

*Christopher Latkoczy,<sup>1</sup> Ph.D.; Stefan Becker,<sup>2</sup> Ph.D.; Marc Dücking,<sup>2</sup> Chem.Ing.; Detlef Günther,<sup>1</sup> Ph.D.; Jurian A. Hoogewerff,<sup>3</sup> Ph.D.; Jose R. Almirall,<sup>4</sup> Ph.D.; JoAnn Buscaglia,<sup>5</sup> Ph.D.; Andrew Dobney,<sup>6</sup> Ph.D.; Robert D. Koons,<sup>5</sup> Ph.D.; Shirly Montero,<sup>6</sup> Ph.D.; Gerard J. Q. van der Peijl,<sup>6</sup> Ph.D.; Wilfried R. S. Stoecklein,<sup>2</sup> Ph.D.; Tatiana Trejos,<sup>4</sup> M.Sc.; John R. Watling,<sup>7</sup> Ph.D.; and Vincent S. Zdanowicz,<sup>8</sup> Ph.D.*

## Development and Evaluation of a Standard Method for the Quantitative Determination of Elements in Float Glass Samples by LA-ICP-MS

**ABSTRACT:** Forensic analysis of glass samples was performed in different laboratories within the NITE-CRIME (Natural Isotopes and Trace Elements in Criminalistics and Environmental Forensics) European Network, using a variety of Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) systems. The main objective of the interlaboratory tests was to cross-validate the different combinations of laser ablation systems with different ICP-MS instruments. A first study using widely available samples, such as the NIST SRM 610 and NIST SRM 612 reference glasses, led to deviations in the determined concentrations for trace elements amongst the laboratories up to 60%. Extensive discussion among the laboratories and the production of new glass reference standards (FGS 1 and FGS 2) established an improved analytical protocol, which was tested on a well-characterized float glass sample (FG 10-1 from the BKA Wiesbaden collection). Subsequently, interlaboratory tests produced improved results for nearly all elements with a deviation of <10%, demonstrating that LA-ICP-MS can deliver absolute quantitative measurements on major, minor and trace elements in float glass samples for forensic and other purposes.

**KEYWORDS:** forensic science, float glass, trace element analysis, laser ablation, ICP-MS

Float glass is one of the major types of evidence encountered in crimes such as burglary, traffic accidents, and vandalism (1–5). The most frequently investigated property of glass has been its refractive index (RI) (6,7). Several analytical techniques for elemental analysis of float glasses have been employed to classify glass as to product end use type and to provide enhanced discrimination among glass sources beyond that provided by RI measurements alone (8,9). Elemental techniques generally employed for forensic glass analysis include scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) or wavelength dispersive spectroscopy (WDS), energy dispersive and wavelength dispersive X-ray fluorescence spectroscopy (EDXRF and WDXRF), inductively coupled plasma optical emission spectroscopy (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) (10,11).

Since many forensic glass investigations involve the comparison of glasses from a scene of crime with glasses from a suspect, ap-

proaches using elemental ratios for a semi-quantitative analysis can also be utilized. An advantage of quantitative glass analysis is that results can easily be compared amongst various techniques such as XRF,  $\mu$ -XRF or SEM-EDS. Furthermore, a quantitative analytical protocol can be established as a pre-cursor to the incorporation of the data into appropriate LA-ICP-MS forensic float glass databases. As a virtually non-destructive method and with the merits of low limits of detection for most elements, LA-ICP-MS can be considered as a suitable method for elemental analysis in forensic float glass analysis (12). A general overview on the chemical analysis of glasses by LA-ICP-MS has been given by Strubel et al. (13). All these studies have shown that the heterogeneity of trace elements in bulk float glass samples is small enough to allow a significant discrimination of different samples on the basis of their trace elemental concentrations (8–13).

As an European initiative, the NITE-CRIME (Natural Isotopes and Trace Elements in Criminalistics and Environmental Forensics) Network aims at providing a forum for the development of analytical protocols involving trace element and isotope analysis in forensic science. Within the Network there is an emphasis on developing protocols for laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). An additional fundamental aim is to ensure that databases created with established forensic technologies, such as X-ray fluorescence spectrometry (XRF), will maintain their validity when adding LA-ICP-MS data. The best way to ensure the comparability of results obtained by different laboratories or using different instruments is by requiring all results to have ranges of accuracy and precision no larger than expected for the chosen methodology when earlier studies are considered. This can be achieved and checked by comparative studies using Certified Reference Materials (CRM). In the early phase of the collaboration,

<sup>1</sup> Swiss Federal Institute of Technology Zurich (ETH Zurich), Laboratory of Inorganic Chemistry, Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland.

<sup>2</sup> Bundeskriminalamt (BKA) Wiesbaden, Forensic Science Institute, Thaeerstrasse 11, 65173 Wiesbaden, Germany.

<sup>3</sup> Institute of Food Research, Norwich Research Park, Norwich NR4 7UA, United Kingdom.

<sup>4</sup> Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199.

<sup>5</sup> Counterterrorism and Forensic Science Research Unit, FBI Laboratory, FBI Academy, Quantico, VA 22135.

<sup>6</sup> Netherlands Forensic Institute, The Hague 2490 AA, The Netherlands.

<sup>7</sup> School of Applied Chemistry, Curtin University of Technology, Perth, Western Australia.

<sup>8</sup> Bureau of Customs and Border Protection, Research Laboratory, Springfield, VA 22153.

Received 5 March 2005; and in revised form 4 June 2005; accepted 9 June 2005; published 14 Sept. 2005.

emphasis was placed on comparison of analytical results as a function of the specific equipment used at the participating laboratories. For example, the laser wavelengths used by the various commercial laser ablation systems ranges from infrared to ultraviolet. In addition, several designs of mass spectrometers including quadrupole-, sector field-, time-of-flight and multi-collector systems are in use. Because of these differences, instrumental bias may be included in analytical data and, consequently, generate ambiguous results. In order to determine, understand and to reduce this potential bias, it was necessary to undertake a judicious program of circulation and analysis of certified reference materials appropriate to forensic science investigations. The critical step in this program was to design and test measurement protocols that make it possible to compare measurements carried out using different instruments in order to produce equivalent data from different laboratories. In addition, validation of quantitative analytical protocols was undertaken as a pre-cursor to the incorporation of these data into an equivalent database. As an important forensic matrix, glass samples were chosen as a first model for this aim.

Quantitative analysis using LA-ICP-MS for float glasses was carried out by using the external calibration standards such as the NIST SRM 61x series or other standards available from the glass industry. Float glass has an approximate average matrix composition of 72 wt% SiO<sub>2</sub>, 13 wt% Na<sub>2</sub>O, 8 wt% CaO, and 4 wt% MgO (14). In contrast, the NIST SRM 610/612 glasses have a slightly different composition of 72 wt% SiO<sub>2</sub>, 14 wt% Na<sub>2</sub>O, 12 wt% CaO, 2 wt% Al<sub>2</sub>O<sub>3</sub>, and MgO only at mg kg<sup>-1</sup> level, respectively (15–17). However, these glass reference materials are the ones most often used as external calibration standards. To improve the accuracy of the quantitative analysis of float glasses by LA-ICP-MS, two matrix-matched standards were produced (18). These forensic “float glass standards” (FGS) resemble soda-lime glass composition, but vary in their concentration of doped elements by a factor of 5. The concentration ranges of the doped elements were chosen according to their expected abundances based on the results of quantitative analysis of 61 float glasses of global origin by ICP-MS. Due to their discriminating power for forensic applications, the elements Al, K, and Fe were selected as minor elements and Li, Ti, Mn, Rb, Sr, Zr, Sn, Ba, La, Ce, Nd, Hf, and Pb were chosen as trace elements in varying concentrations (11). The main aim of the study was to finally reach a level of instrumental accuracy and precision (<10% RSD) among different forensic laboratories, which is in the range of the overall variability of trace elements in float glass samples, allowing LA-ICP-MS to become a routine forensic technique for glass analysis in the future.

## Experimental

### Instrumentation and Measurement Parameters

Within the various interlaboratory test studies, several different ICP-MS instruments were used in standard operation modes: HP-4500 (Agilent Technologies, Palo Alto), ELAN 6100 DRC II, ELAN 6100 DRC+ (Perkin Elmer, Norwalk), Element2 (Thermo Electron GmbH, Bremen, Germany), VG PlasmaQuad 2+ with S-Option, VG PlasmaQuad 3 (Thermo Electron Cooperation, Waltham). For the first two interlaboratory test studies, the following elements were measured: Major element isotopes: <sup>23</sup>Na, <sup>25</sup>Mg, <sup>27</sup>Al, <sup>29</sup>Si, <sup>39</sup>K, <sup>42</sup>Ca, <sup>49</sup>Ti, <sup>55</sup>Mn, <sup>57</sup>Fe and trace element isotopes: <sup>7</sup>Li, <sup>11</sup>B, <sup>59</sup>Co, <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>71</sup>Ga, <sup>75</sup>As, <sup>85</sup>Rb, <sup>88</sup>Sr, <sup>90</sup>Zr, <sup>93</sup>Nb, <sup>118</sup>Sn, <sup>123</sup>Sb, <sup>133</sup>Cs, <sup>137</sup>Ba, <sup>139</sup>La, <sup>140</sup>Ce, <sup>151</sup>Eu, <sup>159</sup>Tb, <sup>165</sup>Ho, <sup>169</sup>Tm, <sup>175</sup>Lu, <sup>178</sup>Hf, <sup>181</sup>Ta, <sup>182</sup>W, <sup>197</sup>Au, <sup>208</sup>Pb, <sup>209</sup>Bi, <sup>232</sup>Th, <sup>238</sup>U. For the third and the fourth interlaboratory test studies, the list of

elements for use in forensic glass analysis was decreased to twenty-one isotopes: major element isotopes: <sup>25</sup>Mg, <sup>27</sup>Al, <sup>29</sup>Si, <sup>39</sup>K, <sup>42</sup>Ca, <sup>57</sup>Fe and trace element isotopes: <sup>7</sup>Li, <sup>49</sup>Ti, <sup>55</sup>Mn, <sup>85</sup>Rb, <sup>88</sup>Sr, <sup>90</sup>Zr, <sup>118</sup>Sn, <sup>137</sup>Ba, <sup>139</sup>La, <sup>140</sup>Ce, <sup>146</sup>Nd, <sup>178</sup>Hf, <sup>206</sup>Pb, <sup>207</sup>Pb, <sup>208</sup>Pb. The instrumental ICP parameters were individually optimized to maximum performance for laser ablation analysis, using parameters such as maximizing signal-to-noise ratio and minimizing ThO<sup>+</sup>/ThO<sup>+</sup> ratio using a glass standard reference material.

Laser ablation analyses were performed with three solid state Q-switched Nd:YAG systems operating at 266 nm (LSX 200, LSX 500; Cetac, Omaha, US, and the VG Microprobe; Thermo Electron Cooperation, Waltham), one solid state Nd:YAG laser system operating at 213 nm (UP 213; New Wave Research, Fremont, US), and one Excimer ArF laser system operating at 193 nm (GeoLas M; Lambda Physik AG, Göttingen, Germany).

