



# Isotope dilution mass spectrometry for quantitative elemental analysis of powdered samples by radiofrequency pulsed glow discharge time of flight mass spectrometry



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## ABSTRACT

In recent years particular effort is being devoted to the development of pulsed glow discharges (PGDs) for mass spectrometry because this powering operation mode could offer important ionization analytical advantages. However, the capabilities of radiofrequency (RF) PGD coupled to a time of flight mass spectrometry (ToFMS) for accurate isotope ratio measurements have not been demonstrated yet. This work is focused on investigating different time positions along the pulse profile for the accurate measurement of isotope ratios. As a result, a method has been developed for the direct and simultaneous multielement determination of trace elements in powdered geological samples by RF-PGD-ToFMS in combination with isotope dilution mass spectrometry (IDMS) as an absolute measurement method directly traceable to the International System of Units. Optimized operating conditions were 70 W of applied radiofrequency power, 250 Pa of pressure, 2 ms of pulse width and 4 ms of pulse period, being argon the plasma gas used. To homogeneously distribute the added isotopically-enriched standards, lithium borate fusion of powdered solid samples was used as sample preparation approach. In this way, Cu, Zn, Ba and Pb were successfully determined by RF-PGD-ToF(IDMS) in two NIST Standard Reference Materials (SRM 2586 and SRM 2780) representing two different matrices of geological interest (soil and rock samples). Cu, Zn, Ba and Pb concentrations determined by RF-PGD-ToF(IDMS) were well in agreement with the certified values at 95% confidence interval and precisions below 12% relative standard deviation were observed for three independent analyses. Elemental concentrations investigated were in the range of 81–5770 mg/kg, demonstrating the potential of RF-PGD-ToF(IDMS) for a sensitive, accurate and robust analysis of powdered samples.

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## 1. Introduction

Pulsed radiofrequency glow discharge (RF-PGD) coupled to time of flight mass spectrometry (ToFMS) is demonstrating advantageous features for direct solid analysis [1]. In contrast to direct current glow discharge analyses, RF-PGDs allow directly analyzing both conducting and insulating samples. Besides, the thermal stress on solid samples produced when GDs are operated in continuous mode is minimized, enabling RF-PGD-ToFMS to offer robust analysis of a wide variety of samples such as thermoelectric layers [2], polymers [3] and glasses [4]. The pulsed cycle of a PGD

can be separated into three temporal regions (denoted as prepeak, plateau and afterpeak) with different predominant ionization mechanisms. ToF mass spectrometers are the detectors of choice when high acquisition rates are required as it is the case to follow the time regimes in ms pulsed GD. Thus, the combination of PGD ion source with a ToFMS analyzer permits the selection of appropriate delay and integration time for many detection windows along a given pulse. Such flexibility should enable the selection of the highest analyte signals with minimum spectral interferences [5].

Concerning elemental quantitative analysis using a GD-MS, the concept of relative sensitivity factors (RSF) related to an internal standard is traditionally employed [6]. The intrinsic low matrix dependence of GD-MS signals provides absolute sensitivity factors which can be considered matrix independent in the first approximation. Nevertheless, when needed to perform quantitative

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analyses by GD-MS with a high accuracy the determination of matrix-matched element-specific RSF should be carried out, whenever suitable reference materials are available. Additionally, the models and methods used to compute quantitative depth profiles by GD-MS are at a primitive stage compared to those developed for GD-OES, particularly in the case of PGD sources.

Isotope dilution mass spectrometry (IDMS) is internationally regarded as an absolute measurement method directly traceable to the International System of Units [7,8]. In contrast to other calibration strategies, reference materials are not required and the analytical result is not affected by signal drifts, matrix effects or analyte losses during the sample preparation processes. IDMS has been already successfully applied for the direct quantification of solid samples by using different solid-state spectrometric techniques, e.g. laser ablation (LA) ICP-MS [9,10]. However, investigations to assess the analytical performance of IDMS approaches in GD-MS are scarce and studies about the potential of IDMS in state of the art PGDs are still lacking.

To our knowledge, only one work reported by Barshick et al. [11], investigated lead elemental analysis in waste oil samples using IDMS with a direct current GD-MS (working in continuous mode) and a double-focusing mass spectrometer. Of course, as for any isotope dilution analysis, accurate measurement of isotope ratios is crucial for accurate results [7]. Previous GD-MS studies utilizing isotope ratio measurements used quadrupole and double-focusing mass analyzers [12–14], both of them sequential mass analyzers. That is, double-focusing mass analyzers provide high resolution and sensitivity, which are excellent qualities for isotope ratio measurements, but they are not able to simultaneously acquire complete mass spectra and such measurements can be affected by mass bias [15]. An advantage of ToFMS is that all ions measured in a given mass spectrum represent the same sputtered sample material which is a condition for precise isotope ratios measurement [16].

Therefore, the aim of this work is the development of a RF-PGD-ToF(IDMS) methodology to achieve an accurate quantification of trace elements in solid powdered samples of geological interest. Two Standard Reference Materials (SRMs) have been chosen as model samples as representatives of soil and a rock mine waste. Appropriate mixing of the needed enriched isotopes with natural elements is an essential step to successfully carry out isotope dilution analyses. However, the operation of homogeneous distributions when spiking a solid with a liquid can be troublesome [17]. In this work, we have investigated lithium borate fusion of the powdered solid samples in order to achieve a homogeneous mixing of the analyte elements and the added isotopically-enriched standards [18] for RF-PGD-ToF(IDMS). This classical sample preparation procedure in X-ray fluorescence has been proposed by Luesaiwong et al. [19] for the qualitative analysis of natural abundance coal ash samples by RF-GD-OES. In that work, problems related to sample-to-sample variability were found and were associated due to problems associated with continuous RF power coupling. In the present work, the accurate measurement of isotope ratios by RF-PGD-ToFMS was first investigated using two different GD ion source designs and the proposed IDMS quantification approach is shown and validated by the analysis of Cu, Zn, Ba and Pb in SRM 2586 and 2780.

## 2. Experimental

### 2.1. Samples, standards and reagents

The studies related to the optimization of GD experimental conditions were carried out using non-conductive silicate glasses of 6 mm thickness for XRF monitoring from Breitländer (Hamm,

**Table 1**

Mass fractions and abundance of the isotopically-enriched spike solutions. Uncertainties represent the standard deviations of the mean of 4 independent mass fraction determinations conducted over a one year period.

