Elemental analyses of soil and sediment fused with lithium borate using isotope dilution laser ablation-inductively coupled plasma-mass spectrometry

Julien Malherbe [a],[*], Fanny Claverie [a], Aitor Alvarez [b], Beatriz Fernandez [b], Rosario Pereiro [b], John L. Molloy [a]
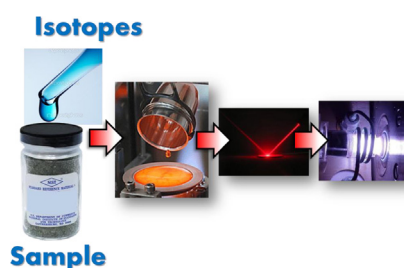
[a] *Chemical Sciences Division, Material Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8391, Gaithersburg, MD 20899, USA*
[b] *Department of Physical and Analytical Chemistry, Faculty of Chemistry, University of Oviedo, Julian Clavería, 8, 33006 Oviedo, Spain*

GRAPHICAL ABSTRACT

ABSTRACT

Quantitative analysis using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) remains challenging primarily due to the lack of appropriate reference materials available for the wide variety of samples of interest and to elemental fractionation effects. Isotopic dilution mass spectrometry (IDMS) is becoming the methodology of choice to address these issues because the different isotopes of an element represent near-perfect internal standards. In this work, we investigated the lithium borate fusion of powdered solid samples, including soils, sediments, rock mine waste and a meteorite, as a strategy to homogenously distribute, i.e. equilibrate the elements and the added isotopically enriched standards. A comparison of this methodology using two pulsed laser ablation systems (ArF* excimer and Nd:YAG) with different wavelengths as well as two ICP-MS instruments (quadrupole and double-focusing sector field) was performed. Emphasis was put on using standard equipment to show the potential of the proposed strategy for its application in routine laboratories. Cr, Zn, Ba, Sr and Pb were successfully determined by LA-ICP-IDMS in six Standard Reference Materials (SRMs) representing different matrices of environmental interest. Experimental results showed the SRM fused glasses exhibited a low level of heterogeneity (intra- and inter-sample) for both natural abundance and isotopically enriched samples (RSD <3%, $n = 3$, 1σ). A good agreement between experimental results and the certified values was also observed.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Traditional methods to determine the mass fractions of metals in soils and sediments involve an acid digestion step that is time consuming, prone to contamination and analyte loss. A complete

* Corresponding author. Tel.: +33 540175035.
  E-mail address: malherbe.julien@hotmail.fr (J. Malherbe).

dissolution of the sample can sometimes prove difficult [1] when refractory phases are present. Several solid-state techniques that do not require prior dissolution of the sample can be used to determine metals mass fraction at the mg kg^{-1} level or below in soils and sediment, such as neutron activation analysis [1], solid-state graphite furnace atomic absorption spectroscopy [2], solid-state electro thermal vaporization inductively coupled plasma mass spectrometry [2,3] or laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [4,5] each of them having their pros and cons.

LA-ICP-MS is a versatile tool and has been widely investigated as a powerful technique for the direct analysis of different types of materials, allowing elemental and isotopic analyses of solids, including microanalysis and depth profiling, at trace concentration levels. However, the lack of appropriate reference materials and elemental fractionation effects (i.e. the preferential ablation of one element compared to another) can severely limit the quantification capabilities of LA-ICP-MS. In other words, a non-stoichiometric ablation process [6,7] can take place, specifically with lasers working in the nanosecond (ns) time regime, which are the most widespread type of laser ablation systems. These issues will have a negative impact on the quantification of the elements, typically performed using an external calibration with matrix-matched reference materials in conjunction with an internal standard (generally the major element of the matrix).

One way to get around these limitations is to use isotope dilution mass spectrometry (IDMS) [8] because the different isotopes of an element are expected to behave similarly (at least at the level of precision required for isotope dilution) and can be considered as almost perfect internal standards. The feasibility of using isotope dilution LA-ICP-MS has been investigated by several groups using four different strategies: by direct spiking of the solid [9–14], by using a nebulizer inserted in the ablation chamber to introduce the isotopically enriched solution [15,16], by mixing the spike and sample aerosols in the ablation cell using a laser scanner [17,18] or a spinning platform [19], or by fusing the sample and spike into a glass [20]. It should be stated that the studies involving direct spiking of the solid were mainly performed with non-standard equipment [14] and used a laser system dedicated to bulk analysis (crater of 4 mm) to minimize heterogeneity issues of the spike/sample mixture [9]. On the other hand, the use of isotopically enriched solutions [15] does not correct for variations in ablated mass. The knowledge of one homogeneously distributed element mass fraction in the sample is also required to correct for instrumental drift. A new approach which removed the need for a known element in the sample has been proposed [16] but it is based on the precise mass determination of both the spike consumed and the ablated sample, which is a difficult task. The mixing aerosol strategy [17,19] requires a laser system equipped with a scanner (that allows fast movement of the beam between the sample and the spike pellets) or a spinning platform. Nevertheless, currently most laser systems are dedicated to microanalysis and are not equipped with scanning capabilities or with a spinning platform.