Laboratory numbers, referred to throughout this text, were assigned to the following LA-ICP-MS combinations: lab 1 (VG Microprobe (266 nm) + VG PlasmaQuad 3), lab 2 (VG Microprobe (266 nm) + VG PlasmaQuad 2+), lab 3 (GeoLas M (193 nm) + ELAN 6100 DRC+), lab 4 (New Wave UP 213 (213 nm) + HP-4500), lab 5 (New Wave UP 213 (213 nm) + Element2), lab 6 (New Wave UP 213 (213 nm) + ELAN 6100 DRC+), lab 7 (Cetac LSX 200 (266 nm) + HP-4500), lab 8 (CETAC LSX 500 (266 nm) + HP-4500), lab 9 (CETAC LSX 500 (266 nm) + ELAN 6100 DRC II).

All samples were analyzed in transient mode with a 30 sec gas blank followed by a 60 sec ablation of the corresponding sample. The laser repetition rate was set to 10 Hz with a maximum laser energy output that did not produce excessive spattering and cracking of the glass samples. The laser energy density ranged between 10–40 J cm<sup>-2</sup> across the individual laboratories. Laser spot sizes varied between 40 to 100 μm for the different instruments used within these studies. The ranges for the experimental parameters used for the analysis of glass samples for all systems are summarized in Table 1.

### Quantification Procedure

The calibration procedure used for this work was an external calibration with glass standard reference materials using Si on mass 29 for internal standardization. Using both an external standard together with internal standardization corrects for different laser ablation yields and instrumental drifts and is, therefore, the calibration method of choice for laser-based analysis of forensic glass samples (5). Furthermore, the range of Si concentrations in float glasses is very low, making internal standardization procedure work well for quantification.

TABLE 1—Instrumental parameters used for elemental analysis by LA-ICP-MS.

|   |                 |
|---|-----------------|
| General setup                                   |                 |
| RF power/W                                      | 1300–1400       |
| Argon make up gas flow rate/L min <sup>-1</sup> | 0.85–1.30       |
| Isotopes  | max. 40 per run |
| Sweeps/s  | 0.5–2.4         |
| Sampling and skimmer cones                      | Al, Pt, Ni      |
| Laser ablation parameters                       |                 |
| Spot diameter/μm                                | 40–100          |
| Repetition rate/Hz                              | 10              |
| Energy density/J cm <sup>-2</sup>               | variable        |
| Ablation cell volume/cm <sup>3</sup>            | 30–140          |
| Tube length/cm                                  | 50–400          |

### Time Resolved Analysis and Data Calculation

The procedure for acquisition and calculation of transient analyte signals is derived from Longerich et al. (19), employing commercially available time resolved software programs (LAMTRACE and GLITTER software; GEOMAC, Macquarie University, Australia) and transferring the raw data to a spreadsheet program for evaluation and quantification. Instrumental drift was calculated and corrected for by measuring the calibration standards at the beginning (first two measurements) and at the end of the procedure (last two measurements).

### Reagents, Standards, and Samples

The reference materials NIST SRM 610, NIST SRM 612, NIST SRM 1831, NIST SRM 621 (National Institute of Standards and Technology, Gaithersburg, MD), and DGG 1 (Deutsche Glastechnische Gesellschaft, Offenbach, Germany) were used for the different interlaboratory test investigations. Furthermore, two float glasses (10-1 & 56-3) from the float glass collection of the BKA Wiesbaden were used for analysis. Sample 10-1 originated from a German float glass manufacturer, sample 56-3 originated from an American float glass plant, and both samples are of known origin and production date. In addition, two new glass standard materials (FGS 1, FGS 2), produced and provided by SCHOTT Glas, Germany, were supplied to the participating laboratories to overcome matrix-dependent problems related to the quantitative analysis by LA-ICP-MS. The glass production protocol is given in the following section.

### Production of New Glass Standards

The glasses (FGS1 and FGS2) were produced by the German glass manufacturer SCHOTT Glas in 2002 as part of a BKA—SCHOTT Glas joint research activity. The 16 selected elements were added as carbonates or oxides to the soda-lime glass matrix and fused/melted at 1550°C using platinum cups. The melt was then refined and homogenized by stirring. The melt was kept at 1540°C for a period of two hours before being allowed to cool down during mixing. In order to reduce micro bubbles, the glasses were again melted and heated for eight hours at 1650°C in platinum cups. After final cooling, two cylinders with a diameter of approximately 10 cm and a height of approximately 10 cm with no visible/detectable inclusions were obtained. Small samples with a diameter of 10 mm and a thickness of 3 mm suitable for laser ablation analysis were cut out of the produced glass cylinder blocks and finally ground and polished (see Fig. 1).

The concentrations of selected elements in the two new matrix-matched glass standards FGS 1 (low concentration standard) and FGS 2 (high concentration standard) were determined using several techniques (AAS, ICP-OES, ICP-MS, LA-ICP-MS, SEM-EDS, XRF) by different laboratories. Table 2 lists the concentration values of elements analyzed in FGS 1 and FGS 2 that were further used as consensus and target values for the quantitative analysis of float glass samples using LA-ICP-MS.

### Sample Preparation for LA-ICP-MS

Glass samples were cut using a diamond wire saw type 4240 (Well/Mannhein, Germany). For float glass samples, the tin side was detected using a UV light source operating at 254 nm. Samples were embedded using a Heraeus Kulzer Technovit 2000<sup>®</sup> resin with blue light polymerization. The float glass samples were embedded with the tin side facing down (towards the embedding material). The

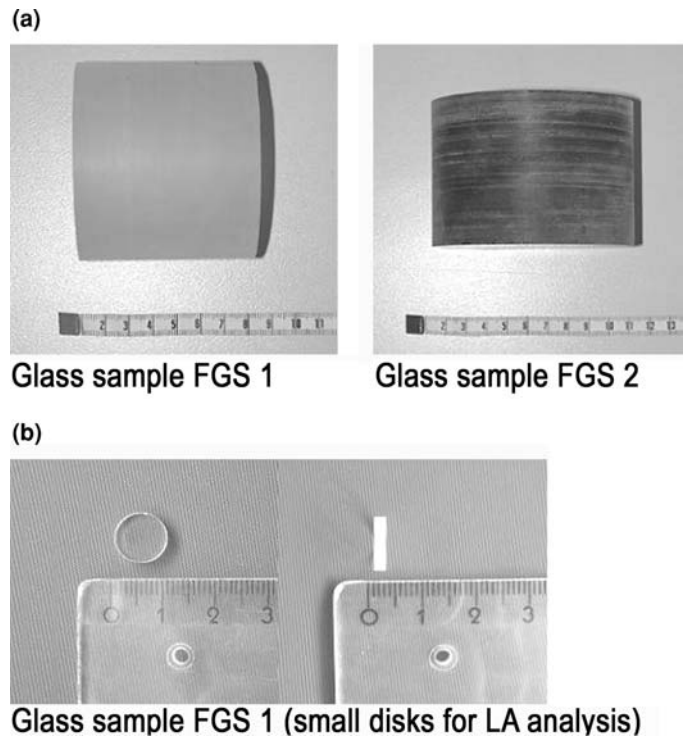


FIG. 1—(a) Produced glass cylinder blocks of new glass reference standards (FGS 1, FGS 2) and (b) final sample size dimensions for laser ablation analysis.

TABLE 2—Consensus values in  $\text{mg kg}^{-1}$  for elements for the float glass reference samples FGS 1 and FGS 2 (mean  $\pm$  std. dev.,  $N = 5-10$ ) validated by different analytical techniques.

| Sample | FGS 1<br>Avg. $\pm$ 1 SD<br>[ $\text{mg kg}^{-1}$ ] | FGS 2<br>Avg. $\pm$ 1 SD<br>[ $\text{mg kg}^{-1}$ ] |
|--------|---|---|
| Si     | 341900 $\pm$ 1300                                   | 335200 $\pm$ 1800                                   |
| Na     | 102800 $\pm$ 2100                                   | 100500 $\pm$ 2500                                   |
| Ca     | 60600 $\pm$ 4200                                    | 59300 $\pm$ 4100                                    |
| Mg     | 23900 $\pm$ 3200                                    | 23400 $\pm$ 3600                                    |
| Li     | 6.0 $\pm$ 1.0                                       | 29 $\pm$ 2  |
| Al     | 1500 $\pm$ 150                                      | 7400 $\pm$ 100                                      |
| K      | 920 $\pm$ 20  | 4600 $\pm$ 200                                      |
| Ti     | 69 $\pm$ 7  | 326 $\pm$ 20  |
| Mn     | 43 $\pm$ 6  | 221 $\pm$ 20  |
| Fe     | 580 $\pm$ 60  | 2600 $\pm$ 100                                      |
| Rb     | 8.6 $\pm$ 0.5                                       | 35 $\pm$ 3  |
| Sr     | 57 $\pm$ 4  | 253 $\pm$ 13  |
| Zr     | 49 $\pm$ 3  | 223 $\pm$ 15  |
| Sn     | 19 $\pm$ 3  | 94 $\pm$ 12   |
| Ba     | 40 $\pm$ 3  | 199 $\pm$ 15  |
| La     | 4.3 $\pm$ 0.5                                       | 18 $\pm$ 1  |
| Ce     | 5.2 $\pm$ 0.5                                       | 23 $\pm$ 2  |
| Nd     | 5.1 $\pm$ 0.5                                       | 25 $\pm$ 2  |
| Hf     | 3.2 $\pm$ 0.3                                       | 15 $\pm$ 1  |
| Pb     | 5.8 $\pm$ 1.0                                       | 24 $\pm$ 2  |

diameter of the resin block was approximately 25 mm (1 in.). This block was then ground and polished using a Struers RotoSystem polishing system.

In many forensic glass investigations, the relevant glass fragments are of small size with irregular shape (below 1 mm in size or less than 0.5 mg in weight), so that embedding is not possible because of the high likelihood of destruction or loss of sample during preparation. In these cases, fixation of the samples with Blue Tack<sup>®</sup>

(Bostik, Burgholzhausen, Germany) or double sided tape could be used, but these procedures were not used in these studies as all samples were of suitable size for direct embedding. Due to specific transport characteristics of the ablated material by the carrier gas, it is very important to place the samples close together in the centre of the ablation cell for optimum transport efficiency (20).

## Results and Discussion

In total, a series of four tests were carried out to define a general protocol that resulted in accurate and precise results for nearly all elements amongst the participating laboratories, demonstrating the suitability of LA-ICP-MS to produce quantitative results on major and trace elements in forensic float glass samples. In the following section the individual improvements made with each successive test measurement are explained and discussed.

The first study using "simple" samples such as the NIST SRM 610 and NIST SRM 612 reference glasses led to results that varied by up to 60% among the different partners. Therefore, in the second study, new float glass reference standards were used with an improved acquisition protocol and a well-characterized float glass sample was tested. Within the third study, a new, improved matrix-matched glass calibration standard was used and the analysis protocol was revised. In the fourth study, a single protocol involving detailed instructions for ICP and laser tuning parameters was utilized by each participant.