Element	Abundance of enriched isotope (%)	Abundance of reference isotope (%)	Mass fraction (mg/kg)
Cu	<sup>65</sup> Cu: 99.70 ± 0.10	<sup>63</sup> Cu: 0.30 ± 0.02	804.2 ± 7.3
Zn	<sup>68</sup> Zn: 99.23 ± 0.10	<sup>66</sup> Zn: 0.10 ± 0.01	939.1 ± 11.0
Ba	<sup>135</sup> Ba: 94.00 ± 0.05	<sup>138</sup> Ba: 2.33 ± 0.02	1186.1 ± 36.1
Pb	<sup>206</sup> Pb: 92.15 ± 0.01	<sup>208</sup> Pb: 1.25 ± 0.01	14427.9 ± 527.0

Germany). In this work, glasses E2 (0.6% Cr<sub>2</sub>O<sub>3</sub>, 0.8% CuO, 1% ZnO, 4.6% BaO, 0.45% PbO, 0.6% SnO, 0.13% Ag<sub>2</sub>O, 0.31% SrO) and B1 (0.5% CuO) were employed.

Concerning the assayed powdered samples, two SRMs were investigated to demonstrate the suitability of the proposed RF-PGD-ToF(IDMS) strategy for the determination of elemental mass fractions: SRM 2586 (trace elements in soil containing lead from paint) and SRM 2780 (hard rock mine waste) from NIST (National Institute of Standards and Technology (Gaithersburg, MD, USA).

Isotopically-enriched spike solutions were prepared by dissolution in nitric acid of an accurately weighted 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 monoelemental solutions of Cu, Zn, Ba and Pb from NIST were used for the characterization of the corresponding spike abundances and mass fractions by reverse isotope dilution ICP-MS (see Table 1).

### 2.2. Samples preparation by lithium borate fusion

Glasses of each SRM were prepared by lithium borate fusion by mixing an accurately weighted amount of SRM (≈0.75 g) with an accurately weighted amount of flux (≈4 g) of lithium borate (67% Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>–33% LiBO<sub>2</sub>) from Spex (New Jersey, USA) in a 30 mL capacity platinum crucible. These 4.75 g of material were then spiked with the different isotopically-enriched solutions, then dried in an oven and finally fused. The amount of spike was optimized with respect to the influence of the error multiplication factor [8] (it was sample dependent).

The fusion was performed by the Perl'x31 induction-heated machine (PANalytical, Almelo, The Netherlands) using a 7 steps 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 lasts approximately 40 min. In a previous study [20] it was shown for Zn, Ba and Pb that no significant analyte loss occurs during the fusion step and thus the fusion process is suitable for quantitative analysis. In addition to the isotopically-enriched SRMs, a natural abundance glass of each SRM was fused to correct for mass bias.

### 2.3. Instrumentation

The RF-PGD-ToFMS instrument consists of a RF-PGD bay unit (pulsed RF generator, matching box, RF-connector and mounting system with a pneumatic piston to press the sample against the GD) from Horiba Jobin Yvon (Longjumeau, France). It was coupled to an orthogonal time-of-flight mass spectrometer (TOFWERK,

Switzerland) equipped with a microchannel plate detector [21]. The sampler and skimmer orifice diameters are 0.5 mm and 1 mm, respectively, and the distance between these cones is fixed to 7 mm. The ion response was monitored along 100 successive TOF extractions, being the time resolution of 33  $\mu$ s (1 TOF extraction every 33  $\mu$ s). A delay of 150 ns was used to ensure a complete acquisition of MS signals between GD pulses. Further details of this GD-MS instrument can be found elsewhere [22].

Concerning the discharge chamber, two GD ion sources were investigated here. One of them, denoted as GD.1, is a copper-based modified Grimm-type chamber similar to those used in the commercial GD-OES instruments from Horiba Jobin Yvon (4 mm diameter cylindrical anode and 15.5 mm thickness). The main body of the anode contains at one side of the cylinder a base with 16 concentric holes through which the Ar enters and flows into the region between the anode and the ceramic piece. A 2.5 mm inner diameter flow tube (EMPA, Switzerland) is inserted from the back of the anode to face the gas flow towards the cathode. This source allows the use of a fast Ar flow directed towards the sample surface aiming at improving the sputtering process, as well as the ion transport efficiency into the MS [21]. The second GD design, which will be named as UniOvi GD, consists of a stainless steel disk of 45 mm diameter and 7 mm thickness allowing a short distance from the sample surface to the sampler cone (approximately 8.8 mm). The UniOvi GD has no flow tube and has eight concentric inner gas channels that constrain the GD plasma in a symmetric