The mixing and equilibration of enriched isotopes with natural elements is an essential step to successfully carry out isotope dilution analyses. However, the spiking of a solid with a solution can sometimes be troublesome [21]: analyte in liquid state can gradually concentrate in isolated droplet as water evaporates during the sample drying process leading to improper mixing. Additional grinding and homogenization may not be enough to overcome this problem, depending on the required homogeneity scale [21]. Finally, pelletization can prove difficult with certain matrices without the use of binders, which may represent a source of metallic contamination. Alternatively, the glass fusion approach [20,22] seems promising in terms of measurement accuracy and precision

and homogeneity but no follow-up studies were performed since its publication in 1999 and quantification was limited to Zr and Hf in materials of geological interest (basaltic-andesitic matrices).

The aim of our study is to broaden the applicability of this strategy to other elements (Cr, Zn, Ba, Sr and Pb) and samples of interest for the environmental field. In the present study, a new variation of the Reid et al. scheme was used to perform LA-ICP-IDMS by fusing the powdered samples and the spikes solution into a glass using lithium borate (67% $Li_2B_4O_7$–33% $LiBO_2$) as fusing matrix. The use of fused lithium borate glasses in LA-ICP-MS has already been discussed by several authors [23–26] for quantification purposes by external calibration. The advantages of using such a procedure include: homogeneous mixing of analytes, possible dilution for highly concentrated elements, complete digestion of refractory phases and stability of fused glass samples over time. The present practical study was focused on using standard instrumentation and on saving time for its possible use as routine methodology. A comparison of two pulsed laser ablation systems (ArF* excimer and Nd:YAG) as well as two ICP-MS instruments (quadrupole (Q) and double-focusing sector field (SF)) was carried out. Several soil and sediment reference materials as well as a rock mine waste and a meteorite were analyzed by LA-ICP-IDMS. Homogeneity of the glasses made from the reference materials was carefully investigated and limits of detection were evaluated with the two instrumental configurations.

2. Materials and methods

2.1. Samples, reference materials and reagents

Six Standard Reference Materials (SRMs) were investigated to demonstrate the suitability of the proposed LA-ICP-IDMS strategy for the determination of elemental mass fractions in powdered samples: SRM 1944 (New York/New Jersey waterway sediment), SRM 2586 (trace elements in soil containing lead from paint), SRM 2702 (inorganics in marine sediment), SRM 2710a (Montana I soil), SRM 2711a (Montana II soil) and SRM 2780 (hard rock mine waste) from NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA). Furthermore, the Allende meteorite (USNM 3529 Split 5 pos. 20) in powdered form was fused and analyzed by LA-ICP-IDMS to demonstrate the potential of this methodology.

Isotopically enriched spike solutions were prepared by dissolution in nitric acid of an accurately weighed amount of enriched powders purchased from Trace Science International (Richmond Hill, ON Canada) and Oak Ridge National Laboratory (Oak Ridge, TN, USA). SRM series 3100 elemental spectrometric solutions of Cr, Zn, Ba, Sr and Pb from NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) were used for the characterization of spike abundances and mass fractions by reverse isotope dilution ICP-MS (see Table 1).

2.2. Samples preparation

Glasses of each SRM were prepared by lithium borate fusion by mixing an accurately weighed amount of SRM (≈0.75 g) with an accurately weighed amount of flux (≈4 g) of Lithium borate (67% $Li_2B_4O_7$–33% $LiBO_2$) from Spex (New Jersey, USA) in a 30 mL capacity platinum crucible. These 4.75 g of material were then spiked with the different spike solutions, dried in an oven and then fused. The amount of spike added was optimized with respect to the influence of the error multiplication factor [8] and, therefore, it was sample dependent.

The fusion was performed using the Perl'x31 induction-heated machine (PANalytical, Almelo, The Netherlands) using a 7 steps

Table 1

Elemental mass fractions and isotopic abundances of the isotope enriched spike solutions. Uncertainties represent the standard deviations of the mean of 4 independent mass fraction and abundance determinations conducted over a one year period.

Element	Mass fraction (mg kg^{-1})	Abundance of enriched isotope (%)	Abundance of reference isotope (%)
Cr	321.9 ± 10.6	^{53}Cr: 97.70 ± 0.20	^{52}Cr: 2.19 ± 0.01
Zn	939.1 ± 11.0	^{68}Zn: 99.23 ± 0.10	^{66}Zn: 0.10 ± 0.01
Sr	46.1 ± 3.7	^{86}Sr: 97.60 ± 0.05	^{88}Sr: 1.73 ± 0.05
Ba	1186.1 ± 36.1	^{135}Ba: 94.00 ± 0.05	^{138}Ba: 2.33 ± 0.02
Pb	14,427.9 ± 527.0	^{206}Pb: 92.15 ± 0.01	^{208}Pb: 1.25 ± 0.01

fusion program: (1) heating at 850 °C for 1 min 30 s, (2) heating at 975 °C for 5 min, (3) heating at 975 °C for 7 min with mixing by rocking the crucible, (4) cooling to room temperature (with mixing), (5) manual addition of one drop of a 20% LiI (aq) non-wetting agent, (6) heating at 975 °C for 4 min (with mixing), (7) casting into a Pt dish (1 min 40 s at 975 °C) followed by forced-air cooling from under the dish (30 s). A 3 cm diameter glass with a ≈1:6 dilution ratio was then obtained in the casting dish. The whole sample preparation takes approximately 1 h and the fusion step itself requires approximately 40 min. In a previous study [19] it was shown for Zn, Sr, Ba and Pb that no significant analyte loss occurs during the fusion step and thus the fusion process is suitable for quantitative analysis. While Cr was not studied previously, it is more refractory than the other analytes and thus less likely to be lost. Moreover, the chosen isotope dilution approach, which involves the addition of spike before the fusion, is able to correct for eventual losses because the enriched isotopes of the spike will react the same way as the analytes from the sample.

