

Determination of Seventeen Major and Trace Elements in New Float Glass Standards for Use in Forensic Comparisons using Laser Ablation Inductively Coupled Plasma Mass Spectrometry

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Abstract

Consensus concentration values for seventeen (17) major and trace elements typically present in soda-lime glass manufactured using the “float” process and used in the quantitative analysis and forensic comparison of glass samples were determined using laser ablation (LA) micro sampling coupled to inductively coupled plasma mass spectrometry (ICP-MS). This is the first reporting of the chemical characterization of a new set of float glass intended for use as matrix-matched calibration standards in the forensic analysis and comparison of glass by LA-ICP-MS using a standard test method (ASTM E2927-16e1). Three Corning Float Glass Standards (CFGs) were manufactured at low, medium, and high concentrations of 32 elements typically encountered in float glass samples as found in forensic casework. This work describes an international collaboration amongst seven (7) laboratories to evaluate the homogeneity of the three glass materials and reports the consensus concentrations values of 17 elements at three concentration levels. Eight (8) sets of independent results from LA-ICP-MS analysis using the standard test method of analysis and one set of micro-X-ray Fluorescence Spectrometry (μ XRF) data (using method ASTM E2926-17) resulted in typically < 3 % relative standard deviation (RSD) within each lab and < 5 % RSDs among all labs participating in the study for the concentration ranges using sampling spots between 50 μ m - 100 μ m in diameter. These results suggest that the new calibration standards are homogeneous for most elements at the small sampling volumes (\sim 90 μ m deep by \sim 80 μ m in diameter) reported and show excellent agreement among the different participating labs. Consensus concentration values are determined using a previously reported calibration standard (FGS 2) and checked with a NIST 1831 SRM[®]. A collaboration with National Institute of Standards and Technology (NIST) scientists to certify these glasses as SRMs, including the certification of the quantitative analysis of the minor and trace element content, for future distribution by NIST is ongoing.

Keywords: LA-ICP-MS, glass calibration standards, forensic analysis and comparisons

1. Introduction

The Russo group at Lawrence Berkeley National Laboratory (LBNL) has been one of the most prolific promoters of the fundamental understanding of laser-material interactions including the development of strategies for quantitative analysis of solid matrices using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [1-12]. The Günther group at the Swiss Federal Institute of Technology (ETH Zürich) has equally advanced the basic understanding of laser ablation processes within the analytical sciences [13-18] including the application of LA-ICP-MS for quantitative analysis of different matrices. Mank and Mason [19] conducted an assessment of ablation depth versus analytical spot size that contributed to a better understanding of this important parameter during the ablation process followed by other fundamental studies by other researchers [20-22]. A European-led effort to develop a standard method for the forensic analysis of soda-lime glass made by the float process for forensic comparisons included many of the lessons learned from the fundamental work described above, including: the importance of the correct choice of the laser fluence, the use of Helium as a carrier gas instead of Argon, the use of short wavelength lasers and short (ns-fs) pulses, the importance of particle size distributions on the transport to and vaporization and ionization within the inductively coupled plasma (ICP), the preference of drilling a single spot rather than a line raster to avoid large particle sizes, the need of limiting the depth as related to the spot diameter, and finally, the importance of using matrix-matched calibration standards that are similar to typical soda-lime glass both in composition (assuming a $\sim 72\%$ SiO_2 matrix concentration) and in optical absorption properties. The Natural Isotopes and Trace Elements in Criminalistics and Environmental Forensics (NITECRIME) network engaged several laboratories in a series of interlaboratory exercises over 5 years and published a standard method based on the optimization of the analytical parameters for LA-ICP-MS of glass [23]. Additional work in the standardization of glass analysis using LA-ICP-MS resulted in corroborating reports and further promoted the utility of this technique in forensic analysis and comparisons of glass [24-29], culminating in the publication of an ASTM test method of analysis [30].

Soda-lime glass is used in the manufacture of vehicle windows, architectural windows, store display cases, containers, and smartphones, which use a variation in formulation known as “gorilla” glass. The relatively fragile nature of glass lends itself to breaking during violent interactions such as vehicle accidents and therefore becomes potential evidence in many different types of crime scenes ranging from hit-and-run accidents to breaking-and-entering events. Trace amounts of glass fragments can transfer from the broken object(s) to people, and to other objects, or to a location, therefore providing evidence of an activity during the breaking event. It has also been widely reported that glass evidence recovered from crime scenes can provide useful information to aid an investigation that leads to identifying a suspect and can also provide strong associations between the suspect and a crime event. A standard test method (ASTM E2927-16e1) describes a consensus-based approach to sampling, sample preparation, quantitative analysis by LA-ICP-MS, comparison, and interpretation of the resulting elemental data that is derived from fundamental studies and from several cooperative studies [23-29]. The quantitative analysis and forensic comparison method recommended in ASTM E2927-16e1 is based on previously reported work by the NITECRIME network in Europe [23]. A series of four interlaboratory tests conducted by several laboratories resulted in the development of a quantitative analysis method using NIST SRM[®] 610, NIST SRM[®] 612, NIST SRM[®] 1831, NIST SRM[®] 621 and other glass standards to evaluate the performance of the participating laboratories [23]. The main lessons learned from these studies included the need for the use of matrix-matched standards as well as the need to prescribe both laser parameters and ICP-MS parameters. This effort also resulted in the recommendation for the use of a new series of glasses (BKA-Schott FGS series) containing ~ 72% SiO₂ for monitoring ²⁹Si as an internal standard and containing analyte elements of interest in approximately similar concentrations as float glass samples, for external calibration. The results reported from the NITECRIME effort were reproduced in a different series of interlaboratory studies in the USA [29] and by groups in The Netherlands [25] and in Germany [27].

This method is now considered the “gold standard” for the quantitative analysis and comparison of small (as small as $\approx 150 \mu\text{m}$ length) soda-lime glass fragments that transfer from a glass breaking event to a person, or to a crime scene, or to another object.

Micro-X-ray Fluorescence Spectrometry (μXRF) is another sensitive tool that is commonly used for the comparison of glass in forensic casework. While laser ablation has a constant sampling volume for each element (ablation depth $\approx 80 \mu\text{m}$ – $150 \mu\text{m}$, depending on the laser analysis parameters), the sampling volume for μXRF varies widely and depends on the element’s X-ray energy and the sample matrix. Low atomic number elements (e.g., Na) have effective penetration depths of a few μm in glass, while high atomic number elements (e.g., Zr) have effective penetration depths of a few mm in glass [31]. Thus, for μXRF analysis, some elements have a much smaller sampling volume and some elements have a much larger sampling volume compared to LA-ICP-MS. This is an important consideration since larger sampling volumes generally result in improved precision. A standard test method (ASTM E2926-17) provides recommendations on the sampling, analysis by μXRF , and comparison of the elemental data using a semi-quantitative approach (element ratios) [32]. Quantitative XRF analysis using the fundamental parameters method or a multivariate calibration approach has been reported for geological materials [33, 34]. However, accurate quantitative analysis depends on the sample characteristics (ideally a homogeneous, infinitely thick sample with a flat and preferably polished surface) and on the calibration standards used; although the fundamental parameters method is a standardless approach, improved quantitative results can be achieved by using calibration standards. Because of the challenges in obtaining accurate quantitative μXRF results, μXRF is included in this study solely as an additional means of evaluating the homogeneity of the three CFGS glasses. XRF is reported as a technique used to characterize the homogeneity of NIST SRM[®] 1830 and 1831 in their respective Certificates of Analysis [40,41]. It should be noted that the three new Corning Float Glass Standards (CFGS) can potentially be useful to improve and validate quantitative results using μXRF .

While soda-lime glass matrix-matched standards have been developed by a joint BKA-Schott effort for calibration purposes [23], these FGS 1 and FGS 2 series of glasses are not certified materials and are available only upon request to the BKA in Germany. The aim of the current effort is to develop similar concentration matrix-matched glass standards to the BKA-Schott FGS series of glasses (FGS 1 and FGS 2) that are sufficiently homogeneous for use in micro sampling methods such as LA-ICP-MS, and potentially μ XRF, and to collaborate with NIST scientists to certify these glasses as standard reference materials for future distribution to the wider scientific community.