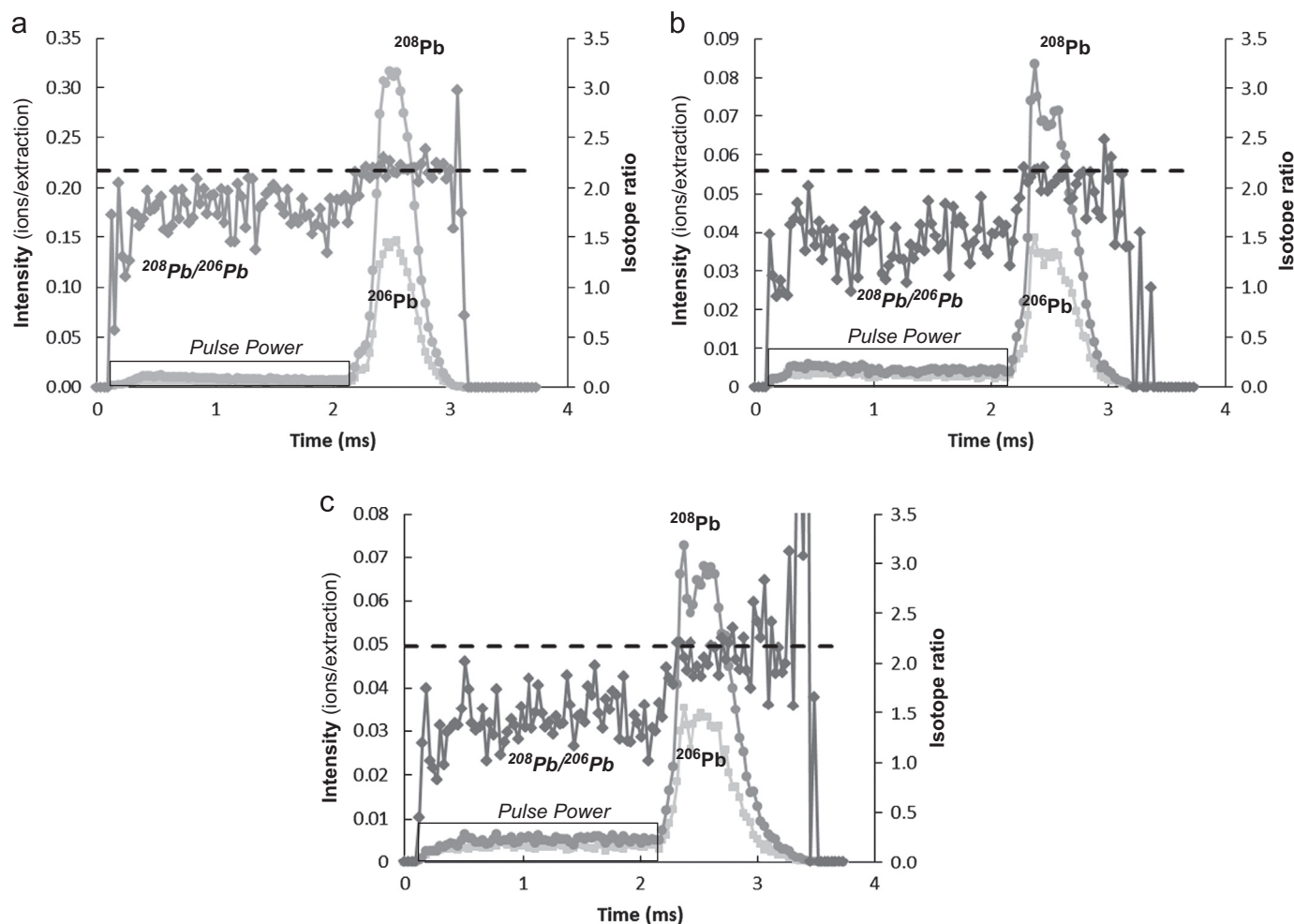
way. The cylindrical orifice of the anode is also 4 mm diameter. More information and comparison of both GD chambers can be found in a previous publication [23].

The radiofrequency power is supplied to both GD designs through the back side of the sample by a RF-power generator operating at 13.56 MHz and a refrigerating disc is used to keep the samples at low temperatures ( $< 4^\circ\text{C}$ ). A pulse width of 2 ms and a pulse period of 4 ms (50% duty cycle) were selected as experimental parameters. Values given along the text for GD power always correspond to applied power during the power-on part of the cycle. The discharge gas was high purity Ar (99.999% minimum purity), supplied by Air Liquide (Oviedo, Spain).

### 3. Results and discussion

#### 3.1. Evaluation of pulse profiles for accurate isotope ratio measurements

Prior to the analysis of lithium borate glasses, a preliminary investigation to ensure accurate isotope ratio measurement by using RF-PGD-ToFMS was performed. Optimization of RF-PGD experimental conditions were first carried out by measuring the 6 mm thick E2 standard glass where analyte concentrations are higher than those expected in the lithium borate samples to be analyzed. In order to minimize interferences for each analyte a



**Fig. 1.** Pulse profiles obtained by RF-PGD-ToFMS at different GD Ar pressures for  $^{206}\text{Pb}^+$  and  $^{208}\text{Pb}^+$  isotopes and  $^{208}\text{Pb}/^{206}\text{Pb}$  isotope ratio along the pulse profile. Analysis of E2 glass using the UniOvi GD source (100 W, 2 ms pulse width, 4 ms pulse period). Dashed lines represent the natural isotope abundance ratio. (a) 250 Pa; (b) 350 Pa; and (c) 450 Pa.

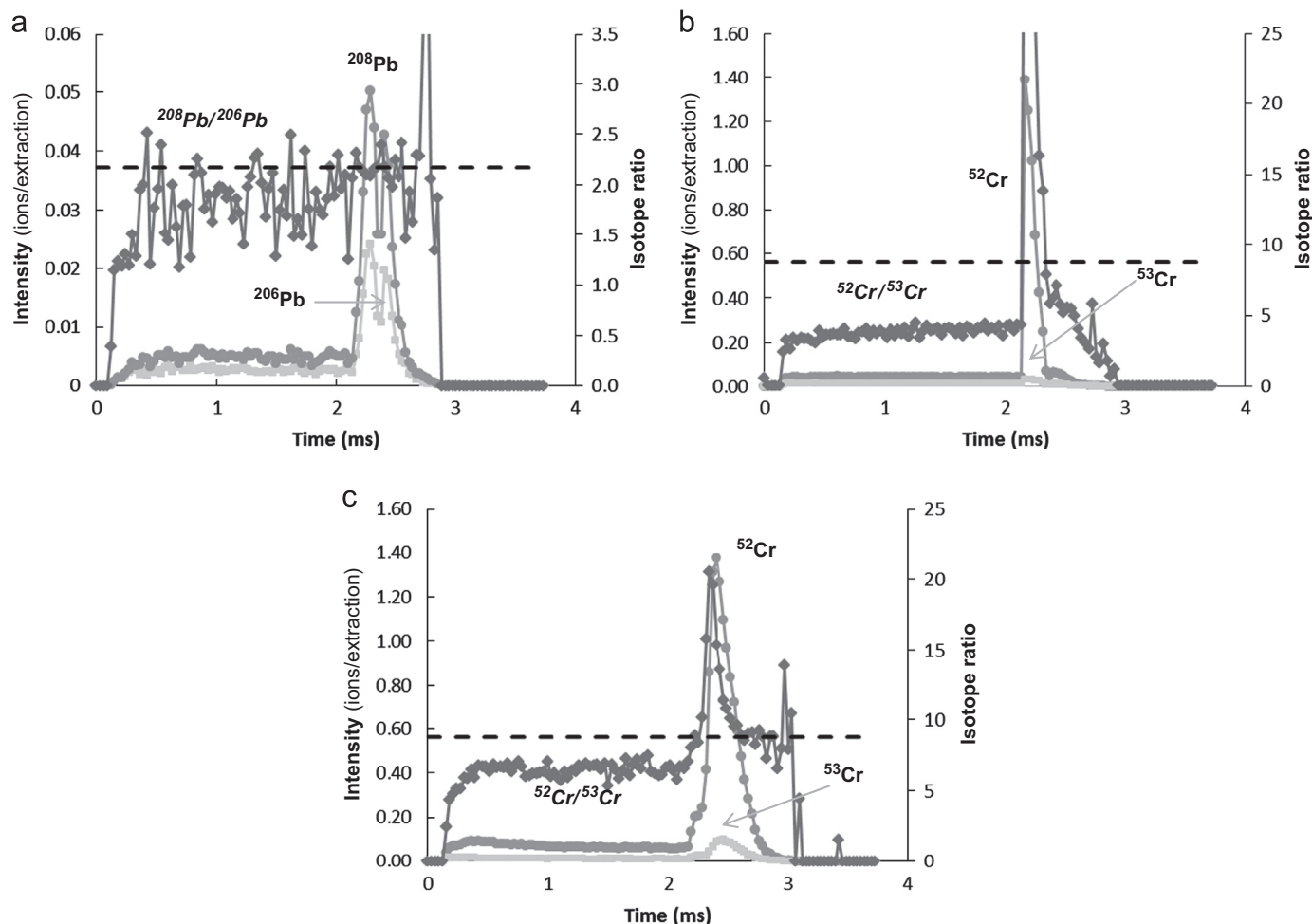
careful selection of the proper time of measurement within a pulse profile (for data treatment) was also performed. Both the optimization of RF-PGD experimental parameters and the selection of measurement time in a pulse were aimed at achieving higher analytical sensitivity and more accurate isotope ratios.

