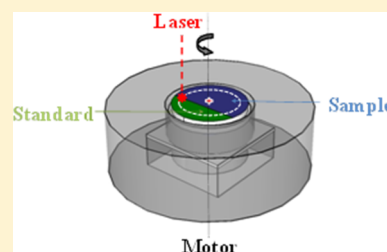# Standard Addition Method for Laser Ablation ICPMS Using a Spinning Platform

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S *Supporting Information*

ABSTRACT: A method has been developed for the fast and easy determination of Pb, Sr, Ba, Ni, Cu, and Zn, which are of geological and environmental interest, in solid samples by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) using a spinning sample platform. The platform, containing a sample and a standard, is spun during the ablation, allowing the quasi-simultaneous ablation of both materials. The aerosols resulting from the ablation of sample and standard were mixed in the ablation cell allowing quantification of analytes by standard additions. The proportion of standard versus sample of the mixing can be increased by performing the ablation further from the axis of rotation. The ablated masses have been determined using a new strategy based on isotope dilution analysis. This spinning laser ablation method has been applied to the Allende meteorite and four powdered standard reference materials (SRMs) fused in lithium borate glasses: two sediments as well as a soil and a rock material. SRM 612 (Trace Elements in Glass) was also analyzed despite having a matrix slightly different from the glass standard obtained by lithium borate fusion. The deviation from the certified values was found to be less than 15% for most of the mass fractions for all the elements and samples studied, with an average precision of 10%. These results demonstrate the validity of the proposed method for the direct and fast analysis of solid samples of different matrixes by standard additions, using a single standard sample.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is considered one of the most powerful techniques for the direct trace elemental analysis of solid materials and is now largely used in geological, archeological, environmental, and biological studies. LA-ICPMS is fast, sensitive, and able to probe microscale features, but it is still held back by the occurrence of fractionation and matrix effects making accurate quantification a hard task to achieve.[1,2] Many researchers use custom matrix-matched standards or develop new quantification strategies to overcome these obstacles. External calibration using homemade matrix-matched standards, liquid ablation, dual introduction (sample plus standard), and the use of isotope dilution are some of the possible ways to accurately determine elemental content of solid material by LA-ICPMS.[1,3]

Standard addition has been rarely used in conjunction with laser ablation mostly because it involves a time-consuming sample preparation when applied to solid sampling. The sample preparation usually includes spiking, homogenizing, drying, and pelletizing steps that need to be repeated for each addition of a single sample.[4] Nevertheless, this method has been successfully used for the analysis of viscous crude oil,[5] zircons fused in glass,[6] and intractable samples prepared with a gluing technique.[7] Online solution-based addition approaches developed by Thompson et al.[8] for laser ablation microprobe ICPMS and Leach et al.[9] for LA-ICPMS analysis have been shown to minimize the time-consuming nature of standard additions when used with laser ablation. This method consists of performing the addition by mixing the ablated sample with a nebulized elemental solution using a Y connection. Pickhardt et al.[10] developed a similar approach by mixing the aerosol coming from an ultrasonic nebulizer with the ablated particles directly inside the ablation cell. Even though these techniques have shown promising results, it requires the knowledge of one element and/or the ablation rate.

Recently a novel approach involving the mixing of two aerosols has been investigated by Fernandez et al.[11] This technique is based on a system equipped with a galvanometric scanning beam device that allowed the laser to rapidly move with high repositioning precision. Using such a device, the quasi-simultaneous ablation of the sample and an isotopically enriched pellet was realized, thus performing the isotope dilution (ID) directly inside the ablation cell. Yokoyama et al.[12] used a similar scanning beam device to perform standard addition by ablating a sample, standard reference material (SRM) 612 (Trace Elements in Glass) and a blank glass quasi-simultaneously with different proportions. However, these rather elegant methods rely on the availability of specialized instrumentation and assume that the same amount of material has been ablated between the sample and the standard (spike pellet or SRM 612).

In the present paper, a spinning LA-ICPMS method to perform standard additions by mixing the aerosol of two solid materials (a sample and a standard) directly inside the ablation cell is described. This method does not require the use of an expensive galvanometric scanner but relies on a modified ablation chamber equipped with a fast spinning sample platform.

It has been demonstrated to accurately quantify one meteorite sample and four powdered SRMs (soil, sediment, glass, and rock) fused as glasses using lithium borate as well as the glass SRM 612.

■ EXPERIMENTAL SECTION

Sample, Standards, and Reagents. Five SRMs were investigated to demonstrate the suitability of the standard addition technique using a spinning ablation cell platform for the determination of elemental mass fractions in a variety of 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 688 (Basalt Rock), and SRM 612 (Trace Elements in Glass) from NIST (National Institute of Standards and Technology, Gaithersburg, U.S.A.). Additionally, the Allende meteorite (USNM 3529 Split 5 pos. 20) in a powdered form was graciously provided by the Smithsonian Institution (Washington, DC. U.S.A.).

