^-	< 10
Fluoride	F^-	< 15
Iron	Fe	< 20
Magnesium	Mg	20
Phosphate	PO_4^{3-}	15
Potassium	K	10
Sodium	Na	16
Strontium	Sr	125
Sulfate	SO_4^{2+}	0.03

A 15 g composite sample was prepared using ≈ 0.7 g of material taken from each of 20 bottles of SRM 915c that had been set aside for possible analysis. This sample and a bottle of SRM 915b [1] for use as a control were sent to Northern Analytical Laboratory, Inc. (NAL, Londonderry, NH, USA) for semi-quantitative analysis by inductively coupled plasma mass spectrometry (ICP-MS). Table 2 lists the element impurity results reported by NAL.

Table 2. Results from ICP-MS Semi-Quantitative Analysis.

Element		µg/g
Aluminum	Al	0.70
Antimony	Sb	< 0.1
Arsenic	As	0.21
Barium	Ba	1.5
Beryllium	Be	< 0.1
Bismuth	Bi	< 0.1
Boron	B	≤ 0.5
Cadmium	Cd	≤ 0.2
Cerium	Ce	< 0.05
Cesium	Cs	< 0.1
Chromium	Cr	1.3
Cobalt	Co	0.42
Copper	Cu	≤ 0.1
Dysprosium	Dy	< 0.05
Erbium	Er	< 0.05
Europium	Eu	< 0.05
Gadolinium	Gd	< 0.05
Gallium	Ga	< 0.1
Germanium	Ge	< 0.5
Gold	Au	< 0.5
Hafnium	Hf	< 0.1
Holmium	Ho	< 0.05
Iridium	Ir	< 0.1
Iron	Fe	≤ 1
Lanthanum	La	< 0.05
Lead	Pb	0.35
Lithium	Li	≤ 0.1
Lutetium	Lu	< 0.05
Magnesium	Mg	20
Manganese	Mn	0.4
Mercury	Hg	< 0.5
Molybdenum	Mo	0.25
Neodymium	Nd	< 0.05
Nickel	Ni	0.32
Niobium	Nb	≤ 0.1
Osmium	Os	< 0.1
Palladium	Pd	< 0.1
Phosphorus	P	≤ 50
Platinum	Pt	< 0.1
Praseodymium	Pr	< 0.05
Rhenium	Re	< 0.1
Rhodium	Rh	< 0.1
Rubidium	Rb	0.26
Ruthenium	Ru	≤ 0.1
Samarium	Sm	< 0.05
Scandium	Sc	≤ 0.5
Selenium	Se	≤ 1
Silicon	Si	≤ 50
Silver	Ag	< 0.1
Sodium	Na	9.2
Strontium	Sr	100
Tantalum	Ta	< 0.1
Tellurium	Te	< 0.5
Terbium	Tb	< 0.05
Thallium	Tl	< 0.1
Thorium	Th	< 0.1
Thulium	Tm	< 0.05
Tin	Sn	< 0.1
Titanium	Ti	0.37
Tungsten	W	< 0.5
Vanadium	V	< 0.1
Ytterbium	Yb	< 0.05
Yttrium	Y	≤ 0.5
Zinc	Zn	0.35
Zirconium	Zr	0.49

Results reported as less-than values are assigned as having a value of one-half of the reported value with a uniformly distributed uncertainty of one-half of the reported value. The contribution from any impurity determined to be < 1 µg/g was ignored since values at this low level would insignificantly contribute to impurity bias. Table 3 lists the values for the impurities determined to be at a mass fraction ≥ 1 µg/g. These values were used to make very small corrections to the gravimetric and coulometric assays. The uncertainties of the impurities are relatively large; however, because the impurity corrections are very small, their uncertainty had a very minor influence on the uncertainty of the assay.

Table 3. Values Assigned for Significant Impurities (≥ 1 µg/g).

		Value, µg/g			Uncertainty		
Impurity	As[a]	Source	Reported	Used[b]	%[c]	Factor[d]	µg/g[e]
Ba	$BaCO_3$	GFS	1	1	50	$1/\sqrt{6}$	0.2
Cl	$CaCl_2$	GFS	< 10	5	100	$1/\sqrt{3}$	2.9
Cr	$Cr_2(CO_3)_3$	NAL	1.3	1.3	100	$1/\sqrt{6}$	0.5
F	CaF_2	GFS	< 15	7.5	100	$1/\sqrt{3}$	4.3
K	K_2CO_3	GFS	10	10	10	$1/\sqrt{6}$	0.4
Mg	$MgCO_3$	GFS	20	20	10	$1/\sqrt{6}$	0.8
Na	Na_2CO_3	GFS	16	16	10	$1/\sqrt{6}$	0.7
NH_4	$(NH_4)_2CO_3$	GFS	< 30	15	100	$1/\sqrt{3}$	8.7
PO_4	$CaHPO_4$	GFS	15	15	10	$1/\sqrt{6}$	0.6
HPO_4[f]	$CaHPO_4$	GFS	-	15	10	$1/\sqrt{6}$	0.6
P[g]	$CaHPO_4$	GFS	-	5	10	$1/\sqrt{6}$	0.2
Si	SiO_2	NAL	≤ 50	25	100	$1/\sqrt{3}$	14
Sr	$SrCO_3$	GFS	125	125	10	$1/\sqrt{6}$	5.1

a) Compound that the impurity is assumed to be present as in the $CaCO_3$.
b) Impurity value, *x*, used in subsequent calculations as estimated from reported values and detection limits.
c) Relative uncertainty estimated from instrument capability assessments.
d) Normalization factor. Results reported as values are assumed to be triangularly distributed (centered within their uncertainty) with a normalization factor of $1/\sqrt{6}$; values reported as a detection limit are uniformly distributed with a normalization factor of $1/\sqrt{3}$.
e) Standard uncertainty, $u(x)$, estimated the product of *x*, the relative uncertainty divided by 100, and the normalization factor.
f) Calculated from reported PO_4 assuming HPO_4 is the only form of phosphorus present as an impurity.
g) Calculated from reported PO_4 assuming P is the only form of phosphorus present as an impurity.

No uncertainties were provided by either GFS or NAL. The percent relative uncertainty uncertainties (%) given in Table 3 for the non-less-than values are based on method-capability assessments made by NIST and GFS staff. The ICP-MS values reported by NAL are assumed to have a relative uncertainty of 100 % since semi-quantitative ICP-MS values typically have a 50 % relative uncertainty coupled with a desire to apply a conservative estimate based on the lack of knowledge about NAL's specific analytical process. The ICP-OES values reported by GFS are assumed to have relative uncertainties of 10 %. While elements determined by ICP-OES generally have uncertainties lower than 2 %, a 5 % relative uncertainty is considered reasonable given the $CaCO_3$ matrix. The 10 % value is a conservative estimate based on the lack of knowledge about GFS's specific analytical process and the low resolution of the reported values. The 1 µg/g Ba mass fraction is assigned a relative uncertainty of 50 % since it was reported as a single digit rather than 1.0. All uncertainties for the non-less-than values are modelled as following triangular distributions.

The standard uncertainties (µg/g) assigned to the impurity values are estimated as the product of the assessed value ("Used"), the estimated relative uncertainties divided by 100, and the normalization factor for the assumed distribution (uniform or triangular) describing the uncertainty.

Values were reported by both GFS and NAL for Fe and PO_4. For Fe, both values are reported as less than values. Since the NAL value (< 1 µg/g) is lower than the GFS value (≤ 20 µg/g), the GFS value was ignored and the impurity contribution from Fe considered insignificant. The value reported by NAL for PO_4 was considered as a confirmatory value since it is a less than value (≤ 50 µg/g); only the GFS value (15 µg/g) was used. Values for HPO_4 and P were calculated based on gravimetric factors calculated from atomic weights [2] to provide values useful to correct assays for impurities.

Both GFS and NAL reported values for Ba, Mg, Na, and Sr. The NAL determined values have significantly higher uncertainties than do those from GFS values and so are considered confirmatory. Only the GFS values for these four elements were used in the calculations. The only NAL values used for corrections are for Cr and Si.

For ammonium, the NH_4 impurity was assumed based on the cation that would form with carbonate. For phosphate, the HPO_4 impurity was assumed based on the anion that would form with calcium.

4. Gravimetric Determinations

Gravimetric determinations of the mass fraction of calcium (w_{Ca}), carbonate (w_{CO3}), and calcium carbonate (w_{CaCO3}) were made for nine bottles of SRM 915c and two bottles of SRM 915b using the current Standard Operating Procedure (SOP) for Gravimetry. Only w_{Ca} was determined directly by gravimetry, w_{CO3} and w_{CaCO3} were determined indirectly.

4.1. Measurement Procedure

Calcium was determined in test portions of SRM 915c and control SRM 915b. Each test portion was dissolved in dilute hydrochloric acid, HCl, and a solution aliquot was transferred to a platinum, Pt, crucible. The solution, along with additions of H_2SO_4, was evaporated on a hotplate to dryness and heated at 875 ºC to constant mass as impure $CaSO_4$. Impurities in the calcium carbonate are listed in Table 3. These impurities, calculated as sulfate salts, are subtracted from the gravimetrically determined impure $CaSO_4$ to calculate the mass of pure $CaSO_4$. Four calculations are performed.

First, the mass fraction of Ca, w_{Ca}, is calculated by multiplying the $CaSO_4$ mass, corrected for impurities (calculated based on Ba, Cr, K, Mg, Na, and Sr assumed present as sulfates), by a gravimetric factor and dividing by the equivalent test portion mass based on the mass of $CaCO_3$ dissolved in the original solution and the mass of the solution aliquot taken. Possible transfer and evaporative losses are accounted for by the method used to calculate sample aliquot mass.

Second, an intermediate calculation is made for the stoichiometrically calculated CO_3 mass fraction, $w_{\mathrm{CO3\text{-}Stoich}}$ (the mass fraction of CO_3 needed to combine with Ca to form $CaCO_3$), by multiplying the mass fraction of Ca by the ratio of the relative molecular mass (RMM) of CO_3 to the relative atomic mass (RAM) of Ca.

Third, the mass fraction of $CaCO_3$, w_{CaCO3}, is calculated by adding w_{Ca} and $w_{\mathrm{CO3\text{-}Stoich}}$ and subtracting the mass fractions of $CaCl_2$, CaF_2, and $CaHPO_4$ (calculated based on the trace Cl, F, and P impurities, respectively) taken as $CaCO_3$.

Fourth, the mass fraction of carbonate determined indirectly from the gravimetry, $w_{\mathrm{CO3(grav)}}$, is calculated by adding $w_{\mathrm{CO3\text{-}Stoich}}$ and the sum of stoichiometric CO_3 in the assumed carbonate compound impurities (calculated based on the trace Ba, Cr, K, Mg, Na, NH_4, and Sr), and subtracting the sum of stoichiometric Ca^{2+} in the assumed calcium compound impurities (calculated based on the trace Cl, F, and P).

Six separate runs were performed, although the results from some runs are excluded from the final calculations.

4.1.1. Reagents

All acids used were high-purity unless otherwise noted. Redistilled HCl was obtained from GFS Chemicals, Item 504, Lot # L029051. Sulfuric acid, H_2SO_4, double-distilled from Vycor® was obtained from GFS Chemicals, Item 273, Lot # X100. All water used was collected from an 18 MΩ·cm water source.

4.1.2. Samples, Controls, and Blanks

Nine bottles of SRM 915c (2, 257, 672, 834, 1097, 1702, 1800, 2225, and 2455) and two bottles of the SRM 915b control were analyzed. The analysis was performed in a series of runs with each run consisting of test portions from four different bottles of SRM 915c, one bottle of SRM 915b, and one blank. All blanks were carried through the procedure as if they were actual test portions. The bottles of SRM 915c for each run were chosen based on a random order that allowed for duplicates from seven of the SRM 915c bottles over four successful runs plus two single analyses of bottles 257 and 2225 for a total of 16 determinations of SRM 915c.

4.1.3. Initial Test Portion Mass and Mass Loss on Drying

A nominal 1 g test portion of SRM 915b or SRM 915c was transferred to a glass weighing bottle (WB) and covered with its corresponding glass cover. After a preliminary "as is" mass was obtained, bottles containing test portions and blanks were then heated to dryness at 205 °C for 4 h. The heated test portions were transferred to desiccators containing anhydrous magnesium perchlorate and their mass was measured after they equilibrated to ambient room temperature. The heating and mass measurement steps were repeated to establish constant mass (mean mass loss $\leq 30\ \mu g$) and allow for calculation of a mean mass loss.

4.1.4. Test Portion Taken for Dissolution

Nominal 0.7 g dried test portions were transferred from a WB to a Pt weighing boat and the combined mass of the Pt boat and test portion was measured. The test portion was delivered into a 60 mL low density polyethylene (LDPE) wide-mouth (WM) screw-cap bottle. The bottle was sealed with the screw cap and the Pt boat mass was re-measured. The mass measurement procedure was performed in a similar manner for the Pt boat with the test portion and the Pt boat after the test portion was delivered, the empty bottle and the bottle after the test portion was received, and the blanks.

All masses are corrected for the average blank and for buoyancy. The mass of $CaCO_3$ is calculated as the mean of the average mass of $CaCO_3$ delivered from the Pt boat and the average mass of $CaCO_3$ received by the LDPE bottle.

4.1.5. Dissolution of Test Portions

Dilute HCl was prepared from redistilled HCl and water to nominal amount concentrations of (0.01, 0.2, 0.5, 0.75, 1) mol/L. Progressively higher amount concentrations of dilute HCl were used to dissolve the $CaCO_3$ in a manner that seemed to avoid any mechanical loss. Initially, ≈ 5 g of 0.01 mol/L HCl was added drop-wise down the inside wall of the tilted LDPE bottle containing the test portion in a manner that transferred all of the residual $CaCO_3$ powder on the inside wall to the bottom of the bottle without any loss of $CaCO_3$ powder. The dissolution was continued with the addition of dilute HCl down the inside walls of the LDPE bottle using a LDPE squirt bottle.

These additions resulted in the evolution of small bubbles of CO_2. The addition of dilute HCl was followed by immediate capping with the screw cap, which was lightly tightened to allow dissipation of evolved gas. At least 1 h later, the bottle was uncapped and the solution was observed to determine if CO_2 was still being produced. If bubbles were being produced, the bottle was recapped as before and checked again at least 30 min later. Once gas evolution decreased to a barely significant rate, so that only tiny bubbles were being produced slowly, additional dilute HCl was added. A similar procedure of observing the production of CO_2 and adding dilute acid, once the reaction rate seemed barely significant, was continued until the total amount of HCl added was slightly in excess of the calculated amount needed to dissolve all of the $CaCO_3$.

The resulting final solution mass was approximately 30 g. This dissolution proceeded slowly over at least three days to avoid mechanical loss from aerosols created by the bubbles of CO_2. Once dissolution was deemed complete, the solution was gently swirled and allowed to settle. Then a laser light was shined through the solution to check for particles that would reflect the laser light. In all cases, no particles were detected. The bottle was capped and shaken and retested with the laser light; again, no particles were detected. The cap was tapped to promote dislodging droplets back into the solution.

4.1.6. Transfer of Solution Aliquots

A nominal 10 g aliquot from each solution was transferred from its 60 mL bottle to a nominal 25 mL Pt crucible of known mass that had been pre-treated with dilute H_2SO_4 and ignited to 900 °C. The mass of the bottle with the solution and its mass after the aliquot had been delivered to the Pt crucible were measured.

The mass of the solution aliquot is calculated by combining the mass delivered from the bottle and the mass received by the crucible using a weighting factor that favored the mass delivered from the bottle.

4.1.7. Evaporation with Sulfuric Acid

Each solution in the Pt crucibles was evaporated down on a hotplate to ≈ 0.5 mL volume and then was allowed to cool to ambient temperature. The inside walls of each crucible were rinsed down dropwise with ≈ 1.5 g of ≈ 0.2 mol/L HCl (to move all Ca to the base of the crucible), evaporated on a hotplate to ≈ 0.5 mL, and allowed to cool. Each crucible was then rinsed down dropwise with ≈ 2 g of ≈ 0.5 mmol/g H_2SO_4. Soon after these solutions were heated on a hotplate, a white precipitate formed and evaporation continued carefully to remove excess solution to obtain a moist precipitate, after which samples were allowed to cool. Precipitates were not allowed to go to dryness at this point because doing so could result in mechanical loss of Ca as a chloride. The rinsing and evaporation to obtain a moist precipitate were repeated with ≈ 2 g of ≈ 2 mmol/g H_2SO_4. Rinsing was repeated with 0.5 g to 1 g of ≈ 2 mmol/g H_2SO_4 so that an excess of ≈ 2.7 times the amount needed to form $CaSO_4$ was added. This large excess is added because the evaporation results in the formation of calcium bisulfate, $Ca(HSO_4)_2$. The evaporation was continued with more rapid heating to a temperature at which fumes of sulfur trioxide formed. Once the fumes had mostly dissipated, heating was continued gradually to the maximum setting displayed on the hotplate (550). After the solutions in the Pt crucibles had evaporated to dryness, they were allowed to cool for ≈ 5 min and covered. The evaporation was done carefully to avoid mechanical losses.

4.1.8. Ignition of the Calcium Sulfate Precipitate to Constant Mass

Within 15 minutes after the cooled crucibles had been covered, they were placed in a muffle furnace set at ≈ 200 ºC and heated very gradually over at least 12 h to 850 ºC. The crucibles were heated at 850 ºC for 10 h, transferred to desiccators containing anhydrous magnesium perchlorate, and allowed to equilibrate to ambient room temperature next to the balance used for mass determination for at least 3 h. After the mass of the precipitates were measured, the crucibles were heated more rapidly to 850 ºC for 5 h, then transferred to desiccators and masses were measured in the same previous manner. The heating and mass measurement were repeated three times at 875 ºC and then twice at 900 ºC. The three sets of temperature programs used to ignite the $CaSO_4$ precipitate are listed in Table 4.

Table 4. Temperature Programs Used to Ignite the $CaSO_4$ Precipitate.

	Initial heating					Repeat heating				
Step	Temp, °C	Ramp, °C/min	Hold, h	Req [a], h	Cum [b], h	Temp, °C	Ramp, °C/min	Hold, h	Req [a], h	Cum [b], h
Start	200					80				
1	300	1	0	1.7	1.7	130	0.5	0	1.7	1.7
2	650	0.5	0	10.6	12.3	600	10	0	0.8	2.5
3	845	1	0	4.2	16.5	845	3	0	1.4	3.9
4	850	0.5	0	0.2	16.7	850	1	0	0.1	4.0
5	850	0	12	12	28.7	850	0	5	5	9.0
6	300	10	0	2	30.7	300	10	0	2	11.0
Finish	300	0	∞			300	0	∞		
Start	80					80				
1	130	0.5	0	1.7	1.7	130	0.5	0	1.7	1.7
2	600	10	0	0.8	2.5	600	10	0	0.8	2.5
3	850	3	0	1.4	3.9	865	3	0	1.5	4.0
4	875	1	0	0.4	4.3	875	1	0	0.2	4.2
5	875	0	5	5	9.3	875	0	5	5	9.2
6	300	10	0	2	11.3	300	10	0	2	11.2
Finish	300	0	∞			300	0	∞		
Start	80					80				
1	130	0.5	0	1.7	1.7	130	0.5	0	1.7	1.7
2	600	10	0	0.8	2.5	600	10	0	0.8	2.5
3	865	3	0	1.5	4.0	885	3	0	1.6	4.1
4	900	1	0	0.6	4.6	900	1	0	0.3	4.4
5	900	0	5	5	9.6	900	0	5	5	9.4
6	300	10	0	2	11.6	300	10	0	2	11.4
Finish	300	0	∞			300	0	∞		

a) Time required at each step.
b) Cumulative time required to accomplish the complete program.

4.2. Gravimetric Measurement Functions

The total mass of the pure $CaSO_4$ precipitate, $m_{\text{Total CaSO4}}$, is calculated by subtracting the sum of calculated sulfate impurities, $m_{\text{Cont CaSO4}}$, from the mass of the gravimetrically determined $CaSO_4$, $m_{\text{Grav CaSO4}}$:

$$m_{\text{Total CaSO4}} = m_{\text{Grav CaSO4}} - \Sigma m_{\text{Cont CaSO4}}. \tag{1}$$

The total mass of impurities in the $CaSO_4$ precipitate is calculated from the sum of the amount content of the Ba, Cr, K, Mg, Na, and Sr impurities in the $CaCO_3$ divided by a gravimetric factor which is equal to the ratio of z times the RAM of the impurity to the RMM of the assumed impurity compound in the $CaSO_4$ precipitate. Gravimetric factors are based on 2017 values for the RAMs [2]. The factor z is calculated as the ratio of the number of atoms of the impurity (e.g., Cr) to the number of atoms of the counter ion (e.g., SO_4^{2-}), where $z = 2$ for K and Na, 2/3 for Cr, and 1 for the other elements. For example, $m_{\text{Cont Cr2(SO4)3}}$, the calculated mass of the Cr impurity, as $Cr_2(SO_4)_3$ is

$$m_{\text{Cont Cr2(SO4)3}} = m_{\text{CaCO3}}(w_{\text{Cr}})/(2A_{\text{Cr}}/3M_{\text{Cr2(SO4)3}}) \tag{2}$$

where w_{Cr} is the mass fraction of Cr impurity in the $CaCO_3$, m_{CaCO3} is the calculated mass of the $CaCO_3$, A_{Cr} is the RAM of Cr, and $M_{\text{Cr2(SO4)3}}$ is the RMM of $Cr_2(SO_4)_3$.

The mass of Ca in the precipitate, m_{Ca}, is calculated from $m_{\text{Total CaSO4}}$ and a gravimetric factor:

$$m_{\text{Ca}} = (m_{\text{Total CaSO4}})A_{\text{Ca}}/M_{\text{CaSO4}} \tag{3}$$

where A_{Ca} is the RAM of Ca and M_{CaSO4} is the RMM of $CaSO_4$.

The initial mass of the $CaCO_3$ test portion, m_{testp}, is calculated from the average of the mass of the test portion delivered from the Pt boat and the mass received by the LDPE bottle. The mass of the aliquot of $CaCO_3$ dissolved solution, m_{aliq}, is calculated as the weighted sum of the mass of aliquot delivered from the LDPE bottle (70 %) and the mass of the aliquot received by the Pt crucible (30 %): see Section 4.3.3.6. The calculation of m_{CaCO3} is based on m_{testp}, m_{aliq}, and the final mass of solution in which it was dissolved, m_{soln}:

$$m_{\text{CaCO3}} = m_{\text{testp}}(m_{\text{aliq}}/m_{\text{soln}}). \tag{4}$$

The mass fraction of Ca, w_{Ca}, is calculated:

$$w_{\text{Ca}} = m_{\text{Ca}}/m_{\text{CaCO3}}. \tag{5}$$

Combining the previous five equations, w_{Ca} is then:

$$w_{\text{Ca}} = (m_{\text{Grav CaSO4}} - \Sigma m_{\text{Cont CaSO4}})(A_{\text{Ca}}/M_{\text{CaSO4}})/(m_{\text{testp}}(m_{\text{aliq}}/m_{\text{soln}})) \tag{6}$$

where the $\Sigma m_{\text{Cont CaSO4}}$ is calculated for the impurities Ba, Cr, K, Mg, Na, and Sr in the manner described above for Eq. 2.

An intermediate value, $w_{\text{CO3-Stoich}}$, is based on the stoichiometric relationship of Ca to CO_3 in $CaCO_3$ calculated from w_{Ca} using the ratio M_{CO3}, the RMM of CO_3, to A_{Ca}:

$$w_{\mathrm{CO3\text{-}Stoich}} = w_{\mathrm{Ca}}(A_{\mathrm{C}} + 3A_{\mathrm{O}})/A_{\mathrm{Ca}} \tag{7}$$

where M_{CO3} is expressed in terms of the RAMs of C (A_{C}) and O (A_{O}) for ease of uncertainty calculation.

The sum of the mass fraction of Ca salt trace impurities taken as carbonates, $\Sigma w'_{\mathrm{imp\ CaCO3}}$, is calculated:

$$\Sigma w'_{\mathrm{imp\ CaCO3}} = w'_{\mathrm{CaCl2}} + w'_{\mathrm{CaF2}} + w'_{\mathrm{CaHPO4}} \tag{8}$$

where the symbol w' is used to denote the mass fraction taken as $CaCO_3$. The only significant trace anionic impurities detected in the impure $CaCO_3$ material used to produce SRM 915c are Cl, F, and P, which are assumed to be present as $CaCl_2$, CaF_2, and $CaHPO_4$, respectively.