The UniOvi GD chamber was investigated in the first place because it has proven to be more suitable for analysis of glasses [23]. Concerning the RF forward power, the interval between 60 W and 100 W was studied. As expected, the higher the RF power, the higher the sensitivity. 100 W power was chosen eventually as the optimum value (powers higher than that were found to significantly worsen MS signals reproducibility). Regarding Ar pressure, the interval between 150 Pa and 650 Pa was investigated and 250 Pa was found to be the optimum pressure for maximum sensitivity. Fig. 1 collects the pulse profiles obtained by RF-PGD-ToFMS for  $^{206}\text{Pb}^+$  and  $^{208}\text{Pb}^+$  isotopes at different pressures (250 Pa, 350 Pa and 450 Pa) as well as the  $^{208}\text{Pb}/^{206}\text{Pb}$  isotope ratio along the pulse profile. As can be observed, the isotopic ratio  $^{208}\text{Pb}/^{206}\text{Pb}$  in the afterpeak region, particularly at 250 Pa (Fig. 1a), was found to be in good agreement with the expected natural isotope abundance ratio. Accurate isotope ratio measurements could also be performed at higher pressures, by selecting an appropriate pulse interval in the afterpeak region (Fig. 1b and c). However, that isotopic ratio  $^{208}\text{Pb}/^{206}\text{Pb}$  cannot be correctly measured neither in the prepeak nor in the plateau regions of the pulse whatever the Ar pressure (the low sensitivity observed

in such regions could account for the irreproducible values of isotopic ratios, being the isotope ratio observed always lower than the natural abundance value expected).

For comparison purposes, preliminary studies were also carried out using the GD.1 ion source for the measurement of isotope ratios. Fig. 2a collects the pulse profiles obtained for  $^{206}\text{Pb}^+$  and  $^{208}\text{Pb}^+$  isotopes and their isotope ratio along the pulse profile with that ion source. As can be seen, the isotopic ratio  $^{208}\text{Pb}/^{206}\text{Pb}$  can be correctly measured in the afterpeak region using the GD.1 chamber. However, the signals obtained for Pb isotopes were significantly lower than those achieved with the UniOvi GD (Fig. 1a). In any case, the measurements with the GD.1 chamber were carried out at a RF forward power of 60 W due to glass sample overheating at higher RF powers [23].

On the other hand, Fig. 2b and c collects the pulse profiles obtained for  $^{52}\text{Cr}^+$  and  $^{53}\text{Cr}^+$  isotopes and the  $^{52}\text{Cr}/^{53}\text{Cr}$  isotope ratios with both ion sources under scrutiny. Signals for  $^{53}\text{Cr}^+$  in the afterpeak region were higher using the UniOvi GD source. In addition, it should be highlighted that in both cases the  $^{52}\text{Cr}^+$  signal was seriously affected by polyatomic interferences ( $^{40}\text{Ar}^{12}\text{C}^+$ ) in the early afterpeak region, this effect being more notorious (i.e. higher deviations from the natural  $^{52}\text{Cr}/^{53}\text{Cr}$  isotope ratio) with GD.1 source (Fig. 2b). By using the UniOvi GD chamber (Fig. 2c), we observed that an optimum position in the afterpeak region (in the late afterpeak) can be selected to obtain isotope ratios close to the expected natural isotope abundance ratio. In any