2. Experimental Section

2.1. Production of New Glass Standards

Three new glasses (CFGS1, CFGS2 and CFGS3) were produced by Corning Research and Development Corporation in 2020 as part of an FIU-Corning joint research activity. In total, 32 selected elements were added as carbonates or oxides to the soda-lime glass matrix and fused/melted at high temperature using platinum cups at three (3) different target concentrations representing low, medium and high concentration ranges for each of the 32 selected elements. Seventeen elements (shown in Fig. 1 and listed in Table 3) were analyzed for this study and an additional 15 elements (B, Na, Sb, Ni, Cu, Co, Mo, Y, W, Sn, Si, Cr, V, Zn, Ga) were added to the melt but not analyzed for this study. The melt was then refined and homogenized by stirring and re-melted to improve the homogeneity of the melt. Nine different canes (aka rods) with no visible or detectable inclusions were obtained. The target concentrations of the elements in three standards were informed by the expected range in concentrations for soda-lime glass samples expected to be encountered in forensic casework. Figure 1 illustrates the distribution of two different databases of glass collected from the elemental analysis of vehicle windows at Florida International University (FIU) in the USA (n=420) and from a much larger variety of glass sources derived from casework submitted to the Bundeskriminalamt (BKA) in Germany (n=385).

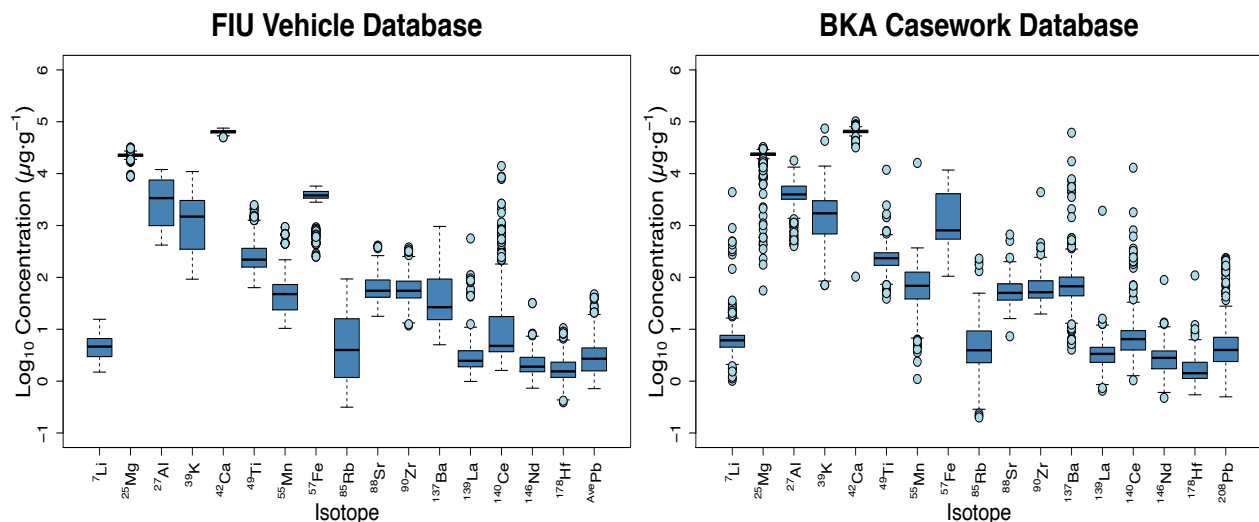


Figure 1. (Left) Box-and-whisker plot for the log₁₀ concentration ($\mu\text{g}\cdot\text{g}^{-1}$) range for 420 vehicle samples collected and analyzed at FIU. (Right) Box-and-whisker plot for the range of 385 BKA casework samples.

Sub samples from three rods (#1, #5 and #9) for each of the CFGS glasses were collected in triplicate for initial analysis by LA-ICP-MS and by μXRF (Figure 2 shows the set of CFGS2 and CFGS3 glass sub-samples). The target concentrations of the analytes in CFGS1 and in CFGS2 were designed to closely match the previously used BKA-Schott FGS 1 and FGS 2 series of calibration standards [23] so that any databases created using the FGS 2 as a calibration standard would potentially be compatible with databases created with the new CFGS2 standard. Additional details of the manufacture of the glass are proprietary and not included in this manuscript.

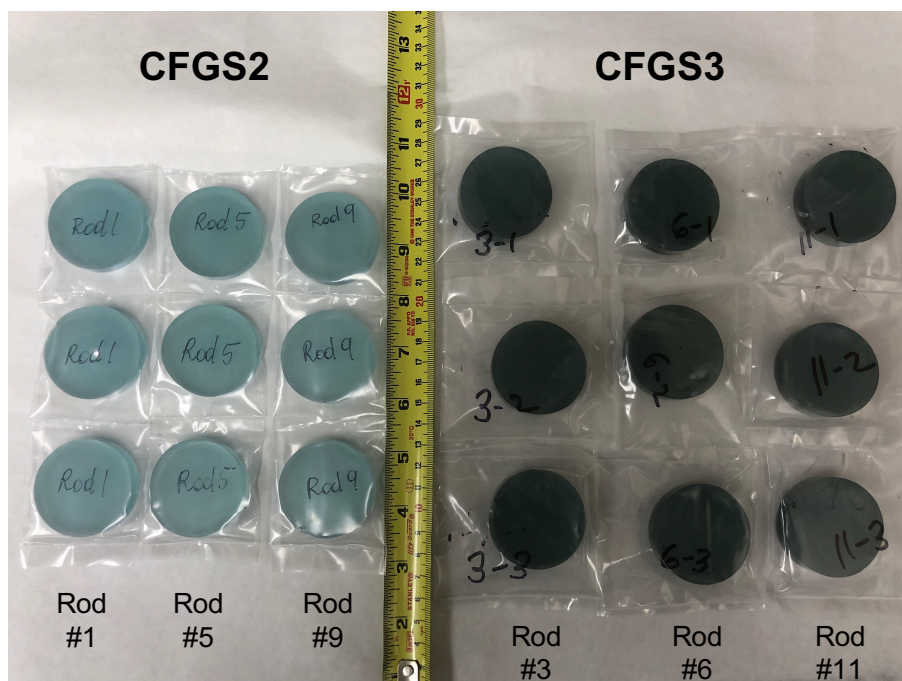


Figure 2. Sub-samples from CFGS2 (left) rods #1, #5 and #9 and CFGS3 (right) rods #3, #6 and #11 with each sub-sample measuring 4.5 cm in diameter and 1.0 cm in thickness.

The concentrations of the selected elements in the three new matrix-matched glass standards CFGS1 (low concentration), CFGS2 (medium concentration) and CFGS3 (high concentration) were determined using the ASTM E2927-16e1 test method by 8 independent data acquisitions at 7 different laboratories. The measurement of several isotopes of the target elements (other than Pb) is not important for the forensic analysis and comparison of glass and not recommended.

2.2. Experimental Parameters

Table 1 lists the instrumental parameters used for both the LA sampling and for the ICP-MS data acquisition in use by all the participating laboratories. The analytical parameters described in ASTM “*Standard Test Method for Determination of Trace Elements in Soda-Lime Glass Samples Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry for Forensic Comparisons*” [30] were followed closely but some flexibility in adjusting parameters is permitted by the method. A particular manufacturer of either the LA or the ICP-MS instrumentation is not prescribed, however. Glass samples are recommended to be washed, pre-ablated, or both but do not necessarily need to be embedded in a media prior to ablation. Well-characterized standards such as

the NIST SRM[®] 612 or, preferably, the BKA FGS 2 glass (both with a ~ 72% SiO₂ matrix concentration) are used as a single-point calibration standard. After a ~ 20 s blank is collected, the signal from the ablation of a single laser spot is collected for sufficient time (~ 60 s) with the first 20 s of the ablation signal ignored to improve signal stability. The signal acquired from ²⁹Si is used in normalization of all other signals and to account for ablation yield. The area of the transient signal resulting from the ablation for each isotope analyte is integrated and compared to the area of the same isotopes of the FGS 2 (or similar glass calibration standard) to convert counts per second (cps) to concentration. A suitable reference material (e.g., NIST SRM[®] 1831 glass) is used as a calibration check to compare the previously determined (consensus) values for the reference material to the measured values. Some important parameters recommended include the use of a matrix-matched standard and the selection of a range of ablation spot size (~ 50 μm - 100 μm) with a corresponding ablation depth range between ~ 80 μm - 150 μm deep. Sufficient fluence is used to reach the photochemical regime and a minimum number of replicates for each of the calibration standards, check standards, and glass samples to be compared are prescribed within the method. As stated in the ASTM method, if this method is used for other than soda-lime glass, the concentration of the normalization standard shall be determined prior to quantification.