The mass fraction of $CaCO_3$, w_{CaCO3}, is calculated as the sum of w_{Ca}, and $w_{\mathrm{CO3\text{-}Stoich}}$, the stoichiometrically calculated CO_3 mass fraction (the mass fraction of CO_3 needed to stoichiometrically combine with Ca to form $CaCO_3$), minus the sum of the mass fraction of Ca salt trace impurities taken as carbonates, $\Sigma w'_{\mathrm{imp\ CaCO3}}$. w_{CaCO3} is calculated:

$$w_{\mathrm{CaCO3}} = w_{\mathrm{Ca}} + w_{\mathrm{CO3\text{-}Stoich}} - \Sigma w'_{\mathrm{imp\ CaCO3}}. \tag{9}$$

The calculations for the impurity mass fractions are all done in the same manner. The w'_{CaCl2} is calculated as the product of the $CaCl_2$ impurity mass fraction, w_{CaCl2}, and the ratio of the $CaCO_3$ RMM, M_{CaCO3}, to the $CaCl_2$ RMM, M_{CaCl2}. The equation can be simplified since the RAMs for Ca and O cancel out. The factor z is calculated in the same manner as for the sulfate impurities as the ratio of the number of atoms of the impurity (e.g., Cl) to the number of atoms of the counter ion (e.g., CO_3^{2-}), where $z = 2$ for Cl and F and $z = 1$ for P. The correction for the Cl impurity is expressed in terms of RAMs for ease of uncertainty as:

$$\begin{aligned} w'_{\mathrm{CaCl2}} &= w'_{\mathrm{CaCl2}}(M_{\mathrm{CaCO3}}/M_{\mathrm{CaCl2}}) \\ &= w_{\mathrm{Cl}}(M_{\mathrm{CaCO3}}/2A_{\mathrm{Cl}}) \\ &= w_{\mathrm{Cl}}(A_{\mathrm{Ca}} + A_{\mathrm{C}} + 3A_{\mathrm{O}})/2\mathrm{A}_{\mathrm{Cl}}. \end{aligned} \tag{10}$$

The stoichiometrically calculated CO_3 mass fraction, $w_{\mathrm{CO3\text{-}Stoich}}$, calculated in Eq. 7, is used as part of the calculation of w_{CaCO3} (Eq. 8). The actual mass fraction of CO_3 in the $CaCO_3$ also includes CO_3 associated with the carbonate impurities. The indirect gravimetrically determined CO_3 mass fraction is symbolized here as w_{CO3}(grav), with “(grav)” denoting that the value is obtained indirectly from the gravimetrically determined w_{Ca}.

The w_{CO3}(grav) is calculated from the stoichiometric amount of CO_3^{2-} expected from the w_{Ca} plus the sum of stoichiometric CO_3^{2-} in the assumed carbonate impurities {$BaCO_3$, $Cr_2(CO_3)_3$, K_2CO_3, $MgCO_3$, Na_2CO_3, $(NH_4)_2CO_3$, and $SrCO_3$} minus the sum of stoichiometric Ca^{2+} in the assumed calcium impurities {$CaCl_2$, CaF_2, and $CaHPO_4$} all taken as carbonates and based on the determinations of trace impurities. The carbonate and calcium impurities are added and subtracted based on gravimetric factors for the RAMs of the elemental impurities, rather than the RMMs of the compounds, because the RMMs cancel out in the calculation. The value of w_{CO3}(grav) is thus:

$$\begin{aligned} w_{\mathrm{CO3}}(\mathrm{grav}) = \;& w_{\mathrm{Ca}}(M_{\mathrm{CO3}}/A_{\mathrm{Ca}}) + (M_{\mathrm{CO3}})[(w_{\mathrm{Ba}}/A_{\mathrm{Ba}}) + (w_{\mathrm{Cr}}(3/2)/A_{\mathrm{Cr}}) + (w_{\mathrm{K}}(1/2)/A_{\mathrm{K}}) \\ & + (w_{\mathrm{Mg}}/A_{\mathrm{Mg}}) + (w_{\mathrm{NH4}}(1/2)/M_{\mathrm{NH4}}) + (w_{\mathrm{Na}}(1/2)/A_{\mathrm{Na}}) + (w_{\mathrm{Sr}}/A_{\mathrm{Sr}})] \\ & - (M_{\mathrm{CO3}})[(w_{\mathrm{Cl}}(1/2)/A_{\mathrm{Cl}}) + w_{\mathrm{F}}(1/2)/A_{\mathrm{F}}) + (w_{\mathrm{P}}/A_{\mathrm{P}})]. \end{aligned} \tag{11}$$

4.3. Measurements

Data for mass changes on drying are reported in Table 5. The data and values used to calculate the effective mass of the $CaCO_3$ test portion, m_{CaCO3}, for each run are reported in Table 6. The data and values used to calculate the mass fraction of Ca for each run, w_{Ca}, are reported in Table 7.

Table 5. Mass Change on Drying.[a,b]

Run	Bottle ID	As-received, mg	Mean dry mass, mg	Mass gain/loss, mg	Mass gain/loss, % relative
1	2	1005.81	1005.78	-0.03	-0.003
1	672	1118.96	1119.00	0.04	0.004
1	2455	1036.78	1036.81	0.03	0.003
1	1097	1054.82	1054.82	0.00	0.000
2	834	1028.30	1028.06	-0.24	-0.023
2	1097	1026.70	1026.47	-0.23	-0.022
2	672	1022.73	1022.63	-0.10	-0.010
2	1702	1038.57	1038.47	-0.10	-0.010
3	1702	1008.04	1007.86	-0.18	-0.018
3	2225	1016.24	1015.98	-0.26	-0.026
3	2	1010.06	1009.63	*-0.43*	*-0.043*
3	1800	1028.92	1027.41	*-1.51*	*-0.147*
4	834	1169.06	1168.50	*-0.56*	*-0.048*
4	257	1038.60	1038.53	-0.07	-0.007
4	2455	1023.53	1023.39	-0.14	-0.014
4	1800	1030.84	1030.78	-0.06	-0.006
5	2	1118.11	1117.89	-0.22	-0.020
5	672	1034.83	1034.78	-0.06	-0.006
5	1097	1026.40	1025.78	-0.62	-0.060
5	2455	1057.72	1057.44	-0.28	-0.026
6	834	1050.64	1049.75	*-0.89*	*-0.085*
6	257	1046.69	1045.90	*-0.79*	*-0.076*
6	2455	1063.12	1062.55	*-0.57*	*-0.054*
6	1800	1149.50	1149.20	-0.30	-0.026
1	915b	1024.08	1024.11	0.03	0.003
2	915b	1072.87	1072.65	-0.22	-0.021
3	915b	1015.88	1015.55	-0.33	-0.032
4	915b	983.52	983.26	-0.26	-0.026
5	915b	1021.58	1021.48	-0.10	-0.010
6	915b	1108.34	1108.15	-0.19	-0.017

[a] Buoyancy correction not applied.

[b] Negative values indicate mass loss, positive values indicate mass gain. Relatively large mass losses, which suggest possible mechanical loss, are shown in italic font.

Table 6. Calculated CaCO$_3$ Test Portion, m_{CaCO3}, in Pt Crucible.[a,b]

Run	Bottle ID	WB	Pt crucible	CaCO$_3$ delivered, g	CaCO$_3$ received, g	Average CaCO$_3$, g	Total solution mass, g	From WM solution delivered, g	To Pt solution received, g	Difference, % relative	Solution calculated, g[c]	CaCO$_3$ in Pt calculated, g
1	2	52	V2	0.657 54	0.657 45	0.657 49	30.055 11	10.323 60	10.320 64	0.029	10.322 71	0.225 823
1	672	53	V3	0.663 33	0.663 27	0.663 30	30.119 09	9.444 91	9.443 39	0.016	9.444 45	0.207 991
1	2455	54	V5	0.665 74	0.665 71	0.665 72	30.081 54	9.095 89	9.093 91	0.022	9.095 29	0.201 284
1	1097	55	V7	0.661 12	0.661 01	0.661 06	30.054 08	9.268 29	9.265 56	0.029	9.267 47	0.203 856
2	834	12	V8	0.654 43	0.654 38	0.654 40	29.317 46	10.434 28	10.431 68	0.025	10.433 50	0.232 888
2	1097	13	V9	0.656 86	0.656 67	0.656 76	29.230 27	9.500 74	9.498 22	0.027	9.499 98	0.213 452
2	672	14	V11	0.657 46	0.657 43	0.657 44	29.279 92	10.039 74	10.037 60	0.021	10.039 10	0.225 415
2	1702	15	V12	0.660 37	0.660 27	0.660 32	29.301 71	9.685 33	9.683 07	0.023	9.684 65	0.218 246
3	1702	42	V2	0.705 86	0.705 76	0.705 81	30.345 51	9.128 70	9.118 00	0.117	9.125 49	0.212 250
3	2225	43	V3	0.680 11	0.680 01	0.680 06	30.195 12	11.484 86	11.472 72	0.106	11.481 21	0.258 581
3	2	44	V5	0.680 16	0.680 02	0.680 09	29.824 79	8.972 26	8.960 86	0.127	8.968 84	0.204 515
3	1800	45	V6	0.675 94	0.675 94	0.675 94	29.825 00	9.886 45	9.873 59	0.130	9.882 59	0.223 974
4	834	8	V8	0.695 51	0.695 37	0.695 44	30.833 13	11.622 59	11.616 61	0.051	11.620 79	0.262 108
4	257	3	V9	0.700 77	0.700 61	0.700 69	31.000 82	10.400 77	10.394 34	0.062	10.398 84	0.235 038
4	2455	7	V11	0.697 01	0.696 89	0.696 95	30.953 62	11.220 52	11.213 22	0.065	11.218 33	0.252 591
4	1800	6	V12	0.694 41	0.694 28	0.694 34	30.868 45	11.049 59	11.043 74	0.053	11.047 84	0.248 506
5	2	33	V2	0.690 49	0.690 38	0.690 43	30.651 18	10.393 89	10.391 43	0.024	10.393 15	0.234 111
5	672	34	V3	0.701 66	0.701 57	0.701 62	30.886 65	10.972 58	10.970 70	0.017	10.972 01	0.249 239
5	1097	35	V5	0.704 06	0.704 03	0.704 05	30.902 48	10.001 69	10.000 46	0.012	10.001 32	0.227 858
5	2455	36	V6	0.705 35	0.705 31	0.705 33	30.934 70	13.108 59	13.107 23	0.010	13.108 18	0.298 874
6	834	2	V8	0.712 37	0.712 32	0.712 35	33.182 56	11.660 20	11.649 94	0.088	11.657 12	0.250 249
6	257	3	V9	0.709 18	0.709 07	0.709 12	33.007 81	13.475 67	13.465 88	0.073	13.472 73	0.289 442
6	2455	21	V11	0.707 91	0.707 75	0.707 83	33.021 17	13.796 24	13.784 91	0.082	13.792 84	0.295 660
6	1800	39	V12	0.700 42	0.700 24	0.700 33	32.899 42	11.061 54	11.052 45	0.082	11.058 81	0.235 407
1	915b	51	V1	0.657 49	0.657 43	0.657 46	30.037 32	9.937 67	9.935 83	0.019	9.937 12	0.217 505
2	915b	9	V6	0.655 98	0.655 97	0.655 97	29.199 90	8.911 29	8.909 64	0.018	8.910 79	0.200 180
3	915b	54	V1	0.683 60	0.683 53	0.683 57	29.928 21	11.502 56	11.494 10	0.074	11.500 02	0.262 662
4	915b	2	V7	0.704 69	0.704 65	0.704 67	30.911 46	10.612 35	10.608 28	0.038	10.611 13	0.241 896
5	915b	53	V1	0.691 66	0.691 64	0.691 65	30.733 57	8.254 76	8.253 12	0.020	8.254 27	0.185 761
6	915b	11	V7	0.700 84	0.700 74	0.700 79	32.695 58	10.654 86	10.646 24	0.081	10.652 27	0.228 319

a All values corrected for blank and buoyancy
b Values highlighted in gray were not used in the final calculations
c Solution mass calculated by weighting 70 % delivered mass and 30 % received mass

Table 7. Calcium Mass Fractions, w_{Ca}, for Each Test Portion.[a,b]

Run	Bottle ID	WB	Pt Crucible	Calculated mass $CaCO_3$, g[c]	Ignited $CaSO_4$ mass, g	Calculated sulfate impurities, µg[d]	Total $CaSO_4$ mass, g	Total Ca mass, g	Mass Fraction Ca, g/g
1	2	52	V2	0.225 823	0.307 081	101.4	0.306 980	0.090 371	0.400 186 9
1	672	53	V3	0.207 991	0.282 878	93.4	0.282 784	0.083 248	0.400 249 4
1	2455	54	V5	0.201 284	0.273 775	90.4	0.273 685	0.080 570	0.400 279 0
1	1097	55	V7	0.203 856	0.277 049	91.6	0.276 957	0.081 533	0.399 953 5
2	834	12	V8	0.232 888	0.316 681	104.6	0.316 576	0.093 196	0.400 176 4
2	1097	13	V9	0.213 452	0.290 275	95.9	0.290 179	0.085 425	0.400 209 6
2	672	14	V11	0.225 415	0.306 523	101.3	0.306 422	0.090 207	0.400 182 6
2	1702	15	V12	0.218 246	0.296 799	98.0	0.296 701	0.087 345	0.400 214 7
3	1702	42	V2	0.212 250	0.288 560	95.3	0.288 464	0.084 921	0.400 096 2
3	2225	43	V3	0.258 581	0.351 596	116.2	0.351 480	0.103 472	0.400 151 3
3	2	44	V5	0.204 515	0.278 011	91.9	0.277 919	0.081 816	0.400 049 6
3	1800	45	V6	0.223 974	0.304 461	100.6	0.304 360	0.089 600	0.400 046 5
4	834	8	V8	0.262 108	0.356 484	117.7	0.356 366	0.104 910	0.400 255 9
4	257	3	V9	0.235 038	0.319 844	105.6	0.319 739	0.094 127	0.400 477 8
4	2455	7	V11	0.252 591	0.343 638	113.5	0.343 525	0.101 130	0.400 369 5
4	1800	6	V12	0.248 506	0.338 056	111.6	0.337 945	0.099 487	0.400 340 0
5	2	33	V2	0.234 111	0.318 397	105.2	0.318 292	0.093 701	0.400 243 9
5	672	34	V3	0.249 239	0.338 977	112.0	0.338 865	0.099 758	0.400 251 4
5	1097	35	V5	0.227 858	0.309 880	102.4	0.309 778	0.091 195	0.400 227 2
5	2455	36	V6	0.298 874	0.406 496	134.3	0.406 362	0.119 628	0.400 263 2
6	834	2	V8	0.250 249	0.340 285	112.4	0.340 172	0.100 143	0.400 172 3
6	257	3	V9	0.289 442	0.393 638	130.0	0.393 508	0.115 844	0.400 233 4
6	2455	21	V11	0.295 660	0.402 084	132.8	0.401 951	0.118 330	0.400 222 7
6	1800	39	V12	0.235 407	0.320 105	105.7	0.319 999	0.094 204	0.400 175 1
1	915b	51	V1	0.217 505	0.295 808	123.6	0.295 685	0.087 044	0.400 193 3
2	915b	9	V6	0.200 180	0.272 098	113.7	0.271 984	0.080 067	0.399 975 1
3	915b	54	V1	0.262 662	0.357 080	149.2	0.356 931	0.105 074	0.400 034 2
4	915b	2	V7	0.241 896	0.328 977	137.4	0.328 840	0.096 804	0.400 188 9
5	915b	53	V1	0.185 761	0.252 593	105.5	0.252 487	0.074 328	0.400 125 2
6	915b	11	V7	0.228 319	0.310 426	129.7	0.310 296	0.091 345	0.400 078 6

a All values corrected for blank and buoyancy.

b Values highlighted in gray were not used in the final calculations.

c From Table 6.

d Calculated by multiplying the $CaSO_4$ mass by the sum of the sulfate impurity factors.

4.3.1. Excluded Results

Values from all of the runs are listed in the above tables; however, some of the values are not included in the final calculations of the values and uncertainties. All values from Run 1, the value for the SRM 915b control in Run 2, and all values from Run 4 are excluded. The excluded values are highlighted in light gray.

4.3.1.1. Run 1

The values from Run 1 are excluded because a slight discoloration of the sulfate precipitate may indicate an unknown contaminant or incomplete conversion to $CaSO_4$. For all subsequent runs, the evaporation of the solution on the hot plate was treated with extra steps intended to prevent entrapment of contaminants in the sulfate precipitate. The discoloration seen for Run 1 was not present in any of the subsequent sulfate precipitates.

4.3.1.2. Run 2

In Run 1, one solution in a Pt crucible spilled (Bottle 1097, crucible V6). An immediate attempt was made to obtain a second aliquot of solution, which was transferred to crucible V7. As shown in Table 7, the results for w_{Ca} in this second aliquot are significantly lower than the other three test portions. As a consequence of using crucible V7, the number of pre-treated crucibles for Run 2 was reduced. Pt crucible V6 was rinsed and pre-treated separately and then its mass was measured with the other crucibles from Run 2. Pt crucible V6 was used to contain the SRM 915b control in Run 2. The results for w_{Ca} in this control are significantly lower than the other results for SRM 915b. It is likely that the separate pre-treatment process resulted in different conditions for the empty pre-treated crucible compared to the other crucibles. Thus, the values for SRM 915b from Run 2 are excluded. The values for SRM 915c from Run 2 are in good agreement with the values from the other runs so they are not excluded from the final calculations. The apparent bias in the mass of Pt V6 in Run 2 supports the importance of conducting the pre-treatment of the Pt crucibles as sets in a precise manner.

4.3.1.3. Run 4

Although, as shown in Table 6 the relative difference between the masses for the solution delivered and received are small for Runs 1 and 2 (nominally 0.025 %), the relative difference is significantly greater for Run 3 (nominally 0.12 %). It is unclear how the manipulations of the solutions were different in Run 3; however, the difference may have been caused by significantly greater evaporation of the solution during the delivery to the Pt crucible or a compromised seal between the cap and the bottle. This 0.12 % difference is of concern because the relative expanded uncertainty for w_{Ca} in SRM 915b is only 0.02 %. In Run 4, an attempt was made to eliminate any evaporation of solution droplets on the bottle cap by replacing the bottle cap with a clean and dry cap (after the solution had been measured with the original cap) and re-measuring the solution and bottle mass with the new cap. Although the relative difference between delivered and received for Run 4 is half of the difference from Run 3 (nominally 0.06 %), it is still roughly double the nominal difference for Runs 1 and 2. The results for w_{Ca} for both SRM 919c and the SRM 919b control in Run 4 are also much higher than the results from the other runs, which could have been caused by evaporation (and concentration) of the solution during the replacement of the caps. In addition, the standard deviation of the results for Run 4 is much higher than for Runs 2 and 3. Thus, because of the higher results, greater variability, and the likelihood that the change in the procedure resulted in a bias, the values from Run 4 are considered suspect.

4.3.2. Accepted Results

New test portions replacing the excluded ones from Run 1 and the suspected Run 4 were determined in Runs 5 and 6. As shown in Table 6 a relatively small difference between delivered and received is obtained for Run 5 (nominally 0.02 %), while a significantly larger difference is obtained for Run 6 (nominally 0.08 %). Although the difference between delivered and received for Run 6 is relatively high, the procedure followed and the result obtained agree well with Runs 2, 3, and 5 and the relative variability is of a similar magnitude. Thus, the SRM 915c results for Runs 2, 3, 5, and 6 are accepted.

Table 8 lists the 16 accepted calcium mass fraction, w_{Ca}, results for SRM 915c; Table 9 lists the three accepted values for the SRM 915b control. The standard deviation is denoted as "*s*" and the relative standard deviation is denoted as "RSD". The values are displayed in Fig. 2 as a function of the production sequence.

Table 8. Summary of SRM 915c Gravimetric Calcium Mass Fraction, w_{Ca}, Results.[a]

Run 2		Run 3		Run 5		Run 6		
ID	g/100g	ID	g/100g	ID	g/100g	ID	g/100g	
834	40.0176	1702	40.0096	2	40.0244	834	40.0172	
1097	40.0210	2225	40.0151	672	40.0251	257	40.0233	
672	40.0183	2	40.0050	1097	40.0227	2455	40.0223	
1702	40.0215	1800	40.0046	2455	40.0263	1800	40.0175	Combined
Mean:	40.0196		40.0086		40.0246		40.0201	40.0182
s:	0.0019		0.0049		0.0015		0.0032	0.0068
RSD:	0.0048 %		0.0120 %		0.0038 %		0.0079 %	0.017 %

a All values corrected for blank and buoyancy.

Table 9. Summary of SRM 915b Gravimetric Calcium Mass Fraction, w_{Ca}, Results.[a]

ID	g/100g
Run 3	40.0034
Run 5	40.0125
Run 6	40.0079
Mean:	40.0079
s:	0.0046
RSD:	0.011 %

a All values corrected for blank and buoyancy.

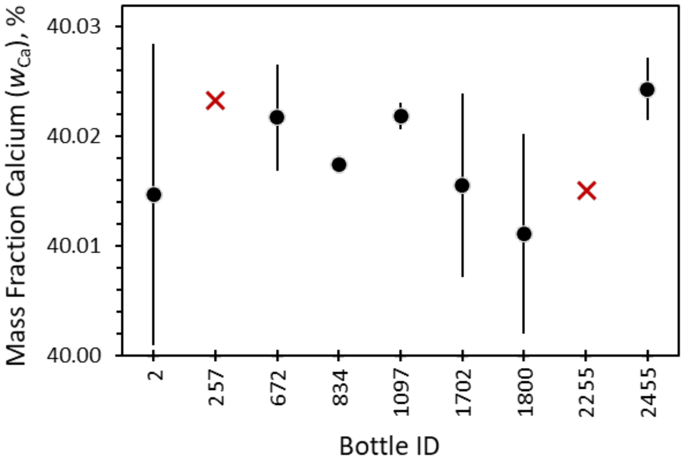

Fig. 2. Gravimetric Calcium Mass Fractions, w_{Ca}, as a Function of Production Sequence.

Dots denote means of duplicate determinations; error bars represent standard deviations (SDs). Crosses denote single determinations.

The w_{Ca} results are displayed in Fig. 3 as functions of run. The greater imprecision (longer error bars) for SRM 915c in Runs 3 and 6 likely reflects the still significant influence of the greater relative difference between mass delivered and received in those two runs compared to Runs 2 and 5. The results for the SRM 915b control agree well with the certified value, all three measurements being within the certified 95 % confidence limits. However, the pattern of differences between Runs 3, 5 and 6 are the same as for the SRM 915c results, providing supporting evidence for small run-specific biases.

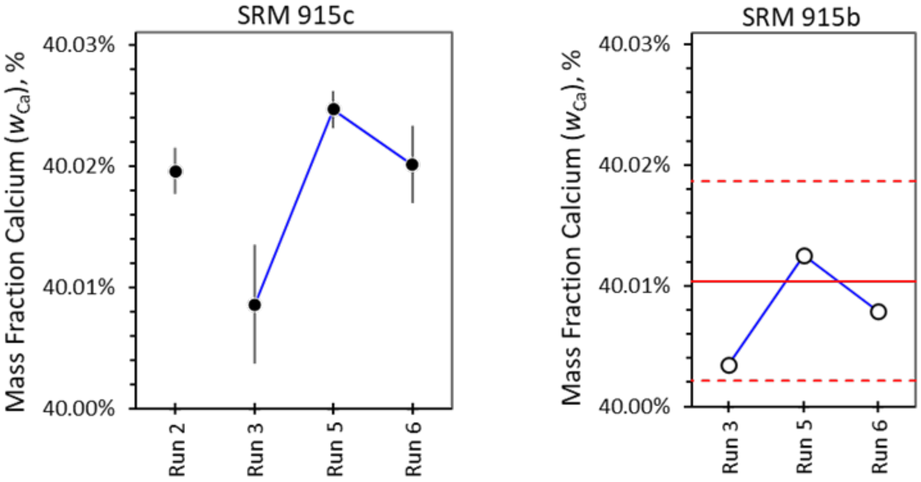

Fig. 3. Gravimetric Calcium Mass Fractions, w_{Ca}, as a Function of Run.