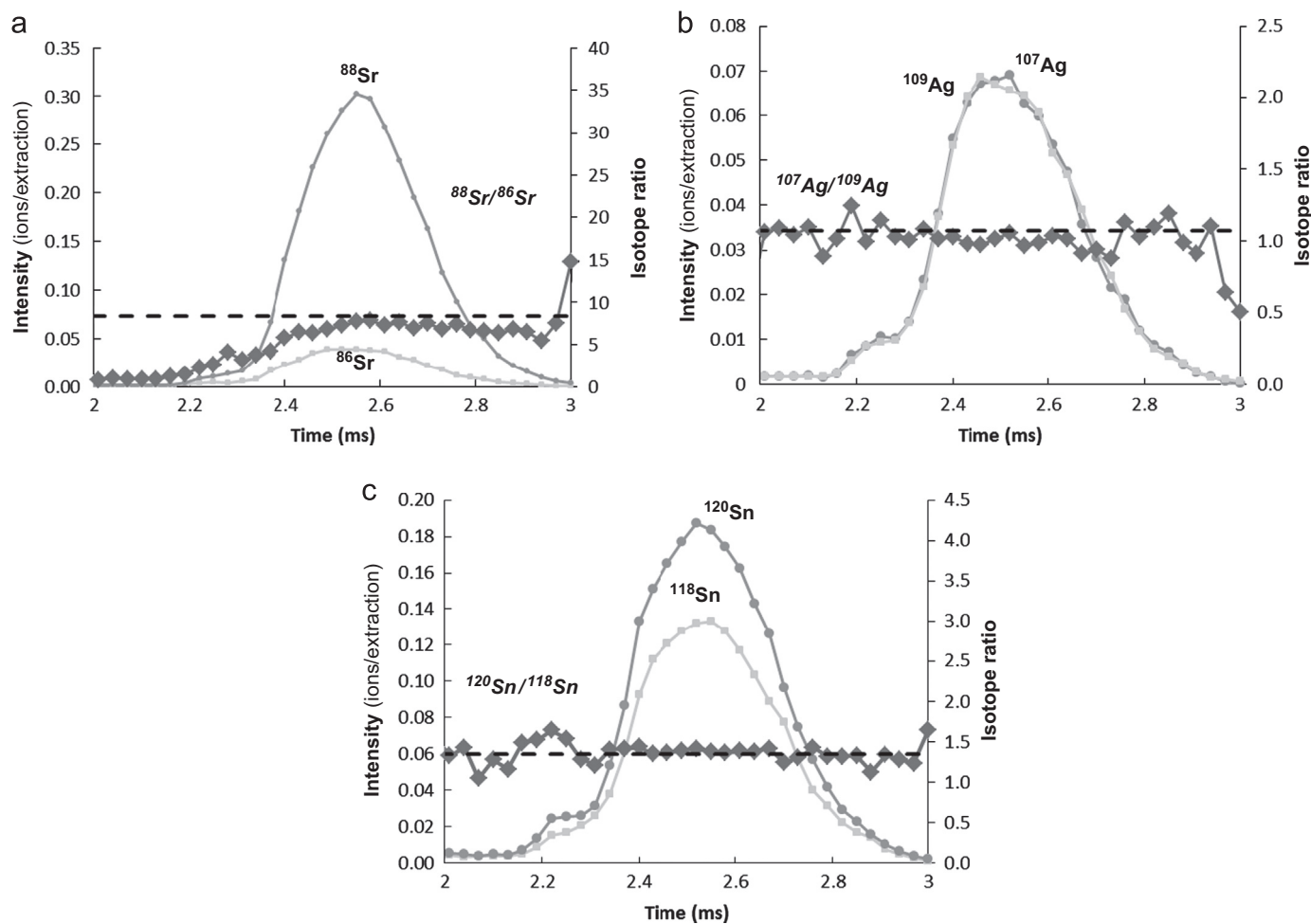
**Fig. 2.** Pulse profiles obtained by RF-PGD-ToFMS for  $^{206}\text{Pb}^+$ ,  $^{208}\text{Pb}^+$ ,  $^{52}\text{Cr}^+$  and  $^{53}\text{Cr}^+$  isotopes and the corresponding isotope ratios along the pulse profile. Analysis of E2 glass using the GD.1 chamber (250 Pa, 60 W, 2 ms pulse width, 4 ms pulse period) and the UniOvi GD source (250 Pa, 100 W, 2 ms pulse width, 4 ms pulse period). Dashed lines represent the natural isotope abundance ratios. (a)  $^{206}\text{Pb}^+$  and  $^{208}\text{Pb}^+$  signals using GD.1 source; (b)  $^{52}\text{Cr}^+$  and  $^{53}\text{Cr}^+$  ion signals using GD.1 source; (c)  $^{52}\text{Cr}^+$  and  $^{53}\text{Cr}^+$  ion signals using UniOvi GD source.



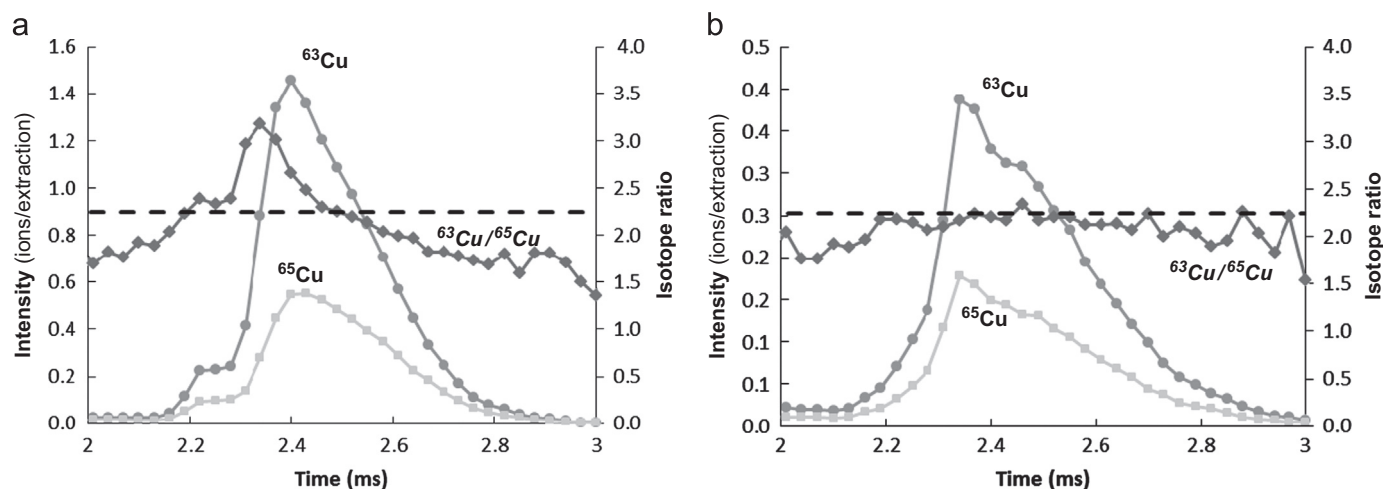
case, to select an interval in the pulse profile free of interferences for the accurate isotope ratio measurement using the GD.1 ion source proved to be difficult. Therefore, the UniOvi GD design was selected for further experiments.

As observed for Pb and Cr analytes (Figs. 1 and 2), low analytical signals have a direct influence not only in the isotope ratio

precision but also in its deviation from the natural isotope ratios. For that reason only the afterpeak region is shown for subsequent experiments. Fig. 3 collects the afterpeak pulse region observed for two isotopes of each of three elements selected as models (Sr, Ag and Sn) and the corresponding isotope ratios ( $^{88}\text{Sr}/^{86}\text{Sr}$ ,  $^{107}\text{Ag}/^{109}\text{Ag}$  and  $^{120}\text{Sn}/^{118}\text{Sn}$ ) in the RF-PGD-ToFMS analysis of E2 glass. As can be



**Fig. 3.** Pulse profiles (afterpeak region) obtained by RF-PGD-ToFMS for  $^{88}\text{Sr}^+$ ,  $^{86}\text{Sr}^+$ ,  $^{107}\text{Ag}^+$ ,  $^{109}\text{Ag}^+$ ,  $^{120}\text{Sn}^+$  and  $^{118}\text{Sn}^+$  isotopes and the corresponding isotope ratios. Analysis of E2 glass using the UniOvi GD source (250 Pa, 100 W, 2 ms pulse width, 4 ms pulse period). Dashed lines represent the natural isotope abundance ratios. (a)  $^{88}\text{Sr}^+$  and  $^{86}\text{Sr}^+$  isotopes; (b)  $^{107}\text{Ag}^+$  and  $^{109}\text{Ag}^+$  isotopes; (c)  $^{120}\text{Sn}^+$  and  $^{118}\text{Sn}^+$  isotopes.