Table 1. Instrumental parameters used for the elemental analysis of glass fragments using LA-ICP-MS and ASTM E2927-16e1.

Lab ID	A	B	C	D	E	F	G	H
ICPMS instrument	Agilent Tech. 7900	Agilent Tech. 7700	Agilent Tech. 7700	Thermo iCAP-Q	Thermo iCAP Q	Agilent Tech. 7800	Perkin Elmer Nexion 350X	Agilent Tech. 7700
RF power (W)	1540	1550	1350	1450	1500	1550	1600	1550
Ar gas flow (Lmin ⁻¹)	0.75	1.0	0.40	1.0	0.70	0.90	1.0	1.0
LA instrument	ESI NWR213	New Wave UP213	CETAC LSX-213 G2	New Wave NWR193 (Excimer)	Applied Spectra J200	Applied Spectra J200	Applied Spectra J200	New Wave UP213
Carrier gas and flow rate (Lmin ⁻¹)	He, 0.8	He, 0.9	He, 0.8	He, 0.95	He, 0.90	He, 0.90	He, 0.6	He, 0.90
Wavelength (nm)	213	213	213	193	213	266	266	213
Spot size (μm)	80	90	50	80	100	50	50	90
Fluence (Jcm ⁻²)	10	~ 25	~ 10	2.0	35	20	15	~ 25
Tube length (m)	2	3.8	0.8	1.5	0.85	4.7	0.7	3.8
Ablation cell volume (cm ³)	TwoVol2	25-50	50	TwoVol2	25	35-41	25	25-50

As stated within the ASTM E2927-16 method, the laser beam is focused at the surface of the sample and a single spot ablation mode is used at the spot size and depth ranges recommended above with a laser ablation repetition rate of 10 Hz. A minimum of three replicates on each sample is measured and, a minimum of three fragments are measured when enough sample is available such as when a known source is characterized. A minimum of three (3) replicates from three different samples of the known source are collected in order to characterize any heterogeneities within the known source.

Micro XRF analyses were conducted on a Bruker M4 Tornado, equipped with a Rh X-ray tube with an incident angle of $\approx 50^\circ$ and a beryllium window with a 100 μm thickness, poly-capillary optics with a 20 μm spot size, and two Silicon Drift Detectors (SDD), each with a detection area of 60 mm^2 and a beryllium window with a 13 μm thickness. The following parameters were used for analysis: 50 kV accelerating voltage, 300 μA filament current (deadtime $\approx 7\%$), 600 s live acquisition time, and 130 kilo counts per second (kcps) pulse throughput (resolution ≈ 143 eV FWHM Mn K_α). Prior to analysis, the detector energy calibration was completed using Zr. Additionally, NIST SRM[®] 1831 was analyzed daily to ensure a limit of detection ≤ 75 $\mu\text{g}\cdot\text{g}^{-1}$ for Ti and Sr, as recommended in ASTM E2926.

3. Results and Discussion

3.1 Consensus Concentration Values for CFGS1, CFGS2 and CFGS3

Table 2 lists the individual results for each of the participating labs for the analysis of the CFGS2 glass sample, when using FGS 2 as a calibration standard. Table 3 provides the consensus concentration values (and related uncertainties) for the 17 elements analyzed in CFGS1, CFGS2 and CFGS3 reporting the mean and standard deviations (SD) and relative standard deviations (reported as % RSD) for 8 independent analyses at 7 different laboratories (n= 369 replicate measurements).

Table 3. Consensus concentrations in $\mu\text{g}\cdot\text{g}^{-1}$ for the seventeen elements analyzed in the new CFGS series of glass standards (mean \pm one standard deviation and relative standard deviation (as % RSD) for n= 369 replicate measurements) with 45-54 replicates analyzed by 8 different analysts at 7 different labs.

Element	CFGS1			CFGS2			CFGS3		
	Mean $\mu\text{g}\cdot\text{g}^{-1}$	± 1 SD $\mu\text{g}\cdot\text{g}^{-1}$	% RSD	Mean $\mu\text{g}\cdot\text{g}^{-1}$	± 1 SD $\mu\text{g}\cdot\text{g}^{-1}$	% RSD	Mean $\mu\text{g}\cdot\text{g}^{-1}$	± 1 SD $\mu\text{g}\cdot\text{g}^{-1}$	% RSD
⁷ Li	4.1	0.2	4.7	9.7	0.3	3.1	23.2	0.7	3.0
²⁴ Mg	23200	420	1.8	23700	480	2.0	10000	190	1.9
²⁷ Al	1330	52	3.9	7500	210	2.8	10400	480	4.6
³⁹ K	940	24	2.6	4600	110	2.4	6870	190	2.8
⁴² Ca	59000	1400	2.4	60200	1700	2.8	60600	1800	3.0
⁴⁹ Ti	100	3	3.4	354	9	2.6	2480	74	3.0
⁵⁵ Mn	55	1	2.6	239	6	2.4	929	24	2.5
⁵⁷ Fe	517	33	6.4	2270	42	1.9	5210	111	2.1
⁸⁵ Rb	9.4	0.3	2.9	33	1	2.7	91	3	3.2
⁸⁸ Sr	127	4	3.1	319	11	3.6	457	16	3.5
⁹⁰ Zr	65	3	4.0	227	9	4.0	396	18	4.6
¹³⁷ Ba	43	2	3.5	199	6	3.2	978	35	3.5
¹³⁹ La	4.4	0.2	4.2	12.4	0.5	3.9	37.7	1.6	4.2
¹⁴⁰ Ce	4.9	0.2	3.8	12.8	0.4	3.4	33.2	1.2	3.6
¹⁴⁶ Nd	4.1	0.2	5.0	12.2	0.5	4.1	31.6	1.5	4.7
¹⁷⁸ Hf	5.3	0.2	4.5	17.9	0.8	4.4	43.7	2.4	5.5
AvePb	4.5	0.3	6.2	14.5	0.5	3.6	38.2	1.8	4.8

One lab conducted 54 replicate measurements and the other 7 labs conducted 44-45 replicate measurements (three separate samples from each of the three rods (Rod #1, #5 and #9) were each measured with 5 replicates). Table 4 lists the consensus concentration values (and related uncertainties) for the 17 elements in the CFGS series of glass standards reporting the laboratory grand mean \pm one standard deviation and relative standard deviation (as % RSD) for n= 8 laboratories.

Table 4. Consensus concentrations in $\mu\text{g}\cdot\text{g}^{-1}$ for the seventeen elements in the CFGS series of glass standards (grand mean \pm one standard deviation and relative standard deviation (as % RSD) for N = 8 laboratories) with 45-54 replicates analyzed by 8 different analysts at 7 different labs.