### First Interlaboratory Test Analysis

In the first interlaboratory test, two silicate glass samples (NIST SRM 610, NIST SRM 612) and one float glass sample (FG 56-3) from the BKA Wiesbaden collection were analyzed in six laboratories using their individual LA-ICP-MS systems. Each laboratory was instructed to use a measurement protocol (see experimental section) containing 40 isotopes, a total measurement time of 90 seconds per sample, with a laser crater size of 40–60  $\mu\text{m}$  and a laser repetition rate of 10 Hz. The main objective of the first interlaboratory test was to compare the capabilities of the commonly used NIST SRM 61x series for the quantitative analysis of one float glass sample FG 56-3 (major, minor and trace elements) with various laser ablation systems and different ICP-MS instruments. In this first test, calibration was based on the reference glass materials NIST SRM 612 and NIST SRM 610 as available among the different partners. The reference values of the two NIST SRM glasses used for the evaluation have been given by Pearce et al. (16). The six laboratories were asked to analyze the samples based on their own experience with their own optimization procedure without a detailed tuning procedure stated in the protocol. However,  $^{29}\text{Si}$  was used as internal standard element. One reason for choosing Si as internal standard is that the concentration of  $\text{SiO}_2$  is consistently 72 wt% for float glass samples with only minor differences between different float glass samples. Therefore, for forensic float glass analysis, this specific concentration value can be used for elemental analysis, even for soda-lime glass samples of unknown composition (1,2,14,21).

The sensitivity and the limits of detection indicate differences among the individual LA-ICP-MS systems reaching up to 2 orders of magnitude. The highest sensitivities do not always correspond with the lowest limits of detection because of significant background differences for individual elements on various ICP-MS systems (especially for Na, Mg, Si, K and Fe) as shown in Fig. 2. The results for the quantitative analysis of FG 56-3 illustrate significant differences for selected elements (e.g., Na, Mg, K, Ca, Ti, Mn, Fe, Sr, Zr, Ba, Th) using either NIST SRM 610 or NIST SRM 612 as the

external calibration standards. These differences can be partly explained by the different transparency properties of these two NIST glass samples. Therefore, depending on the laser wavelength used, the coupling of the laser light into the samples varies, leading to distinctly different penetration depths and absorption characteristics (22–24). These processes result in significant variation in ablation yields and possibly in different laser-induced particle sizes, which lead to altered excitation conditions in the ICP and, therefore, to different elemental responses (25–28). In addition, the relative standard deviations of four individual sample spots showed differences (RSD = 2–10%) between the various laboratory systems. As an example and to illustrate the spread among the laboratories, results for the determination of Zr are given in Fig. 3.

To minimize the effects of different laser-induced ablation yields for samples with different optical properties, NIST SRM 612 was chosen as external reference material for the next interlaboratory study, since the optical properties of NIST SRM 612 are closer to those of the float glass samples than are the optical properties of NIST SRM 610. In addition, the concentrations of trace elements in NIST SRM 612 are lower (nominal concentration of 40  $\text{mg kg}^{-1}$ ) compared to NIST SRM 610 (nominal concentration of 400  $\text{mg kg}^{-1}$ ) and thus within the expected range of elements in float glass samples. Based on the evaluation of the first tests, a new analysis protocol for use in a second interlaboratory study was established.

### Second Interlaboratory Test Analysis

Five glass samples (maximum dimensions <8 mm) were embedded and polished within a single block with a diameter of 25 mm, minimizing the risk of influences from the sample fragment size and surface morphology between different batches of samples. NIST SRM 612 was used as an external calibration standard for the reasons stated above in the discussion of the results of the first interlaboratory test analysis. FG 10-1 (provided by BKA Wiesbaden) was introduced as a float glass sample, because the elemental composition of this sample is well characterized by various analytical methods (XRF and solution-based ICP-MS) compared to FG 56-3. Additionally, two reference materials, a container glass (NIST SRM 621) and a sheet glass (NIST SRM 1831), were included for testing the applied measurement procedure (comparison to reference values). The list of elements to be measured contained 40 isotopes and data acquisition was performed in transient mode by single hole drilling with a laser spot size of 40–60  $\mu\text{m}$  and a laser repetition rate of 10 Hz. As in the first interlaboratory test, no detailed instructions were given for ICP parameters to be used. However, all parameters, such as rf-power, gas flow conditions, details of the laser cell geometry, the tube length between the laser cell and the ICP and the output energy of the laser ablation system with its corresponding laser fluence on the sample were reported. For this interlaboratory test, the samples were sent to seven laboratories.

The results for this interlaboratory test revealed that the high standard deviations (up to 12%) for some elements (Li, Mg, Ca, Ti, Ba, La, Pb) obtained by several laboratories were not significantly improved by the new analysis procedure. Concentration values obtained for calcium suggest that the selection of the internal standard is a very critical parameter (laser dependent), and some of the uncertainties seen in the trace element determinations (e.g., Ba, see Fig. 4) are attributed to the use of silicon as internal standard. It can be concluded that the use of calcium as internal standard would have improved both the accuracy and precision of the results for the analysis of strontium, zirconium, barium, lanthanum, and cerium. It has already been demonstrated by Longerich et al. that, in terms of ablation behaviour using a 266 nm laser wavelength, elements

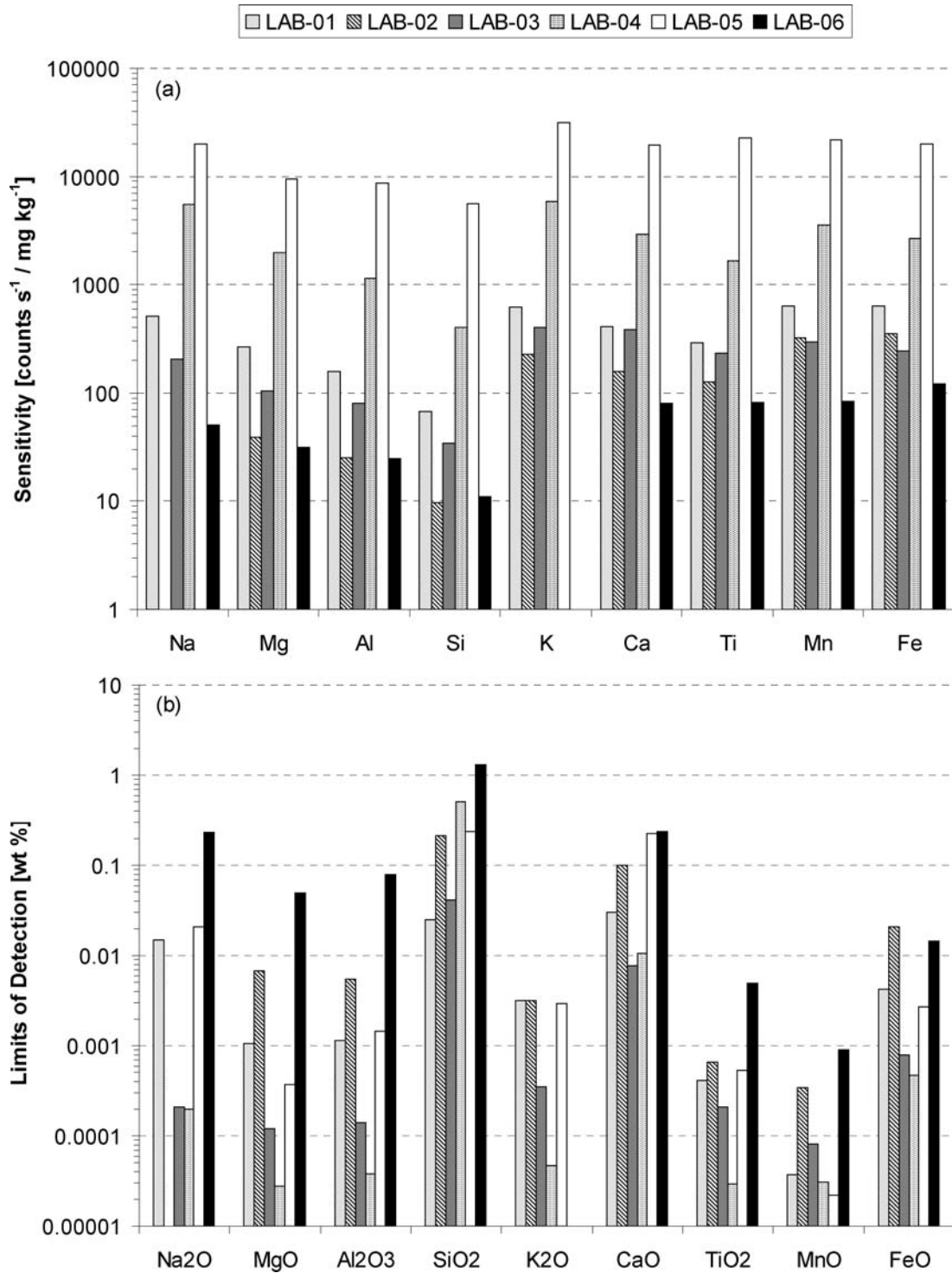


FIG. 2—(a) Sensitivity shown as counts s<sup>-1</sup>/mg kg<sup>-1</sup> obtained by the different laboratories for main elements. (b) Limits of Detection in wt% for main element oxides using different LA-ICP-MS combinations.

fall into several distinct clusters and that the elements within these clusters correlate well with each other during a period of ablation. Thus, elements within a cluster can be determined using an internal reference element from within the same cluster (29). This implies that specific 266 nm LA-ICP-MS combinations (laboratories 1, 2, and 7) show a much more pronounced matrix dependence for the determination of trace elements in glass samples compared to the other setups. Therefore, it is concluded that using a matrix-matched external standard will improve the accuracy for the quantitative de-

termination of elements for laser systems showing such a matrix dependence.

### Third Interlaboratory Test Analysis

In the third interlaboratory test analysis, the new glass standard, FGS 1, doped with 20 elements in various concentrations, was provided by BKA Wiesbaden (see experimental section) as an external calibration standard to better match the matrix of the float

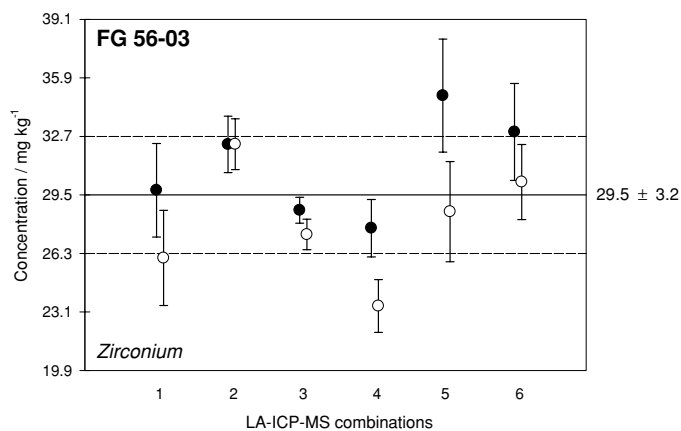


FIG. 3—Quantitative results (mean  $\pm$  std. dev.) for Zr in FG 56-03 using NIST SRM 610 (closed circles) and NIST SRM 612 (open circles) as external standards. The mean and standard deviation are calculated on the basis of four individual single spot analysis ( $N=4$ ). Horizontal lines indicate the consensus value ( $\pm$ std. dev.) determined using liquid ICP-MS and XRF analysis.

glass sample FG 10-1. A German glass standard, DGG1, a second float glass with a high iron content, FG 1-1, and NIST SRM 612, were also included. Again, individual embeddings containing several sample blocks were sent to each of six different laboratories. The analysis protocol used for this round of testing was altered such that only 21 isotopes were measured ( $^7\text{Li}$ ,  $^{25}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{39}\text{K}$ ,  $^{42}\text{Ca}$ ,  $^{49}\text{Ti}$ ,  $^{55}\text{Mn}$ ,  $^{57}\text{Fe}$ ,  $^{85}\text{Rb}$ ,  $^{88}\text{Sr}$ ,  $^{90}\text{Zr}$ ,  $^{118}\text{Sn}$ ,  $^{137}\text{Ba}$ ,  $^{139}\text{La}$ ,  $^{140}\text{Ce}$ ,  $^{146}\text{Nd}$ ,  $^{178}\text{Hf}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ ). The selection of these 21 isotopes was based on their potential for discrimination among glass sources (30). The results were improved compared to prior tests, but retained enough uncertainty that a fourth test including a specific measurement protocol was required.