The plot to the left displays the mean and ± SD w_{Ca} values for SRM 915c in the four accepted runs. The plot to the right displays the three results for the SRM 915b control. The lines connecting the Run 3, 5, and 6 values provide visual emphasis of the similar bias pattern for both SRM 915c and SRM 915b. The solid horizontal line in the SRM 915b plot represents the material's w_{Ca} certified value; the dashed lines bound the certified 95 % uncertainty interval [1].

Table 10 lists the gravimetrically-determined mass fractions w_{Ca}, w_{CO3}, and w_{CaCO3} for SRM 915c. The effective degrees of freedom are denoted as ν_{eff}, which is calculated from the Welch-Satterthwaite equation [3, Section G.4.1]. The coverage factor, k, that corresponds to approximately 95 % coverage of the Student's t distribution is determined from ν_{eff}. The expanded uncertainty, $U_{95\%}$, is then calculated as the product of k and u and represents an approximately 95 % coverage interval.

Table 10. Gravimetrically Determined Mass Fractions Results for SRM 915c.

Parameter	Ca	CO_3	$CaCO_3$
w, %	40.0182	59.9359	99.933
$u(w)$, %	0.0061	0.0090	0.015
ν_{eff}	31	28	27
k	2.040	2.048	2.052
$U_{95\%}(w)$, %	0.012	0.018	0.030

4.3.3. Uncertainties

Uncertainties based on evaluation by Type A methods are standard errors of the mean for the determined assay value. Because any uncertainties evaluated by Type A methods for the measurement of the blank and the test portion mass are incorporated into the determined assay value for each run, they are already accounted for in the measurement replication for the mean of the runs. The overall mean is calculated from the mean assay value of each run, as if there were a run-to-run difference, because the calculation based on the mean for each run incorporates the uncertainties evaluated by Type A methods of the blank and test portion mass.

Uncertainties based on evaluation by Type B methods in the determination of w_{Ca}, w_{CO3}, and w_{CaCO3} have been assessed for the following procedural components of the determination: RAMs, general mass measurement, mass loss on drying, test portion mass, dissolved solution mass, solution aliquot mass, heating and treatment of sulfate precipitate, precipitate mass, and contaminants and impurities. Since the uncertainty of the buoyancy corrections is considered insignificant (< 0.001 %, relative to the combined standard uncertainty), it is not quantified.

In general, all uncertainties are evaluated and calculated based on published information, previous work, and the limited knowledge of the uncertainties for the impurity values. The calculations of the uncertainties based on evaluation by Type B methods are discussed in the following sections, along with discussion of the procedural components of the determination. Generally, the uncertainties based on evaluation by Type B methods for the SRM 915b control are of a relatively similar magnitude as those for SRM 915c (except that impurities are present in different amounts).

Uncertainties in the determinations discussed in this section are propagated using the Guide to the Expression of Uncertainty in Measurement (GUM) [3] and NIST [4] guidelines for the propagation of uncertainty.

4.3.3.1. Gravimetric Factors and Relative Atomic Masses (RAMs)

The RAM values and uncertainties for the elements of interest to SRM 915c are listed in Table 11. The RAM values used to calculate the gravimetric factors are from the 2017 Commission on Isotopic Abundances and Atomic Weights (CIAAW) standard atomic weights [2, Fig. 9]. The standard uncertainty of each of the RAMs is modeled as a uniform distribution [5]. The standard uncertainties for multiple occurrences of an element in the molecular formula (e.g., O = 4) are summed arithmetically.

Table 11. Values and Uncertainties of Relative Atomic Masses (RAM), g/mol.[a,b]

Element Name	Symbol	Atomic Number	CIAAW standard RAM (Atomic Weight)	Assigned value[c]	Assigned U[d]	Calculated u[e]
Barium	Ba	56	137.327(7)	137.327	7.00E-03	4.04E-03
Carbon	C	6	[12.0096, 12.0116]	12.0106	1.00E-03	5.77E-04
Calcium	Ca	20	40.078(4)	40.078	4.00E-03	2.31E-03
Chlorine	Cl	17	[35.446, 35.457]	35.4515	5.50E-03	3.18E-03
Chromium	Cr	24	51.9961(6)	51.9961	6.00E-04	3.46E-04
Fluorine	F	9	18.998 403 163(6)	18.998 403 163	6.00E-09	3.46E-09
Hydrogen	H	1	[1.007 84, 1.008 11]	1.007 98	1.30E-04	7.79E-05
Potassium	K	19	39.0983(1)	39.0983	1.00E-04	5.77E-05
Magnesium	Mg	12	[24.304, 24.307]	24.3055	1.50E-03	8.66E-04
Nitrogen	N	7	[14.006 43, 14.007 28]	14.006 86	4.20E-04	2.45E-04
Sodium	Na	11	22.989 769 28(2)	22.989 769 28	2.00E-08	1.16E-08
Oxygen	O	8	[15.999 03, 15.999 77]	15.999 40	3.70E-04	2.14E-04
Phosphorus	P	15	30.973 761 998(5)	30.973 761 998	5.00E-09	2.89E-09
Sulfur[f]	S	16	[32.0635, 32.0650]	32.064 25	2.20E-03	1.30E-03
Sulfur[g]	S	16	[32.059 32.076]	32.0675	8.50E-03	4.91E-03
Strontium	Sr	38	87.62(1)	87.62	1.00E-02	5.77E-03

a The term relative atomic mass (RAM) is the preferred name and a synonym for the atomic weight.
b Values and uncertainties as listed in the 2017 CIAAW standard atomic weights [2].
c Values taken as listed value or, if an interval of values is listed, taken as the mid-point of the interval.
d Values taken as the uncertainty listed in parentheses, or, if an interval of values is listed, taken as one-half of the interval.
e Calculated assuming a uniform distribution: $u = U/\sqrt{3}$.
f Value for S based on H_2SO_4 source [2, Fig. 9]: used for SRM 915c only.
g Value and uncertainty for S based on CIAAW values [2]: used for SRM 915b control only.

4.3.3.1.1. Exception for the Sulfur RAM

The RAM of sulfur is stated as the interval 32.059 g/mol to 32.076 g/mol [2]. Absent additional information, the RAM can be calculated as the midpoint of the interval (32.0675 g/mol) with U = half of the interval (0.0085 g/mol). However, the actual RAM and uncertainty of sulfur are likely to be significantly different than the above calculations because the RAM for sulfur in H_2SO_4 (the source of sulfur in the $CaSO_4$ precipitate) has an interval from about 32.0635 g/mol to 32.0650 g/mol [2]. Using the assumptions above, the RAM can be calculated as 32.064 25 g/mol, with U = 0.000 75 g/mol and, assuming a uniform distribution, u = 0.000 43 g/mol. This RAM based on the H_2SO_4 source is 0.01 %, relative, lower than the previously calculated value above and its u is only 9 % of the previous value. Based on a conservative estimate that the RAM of the sulfur could be within the bounds of the interval for the S RAM for sulfur in reagents [2], which is about three times greater than the interval for H_2SO_4, the value for U and u based on the H_2SO_4 interval are multiplied by a factor of 3 to yield values of $U = 0.00225$ g/mol and $u = 0.00130$ g/mol. Relative to the stated CIAAW values for the S RAM, the revised S RAM values increase the w_{Ca} values determined by gravimetry by about 0.002 % (absolute) and the revised S RAM contributes about 0.4 %, relative, to the variance.

4.3.3.2. General Mass Measurement

All measured masses are corrected for air buoyancy using a formula for air density [6]; the densities of $CaCO_3$, $CaSO_4$, and water [7]; 6 mol/L HCl [8], and estimated densities of more dilute HCl solutions, as appropriate to the mass being measured. Blank and/or tare corrections are applied to correct the mass of the Pt boat, Pt crucibles, and LDPE bottles. All masses used in the calculations were determined to a resolution of 10 µg.

The variability in all mass determinations was monitored by measuring standard masses of 0.5 g, 20 g, 50 g and a Pt crucible during every event when a mass critical to calculations was determined. Data to determine the replication uncertainty of the mass determination based on the standard deviation of the average mass value for a 20 g mass standard for all the mass determinations was recorded. This replication uncertainty is not included as part of the combined uncertainty of the mass determination because it is already accounted for in the replication uncertainty of the assay values.

The balance has specifications for resolution, reproducibility, eccentricity, linearity, and span while the calibration certificate lists values for repeatability, eccentricity, and error of indication both for the balance as found and as left. In addition, a measurement function is provided in the balance calibration certificate to calculate the expanded uncertainty. The measurement uncertainty stated in the calibration certificate is likely to be greater than the actual mass uncertainty because (a) the measurement replication is already accounted for, as stated above for the Type A method of evaluation, (b) eccentricity (dependent on the location of the mass on the balance pan) was minimized by placing all items near the center of the balance pan, and (c) determined values are based on the mass of the $CaCO_3$ relative to the mass of $CaSO_4$, so that biases in determining their mass are likely to cancel out. However, the measurement function in the calibration certificate is used for lack of a better alternative.

4.3.3.3. Mass Loss on Drying of $CaCO_3$ Test Portions

All $CaCO_3$ dried test portions came to a constant mass after the first heating. The recorded masses are used to determine a mass loss on drying. This mass loss value is subject to significant bias because the fine $CaCO_3$ powder tended to creep up the sides of the WBs and be subject to mechanical loss each time the open bottle was handled. It is likely that the lower recorded absolute mass losses on drying are the most accurate since the higher losses probably are biased by partial mechanical loss. The higher mass losses are shown in a lighter shade in Table 4. Based on discarding the higher mass losses, the mass loss on drying is calculated as 0.012 % for SRM 915c and 0.017 % for SRM 915b. These mass loss values were recorded for informational purposes and are not used in the calculations, which are based on measurement of the test portion dry mass.

4.3.3.4. Measurement of $CaCO_3$ Test Portion Masses to Calculate the Mass Contained in the Bottle

The mass of $CaCO_3$ that was transferred from a Pt boat (delivered) to a LDPE bottle (received) was recorded and calculated as the average of the mass delivered and the mass received. The masses were recorded in replicate as part of the effort to accurately determine the mass. The uncertainty of the mass contained in the LDPE bottle is calculated from the sum of the uncertainty of the balance and the uncertainty of using the average of the delivered and received values. The uncertainty of this calculated value is represented in the uncertainty calculations as the uncertainty of the "test portion calculated" dimensionless factor K_{tpc}. The uncertainty of the average mass is calculated as the difference of the average from the mass delivered and, because the average mass is assumed to have a central tendency, it is modeled as a triangular distribution so that it is divided by $\sqrt{6}$.

4.3.3.5. Dissolved Solution Total Mass

The total mass of the dissolved test portion solution is determined as the difference of the mass of the bottle full of solution and its mass empty with its uncertainty calculated based on the balance uncertainty.

4.3.3.6. Solution Aliquot Mass

The mass of the aliquot of the test portion solution delivered from the LDPE bottle to the Pt crucible is determined as the difference of the mass of the bottle full of solution and its mass after the aliquot was transferred. The mass of the aliquot received by the Pt crucible is determined as the difference of the mass of the Pt crucible with the aliquot and its empty mass.

Experiments to determine the expected mass loss from evaporation during the transfer of solution from the bottle to a Pt crucible indicated that a mass loss of at least 0.02 % should be expected. A weighting of 70 % delivered and 30 % received resulted in the smallest difference between delivered and received for an aliquot transfer of nominally 0.02 %. The weighting scheme had the effect of allowing the aliquot mass received by the Pt crucible to have some influence on the aliquot mass value, but not an overwhelming influence because the relatively fast evaporation rate from the solution in the Pt crucible after the aliquot had been delivered could bias the results. The uncertainty of this calculated value is represented in the uncertainty calculations as the uncertainty of the "weighted aliquot" dimensionless factor K_{waliq}. The calculated value based on this weighting scheme is assumed to have an uncertainty interval equal to the difference between the aliquot mass delivered and the calculated aliquot mass based on the weighting factors. The weighted aliquot mass value is assumed to have a central tendency so that the uncertainty is modeled as having a triangular distribution. No corrections are applied for unobserved mechanical losses in the solution transfer.

4.3.3.7. Heating and Treatment of Sulfate Precipitate

Preliminary method development performed with SRM 915a had shown that the sulfate precipitate gradually lost mass as the temperature was raised in 25 °C increments (≈ 0.8 % between 300 °C and 650 °C and ≈ 0.1 % between 650 °C and 850 °C) up to an ignition temperature of 850 ºC and remained at an approximate plateau through about 925 ºC. An ignition temperature of 875 °C has been chosen for the determination. The greater of the difference between the mass determined at 875 ºC and the mass determined at 850 ºC or 900 °C is used to estimate the uncertainty of the ignition temperature. A triangular distribution is assumed because the mass is determined using the central value at 875 °C. This mass difference between the ignition temperatures is calculated from the mean values for the four runs.

4.3.3.8. Sulfate Precipitate Mass

The precipitate mass is determined from the difference of the mass of the crucible with the precipitate and the mass of the empty crucible. The uncertainty of the precipitate mass is calculated from the uncertainty of the balance mass in the same manner as the uncertainty of the test portion mass.

4.3.3.9. Contaminants and Impurities

Impurities in the $CaSO_4$ precipitate are subtracted to determine w_{Ca} and impurities in the $CaCO_3$ test portion are subtracted to determine w_{CO3}(grav) and w_{CaCO3}. The impurities in the $CaSO_4$ precipitate are assumed based on reported impurities in the $CaCO_3$ (Table 3). Since only high-purity acids and water were used to convert the $CaCO_3$ to $CaSO_4$, it is assumed that no significant contaminants are added to the $CaSO_4$ precipitate in the analytical procedure. In addition, it is assumed that there is no significant volatilization of the impurities in the ignition to 875 °C, except that any impurity from NH_4 would be volatilized prior to the ignition. Additional determination of possible impurities and contaminants in the $CaSO_4$ precipitate was not done because of the time and cost required.

4.3.3.9.1. Calculation of Impurities

Reported values of impurities in the $CaCO_3$ starting material are used to make corrections for the impurities listed in Table 3. Table 12 lists the calculated values of the subtracted impurities and their standard uncertainties. The sum of the calculated sulfate impurities is subtracted from each individual $CaSO_4$ precipitate.

Table 12. Impurity Corrections in SRM 915c.[a]

Impurity	x_i, µg/g	$u(x_i)$, µg/g	$100u(x_i)/x$, %	Assumed Compound	Sulfate Impurity Factor [b]
Ba	1	0.2	20	$BaSO_4$	1.70
Cl	5	2.9	58	-	-
Cr	1.3	0.5	41	$Cr_2(SO_4)_3$	14.71
F	7.5	4.3	58	-	-
K	10	0.4	4	K_2SO_4	22.28
Mg	20	0.8	4	$MgSO_4$	99.05
Na	16	0.7	4	Na_2SO_4	49.43
NH_4	15	8.7	58	-	c
PO_4	15	0.6	4	-	-
HPO_4	15	0.6	4	-	-
P	5	0.2	4	-	-
Si	25	14	58	SiO_2	d
Sr	125	5.1	4	$SrSO_4$	262.04
Sum					449.21

[a] Details on calculation of impurities are provided in Section 3.

[b] Calculated as z multiplied by the impurity mass fraction multiplied by the RMM of the impurity as a sulfate and divided by the RAM of the impurity ($z = 1/2$ for K and Na, $z = 3/2$ for Cr, and $z = 1$ for all other elements).

[c] NH_4 is not an impurity in $CaSO_4$ because it volatilized prior to ignition.

[d] No correction applied based on assumption that SiO_2 would settle to bottle of dissolved solution of $CaCO_3$.

4.3.3.9.2. Correction to Cations in $CaSO_4$ Precipitate

Corrections are made for Ba, Cr, K, Mg, Na, and Sr in the $CaSO_4$ precipitate (Eq. 1) to determine w_{Ca}. The impure $CaSO_4$ precipitate contained an average of 109 µg of total sulfate impurities.

4.3.3.9.3. Si and NH_4 Ignored as Impurities in the $CaSO_4$ Precipitate

Although NAL reported a trace Si impurity of ≤ 50 µg/g, no correction is made for Si as SiO_2 in the $CaSO_4$ precipitate because it is unlikely that the SiO_2 in the $CaCO_3$ would have been dissolved and transferred as part of the dissolved solution aliquot. The uncertainty of whether any SiO_2 would be present in the $CaSO_4$ precipitate is no greater than the mean mass expected if all the Si was transferred and present as SiO_2, 18 µg, and its standard uncertainty, modeled as a uniform uncertainty, is 10 µg. If all of the SiO_2 in the solution aliquot was present as SiO_2 in the $CaSO_4$ precipitate, it's subtraction as an impurity would decrease the w_{Ca} by 0.005 %, relative, which would be seen as a decrease in the determined w_{Ca} (from 40.018 % to 40.016 %). Although this decrease is significant, the transfer of SiO_2 to the Pt crucible is not likely and the Si impurity could be much less than 25 µg/g. The Si impurity in SRM 915b was determined by glow discharge mass spectrometry to be only 5 µg/g. An impurity from NH_4, as $(NH_4)_2SO_4$, in the $CaSO_4$ precipitate is not considered because the ammonium would be volatilized prior to the ignition of the precipitate.

4.3.3.9.4. Correction to Cations for w_{CaCO3}

Corrections are made for Cl, F, and P to determine w_{CaCO3} (Eq. 8) assuming they are present in the $CaCO_3$ as $CaCl_2$, CaF_2, and $CaHPO_4$. The average calculated mass of $CaCO_3$ present in the aliquot of dissolved solution transferred to the Pt crucible contained 10 µg of total impurities.

4.3.4. Expanded Measurement Functions for Calculating Uncertainty

Estimating uncertainties using the standard GUM approach requires measurement functions that explicitly capture all the known sources of uncertainty expressed as standard deviations.

The calculated mass of $CaCO_3$, m_{CaCO3}, defined in Eq. 4 can be expanded to include the uncertainty in the test portion and aliquot masses:

$$m_{CaCO3} = K_{tpc} \cdot m_{testp}\ K_{waliq} \cdot m_{aliq}/m_{soln} \qquad (12)$$

where K_{tpc} is a dimensionless value of one (1) placeholder with an uncertainty calculated as the difference between the calculated average test portion mass (average of masses delivered and received) and K_{waliq} is a dimensionless value of 1 placeholder having uncertainty calculated from the difference between the aliquot mass delivered and the calculated aliquot mass based on the weighting factors.

The mass fraction of Ca, w_{Ca}, defined in Eq. 6 can be expanded to include replication uncertainty and the uncertainty in the measurement of the mass after ignition as well as the individual components of the sulfate impurities, $\Sigma m_{Cont\ CaSO4}$, expressed in RAMs:

$$\begin{aligned} w_{Ca} = (&R\ I\ m_{Grav\ CaSO4} - (K_{tpc}\ m_{testp}\ K_{waliq}\ m_{aliq}/m_{soln}) \\ &- (w_{Ba}(A_{Ba} + A_S + 4A_O)/A_{Ba} + w_{Cr}(3/2)(2A_{Cr} + 3(A_S + 4A_O))/A_{Cr} \\ &+ w_K(1/2)(2A_K + A_S + 4A_O)/A_K + w_{Mg}(A_{Mg} + A_S + 4A_O)/A_{Mg} \\ &+ w_{Na}(1/2)(2A_{Na} + A_S + 4A_O)/A_{Na} + w_{Sr}(A_{Sr} + A_S + 4A_O)/A_{Sr})) \\ &- (A_{Ca}/(A_{Ca} + A_S + 4A_O))/(K_{tpc}\ m_{testp}\ K_{waliq}\ m_{aliq}/m_{soln}) \end{aligned} \qquad (13)$$

where R is a dimensionless value of 1 placeholder for the uncertainty in replication of the mean values of the four runs and I is a dimensionless value of 1 placeholder with an uncertainty calculated from the maximum difference between the mass measured at an ignition temperature of 875 °C and either 850 °C or 900 °C. Since the mass difference between the masses measured at 875 °C and 850 °C is more than twice the difference between the masses measured at 875 °C and 900 °C, the difference between the masses measured at 875 °C and 850 °C is used in the calculation.

The stoichiometrically-calculated CO_3 mass fraction, $w_{CO3\text{-}Stoich}$, defined in Eq. 7 can then be expanded as:

$$\begin{aligned} w_{CO3\text{-}Stoich} = (&A_C + 3A_O)/A_{Ca}) \\ &- (R\ I\ m_{Grav\ CaSO4} - (K_{tpc}\ m_{testp}\ K_{waliq}\ m_{aliq}/m_{soln}) \\ &- (w_{Ba}(A_{Ba} + A_S + 4A_O)/A_{Ba} + w_{Cr}(3/2)(2A_{Cr} + 3(A_S + 4A_O))/A_{Cr} \\ &+ w_K(1/2)(2A_K + A_S + 4A_O)/A_K + w_{Mg}(A_{Mg} + A_S + 4A_O)/A_{Mg} \end{aligned}$$

$$\begin{aligned}
&+ w_{\mathrm{Na}}(1/2)(2A_{\mathrm{Na}} + A_{\mathrm{S}} + 4\mathrm{A}_{\mathrm{O}})/A_{\mathrm{Na}} + w_{\mathrm{Sr}}(A_{\mathrm{Sr}} + A_{\mathrm{S}} + 4A_{\mathrm{O}})/A_{\mathrm{Sr}})\\
&- (A_{\mathrm{Ca}}/(A_{\mathrm{Ca}} + A_{\mathrm{S}} + 4A_{\mathrm{O}}))/(K_{\mathrm{tpc}}\ m_{\mathrm{testp}}\ K_{\mathrm{waliq}}\ m_{\mathrm{aliq}}/m_{\mathrm{soln}}).
\end{aligned} \tag{14}$$

The measurement function defined in Eq. 8 for the sum of the mass fraction of Ca salt trace impurities taken as $CaCO_3$, $\Sigma w'_{\mathrm{imp\ CaCO3}}$, can be expanded as:

$$\Sigma w'_{\mathrm{imp\ CaCO3}} = (A_{\mathrm{Ca}} + A_{\mathrm{C}} + 3A_{\mathrm{O}})(\ w_{\mathrm{Cl}}/2A_{\mathrm{Cl}} + w_{\mathrm{F}}/2A_{\mathrm{F}} + w_{\mathrm{P}}/A_{\mathrm{P}}). \tag{15}$$

The measurement function defined in Eq. 9 for the mass fraction of $CaCO_3$, w_{CaCO3}, can be expanded to:

$$\begin{aligned}
w_{\mathrm{CaCO3}} = (1 + (A_{\mathrm{C}} + 3A_{\mathrm{O}})/A_{\mathrm{Ca}})&\\
&- (R\ I\ m_{\mathrm{Grav\ CaSO4}} - (K_{\mathrm{tpc}}\ m_{\mathrm{testp}}\ K_{\mathrm{waliq}}\ m_{\mathrm{aliq}}/m_{\mathrm{soln}})\\
&- (w_{\mathrm{Ba}}(A_{\mathrm{Ba}} + A_{\mathrm{S}} + 4A_{\mathrm{O}})/A_{\mathrm{Ba}} + w_{\mathrm{Cr}}(3/2)(2A_{\mathrm{Cr}} + 3(A_{\mathrm{S}} + 4A_{\mathrm{O}}))/A_{\mathrm{Cr}}\\
&+ w_{\mathrm{K}}(1/2)(2A_{\mathrm{K}} + A_{\mathrm{S}} + 4A_{\mathrm{O}})/A_{\mathrm{K}} + w_{\mathrm{Mg}}(A_{\mathrm{Mg}} + A_{\mathrm{S}} + 4A_{\mathrm{O}})/A_{\mathrm{Mg}}\\
&+ w_{\mathrm{Na}}(1/2)(2A_{\mathrm{Na}} + A_{\mathrm{S}} + 4\mathrm{A}_{\mathrm{O}})/A_{\mathrm{Na}} + w_{\mathrm{Sr}}(A_{\mathrm{Sr}} + A_{\mathrm{S}} + 4A_{\mathrm{O}})/A_{\mathrm{Sr}})\\
&- (A_{\mathrm{Ca}}/(A_{\mathrm{Ca}} + A_{\mathrm{S}} + 4A_{\mathrm{O}}))/(K_{\mathrm{tpc}}\ m_{\mathrm{testp}}\ K_{\mathrm{waliq}}\ m_{\mathrm{aliq}}/m_{\mathrm{soln}}))\\
&- (A_{\mathrm{Ca}} + A_{\mathrm{C}} + 3A_{\mathrm{O}})(w_{\mathrm{Cl}}/2A_{\mathrm{Cl}} + w_{\mathrm{F}}/2A_{\mathrm{F}} + w_{\mathrm{P}}/A_{\mathrm{P}}).
\end{aligned} \tag{16}$$