SRM 3100 series standard solutions from NIST were used to prepare a multielement doped glass. Ni, Cu, Zn, Sr, Ba, and Pb were considered in this work to cover a wide mass range, but the methodology is, in principle, applicable to all elements. This glass was also spiked with an accurately weighed amount of isotopically enriched ^{157}Gd solution, whereas each SRM was spiked with a solution of natural Gd (SRM NIST 3118a). A spike solution of ^{157}Gd was prepared by dissolution in nitric acid of an accurately weighed amount of enriched gadolinium oxide (Gd_2O_3, ^{157}Gd = 88.63%) purchased from Trace Sciences International (Richmond Hill, ON, Canada). This enriched ^{157}Gd solution was diluted and analyzed by ICPMS to determine its isotopic abundance and by reverse ID-ICPMS for the elemental mass fraction.

Sample Preparation. Glasses of the meteorite sample and each SRM were prepared by lithium borate fusion. This technique produces time-stable and homogeneous glasses, eliminating the effect of particle size variations and compositions of the sample.[13] The borate fusion method consisted of mixing an SRM (~0.3 g) with flux (~1.7 g of lithium borate: 67% $Li_2B_4O_7$– 33% $LiBO_2$ from Spex, New Jersey U.S.A.) in a 30 mL capacity platinum crucible. This mixture was spiked with a solution of natural Gd, dried in an oven, and fused using a Perl'x3 induction-heated machine (PANalytical, Almelo, The Netherlands). The fusion program consisted of seven steps: (1) heat at 850 °C for 1 min 30 s, (2) heat at 975 °C for 5 min, (3) heat at 975 °C for 7 min with mixing by rocking the crucible, (4) cool to room temperature (with mixing), (5) manually add one drop of a 20% LiI (aq) nonwetting agent, (6) heat at 975 °C for 4 min (with mixing), (7) cast into Pt dish (1 min 40 s at 975 °C) followed by forced-air cooling from under the dish (30 s). A 2 cm diameter glass with a nominal 3:20 dilution ratio was then obtained in the casting dish.

One multielement glass was prepared by spiking flux (~2 g) with a multielemental solution of Ni, Cu, Zn, Sr, Ba, Pb, and an isotopically enriched solution of ^{157}Gd. The nominal mass fraction of each of the analytes was ~250 mg/kg. The mixture was then dried in an oven and fused using the same protocol as described in the preceding paragraph. Each lithium borate glass was then cut in half using a custom-built diamond saw. Table 1 shows the mass fraction of the multielement glass determined by ID-ICPMS after dissolution in nitric acid and the isotopic abundances obtained for Gd.

Gadolinium was chosen because it is not present in the soils to be analyzed and because most of its isotopes are not prone to

Table 1. Mass Fraction of Multielemental Glass Determined by ID-ICPMS after Digestion in Nitric Acid[a]

	theor value based on gravimetric data (mg/kg)	mass fraction by ID-ICPMS (mg/kg)	deviation from theor value (%)
Ni	272.6 ± 0.6	263.5 ± 16.2	−3.3
Cu	268.0 ± 0.4	252.2 ± 5.3	−5.8
Zn	266.9 ± 0.7	298.8 ± 11.2	11.9
Sr	268.3 ± 0.9	259.9 ± 0.9	−3.1
Ba	251.6 ± 0.9	253.8 ± 6.8	0.9
Pb	249.3 ± 0.3	257.3 ± 1.6	3.2
Gd	161.8 ± 0.5	159.4 ± 1.2	−1.5

[a]Uncertainties for the theoretical values were calculated using weighing uncertainties and uncertainties of the mass fraction values for the SRM 3100 standard solutions. Uncertainties on ID-ICPMS results represent the standard deviation of the mean of three replicate analyses of the digested glass sample.

interferences due to elements in the sample matrixes. The gadolinium additions (natural and isotopically enriched), which allow calculations of the amount of material ablated from the sample, need to be optimized because it is known that this parameter influences the precision of the isotope dilution calculation (as discussed later). To do so, the respective amounts of natural and isotopic gadolinium added were determined to minimize the error multiplication factor.[14,15]

It is worth noting that elemental and isotopic fractionations, two known problems of laser ablation, are not expected to have a significant impact because the standard and the sample are in a similar matrix of lithium borate (due to the fusion process).

Table 1 compares the theoretical values (calculated using certified mass fractions of SRM 3100 series standards and gravimetric data) and the mass fractions obtained after glass dissolution and ID-ICPMS. No significant and systematic deviation can be noticed except for zinc and copper for reasons that are unclear. This means that the fusion process does not induce significant loss of these analytes and is therefore suitable for quantification purposes. It should be highlighted that only the mass fractions obtained by ID-ICPMS after dissolution of the multielement glass were used in the standard additions calculations, rather than the values arising from gravimetric data.