#### Fourth Interlaboratory Test Analysis

Based on the results of the first three interlaboratory tests, a protocol that included ICP and laser tuning parameters for each analysis was established. These parameters include optimization of the signal-to-noise ratio (S/N-ratio) on selected isotopes ( $^{29}\text{Si}$ ,  $^{57}\text{Fe}$ ,  $^{139}\text{La}$ ), optimization of parameters to give a minimum double-charged ratio ( $\text{Ba}^{++}/\text{Ba}^+ < 1\%$ ) and a minimum oxide formation

( $\text{CeO}^+/\text{Ce}^+ < 1\%$ ). As a general rule, count rates of 700–1000 counts  $\text{ppm}^{-1}$  should be reached with a laser spot diameter between 40–60  $\mu\text{m}$ , using these optimized conditions. All parameters were checked on the new glass reference material, FGS 2, which was also used as an external standard for quantitative analysis. In contrast to the glass standard reference NIST SR 61 $\times$  series, the determination of the doubly charged barium ion ( $\text{Ba}^{++}$ ) on mass  $m/z$  69 was possible and oxide formation on mass 156 ( $\text{CeO}^+$ ) was measurable within this standard, since the elements Ga, Gd, Dy were not included in the production of the glass reference standards FGS 1 and FGS 2. Therefore, these new glass standards are well suited as tuning samples for laser ablation analysis. Seven different laboratories carried out laser ablation analyses on embedded sample blocks containing the float glass sample FG 10-1, along with various standards. FGS 2 was used as external reference material (calibration standard). However, although improved concentration results were obtained using Ca as an internal standard, the sample matrix element Si at mass 29 was again used for internal standardization due to its low variability within float glass samples. The results of all four interlaboratory tests are summarized in the following results and discussion section.

#### Results and Discussion of Interlaboratory Tests

A comparison of the results of three interlaboratory tests obtained by different laboratories on the float glass sample FG 10-1 is given in Figs. 5 through 17 and Table 3 for the following elements: Li, Mg, Ca, Ti, Fe, Rb, Sr, Zr, Ba, La, Ce, Hf and Pb. Results for sample FG 10-1 were selected and used for illustration purposes. The results for the other samples are similar, but are not shown in the text for the sake of clarification.

The determination of lithium (Fig. 5) reveals problems in the first interlaboratory test due to the very low count rates obtained by two laboratories. These low count rates result in a high standard deviation ( $>80\%$  RSD) for individual analysis spots. The most accurate results were obtained, using FGS 1 as the external standard and by improving instrumental conditions, because of the similar concentration ranges of sample and standard.

The results obtained for magnesium (Fig. 6), titanium (Fig. 8), and hafnium (Fig. 16) show that the published values given for NIST SRM 612 lead to a constant deviation of 10–15% RSD for most laboratories. These findings support the conclusion that the

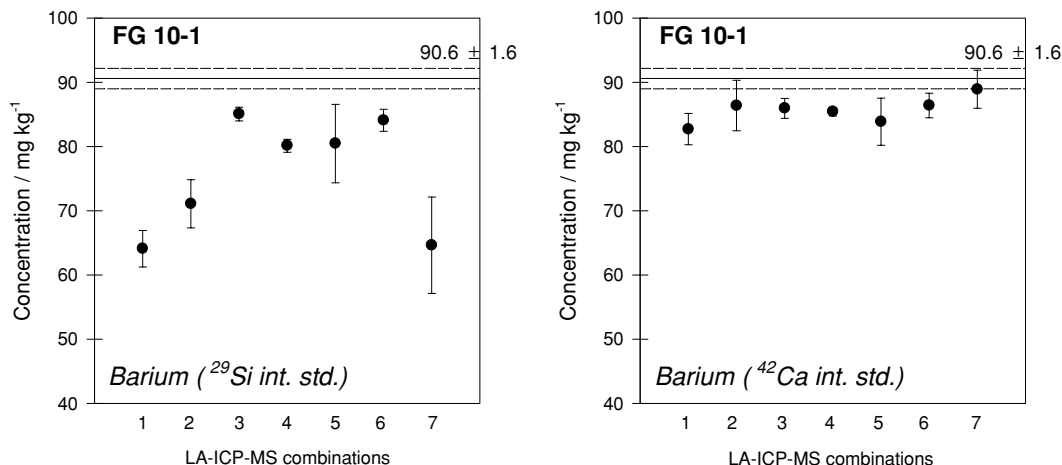


FIG. 4—Concentration values for barium in FG 10-1 (mean  $\pm$  std. dev.,  $N=4$ ) using NIST SRM 612 as external standard and mass 29 or mass 42 for internal standardization. Horizontal lines indicate the consensus value ( $\pm$ std. dev.) determined using liquid ICP-MS.

TABLE 3—Quantitative LA-ICP-MS results for elements in FG 10-1 in  $\text{mg kg}^{-1}$  for three interlaboratory test studies using three different external glass reference material (mean  $\pm$  std. dev.,  $N = 4$ ). The fourth column shows the consensus results obtained using other techniques (ICP-MS, XRF).

| Sample Standard | FG 10-1<br>NIST SRM 612<br>[ $\text{mg kg}^{-1}$ ] | FG 10-1<br>FGS 1<br>[ $\text{mg kg}^{-1}$ ] | FG 10-1<br>FGS 2<br>[ $\text{mg kg}^{-1}$ ] | FG 10-1<br>ICP-MS, XRF<br>[ $\text{mg kg}^{-1}$ ] |
|-----------------|--|---|---|---|
| Li              | 3.5 $\pm$ 3.6                                      | 3.8 $\pm$ 0.6                               | 4.3 $\pm$ 1.3                               | 4.1 $\pm$ 0.25                                    |
| Mg              | 27390 $\pm$ 2400                                   | 24520 $\pm$ 1070                            | 24280 $\pm$ 780                             | 24570 $\pm$ 900                                   |
| Al              | 3380 $\pm$ 500                                     | 3650 $\pm$ 400                              | 3650 $\pm$ 310                              | 3670 $\pm$ 160                                    |
| K               | 1650 $\pm$ 260                                     | 1920 $\pm$ 180                              | 1830 $\pm$ 90                               | 1910 $\pm$ 210                                    |
| Ca              | 58130 $\pm$ 7900                                   | 63120 $\pm$ 6500                            | 63280 $\pm$ 2820                            | 63300 $\pm$ 1800                                  |
| Ti              | 227 $\pm$ 39                                       | 199 $\pm$ 19                                | 195 $\pm$ 14                                | 213 $\pm$ 13                                      |
| Mn              | 62 $\pm$ 8   | 62 $\pm$ 4                                  | 64 $\pm$ 4                                  | 68 $\pm$ 3  |
| Fe              | 770 $\pm$ 140                                      | 750 $\pm$ 60                                | 670 $\pm$ 60                                | 740 $\pm$ 20                                      |
| Rb              | 3.9 $\pm$ 1.2                                      | 4.6 $\pm$ 0.6                               | 3.8 $\pm$ 0.6                               | 4.4 $\pm$ 0.8                                     |
| Sr              | 86 $\pm$ 12  | 94 $\pm$ 10                                 | 96 $\pm$ 9                                  | 96 $\pm$ 5  |
| Zr              | 41 $\pm$ 7   | 49 $\pm$ 7                                  | 47 $\pm$ 6                                  | 48 $\pm$ 2  |
| Sn              | 9.4 $\pm$ 1.7                                      | 9.6 $\pm$ 1.2                               | 11.5 $\pm$ 1.2                              | n.d.  |
| Ba              | 76 $\pm$ 11  | 83 $\pm$ 8                                  | 88 $\pm$ 5                                  | 91 $\pm$ 2  |
| La              | 2.8 $\pm$ 0.7                                      | 3.2 $\pm$ 0.4                               | 3.1 $\pm$ 0.4                               | 3.2 $\pm$ 0.1                                     |
| Ce              | 4.6 $\pm$ 0.5                                      | 5.1 $\pm$ 0.4                               | 5.0 $\pm$ 0.3                               | 4.9 $\pm$ 0.5                                     |
| Nd              | n.d.   | 2.5 $\pm$ 0.4                               | 2.4 $\pm$ 0.4                               | n.d.  |
| Hf              | 1.0 $\pm$ 0.3                                      | 1.3 $\pm$ 0.3                               | 1.2 $\pm$ 0.4                               | 1.4 $\pm$ 0.1                                     |
| Pb              | 8.8 $\pm$ 2.1                                      | 9.9 $\pm$ 2.1                               | 10.0 $\pm$ 2.3                              | 10 $\pm$ 1  |

published (Pearce) reference values are not correctly determined for NIST SRM 612. Comparing the results with Gao et al. indicate that the reported values of  $67 \text{ mg kg}^{-1}$  lead to greatly improved agreement for magnesium (15). In addition, the higher concentration values for Mg in FGS 1 and FGS 2 improved the precision and accuracy for the quantitative determination of Mg in float glass samples.

Quantitative results for calcium (Fig. 7), strontium (Fig. 11), zirconium (Fig. 12), barium (Fig. 13), lanthanum (Fig. 14), and cerium (Fig. 15) clearly show that using NIST SRM 612 as the external standard and Si on mass 29 for internal standardization leads to biased results for some laser systems (LA-ICP-MS combinations

1, 2, and 7) due to elemental fractionation, which has previously been observed in studies using the same wavelength (28,29). Using a matrix-matched external standard, such as FGS 1 or FGS 2, matrix effects are significantly improved and the deviations in the determined concentrations are reduced. The use of either another matrix element (Ca at mass 42) as internal standard or the use of a matrix-matched external standard, such as FGS 1 or FGS 2, greatly improves the overall accuracy for the analysis of these elements by LA-ICP-MS.