Element	CFGS1			CFGS2			CFGS3		
	Mean $\mu\text{g}\cdot\text{g}^{-1}$	± 1 SD $\mu\text{g}\cdot\text{g}^{-1}$	% RSD	Mean $\mu\text{g}\cdot\text{g}^{-1}$	± 1 SD $\mu\text{g}\cdot\text{g}^{-1}$	% RSD	Mean $\mu\text{g}\cdot\text{g}^{-1}$	± 1 SD $\mu\text{g}\cdot\text{g}^{-1}$	% RSD
⁷ Li	4.1	0.1	2.0	9.7	0.2	1.6	23.2	0.4	1.6
²⁴ Mg	23200	260	1.1	23700	350	1.5	10000	94	0.9
²⁷ Al	1330	44	3.3	7500	150	2.0	10400	460	4.4
³⁹ K	940	18	1.9	4600	76	1.6	6870	124	1.8
⁴² Ca	59000	640	1.1	60200	1180	1.9	60600	1140	1.9
⁴⁹ Ti	100	2	2.1	354	5	1.5	2480	54	2.2
⁵⁵ Mn	54.5	1.2	2.2	239	5	2.0	928	17	1.9
⁵⁷ Fe	517	33	6.4	2270	22	1.0	5210	63	1.2
⁸⁵ Rb	9.4	0.1	1.5	32.8	0.6	1.7	90.5	2.2	2.4
⁸⁸ Sr	127	2	1.5	319	9	3.0	457	12	2.6
⁹⁰ Zr	65.2	1.8	2.7	227	7	2.9	396	15	3.8
¹³⁷ Ba	42.7	0.7	1.6	199	5	2.4	978	18	1.8
¹³⁹ La	4.4	0.1	2.2	12.4	0.3	2.7	37.7	1.0	2.7
¹⁴⁰ Ce	4.9	0.1	1.9	12.8	0.3	2.5	33.2	0.6	1.8
¹⁴⁶ Nd	4.1	0.1	2.3	12.1	0.3	2.7	31.6	1.0	3.1
¹⁷⁸ Hf	5.3	0.1	2.3	17.9	0.6	3.2	43.6	1.9	4.2
AvePb	4.5	0.2	5.2	14.5	0.3	2.2	38.2	1.0	2.5

3.2 Homogeneity Study

One-way Analysis of Variance (ANOVA) followed by Tukey's Honestly Significant Difference (HSD) was used to determine any significant differences between the rods for the reported concentrations of each of the 17 elements. The reported concentrations from the 8 independent sets of data collected from the participating laboratories were used as input for the ANOVA. Although the overall variance within a lab (Table 2) and between the labs (Tables 3 and 4) are low (typically < 5% RSD), suggesting that the three glass rods (1,5 and 9) are very homogeneous, the more sensitive ANOVA results in significant differences (95% confidence) between the middle rods and the last rods for CFGS1 and for CFGS3 for some of the elements using the ANOVA followed by Tukey's HSD. CFGS2 produces very homogeneous results, according to ANOVA followed by Tukey's HSD with only Ca resulting in a significant difference between the middle rod (#5) and the last rod (#9) and all other analytes in CFGS2 resulting in no significant differences between all three rods. Figure 3 illustrates the distribution of all of the measurements (n=369) for the Ca values reported in the eight sets of data for CFGS2 when calibrated with FGS2. The CFGS1 and CFGS3 results show more pronounced differences for additional elements but only between the last two rods compared. These results may limit which rods may be selected for grouping as calibration standards for distribution in the future, but analysis of additional data is needed to make this determination.

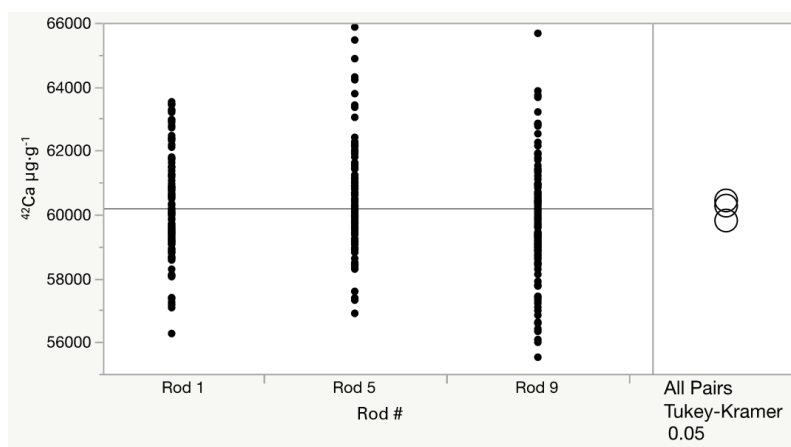


Figure 3. Distribution of the ^{42}Ca concentration ($\mu\text{g}\cdot\text{g}^{-1}$) values from all of the measurements (n=369) reported in the eight sets of data for the CFGS2 glass using FGS2 as a calibration standard.

The homogeneity of CFGS1, CFGS2, and CFGS3 was also evaluated, and compared to NIST SRM[®] 1831, using μ XRF. Elements were considered above the limit of detection (LOD) if the signal-to-noise (SNR) ratio was greater than 3 and above the limit of quantitation (LOQ) if the SNR was greater than 10. SNR calculations were completed following the recommendations given by Ernst et al. in [35]. Nine replicate measurements were collected on each of 9 fragments (3 fragments each from rod 1, 5, and 9) for CFGS1 ($n = 81$), and 6 replicate measurements were collected on each of 9 fragments for CFGS2 and CFGS3 ($n = 54$). For NIST SRM[®] 1831, 3 replicate measurements were collected on each of 16 days of analysis, for a total of 48 replicate measurements. Quantitative analysis was accomplished using the Bruker M4 software, which applies the fundamental parameters method but are not reported here because of the challenges in obtaining accurate quantitative results using μ XRF. Instead, RSDs are reported to provide a measure of homogeneity within each CFGS glass (and between the rods of the same CFGS glass). Table 5 lists the RSDs for the three CFGS glasses and for NIST SRM[®] 1831. The RSDs are below 3% for most elements, which are comparable to the benchmark of the well-characterized NIST SRM 1831, indicating excellent homogeneity for the new CFGS glasses. Elements with slightly higher RSDs (5 % - 10 %) had relatively low SNRs (≈ 25) compared to elements with RSDs below 5 % ($\text{SNR} > 50$). Aluminum in CFGS1 was the only element that resulted in a high RSD (> 20 %). This is partly due to the difficulty of deconvoluting the Al peak from the neighboring large Si peak when the concentration of Al is relatively low ($\leq 1500 \mu\text{g}\cdot\text{g}^{-1}$). At the higher concentrations ($> 5000 \mu\text{g}\cdot\text{g}^{-1}$) present in CFGS2, CFGS3, and NIST SRM 1831, the Al RSD is below 2 %.

Table 5. RSD (%) for n μ XRF measurements collected on CFGS1, CFGS2, CFGS3, and NIST SRM1831. The RSD is reported for elements above the LOD (SNR > 3). Bracketed values indicate SNR < 10.

Element	CFGS1 (n = 81)	CFGS2 (n = 54)	CFGS3 (n = 54)	NIST SRM 1831 (n = 48)
Na	1.14	1.05	1.94	0.71
Mg	1.06	1.00	1.94	0.69
Al	23.71	0.88	1.77	1.06
K	3.96	0.72	0.59	0.88
Ca	0.46	0.70	0.50	0.40
Ti	2.04	1.00	0.63	1.55
Mn	2.25	1.38	0.68	7.07
Fe	1.73	1.34	0.71	0.88
Zn	5.37	3.73	3.01	4.68
Rb	7.18	2.35	1.20	[13.14]
Sr	0.84	1.86	0.81	2.28
Zr	1.40	2.29	1.00	3.56
Ba	< LOD	4.04	1.74	< LOD
Pb	< LOD	[6.49]	3.90	< LOD

3.3 Continuity Study Comparing FGS 2 and CFGS2 as Calibration Standards

In order to establish elemental analysis databases of glass samples that are comparable over time within the same lab and also to share between labs, the continuity in reporting concentration results is necessary. The NIST SRM[®] 1831 has been incorporated as a calibration check during every analytical run and is used to establish continuity between the use of FGS 2 and CFGS2 as calibrants for the method [30]. The NIST SRM[®] 1831 values generated by all the participating laboratories using FGS 2 and CFGS2 (itself calibrated using FGS 2 glass) were used to determine any differences between the FGS 2-calibrated values and the CFGS2-calibrated values. Table 6 lists the NIST SRM[®] 1831 previously reported values (when available) compared to lab mean NIST SRM[®] 1831 values determined using FGS 2 and CFGS2 as calibration standards (n=6-27). Table 7 lists the NIST SRM 1831 values reported by each participating laboratory for both FGS 2 and CFGS2 and also shows any differences between the FGS 2-calibrated and CFGS2-calibrated data for NIST SRM[®] 1831. All of the participating laboratories report relative differences (as reported by %) below 5 % and most laboratories report differences below 2 % for most analytes.