Instrumentation. *LA-ICPMS Coupling.* An ArF 193 nm excimer laser ablation system (Photon Machine Analyte 193) which delivers 4 ns pulses at repetition rates ranging from 1 to 300 Hz was employed in this work. The laser was coupled to an ICPMS PQ3 (Thermo Elemental) under wet plasma configuration to ensure a high robustness of the ICP.[16,17] The laser-generated aerosol and a nebulized 2% mass fraction nitric acid solution were mixed together using a Y connection. Helium was used as carrier gas in the ablation cell. The optimization of the coupling was performed with a 2 ng g^{-1} multielemental solution in order to achieve higher sensitivity with low oxide level (CeO/Ce below 3%). The ICPMS detector dead-time was also determined. Table 2 summarizes the conditions used for LA-ICPMS analysis.

Spinning Motor Setup. A brushless flat dc micromotor (series 2610T012B) was used in combination with a speed controller (SC1801S) and a programming adapter, all obtained from Faulhaber (Schonaich, Germany). The "Faulhaber Motion Manager" software was used to operate the motor with controlled revolutions (up to 7000 rpm). In order for the motor to fit inside the original ablation cell of the laser ablation system, a special sample holder was designed and constructed in-house. As can be seen in Figure 1, the motor was fixed from the

Table 2. Operating Conditions of the ICPMS and Laser Ablation System

ICPMS	Thermo Elemental, PQ3
argon flow rates	
plasma gas	13.6 L min^{-1}
auxiliary gas	0.88 L min^{-1}
carrier gas	0.85 L min^{-1}
cones material	Ni
dwell time	20 ms
isotopes	^{60}Ni, ^{63}Cu, ^{66}Zn, ^{88}Sr, ^{138}Ba, ^{157}Gd, ^{158}Gd, ^{208}Pb
laser ablation system	Photon Machines, Analyte 193
wavelength	193 nm
pulse duration	4 ns
fluence	7 J/cm^2
repetition rate	20 Hz
spot size	138 μm
carrier gas flow rate	550 mL min^{-1} of He
motor speed rate	2000 rpm

top in the square shaped hole to allow air circulation and avoid overheating. A flat and horizontal platform was attached on the axis of the motor. For easier handling, samples were placed on a disc that could be fixed to the platform. Finally, a 9 mm diameter hole was drilled in the drawer containing the sample holder in order to provide a path for wires used to control the micromotor out of the ablation cell. This hole was then sealed with Epoxy resin to ensure the ablation cell was airtight.

Spinning LA-ICPMS Combined with Standard Addition. See the flowchart displayed in Figure S1 in the Supporting Information.

Ablation Strategy. The principle of this new spinning LA-ICPMS method combined with standard addition is based on the mixing of different proportions of the standard and the sample as aerosols directly inside the ablation chamber. To do so, two halves of glasses were placed close together on the spinning platform in order to ablate both samples during the motor rotation. They were shifted around 1.5 mm away from the axis of the motor as shown in Figure 1. This way, it was possible to ablate only the SRM glass when using a small circle diameter (<3 mm)

and then increase the proportion of the ablated multielemental glass versus sample glass by increasing the ablation circle diameter. The repetition rate was chosen so that the method could be applicable to common laser ablation systems. It should be noted that an optimization of the setup has been performed and that the repetition rate had little influence on the accuracy and precision of the method (paper in preparation). The diameter of the circle varied from 1 to 6.5 mm.

Standard Addition Calculation. Standard addition is a well-known and established method which was developed for liquid analysis to eliminate interferences due to the matrix of the sample.[18] Although it was based on the use of volumetric dilutions, the appearance of new high-performance analytical balances made gravimetric dilution more common in order to obtain better precision and accuracy. Kelly et al.[19] described a general solution to the standard additions problem based on gravimetry by using eq 1:

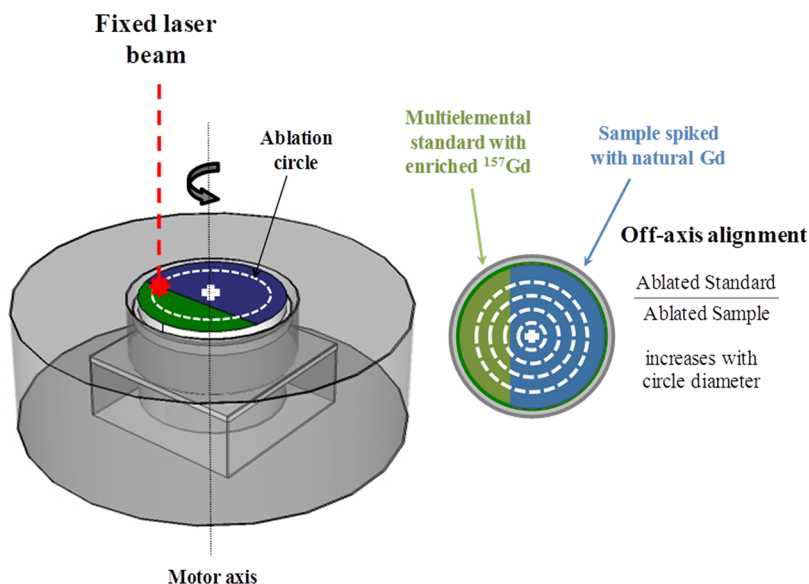$$\left(\frac{m_x + m_s + m_d}{m_x}\right)I = k\left(\frac{m_s}{m_x}C_s\right) + kC_x \qquad (1)$$