For titanium (Fig. 8) and iron (Fig. 9), an offset for all laboratories was observed for FG 10-1 using FGS 2 as calibration standard. Still, all the laser ablation data are very consistent and most values agree within the confidence interval of the liquid analysis. These results for iron and titanium show the advantages of the new reference materials (e.g., higher concentration of iron), leading to smaller standard deviations comparing the quantitative results from different laboratories. Furthermore, problems associated with low signal-to-noise ratios obtained due to the lack of a proper optimization procedure as in the first interlaboratory test, are quite obvious for these two elements. However, the constant deviations indicate other sources of uncertainty, which cannot be explained and more data for FGS 2 are required.

Concentration values for rubidium (Fig. 10), strontium (Fig. 11), cerium (Fig. 15), and lead (Fig. 17) show that the precision obtained among different laboratories by laser ablation analysis is much better than the precision of liquid-based analysis.

Finally, problems related to high background signals for some elements such as lead, which were encountered by a few laboratories, can be partly explained by the use of their ICP-MS equipment for other applications, such as the liquid analysis of bullets. Such analyses result in a high memory effect for these elements. These effects might be reduced to a certain extent by using dedicated parts, such as the torch system, sampler and skimmer cones, and tubing for laser ablation work only. However, this was not an aim of this study and is only intended as a recommendation.

The above results were obtained using float glass samples that were larger than the samples commonly analyzed within forensic

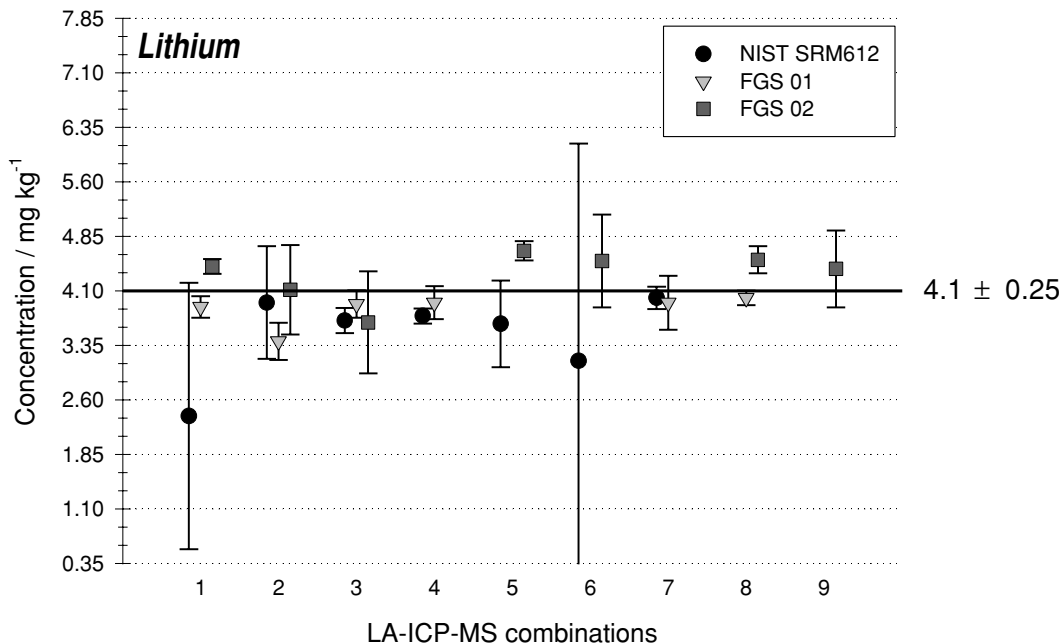


FIG. 5—FG 10-1 concentration values for Lithium in  $\text{mg kg}^{-1}$  (mean  $\pm$  std. dev.,  $N=4$ ) for three interlaboratory test studies using NIST SRM 612, FGS 1, and FGS 2 as external standards, respectively. The bold horizontal line indicates the mean value determined using liquid ICP-MS.

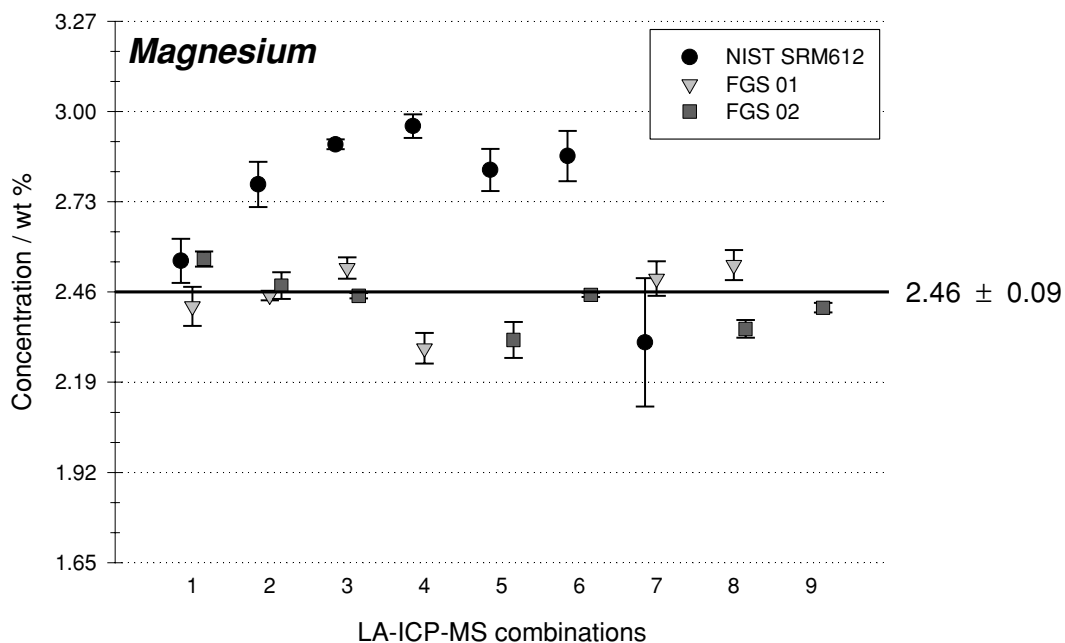


FIG. 6—FG 10-1 concentration values for Magnesium in wt% (mean  $\pm$  std. dev.,  $N=4$ ) for three interlaboratory test studies using NIST SRM 612, FGS 1, and FGS 2 as external standards, respectively. The bold horizontal line indicates the mean value determined using liquid ICP-MS.

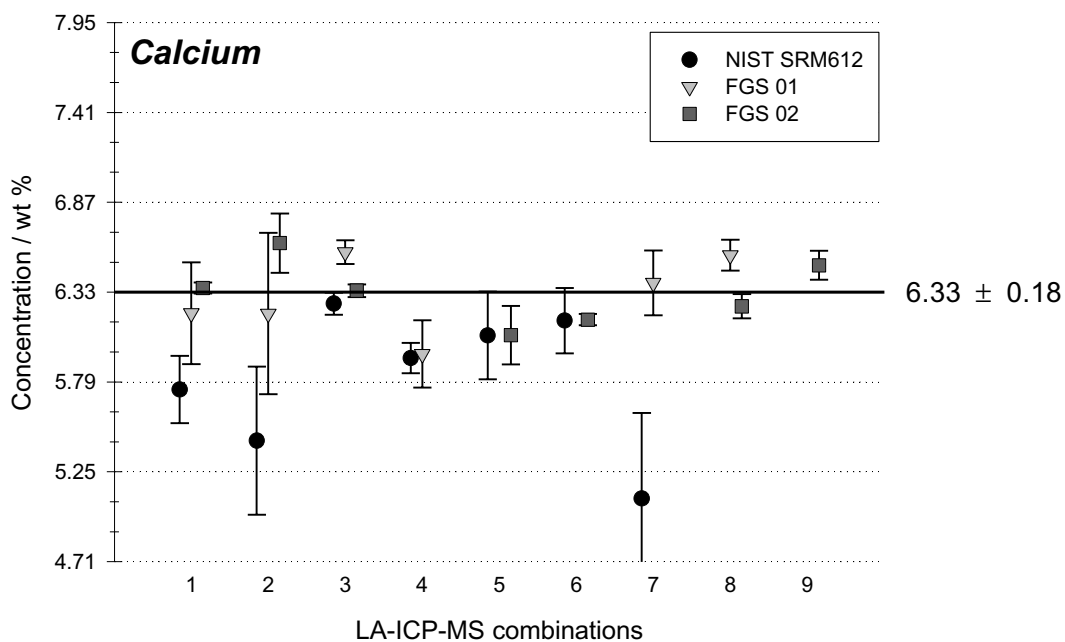


FIG. 7—FG 10-1 concentration values for Calcium in wt% (mean  $\pm$  std. dev.,  $N=4$ ) for three interlaboratory test studies using NIST SRM 612, FGS 1, and FGS 2 as external standards, respectively. The bold horizontal line indicates the mean value determined using liquid ICP-MS.



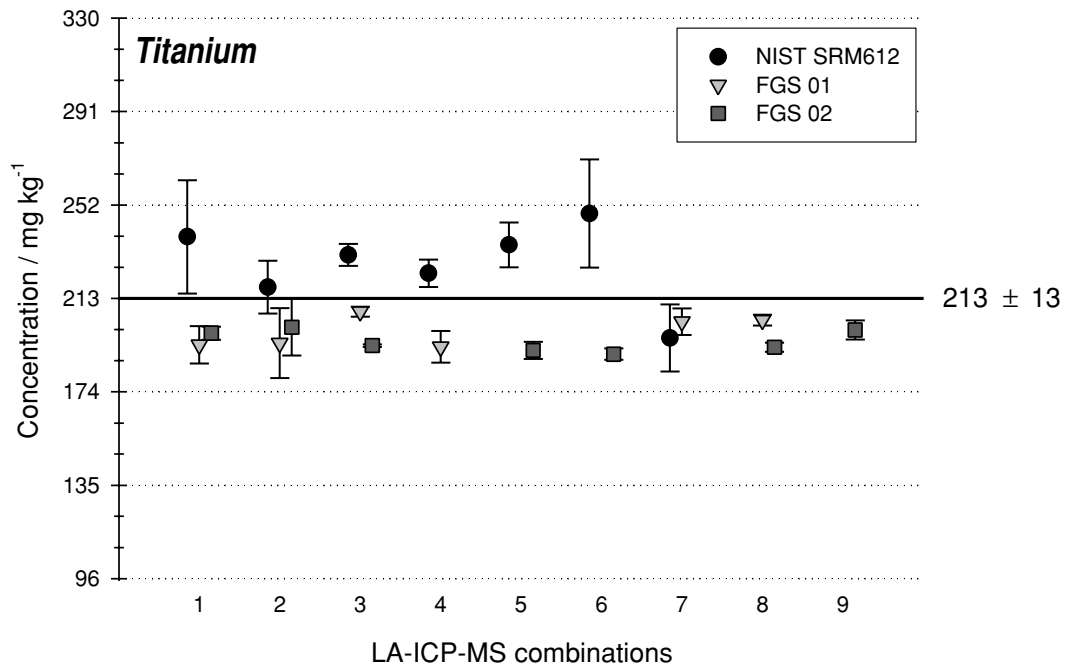


FIG. 8—FG 10-1 concentration values for Titanium in  $\text{mg kg}^{-1}$  (mean  $\pm$  std. dev.,  $N=4$ ) for three interlaboratory test studies using NIST SRM 612, FGS 1, and FGS 2 as external standards, respectively. The bold horizontal line indicates the mean value determined using liquid ICP-MS.