4. Conclusion

Good data agreement among the 8 independent sets of measurements results from following the prescribed analytical parameters within the ASTM standard test method, regardless of the laser manufacturer, laser wavelength used, or the ICP-MS instrument manufacturer used in the data acquisition. The consistency in the quantitative analysis of the trace elements in float glass samples (assuming ~ 72% SiO₂ matrix concentration) also allows for the development of LA-ICP-MS databases over time in the same laboratory and potentially for sharing databases between different laboratories. The development of the CFGS glasses may also be suitable to improve and validate the quantitative analysis of glass using μ XRF in the future. The development of databases is important because, while the use of the LA-ICP-MS ASTM method results in excellent analytical figures of merit and allows for the comparison between a glass fragment collected at a crime scene and glass collected from a known source for association questions, it is also important to qualify the significance of finding glass with that particular elemental profile within the population of glass in circulation that could serve as a potential source(s), other than the source in question for a particular case. In order to answer this question, databases that include many different sources of glass are needed to determine the “random match probability” (or a reasonable estimate, as best that can be achieved) as evidenced by the frequency of a given glass composition profile that is encountered in a given laboratory. The interpretation of the analytical results of the ASTM method currently involves a binary decision of either finding a difference in all of the elements of the compared items and arriving at the conclusion that “...the questioned fragment did not originate from the same source of broken glass,” or not finding a difference in their elemental profile, resulting in a conclusion that the “possibility that the fragments originated from the same source of glass may not be eliminated”. Recent studies [36-39] describe an alternative approach to the interpretation of glass comparisons by calculating a source likelihood ratio (LR) for the multivariate comparisons of the elements in glass, providing an expanded range of “significance” statements over the binary decision of “exclude” or “fail to exclude” and now allowing for a numerical assessment of

the strength of the evidence comparison. This provides a numerical LR value for the multi-element comparison that results in low LRs (equivalent to exclusion) or high LRs (equivalent to high confidence of an association) and values in between these upper and lower bounds. In addition, studies show that “ambiguous” LR values (values not supporting either proposition) are explained by small but noticeable systematic deviations in the data acquisition over time, heterogeneity of the glass samples in question, or chemical relatedness between samples from different sources (e.g., the glass samples originated from different glass objects, but the glass was manufactured in the same plant within a relatively small time span) [38-39]. Relevant glass databases containing background information related to the elemental composition of glass are needed for these LR calculations and matrix-matched calibration standards that are certified and widely available are, in turn, needed to create the databases. The LA-ICP-MS and μ XRF results for the CFGS series of glasses suggest that these new glasses are sufficiently homogeneous for micro sampling. In addition, the reported consensus values for the CFGS2 glass, the most similar in concentration ranges to soda-lime glass made by the float process expected to be submitted to the forensic laboratory, may be used as a calibration standard to replace or complement the FGS 2 calibration standard currently in wide use. Finally, in addition to the 17 elements reported here, another 15 elements (B, Na, Sb, Ni, Cu, Co, Mo, Y, W, Sn, Si, Cr, V, Zn, Ga) were included in the formulations of the CFGS series at different concentration levels for each of the CFGS glasses. These additional 15 elements were not measured for this study but may be used in calibration strategies in the future.

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are identified in this manuscript in order to specify the experimental procedures adequately. Such identification is not intended to imply recommendation or endorsement by any of the authors and their respective organizations, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose. Ms. Oriana Ovide assisted CLM at WVU in collecting data.

References

1. O.V. Borisov, X.L. Mao, R.E. Russo, Effects of crater development on fractionation and signal intensity during laser ablation inductively coupled plasma mass spectrometry, *Spectrochim. Acta. B* 55 (11) (2010) 1693–1704. [https://doi.org/10.1016/S0584-8547\(00\)00272-X](https://doi.org/10.1016/S0584-8547(00)00272-X)
2. O. Borisov, C. Bannochie, and R. Russo, Laser Ablation Inductively Coupled Plasma Mass Spectrometry of Pressed Pellet Surrogates for Pu Materials Disposition, *Appl. Spectrosc.* 55 (2001) 1304-1311.
3. J.H. Yoo, O.V. Borisov, X. Mao, R.E. Russo, Existence of Phase Explosion during Laser Ablation and Its Effects on Inductively Coupled Plasma-Mass Spectroscopy, *Anal. Chem.* 73 (2001) 2288-2293.
4. F. Poitrasson, X. Mao, S.S. Mao, R. Freydier, R.E. Russo, Comparison of Ultraviolet Femtosecond and Nanosecond Laser Ablation Inductively Coupled Plasma Mass Spectrometry Analysis in Glass, Monazite, and Zircon, *Anal. Chem.* 75 (2003) 6184-6190.
5. H. Liu, O.V. Borisov, X. Mao, S. Shuttleworth, R.E. Russo, Pb/U Fractionation during Nd:YAG 213 nm and 266 nm Laser Ablation Sampling with Inductively Coupled Plasma Mass Spectrometry, *Appl. Spectrosc.* 54 (2000) 1435-1442.
6. H. Liu, X. Mao, R.E. Russo, Representative sampling using single-pulse laser ablation with inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 16 (2001) 1115-1120.
7. R.E. Russo, X. Mao, J.J. Gonzalez, S.S. Mao, Femtosecond laser ablation ICP-MS, *J. Anal. At. Spectrom.* 17 (2002) 1072-1075.
8. J. Gonzalez, X.L. Mao, J. Roy, S.S. Mao, R.E. Russo, Comparison of 193, 213 and 266 nm laser ablation ICP-MS, *J. Anal. At. Spectrom.* 17 (2002) 1108-1113.
9. Q. Lu, S.S. Mao, X. Mao, R.E. Russo, A thermal model of phase explosion for high-power laser ablation, In: *Proceedings of Society of Photo-optical Instrumentation engineers*, 4760, (2202) S. 959–964.
10. R.E. Russo, X. Mao, S.S. Mao, The Physics of Laser Ablation in Microchemical Analysis, *Anal. Chem.* 74(3)(2002) 71A-77A.

11. J. González, C. Liu, X. Mao, R.E. Russo, UV-femtosecond laser ablation-ICP-MS for analysis of alloy samples, *J. Anal. At. Spectrom.* 19 (2004) 1165-1168.
12. C. Liu, X.L. Mao, S.S. Mao, X. Zeng, R. Greif, R.E. Russo, Nanosecond and Femtosecond Laser Ablation of Brass: Particulate and ICPMS Measurements, *Anal. Chem.* 76 (2004) 379-383.
13. I. Horn, D. Günther, The influence of ablation carrier gasses Ar, He and Ne on the particle size distribution and transport efficiencies of laser ablation-induced aerosols: implications for LA-ICP-MS, *Appl. Surf. Sci.* 207 (2003) 144-157.
14. M. Guillong, D. Günther, Effect of particle size distribution on ICP-induced elemental fractionation in laser ablation-inductively coupled plasma-mass spectrometry, *J. Anal. At. Spectrom.* 17 (2002) 831-837.
15. M. Guillong, I. Horn, D. Günther, A comparison of 266 nm, 213 nm and 193 nm produced from a single solid state Nd:YAG laser for laser ablation ICP-MS, *J. Anal. At. Spectrom.* 18 (2003) 1224-1230.
16. H. R. Kuhn, M. Guillong, D. Günther, Size-related vaporisation and ionisation of laser-induced glass particles in the inductively coupled plasma, *Anal. Bioanal. Chem.* 378 (2004) 1069-1074.
17. H. R. Kuhn, D. Günther, Laser ablation-ICP-MS: particle size dependent elemental composition studies on filter-collected and online measured aerosols from glass, *J. Anal. At. Spectrom.* 19 (2004) 1158-1164.
18. P. Weis, H.P. Beck, D. Günther, Characterizing ablation and aerosol generation during elemental fractionation on absorption modified lithium tetraborate glasses using LA-ICP-MS, *Anal. Bioanal. Chem.* 381 (2005) 212-224.
19. A. J. G. Mank, P. R. D. Mason, A critical assessment of laser ablation ICP-MS as an analytical tool for depth analysis in silica-based glass samples, *J. Anal. At. Spectrom.* 14 (1999) 1143-1153.
20. T. Trejos, S. Montero, J.R. Almirall, Analysis and comparison of glass fragments by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and ICP-MS, *Anal. Bioanal. Chem.* 376 (2003) 1255-1264.
21. T. Trejos, J.R. Almirall, Sampling strategies for the analysis of glass fragments by LA-ICP-MS: Part I. Micro-homogeneity study of glass and its application to the interpretation of forensic evidence, *Talanta.* 67 (2005) 388-395.
22. T. Trejos, J.R. Almirall, Sampling strategies for the analysis of glass fragments by LA-ICP-MS: Part II: Sample size and sample shape considerations, *Talanta.* 67 (2005) 396-401.