In addition to the isotopically enriched SRMs, a glass of each SRM without any spike was fused to study the influence of mass bias correction. Finally, to compare our approach with the traditional method involving pelletization, a pellet of SRM 1944 (spiked with the same amount of spikes as the glass) was made using the following procedure: (1) spiking of 0.75 g of soil with the isotopically enriched solution, (2) drying in oven at 105 °C until dryness, (3) homogenization by grinding using an agate mortar, (4) pelletization using a 10 mm die with a pressure of 2 tons for 5 min.

2.3. Instruments and procedure

Two different instrumental configurations were employed in this work. First, an ArF* 193 nm excimer laser ablation system (Photon Machine Analyte.193, San Diego, CA, USA) which delivers 4 ns pulses at repetition rates ranging from 1 Hz to 300 Hz was employed

at NIST. In this study, a repetition rate of 20 Hz was chosen to mimic the conditions available to most laser systems. It was coupled to an ICP-MS X7 (Thermo Elemental, Waltham, MA, USA) under wet plasma configuration. The laser generated aerosol and a nebulized 2% nitric acid solution were mixed together using a Y-connection to obtain a more robust condition of the ICP [27] No collision cell was used in this study because the plasma conditions were chosen so that the ratio CeO/Ce was below 2% and because the analysis of the glass made to correct mass bias did not reveal deviations in the isotopic ratios higher than 5% thus excluding major spectral interferences. Moreover, in the context of multi-elemental analyses, the use of collision cell can sometimes induce further complications on the non-interfered elements such as a decrease of the LODs or the formation of new interferences with the atoms of the collision gas. Next, a Nd:YAG 213 nm laser system (Cetac Technologies, USA) coupled to a double-focusing sector field ICP-MS (Element 2, Thermo Fisher Scientific, Germany) was employed at the University of Oviedo. In this case, dry plasma conditions were used. Table 2 summarizes the conditions used for LA-ICP-MS analysis in both cases.

Measured isotope ratios were corrected for detector dead-time [8]. At the optimized experimental conditions, two replicate ablations of the natural abundance SRM glass were performed before and after the analysis of isotopically enriched SRM glass to correct for mass bias. The final calculation of the LA-ICP-IDMS results was carried out by using the conventional isotope dilution equation [8].

3. Results and discussion

3.1. Method validation on standard reference materials

Fig. 1 presents the typical ablation profile obtained by LA-ICP-MS for the fused samples. In the case of the ArF* excimer laser coupled to a quadrupole ICP-MS, the calculation of isotope ratios is

Table 2

Operating conditions of the laser and ICP-MS systems.

ICP-MS	Thermo Elemental, X7 series (Q-ICP-MS)	Thermo Element 2 (SF-ICP-MS)
Argon flow rates		
• Plasma gas	13.6 L min^{-1}	15.5 L min^{-1}
• Auxiliary gas	0.86 L min^{-1}	0.8 L min^{-1}
• Nebulization gas	0.71 L min^{-1}	0.4 L min^{-1}
RF power	1200 W	1350 W
Cones material	Ni	Ni
Dwell time	50 ms	10 ms (10 samples per peak, 75% mass window)
Isotopes	^{52}Cr, ^{53}Cr, ^{66}Zn, ^{68}Zn, ^{86}Sr, ^{88}Sr, ^{135}Ba, ^{138}Ba, ^{206}Pb, ^{208}Pb	^{52}Cr, ^{53}Cr, ^{66}Zn, ^{68}Zn (Medium Resolution) ^{86}Sr, ^{88}Sr, ^{135}Ba, ^{138}Ba, ^{206}Pb, ^{208}Pb (low resolution)

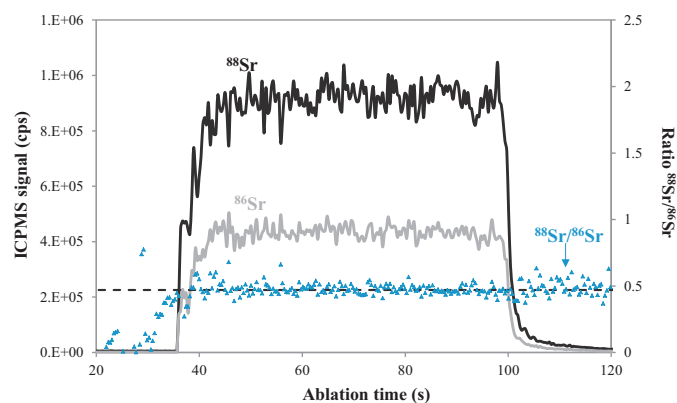| Laser ablation system	Photon Machines, Analyte 193 (ArF* excimer)	Cetac Technologies, LSX-213 (Nd:YAG)
Wavelength	193 nm	213 nm
Pulse duration	4 ns	<6 ns
Fluence	7 J cm^{-2}	13.4 J cm^{-2}
Repetition rate	20 Hz	20 Hz
Spot size	34–138 μm	200 μm
Carrier gas flow rate (He)	0.550 L min^{-1}	1 L min^{-1}
Raster length	1200 μm	2400 μm
Stage displacement speed	10 μm s^{-1}	20 μm s^{-1}