The measurement function defined in Eq. 11 for the indirect gravimetrically determined CO_3 mass fraction, w_{CO3}(grav), can be expanded in terms of RAMs as:

$$\begin{aligned}
w_{\mathrm{CO3}}(\mathrm{grav}) = (A_{\mathrm{C}} + 3A_{\mathrm{O}})(&w_{\mathrm{Ca}}/A_{\mathrm{Ca}} + w_{\mathrm{Ba}}/A_{\mathrm{Ba}} + w_{\mathrm{Cr}}(3/2)/A_{\mathrm{Cr}} + w_{\mathrm{K}}(1/2)/A_{\mathrm{K}}\\
&+ w_{\mathrm{Mg}}/A_{\mathrm{Mg}} + w_{\mathrm{NH4}}(1/2)/(A_{\mathrm{N}} + 4A_{\mathrm{H}}) + w_{\mathrm{Na}}(1/2)/A_{\mathrm{Na}} + (w_{\mathrm{Sr}}/A_{\mathrm{Sr}})\\
&- w_{\mathrm{Cl}}(1/2)/A_{\mathrm{Cl}} - w_{\mathrm{F}}(1/2)/A_{\mathrm{F}} - w_{\mathrm{P}}/A_{\mathrm{P}}).
\end{aligned} \tag{17}$$

The full measurement function to calculate the uncertainties for w_{CO3}(grav) is then:

$$\begin{aligned}
w_{\mathrm{CO3}}(\mathrm{grav}) = (A_{\mathrm{C}} + 3A_{\mathrm{O}})&\\
&- ((((R\ I\ m_{\mathrm{Grav\ CaSO4}} - (K_{\mathrm{tpc}}\ m_{\mathrm{testp}}\ K_{\mathrm{waliq}}\ m_{\mathrm{aliq}}/m_{\mathrm{soln}})\\
&- (w_{\mathrm{Ba}}(A_{\mathrm{Ba}} + A_{\mathrm{S}} + 4A_{\mathrm{O}})/A_{\mathrm{Ba}} + w_{\mathrm{Cr}}(3/2)(2A_{\mathrm{Cr}} + 3(A_{\mathrm{S}} + 4A_{\mathrm{O}}))/A_{\mathrm{Cr}}\\
&+ w_{\mathrm{K}}(1/2)(2A_{\mathrm{K}} + A_{\mathrm{S}} + 4A_{\mathrm{O}})/A_{\mathrm{K}} + w_{\mathrm{Mg}}(A_{\mathrm{Mg}} + A_{\mathrm{S}} + 4A_{\mathrm{O}})/A_{\mathrm{Mg}}\\
&+ w_{\mathrm{NH4}}(1/2)/(A_{\mathrm{N}} + 4A_{\mathrm{H}}) + w_{\mathrm{Na}}(1/2)(2A_{\mathrm{Na}} + A_{\mathrm{S}} + 4\mathrm{A}_{\mathrm{O}})/A_{\mathrm{Na}}\\
&+ w_{\mathrm{Sr}}(A_{\mathrm{Sr}} + A_{\mathrm{S}} + 4A_{\mathrm{O}})/A_{\mathrm{Sr}}))\\
&- (A_{\mathrm{Ca}}/(A_{\mathrm{Ca}} + A_{\mathrm{S}} + 4A_{\mathrm{O}}))/(K_{\mathrm{tpc}}\ m_{\mathrm{testp}}\ K_{\mathrm{waliq}}\ m_{\mathrm{aliq}}/m_{\mathrm{soln}}))/A_{\mathrm{Ca}})\\
&+ w_{\mathrm{Ba}}/A_{\mathrm{Ba}} + w_{\mathrm{Cr}}(3/2)/A_{\mathrm{Cr}} + w_{\mathrm{K}}(1/2)/A_{\mathrm{K}} + w_{\mathrm{Mg}}/A_{\mathrm{Mg}} + w_{\mathrm{Na}}(1/2)/A_{\mathrm{Na}}\\
&+ (w_{\mathrm{Sr}}/A_{\mathrm{Sr}}) - w_{\mathrm{Cl}}(1/2)/A_{\mathrm{Cl}} - w_{\mathrm{F}}(1/2)/A_{\mathrm{F}} - w_{\mathrm{P}}/A_{\mathrm{P}}).
\end{aligned} \tag{18}$$

4.3.5. Summary Tables

Components of uncertainty are listed in Table 13 for calcium (w_{Ca}), Table 14 for carbonate (w_{CO3}), and Table 15 for calcium carbonate (w_{CaCO3}). The particular values listed in the tables are based on results for Run 2, of Bottle 834 but are characteristic for all of the accepted measurements. Table 16 summarizes the basis for the evaluation of the uncertainty components.

Table 13. Uncertainty Components for Calcium Mass Fraction, w_{Ca}.[a]

Component	Symbol	Type	x_i	$u(x_i)$	Units	Distribution	c_i [b]	$c_iu(x_i)$	ν_{eff}	$\%V_i$ [c]
Measurement replication	R	A	1.000E+00	8.513E-05	1	normal	4.003E-01	3.408E-05	3	30.9
Ignition temperature	I	B	1.000E+00	5.039E-05	1	triangular	4.003E-01	2.017E-05	60	10.8
Mass of $CaSO_4$ precipitate at 875 °C	$m_{CaSO4\ ppt}$	U	3.167E-01	2.107E-05	g	$U_{k=2}$	1.264E+00	2.663E-05	60	18.9
Calculated value of the $CaCO_3$ test portion	K_{tpc}	B	1.000E+00	2.698E-05	1	triangular	-4.003E-01	-1.080E-05	60	3.1
Mass of calculated value of the $CaCO_3$ test portion	m_{testp}	U	6.544E-01	2.278E-05	g	$U_{k=2}$	-6.117E-01	-1.394E-05	60	5.2
Solution aliquot $CaCO_3$ test portion calculated value	K_{waliq}	B	1.000E+00	7.339E-05	1	triangular	-4.003E-01	-2.938E-05	60	23.0
Mass of the solution aliquot	m_{aliq}	U	1.043E+01	7.130E-05	g	$U_{k=2}$	-3.837E-02	-2.736E-06	60	0.2
Total mass of solution of dissolved $CaCO_3$	m_{soln}	U	2.932E+01	1.666E-04	g	$U_{k=2}$	1.365E-02	2.274E-06	60	0.1
Mass fraction of barium impurity	w_{Ba}	B	1.000E-06	1.179E-07	g/g	u_c	-5.003E-01	-5.896E-08	60	< 0.1
Mass fraction of chromium impurity	w_{Cr}	B	1.300E-06	3.064E-07	g/g	uniform	-4.245E-05	-1.301E-11	60	< 0.1
Mass fraction of potassium impurity	w_K	B	1.000E-05	2.357E-07	g/g	uniform	-6.560E-01	-1.546E-07	60	< 0.1
Mass fraction of magnesium impurity	w_{Mg}	B	2.000E-05	4.714E-07	g/g	u_c	-1.458E+00	-6.873E-07	60	< 0.1
Mass fraction of sodium impurity	w_{Na}	B	1.600E-05	3.771E-07	g/g	u_c	-9.094E-01	-3.430E-07	60	< 0.1
Mass fraction of strontium impurity	w_{Sr}	B	1.250E-04	2.946E-06	g/g	u_c	-6.171E-01	-1.818E-06	60	0.1
Barium RAM	A_{Ba}	B	1.373E+02	4.041E-03	g/mol	uniform	1.500E-09	6.060E-12	60	< 0.1
Chromium RAM	A_{Cr}	B	5.200E+01	3.464E-04	g/mol	uniform	1.522E-12	5.274E-16	60	< 0.1
Potassium RAM	A_K	B	3.910E+01	5.774E-05	g/mol	uniform	9.250E-08	5.340E-12	60	< 0.1
Magnesium RAM	A_{Mg}	B	2.431E+01	8.660E-04	g/mol	uniform	9.574E-07	8.291E-10	60	< 0.1
Sodium RAM	A_{Na}	B	2.299E+01	1.155E-08	g/mol	uniform	4.279E-07	4.940E-15	60	< 0.1
Sulfur RAM based on H_2SO_4 as source of S	A_S	B	3.206E+01	1.299E-03	g/mol	uniform	-2.940E-03	-3.820E-06	60	0.4
Strontium RAM	A_{Sr}	B	8.762E+01	5.774E-03	g/mol	uniform	4.604E-07	2.658E-09	60	< 0.1
Calcium RAM	A_{Ca}	B	4.008E+01	2.309E-03	g/mol	uniform	7.046E-03	1.627E-05	60	7.1
Oxygen RAM	A_O	B	1.600E+01	2.136E-04	g/mol	uniform	-1.176E-02	-2.512E-06	60	0.2
							combined relative standard, $u_{c\text{-rel}}$ (%, rel)[d]	0.01531	31	100

a Based on results for Run 2, Bottle 834, which represents a typical test portion.

b The sensitivity coefficients, c_i, are here estimated using Kragten spreadsheets [9,10] using other information provided in this table.

c $\%V_i$ reflects the relative contribution of the component to the total variance. It is calculated: $\%V_i = 100\left(c_iu(x_i)\right)^2/\sum\left(c_iu(x_i)\right)^2$.

d $u_{c\text{-rel}}$ is calculated on a relative basis and multiplied by the calculated summary mass fraction to calculate u_c in units of % absolute.

Table 14. Uncertainty Components for Carbonate Mass Fraction, w_{CO3}.[a]

Component	Symbol	Type	x_i	$u(x_i)$	Units	Distribution	c_i [b]	$c_iu(x_i)$	ν_{eff}	$\%V_i$ [c]
Measurement replication	R	A	1.000E+00	8.513E-05	1	normal	5.994E-01	5.103E-05	3	32.4
Ignition temperature	I	B	1.000E+00	5.039E-05	1	triangular	5.994E-01	3.020E-05	60	11.4
Mass of $CaSO_4$ precipitate at 875 °C	$m_{CaSO4\ ppt}$	U	3.167E-01	2.107E-05	g	$U_{k=2}$	1.893E+00	3.988E-05	60	19.8
Calculated value of the $CaCO_3$ test portion	K_{tpc}	B	1.000E+00	2.698E-05	1	triangular	-5.994E-01	-1.617E-05	60	3.3
Mass of calculated value of the $CaCO_3$ test portion	m_{testp}	U	6.544E-01	2.278E-05	g	$U_{k=2}$	-9.159E-01	-2.087E-05	60	5.4
Solution aliquot $CaCO_3$ test portion calculated value	K_{waliq}	B	1.000E+00	7.339E-05	1	triangular	-5.994E-01	-4.399E-05	60	24.1
Mass of the solution aliquot	m_{aliq}	U	1.043E+01	7.130E-05	g	$U_{k=2}$	-5.745E-02	-4.096E-06	60	0.2
Total mass of solution of dissolved $CaCO_3$	m_{soln}	U	2.923E+01	1.666E-04	g	$U_{k=2}$	2.044E-02	3.405E-06	60	0.1
Mass fraction of barium impurity	w_{Ba}	B	1.000E-06	1.179E-07	g/g	u_c	-3.121E-01	-3.679E-08	60	< 0.1
Mass fraction of chloride impurity	w_{Cl}	B	5.000E-06	1.667E-06	g/g	uniform	-8.464E-01	-1.411E-06	60	< 0.1
Mass fraction of chromium impurity	w_{Cr}	B	1.3000E-06	3.064E-07	g/g	uniform	-3.256E+00	-9.976E-07	60	< 0.1
Mass fraction of fluoride impurity	w_F	B	7.500E-06	2.500E-06	g/g	uniform	-1.579E+00	-3.948E-06	60	0.2
Mass fraction of potassium impurity	w_K	B	1.000E-05	2.357E-07	g/g	uniform	-2.149E-01	-5.065E-08	60	< 0.1
Mass fraction of magnesium impurity	w_{Mg}	B	2.000E-05	4.714E-07	g/g	u_c	2.860E-01	1.348E-07	60	< 0.1
Mass fraction of ammonium impurity	w_{NH4}	B	1.500E-05	5.000E-06	g/g	u_c	1.663E+00	8.317E-06	60	0.9
Mass fraction of sodium impurity	w_{Na}	B	1.600E-05	3.771E-07	g/g	u_c	-5.658E-02	-2.134E-08	60	< 0.1
Mass fraction of phosphorus impurity	w_P	B	4.892E-06	1.153E-07	g/g	u_c	-1.937E+00	-2.234E-07	60	< 0.1
Mass fraction of strontium impurity	w_{Sr}	B	1.250E-04	2.946E-06	g/g	u_c	-2.392E-01	-7.047E-07	60	< 0.1
Barium RAM	A_{Ba}	B	1.373E+02	4.041E-03	g/mol	uniform	-9.368E-10	-3.786E-12	60	< 0.1
Chlorine RAM	A_{Cl}	B	3.545E+01	3.175E-03	g/mol	uniform	1.194E-07	3.790E-10	60	< 0.1
Chromium RAM	A_{Cr}	B	5.200E+01	3.464E-04	g/mol	uniform	4.834E-08	1.675E-11	60	< 0.1
Fluoride RAM	A_F	B	1.900E+01	3.464E-09	g/mol	uniform	6.410E-07	2.220E-15	60	< 0.1
Hydrogen RAM	A_H	B	1.008E+00	7.794E-05	g/mol	uniform	-5.533E-06	-4.312E-10	60	< 0.1
Potassium RAM	A_K	B	3.910E+01	5.774E-05	g/mol	uniform	-5.778E-08	-3.336E-12	60	< 0.1
Magnesium RAM	A_{Mg}	B	2.431E+01	8.660E-04	g/mol	uniform	-5.981E-07	-5.179E-10	60	< 0.1
Nitrogen RAM	A_N	B	1.401E+01	2.454E-04	g/mol	uniform	-1.383E-06	-3.394E-10	60	< 0.1
Sodium RAM	A_{Na}	B	2.299E+01	1.155E-08	g/mol	uniform	-2.692E-07	-3.109E-15	60	< 0.1
Phosphorus RAM	A_P	B	3.097E+01	2.887E-09	g/mol	uniform	3.077E-07	8.882E-16	60	< 0.1
Sulfur RAM based on H_2SO_4 as source of S	A_S	B	3.206E+01	1.299E-03	g/mol	uniform	-4.402E-03	-5.719E-06	60	0.4
Strontium RAM	A_{Sr}	B	8.762E+01	5.774E-03	g/mol	uniform	-2.876E-07	-1.661E-09	60	< 0.1
Carbon RAM	A_C	B	1.201E+01	5.774E-04	g/mol	uniform	9.988E-03	5.766E-06	60	0.4
Calcium RAM	A_{Ca}	B	4.008E+01	2.309E-03	g/mol	uniform	-4.401E-03	-1.016E-05	60	1.3
Oxygen RAM	A_O	B	1.600E+01	2.136E-04	g/mol	uniform	1.235E-02	2.639E-06	60	0.1
							combined relative standard, $u_{c\text{-}rel}$ (%, rel)[d]	0.01495	28	100

a Based on results for Run 2, Bottle 834, which represents a typical test portion.

b The sensitivity coefficients, c_i, are here estimated using Kragten spreadsheets [9,10] using other information provided in this table.

c $\%V_i$ reflects the relative contribution of the component to the total variance. It is calculated: $\%V_i = 100\left(c_iu(x_i)\right)^2/\sum\left(c_iu(x_i)\right)^2$.

d $u_{c\text{-}rel}$ is calculated on a relative basis and multiplied by the calculated summary mass fraction to calculate u_c in units of % absolute.

Table 15. Uncertainty Components for Calcium Carbonate Mass Fraction, w_{CaO3}.[a]

Component	Symbol	Type	x_i	$u(x_i)$	Units	Distribution	c_i [b]	$c_iu(x_i)$	ν_{eff}	$\%V_i$ [c]
Measurement replication	R	A	1.000E+00	8.513E-05	1	normal	9.997E-01	8.510E-05	3	33.1
Ignition temperature	I	B	1.000E+00	5.039E-05	1	triangular	9.997E-01	5.037E-05	60	11.6
Mass of $CaSO_4$ precipitate at 875 °C	m_{CaSO4ppt}	U	3.167E-01	2.107E-05	g	$U_{k=2}$	3.157E+00	6.652E-05	60	20.2
Calculated value of the $CaCO_3$ test portion	K_{tpc}	B	1.000E+00	2.698E-05	1	triangular	-9.997E-01	-2.698E-05	60	3.3
Mass of calculated value of the CaCO3 test portion	m_{testp}	U	6.544E-01	2.278E-05	g	$U_{k=2}$	-1.528E+00	-3.480E-05	60	5.5
Solution aliquot $CaCO_3$ test portion calculated value	K_{waliq}	B	1.000E+00	7.339E-05	1	triangular	-9.997E-01	-7.337E-05	60	24.6
Mass of the solution aliquot	m_{aliq}	U	1.043E+01	7.130E-05	g	$U_{k=2}$	-9.582E-02	-6.832E-06	60	0.2
Total mass of solution of dissolved $CaCO_3$	m_{soln}	U	2.932E+01	1.666E-04	g	$U_{k=2}$	3.410E-02	5.680E-06	60	0.1
Mass fraction of barium impurity	w_{Ba}	B	1.000E-06	1.179E-07	g/g	u_{c}	-1.249E+00	-1.472E-07	60	< 0.1
Mass fraction of chloride impurity	w_{Cl}	B	5.000E-06	1.667E-06	g/g	uniform	-1.412E+00	-2.353E-06	60	< 0.1
Mass fraction of chromium impurity	w_{Cr}	B	1.300E-06	3.064E-07	g/g	uniform	-8.318E+00	-2.549E-06	60	< 0.1
Mass fraction of fluoride impurity	w_{F}	B	7.500E-06	2.500E-06	g/g	uniform	-2.634E+00	-6.585E-06	60	0.2
Mass fraction of potassium impurity	w_{K}	B	1.000E-05	2.357E-07	g/g	uniform	-1.638E+00	-3.862E-07	60	< 0.1
Mass fraction of magnesium impurity	w_{Mg}	B	2.000E-05	4.714E-07	g/g	u_{c}	-3.641E+00	-1.716E-06	60	< 0.1
Mass fraction of sodium impurity	w_{Na}	B	1.600E-05	3.771E-07	g/g	u_{c}	-2.271E+00	-8.565E-07	60	< 0.1
Mass fraction of phosphorus impurity	w_{P}	B	4.892E-06	1.667E-06	g/g	u_{c}	-3.231E+00	-5.386E-06	60	0.1
Mass fraction of strontium impurity	w_{Sr}	B	1.250E-04	2.946E-06	g/g	u_{c}	-1.541E+00	-4.541E-06	60	0.1
Barium RAM	A_{Ba}	B	1.373E+02	4.041E-03	g/mol	uniform	3.745E-09	1.513E-11	60	< 0.1
Chlorine RAM	A_{Cl}	B	3.545E+01	3.175E-03	g/mol	uniform	1.991E-07	6.322E-10	60	< 0.1
Chromium RAM	A_{Cr}	B	5.200E+01	3.464E-04	g/mol	uniform	1.528E-07	5.294E-11	60	< 0.1
Fluoride RAM	A_{F}	B	1.900E+01	3.464E-09	g/mol	uniform	1.042E-06	3.608E-15	60	< 0.1
Potassium RAM	A_{K}	B	3.910E+01	5.774E-05	g/mol	uniform	2.310E-07	1.334E-11	60	< 0.1
Magnesium RAM	A_{Mg}	B	2.431E+01	8.660E-04	g/mol	uniform	2.391E-06	2.071E-09	60	< 0.1
Sodium RAM	A_{Na}	B	2.299E+01	1.155E-08	g/mol	uniform	1.067E-06	1.232E-14	60	< 0.1
Phosphorus RAM	A_{P}	B	3.097E+01	2.887E-09	g/mol	uniform	5.000E-07	1.443E-15	60	< 0.1
Sulfur RAM based on H_2SO_4 as source of S	A_{S}	B	3.206E+01	1.299E-03	g/mol	uniform	-7.343E-03	-9.539E-06	60	0.4
Strontium RAM	A_{Sr}	B	8.762E+01	5.774E-03	g/mol	uniform	1.150E-06	6.639E-09	60	< 0.1
Carbon RAM	A_{C}	B	1.201E+01	5.774E-04	g/mol	uniform	9.985E-03	5.765E-06	60	0.2
Calcium RAM	A_{Ca}	B	4.008E+01	2.309E-03	g/mol	uniform	2.644E-03	6.106E-06	60	0.2
Oxygen RAM	A_{O}	B	1.600E+01	2.136E-04	g/mol	uniform	5.824E-04	1.244E-07	60	< 0.1
							combined relative standard, $u_{\mathrm{c\text{-}rel}}$ (%, rel)[d]	0.01480	27	100

a Based on results for Run 2, Bottle 834, which represents a typical test portion.

b The sensitivity coefficients, c_i, are here estimated using Kragten spreadsheets [9,10] using other information provided in this table.

c $\%V_i$ reflects the relative contribution of the component to the total variance. It is calculated: $\%V_i = 100\left(c_iu(x_i)\right)^2/\sum\left(c_iu(x_i)\right)^2$.

d $u_{\mathrm{c\text{-}rel}}$ is calculated on a relative basis and multiplied by the calculated summary mass fraction to calculate u_{c} in units of % absolute.

Table 16. Basis for the Evaluation of the Uncertainty Components.

Input	Symbol	Uncertainty source	Basis	Distribution	Factor
Measurement replication	R	Replication of n = 4 runs	RSD of a single determination	normal	$1/\sqrt{n}$
Ignition temperature	I	Maximum difference between mass of $CaSO_4$ precipitate at 850 °C and 900 °C and the mass at 875°C	-	triangular	$1/\sqrt{6}$
Mass of $CaSO_4$ precipitate at 875 °C	$m_{CaSO4\ ppt}$	Balance calibration Certificate	U = (0.039 + 0.00955x)/1000 [a]	$U_{k=2}$	$1/k$
Calculated value of the $CaCO_3$ test portion	K_{tpc}	Delivered and received mass	|Average – Received|/Average [b]	triangular	$1/\sqrt{6}$
Mass of calculated value of the $CaCO_3$ test portion	m_{testp}	Balance calibration Certificate	U = (0.039 + 0.00955x)/1000 [a]	$U_{k=2}$	$1/k$
Calculated value of the solution aliquot $CaCO_3$ testportion	K_{waliq}	Delivered aliquot and weighted calculated value [c]	(Delivered - Weighted)/Weighted [c]	triangular	$1/\sqrt{6}$
Mass of the solution aliquot	m_{aliq}	Balance calibration Certificate	U = (0.039 + 0.00955x)/1000 [a]	$U_{k=2}$	$1/k$
Total mass of solution of dissolved $CaCO_3$	m_{soln}	Balance calibration Certificate	U = (0.039 + 0.00955x)/1000 [a]	$U_{k=2}$	$1/k$
Mass fraction of barium impurity	w_{Ba}	Table 3	50 % of value	triangular	$1/\sqrt{6}$
Mass fraction of chloride impurity	w_{Cl}	Table 3	50 % of less than value	uniform	$1/\sqrt{3}$
Mass fraction of chromium impurity	w_{Cr}	Table 3	100 % of value	triangular	$1/\sqrt{6}$
Mass fraction of fluoride impurity	w_{F}	Table 3	50 % of less than value	uniform	$1/\sqrt{3}$
Mass fraction of potassium impurity	w_{K}	Table 3	10 % of value	triangular	$1/\sqrt{6}$
Mass fraction of magnesium impurity	w_{Mg}	Table 3	10 % of value	triangular	$1/\sqrt{6}$
Mass fraction of ammonium impurity	w_{NH4}	Table 3	50 % of less than value	uniform	$1/\sqrt{3}$
Mass fraction of sodium impurity	w_{Na}	Table 3	10 % of value	triangular	$1/\sqrt{6}$
Mass fraction of phosphorus impurity	w_{P}	Table 3	10 % of value	triangular	$1/\sqrt{6}$
Mass fraction of strontium impurity	w_{Sr}	Table 3	10 % of value	triangular	$1/\sqrt{6}$
Barium RAM	A_{Ba}	Table 11	Literature	uniform	$1/\sqrt{3}$
Chlorine RAM	A_{Cl}	Table 11	Literature	uniform	$1/\sqrt{3}$
Chromium RAM	A_{Cr}	Table 11	Literature	uniform	$1/\sqrt{3}$
Fluoride RAM	A_{F}	Table 11	Literature	uniform	$1/\sqrt{3}$
Hydrogen RAM	A_{H}	Table 11	Literature	uniform	$1/\sqrt{3}$
Potassium RAM	A_{K}	Table 11	Literature	uniform	$1/\sqrt{3}$
Magnesium RAM	A_{Mg}	Table 11	Literature	uniform	$1/\sqrt{3}$
Nitrogen RAM	A_{N}	Table 11	Literature	uniform	$1/\sqrt{3}$
Sodium RAM	A_{Na}	Table 11	Literature	uniform	$1/\sqrt{3}$
Phosphorus RAM	A_{P}	Table 11	Literature	uniform	$1/\sqrt{3}$
Sulfur RAM for SRM 915c	A_{S}	Table 11	Literature	uniform	$1/\sqrt{3}$
Sulfur RAM for SRM 915b	A_{Sr}	Table 11	Literature	uniform	$1/\sqrt{3}$
Strontium RAM	A_{C}	Table 11	Literature	uniform	$1/\sqrt{3}$
Carbon RAM	A_{Ca}	Table 11	Literature	uniform	$1/\sqrt{3}$
Calcium RAM	A_{O}	Table 11	Literature	uniform	$1/\sqrt{3}$
Oxygen RAM	R	Table 11	Literature	uniform	$1/\sqrt{3}$

a x is the recorded mass.

b Average is (delivered mass + received mass)/2.

c Weighted is the sum of the mass of aliquot delivered from the LDPE bottle (70 %) and the mass of the aliquot received by the Pt crucible (30 %).