with m_x = mass of sample, m_s = mass of standard, m_d = mass of diluent, I = instrumental response for analyte, C_s = mass fraction of the analyte in the standard, C_x = mass fraction of the analyte in the sample, and k = instrument sensitivity (response units per unit of mass fraction). In our case, $m_d = 0$; therefore, eq 1 can be rewritten as follows:

$$\left(1 + \frac{m_s}{m_x}\right)I = k\left(\frac{m_s}{m_x}C_s\right) + kC_x \qquad (2)$$

Usually, the masses of sample and standard are determined during the sample preparation and eq 2 can be plotted as $y = ax + b$ with $a = k$ and $b = kC_x$. C_x can then be determined by dividing the y-intercept by the slope of the linear regression ($C_x = b/a$).

Therefore, in standard addition analyses, the amount of sample and standard mixed together is a crucial parameter.

Determination of the Proportion of Ablated Standard and Sample. The ablated masses are too small to be measurable with five-place balances, can vary during the course of the ablation,

Figure 1. Illustration of the modified ablation cell showing the ablation strategy chosen to perform standard addition.
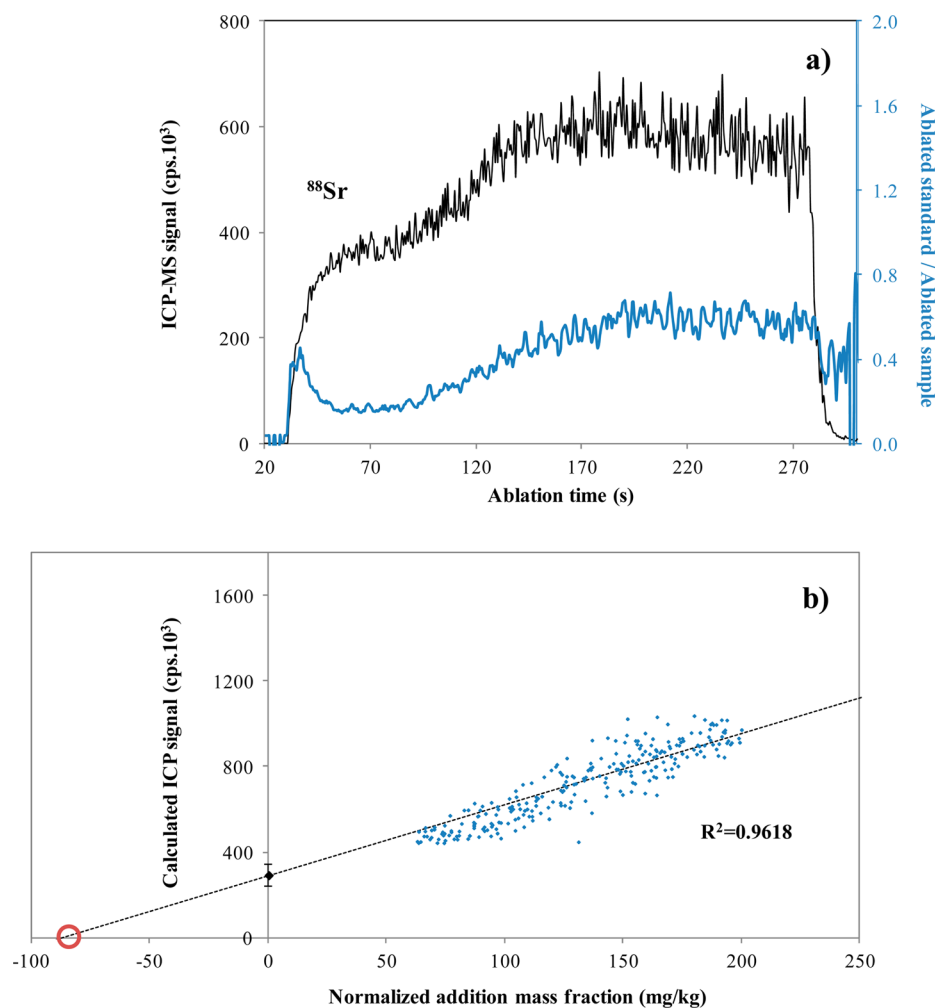
Figure 2. Ablation of NIST SRM 612 glass and standard glass having nominal analyte mass fractions of 250 mg/kg placed on the spinning device at 2000 rpm. (a) Signal of [88]Sr (left scale) superimposed with the ablated ratio of the standard compared to the sample (right scale). After calculation, these two data will give (b) the mass fraction of strontium (red circle).

and will be different depending on the diameter of the ablated circle. A novel way of determining the respective masses of sample and standard (m_s/m_x) ablated was developed using isotope dilution.