23. C. Latkoczy, S. Becker, M. Dücking, D. Günther, J.A. Hoogewerff, J.R. Almirall, J. Buscaglia, A. Dobney, R.D. Koons, S. Montero, G.J.Q. van der Peijl, W.R.S. Stoecklein, T. Trejos, J.R. Watling, V.S. Zdanowicz, Development and Evaluation of a Standard Method for the Quantitative Determination of Elements in Float Glass Samples by LA-ICP-MS, *J. Forensic Sci.* 50 (2005) 1-15.
24. K. Smith, T. Trejos, R.J. Watling, J. Almirall, A guide for the quantitative elemental analysis of glass using laser ablation inductively coupled plasma mass spectrometry. *Spectrosc.* 27 (3) (2006) 69.
25. S. Berends-Montero, W. Wiarda, P. de Joode, G. van der Peijl, Forensic analysis of float glass using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS): validation of a method, *J. Anal. At. Spectrom.* 21 (2006) 1185-1193.
26. B.E. Naes, S. Umpierrez, S. Ryland, C. Barnett, J.R. Almirall, A comparison of laser ablation inductively coupled plasma mass spectrometry, micro X-ray fluorescence spectroscopy, and laser induced breakdown spectroscopy for the discrimination of automotive glass, *Spectrochimica Acta Part B: Spectrosc.* 63 (2008) 1145-1150.
27. P. Weis, M. Dücking, P. Watzke, S. Menges, S. Becker, Establishing a match criterion in forensic comparison analysis of float glass using laser ablation inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 26 (2011) 1273-1284.
28. T. Trejos, R. Koons, P. Weis, S. Becker, T. Berman, C. Dalpe, M. Dücking, J. Buscaglia, T. Eckert-Lumsdon, T. Ernst, C. Hanlon, A. Heydon, K. Mooney, R. Nelson, K. Olsson, E. Schenk, C. Palenik, E.C. Pollock, D. Rudell, S. Ryland, A. Tarifa, M. Valadez, A. van Es, V. Zdanowicz, J. Almirall, Forensic analysis of glass by μ -XRF, SN-ICP-MS, LA-ICP-MS and LA-ICP-OES: evaluation of the performance of different criteria for comparing elemental composition, *J. Anal. At. Spectrom.* 28 (2013) 1270-1282.
29. T. Trejos, R. Koons, S. Becker, T. Berman, J. Buscaglia, M. Dücking, T. Eckert-Lumsdon, T. Ernst, C. Hanlon, A. Heydon, K. Mooney, R. Nelson, K. Olsson, C. Palenik, E. Pollock, D. Rudell, S. Ryland, A. Tarifa, M. Valadez, P. Weis, J. R. Almirall, Cross-validation and evaluation of the performance of methods for the elemental analysis of forensic glass by μ -XRF, ICP-MS, and LA-ICP-MS, *Anal. Bioanal. Chem.* 405 (2013) 5393-5409.
30. E2927-16e1 In Standard Test Method for the Determination of Trace Elements in Soda-Lime Glass Samples Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry for Forensic Comparisons, ASTM International: 2016.
31. M. Haschke. Laboratory Micro-X-Ray Fluorescence Spectroscopy: Instrumentation and Applications. Springer, New York, 2014.
32. E2926-17 In Standard Test Method for the Forensic Comparison of Glass Using Micro X-ray Fluorescence (μ XRF) Spectrometry, ASTM International: 2017.
33. S. Akbulut. Validation of classical quantitative fundamental parameters method using multivariate calibration procedures for trace element analysis in ED-XRF, *J. Anal. At. Spectrom.* 28 (2014) 853-860.

34. R. Rosseau. How to Apply the Fundamental Parameters Method to the Quantitative X-ray Fluorescence Analysis of Geological Materials, *J. of Geosciences and Geomatics*, 1 (2013) 1-7.
35. T. Ernst, T. Berman, J. Buscaglia, T. Eckert-Lumsdon, C. Hanlon, K. Olsson, C. Palenik, S. Ryland, T. Trejos, M. Valdez, and J. Almirall. Signal-to-noise ratios in forensic glass analysis by micro X-ray fluorescence spectrometry, *XRay Spectrom.* 43 (2014) 13-21.
36. R. Corzo, T. Hoffman, P. Weis, J. Franco-Pedroso, D. Ramos, J.R. Almirall, The Use of LA-ICP-MS Databases to Estimate Likelihood Ratios for the Forensic Analysis of Glass Evidence, *Talanta*. 186 (15) (2018) 655-661.
37. T. Hoffman, R. Corzo, P. Weis, E. Pollock, A. v Es, W. Wiarda, A Stryjnik, H Dorne, A Heydon, E Hoise, S Le Franc, X Huifang, B Pena, T Scholz, J Gonzalez, J.R. Almirall, An Interlaboratory Evaluation of LA-ICP-MS Analysis of Glass and the Use of a Database for the Interpretation of Glass Evidence, *J of For. Chem.* (11) (2018) 65-76.
38. A. Akmeemana, P. Weis, R. Corzo, D. Ramos, P. Zoon, T. Trejos, T. Ernst, E. Pollock, E. Bakowska, C. Neumann, J.R. Almirall, Interpretation of Chemical Data from Glass Analysis for Forensic Purposes, *J. Chemom.* (2020), e3267.
39. A. Gupta, R. Corzo, A. Akmeemana, K. Lambert, K. Jimenez, J.M. Curran, J.R. Almirall, Dimensionality reduction of multielement glass evidence to calculate likelihood ratios, *J. Chemom.* (2020) , DOI: 10.1002/cem.3298.
40. SRM 1830; *Soda-Lime Float Glass*; National Institute of Standards and Technology OR National Bureau of Standards; U.S. Department of Commerce: Gaithersburg, MD (12 July 2017).
41. SRM 1831; *Soda-Lime Sheet Glass*; National Institute of Standards and Technology OR National Bureau of Standards; U.S. Department of Commerce: Gaithersburg, MD (12 July 2017).

Table 2. Individual laboratory results for the CFGS2 glass concentrations using FGS 2 as the calibration standard (n=45-54).