Fig. 1. Strontium signals during the ablation of the fused spiked SRM 2710a (ArF* excimer laser and Q-ICP-MS).

accomplished using the net intensities, i.e. intensities substracted of the gas blank recorded in the first 30 s. The average of this ratio over the ablation time is then used in the isotope dilution equation. In contrast, using the Nd:YAG laser and the sector field ICP-MS the isotope ratios were calculated by a new strategy recently described [28]. The INDEX and LINEST functions of Microsoft EXCEL calculate the statistics for a line by using the "least squares" method to determine a straight line that best fits the obtained data, and return an array that describes the line. In this way, background correction and the subjective influence which may occur by setting the integration limits were avoided, simplifying the evaluation of data enormously. It should be stated that differences below 0.5% were found between the isotope ratio values determined by the two different strategies on a given dataset and the measurement precision were almost identical.

The goal of this study was to demonstrate that the proposed methodology was suited for fast, routine analyses. Therefore, the five elements were quantified using the same ablation line which permits to save time. The average measurement bias considering all elements and all SRMs was about 4.2% on both systems (error ranging from 0% to 16.5%). Moreover, the average measurement precision for 5 replicates was 1.7% RSD (ArF* excimer and Q-ICP-MS) and 0.9% RSD for 3 replicates (Nd:YAG and SF-ICP-MS). As can be seen on Fig. 2 and Table 3,[1] the studied mass fraction ranges from 23 mg kg^{-1} to 5770 mg kg^{-1}. Lower mass fraction values have been studied in the literature for elements having low background levels [24]. Detection limits obtained for both LA-ICP setups were calculated by using the natural abundance SRM glasses. The 3s criterion (3s_b/S) was employed to calculate the limits of detection (LODs), where s_b is the standard deviation of 3 independent measurements of the gas blank value in cps and S is the sensitivity for the corresponding analyte isotope. Table 4 collects the LODs obtained for three different matrices. In all cases LODs were in the low mg kg^{-1} range. As expected, lower LODs can be generally achieved using the Nd:YAG laser with the SF-ICP-MS because of the lower background and higher sensitivity obtained with the high resolution sector field mass spectrometer compared to the quadrupole mass spectrometer.

It should be stated that for the experiments carried out using the quadrupole ICP-MS no reaction cell was used during this study to eliminate possible isobaric interferences, as explained in Section 2. The differences observed for Zn concentration in the SRMs between the analyses performed using the quadrupole and the sector field ICP-MS could be attributed to the presence of
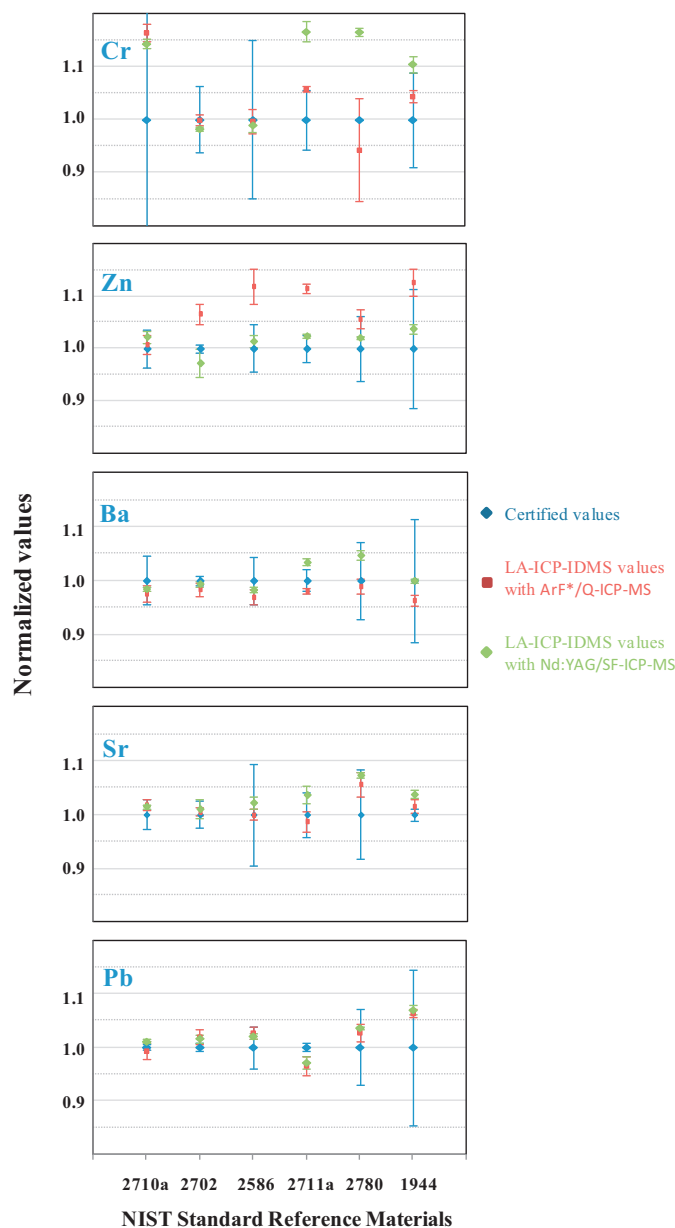

Fig. 2. Results obtained by LA-ICP-IDMS for Cr, Zn, Sr, Ba and Pb for the six NIST SRMs (results were normalized by the certified value). Uncertainties shown result from standard deviations of the mean of 5 (ArF*/Q-ICP-MS) and 3 (Nd:YAG/SF-ICP-MS) independent ablations.

polyatomic interferences for ^{66}Zn and ^{68}Zn (possibly ^{28}Si^{40}Ar) considering that any deviations from certified values are much smaller using the medium resolution of the sector field mass spectrometer.