An isotopically enriched element ([157]Gd enriched at 88.63%) was added to the standard glass during its preparation, and the same element of natural isotopic composition (Gd) was added to all sample glasses. Knowing the mass fraction and the abundance of gadolinium in the sample and the standard, the term m_s/m_x can be calculated using the following isotope dilution equation (adapted from ref 14):

$$\frac{m_s}{m_x} = \frac{C_{Gd_x}}{C_{Gd_s}} \frac{M_s}{M_x} \frac{R_{Gd}A_X^2 - A_X^1}{A_S^1 - R_{Gd}A_S^2} \tag{3}$$

where C_{Gd_s} = gadolinium mass fraction in the standard (μg/g), C_{Gd_x} = gadolinium mass fraction in the sample (μg/g), M_s = molar mass of isotopically enriched gadolinum in the standard (g/mol), M_x = molar mass of natural gadolinium in the sample (g/mol), $A_s^{1,2}$ = Gd isotope abundance of isotope 1 and 2 in the spike (%), $A_x^{1,2}$ = Gd isotope abundance of isotope 1 and 2 in the sample (%), and R_{Gd} = measured ratio of isotope 1/isotope 2 in the aerosol.

This mass ratio can be determined in real time, and online by a point per point data treatment. This way, it is possible to access different mass ratios during the course of one unique "mixing ablation" (quasi-simultaneous ablation of the sample and standard during the spinning). Additionally, even though the sample has a different ablation rate (due to its transparency, matrix composition, or level position) than the multielemental glass, it can be analyzed using our method because the mass ratio provides the amount of both materials reaching the ICPMS.

RESULTS AND DISCUSSION

Measurement by Spinning LA-ICPMS. Using the proposed method, two aerosols were mixed together directly in the ablation cell. The transient signal obtained for the mixing ablation shows variations due to changes of the mass of standard versus the mass of sample ablated during the course of the ablation (see Figure 2). The variation of this ratio over time can be explained by a necessary equilibration time of the aerosol at the beginning of the ablation and different heights of the standard and the sample inducing a variation of the focus for both materials as the ablation occurs. No particular attention was taken to get a constant ablation since a variation of the additions was preferred to simulate additions of different amounts of standard. More material is typically ablated from the sample than

the standard because of the off-axis alignment of the two glasses on the spinning stage (see Figure 1), with the trajectory of the laser beam spending more time on the sample. However, in some cases, more material from the standard can be ablated due to a small difference in ablation rate even though the sample and standard matrixes are almost matrix-matched. Differences of laser focus or glass transparency can affect ablation depth and, consequently, the respective amount of material ablated.

To calculate an elemental mass fraction, a linear regression was obtained for each "mixing ablation" as shown in Figure 2. The data acquisition consisted of recording 30 s of gas blank (i.e., with no ablation) in order to subtract the background level from each isotope before the ablation. Then, the ablation was performed on the sample alone (diameter circle less than 3 mm) and on both samples (diameter circle greater than 3 mm) while the sample platform was spun. Three replicates of the sample alone ("no addition" ablation) and five replicates of the mixing were collected with a range of diameter circles less than 13 mm. The isotopic ratio ^{157}Gd/^{158}Gd was monitored in order to know the exact ablation ratio between the sample glass and the multielemental glass standard. This ratio was corrected for mass bias using the "no addition" ablation (with natural abundance Gd).

The ICPMS signal of the three replicates of the sample alone were averaged and used as the "no addition" point for the five linear regressions obtained with the five replicates of the "mixing ablation". Each regression line was forced to pass through the "no-addition" point for each sample. Each point of the ICPMS signals was considered as one addition. An initial homogenization time was required to obtain a complete mixing of the aerosols; therefore, the first 30 s of ablation was discarded. A selection of the additions was then collected in accordance with the expected mass fraction. Usually, the calculated additions were found to vary from 50 to 400 mg/kg when using the 250 mg/kg multielemental glass standard. These variations depended on the ablation rate, the position of both samples, and the location of the ablation on the glasses. For expected sample mass fractions lower than 100 mg/kg, additions higher than 250 mg/kg were filtered out, and the opposite for higher expected sample mass fractions.