CFGS2	Lab A (n=54)			Lab B (n=45)			Lab C (n=45)			Lab D (n=45)			Lab E (n=45)			Lab F (n=45)			Lab G (n=45)			Lab H (n=45)		
Element Isotope	Lab Mean (µg·g ⁻¹)	± 1 SD	Lab %RSD	Lab Mean (µg·g ⁻¹)	± 1 SD	Lab %RSD	Lab Mean (µg·g ⁻¹)	± 1 SD	Lab %RSD	Lab Mean (µg·g ⁻¹)	± 1 SD	Lab %RSD	Lab Mean (µg·g ⁻¹)	± 1 SD	Lab %RSD	Lab Mean (µg·g ⁻¹)	± 1 SD	Lab %RSD	Lab Mean (µg·g ⁻¹)	± 1 SD	Lab %RSD	Lab Mean (µg·g ⁻¹)	± 1 SD	Lab %RSD
⁷ Li	9.6	0.1	1.3	9.7	0.3	2.6	9.6	0.2	2.1	9.9	0.5	4.8	9.6	0.3	3.2	9.8	0.2	2.5	9.5	0.2	2.2	9.9	0.3	2.5
²⁴ Mg	23700	180	0.8	23700	160	0.7	23200	400	1.7	23500	400	1.7	24200	510	2.1	23900	400	1.7	23400	300	1.3	24100	390	1.6
²⁷ Al	7590	88	1.2	7490	41	0.5	7240	170	2.3	7370	210	2.9	7720	180	2.3	7480	180	2.4	7490	160	2.1	7590	180	2.4
³⁹ K	4600	30	0.6	4570	28	0.6	4500	41	0.9	4600	120	2.6	4690	128	2.7	4690	95	2.0	4550	73	1.6	4730	103	2.2
⁴² Ca	60000	730	1.2	59500	410	0.7	58800	1330	2.3	59300	1610	2.7	62200	1870	3.0	60800	1520	2.5	59700	1060	1.8	615004	1340	2.2
⁴⁹ Ti	355	4	1.1	351	4	1.1	345	8	2.4	350	11	3.0	360	9	2.5	358	10	2.8	352	5	1.5	361	8	2.3
⁵⁵ Mn	238	2	0.9	236	1	0.6	237	5	2.0	237	4	1.6	250	5	1.9	239	5	2.0	236	4	1.5	240	4	1.5
⁵⁷ Fe	2290	21	0.9	2250	18	0.8	2280	48	2.1	2250	48	2.1	2310	40	1.8	2270	44	1.9	2260	36	1.6	2290	31	1.3
⁸⁵ Rb	32.5	0.4	1.1	32.1	0.4	1.2	32.4	0.7	2.0	32.8	0.9	2.8	33.7	1.0	3.0	33.2	0.8	2.4	32.2	0.5	1.7	33.4	0.8	2.3
⁸⁸ Sr	320	5	1.6	312	3	0.8	308	8	2.5	314	8	2.7	339	11	3.3	320	7	2.3	314	6	1.9	322	7	2.3
⁹⁰ Zr	229	4	1.7	224	2	0.8	219	6	2.9	222	8	3.7	241	7	2.9	225	8	3.6	230	8	3.6	229	8	3.5
¹³⁷ Ba	198	2	0.9	195	3	1.3	197	5	2.6	197	4	2.0	210	8	3.6	199	5	2.6	196	4	2.0	202	5	2.3
¹³⁹ La	12.4	0.2	1.3	12.2	0.2	1.6	12.2	0.4	3.4	12.1	0.4	3.1	13.2	0.5	4.0	12.4	0.4	2.8	12.4	0.5	4.1	12.6	0.4	2.8
¹⁴⁰ Ce	12.7	0.1	1.1	12.7	0.2	1.8	12.7	0.3	2.4	12.6	0.3	2.1	13.5	0.5	3.5	12.8	0.3	2.5	12.6	0.5	3.7	13.0	0.3	2.2
¹⁴⁶ Nd	12.2	0.2	1.8	11.8	0.3	2.4	11.9	0.4	3.2	12.0	0.5	4.3	12.9	0.5	4.1	12.2	0.4	2.9	12.1	0.5	4.3	12.3	0.3	2.6
¹⁷⁸ Hf	17.9	0.3	1.7	17.6	0.4	2.0	17.3	0.6	3.2	17.3	0.7	4.3	19.1	0.6	3.1	17.8	0.6	3.6	18.0	0.7	3.7	17.9	0.7	3.9
Ave Pb	14.2	0.4	2.7	14.6	0.3	1.8	14.4	0.4	2.6	14.2	0.5	3.8	15.0	0.3	2.1	15.0	0.5	3.0	14.3	0.6	4.0	14.4	0.4	3.1

Table 6. NIST SRM 1831 reported* (and consensus data*) compared to mean NIST 1831 values determined using FGS 2 and CFGS2 as calibration standards (n=15-27).

Element Isotope	Reported µg·g ⁻¹	FGS 2 Calibrated µg·g ⁻¹	CFGS2 Calibrated µg·g ⁻¹
⁷ Li	5.00	5.9	5.8
²⁴ Mg	21200	21100	20900
²⁷ Al	6380	6250	6180
³⁹ K	2740	2470	2440
⁴² Ca	58600	57900	57300
⁴⁹ Ti	114	108	107
⁵⁵ Mn	15.00	13.1	13.0
⁵⁷ Fe	608	590	585
⁸⁵ Rb	6.11	5.6	5.5
⁸⁸ Sr	89.12	81.6	80.1
⁹⁰ Zr	43.36	34.8	34.5
¹³⁷ Ba	31.50	30.3	29.8
¹³⁹ La	2.12	2.1	2.0
¹⁴⁰ Ce	4.54	4.2	4.2
¹⁴⁶ Nd	1.69	1.7	1.7
¹⁷⁸ Hf	1.10	1.0	1.0
Ave Pb	1.99	1.9	1.9

* Sources of Li, La and Nd reported values are historical data from a single lab over one year period (N = 42 days over a period of a year) [30], Mg, Al, K, Ca, Fe and Ti values are certified by NIST (NIST 1831 SRM Certificate), and the remaining elements (Mn, Rb, Sr, Zr, Ba, Ce, Hf and Pb) are reported in ASTM Test Method E2330 (values obtained by acid digestion ICP-MS during an interlaboratory study).

Table 7. NIST SRM 1831 values reported by each participating laboratory for both FGS 2 and CFGS2 and differences between the data for NIST 1831 (n=15-27).

Table 7.a NIST SRM 1831 values using FGS 2 as a calibration standard.

NIST SRM 1831	Lab A (n=27)			Lab B (n=15)			Lab C (n=15)			Lab D (n=15)			Lab E (n=15)			Lab F (n=15)			Lab G (n=15)			Lab H (n=15)		
	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD
⁷ Li	5.9	0.1	1.5	5.9	0.2	3.0	5.7	0.2	3.0	6.2	0.4	7.2	5.7	0.1	2.5	5.9	0.2	2.6	5.7	0.1	2.2	5.9	0.2	2.8
²⁴ Mg	21100	180	0.9	21200	188	0.9	20800	270	1.3	21300	450	2.1	21700	239	1.1	20800	341	1.6	20700	343	1.7	21200	372	1.8
²⁷ Al	6390	110	1.7	6330	34.9	0.6	6070	40.4	0.7	6140	217	3.5	6450	60.6	0.9	6140	111	1.8	6170	179	2.9	6300	121	1.9
³⁹ K	2530	30	1.2	2480	14	0.6	2420	19	0.8	2440	53	2.2	2520	48	1.9	2470	61	2.5	2480	55	2.2	2520	58	2.3
⁴⁰ Ca	58200	860	1.5	58200	490	0.8	57100	680	1.2	58000	2280	3.9	60600	1210	2.0	57100	1170	2.0	57800	1390	2.4	58700	1240	2.1
⁴⁸ Ti	110	1.9	1.7	109	1.4	1.3	105	2.1	2.0	108	6.3	5.8	110	2.2	2.0	106	3.9	3.6	108	3.3	3.0	110	2.5	2.3
⁵⁵ Mn	13.5	0.1	0.9	13.6	0.2	1.3	13.2	0.3	2.0	13.2	0.5	3.7	12.8	0.2	1.6	13.2	0.3	2.2	11.7	0.1	1.1	13.4	0.2	1.6
⁵⁷ Fe	577	5.6	1.0	560	7.5	1.3	639	12	1.9	538	20	3.7	585	9.4	1.6	591	16	2.8	641	8.3	1.3	590	10	1.7
⁸⁵ Rb	5.7	0.1	1.9	5.6	0.1	1.8	5.6	0.1	1.9	5.5	0.3	4.9	5.5	0.1	2.5	5.6	0.2	3.1	5.6	0.1	2.2	5.7	0.2	3.1
⁸⁶ Sr	88	1.3	1.4	87	1.2	1.4	75	0.8	1.1	81	1.6	1.9	83	2.5	3.0	80	4.9	6.1	80	4.5	5.7	84	3.9	4.6
⁹⁰ Zr	39	1.0	2.5	38	1.2	3.0	31	0.2	0.7	35	1.8	5.2	36	0.9	2.6	33	1.8	5.3	33	2.2	6.6	36	1.5	4.2
¹³⁷ Ba	31	0.6	1.8	31	0.6	1.9	30	0.6	2.1	31	1.3	4.2	30	1.1	3.6	30	0.7	2.4	30	0.8	2.6	31	0.7	2.2
¹³⁹ La	2.1	0.1	2.5	2.1	0.1	2.9	2.0	0.05	2.2	2.1	0.1	4.0	2.0	0.1	3.3	2.1	0.1	3.5	2.1	0.1	3.5	2.1	0.05	2.2
¹⁴⁰ Ce	4.3	0.1	1.5	4.3	0.1	1.6	4.2	0.1	2.1	4.3	0.1	2.4	4.2	0.09	2.2	4.2	0.1	2.7	4.3	0.1	1.8	4.3	0.1	2.5
¹⁴⁰ Nd	1.8	0.04	2.2	1.7	0.1	5.2	1.7	0.04	2.7	1.7	0.3	15	1.7	0.1	4.6	1.7	0.1	5.5	1.7	0.1	3.5	1.7	0.1	4.4
¹⁷³ Hf	1.1	0.04	3.5	1.0	0.1	5.9	0.9	0.03	2.8	0.9	0.1	16	1.0	0.05	5.5	0.9	0.1	5.6	1.0	0.1	6.6	1.0	0.1	5.7
Ave Pb	2.1	0.05	2.2	2.0	0.1	3.3	1.7	0.04	2.6	1.9	0.2	8.1	1.7	0.1	4.1	1.9	0.1	5.7	1.9	0.1	7.0	2.0	0.1	6.0