Different factors can influence the measurement uncertainties of analyses using the proposed methodology. Using Kragten et al. calculations [29],[2] it was found that the main sources of uncertainty for most samples were the measurements of the isotopic ratios in the natural abundance glasses (for mass bias correction) and the isotopically enriched glasses, as well as the spike mass fractions. The measurement precision of the isotopic ratios can also be influenced by the homogeneity of the spiked and unspiked glasses and by Poisson counting statistics [20]. In all cases except Zn, the

---

[1] See also Figure S1 in Supplementary material.

[2] See Figure S2 in Supplementary material.

Table 3
Detailed results obtained by LA-ICP-IDMS for Cr, Zn, Sr, Ba and Pb for the six NIST SRMs. Uncertainties shown result from standard deviations of the mean of 5 and 3 independent ablations (ArF* and Nd:YAG laser systems, respectively). Combined uncertainties resulting from Kragten et al. calculations are indicated in parenthesis.

SRM	Elements	Certified concentration (mg kg^{-1})	LA-ICP-IDMS concentration (mg kg^{-1}) Nd:YAG laser + SF-ICP-MS	LA-ICP-IDMS concentration (mg kg^{-1}) ArF* + Q-ICP-MS
2710a	Cr	23.0 ± 6.0	26.3 ± 0.2 (2.1)	26.8 ± 0.4 (2.8)
	Zn	4180.0 ± 150.0	4275.0 ± 49.0 (145.4)	4213.3 ± 77.9 (470.1)
	Ba	792.0 ± 36.0	780.0 ± 3.0 (41.8)	772.9 ± 11.9 (74.1)
	Sr	255.0 ± 7.0	259.0 ± 1.0 (10.5)	259.8 ± 2.6 (12.4)
	Pb	5520.0 ± 30.0	5580.0 ± 21.0 (278.8)	5484.3 ± 93.1 (555.1)
2702	Cr	352.0 ± 22.0	346.0 ± 1.0 (23.4)	351.9 ± 3.2 (26.1)
	Zn	485.3 ± 4.2	472.0 ± 13.0 (22.7)	517.7 ± 9.4 (23.2)
	Ba	397.4 ± 3.2	395.0 ± 2.0 (20.4)	391.1 ± 4.9 (23.4)
	Sr	119.7 ± 3.0	121.0 ± 2.0 (5.4)	120.3 ± 0.9 (6.3)
	Pb	132.8 ± 1.1	135.0 ± 1.0 (7.2)	135.4 ± 1.9 (9.3)
2586	Cr	301.0 ± 45.0	298.0 ± 4.0 (22.9)	300.3 ± 6.9 (30.5)
	Zn	352.0 ± 16.0	357.0 ± 4.0 (14.2)	393.9 ± 12.0 (23.3)
	Ba	413.0 ± 18.0	406.0 ± 2.0 (18.3)	400.4 ± 5.5 (26.3)
	Sr	84.1 ± 8.0	86.0 ± 1.0 (3.7)	84.1 ± 0.8 (4.8)
	Pb	432.0 ± 17.0	441.0 ± 2.0 (24.1)	443.7 ± 4.5 (28.6)
2711a	Cr	52.3 ± 2.9	61.0 ± 1.0 (13.7)	55.3 ± 0.3 (8.2)
	Zn	414.0 ± 11.0	424.0 ± 2.0 (24.1)	461.7 ± 3.5 (29.5)
	Ba	730.0 ± 15.0	755.0 ± 5.0 (48.3)	715.9 ± 4.5 (44.2)
	Sr	242.0 ± 10.0	251.0 ± 4.0 (16.5)	239.1 ± 4.6 (18.1)
	Pb	1400.0 ± 10.0	1360.0 ± 15.0 (99.2)	1352.0 ± 25.4 (121.3)
2780	Cr[a]	44.0	51.3 ± 0.3 (16.1)	41.5 ± 4.2 (6.2)
	Zn	2570.0 ± 160.0	2624.0 ± 6.0 (102.0)	2715.6 ± 44.7 (147.8)
	Ba[b]	993.0 ± 71.0	1040.0 ± 8.0 (50.5)	982.6 ± 14.7 (66.5)
	Sr[b]	217.0 ± 18.0	233.0 ± 1.0 (8.8)	229.3 ± 4.8 (19.4)
	Pb	5770.0 ± 410.0	5980.0 ± 18.0 (326.9)	5928.6 ± 93.7 (431.4)
1944	Cr	266.0 ± 24.0	294.0 ± 4.0 (27.4)	277.8 ± 3.2 (22.6)
	Zn	656.0 ± 75.0	681.0 ± 6.0 (27.8)	739.1 ± 17.3 (40.6)
	Ba[a]	499.0 ± 57.0	499.0 ± 2.0 (23.4)	480.8 ± 4.7 (28.9)
	Sr[c]	136.8 ± 1.5	142.0 ± 1.0 (8.3)	139.0 ± 1.6 (10.0)
	Pb	330.0 ± 48.0	353.0 ± 3.0 (28.0)	351.0 ± 2.5 (22.4)

[a] Information value.
[b] Reference values.
[c] Not certified but determined by liquid ICP-IDMS.