5. Coulometry

Test portions from nine bottles of the SRM 915c material were analyzed in triplicate by coulometric acidimetry for the mass fractions (g/g) of calcium, w_{Ca}, carbonate, w_{CO3}, and calcium carbonate, w_{CaCO3}. Coulometric analyses were conducted in conformance with the current SOP for controlled-current coulometry. Only w_{CO3} was determined directly by gravimetry, w_{Ca} and w_{CaCO3} were determined indirectly.

5.1. Measurement Procedure

The amount content of total titratable alkalinity in the SRM 915c test portion, ν_{CO3} (mol/kg), is based on acidimetric neutralization of the material by addition of coulometrically-standardized HCl. The amount of standardized HCl remaining after neutralization is determined by back-titration with coulometrically-generated hydroxide, OH^-. The mass fractions of Ca, CO_3, and $CaCO_3$ are calculated from the determined amount-of-substance contents and the relative molecular mass (RMM) or relative atomic mass (RAM, A_r), of the material. The mass fractions are corrected for co-titrated interferences and other trace impurities. Values for trace impurities are calculated using the results discussed in Section 3.

5.1.1. Reagents

All chemicals used were reagent grade. All water was Type I (resistivity > 18 MΩ cm, and total organic carbon mass concentration < 50 µg/L) that was passed through a 0.22 µm filter before use. The coulometric catholyte and anolyte were prepared with a reagent grade potassium chloride, KCl. A nominal 0.2 mol/kg HCl solution was prepared from concentrated HCl by dilution with water and assayed by coulometric acidimetry.

SRM 915b Calcium Carbonate [1], was used as the control. The material used was a composite prepared from approximately equal proportions of material from 2 units.

5.1.2. Experimental Design

The experimental plan was designed for 3 titrations per day. The SRM 915c bottles (2, 330, 537, 947, 1138, 1546, 1757, 2248, and 2455) were randomly selected except for 2 and 2455. The material in these next-to-first and next-to-last bottles was also assayed by gravimetry (Section 4.1.2). Each of the selected bottles was assayed in triplicate. Excluding days where the HCl was standardized by titration, a single titration of the SRM 915b composite material was made every other day along with two titrations of SRM 915c.

The original experimental plan was for three days of HCl standardization titrations to occur before, during and after the SRM 915b and SRM 915c titrations. A scheduling conflict, which led to a 2 week break during the middle of the titrations, caused an additional day of HCl titrations to be added to the plan. The realized experimental design was: 1 day of HCl titrations, 6 days of CO_3 back-titrations, 1 day of HCl titrations, a 2 week break where no titrations were completed, 1 day of HCl titrations, 5 days of CO_3 back-titrations, and a final day of HCl titrations.

5.1.3. Preparation and Storage of Reagents

The containers used for drying and storage of the solid materials were glass WBs.

Nominal 0.5 g to 1 g aliquots from each SRM 915c unit were collected in individual WBs. A single 2 g test portion of SRM 915b was also collected. The test portions were dried at 210 °C in a muffle furnace for 4 h. The furnace temperature was then reduced and maintained at 150 °C until the test portions were collected and placed in a borosilicate glass desiccator over anhydrous magnesium perchlorate.

The HCl was stored in a borosilicate glass sphere with an inlet and outlet at the top of the sphere. The interior end of the outlet extended below the solution surface and the exterior end was stoppered with a polytetrafluoroethylene (PTFE) stopcock and terminated by a section of flexible tubing. The glass sphere inlet vented to the laboratory atmosphere via a medium porosity glass frit set in a secondary borosilicate glass vessel. The secondary vessel was partially filled with HCl from the glass sphere. As solution was removed from primary spherical vessel, atmospheric gas was vented through the solution in the secondary vessel into the sphere. Venting served to reduce the loss, or gain, of solvent from the HCl solution in the primary spherical vessel by equilibration of atmospheric gas with HCl in the secondary vessel.

5.1.4. Methods and Procedure

For the acidimetric certification measurements of SRM 915c, two general methods were applied: titration and back-titration. The titrations (assay of the HCl titrant) and back-titrations (assay of SRM 915b and 915c) were performed by automated high-precision coulometry [11,12]. Except for details specific to the back-titrations described in Section 5.1.4.7, the following procedures apply to both the HCl titrant titrations and the $CaCO_3$ back-titrations.

5.1.4.1. Mass Determination

All masses (m) are determined from measured apparent masses (m') by applying corrections for air buoyancy. Corrections for air buoyancy are based on densities for $CaCO_3$ (calcite structure[*]) of 2.71 g/cm^3 [13], 8.0 g/cm^3 for the reference density of the stainless-steel calibration weights, ρ_{ref}, and the density of air, ρ_{air}, calculated from the measured room temperature, T, and air pressure, p_{atm}, at the time of each titration. The air density calculations use the formula recommended by [6]. This formula assumes that moist air behaves as an ideal gas over the range of temperatures and pressures over which the correction is made. For the air density calculations, the reference values p_{ref} and T_{ref} are 101.325 kPa and 273.15 K.

The density of the HCl titrant, ρ_{HCl}, is estimated using the nominal expected molality of the solution using a linear interpolation of the density and molality data [14]. The change in

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[*] The uncertainty was estimated as 0.0845 g/cm^3 by calculating the standard deviation of the mean density for calcite (2.710 g/cm^3), aragonite (2.930 g/cm^3) and vaterite (2.653 g/cm^3) [13].

value for the HCl density calculated using the initial estimate of the nominal molality versus the value calculated from the mean coulometric assay value is negligible.

5.1.4.2. Estimation of the Relative Atomic and Molecular Masses

Values for the RAMs are the 2017 values and were copied from the "Standard Atomic Weights" table maintained by the CIAAW [2]. Using RAM for isotopic species with intervals given for the standard values, the RAM is estimated as the mean of the interval and the standard uncertainty is modeled with a uniform distribution (half width of the interval divided by $\sqrt{3}$) [5]. Expanded uncertainties of the RAMs for the other species are assumed to have a uniform distribution and the standard uncertainties are determined with a normalization factor of $\sqrt{3}$. Calculated values and uncertainties of the RAMs used are provided in Table 11.

All dimensionless A_r values are converted to molar masses, M, with dimensions of mol/kg following [15 section 2.10, footnote 8, page 47]. For ions and compounds, M is determined by appropriate summation of A_r values.

5.1.4.3. Coulometric Apparatus

The Faraday constant, F, is taken as 96 485.332 12 C/mol (exact value, u = 0 C/mol) [16]. Values for the constant current, traceable to NIST primary standards, were obtained from calibration of a standard 4 wire resistor [17] and calibration of a standard voltage cell [18]. The constant current for the main titration was maintained to within 2 µA/A (indicated) during the entire period of the respective main titration for each assay. The internal time-base of the counter-timer was synchronized using a time and frequency standard that is traceable to NIST via the Global Positioning System synchronization signal of the cellular network.

The coulometric cell was a horizontal design with 2 intermediate chambers separating the anode and cathode half-cells [11,19]. The cathode half-cell was separated from the first intermediate chamber by a sintered glass frit of a coarse porosity; the intermediate chambers were separated by a medium porosity frit; and the last intermediate chamber was separated from the anode half-cell by a fine porosity frit with an agar-agar gel plug set with 1.0 mol/dm^3 KCl.

The catholyte (solution in the cathode half-cell) and anolyte (solution in the anode half-cell) were each 1.0 mol/dm^3 KCl. Electrical contact between the anode and cathode half cells was achieved by filling the intermediate chambers with catholyte. The nominal catholyte volume was 65 cm^3.

The cathode used was a Pt wire approximately 0.76 mm in diameter and immersed 5 cm in the solution in the titration chamber. The end was melted to form a ball of diameter approximately 1.3 mm to avoid areas of high charge density at the tip of the electrode. The cathodic reaction was reduction of $H_2O(l)$ to $H_2(g)$ and $OH^-(aq)$. The anode was a silver, Ag, rod approximately 20 mm in diameter and approximately immersed 7 cm into the anolyte. The anodic reaction was oxidation of Ag(s) to AgCl(s).

5.1.4.4. Potentiometric Determination of the End Point

In this work, the end point is calculated using the pH measurements taken with a combination glass pH electrode and pH meter. The electrode was calibrated at ambient laboratory temperature (20 °C) against pH SRM 185h Potassium Hydrogen Phthalate pH Standard [20] and SRM 186f Potassium Dihydrogen Phosphate pH Primary Standard [21]. The electrode slope was found to be between 97.94 % and 99.97 % of the theoretical slope. No adjustment was made for changes to the electrode slope resulting from deviations in room temperature (19.7 °C to 21.9 °C) over the course of the titrations.

The titration times for the initial, t_{init}, and final, t_{final}, end points were calculated as the time required to increase the pH to 7. For both the titrations and back-titrations, the same equipment and an identical routine were used to determine the initial and final end points.

5.1.4.5. Initial Titration

An initial titration was performed on a 50 mm^3 spike of dilute HCl (~0.005 mol/dm^3), which resulted in a few µmol/kg H$^+$ added to the catholyte. This initial titration corresponds to the “blank” titrations performed in classical titrimetric analyses. The nominal current for the initial titrations, I_{init}, was 0.964 31 mA.

5.1.4.6. HCl Titrant Addition

Following the initial titration, addition of the nominal 0.2 mol/kg HCl titrant was made. For each titration or back-titration, a fresh ≈ 20 cm^3 aliquot of the HCl titrant was drawn from the previously described glass sphere storage vessel into a 30 cm^3 glass syringe with a Luer-slip connection.

The mass of the syringe-with-titrant was determined using ananalytical balance. After addition of the titrant to the cathode chamber, the mass of the syringe-without-titrant was measured. The apparent mass of the HCl titrant, m'_{HCl}, was determined as the difference in the two measurements (mass of the syringe-with-titrant minus the mass of the syringe-without-titrant).

After the final syringe mass measurement, the syringe was rinsed with water and then sprayed with 100 % ethanol from a wash bottle, which served to rinse the water from the syringe. The ethanol was removed by allowing the syringe to dry in air.

5.1.4.7. Coulometric Acidimetric Back-Titration

Following the HCl titrant addition, the maximum $CaCO_3$ test portion mass is automatically estimated by the software controlling the semi-automated coulometric system. This estimate helps to ensure that excess titrant will be present after the neutralization and the back-titration end point is determinable.

For SRM 915b and SRM 915c, approximately 170 mg of dried $CaCO_3$ was transferred into a Pt weighing boat and its mass was measured. The test portion was transferred to the titration chamber of the coulometric cell and the mass of the Pt boat-minus-test-portion was measured. The test portion mass added, m'_{tp}, was determined as the difference in these two measurements.

On addition of the $CaCO_3$ test portion to the HCl mixture, the neutralization reaction between H^+ and CO_3^{2-} results in the production of a quantitative amount of CO_2. Chemically, the automated coulometric back-titration is similar to the original, non-automated methodology [22] in which the CO_2 formed via neutralization of the $CaCO_3$ test portion was removed from the solution by boiling. For certification of SRM 915a, the neutralization was performed outside the coulometric cell and the neutralized solution was boiled to expel the CO_2 byproduct. Studies conducted as part of the SRM 915b certification demonstrated that expulsion of the CO_2 by bubbling the neutralized solution with high-purity argon yielded results indistinguishable from the earlier results using boiling.

For this work, the CO_2 was quantitatively expelled by introducing high-purity (99.999 %) nitrogen gas, N_2, into the neutralized solution with a 135 mm filter stick of "C" porosity for a period of 30 minutes. The CO_2 expulsion routine occurred immediately after the $CaCO_3$ test portion addition.

5.1.4.8. Main Titration Routine

For the HCl titrations and the $CaCO_3$ back-titrations, the main titration routine assayed approximately 99.8 % to 99.9 % of the test portion and was conducted at a nominal current, I_{main}, of 101.826 mA. The average time of the main titration routine, t_{main}, for the HCl was 3209 s; for the back-titrations the average time was 289 s for the SRM 915b control and 408 s for SRM 915c.

5.1.4.9. CO_2 Removal and Cell Rinsing

Following the main titration routine, the amount of CO_2 present in the titration chamber was reduced by purging of the solution with N_2 through the filter stick for 15 minutes. The intermediate cells were then flushed to recover any H^+ that had migrated from the titration chamber. A maximum of six rinses were made per titration. When the pH change between rinses was less than a threshold value calculated from the titration slope, the H^+ was considered recovered and fewer than six rinses were made.

5.1.4.10. Final Titration

This routine determined the end point time of the test portion titrated and followed the procedure described in Sections 5.1.4.4 and 5.1.4.5. The nominal current for the final titrations, I_{final}, was 0.964 31 mA.

5.1.4.11. Corrections for Coulometric Biases

Coulometric biases arise from the coulometric titration procedure.

With the horizontal style cell, a small (< 1 cm^3) amount of test portion remains un-titrated in the intermediate chambers during the initial and final end point determinations. This residual test portion is necessary to maintain electrical contact between the cathode and anode. As approximately 99.9 % of the test portion is titrated in the main titration routine and the volume of solution in the intermediate chambers with un-titrated test portion is small, this error accounts for less than 0.0005 % (relative) for strong acid titrations. The bias correction factors applied to the initial and final end point determinations are: $corr_{\mathrm{init}}$ and $corr_{\mathrm{final}}$. These factors are estimated by the titration software based on volume estimates determined from the known volume of the intermediate chambers, the time required to fill the full volume of the intermediate chambers, and the time to partially fill the intermediate chambers for the end point determinations.

To account for potential inefficiency of current conversion to OH^- at the Pt electrode [19], a bias correction factor for current inefficiency, $corr_{\mathrm{Ag}}$, is estimated and applied.

Another minor correction is applied for the OH^- added to the coulometric cell in the titration points made past the initial end point. The amount of OH^- added is calculated by the product of the initial titration current difference in the titration time at the initial end point, t_{init}, and the titration time of the final point of the initial titration. t_{f}, which was past the initial end point.

The final coulometric bias correction applied was for the drift in the HCl titrant assay, $corr_{\mathrm{drift}}$. This correction factor accounted for observed shifts in the HCl assay. Observed shifts indicated a decrease in the HCl assay during the period that HCl was collected. When the HCl solution was left quiescent, an increase in the HCl titrant assay was observed.

5.1.4.12. Corrections for Co-titration Biases

This category is for corrections made for impurities co-titrated by the HCl or OH^- titrants. The interfering species considered arise from matrix impurities and the residual CO_2 from incomplete elimination in the solution.

The only interfering matrix impurity detected was phosphorus, P, which is assumed present as calcium hydrogen phosphate, $CaHPO_4$. The correction for P is made assuming HPO_4^{2-} is converted to H_3PO_4 and $H_2PO_4^-$ by addition of HCl. These acidic species are then back-titrated, by coulometrically-generated OH^-, to $H_2PO_4^-$ and HPO_4^{2-}. At the strong acid end point (pH = 7), the ratio of HPO_4^{2-} to total P is approximately 2:3. Combining the $H_2PO_4^{2-}$ ratio with the ratio for the net removal of H^+ by CO_3^{2-} of 2:1, a value of 3 for the stoichiometric titration factor, δ_P, is determined[*].

The value for δ_P is also determined using a titration model for $CaCO_3$ plus a trace amount of $CaHPO_4$. The titration model results are confirmed using a second model, independent of δ_P, derived from mass and charge balance. The titration model and the mass plus charge balance model agree to ± 1 mg/kg in w_{Ca}, w_{CO3}, and w_{CaCO3}. A deviation of about 1 mg/kg between the titration and mass plus charge balance models is also observed when the models are applied to a test case using 100 % $CaCO_3$.

Other potential acid/base species detected in the impurity analyses were Si and NH_4^+. Neither of these species are reasoned to cause appreciable bias in the titration. The determined Si

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[*] The value for δ_P used in certification of SRM 915b was 4. This value was derived under the assumption of a 1:1 ratio between $H_2PO_4^=$ and HPO_4^-. Owing to small amounts of P present in the SRM 915c, this difference in δ_P causes no appreciable difference, > 10 nmol/kg, in the determined $\nu_{\mathrm{CO_3}}$.

impurity is assumed present as SiO_2. Over the period the titration progressed (2 h maximum), it is unlikely that any SiO_2 dissolves to form $Si(OH)_4$ to affect the titration. At the end point pH, less than 1 % of the total detected NH_4^+ is found to deprotonate. This reasoning is confirmed by comparison of two $CaCO_3$ titration models, one with a trace amount of $(NH_4)_2CO_3$ and the other without impurities, which shows no significant difference in the determined CO_3 mass fractions.

The bias associated with incomplete elimination of CO_2, $corr_{\mathrm{CO2}}$, from the titration chamber in the HCl titrations and $CaCO_3$ back-titrations is estimated from the average of the measured maximum slopes of the initial endpoint determination and the average of the measured maximum slopes of the final endpoint determination in the set of SRM 915c back-titrations. A model of the fundamental titration equation for CO_2 is derived, based on literature values for $\mathrm{p}K_{\mathrm{a},1}$ and $\mathrm{p}K_{\mathrm{a},2}$ for CO_2 in 1.0 mol/kg NaCl solution [23] and values for the CO_2, HCO_3^-, CO_3^{2-}, H^+, OH^- single-ion activity coefficients are estimated from data in the literature [23-27]. The $corr_{\mathrm{CO2}}$ bias is estimated as the difference between the calculated molalities of CO_2 that minimized the difference in the observed maximum titration slopes and the calculated slopes of the initial and final endpoint determinations.

5.2. Coulometric Measurement Functions

Definitions and descriptions of the terms in following measurement functions are provided in the above explanations of the methods and procedures.

5.2.1. HCl Titrant Standardization

Individual titration results for the coulometric assay values of the H^+ amount of substance content in the HCl titrant, $\nu_{\mathrm{H^+}}$, are calculated by the measurement function:

$$\nu_{\mathrm{H^+}} = \frac{[I_{\mathrm{main}}\, t_{\mathrm{main}} + I_{\mathrm{init}}\,(t_{\mathrm{f}} - t_{\mathrm{init}}) + I_{\mathrm{final}}\, t_{\mathrm{final}}]}{m'_{\mathrm{HCl}}\left[1 + \rho_{\mathrm{air}}\frac{p_{\mathrm{atm}} T_{\mathrm{ref}}}{p_{\mathrm{ref}}\; T}\left(\frac{1}{\rho_{\mathrm{HCl}}} - \frac{1}{\rho_{\mathrm{ref}}}\right)\right] F}\, corr_{H^+} \qquad (19)$$

where the correction term for the coulometric biases is

$$corr_{H^+} = \left(1 - corr_{\mathrm{init}} + corr_{\mathrm{final}} + corr_{\mathrm{Ag}} + corr_{\mathrm{CO2}} + corr_{\mathrm{drift}}\right). \qquad (20)$$

5.2.2. Coulometric Back-Titration of $CaCO_3$

The measurement function for the CO_3 amount of substance content, ν_{CO3}, is calculated according to the measurement function:

$$\nu_{\mathrm{CO_3}} = \frac{n_{\mathrm{HCl}} - [I_{\mathrm{main}}\, t_{\mathrm{main}} + I_{\mathrm{init}}\,(t_{\mathrm{f}} - t_{\mathrm{init}}) + I_{\mathrm{final}}\, t_{\mathrm{final}}]/F}{2\, m'_{\mathrm{tp}}\left[1 + \rho_{\mathrm{air}}\frac{p_{\mathrm{atm}} T_{\mathrm{ref}}}{p_{\mathrm{ref}}\; T}\left(\frac{1}{\rho_{\mathrm{CaCO_3}}} - \frac{1}{\rho_{\mathrm{ref}}}\right)\right]} + corr_{CO3} \qquad (21)$$

where the numeric factor 2 is the number moles of H necessary to neutralize 1 mole of CO_3,

$$n_{\mathrm{HCl}} = m'_{\mathrm{HCl}}\left[1 + \rho_{\mathrm{air}}\frac{p_{\mathrm{atm}}}{p_{\mathrm{ref}}}\frac{T_{\mathrm{ref}}}{T}\left(\frac{1}{\rho_{\mathrm{HCl}}} - \frac{1}{\rho_{\mathrm{ref}}}\right)\right]\nu_{\mathrm{H^+}} \qquad (22)$$

and

$$corr_{CO3} = corr_{\mathrm{init}} - corr_{\mathrm{final}} - corr_{\mathrm{Ag}} - corr_{CO2} - \frac{w_{\mathrm{P}}}{\delta_{\mathrm{P}}\, M_{\mathrm{P}}}\,. \tag{23}$$

The $corr_{\mathrm{init}}$, $corr_{\mathrm{final}}$, $corr_{\mathrm{Ag}}$ and $corr_{\mathrm{CO2}}$ are analogous to those in Eq. 20, but with opposite mathematical signs appropriate for back-titrations.

The mass fraction of CO_3, w_{CO3}, is then determined from ν_{CO3} and the molar mass of CO_3, M_{CO3}, as

$$w_{\mathrm{CO3}} = M_{\mathrm{CO3}} \nu_{\mathrm{CO3}}. \tag{24}$$

Values of w_{CaCO3} and w_{Ca} are indirectly determined from the acidimetric analysis and the material stoichiometry after correction for the detected impurities. The detected impurities for w_{Ca} are barium, Ba, chloride, Cl, chromium, Cr, fluoride, F, potassium, K, magnesium, Mg, sodium, Na, NH_4^+, P (assumed present as HPO_4^{2-}), and strontium, Sr. The detected impurities for w_{CaCO3} are Ba, Cr, K, Mg, Na, NH_4^+, and Sr. The impurity corrections assume that each impurity species is initially present as the matrix salt (i.e., Ba is present as $BaCO_3$, Cl is present as $CaCl_2$, Cr is present as $Cr_2(CO_3)_3$, F is present as CaF_2, K is present as K_2CO_3, Mg is present as $MgCO_3$, Na is present as Na_2CO_3, NH_4^+ is present as $(NH_4)_2CO_3$, P is present as $CaHPO_4$, and Sr is present as $SrCO_3$). Indirect determinations of w_{Ca} and w_{CaCO3} are made using the measurement functions

$$w_{\mathrm{Ca}} = M_{\mathrm{Ca}} \left(\nu_{\mathrm{CO_3}} + \sum_i \frac{z_i}{z_{\mathrm{CO_3}}} \frac{w_i}{M_i} \right) \tag{25}$$

and

$$w_{\mathrm{CaCO_3}} = M_{\mathrm{CaCO_3}} \left(\nu_{\mathrm{CO_3}} + \sum_i^{z_i > 0} \frac{z_i}{z_{\mathrm{CO_3}}} \frac{w_i}{M_i} \right) \tag{26}$$

where z_i represents the charge and *i* is the summation factor representing the matrix impurities listed above.