Table 7.b NIST SRM 1831 values using CFGS2 as a calibration standard.

NIST SRM 1831	Lab A (n=27)			Lab B (n=15)			Lab C (n=15)			Lab D (n=15)			Lab E (n=15)			Lab F (n=15)			Lab G (n=15)			Lab H (n=15)		
	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD	Lab Mean	Lab STDEV	Lab %RSD
⁷ Li	5.9	0.1	1.3	5.8	0.11	1.9	5.8	0.24	4.1	6.1	0.43	7.0	5.9	0.16	2.8	5.7	0.17	2.9	5.7	0.13	2.3	5.7	0.17	3.0
²⁴ Mg	20900	240	1.1	20900	180	0.9	21200	870	4.1	21400	370	1.7	21900	280	1.3	20300	370	1.8	20800	330	1.6	20500	390	0.2
²⁷ Al	6200	146	2.4	6250	33	0.5	6280	215	3.4	6250	238	3.8	6400	55	0.9	6050	114	1.9	6120	117	1.9	6160	130	2.1
³⁹ K	2520	34.6	1.4	2470	12	0.5	2500	39	1.5	2450	79	3.2	2520	41	1.6	2390	67	2.8	2450	41	1.7	2410	61	2.5
⁴⁰ Ca	57300	890	1.6	57800	450	0.8	59300	1560	2.6	58800	2280	3.9	60100	1140	1.9	55900	1200	2.1	56900	920	1.6	56800	1270	2.2
⁴⁸ Ti	108	1.8	1.7	108	1.3	1.2	109	3.6	3.3	109	5.8	5.3	110	2.4	2.2	104	3.6	3.5	106	2.3	2.1	106	2.5	2.4
⁵⁵ Mn	13.4	0.2	1.1	13.5	0.1	0.9	13.3	0.5	3.5	13.4	0.6	4.2	13.1	0.2	1.5	13.3	0.4	2.7	11.8	0.2	2.0	13.2	0.2	1.7
⁵⁷ Fe	565	6	1.1	556	7	1.3	636	31	4.9	543	19	3.5	590	11	1.8	597	21	3.5	633	10	1.6	585	10	1.7
⁸⁵ Rb	5.7	0.1	1.7	5.6	0.1	1.0	5.5	0.2	4.4	5.5	0.3	6.1	5.5	0.2	2.7	5.5	0.2	3.3	5.6	0.1	1.8	5.5	0.2	3.2
⁸⁶ Sr	85.9	1.7	2.0	87.2	1.0	1.1	76.9	2.6	3.4	81.6	1.4	1.7	83.6	2.7	3.2	78.6	4.8	6.2	78.6	4.6	5.8	82.4	3.9	4.7
⁹⁰ Zr	38.1	1.2	3.1	38.4	1.0	2.7	32.4	0.8	2.4	35.7	1.8	5.0	36.3	1.0	2.8	32.8	1.8	5.6	33.1	1.5	4.6	35.1	1.5	4.4
¹³⁷ Ba	30.7	1.1	3.5	30.6	0.4	1.3	30.3	1.2	3.9	31.2	1.4	4.5	30.1	1.1	3.8	29.6	0.8	2.7	30.1	0.6	2.0	30.0	0.7	2.3
¹³⁹ La	2.1	0.1	2.8	2.1	0.0	2.3	2.1	0.1	5.1	2.1	0.1	4.5	2.1	0.1	3.8	2.0	0.1	4.9	2.1	0.03	1.6	2.1	0.1	2.4
¹⁴⁰ Ce	4.3	0.1	1.4	4.3	0.1	1.2	4.2	0.2	5.4	4.3	0.1	3.0	4.2	0.1	2.5	4.2	0.1	2.8	4.2	0.1	1.3	4.2	0.1	2.6
¹⁴⁰ Nd	1.7	0.05	2.8	1.7	0.1	4.8	1.6	0.1	5.2	1.8	0.2	13	1.7	0.1	4.9	1.7	0.1	5.0	1.7	0.03	1.7	1.7	0.1	4.5
¹⁷³ Hf	1.1	0.04	4.1	1.1	0.1	5.5	0.9	0.04	4.6	0.9	0.2	16	0.9	0.1	5.8	0.9	0.1	6.3	0.9	0.1	5.3	1.0	0.1	6.0
Ave Pb	2.2	0.1	3.5	2.0	0.1	3.6	1.7	0.1	3.7	1.9	0.1	6.1	1.8	0.1	3.8	1.9	0.2	8.4	1.9	0.1	6.5	2.0	0.1	6.1

Table 7.c Relative differences (reported as relative %) between the use of FGS 2 and CFGS2 as calibration standards.

	Lab A (n=27)	Lab B (n=15)	Lab C (n=15)	Lab D (n=15)	Lab E (n=15)	Lab F (n=15)	Lab G (n=15)	Lab H (n=15)
Element Isotope	Relative Difference %	Relative Difference %	Relative Difference %	Relative Difference %	Relative Difference %	Relative Difference %	Relative Difference %	Relative Difference %
⁷ Li	0.1	-0.9	1.5	-1.2	3.2	-1.8	0.5	-3.6
²⁴ Mg	-1.0	-1.3	1.9	0.7	0.9	-2.3	0.4	-3.3
²⁷ Al	-3.0	-1.4	3.3	1.8	-0.7	-1.5	-0.8	-2.8
³⁹ K	-0.3	-0.6	3.2	0.3	0.1	-3.5	-0.9	-4.6
⁴² Ca	-1.1	-0.6	3.8	1.5	-0.7	-2.1	-1.6	-3.4
⁴⁹ Ti	-1.7	-0.9	3.9	1.1	-0.6	-2.1	-1.5	-3.2
⁵⁵ Mn	-0.9	-0.5	1.2	1.2	2.1	0.8	0.1	-1.1
⁵⁷ Fe	-2.1	-0.8	-0.6	0.8	0.9	1.0	-1.2	-0.9
⁸⁵ Rb	0.6	0.3	-1.2	-0.1	0.6	-2.3	-0.6	-3.3
⁸⁸ Sr	-2.6	0.3	1.9	1.3	0.3	-1.8	-1.6	-2.2
⁹⁰ Zr	-2.6	-0.1	3.3	2.6	-0.3	-1.0	1.1	-1.7
¹³⁷ Ba	0.3	-0.2	1.3	0.4	0.6	-1.4	-0.9	-2.8
¹³⁹ La	-1.8	0.1	1.5	2.5	0.6	-0.5	-1.9	-1.9
¹⁴⁰ Ce	-0.4	-0.1	-0.8	1.0	2.3	-0.6	-0.7	-2.5
¹⁴⁶ Nd	-2.2	1.9	-2.3	0.8	2.3	-1.9	-2.2	-1.9
¹⁷⁸ Hf	-2.2	0.4	-1.9	2.5	-1.5	-2.2	-2.6	-0.6
Ave. ^{Pb}	3.2	-0.8	-0.5	1.7	5.4	-2.3	-0.2	0.3