Table 4
Limits of detection obtained by LA-ICP-MS setups for three SRMs.

Element	LODs (mg kg^{-1}) with SRM 2702 (sediment)		LODs (mg kg^{-1}) with SRM 2780 (rock mine waste)		LODs (mg kg^{-1}) with SRM 2710a (soil)	
	Nd:YAG/SF-ICPMS	ArF*/Q-ICPMS	Nd:YAG/SF-ICPMS	ArF*/Q-ICPMS	Nd:YAG/SF-ICPMS	ArF*/Q-ICPMS
^{52}Cr	0.098	0.48	0.032	0.49	0.175	0.34
^{66}Zn	2.99	2.46	1.63	3.88	3.60	72.3
^{88}Sr	0.033	0.032	0.125	0.118	0.180	0.059
^{138}Ba	0.076	0.040	0.051	0.098	0.055	1.53
^{208}Pb	0.019	0.050	0.021	0.020	0.310	3.11

determination of the spike mass fraction dominated the uncertainty of the measurements made.

3.2. Comparison of sample preparation methods: glass fusion versus pelletization

The fusion method can be time consuming compared to simple pelletizing although automated fusion machines combined with a general fusion methodology used can be faster than having to customize each pellet to the physical binding properties of the sample of interest. Borate fusion procedure is also expected to produce a more homogeneous sample and allow a better mixing of elements with their respective isotopically enriched isotopes. In order to ensure the homogeneity of the synthesized glasses, both for the natural abundance and the isotopically enriched lithium borate glasses, the inter-sample and intra-sample homogeneity were investigated by LA-ICP-MS using two different matrices (SRM 2702 and SRM 2780).[3] Table S1 shows the isotope ratios and the standard deviation values obtained for three independent measurements by LA-ICP-MS. As can be seen, measurement precisions better than 1% ($n = 3$, 1σ) were obtained in all cases except for Cr (1–3% RSD, $n = 3$, 1σ), demonstrating that the sample preparation strategy allows obtaining homogeneous distribution of sample and spike analytes.

In order to compare glass fusion to simple spiking of the sample followed by pelletization, both approaches were used on SRM 1944 using the same amount of sample and spikes. The size of the crater produced during the ablation was not the same between the glass (56 μm) and the pellet (7 μm). The size of the laser spot was chosen so that the highest signal (^{138}Ba) in the SRM remains below the upper count limit of the pulse counting detector (i.e. every isotope was counted on the same detector thus removing

---

[3] See Table S1 in Supplementary material.

Table 5
Mass fraction obtained by LA-ICP-IDMS on the Allende meteorite using the two instrumental configurations. Uncertainties shown result from standard deviations of the mean of 5 and 3 independent ablations (ArF* and Nd:YAG laser systems, respectively). Combined uncertainties resulting from Kragten et al. calculations are indicated in parenthesis.

Element	Literature range (mg kg^{-1}) [31]	Mean values (mg kg^{-1})	LA-ICP-IDMS (mg kg^{-1}) ArF*/Q-ICPMS	LA-ICP-IDMS (mg kg^{-1}) Nd:YAG/SF-ICPMS
Cr	2942–4285	3558 ± 344	3827.8 ± 69.4 (352.1)	4074 ± 39 (366)
Zn	100–130	111 ± 13	113 ± 12 (36)	133 ± 4 (8)
Ba	3–12	6 ± 3	7.3 ± 0.3 (1.6)	7 ± 2 (4)
Sr	8–27	14 ± 6	14.1 ± 0.3 (4.9)	19 ± 1 (2)

possible problems with cross calibration). The crater was smaller for the pellet because the sample is diluted during borate fusion. However, the aim of this experiment was to study the influence of the samples preparation method on the accuracy and precision of isotopic ratio measurements, so, obtaining signals of the same intensity was regarded as more important than having the same crater size.

Fig. 3 shows the concentrations obtained by LA-ICP-IDMS for the SRM 1944 using the two sample preparation procedures. The average measurement bias on mass fractions is about 5.7% for the glass and 28.1% for the pellet including all the elements. It should be noted that in the pellet, Sr and Ba mass fraction are significantly different from the expected value indicating a poor mixing of these elements when simply spiking the solid with liquid solution. In addition, sample heterogeneity should have a higher influence on the ICP transient signals for the ablation of the pellet. This can be observed directly as the measurement precision of mass fractions is better for the glass (1.3% of RSD on average, $n = 5$, 1σ) compared to the pellet (2.4% of RSD on average, $n = 5$, 1σ). Fig. 4 shows that the measurement precision on isotopic ratios was strongly affected by the shape and stability of ablation profiles.