Determined values for $\nu_{\mathrm{H+}}$ are given in Table 17. The standard deviation of the mean is denoted by *s*(mean).

Table 17. Individual ν_{H^+} Results Determined for the HCl Titrant.

Index	Date Time	ν_{H^+}, mol/kg
4	25-Sep 11:26:51	0.199 520
5	25-Sep 14:10:11	0.199 524
6	25-Sep 16:44:14	0.199 493
7	4-Oct 11:04:22	0.199 477
8	5-Oct 10:46:22	0.199 487
9	5-Oct 13:37:00	0.199 448
10	5-Oct 16:39:02	0.199 436
11	17-Oct 10:25:35	0.199 504
12	17-Oct 13:21:53	0.199 473
13	17-Oct 16:12:47	0.199 472
14	26-Oct 10:10:19	0.199 457
15	26-Oct 12:36:55	0.199 438
16	26-Oct 15:19:44	0.199 449
	Mean:	0.199 475
	s:	0.000 029
	s(mean):	0.000 008
	n:	13

Measured values of ν_{CO3} and determined values of w_{Ca}, w_{CO3}, and w_{CaCO3} for the SRM 915b control titrations and for the SRM 915c titrations are given in Table 18 and Table 19. All reported mass fractions are the final values with corrections for determined impurities applied.

Table 18. Individual Results for SRM 915b Control Titrations.

n	*n*, (day)	Date	m_{tp}, g	ν_{CO3}, mol/kg	w_{Ca}, %	w_{CO3}, %	w_{CaCO3}, %
1	1	26-Sep	0.168 430	9.994 133	40.0314	59.9736	99.968
2	3	28-Sep	0.190 052	9.987 311	40.0040	59.9327	99.899
3	1	2-Oct	0.201 075	9.981 287	39.9799	59.8965	99.839
4	3	18-Oct	0.150 026	9.987 767	40.0058	59.9354	99.904
5	2	20-Oct	0.184 918	9.987 614	40.0052	59.9345	99.902
6	1	25-Oct	0.159 235	9.988 636	40.0093	59.9406	99.913
		Mean:	0.175 623	9.987 791	40.0059	59.9355	99.904
		s:	0.019 585	0.004 087	0.0164	0.0245	0.041
		s(mean):	0.007 996	0.001 668	0.0067	0.0100	0.017
		n:	6	6	6	6	6

Table 19. Individual Results for SRM 915c Titrations.

n	n, (day)	Bottle	Date	m_{tp}, g	v_{CO3}, mol/kg	w_{Ca}, %	w_{CO3}, %	w_{CaCO3}, %
1	2	330	26-Sep	0.150 541	9.991 769	40.0339	59.9594	99.973
2	3	1138	26-Sep	0.176 897	9.991 184	40.0316	59.9559	99.967
3	1	1757	27-Sep	0.170 497	9.987 803	40.0180	59.9356	99.933
4	2	947	27-Sep	0.153 398	9.999 057	40.0632	60.0031	100.046
5	3	1546	27-Sep	0.178 195	9.994 487	40.0448	59.9757	100.000
6	1	2455	28-Sep	0.160 410	10.003 712	40.0818	60.0311	100.092
7	2	2248	28-Sep	0.181 510	9.993 001	40.0389	59.9668	99.985
8[a,d]	1	1546	29-Sep	0.183 687	9.999 331	40.0643	60.0048	100.048
9	2	2248	29-Sep	0.168 427	9.996 242	40.0519	59.9862	100.017
10	3	2	29-Sep	0.181 594	9.994 134	40.0434	59.9736	99.996
11	2	2	2-Oct	0.210 934	9.990 372	40.0283	59.9510	99.959
12	3	1138	2-Oct	0.204 590	9.986 927	40.0145	59.9303	99.924
13	1	2248	3-Oct	0.196 294	9.983 043	39.9990	59.9070	99.885
14	2	2455	3-Oct	0.174 781	9.989 614	40.0253	59.9465	99.951
15[b,d]	3	947	3-Oct	0.171 238	9.991 909	40.0345	59.9602	99.974
16	1	2	18-Oct	0.118 853	10.000 076	40.0672	60.0093	100.056
17	2	330	18-Oct	0.175 611	9.987 697	40.0176	59.9350	99.932
18	1	947	19-Oct	0.173 132	9.984 672	40.0055	59.9168	99.902
19	2	537	19-Oct	0.140 145	9.992 336	40.0362	59.9628	99.978
20	3	2455	19-Oct	0.165 912	9.985 891	40.0104	59.9241	99.914
21[c,d]	1	1138	20-Oct	0.187 486	9.990 470	40.0287	59.9516	99.960
22	3	330	20-Oct	0.167 399	9.987 635	40.0174	59.9346	99.931
23	1	537	24-Oct	0.161 610	9.982 523	39.9969	59.9039	99.880
24	2	1546	24-Oct	0.151 999	9.986 835	40.0142	59.9298	99.923
25[c,d]	3	1757	24-Oct	0.175 604	9.989 682	40.0256	59.9469	99.952
26	2	1757	25-Oct	0.173 315	9.984 489	40.0048	59.9157	99.900
27	3	537	25-Oct	0.188 622	9.980 409	39.9884	59.8912	99.859
			Mean:	0.171 951	9.990 567	40.0291	59.9522	99.961
			s:	0.019 079	0.005 740	0.0230	0.0344	0.058
			s(mean):	0.003 672	0.001 105	0.0044	0.0066	0.011
			n:	27	27	27	27	27

a pH meter off. Partial data available.

b Detector malfunctioned 1021 min into titration. Partial data available.

c Over-titrated. Partial data available.

d Although only partial data is available, any bias in these values is believed to be small. These titration results are included in the calculations. See text for details.

5.3. Discussion of Results and Description of Uncertainty Estimates

Table 20 lists the coulometrically determined values for the mass fractions w_{Ca}, w_{CO3}, and w_{CaCO3} in SRM 915c.

Table 20. Coulometrically Determined Mass Fractions Results for SRM 915c.

Parameter	Ca	CO_3	$CaCO_3$
w, %	40.0291	59.9522	99.961
$u(w)$, %	0.0069	0.0097	0.016
ν_{eff}	124	96	103
k	1.979	1.985	1.983
$U_{95\%}(w)$, %	0.0137	0.0192	0.033

Estimated uncertainties are calculated for each of the reported measurements following the GUM [3] and NIST [4] guidelines for the propagation of uncertainty. For each estimate of measurement uncertainty, values of the sensitivity factors, c_i, standard uncertainty, $u(x_i)$, uncertainty component for the combined standard uncertainty, $u_i(y)$, and effective degrees of freedom for $u(x_i)$, ν_{eff}, are calculated for each of the components.

Values of c_i are calculated by differentiation and verified by "Kragten" [9,10,28] type calculations. Values of $u_i(y)$ are calculated as the product of c_i and $u(x_i)$. The combined standard uncertainty is the square root of the sum of the $u_i(y)^2$. The ν_{eff} values are the estimated degrees of freedom calculated from the Welch-Satterthwaite equation [3, Section G.4.1]. The coverage factor, k, that corresponds to approximately 95 % coverage of the Student's t distribution is determined from ν_{eff}. The expanded uncertainty, U, is then calculated as the product of k and u. Values used in determination of the estimated uncertainties for w_{Ca}, w_{CO3}, and w_{CaCO3} are provided in Table 21. Values used in determination of the estimated uncertainties for I_{main} are provided in Table 21. Values used in determination of the estimated uncertainties for the m_{HCl} and m_{tp} determinations are provided in Table 22 and Table 23. Component sources of uncertainty for $\nu_{\mathrm{H^+}}$ and ν_{CO3} are given in Table 24 and Table 25. Component sources of uncertainty for w_{CO3}, w_{Ca}, and w_{CaCO3} are provided in Table 26, Table 27, and Table 28.

Table 21. Uncertainty Components for Main Titration Current, I_{main}.

Component	Symbol	Type	x_i	$u(x_i)$	Units	Distribution	c_i	$c_iu(x_i)$	ν_{eff}	%V_i [a]
Current drift	$I_{\mathrm{main\ drift}}$	A	2.00E-06	5.77E-07	A	uniform	1.00E+00	5.77E-07	60	46.5
Voltage reference	E_{std}	B	1.018 210 2	2.00E-07	V	95 % CI	1.00E-01	2.00E-08	60	0.1
Resistance reference	R_{std}	B	9.999 463	6.08E-05	Ω	uniform	1.02E-02	6.19E-07	60	53.5
Main titration current	I_{main}	A+B			A	combined standard		8.47E-07	120	100

[a] %V_i reflects the relative contribution of the component to the total variance. It is calculated: $\%V_i = 100\left(c_iu(x_i)\right)^2/\sum\left(c_iu(x_i)\right)^2$.

Table 22. Uncertainty Components for HCl Mass Determination, m_{HCl}.[a]

Component	Symbol	Type	x_i	$u(x_i)$	Units	Distribution	c_i	$c_iu(x_i)$	ν_{eff}	%V_i [b]
Indication error		B	2.01E-02	1.16E-07	kg	uniform	1.00E+00	1.16E-07	60	89.5
	ρ_{HCl}	B	4.95E-01	2.01E-04	kg/dm^3	normal	9.06E-05	1.82E-08	60	2.2
	ρ_{std}	B	8.00E+00	0.00E+00	kg/dm^3	absolute	3.46E-07	0.00E+00	60	< 0.1
	ρ_{air}	B	1.20E-03	6.93E-07	kg/dm^3	uniform	3.50E-02	2.43E-08	60	3.9
	T	B	2.93E+02	5.77E-02	K	uniform	1.43E-07	8.27E-09	60	0.5
	T_{std}	B	2.73E+02	0.00E+00	K	absolute	1.54E-07	0.00E+00	60	< 0.1
	p_{atm}	B	1.00E+02	5.77E-02	kPa	uniform	4.20E-07	2.43E-08	60	3.9
	p_{std}	B	1.01E+02	0.00E+00	kPa	absolute	4.15E-07	0.00E+00	60	< 0.1
HCl Mass	m_{HCl}	A+B			kg	combined standard		1.23E-07	75	100

[a] Specific values are for the back titration. The same balance was used to determine the mass of added HCl in both titrations.

[b] %V_i reflects the relative contribution of the component to the total variance. It is calculated: $\%V_i = 100\left(c_iu(x_i)\right)^2/\sum\left(c_iu(x_i)\right)^2$.

Table 23. Uncertainty Components Determination of Test Portion Mass, m_{tp}.

Component	Symbol	Type	x_i	$u(x_i)$	Units	Distribution	c_i	$c_iu(x_i)$	ν_{eff}	$\%V_i$ [a]
Measurement replication		A	1.51E-04	2.89E-09	kg	uniform	1.00E+00	2.89E-09	60	43.3
Calibration uncertainty		B	0.00E+00	2.70E-09	kg	uniform	1.00E+00	2.70E-09	60	37.8
	ρ_{CaCO3}	B	2.71E+00	8.45E-02	kg dm^{-3}	uniform	2.26E-08	1.91E-09	60	18.9
	ρ_{std}	B	8.00E+00	0.00E+00	kg dm^{-3}	absolute	2.59E-09	0.00E+00	60	< 0.1
	ρ_{air}	B	1.20E-03	6.93E-07	kg dm^{-3}	uniform	3.37E-05	2.33E-11	60	< 0.1
	T	B	2.94E+02	5.77E-02	K	uniform	1.38E-10	7.94E-12	60	< 0.1
	T_{std}	B	2.73E+02	0.00E+00	K	absolute	1.48E-10	0.00E+00	60	< 0.1
	p_{atm}	B	1.00E+02	5.77E-02	kPa	uniform	4.04E-10	2.33E-11	60	< 0.1
	p_{std}	B	1.01E+02	0.00E+00	kPa	absolute	3.99E-10	0.00E+00	60	< 0.1
Test Portion Mass	m_{tp}	A+B			kg	uniform		4.39E-09	164	100

[a] $\%V_i$ reflects the relative contribution of the component to the total variance. It is calculated: $\%V_i = 100\left(c_iu(x_i)\right)^2/\sum\left(c_iu(x_i)\right)^2$.

Table 24. Uncertainty Components for the Standardization of HCl Titrant, ν_{H^+} Basis.

Component	Symbol	Type	x_i	$u(x_i)$	Units	Distribution	c_i	$c_iu(x_i)$	ν_{eff}	$\%V_i$ [a]
HCl standardization replication		A	1.99E-01	7.79E-06	mol/kg	normal	1.00E+00	7.79E-06	13	40.5
Table 22	m_{HCl}	B	1.70E-02	5.77E-07	kg	uniform	1.17E+01	6.78E-06	75	30.5
	$corr_{\mathrm{CO2}}$	B	5.01E-05	2.89E-05	mol/kg	uniform	1.99E-01	5.77E-06	60	22.1
	$corr_{\mathrm{drift}}$	B	0.00E+00	1.36E-05	mol/kg	triangular	1.99E-01	2.71E-06	60	4.9
	$corr_{\mathrm{Ag}}$	B	0.00E+00	5.77E-07	mol/kg	uniform	1.99E-01	1.15E-07	60	< 0.1
	$corr_{\mathrm{final}}$	B	-6.94E-06	2.00E-06	mol/kg	uniform	1.99E-01	4.00E-07	60	0.1
	$corr_{\mathrm{init}}$	B	-4.24E-06	1.22E-06	mol/kg	uniform	1.99E-01	2.44E-07	60	< 0.1
CODATA 2018	F	B	9.65E+04	0.00E+00	C/mol	absolute	2.07E-06	0.00E+00	60	< 0.1
Table 21	I_{main}	A+B	1.02E-01	8.47E-07	A	uniform	1.96E+00	1.66E-06	120	1.8
	I_{final}	B	9.64E-04	5.57E-07	A	uniform	1.83E-01	1.02E-07	60	< 0.1
	I_{init}	B	9.64E-04	6.12E-07	A	uniform	3.42E-04	2.09E-10	60	< 0.1
	t_{main}	B	3.21E+03	1.85E-06	s	uniform	6.21E-05	1.15E-10	60	< 0.1
	t_{final}	B	3.00E+02	1.73E-07	s	uniform	5.88E-07	1.02E-13	60	< 0.1
	t_{f}	B	2.16E+01	1.25E-08	s	uniform	5.88E-07	7.34E-15	60	< 0.1
	t_{init}	B	2.11E+01	1.22E-08	s	uniform	5.88E-07	7.15E-15	60	< 0.1
HCl titrant		A+B			mol/kg	uniform		1.23E-05	68	100

[a] $\%V_i$ reflects the relative contribution of the component to the total variance. It is calculated: $\%V_i = 100\left(c_iu(x_i)\right)^2/\sum\left(c_iu(x_i)\right)^2$.

Table 25. Uncertainty Components for the Assay of SRM 915c, ν_{CO3} Basis.

Component	Symbol	Type	x_i	$u(x_i)$	Units	Distribution	c_i	$c_iu(x_i)$	ν_{eff}	$\%V_i$
Assay replication		A	9.99E+00	1.10E-03	mol/kg	normal	1.00E+00	1.10E-03	26	47.2
	$corr_{\mathrm{Ag}}$	B	0.00E+00	5.35E-06	mol/kg	uniform	1.00E+00	5.35E-06	60	< 0.1
	$corr_{\mathrm{CO2}}$	B	1.32E-03	7.64E-04	mol/kg	uniform	1.00E+00	7.64E-04	60	22.8
	$corr_{\mathrm{final}}$	B	-3.00E-05	1.73E-07	mol/kg	uniform	1.00E+00	1.73E-07	60	< 0.1
	$corr_{\mathrm{init}}$	B	-2.00E-05	1.15E-07	mol/kg	uniform	1.00E+00	1.15E-07	60	< 0.1
	δ_{P}	B	3.00E+00	5.77E-01	1	uniform	5.38E-05	3.11E-05	60	< 0.1
CODATA 2018	F	B	9.65E+04	0.00E+00	C/mol	absolute	3.45E-05	0.00E+00	60	< 0.1
	I_{final}	B	9.64E-04	5.57E-07	A	uniform	1.06E+01	5.91E-06	60	< 0.1
	I_{init}	B	9.64E-04	5.57E-07	A	uniform	3.97E-03	2.21E-09	60	< 0.1
Table 21	I_{main}	A+B	1.02E-01	8.47E-07	A	combined standard	3.26E+01	2.76E-05	120	< 0.1
Table 22	m_{HCl}	B	2.01E-02	1.23E-07	kg	combined standard	6.63E+02	8.13E-05	75	0.3
Table 23	m_{tp}	A+B	1.51E-04	4.39E-09	kg	combined standard	6.64E+04	2.92E-04	164	3.3
	M_{P}	B	3.10E-02	2.89E-12	kg/mol	uniform	5.21E-03	1.50E-14	60	< 0.1
ν_{HCl} standardization, Table 7		A+B	1.99E-01	1.23E-05	mol/kg	combined standard	6.68E+01	8.19E-04	68	26.3
	t_{f}	B	1.41E+01	8.16E-09	s	uniform	3.32E-05	2.71E-13	60	< 0.1
	t_{final}	B	3.08E+02	1.78E-07	s	uniform	3.32E-05	5.91E-12	60	< 0.1
	t_{init}	B	1.40E+01	8.09E-09	s	uniform	3.32E-05	2.69E-13	60	< 0.1
	t_{main}	B	9.45E+02	5.46E-07	s	uniform	3.51E-03	1.92E-09	60	< 0.1
	w_{P}	B	1.50E-05	6.00E-07	kg/kg	triangular	1.08E+01	6.46E-06	60	< 0.1
	z_{CO3}	B	-2.00E+00	0.00E+00	1	absolute	8.07E-05	0.00E+00	60	< 0.1
	z_{HPO4}	B	-2.00E+00	0.00E+00	1	absolute	8.07E-05	0.00E+00	60	< 0.1
	ν_{CO3}	A+B			mol/kg	combined standard		1.60E-03	95	100

Table 26. Uncertainty Components for Coulometric Assay of SRM 915c, w_{CO3} Basis.

Component	Symbol	Type	x_i	$u(x_i)$	Units	Distribution	c_i	$c_iu(x_i)$	ν_{eff}	$\%V_i$
Table 25	ν_{CO3}	A+B	9.99E+00	1.60E-03	mol/kg	combined standard	6.00E-02	9.62E-05	95	99.2
	M_{CO3}	B	6.00E-02	8.63E-07	kg/mol	combined standard	9.99E+00	8.62E-06	60	0.8
	w_{CO3}	A+B			mol/kg	combined standard		9.66E-05	96	100

Table 27. Uncertainty Components for Coulometric Assay of SRM 915c, w_{Ca} Basis.

Component	Symbol	Type	x_i	$u(x_i)$	Units	Distribution	c_i	$c_iu(x_i)$	ν_{eff}	%V_i
Table 25	ν_{CO3}	A+B	9.99E+00	1.60E-03	mol/kg	combined standard	4.01E-02	6.42E-05	95	86.2
	M_{Ba}	B	1.37E-01	4.04E-06	kg/mol	uniform	2.13E-06	8.59E-12	60	< 0.1
	M_{Ca}	B	4.01E-02	2.31E-06	kg/mol	uniform	9.99E+00	2.31E-05	60	11.2
	M_{Cl}	B	3.55E-02	3.18E-06	kg/mol	uniform	7.97E-05	2.53E-10	60	< 0.1
	M_{Cr}	B	5.20E-02	3.46E-07	kg/mol	uniform	2.89E-05	1.00E-11	60	< 0.1
	M_{F}	B	1.90E-02	3.46E-12	kg/mol	uniform	4.16E-04	1.44E-15	60	< 0.1
	M_{K}	B	3.91E-02	5.77E-08	kg/mol	uniform	1.31E-04	7.57E-12	60	< 0.1
	M_{Mg}	B	2.43E-02	8.66E-07	kg/mol	uniform	1.36E-03	1.18E-09	60	< 0.1
	M_{Na}	B	2.30E-02	1.15E-11	kg/mol	uniform	6.07E-04	7.00E-15	60	< 0.1
	M_{NH4}	B	1.80E-02	3.97E-07	kg/mol	combined standard	9.24E-04	3.66E-10	60	< 0.1
	M_{P}	B	3.10E-02	2.89E-12	kg/mol	uniform	6.27E-04	1.81E-15	60	< 0.1
	M_{Sr}	B	8.76E-02	5.77E-06	kg/mol	uniform	6.53E-04	3.77E-09	60	< 0.1
	w_{Ba}	B	1.00E-06	2.00E-07	kg/kg	triangular	2.92E-01	5.84E-08	60	< 0.1
	w_{Cl}	B	5.00E-06	2.90E-06	kg/kg	uniform	5.65E-01	1.64E-06	60	0.1
	w_{Cr}	B	1.30E-06	5.00E-07	kg/kg	triangular	1.16E+00	5.78E-07	60	< 0.1
	w_{F}	B	7.50E-06	4.30E-06	kg/kg	uniform	1.05E+00	4.54E-06	60	0.4
	w_{K}	B	1.00E-05	4.00E-07	kg/kg	triangular	5.13E-01	2.05E-07	60	< 0.1
	w_{Mg}	B	2.00E-05	8.00E-07	kg/kg	triangular	1.65E+00	1.32E-06	60	< 0.1
	w_{Na}	B	1.60E-05	7.00E-07	kg/kg	triangular	8.72E-01	6.10E-07	60	< 0.1
	w_{NH4}	B	1.50E-05	8.70E-06	kg/kg	uniform	1.11E+00	9.66E-06	60	2.0
	w_{P}	B	1.50E-05	6.00E-07	kg/kg	triangular	1.29E+00	7.76E-07	60	< 0.1
	w_{Sr}	B	1.25E-04	5.10E-06	kg/kg	triangular	4.57E-01	2.33E-06	60	0.1
	z_{Ba}	B	2.00E+00	0.00E+00	1	absolute	1.46E-07	0.00E+00	60	< 0.1
	z_{CO3}	B	-2.00E+00	0.00E+00	1	absolute	4.88E-05	0.00E+00	60	< 0.1
	z_{Cl}	B	-1.00E+00	0.00E+00	1	absolute	2.83E-06	0.00E+00	60	< 0.1
	z_{Cr}	B	3.00E+00	0.00E+00	1	absolute	5.01E-07	0.00E+00	60	< 0.1
	z_{F}	B	-1.00E+00	0.00E+00	1	absolute	7.91E-06	0.00E+00	60	< 0.1
	z_{K}	B	1.00E+00	0.00E+00	1	absolute	5.13E-06	0.00E+00	60	< 0.1
	z_{Mg}	B	2.00E+00	0.00E+00	1	absolute	1.65E-05	0.00E+00	60	< 0.1
	z_{Na}	B	1.00E+00	0.00E+00	1	absolute	1.39E-05	0.00E+00	60	< 0.1
	z_{NH4}	B	1.00E+00	0.00E+00	1	absolute	1.67E-05	0.00E+00	60	< 0.1
	z_{HPO4}	B	-2.00E+00	0.00E+00	1	absolute	9.70E-06	0.00E+00	60	< 0.1
	z_{Sr}	B	2.00E+00	0.00E+00	1	absolute	2.86E-05	0.00E+00	60	< 0.1
	ν_{CO3}	A+B			mol/kg	combined standard		6.92E-05	124	100

Table 28. Uncertainty Components for Coulometric Assay of SRM 915c, w_{CaCO3} Basis.