Influence of Circle Diameter. The spinning LA-ICPMS method relies on the fact that the ICPMS signal from the ablation of one uncut sample alone is not significantly different when using different circle diameters. For the mixing of two materials (one-half of standard and one-half of sample), replicates were generated by ablating different circle diameters (e.g., the distance of the ablation from the axis of rotation changes). This change in diameter of the circle does not change the short time period between the ablation of the first and the second half-samples for a given rotation speed rate (for example, at 2000 rpm, it takes 30 ms to make a complete rotation) when the samples are centered. However, with a larger diameter, the laser will more likely ablate a fresh surface and result in a less deep ablation than with a smaller circle diameter. Therefore, it is important to study the repeatability obtained on a series of ablations spaced by several hundreds of micrometers. For this purpose, an uncut glass of SRM 2586 was placed inside the ablation cell and analyzed with circle diameter from 1 to 13 mm (which correspond to the diameters used during the quantification of the SRM fused in glass). Although the sample was flat, the focus position was checked before each ablation.

Figure 3 shows that the relative standard deviation obtained from 10 circular ablations performed on SRM 2586 glass sample was within 5.3% for Cu to 8.2% for Ni. It should be highlighted
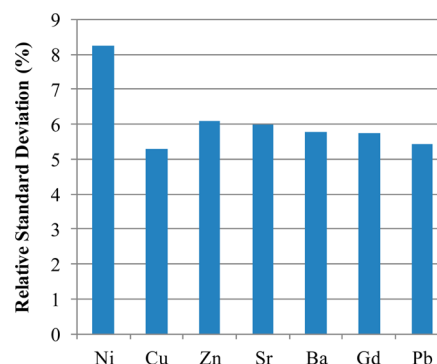

Figure 3. Relative standard deviation calculated from 10 circular ablation signals performed on 2586 glass with diameter circles varying from 1 to 13 mm (spot size 138 μm, 20 Hz, 2000 rpm).

that the spinning platform minimizes redeposition of the particles at the surface of the ablated sample. Therefore, bigger particles that would be deposited without the spinning stage are more likely to be transported to the ICPMS and to induce instability of the signal. Temporal relative standard deviations (TRSDs) of the elemental signal were calculated (results not shown). The TRSD has been previously defined and used to describe LA-ICPMS transient signals.[20] The TRSD is related to the short-term change and was calculated by dividing the standard deviation of the signal average (after background subtraction) by the signal-integrated value obtained for each circle ablation. Although TRSDs varied from 2% to 14% (except for Ni whose sensitivity was low) depending on the element, they were similar from one diameter of the circle to another one: TRSDs varied from 2.0% to 3.3% for Gd (best case) and 9.9% to 14% for Cu (worst case). Taking into account that no internal standard was used, the RSDs and TRSDs obtained showed a good external and internal repeatability of the circle ablation strategy.

Additionally, no particular trend was observed on the signal intensity with the circle diameter of the ablation.

Therefore, the ablation of the sample alone which corresponds to the smallest circle diameter ablation (below 3 mm) can be used as the "no addition point" for linear regression obtained using a large circle diameter (up to 13 mm).

However, it should be noted that, during the mixing ablation of the standard and the sample, the focus was always performed on the sample in order to obtain a similar ablation rate of the sample whatever the circle diameter.

Figures of Merit. The spinning LA-ICPMS method combined with standard addition was applied to four different powdered SRMs fused into beads. Linear regressions for the different mixing replicates (multielemental glass and sample) were obtained with R^2 from 0.94 to 0.99.

Table 3 and Figure 4 show that the average error considering all elements and all SRMs was 9.7%. The deviation from the certified value was found to be below 15% for most of the mass fractions obtained and below 5% in some cases. Errors as low as 0.6% for Pb in SRM 2586, and 0.3% for Ba in SRM 1944 were also observed. The relative standard deviation was calculated based on five mixing ablations and was found to be in the range of 0.6−17% with an average precision of 10%. However, certain elements and SRMs give more accurate and precise results than others. For example, mass fractions obtained for SRM 2586 for the six elements studied showed accuracy in the range of 0.6− 10.9% with an average precision of 6%. These differences in

Table 3. Results from the Spinning LA-ICPMS[a]