3.3. Example of application: the Allende meteorite

The Allende meteorite constitutes an interesting application of the proposed methodology because it is known to contain refractory inclusions (calcium–aluminum-rich inclusions, presolar grains such as SiC, TiO_2, . . .) which can be hard to digest. Because of their pre-solar origin, these refractory inclusions can also have isotopic compositions that differs from that of earth, e.g. anomalies on ^{53}Cr have been reported [30] due to the decay of extinct ^{53}Mn. However, the measured isotopic ratio of glass made out of the meteorite only did not show any suspicious sign of unusual fractionation. As mentioned earlier, the measurement precision required to observe such fractionation in meteorite is certainly out of reach for quadrupole and sector field mass spectrometers as this variation of abundances are generally less than 0.1%. Moreover the relative mass of these inclusions generally does not exceed 10% of the total mass of the
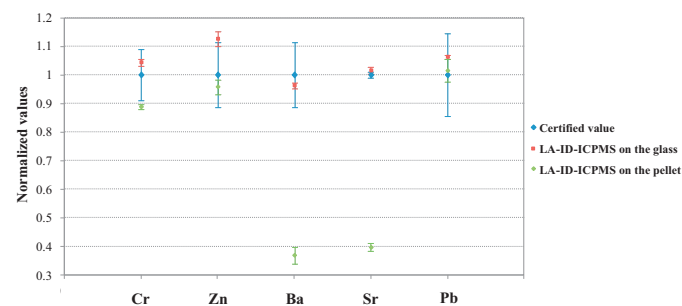

Fig. 3. Comparison of LA-ICP-IDMS results obtained on SRM 1944 after pelletization and glass fusing (ArF* excimer laser coupled to a Q-ICP-MS). Uncertainties shown result from standard deviations of the mean of 5 independent ablations.
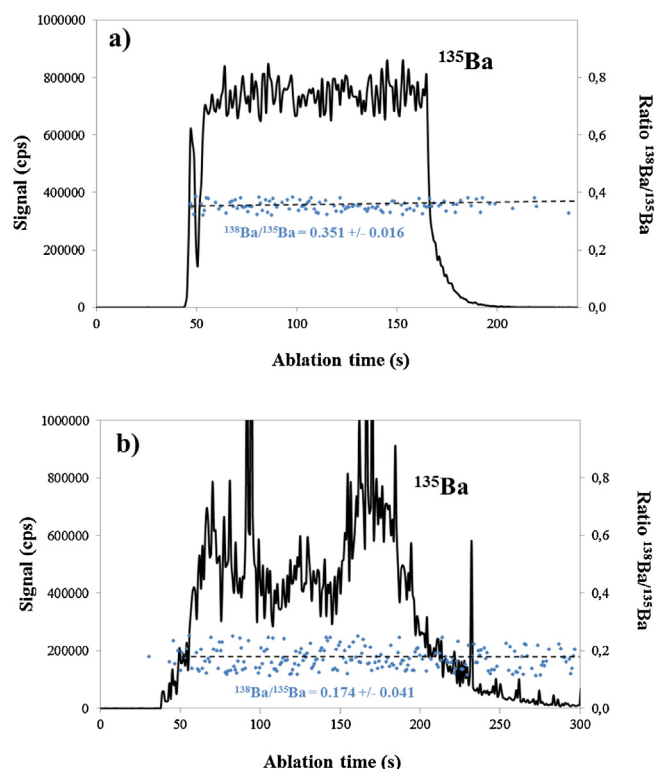

Fig. 4. Ablation profile and isotopic ratio of barium obtained for SRM1944 by LA-ICP-MS (ArF* excimer laser and Q-ICP-MS). a) Glass and b) pressed pellet.

meteorite. Table 5 shows that the mass fractions determined by LA-ICP-IDMS with the proposed methodology were within the range of published values. It should be highlighted that the Allende meteorite is not a certified reference material and therefore may not have the same level of homogeneity, which may explain certain deviations with published values.

4. Conclusion

LA-ICP-IDMS after fusion of samples using lithium borate appears to be a technique suitable for routine bulk elemental analyses of powdered samples with different matrices, including soils, sediments, rock mine wastes and meteorites. Experimental results showed that this method is robust, fast, precise (less than 2% RSDs), and gives low measurement bias (less than 5%), and that the sample preparation can be automated. It is especially well suited for heterogeneously distributed elements that tend to be sequestered in refractory phases which are difficult to dissolve using acids. The very good measurement precisions obtained was mostly rendered possible by the homogeneous distribution of elements in the glasses. Limits of detection for these sample types with standard equipment (i.e. Q-ICP-MS) are better compared to X-ray fluorescence and can be further

improved using more sophisticated instruments (i.e. SF-ICP-MS) which decrease the possible influence of isobaric interferences on isotopic ratios when operated in medium to high resolution. Future work will focus on analyzing samples with lower concentrations to fit the needs of geochemistry/geology applications.

The advantages of borate fusion over the spiking/pellitization approach include a better homogenization of the spike and analytes, the possibility of automation of the sample preparation, the complete digestion of refractory phases (such as chromite and zircons) and easier dilution of samples. The dilution of the sample by the flux enables the making of closely matched samples in terms of chemical composition and physical characteristics [32] removing the need to optimize the laser ablation setup for series of different sample matrices. Alternative fusing methods include strip flux-free fusion [33,34] and Pt-crucible flux-free fusion [35,36] which do not require a dilution with flux and hence appear better for elements present at low mass fraction levels within samples. However, studies are still needed to compare the homogeneity and mixing of these fusion processes.

Some pitfalls need to be acknowledged such as possible reagent impurities (which can be estimated with a blank glass) and sample contamination during preparation which can compromise the analysis of low mass fraction elements as well as the fact that the repeated analysis of lithium borate glasses may contaminate the ICP-MS with Li due to memory effects [37].

Disclaimer

Certain commercial equipment, instruments or materials are identified in this work to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for this purpose.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.aca.2013.07.031.