Component	Symbol	Type	x_i	$u(x_i)$	Units	Distribution	c_i	$c_iu(x_i)$	ν_{eff}	$\%V_i$
Table 25	ν_{CO3}	A+B	9.99E+00	1.60E-03	mol/kg	combined standard	1.00E-01	1.60E-04	95	95.4
	M_{CaCO3}	B	1.00E-01	2.47E-06	kg/mol	combined standard	9.99E+00	2.46E-05	60	2.3
	M_{Ba}	B	1.37E-01	4.04E-06	kg/mol	uniform	5.31E-06	2.14E-11	60	< 0.1
	M_{Cr}	B	5.20E-02	3.46E-07	kg/mol	uniform	7.22E-05	2.50E-11	60	< 0.1
	M_{K}	B	3.91E-02	5.77E-08	kg/mol	uniform	3.27E-04	1.89E-11	60	< 0.1
	M_{Mg}	B	2.43E-02	8.66E-07	kg/mol	uniform	3.39E-03	2.93E-09	60	< 0.1
	M_{Na}	B	2.30E-02	1.15E-11	kg/mol	uniform	1.51E-03	1.75E-14	60	< 0.1
	M_{NH4}	B	1.80E-02	3.97E-07	kg/mol	combined standard	2.31E-03	9.15E-10	60	< 0.1
	M_{Sr}	B	8.76E-02	5.77E-06	kg/mol	uniform	1.63E-03	9.41E-09	60	< 0.1
	w_{Ba}	B	1.00E-06	2.00E-07	kg/kg	triangular	7.29E-01	1.46E-07	60	< 0.1
	w_{Cr}	B	1.30E-06	5.00E-07	kg/kg	triangular	2.89E+00	1.44E-06	60	< 0.1
	w_{K}	B	1.00E-05	4.00E-07	kg/kg	triangular	1.28E+00	5.12E-07	60	< 0.1
	w_{Mg}	B	2.00E-05	8.00E-07	kg/kg	triangular	4.12E+00	3.29E-06	60	< 0.1
	w_{Na}	B	1.60E-05	7.00E-07	kg/kg	triangular	2.18E+00	1.52E-06	60	< 0.1
	w_{NH4}	B	1.50E-05	8.70E-06	kg/kg	uniform	2.77E+00	2.41E-05	60	2.2
	w_{Sr}	B	1.25E-04	5.10E-06	kg/kg	triangular	1.14E+00	5.83E-06	60	0.1
	z_{Ba}	B	2.00E+00	0.00E+00	1	absolute	3.64E-07	0.00E+00	60	< 0.1
	z_{CO3}	B	-2.00E+00	0.00E+00	1	absolute	1.59E-04	0.00E+00	60	< 0.1
	z_{Cr}	B	3.00E+00	0.00E+00	1	absolute	1.25E-06	0.00E+00	60	< 0.1
	z_{K}	B	1.00E+00	0.00E+00	1	absolute	1.28E-05	0.00E+00	60	< 0.1
	z_{Mg}	B	2.00E+00	0.00E+00	1	absolute	4.12E-05	0.00E+00	60	< 0.1
	z_{Na}	B	1.00E+00	0.00E+00	1	absolute	3.48E-05	0.00E+00	60	< 0.1
	z_{NH4}	B	1.00E+00	0.00E+00	1	absolute	4.16E-05	0.00E+00	60	< 0.1
	z_{Sr}	B	2.00E+00	0.00E+00	1	absolute	7.14E-05	0.00E+00	60	< 0.1
	w_{CaCO3}	A+B			mol/kg	combined standard		1.64E-04	104	100

5.3.1. Significant Uncertainty Sources

For $w_{\mathrm{CO3}}$the only significant uncertainty source (one that contributes more than 1 % to the combined variance) is the determination of ν_{CO3} (> 99 %). For w_{Ca} and w_{CaCO3} the significant uncertainty sources are the determination of ν_{CO3} (86 % and 95 %), the RAM of Ca and the RMM of $CaCO_3$ (11 % and 2 %), and the mass fraction of NH_4^+ (2 % and 2 %).

For determination of ν_{CO3}, significant uncertainty sources, are assay replication (48 %). $\nu_{\mathrm{H^+}}$ standardization (26 %), CO_2 interference (23 %), and the determination of the test portion mass (3 %). The assay replication and CO_2 interference sources potentially covary. In this analysis, a single value is estimated for the residual CO_2 bias correction and it is based on data for all SRM 915c titrations. This estimate does not incorporate variability in CO_2 solubility[3], the time between titrations[4], or the mass of $CaCO_3$ test portion titrated.

The uncertainty budget for the HCl standardization also includes a component for CO_2 interference; however, for these HCl titrations, the amount of dissolved CO_2 is relatively low and CO_2 interference is less significant. Conversion of CO_3 to H_2CO_3/CO_2 in the $CaCO_3$ back titrations greatly increases the amount of dissolved CO_2 in solution and the CO_2 interference in these titrations is quite significant. Based on the relative importance of CO_2 interference in the HCl standardization titrations and in the SRM 915c titrations, the risk of this error being double-counted in the determined mass fractions for the SRM 915c is minimal.

5.3.2. HCl Titrant Standardization

Individual $\nu_{\mathrm{H^+}}$ results determined for the HCl titrant are provided in Table 17. Values used in the determination of the combined standard uncertainty $\nu_{\mathrm{H^+}}$ are provided in Table 24.

As shown in Fig. 4, the $\nu_{\mathrm{H^+}}$ values determined for the HCl titrant in the initial series decrease with time ($n = 7$). This trend continues until the 2 week pause in work when the values of $\nu_{\mathrm{H^+}}$ in the HCl titrant increase. Once the titrations resume, the final series of $\nu_{\mathrm{H^+}}$ values determined in the HCl titrant again decrease ($n = 6$). These trends are controlled by competing effects of evaporation, condensation, and CO_2 equilibration. Assay drift is accounted for by splitting the titrations into two groups, split at the 2 week pause in work, and fitting each group to a linear function by least-squares analysis.

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[3] The solubility of CO_2 is, among other factors, controlled by ambient temperature (increased CO_2 solubility at low temperature) and pressure (increased CO_2 solubility at high pressure). A scatter plot (not shown) of the ambient room temperature recorded for each titration reveals a weak linear trend ($R^2 = 0.21$) between temperature and w_{CaCO3}. The highest w_{CaCO3} assay value (1.000 633 kg/kg) occurs at the lowest recorded room temperature (19.7 °C) and one of the lowest assay values (0.998 781 kg/kg) occurs at the highest observed room temperature (21.9 °C). The observed range in atmospheric pressure for the SRM 915c titration (98.9 kPa to 101.8 kPa) is not large enough to significantly impact CO_2 solubility.

[4] Atmospheric CO_2 might permeate into the system during overnight or weekend pauses between titrations where the system is not flushed by N_2 gas. Excess CO_2 in the system might increase amount of acid titrated and cause a positive bias.

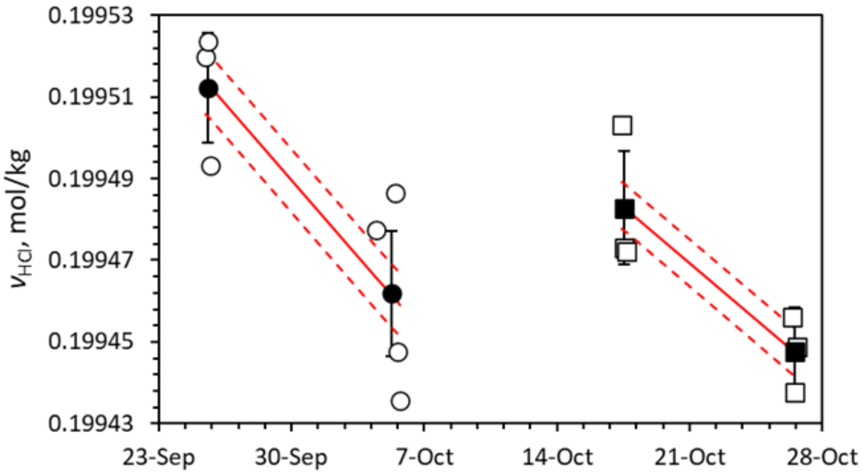

Fig. 4. Time series of the HCl Titrations.

1st half of titrations (circles) completed: 25 September to 5 October; 2nd half of titrations (squares) completed: 17 October to 26 October. Open black symbols are the individual titration results; filled black symbols are daily mean results. The error bars represent standard uncertainties. Solid lines represent the linear regression functions; dashed lines represent the standard deviation of the mean of the regressions.

For each HCl analysis group, the estimated Type A uncertainty, u_A, is taken as the standard error of the mean for the regression line. The mean u_A for the first and second groups are 8 µmol/kg and 6 µmol/kg. As these values are in close agreement, a single value for the u for ν_{H^+} is estimated for both groups by taking the greater of the u_A values. In using a single u_A value for both groups, the estimated u for the second group is increased by 1 µmol/kg, absolute, or about 12 %, relative.

5.3.3. Corrections for Coulometric and Impurity Biases

In the back-titrations for SRM 915c, mean CO_2 biases for the initial endpoint determination and for the final endpoint determination were calculated. The net CO_2 bias is taken as the difference in these values and is 1.32 mmol/kg. For the control titrations on SRM 915b, the net CO_2 bias is 1.30 mmol/kg, which is in satisfactory agreement with the value (0.0104 %, or 1.04 mmol/kg) determined during the original certification titrations.

Uncertainties for impurity mass fraction values reported as less-than-or-equal values were modeled with uniform distributions and the standard uncertainty was estimated by dividing the half width of the mass fraction upper bound by $\sqrt{3}$. For impurities with mass fraction values reported as numeric values, uncertainties were modeled with triangular distributions and the standard uncertainty was estimated by dividing the half width of the triangular distribution by $\sqrt{6}$. Additional detail these uncertainty values is given in Section 3. This modeling approach was used for both co-titrated and non-interfering impurity species.

The magnitude of the interfering P impurity is based on the fraction of H_2PO_4 to total P. This dependency is captured in the δ_P in Eq. 23. A plausible estimate of the uncertainty in δ_P is derived from the titration model by making small adjustments to the H_2PO_4:P ratio around the (pH = 7) titration end point.

5.3.4. Acidimetric Assay

Bias corrected results of the individual determinations of w_{Ca}, w_{CO3}, and w_{CaCO3} for SRM 915c are provided in Table 19. Values used in the determination of the combined standard uncertainty for w_{Ca}, w_{CO3}, and w_{CaCO3}, are provided in Table 26, Table 27, and Table 28. Bias corrected mean values and standard uncertainties for each bottle and the overall set of bottles are plotted in Fig. 5.

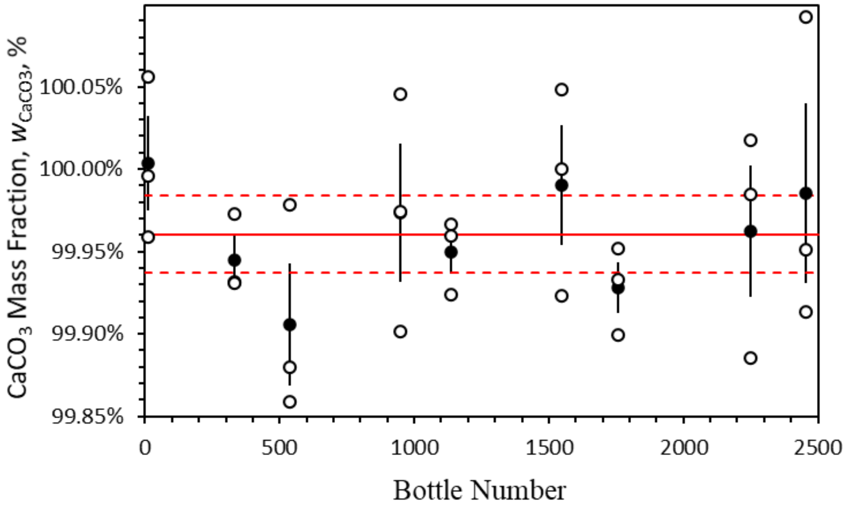

Fig. 5. Titration Results As a Function of Bottle Number.

Open circles denote bias-corrected individual results; filled black circles with standard uncertainty error bars represent mean bottle results. The solid line is the over-all mean value and the dashed lines represent the approximate 95 % expanded uncertainty bounds based only on the measurement results (heterogeneity component not included).

At the 2 week pause in work, the back-titrations are split into two analysis groups. For each back-titration, $\nu_{\mathrm{H^+}}$ is calculated from the date and time of analysis and the least squares coefficients for HCl titrations in the matched group.

Errors occurred during four titrations of SRM 915c and are noted in Table 19. Data for these titrations are incomplete, but enough information is known to estimate the mass fractions. Owing to incomplete data, the end point is not precisely determined for these titrations and calculations of the mass fractions are likely biased. This bias is not expected to be large as the end point routine is responsible for titrating less than the final 0.1 % of the analyte. Excluding the results with incomplete end point information decreases the overall mean value determined for w_{CaCO3} by 49 mg/kg ($n = 24$).

For these titrations, any potential bias in the determined values is believed to be small and these titration results are not excluded from this analysis. The final reported mass fraction values were calculated as the mean of the individual mass fraction results for the entire data set.

5.3.5. SRM 915b Control Titrations

Determination of the w_{CaCO3} control value is made according to Eq. 26 where: ν_{CO3} is determined from Eq. 21 and is based on data from titrations of SRM 915b built into the SRM 915c experimental design. For the control determinations, M_{CaCO3} is calculated as 100.087 g/mol, $corr_{\mathrm{Ag}}$ and $corr_{\mathrm{CO2}}$ are determined by the same procedures described for SRM 915c but using results of the SRM 915b control titrations, and impurity corrections taken from the SRM 915b certification. The SRM 915b control calculations also use the values for the Standard Atomic Weights used in the certification of SRM 915b [29].

6. Comparisons of Mass Fraction Estimates for SRM 915b and SRM 915c

6.1. Confirmatory Mass Balance Calculations

Confirmatory estimates of w_{CaCO3}, w_{Ca}, and w_{CO3} are made from the instrumentally detected impurities using an indirect approach derived from equations for mass and charge balance [30]. The function for determining w_{CaCO3} by this approach is

$$w_{\mathrm{CaCO3}} = 1 - \sum_i \frac{w_i M_j}{\tau_{i,j} M_i} \tag{27}$$

where, M_j is the i impurity as a matrix salt and $\tau_{i,j}$ is the stoichiometric coefficient for i in the j matrix salt. For w_{Ca} and w_{CO3} the functions are:

$$w_{\mathrm{Ca}} = M_{\mathrm{Ca}} \left(\frac{w_{\mathrm{CaCO3}}}{M_{\mathrm{CaCO3}}} + \sum_i^{z_i < 0} \frac{z_i}{z_{\mathrm{CO3}}} \frac{w_i}{M_i} \right) \tag{28}$$

and

$$w_{\mathrm{CO3}} = M_{\mathrm{CO3}} \left(\frac{w_{\mathrm{CaCO3}}}{M_{\mathrm{CaCO3}}} + \sum_i^{z_i > 0} \frac{z_i}{z_{\mathrm{Ca}}} \frac{w_i}{M_i} \right). \tag{29}$$

Values using this “mass balance” or “100 % - trace” approach are confirmatory since they are based upon estimated mass fraction values of impurities present and best approximations of the component sources of uncertainty rather than direct measurements.

6.2. Comparison of the SRM 915b Certification and Control Values

Table 29 summarizes the Ca, CO_3, and $CaCO_3$ mass fractions results of the gravimetric and coulometric measurements used to certify SRM 915b, the SRM 915b certified values, the gravimetric and coulometric measurements made on the SRM 915b control material as part of the certification effort for SRM 915c, and the mass balance estimates based on the impurity estimates. The certification and control estimates are compared in Fig. 6.

The determined values for Ca, $CaCO_3$, and CO_3 in the SRM 915b control agree with the certified values within the uncertainty limits of this determination and the uncertainty limits of the certified value. The derived mass balance values are uniformly higher than the measured values, suggesting that the total mass fraction of impurities in this material might be underestimated.

Table 29. Mass Fraction Estimates for SRM 915b.

Measurand	Purpose	Method	*w*, %	*u*, %	ν_{eff}	*k*	*U*, %	$u_{\text{rel}, \%}$ [a]
Calcium (Ca)	Certification	Gravimetric	40.0135	0.0056	15	2.13	0.012	0.014
		Coulometric	40.0072	0.0049	263	1.97	0.0097	0.012
		Certified	40.0104	0.0041	-	2	0.0083	0.010
	Control	Gravimetric	40.0079	0.0059	132	1.978	0.012	0.015
		Coulometric	40.0059	0.0069	124	1.979	0.014	0.017
		Mass Balance	40.0257	0.0036	188	1.973	0.0071	0.0089
Carbonate (CO_3)	Certification	Gravimetric	59.9281	0.0090	21	2.086	0.019	0.015
		Coulometric	59.9187	0.0066	165	1.975	0.013	0.011
		Certified	59.9230	0.0062	-	2	0.012	0.010
	Control	Gravimetric	59.9197	0.0084	111	1.982	0.017	0.014
		Coulometric	59.9355	0.0097	96	1.985	0.019	0.016
		Mass Balance	59.9524	0.0053	270	1.969	0.010	0.0089
Calcium Carbonate ($CaCO_3$)	Certification	Gravimetric	99.915	0.015	19	2.093	0.031	0.015
		Coulometric	99.899	0.012	165	1.96	0.025	0.012
		Certified	99.907	0.011	-	2	0.021	0.011
	Control	Gravimetric	99.901	0.014	113	1.981	0.028	0.014
		Coulometric	99.904	0.022	14	2.160	0.047	0.022
		Mass Balance	99.9553	0.0064	110	1.982	0.013	0.0064

a Relative uncertainty, 100*u*/*w*

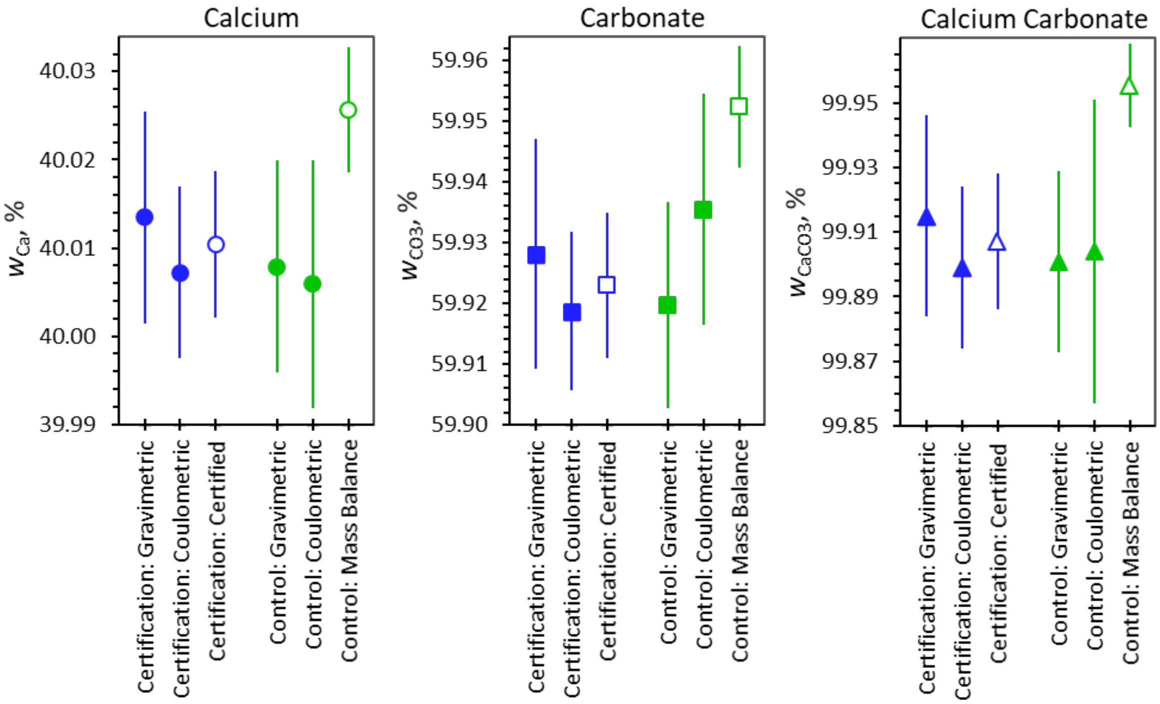

Fig. 6. Comparison of Mass Fraction Estimates for SRM 915b.

Solid symbols represent measurements by analytical assays; open symbols represent certified values or non-assay mass balance assessments. Error bars represent 95 % coverage intervals.

6.3. Comparison of the SRM 915c Mass Fraction Estimates

Table 30summarizes the gravimetric, coulometric, and mass balance estimates of the Ca, CO_3, and $CaCO_3$ mass fractions, expressed as percent of sample mass, for SRM 915c. Fig. 7 compares these estimates. All of the estimates are in good agreement, including the confirmatory values determined by the mass balance approach. This suggests that the identity and the quantity of impurities in SRM 915c have been adequately characterized.

Table 30. Mass Fraction Estimates for SRM 915c.

Measurand	Method	w, %	u, %	ν_{eff}	k	U, %	u_{rel}, % [a]
Calcium (Ca)	Gravimetric	40.0182	0.0061	31	2.040	0.0125	0.015
	Coulometric	40.0291	0.0069	124	1.979	0.0137	0.017
	Mass Balance	40.0243	0.0034	191	1.973	0.0067	0.0085
Carbonate (CO_3)	Gravimetric	59.9359	0.0090	28	2.048	0.0184	0.015
	Coulometric	59.9522	0.0097	96	1.985	0.0192	0.016
	Mass Balance	59.9449	0.0041	217	1.971	0.0081	0.0068
Calcium Carbonate ($CaCO_3$)	Gravimetric	99.9333	0.0148	27	2.052	0.0303	0.015
	Coulometric	99.9605	0.0164	104	1.983	0.0326	0.016
	Mass Balance	99.9484	0.0057	118	1.980	0.0112	0.0057

a Relative uncertainty, $100u/w$

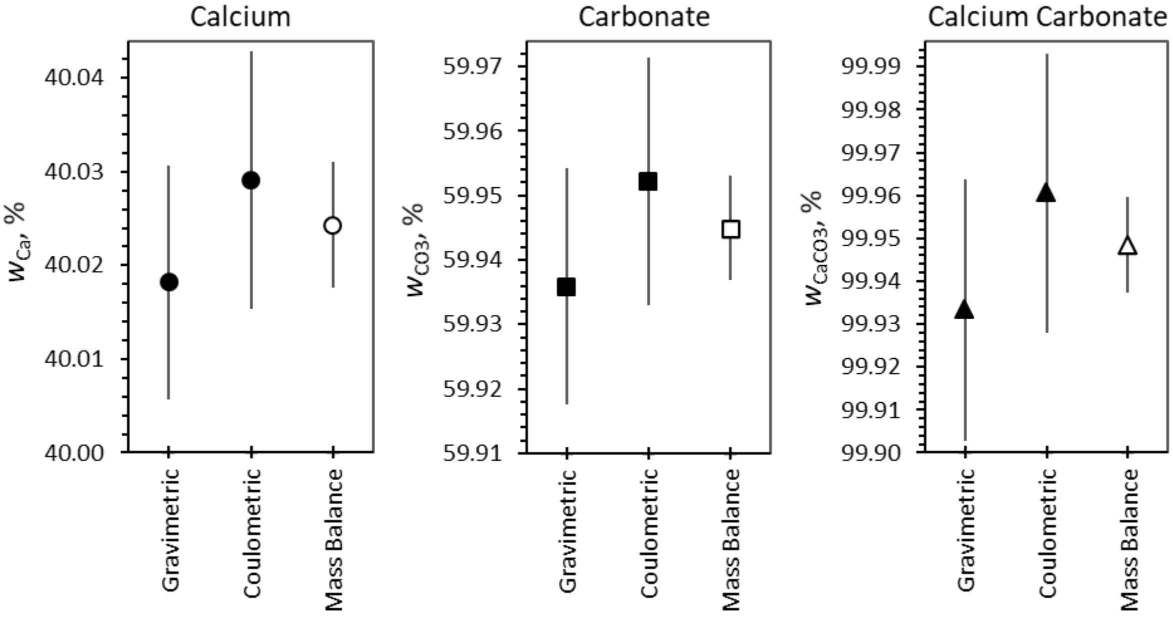

Fig. 7. Comparison of Mass Fraction Estimates for SRM 915c.

Solid symbols represent measurements by analytical assays; open symbols represent certified values or non-assay mass balance assessments. Error bars represent 95 % coverage intervals.

7. Statistical Design and Analysis

The uncertainty evaluations reported in the previous sections used techniques from the GUM [3]. The uncertainty analyses in this section augment the uncertainty analyses of the previous sections in two important ways: 1) correlations between measurements made on the same bottle and run, in the case of gravimetry, are accounted for in the calculation of uncertainty due to measurement replication. And 2) the results from gravimetry and coulometry are combined into a single value and statement of uncertainty. Bayesian data analysis techniques and Monte Carlo uncertainty propagation methods are leveraged to accomplish those goals [31,32].