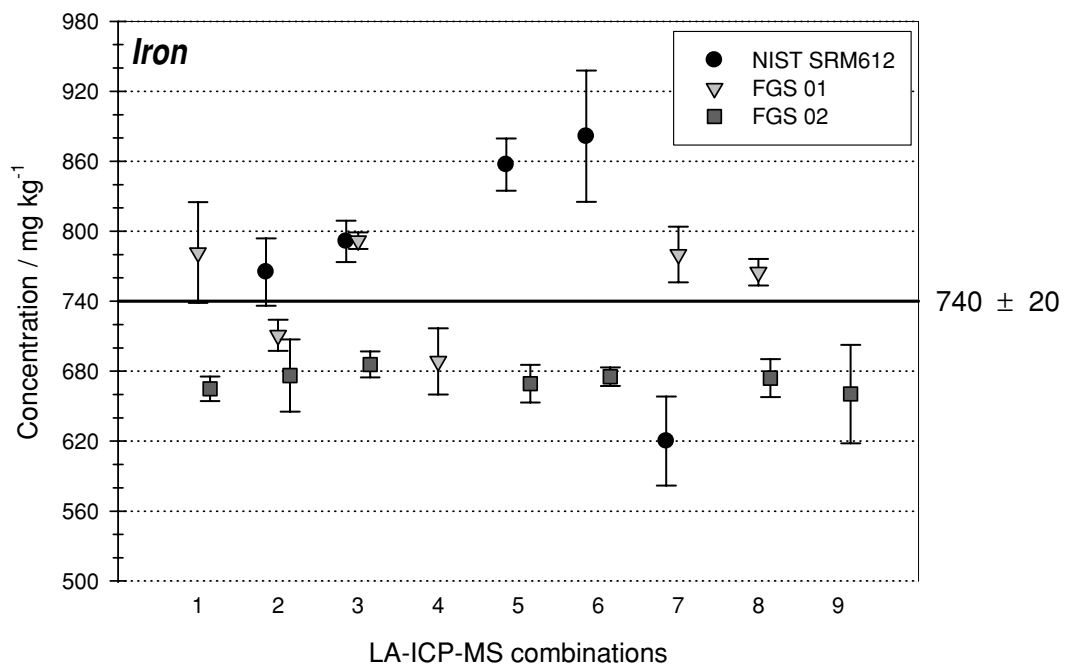


FIG. 9—FG 10-1 concentration values for Iron in  $\text{mg kg}^{-1}$  (mean  $\pm$  std. dev.,  $N=4$ ) for three interlaboratory test studies using NIST SRM 612, FGS 1, and FGS 2 as external standards, respectively. The bold horizontal line indicates the mean value determined using liquid ICP-MS.

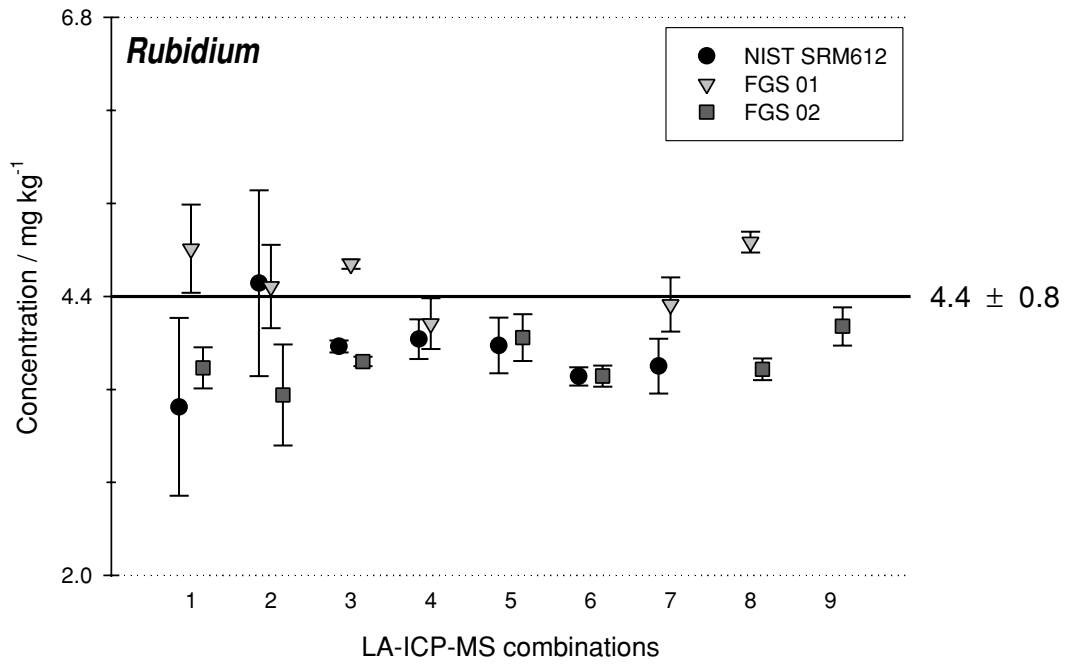


FIG. 10—FG 10-1 concentration values for Rubidium in  $\text{mg kg}^{-1}$  (mean  $\pm$  std. dev.,  $N=4$ ) for three interlaboratory test studies using NIST SRM 612, FGS 1, and FGS 2 as external standards, respectively. The bold horizontal line indicates the mean value determined using liquid ICP-MS.

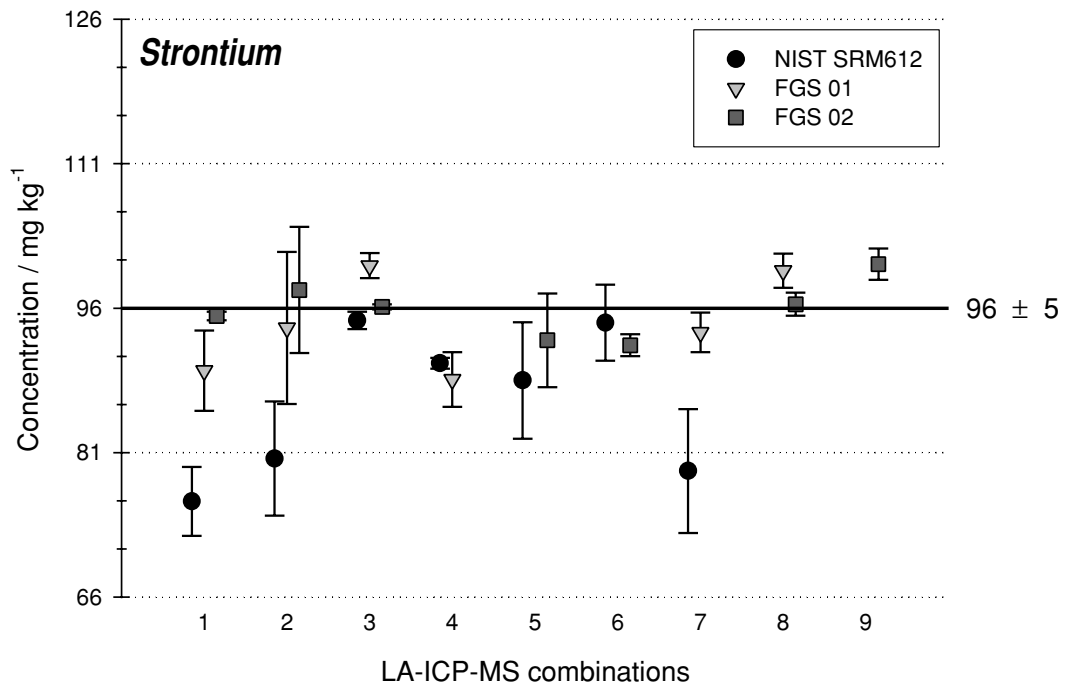


FIG. 11—FG 10-1 concentration values for Strontium in  $\text{mg kg}^{-1}$  (mean  $\pm$  std. dev.,  $N=4$ ) for three interlaboratory test studies using NIST SRM 612, FGS 1, and FGS 2 as external standards, respectively. The bold horizontal line indicates the mean value determined using liquid ICP-MS.

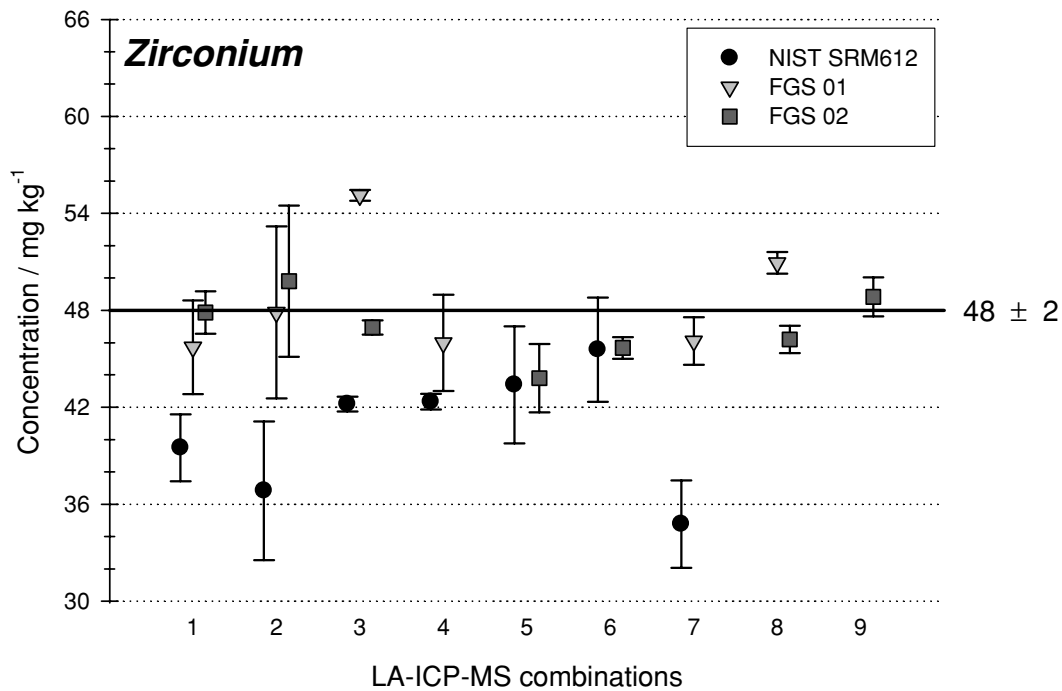


FIG. 12—FG 10-1 concentration values for Zirconium in  $\text{mg kg}^{-1}$  (mean  $\pm$  std. dev.,  $N=4$ ) for three interlaboratory test studies using NIST SRM 612, FGS 1, and FGS 2 as external standards, respectively. The bold horizontal line indicates the mean value determined using liquid ICP-MS.