**Fig. 4.** Pulse profiles (afterpeak region) obtained by RF-PGD-ToFMS for  $^{63}\text{Cu}^+$  and  $^{65}\text{Cu}^+$  isotopes and  $^{63}\text{Cu}/^{65}\text{Cu}$  isotope ratio. Analysis of E2 glass using the UniOvi GD source (100 W, 2 ms pulse width, 4 ms pulse period). Dashed lines represent the natural isotope abundance ratios. (a) 250 Pa; and (b) 450 Pa.

observed, isotope ratios close to the theoretical values can be obtained by RF-PGD-ToFMS selecting the appropriate segments in the pulse profile for each analyte: the whole afterpeak region for Sn (Fig. 3c) and a well-defined time interval within the afterpeak for Sr and Ag (Fig. 3a and b).

The selection of the correct time and integration window in the pulse profile is critical to obtain accurate isotope ratio measurements and, therefore, to apply the proposed RF-PGD-ToFMS quantification methodology based on isotope dilution. Fig. 4a collects the observed profiles along the afterpeak region for  $^{63}\text{Cu}^+$  and  $^{65}\text{Cu}^+$  isotopes at 250 Pa: in this case, the obtained  $^{63}\text{Cu}/^{65}\text{Cu}$  isotope ratio was changing close to the natural abundance isotope ratio just in certain segments. Two peaks can be distinguished in the afterpeak region for  $^{63}\text{Cu}^+$  and  $^{65}\text{Cu}^+$ , the first one being less intense than the second one. As can be observed, the  $^{63}\text{Cu}/^{65}\text{Cu}$  ratio reached values close to the theoretical isotope ratio only in this early peak and after the maximum of the later peak. This fact can be attributed to the presence of spectral interferences ( $^{63}\text{Cu}^+$  is interfered by the polyatomic ion  $^{40}\text{Ar}^{23}\text{Na}^+$ ), as confirmed through the analysis of a B1 standard glass, which does not contain Na. For the RF-PGD-ToFMS analysis of B1 glass, the obtained  $^{63}\text{Cu}/^{65}\text{Cu}$  isotope ratio showed values close to the expected ratio, all along the whole afterpeak region (data not shown). Interestingly, such polyatomic ion is not formed using higher Ar pressures in the chamber because polyatomic ions are less stable at higher pressure. This is confirmed in Fig. 4b, where the  $^{63}\text{Cu}/^{65}\text{Cu}$  isotope ratio obtained for E2 glass at 450 Pa matches well with the natural isotope ratio virtually all over the whole afterpeak.

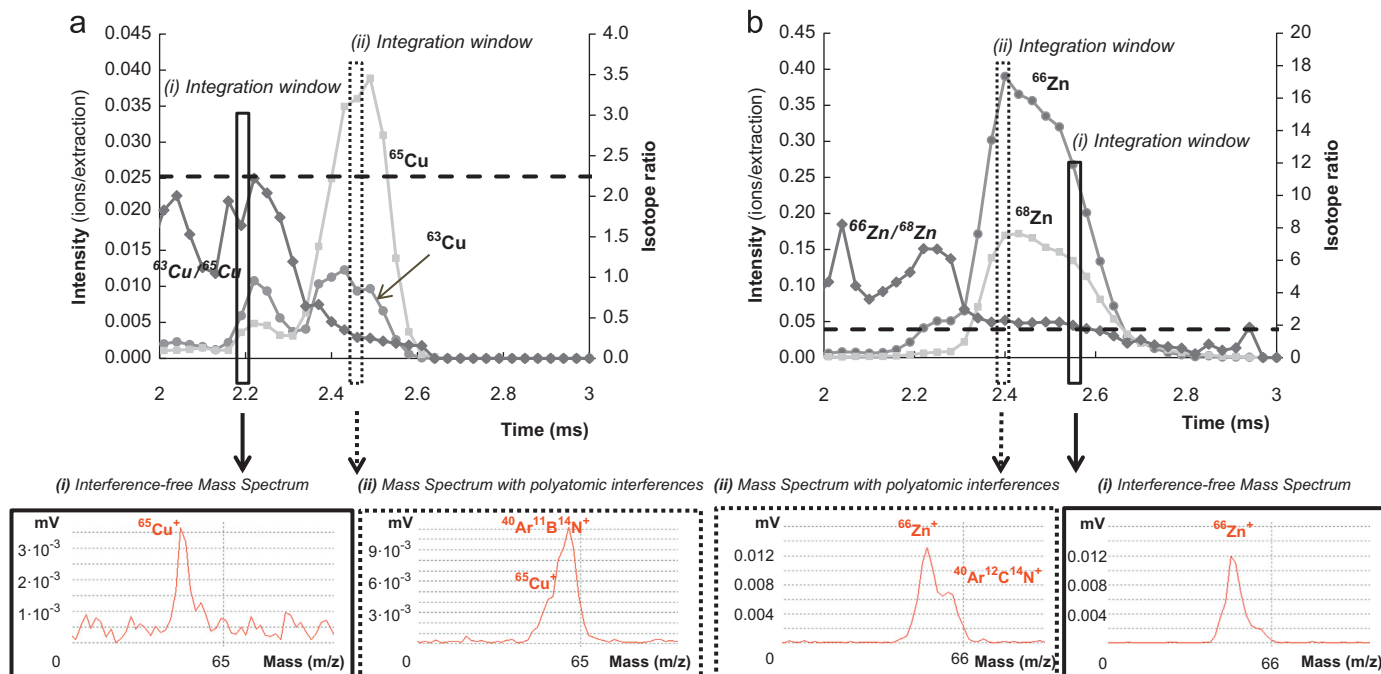
Such studies were carried out with a variety of isotopes in silicate glasses and showed that, as a rule, 250 Pa can be considered optimum GD pressure for isotope ratio measurements (i.e. analytical sensitivity is higher, while polyatomic interferences can be minimized in most cases by appropriate selecting of the pulse measuring window). However, it is important to note that higher pressures could provide more accurate isotope ratios in cases where polyatomic ions can produce serious interferences.