References

[1] W. Kelly, K. Murphy, D. Becker, J. Mann, J. Anal. At. Spectrom. 18 (2003) 166–169.
[2] M. Resano, E. Garcia-Ruiz, F. Vanhaecke, C. Crespo, M. Belarra, J. Anal. At. Spectrom. 19 (2004) 958–965.
[3] M. Belarra, M. Resano, F. Vanhaecke, L. Moens, Trends Anal. Chem. 21 (2002) 828–839.
[4] D. Gunther, I. Horn, B. Hattendorf, Fresenius J. Anal. Chem. 368 (2000) 4–14.
[5] R. Russo, X. Mao, H. Liu, J. Gonzalez, S. Mao, Talanta 57 (2002) 425–451.
[6] H. Kuhn, D. Gunther, Anal. Chem. 75 (2003) 747–753.
[7] M. Motelica-Heino, P. Le Coustumer, O.F.X. Donard, J. Anal. At. Spectrom. 16 (2001) 542–550.
[8] K.G. Heumann, Isotope dilution mass spectrometry, in: Inorganic Mass Spectrometry, Wiley, New York, 1988, pp. 301–376.
[9] S. Boulyga, K. Heumann, J. Anal. At. Spectrom. 19 (2004) 1501–1503.
[10] B. Fernández, F. Claverie, C. Pécheyran, O.F.X. Donard, J. Anal. At. Spectrom. 23 (2008) 367–377.
[11] J. Heilmann, S.F. Boulyga, K.G. Heumann, J. Anal. At. Spectrom. 24 (2009) 385–390.
[12] Y. Lee, C. Chang, S. Jiang, Spectrochim. Acta B 58 (2003) 523–530.
[13] H. Scholze, E. Hoffmann, C. Ludke, A. Platalla, Fresenius J. Anal. Chem. 355 (1996) 892–894.
[14] M. Tibi, K.G. Heumann, J. Anal. At. Spectrom. 18 (2003) 1076.
[15] C. Pickhardt, A. Izmer, M. Zoriy, D. Schaumloffel, J. Becker, Int. J. Mass Spectrom. 248 (2006) 136–141.
[16] C.K. Yang, P.H. Chi, Y.C. Lin, Y.C. Sun, M.-H. Yang, Talanta 80 (2010) 1222–1227.
[17] B. Fernandez, F. Claverie, C. Pecheyran, J. Alexis, O.F.X. Donard, Anal. Chem. 80 (2008) 6981–6994.
[18] T.D. Yokoyama, T. Suzuki, Y. Kon, T. Hirata, Anal. Chem. 83 (2011) 8892–8899.
[19] F. Claverie, J. Malherbe, N. Bier, J.L. Molloy, S.E. Long, Anal. Bioanal. Chem. 405 (2013) 2289–2299.
[20] J. Reid, I. Horn, H. Longerich, L. Forsythe, G. Jenner, Geostand. Newsl. 23 (1999) 149–155.
[21] M. Viger, J. Gravel, D. Brouard, D. Beauchemin, D. Boudreau, Anal. Chem. 77 (2005) 706–710.
[22] B. Stoll, K.P. Jochum, K. Herwig, M. Amini, M. Flanz, B. Kreuzburg, D. Kuzmin, M. Willbold, J. Enzweiler, Geostand. Geoanal. Res. 32 (2008) 5–26.
[23] S. Eggins, Geostand. Newsl. 27 (2003) 147–162.
[24] D. Gunther, A. Von Quadt, R. Wirz, H. Cousin, V. Dietrich, Mikrochim. Acta 136 (2001) 101–107.
[25] T.D.F. Leite, R. Escalfoni, T.C.O. Da Fonseca, N. Miekeley, Spectrochim. Acta B 66 (2011) 314–320.
[26] Z. Yu, M. Norman, P. Robinson, Geostand. Newsl. 27 (2003) 67–89.
[27] C. O'Connor, B.L. Sharp, P. Evans, J. Anal. At. Spectrom. 21 (2006) 556–565.
[28] J. Fietzke, V. Liebetrau, D. Günther, K. Gürs, K. Hametner, K. Zumholz, T.H. Hansteen, A. Eisenhauer, J. Anal. At. Spectrom. 23 (2008) 955–961.
[29] J. Kragten, Analyst 119 (1994) 2161–2165.
[30] P. Hoppe, D. Macdougall, G.W. Lugmair, Meteorit. Planet. Sci. 42 (2007) 1309–1320.
[31] E. Jarosewich, R.S. Clarke, J.N. Barrows, The Allende Meteorite Reference Sample. Smithsonian Contributions to the Earth Sciences, 1987.
[32] M. Odegard, S.H. Dundas, B. Flem, A. Grimstvedt, Fresenius J. Anal. Chem. 362 (1998) 477–482.
[33] J.S. Fedorowich, J.P. Richards, J.C. Jain, R. Kerrich, J. Fan, Chem. Geol. 106 (1993) 229–249.
[34] M.D. Norman, N.J. Pearson, A. Sharma, W.L. Griffin, Geostand. Newsl. 20 (1996) 247–261.
[35] Z. Chen, D. Canil, H.P. Longerich, Fresenius J. Anal. Chem. 368 (2000) 73–78.
[36] M. Kurosawa, K. Shima, S. Ishii, K. Sasa, Geostand. Geoanalyt. Res. 30 (2006) 17–30.
[37] F. Nehring, D.E. Jacob, M.G. Barth, S.F. Foley, Microchim. Acta 160 (2007) 153–163.