SRM	elements	certified mass fraction (mg/kg)	spinning LA-ICPMS mass fraction (mg/kg)	absolute value of deviation from the certified value (%)
612				
	Ni	38.8 ± 0.2	37.2 ± 6.3	4.2
	Cu	37.7 ± 0.9	33.8 ± 2.9	10.5
	Zn	39.1 ± 1.7	32.8 ± 2.3	16.0
	Sr	78.4 ± 0.2	87.1 ± 9.1	11.1
	Ba	39.3 ± 0.9	43.0 ± 4.1	9.3
	Pb	38.6 ± 0.2	38.1 ± 4.0	1.3
2586				
	Ni	75[b]	69.6 ± 1.3	7.2
	Cu	81[b]	74.6 ± 7.3	7.9
	Zn	352.0 ± 16.0	331.3 ± 2.1	5.9
	Sr	84.1 ± 8.0	91.8 ± 5.9	9.1
	Ba	413.0 ± 18.0	458.2 ± 33.9	10.9
	Pb	432.0 ± 17.0	429.6 ± 39.3	0.6
1944				
	Ni	76.1 ± 5.6	70.4 ± 9.4	7.4
	Cu	380.0 ± 40.0	366.1 ± 49.4	3.7
	Zn	656.0 ± 75.0	637.7 ± 97.2	2.8
	Sr	136.8[c]	143.6 ± 21.7	4.9
	Ba	499.0 ± 57.0	500.3 ± 59.5	0.3
	Pb	330.0 ± 48.0	252.7 ± 13.4	23.4
688				
	Ni	150[b]	123.1 ± 12.2	17.9
	Cu	96[b]	80.9 ± 6.0	15.7
	Zn	58[b]	64.6 ± 6.3	11.5
	Sr	169.2 ± 0.7	160.0 ± 20.7	5.5
	Ba	200[b]	170.3 ± 19.2	14.8
	Pb	3.3 ± 0.2	2.6 ± 0.3	21.2
2702				
	Ni	75.4 ± 1.5	66.7 ± 2.2	11.6
	Cu	117.7 ± 5.6	113.2 ± 16.0	3.8
	Zn	485.3 ± 4.2	430.3 ± 56.0	11.3
	Sr	119.7 ± 3.0	105.7 ± 11.0	11.7
	Ba	397.4 ± 3.2	346.1 ± 33.4	12.9
	Pb	132.8 ± 1.1	112.1 ± 19.0	15.6
			av error	9.7

[a]The uncertainties for the spinning LA-ICPMS measurement are standard deviations of the mean from five measurements. [b]Reference value (not certified). [c]Not certified, determined by ID-ICPMS.

accuracy could result from small interferences due to the different matrixes (although they were diluted in the flux) or additions that were not perfectly adapted to the sample mass fraction (because a single multielement glass standard was used).

Spinning LA-ICPMS analysis of SRM 612 was also performed using the multielemental glass obtained by lithium borate fusion. Even though SRM 612 has a different matrix than the standard glass, the average error is 9% considering all elements. SRM 612 was analyzed to demonstrate that even samples with a matrix different from that of the standard can be analyzed as long as one element is known in the sample and its corresponding isotopically enriched counterpart has been added to the standard. In the case of SRM 612, the information value for the mass fraction of gadolinium (39 mg/kg) was used to determine the ratio m_s/m_x.

The repeatability of the ablation of the sample without any addition accounted for the majority of the overall uncertainty, i.e., a 10% decrease of the signal coming from the sample alone leads to a 10% decrease of its determined mass fraction.

Additionally, the ablated masses determined using the ^{157}Gd/^{158}Gd ratio (RSD in the 2−4% range) contribute to the precision of the overall uncertainty.

Advantages and Limitations of the Methodology. The developed approach allows the application of standard addition to solid analysis with less tedious sample preparation. It combines the advantages of the standard addition approach such as reduced matrix effects and the advantages of sample fusion such as an improved homogeneity of analytes in the sample (compared to pellets). The proposed methodology only requires one standard (that can be reused after polishing) but manages to perform multiple standard/sample mixes out of it in one ablation. Once the multielement glass standard is prepared, the whole quantification procedure (fusion, sawing, and replicate ablations of sample alone and sample/standard) can be performed in less than 2 h. This time may be shortened by using a casting dish already in a suitable form for the glass to avoid the sawing step. The fusion step can be automatized and be performed on several sample at the same time with recent instrumentation.

Compared to external calibration, time is spared because there is no need to establish a calibration curve with standards that are scarce and difficult to match with samples in terms of matrix. The accuracy of the methodology on selected elements is similar[21−23] and sometimes better[24] than regular matrix-matched external calibration using samples fused with lithium borate. It is, however, better than external calibrations involving the pelletization of powders with the use of binder.[7,25]

One limitation of the method is the generally less good precision (10% RSD) obtained compared to other methodologies (5−10% RSD), mostly due to the signal drift of the no-addition point as explained in the previous section. However, future work will focus on alternative strategies to try measure the no-addition point at the same time as the spinning ablation using a translation of the spinning platform.