### 3.2. Quantitative analysis of Cu, Zn, Ba and Pb in geological samples by RF-PGD-ToF(IDMS)

Once the measurement of isotope ratios by RF-PGD-ToFMS was investigated and conditions for accurate values were demonstrated, the proposed IDMS quantification methodology was applied to the analysis of the SRMs from NIST. These powdered standards were fused, as indicated in the Experimental section, to form homogeneous lithium borate glasses (30 mm diameter and 2 mm thick). The homogeneity (in natural abundance and isotopically-enriched samples) had been previously demonstrated by LA-ICP-MS measurements [24].

During preliminary analyses it was observed that such lithium borate glasses were damaged from heating rather easily when applying 100 W RF forward power (50% duty cycle), so a lower forward power of 70 W was employed. The mass fractions of the analytes (Cu, Zn, Ba and Pb) in the SRMs are in the low mg/kg range and the analyzed samples were diluted 1:6 during the formation of the lithium borate glasses, high sensitivity of the technique becomes a priority. Therefore, 250 Pa was chosen as discharge pressure and the UniOvi GD source was used. Moreover, as the sample matrix here is different to the E2 standard glass, the interferences can be different. In any case, the two SRMs will have the same lithium borate matrix; that is, interferences should be similar even if original solid matrices are very different (soil and rock mine waste).

Prior to the quantitative analysis of the isotopically-enriched SRMs, the natural abundance of those samples was measured to investigate the isotope ratios possible variations along the pulse profiles in the lithium borate matrices. Fig. 5 collects the pulse profiles obtained by RF-PGD-ToFMS for  $^{63}\text{Cu}^+$ ,  $^{65}\text{Cu}^+$ ,  $^{66}\text{Zn}^+$  and  $^{68}\text{Zn}^+$  isotopes as well as the  $^{63}\text{Cu}/^{65}\text{Cu}$  and  $^{66}\text{Zn}/^{68}\text{Zn}$  isotope ratios along the afterpeak region (by analyzing the natural abundance SRM 2780). As can be seen in Fig. 5a, the  $^{63}\text{Cu}/^{65}\text{Cu}$  isotope ratio can only be correctly measured at the window around the maximum of the first peak of the afterpeak region of the pulse. The values for  $^{63}\text{Cu}/^{65}\text{Cu}$  ratio turned out to be much lower



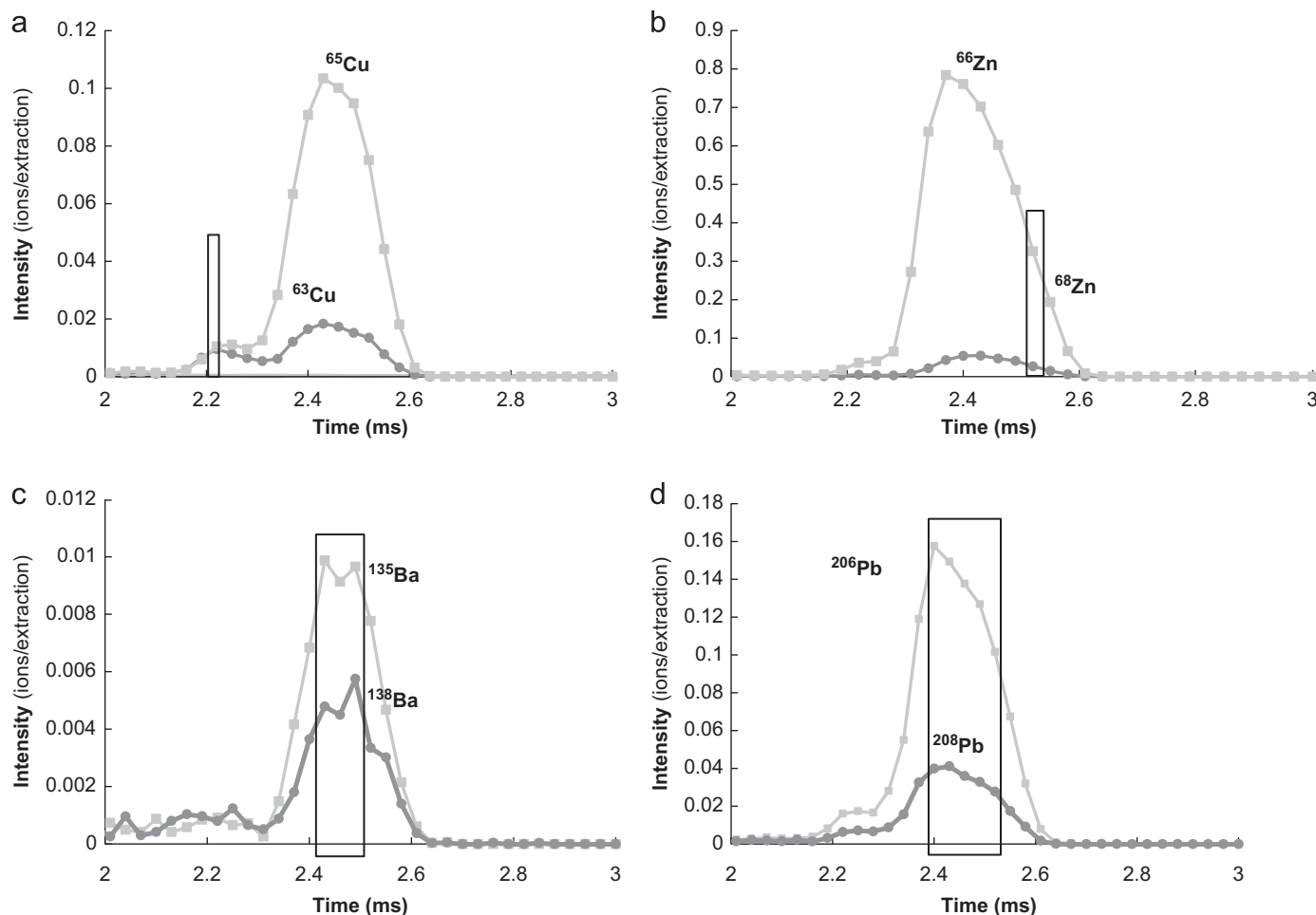
**Fig. 5.** Pulse profiles (afterpeak region) and mass spectra (surroundings of  $m/z=65$ ) obtained by RF-PGD-ToFMS for  $^{63}\text{Cu}^+$ ,  $^{65}\text{Cu}^+$ ,  $^{66}\text{Zn}^+$  and  $^{68}\text{Zn}^+$  isotopes and the corresponding isotope ratios. Analysis of natural abundance SRM 2780 (lithium borate glass) using the UniOvi GD source (250 Pa, 70 W, 2 ms pulse width, 4 ms pulse period). Dashed lines represent the natural isotope abundance ratios. (a)  $^{63}\text{Cu}^+$  and  $^{65}\text{Cu}^+$  isotopes; (b)  $^{66}\text{Zn}^+$  and  $^{68}\text{Zn}^+$  isotopes.