7.1. Data

7.1.1. Gravimetric Mass Fraction Calcium, w_{Ca}

The gravimetric w_{Ca} measurements are provided in Table 8. Additional sources of uncertainty, besides measurement replication, are provided in Table 13.

Not all of the measurements could be made at once, so they were divided into experimental runs. An incomplete block design with four blocks (experimental runs) and four measurements in each block was used. So that bottle-to-bottle differences could be assessed, the factor of interest in the design was the bottle, with eight levels (the original design was for eight bottles). The design was optimally chosen by the *D*-criterion [33,34]. Denote the measurements of w_{Ca} by gravimetry as $y_{\mathrm{G,ij}}(\mathrm{Ca})$, where $i = 1$ to 4 indexes the successful Runs and $j = 1$ to 9 indexes bottle. Note that not all $4 \cdot 9 = 36$ combinations of i and j appear because not all bottles were measured in each run.

7.1.2. Coulometric Mass Fraction Calcium, w_{Ca}

The coulometric v_{CO3} measurements are provided in Table 19. These measurements can be translated into measurements of w_{Ca} using (see Eq. 25)

$$w_{\mathrm{Ca}} = M_{\mathrm{Ca}} \left(v_{\mathrm{CO3}} + \sum_i \frac{z_i}{z_{\mathrm{CO3}}} \frac{w_i}{M_i} \right). \tag{30}$$

The values and associated uncertainties for the z_i, w_i, M_i, and z_{CO3} terms in this equation are provided in Table 27. Additional sources of uncertainty for the measurements of v_{CO3}, besides measurement replication, are provided in Table 25.

The measurements of v_{CO3} are denoted as $y_{\mathrm{C,ij}}(\mathrm{CO_3})$, where $i = 1$ to 9 indexes bottle and $j = 1$ to 3 indexes the replicate measurements of bottle i.

7.1.3. Gravimetric Mass Fraction Carbonate, w_{CO3}

The gravimetric w_{CO3} measurements are derived from the measurements of w_{Ca} using (see Eq. 17):

$$w_{\mathrm{CO3}}(\mathrm{grav}) = (A_{\mathrm{C}} + 3A_{\mathrm{O}})\left(\begin{array}{c} \frac{w_{\mathrm{Ca}}}{A_{\mathrm{Ca}}} + \frac{w_{\mathrm{Ba}}}{A_{\mathrm{Ba}}} + \frac{3w_{\mathrm{Cr}}}{2A_{\mathrm{Cr}}} + \frac{w_{\mathrm{K}}}{2A_{\mathrm{K}}} + \frac{w_{\mathrm{Mg}}}{A_{\mathrm{Mg}}} + \\ \frac{w_{\mathrm{NH4}}}{2(A_{\mathrm{N}} + 4A_{\mathrm{H}})} + \frac{w_{\mathrm{Na}}}{2A_{\mathrm{Na}}} + \frac{w_{\mathrm{Sr}}}{A_{\mathrm{Sr}}} - \frac{w_{\mathrm{Cl}}}{2A_{\mathrm{Cl}}} - \frac{w_{\mathrm{F}}}{2A_{\mathrm{F}}} - \frac{w_{\mathrm{P}}}{A_{\mathrm{P}}} \end{array}\right). \qquad (31)$$

The values and associated uncertainties for the w and A terms are provided in Table 14.

The measurements of w_{CO3} by gravimetry are denoted as $y_{\mathrm{G,ij}}(\mathrm{CO_3})$, where $i = 1$ to 4 indexes the successful Runs and $j = 1$ to 9 indexes bottle. Note that not all $4 \cdot 9 = 36$ combinations of i and j appear because not all bottles were measured in each run.

7.1.4. Coulometric Mass Fraction Carbonate, w_{CO3}

The v_{CO3} measurements can be translated into measurements of w_{CO3} using (see Eq. 24)

$$w_{\mathrm{CO3}} = M_{\mathrm{CO3}} v_{\mathrm{CO3}} \cdot \qquad (32)$$

The value and associated uncertainty for M_{CO3} are provided in Table 26.

7.1.5. Gravimetric Mass Fraction Calcium Carbonate, w_{CaCO3}

The gravimetric w_{CaO3} measurements are derived from the measurements of w_{Ca} using

$$w_{\mathrm{CaCO3}} = w_{\mathrm{Ca}} + \frac{w_{\mathrm{Ca}}(A_{\mathrm{C}} + 3A_{\mathrm{O}})}{A_{\mathrm{Ca}}} - (A_{\mathrm{Ca}} + A_{\mathrm{C}} + 3A_{\mathrm{O}})\left(\frac{w_{\mathrm{Cl}}}{2A_{\mathrm{Cl}}} + \frac{w_{\mathrm{F}}}{2A_{\mathrm{F}}} + \frac{w_{\mathrm{P}}}{A_{\mathrm{P}}})\right) \qquad (33)$$

which combines Eqs. 7, 9, and 15. The values and associated uncertainties for the w and A terms are provided in Table 15.

The measurements of w_{CaCO3} by gravimetry are denoted as $y_{\mathrm{G,ij}}(\mathrm{CaCO_3})$, where $i = 1$ to 4 indexes the successful Runs and $j = 1$ to 9 indexes bottle. Note that not all $4 \cdot 9 = 36$ combinations of i and j appear because not all bottles were measured in each run.

7.1.6. Coulometric Mass Fraction Calcium Carbonate, w_{CaCO3}

The v_{CO3} measurements can be translated into measurements of w_{CaCO3} using (see Eq. 26)

$$w_{CaCO3} = M_{\mathrm{CaCO_3}}\left(v_{CO3} + \sum_i \frac{z_i}{z_{CO3}} \frac{w_i}{M_i}\right). \qquad (34)$$

The values and associated uncertainties for the z_i, w_i, M_i, and z_{CO3} terms are provided in Table 28.

7.2. Model

For each constituent, w_{Ca}, w_{CO3} , and w_{CaCO3}, the values and uncertainties by gravimetry and coulometry are established separately and then combined. The following Section presents the details for each step.

7.2.1. Gravimetric Mass Fraction Calcium, w_{Ca}

The measurements of w_{Ca} by gravimetry, $y_{\mathrm{G},ij}(\mathrm{Ca})$, are modeled:

$$\begin{aligned}
&y_{\mathrm{G},ij}(\mathrm{Ca}) = \mu_{\mathrm{G}}(\mathrm{Ca}) + R_i(\mathrm{Ca}) + B_{\mathrm{G},j}(\mathrm{Ca}) + \varepsilon_{\mathrm{G},ij}(\mathrm{Ca})\\
&R_i(\mathrm{Ca}) \sim \mathrm{Normal}(0, \sigma_{\mathrm{R}}^2(\mathrm{Ca}))\\
&B_{\mathrm{G},j}(\mathrm{Ca}) \sim \mathrm{Normal}(0, \sigma_{\mathrm{BG}}^2(\mathrm{Ca}))\\
&\varepsilon_{\mathrm{G},ij}(\mathrm{Ca}) \sim \mathrm{Normal}(0, \sigma_{\mathrm{G}}^2(\mathrm{Ca}))
\end{aligned} \qquad (35)$$

where $\mu_{\mathrm{G}}(\mathrm{Ca})$ represents the mean value of the $y_{\mathrm{G},ij}(\mathrm{Ca})$, $R_i(\mathrm{Ca})$ represents the effect of Run i, $B_{\mathrm{G},j}(\mathrm{Ca})$ represents the effect of bottle j, and $\varepsilon_{\mathrm{G},ij}(\mathrm{Ca})$ is a random error. The parameter $\sigma_R(\mathrm{Ca})$ represents the run-to-run standard deviation, and $\sigma_{\mathrm{BG}}(\mathrm{Ca})$ represents the bottle-to-bottle standard deviation, which is a measure of heterogeneity.

The parameters $\mu_{\mathrm{G}}(\mathrm{Ca})$, $\sigma_{\mathrm{R}}(\mathrm{Ca})$, $\sigma_{\mathrm{BG}}(\mathrm{Ca})$, and $\sigma_{\mathrm{G}}(\mathrm{Ca})$ are inferred from the measurements using a Bayesian analysis. An improper flat prior distribution is selected for $\mu_{\mathrm{G}}(\mathrm{Ca})$ to express a lack of knowledge *a priori*. For $\sigma_{\mathrm{R}}(\mathrm{Ca})$, $\sigma_{\mathrm{BG}}(\mathrm{Ca})$, and $\sigma_{\mathrm{G}}(\mathrm{Ca})$ a weakly informative half-Cauchy distribution is selected as a prior distribution. The scale of the half-Cauchy distribution is taken to be the median absolute deviation of the measurements, which matches the default for the NIST Consensus Builder (NICOB) [35] when the Hierarchical Bayes (Gaussian) method is selected. Note that the NICOB was not explicitly used for the analyses described in this report; however, the underlying modeling principles were leveraged.

The value and uncertainty for w_{Ca} by gravimetry that does not include heterogeneity is obtained by convolving the posterior distribution of $\mu_{\mathrm{G}}(\mathrm{Ca})$ with all of the distributions from Table 13 except the replication distribution. Measurement replication is accounted for by the posterior distribution of $\mu_{\mathrm{G}}(\mathrm{Ca})$. A random variable following this distribution is denoted by $G(\mathrm{Ca})$. The mean of the distribution of $G(\mathrm{Ca})$ is taken to be the value of w_{Ca} by gravimetry, and the standard deviation of $G(\mathrm{Ca})$ is taken to be the standard uncertainty.

The value and uncertainty for w_{Ca} that does include heterogeneity replaces in the convolution described immediately prior, the posterior distribution of $\mu_{\mathrm{G}}(\mathrm{Ca})$ with the posterior predictive distribution of $\mu_{\mathrm{G}}(\mathrm{Ca}) + B_{\mathrm{G,new}}(\mathrm{Ca})$. The term $B_{\mathrm{G,new}}(\mathrm{Ca})$ represents the effect of a randomly selected bottle of SRM 915c and is Normally distributed with mean zero and standard deviation $\sigma_{\mathrm{BG}}(\mathrm{Ca})$. A random variable following the convolution of the posterior predictive distribution of $\mu_{\mathrm{G}}(\mathrm{Ca}) + B_{\mathrm{G,new}}(\mathrm{Ca})$ and the distributions from Table 13 is denoted by $G_{\mathrm{H}}(\mathrm{Ca})$. The mean and standard deviation of $G_{\mathrm{H}}(\mathrm{Ca})$ are taken to be the value and standard uncertainty for w_{Ca} with heterogeneity measured by gravimetry.

7.2.2. Coulometric Mass Fraction Calcium, w_{Ca}

The measurements of v_{CO3} by coulometry, $y_{\mathrm{C},ij}(\mathrm{CO_3})$, are modeled:

$$\begin{aligned}
&Y_{\mathrm{C},ij}(\mathrm{CO_3}) = \mu_{\mathrm{C}}(\mathrm{CO_3}) + B_{\mathrm{C},j}(\mathrm{CO_3}) + \varepsilon_{\mathrm{C},ij}(\mathrm{CO_3})\\
&B_{\mathrm{C},j}(\mathrm{CO_3}) \sim \mathrm{Normal}(0, \sigma_{\mathrm{BC}}^2(\mathrm{CO_3}))\\
&\varepsilon_{\mathrm{C},ij}(\mathrm{CO_3}) \sim \mathrm{Normal}(0, \sigma_{\mathrm{C}}^2(\mathrm{CO_3}))
\end{aligned} \qquad (36)$$

where $\mu_C(CO_3)$ represents the mean value of the $y_{C,ij}(CO_3)$, $B_{C,j}(CO_3)$ represents the effect of bottle j, and $\varepsilon_{C,ij}(CO_3)$ is a random error. The parameter $\sigma_{BC}(CO_3)$ represents the bottle-to-bottle standard deviation, which is a measure of heterogeneity.

The parameters $\mu_C(CO_3)$, $\sigma_{BC}(CO_3)$, and $\sigma_C(CO_3)$ are inferred from the measurements using a Bayesian analysis. An improper flat prior distribution is selected for $\mu_C(CO_3)$ to express a lack of knowledge *a priori*. For $\sigma_{BC}(CO_3)$, and $\sigma_C(CO_3)$ a weakly informative half-Cauchy distribution is selected as a prior distribution. The scale of the half-Cauchy distribution is taken to be the median absolute deviation of the measurements, which matches the default for the NICOB when Hierarchical Bayes (Gaussian) is selected.

The value and uncertainty for v_{CO3} by coulometry that does not include heterogeneity is obtained by convolving the posterior distribution of $\mu_C(CO_3)$ with all of the distributions from Table 25 except the Assay replication distribution. Measurement replication is accounted for by the posterior distribution of $\mu_C(CO_3)$. The random variable following this distribution is denoted by X_{CO3}.

The value and uncertainty for v_{CO3} that does include heterogeneity replaces in the convolution the posterior distribution of $\mu_C(CO_3)$ with the posterior predictive distribution of $\mu_C(CO_3) + B_{C,new}(CO_3)$. The term $B_{C,new}(CO_3)$ represents the effect of a randomly selected bottle of SRM 915c and is Normally distributed with mean zero and standard deviation $\sigma_{BC}(CO_3)$. A random variable following the convolution of the posterior predictive distribution of $\mu_C(CO_3) + B_{C,new}(CO_3)$ and the distributions from Table 25 is denoted by X^H_{CO3}.

The distributions of X_{CO3} and X^H_{CO3} are translated into distributions for w_{Ca} using Eq. 30, Monte Carlo, and the values from Table 27. Random variables following these distributions are denoted as $C(Ca)$ and $C_H(Ca)$, respectively. The means and standard deviations of $C(Ca)$ and $C_H(Ca)$ are taken to be the values and standard uncertainties for w_{Ca} without and with heterogeneity, respectively, by coulometry.

7.2.3. Gravimetric Mass Fraction Carbonate, w_{CO3}

The measurements of w_{CO3} by gravimetry, $y_{G,ij}(CO_3)$, are modeled:

$$\begin{aligned}
&y_{G,ij}(CO_3) = \mu_G(CO_3) + R_i(CO_3) + B_{G,j}(CO_3) + \varepsilon_{G,ij}(CO_3)\\
&R_i(CO_3) \sim \text{Normal}(0, \sigma^2_R(CO_3))\\
&B_{G,j}(CO_3) \sim \text{Normal}(0, \sigma^2_{BG}(CO_3))\\
&\varepsilon_{G,ij}(CO_3) \sim \text{Normal}(0, \sigma^2_G(CO_3))
\end{aligned} \tag{37}$$

where the parameters are interpreted similarly to Eq. 35, and similar priors were used.

The distributions convolved with the posterior distribution of $\mu_G(CO_3)$ and the posterior predictive distribution of $\mu_G(CO_3) + B_{G,new}(CO_3)$ are found in Table 14. The random variables $G(CO_3)$ and $G_H(CO_3)$ are defined to follow the former and latter resulting distributions, respectively, similarly to $G(Ca)$ and $G_H(Ca)$.

7.2.4. Coulometric Mass Fraction Carbonate, w_{CO3}

The evaluation of w_{CO3} by coulometry proceeds exactly as for w_{Ca} but replacing Eq. 30 by Eq. 32, and Table 27 with Table 26. Random variables from the resulting distributions are denoted by $C(\mathrm{CO_3})$ and $C_{\mathrm{H}}(\mathrm{CO_3})$ for without and with heterogeneity, respectively.

7.2.5. Gravimetric Mass Fraction Calcium Carbonate, w_{CaCO3}

The measurements of w_{CaCO3} by gravimetry, $y_{\mathrm{G},ij}(\mathrm{CaCO_3})$, are modeled:

$$\begin{aligned}
&y_{\mathrm{G},ij}(\mathrm{CaCO_3}) = \mu_{\mathrm{G}}(\mathrm{CaCO_3}) + R_i(\mathrm{CaCO_3}) + B_{\mathrm{G},j}(\mathrm{CaCO_3}) + \varepsilon_{\mathrm{G},ij}(\mathrm{CaCO_3})\\
&R_i(\mathrm{CaCO_3}) \sim \mathrm{Normal}(0, \sigma^2_{\mathrm{R}}(\mathrm{CaCO_3}))\\
&B_{\mathrm{G},j}(\mathrm{CaCO_3}) \sim \mathrm{Normal}(0, \sigma^2_{\mathrm{BG}}(\mathrm{CaCO_3}))\\
&\varepsilon_{\mathrm{G},ij}(\mathrm{CaCO_3}) \sim \mathrm{Normal}(0, \sigma^2_{\mathrm{G}}(\mathrm{CaCO_3}))
\end{aligned} \tag{38}$$

where the parameters are interpreted similarly to Eqs. 35 and 37, and similar priors were used.

The distributions convolved with the posterior distribution of $\mu_{\mathrm{G}}(\mathrm{CaCO_3})$ and the posterior predictive distribution of $\mu_{\mathrm{G}}(\mathrm{CaCO_3}) + B_{\mathrm{G,new}}(\mathrm{CaCO_3})$ are found in Table 15. The random variables $G(\mathrm{CaCO_3})$ and $G_{\mathrm{H}}(\mathrm{CaCO_3})$ are defined to be random variables following the appropriate convolution of distributions, similarly to $G(\mathrm{Ca})$ and $G_{\mathrm{H}}(\mathrm{Ca})$.

7.2.6. Coulometric Mass Fraction Calcium Carbonate, w_{CaCO3}

The evaluation of w_{CaCO3} by coulometry proceeds exactly as for w_{Ca} but replacing Eq. 30 by Eq. 34 and Table 27 with Table 28. Random variables from the resulting distributions are denoted by $C(\mathrm{CaCO_3})$ and $C_{\mathrm{H}}(\mathrm{CaCO_3})$ for without and with heterogeneity, respectively.

7.2.7. Combined

Combining the gravimetry and coulometry values is described only for the w_{Ca} without heterogeneity case. The other five cases are identical.

Let $\bar{x}_{\mathrm{G}}(\mathrm{Ca})$ and $s_{\mathrm{G}}(\mathrm{Ca})$ be the mean and standard deviation of $G(\mathrm{Ca})$. Similarly, let $\bar{x}_{\mathrm{C}}(\mathrm{Ca})$ and $s_{\mathrm{C}}(\mathrm{Ca})$ be the mean and standard deviation of $C(\mathrm{Ca})$. The model used to combine the gravimetry and coulometry values is:

$$\begin{aligned}
&\bar{x}_{\mathrm{G}}(\mathrm{Ca}) \sim \mathrm{Normal}(\mu(\mathrm{Ca}), \sigma^2_M(\mathrm{Ca}) + s^2_G(\mathrm{Ca}))\\
&\bar{x}_{\mathrm{C}}(\mathrm{Ca}) \sim \mathrm{Normal}(\mu(\mathrm{Ca}), \sigma^2_M(\mathrm{Ca}) + s^2_C(\mathrm{Ca}))
\end{aligned} \tag{39}$$

where $\mu(\mathrm{Ca})$ represents the mean value over measurement methods and $\sigma_{\mathrm{M}}(\mathrm{Ca})$ represents the measurement-method-to-measurement-method standard deviation.

The parameters $\mu(\mathrm{Ca})$ and $\sigma_{\mathrm{M}}(\mathrm{Ca})$ in Eq. 39 are inferred from $\bar{x}_{\mathrm{G}}(\mathrm{Ca})$, $\bar{x}_{\mathrm{C}}(\mathrm{Ca})$, $s_{\mathrm{G}}(\mathrm{Ca})$, and $s_{\mathrm{C}}(\mathrm{Ca})$ using a Bayesian analysis. An improper flat prior distribution is selected for $\mu(\mathrm{Ca})$ to express a lack of knowledge. For $\sigma_{\mathrm{M}}(\mathrm{Ca})$ a weakly informative half-Cauchy distribution is selected as a prior distribution. The scale of the half-Cauchy distribution is taken to be the median absolute deviation of all of the Monte Carlo samples of *G*(Ca) and *C*(Ca), which is larger than the default for the NICOB when Hierarchical Bayes (Gaussian) is selected. Since there are only two measurement methods, the NIST Consensus Builder default is inflated to protect against the measurements being relatively near one another by chance.

7.3. Results

Table 31 lists the mean, standard uncertainty, and 95 % coverage intervals for the combined mass fractions w_{Ca}, w_{CO3}, and w_{CaCO3} with and without including between-bottle heterogeneity. The summaries that include heterogeneity are appropriate estimates of the true value of the measurands in single units of SRM 915c.

Table 31. Summary Mass Fraction Values for SRM 915c, %.

	With Heterogeneity			Without Heterogeneity		
Measurand	*x*	*u*(*x*)	*U*(*x*)	*x*	*u*(*x*)	*U*(*x*)
w_{Ca}	40.022	0.009	0.017	40.023	0.009	0.016
w_{CO3}	59.942	0.013	0.026	59.944	0.013	0.023
w_{CaCO3}	99.944	0.022	0.043	99.947	0.021	0.040

The mass fractions determined by gravimetric and coulometric assay and the combined estimates are compared in Fig. 8. The combined estimates are shown with and without considering between-bottle heterogeneity. All estimates are in close agreement.

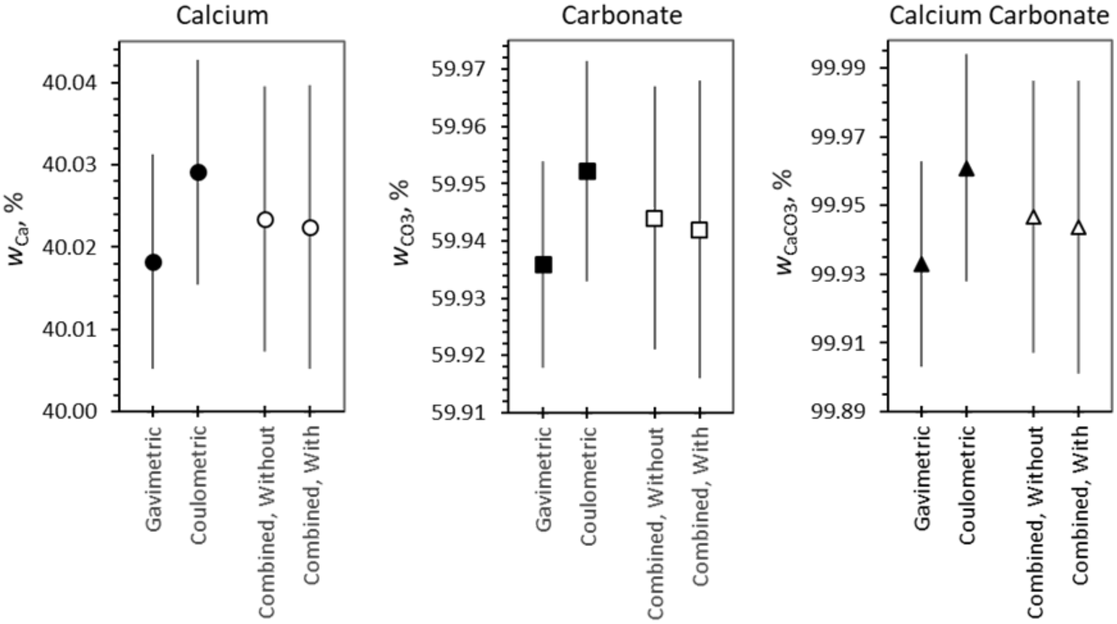

Fig. 8. Comparison of Gravimetric, Coulometric and Combined Mass Fraction Estimates.

Error bars represent 95 % coverage intervals.

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Appendix A. List of Symbols, Abbreviations, and Acronyms

CIAAW	Commission on Isotopic Abundances and Atomic Weights
COA	Certificate of Analysis
GFS	GFS Chemicals, Inc.
GUM	Guide to the Expression of Uncertainty in Measurement
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectroscopy
LDPE	low density polyethylene
NAL	Northern Analytical Laboratory, Inc.
NICOB	NIST Consensus Builder
NIST	National Institute of Standards and Technology
PTFE	polytetrafluoroethylene
RAM	relative atomic mass (“atomic weight”)
RMM	relative molecular mass (“molecular weight”)
SOP	standard operating procedures
SD	standard deviation
SI	International System of Units
SRM	Standard Reference Material®
WB	weighing bottle
WM	wide mouth (bottle)

A_{C}	relative atomic mass of carbon
A_{O}	relative atomic mass of oxygen
A_r	relative atomic mass of a chemical entity “r”
n	number of values
w_{Ca}	mass fraction calcium
w_{CO3}	mass fraction carbonate
w_{CaCO3}	mass fraction calcium carbonate