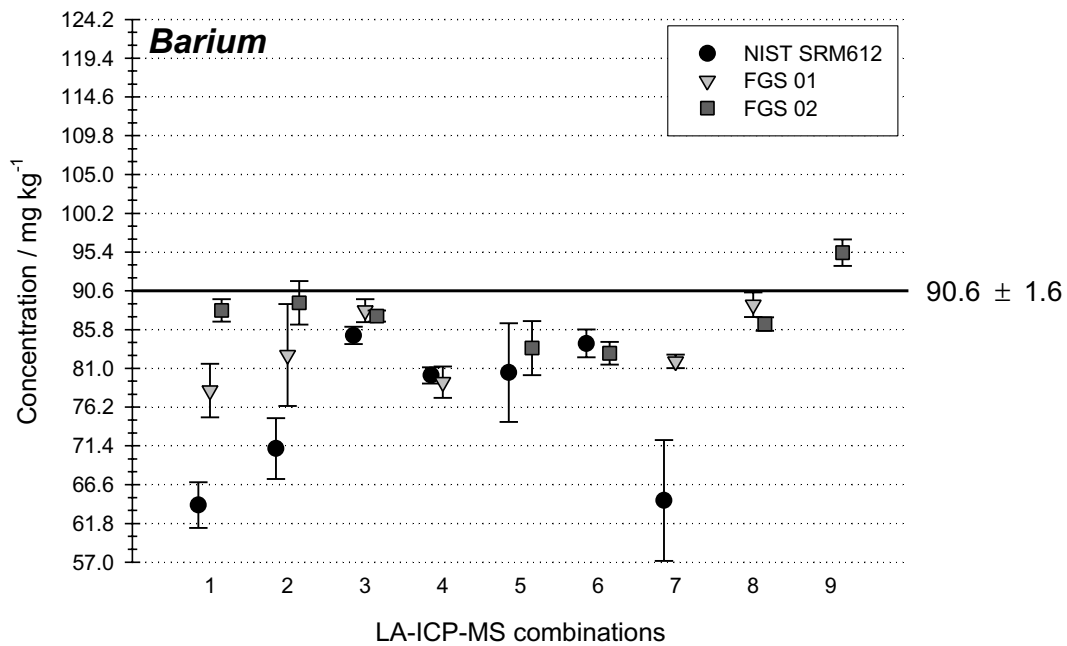


FIG. 13—FG 10-1 concentration values for Barium in  $\text{mg kg}^{-1}$  (mean  $\pm$  std. dev.,  $N=4$ ) for three interlaboratory test studies using NIST SRM 612, FGS 1, and FGS 2 as external standards, respectively. The bold horizontal line indicates the mean value determined using liquid ICP-MS.

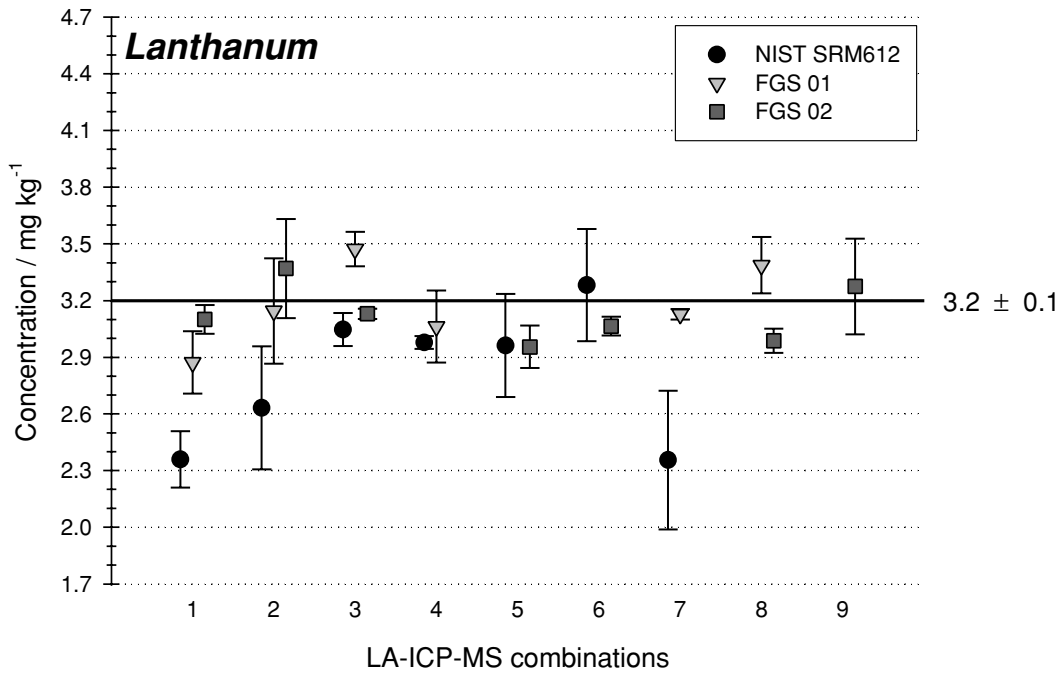


FIG. 14—FG 10-1 concentration values for Lanthanum in  $\text{mg kg}^{-1}$  (mean  $\pm$  std. dev.,  $N=4$ ) for three interlaboratory test studies using NIST SRM 612, FGS 1, and FGS 2 as external standards, respectively. The bold horizontal line indicates the mean value determined using liquid ICP-MS.

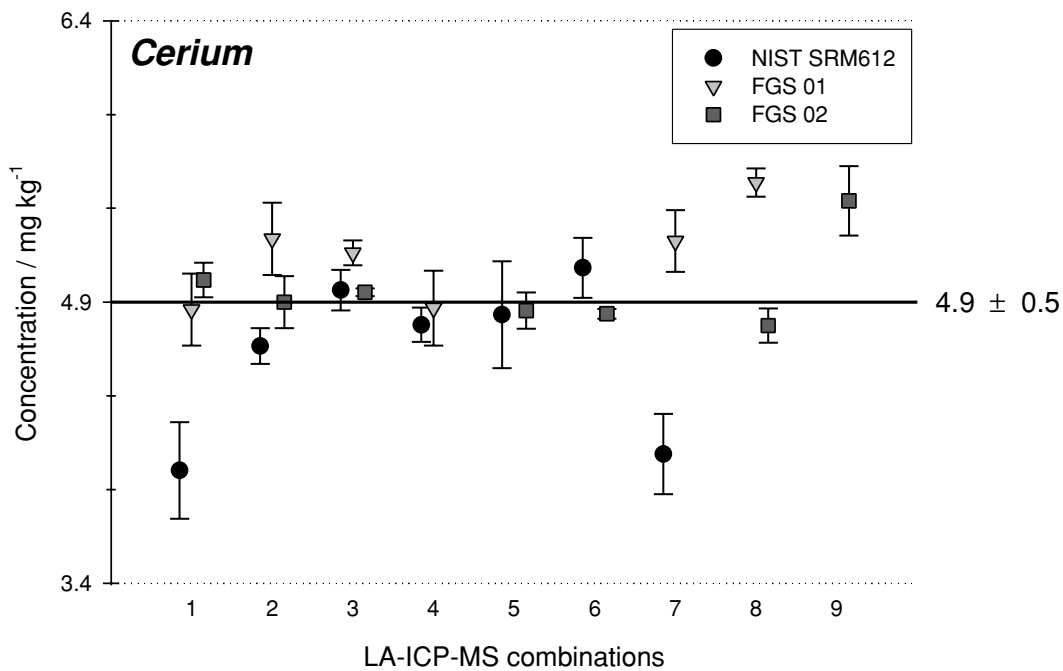


FIG. 15—FG 10-1 concentration values for Cerium in  $\text{mg kg}^{-1}$  (mean  $\pm$  std. dev.,  $N=4$ ) for three interlaboratory test studies using NIST SRM 612, FGS 1, and FGS 2 as external standards, respectively. The bold horizontal line indicates the mean value determined using liquid ICP-MS.

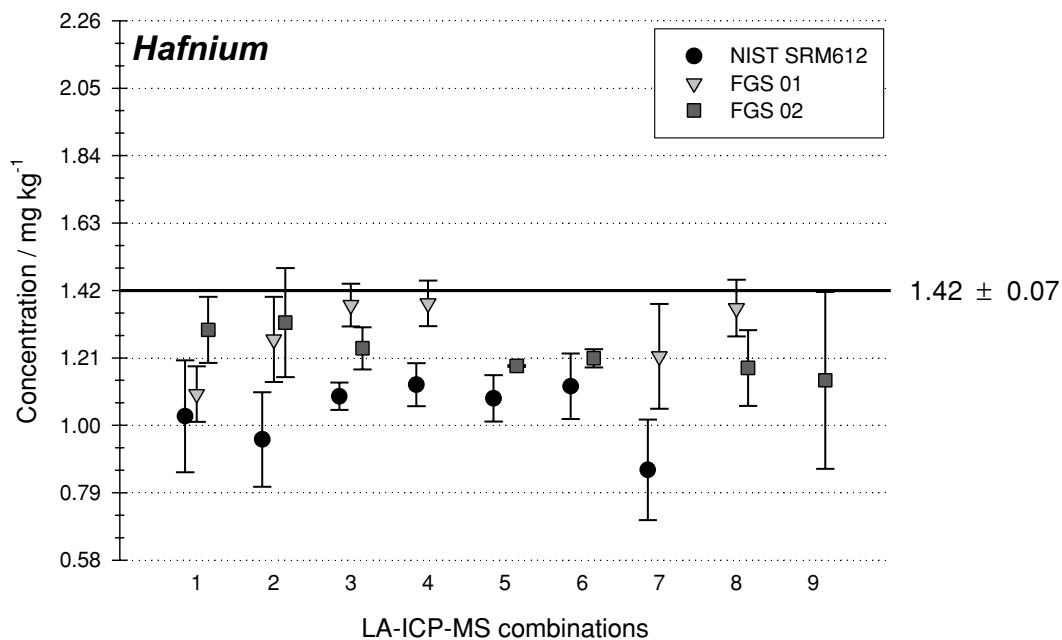


FIG. 16—FG 10-1 concentration values for Hafnium in mg kg<sup>-1</sup> (mean ± std. dev., N=4) for three interlaboratory test studies using NIST SRM 612, FGS 1, and FGS 2 as external standards, respectively. The bold horizontal line indicates the mean value determined using liquid ICP-MS.