Application to Meteorite Quantification. To demonstrate the potential of this technique, a sample of the Allende meteorite in powdered form was prepared using lithium borate fusion and analyzed. Due to the rock matrix, the glass obtained was darker than all the other glasses. The results obtained using spinning LA-ICPMS are in good agreement with the recommended literature values[26] with an average error of 12%. It should be noted that the meteorite Allende is not a certified reference material, and therefore, the values found in the literature may be more biased due to the combination of data from several different analytical techniques. Material homogeneity may also have contributed to differences from the literature values. The average precision is 12%, slightly poorer than for SRMs, mainly because the additions are less adapted to this sample with both high and low constituent elements. For example, the additions were between 300 and 400 mg/kg, and thus were too small for Ni, which has a higher mass fraction in the meteorite. However, as shown in Table 4, the error in the Ni mass fraction is 13%, which is still reasonably good considering such low additions. For low mass fraction elements such Ba and Pb only the lower additions were kept, i.e., between 50 (which was the lowest possible addition) and 200 mg/kg.

■ CONCLUSION

This spinning LA-ICPMS method combined with standard additions allows the quantification of Ni, Cu, Zn, Sr, Ba, and Pb in four different matrixes accurately and with reasonable precision (ca. 10% RSD). The mixing of the aerosols coming from two
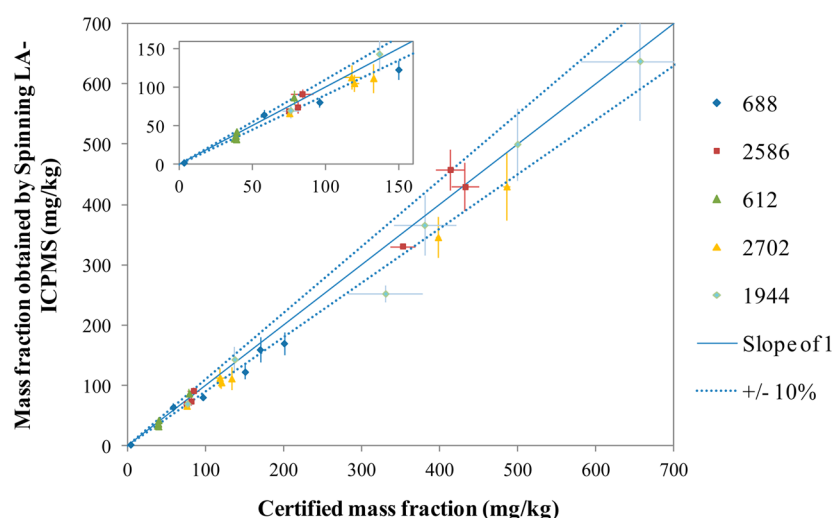
Figure 4. Mass fraction obtained by spinning LA-ICPMS compared to certified concentration of Ni, Cu, Zn, Sr, Ba, and Pb on five NIST SRMs. The uncertainties for the mass fractions obtained by spinning LA-ICPMS are standard deviations of the mean from five measurements.

Table 4. Mass Fractions Obtained by Spinning LA-ICPMS for the Allende Meteorite[a]

elements	mean literature value (mg/kg)[b]	recommended literature value (mg/kg)[b,c]	results obtained by spinning LA-ICPMS (mg/kg)[a]
Ni	13900 ± 700	14200 ± 200	12303.9 ± 1678.3
Cu	135 ± 44	119 ± 19	110.0 ± 9.6
Zn	111 ± 13	110 ± 5	126.0 ± 16.8
Sr	14 ± 6	12 ± 3	11.4 ± 1.6
Ba	6 ± 3	4 ± 1	4.7 ± 0.7
Pb	4.04 ± 4.92	1.39 ± 0.25	1.2 ± 0.1

[a]The uncertainties for the spinning LA-ICPMS measurement are standard deviations of the mean from five measurements. [b]Values from ref 26. [c]Values with outliers removed.

different samples was performed using a standard laser ablation system equipped with a new spinning sample holder.

The main advantage of using this newly developed method to perform standard addition is the possibility of analyzing a high number of samples with a limited sample preparation. Multiple additions can be carried out using only two glasses: the sample and the multielemental standard. This single multielemental glass standard can also be reused several times by polishing it to remove the previous ablations. The same standard glass has been used to quantify powdered materials of three different matrixes (rock, soil, and sediment). Although they were fused in glass, which means 85% of the sample was made from lithium borate, very different opacities and colors were observed. This difference in matrix composition was not problematic, since even the analysis of glass SRM 612, whose composition differs from lithium borate, gave accurate and precise mass fractions. Future work will expand the methodology to other matrixes.

The determination of the ablated masses applying the isotope dilution technique to a known element (gadolinium) present in both the sample and the standard is a powerful tool to characterize the aerosol mixture. The exact proportion of standard and sample can be calculated in real time, allowing the determination of the addition from the standard glass. This spinning LA-ICPMS technique combined with standard addition can be applied directly to the material without any sample preparation providing one element is known in the sample as demonstrated with SRM 612.

Finally, this proposed methodology was realized on standard equipment that can be found in most laboratories. The analytical figures of merit may be further improved using higher technology equipment allowing higher repetition rates, femtosecond impulsions, or high-resolution mass separation.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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. The authors declare no competing financial interest.

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