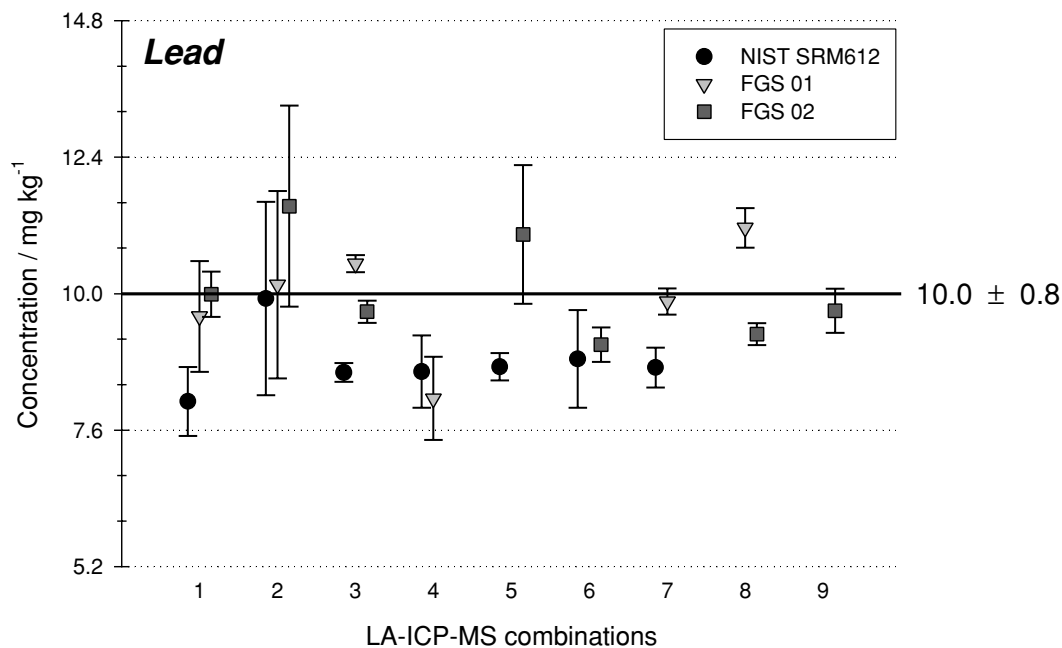


FIG. 17—FG 10-1 concentration values for Lead in mg kg<sup>-1</sup> (mean ± std. dev., N=4) for three interlaboratory test studies using NIST SRM 612, FGS 1, and FGS 2 as external standards, respectively. The bold horizontal line indicates the mean value determined using liquid ICP-MS.

case studies. Some NITE-CRIME (Natural Isotopes and Trace Elements in Criminalistics and Environmental Forensics) network partners considered the sample size in their glass studies and confirmed that results are sample size independent and similar results are obtained for glasses with a rough and untreated surface. Samples with dimensions as low as 100  $\mu\text{m}$  have been analyzed (S. Montero, NFI Scientific Report 2004, Netherlands Forensic Institute; 31).

## Conclusions

Evaluating the results of the four interlaboratory tests, it is concluded that for the analysis of forensic glass fragments it is essential to follow a dedicated laser ablation optimization protocol. However, since the operating conditions of various laser ablation-ICP-MS systems are so significantly different, matrix-matched float glass calibration standards are required to produce comparable concentration values. In general, the various interlaboratory tests indicate that a very detailed list of operating conditions, including a protocol for optimized laser ablation conditions and ICP-MS conditions (as given in the fourth interlaboratory test), leads to improved (in terms of precision and accuracy) concentration values. Furthermore, it also indicates if LA-ICP-MS is to become a routine forensic technique, further studies must be carried out on the effects of a number of parameters, including instrumental variations.

However, the introduction of matrix-matched standards (FGS 1 and FGS 2, respectively) helped to overcome problems related to elements susceptible to elemental fractionation processes. It was demonstrated that the new matrix-matched glass reference standards FGS 1 and FGS 2 can be used as calibration or tuning standards for the quantitative analysis of float glass. The two standards are available to the (forensic) LA-ICP-MS community, and can be used as calibration standards for forensic float glass LA-ICP-MS analysis.

Further tasks are focused on thorough chemical characterization of the two new glass calibration standards FGS 1 and FGS 2, so that these materials may be used as standard reference materials for forensic float glass analysis. In addition, a standardized guideline for the determination of trace elements in glass samples using LA-ICP-MS, including both laser ablation- and ICP parameters, is one of the future goals of the European Union NITE-CRIME (Natural Isotopes and Trace Elements in Criminalistics and Environmental Forensics) network to establish this technique as a routine method for crime scene investigations.

## Acknowledgments

Financial support granted through the Federal Office for Education and Science, Switzerland, and through the EU project G6RT-CT-2001-05025 (NITE-CRIME, Natural Isotopes and Trace Elements in Criminalistics and Environmental Forensics) is greatly acknowledged. Additional thanks go to Annette Walther (SCHOTT Glas) for her co-operation in the production of the new glass standard materials, and to Carolin Schmid and Thomas Fedgenhaeuer (BKA Wiesbaden) for sample preparation.

## References

1. Watling RJ, Lynch BF, Herring D. [Use of laser ablation inductively coupled plasma mass spectrometry for fingerprinting scene of crime evidence.](#) *J Anal At Spectrom* 1997;12:195–203.
2. Duckworth DC, Morton SJ, Bayne CK, Koons RD, Montero S, Almirall JR. [Forensic glass analysis by ICP-MS: a multi-element assessment of discriminating power via analysis of variance and pairwise comparisons.](#) *J Anal At Spectrom* 2002;17:662–8.
3. Hordijk M, Wiarda W, de Joode P, van der Peijl GJQ, Montero S. LA-ICP-MS method for the elemental profiling of forensic glass: A study of a float glass sample set collected in the Netherlands. *Forensic Sci Int* 2003;136:358–9.
4. Montero S, Hobbs AL, French TA, Almirall AR. Elemental analysis of glass fragments by ICP-MS as evidence of association: Analysis of a case. *J Forensic Sci* 2003;48:1101–7. [[PubMed](#)]
5. Trejos T, Montero S, Almirall JR. [Analysis and comparison of glass fragments by laser ablation inductively coupled plasma mass spectrometry \(LA-ICP-MS\) and ICP-MS.](#) *Anal Bioanal Chem* 2003;376:1255–64. [[PubMed](#)]
6. Koons RD, Buscaglia J. The forensic significance of glass composition and refractive index measurements. *J Forensic Sci* 1999;44:496–503.
7. Curran JM, Hicks T, Buckleton JS. *Forensic interpretation of glass evidence.* Boca Raton: CRC Press, 2000;17.
8. Parouchais T, Warner IM, Palmer LT, Kobus H. The analysis of small glass fragments using inductively coupled plasma mass spectrometry. *J Forensic Sci* 1996;41:351–60.
9. Becker S, Gunaratnam L, Hicks T, Stoecklein W, Warman G. The differentiation of float glass using refractive index and elemental analysis: comparisons of techniques. *Probl Forensic Sci* 2001;XLVII:80–92.
10. Buscaglia J. [Elemental analysis of small glass fragments in forensic science.](#) *Anal Chim Acta* 1994;288:17–24.
11. Almirall JR. Elemental analysis of glass fragments. In: *Forensic examination of glass and paint: Analysis and interpretation.* London, New York: Taylor & Francis, 2001; 65–83.
12. Aeschliman DB, Bajic SJ, Baldwin DP, Houk RS. [Multivariate pattern matching of trace elements in solids by laser ablation inductively coupled plasma-mass spectrometry: Source attribution and preliminary diagnosis of fractionation.](#) *Anal Chem* 2004;76:3119–25. [[PubMed](#)]
13. Strubel C, Meckel L, Effenberger R. Determination of the composition of glass, glass-ceramics and glass raw materials with laser-ICP-MS. *Glastech* 1999;72:15–20.
14. Caddy B. *Forensic examination of glass and paint: Analysis and interpretation.* London, New York: Taylor & Francis, 2001.
15. Gao S, Liu XM, Yuan HL, Hattendorf B, Günther D, Chen L, Hu SH. Determination of forty two major and trace elements in USGS and NIST SRM glasses by laser ablation-inductively coupled plasma-mass spectrometry. *Geostand News* 2002;26:181–96.
16. Pearce NJG, Perkins WT, Westgate JA, Gorton MP, Jackson SE, Neal CR, Chenery SP. A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. *Geostand News* 1997;21:115–44.
17. Hollocher K, Ruiz J. Major and trace-element determinations on NIST glass standard reference material-611, material-612, material-614, and material-1834 by ICP-MS. *Geostand News* 1995;19:27–34.
18. Becker S, Ducking M, Watzke P, Stoecklein W. Laser ablation in forensic glass analysis: The use of matrix matched standards for quantitative float glass analysis. *Forensic Sci Int* 2003;136:361.
19. Longerich HP, Jackson SE, Günther D. [Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation.](#) *J Anal At Spectrom* 1996;11: 899–904.
20. Bleiner D, Günther D. [Theoretical description and experimental observation of aerosol transport processes in laser ablation inductively coupled plasma mass spectrometry.](#) *J Anal At Spectrom* 2001;16:449–56.
21. Almirall JR, Furton KG, Duckworth DC, Morton SJ, Bayne CK, Montero S. Trace-elemental analysis of forensic glass samples by ICP-MS. *Abstr Pap Amer Chem Soc* 2000;219:108-ANYL.
22. Horn I, Guillong M, Günther D. [Wavelength dependant ablation rates for metals and silicate glasses using homogenized laser beam profiles—implications for LA-ICP-MS.](#) *Appl Surf Sci* 2001;182:91–102.
23. Gonzalez J, Mao XL, Roy J, Mao SS, Russo RE. [Comparison of 193, 213 and 266 nm laser ablation ICP-MS.](#) *J Anal At Spectrom* 2002;17: 1108–13.
24. Guillong M, Horn I, Günther D. [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* 2003;18:1224–30.
25. Rodushkin I, Axelsson MD, Malinovsky D, Baxter DC. [Analyte- and matrix-dependent elemental response variations in laser ablation inductively coupled plasma mass spectrometry—Part 2. Implications for multi-element analyses.](#) *J Anal At Spectrom* 2002;17:1231–9.

26. Guillon M, Kuhn HR, Günther D. Application of a particle separation device to reduce inductively coupled plasma-enhanced elemental fractionation in laser ablation-inductively coupled plasma-mass spectrometry. *Spectrochim Acta B* 2003;58:211–20.
27. Kuhn HR, Guillon M, Günther D. Size-related vaporisation and ionisation of laser-induced glass particles in the inductively coupled plasma. *Anal Bioanal Chem* 2004;378:1069–74. [PubMed]
28. Trejos T, Almirall JR. Effect of fractionation on the forensic elemental analysis of glass using laser ablation inductively coupled plasma mass spectrometry. *Anal Chem* 2004;76:1236–42. [PubMed]
29. Longerich HP, Günther D, Jackson SE. Elemental fractionation in laser ablation inductively coupled plasma mass spectrometry. *Fresenius J Anal Chem* 1996;355:538–42.
30. Becker S, Chadzelek A, Stoecklein W. Classification of float glasses with respect to their origin by chemometric analysis of elemental concentrations and the use of LA-ICP-MS as a tool in forensic science. Proceedings of the European Winter Conference on Plasma Spectrochemistry, January 10–15, 1999, organized and published by the Université de Pau et des Pays de l'Adour, 64016 Pau, France, 113–4.
31. Trejos T, Almirall JR. Sampling strategies for the analysis of glass fragments by LA-ICP-MS. Part II: sample size and sample shape considerations. *Talanta*, in press.

Additional information and reprint requests:  
Christopher Latkoczy, Ph.D.  
Lab of Inorg Chem—ETH Zurich  
Hoenggerberg—HCI G111  
Wolfgang-Pauli Strasse 10  
CH—8093 Zurich  
Switzerland  
Fax: +41-1-633-1071  
E-mail: Latkoczy@inorg.chem.ethz.ch  
Web: <http://www.analytica.ethz.ch/>