(i.e.  $^{65}\text{Cu}^+$  is interfered). As can be observed in the mass spectrum collected below Fig. 5a, the surroundings of  $m/z=65$  for the afterpeak first maximum showed only one mass peak that corresponds to  $^{65}\text{Cu}^+$ . However, for the larger second afterpeak maximum at least two peaks can be observed around  $m/z=65$ . Such peaks were not resolved but one corresponded to  $^{65}\text{Cu}^+$  (shoulder in the figure) and the other to the polyatomic ion  $^{40}\text{Ar}^{11}\text{B}^{14}\text{N}^+$  (boron is coming from the borate sample matrix). Therefore, despite the lower signal of the first peak in the pulse profile, this temporal region was found to be the most suitable for accurate  $^{63}\text{Cu}/^{65}\text{Cu}$  isotope ratio measurement because no polyatomic interferences were present. A similar behavior was also observed for the analysis of Zn:  $^{66}\text{Zn}^+$  isotope was interfered in some regions of the pulse and thus a careful selection of the correct integration window in the pulse profile is again critical to obtain accurate isotope ratio measurements. The mass spectrum collected below Fig. 5b shows that the  $^{66}\text{Zn}^+$  isotope suffered from interference from the polyatomic ion  $^{40}\text{Ar}^{12}\text{C}^{14}\text{N}^+$ . In this case, the  $^{66}\text{Zn}/^{68}\text{Zn}$  isotope ratio could be correctly measured only by selecting the later afterpeak region (second window in Fig. 5b).

Once the segments of the pulse profile for the correct isotope ratio measurement were selected for each analyte, the validation of the RF-PGD-ToF(IDMS) methodology was carried out by measuring the different isotopically-enriched SRMs. Fig. 6 shows examples of the pulse profiles obtained in the afterpeak region for Cu, Zn, Ba and Pb analytes in the case of isotopically-enriched lithium borate glass of SRM 2586 sample, as well as the time intervals selected for the isotope ratios measurement. According to

previous observations with the corresponding natural abundance SRMs (Fig. 5), a narrow interval in the afterpeak region was selected for the measurement of  $^{63}\text{Cu}/^{65}\text{Cu}$  and  $^{66}\text{Zn}/^{68}\text{Zn}$  isotope ratios (Fig. 6a and b, respectively). Nevertheless, further experiments demonstrated that Ba and Pb analytes (Fig. 6c and d, respectively) did not have significant interferences present. Therefore, the whole region corresponding to the maximum of the afterpeak was selected for the measurement of  $^{138}\text{Ba}/^{135}\text{Ba}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  isotope ratios (see broader windows in Fig. 6c and d).

Quantitative results of the determinations of Cu, Zn, Ba, and Pb in the two SRMs by RF-PGD-ToF(IDMS) are summarized in Table 2. Multiplex  $^{63}\text{Cu}/^{65}\text{Cu}$ ,  $^{66}\text{Zn}/^{68}\text{Zn}$ ,  $^{138}\text{Ba}/^{135}\text{Ba}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  isotope ratio measurements of isotopically-enriched glasses were carried out and three successive replicates per sample were performed in all cases. The corresponding isotope ratios were corrected for mass bias using the bracketing method (two analyses of the natural abundance SRM glass were performed before and after the analysis of the corresponding isotopically-enriched glass) [25]. The final calculation of the RF-PGD-ToF(IDMS) results was carried out by using the conventional isotope dilution equation [26]. As can be seen in Table 2, except for Zn in SRM 2586, the mass fraction values determined by RF-PGD-ToF(IDMS) were in agreement with the certified values at 95% confidence interval. Concerning Zn in SRM 2586, the low mass fraction of Zn (352 mg/kg diluted 1:6 in the lithium borate glass) could explain, at least partly, the inferior accuracy obtained due to low ions statistics and the higher influence of the spectral interference coming from the polyatomic ion  $^{40}\text{Ar}^{12}\text{C}^{14}\text{N}^+$ . The precision of Cu, Zn, Ba and Pb



**Fig. 6.** Pulse profiles (afterpeak region) obtained by RF-PGD-ToFMS for Cu, Zn, Ba and Pb analytes in the isotopically-enriched SRM 2586 (250 Pa, 70 W, 2 ms pulse width, 4 ms pulse period). (a)  $^{63}\text{Cu}^+$  and  $^{65}\text{Cu}^+$  isotopes; (b)  $^{66}\text{Zn}^+$  and  $^{68}\text{Zn}^+$  isotopes; (c)  $^{135}\text{Ba}^+$  and  $^{138}\text{Ba}^+$  isotopes; (d)  $^{206}\text{Pb}^+$  and  $^{208}\text{Pb}^+$  isotopes.

**Table 2**

Results obtained by RF-PGD-ToF(IDMS) for Cu, Zn, Ba and Pb in two NIST SRMs. Uncertainties shown result from standard deviations of the mean of 3 independent analyses.

SRM	Elements	Certified concentration (mg/kg)	RF-PGD-ToF(IDMS) concentration (mg/kg)
2586	Cu <sup>a</sup>	81 ± –	53 ± 4
	Zn	352 ± 16	209 ± 26
	Ba	413 ± 18	444 ± 12
	Pb	432 ± 17	436 ± 14
2780	Cu	215.5 ± 7.8	242 ± 29
	Zn	2570 ± 160	1942 ± 158
	Ba <sup>b</sup>	993 ± 71	942 ± 2
	Pb	5770 ± 410	5969 ± 47

<sup>a</sup> Information value.

<sup>b</sup> Reference values.

mass fractions obtained using the IDMS procedure were always better than 12% for three independent replicates, in some cases being as good as 1% (Ba and Pb in SRM 2780). It should be highlighted that mass fractions refer to the original powders (before fusion); in fact, the measured samples (lithium borate glasses) have mass fractions about six times lower than the powdered SRMs, demonstrating the potential of the proposed quantification methodology for the analysis of trace elements.

#### 4. Conclusions

RF-PGD-ToFMS has been evaluated for the first time for the accurate and precise quantitative analysis of powdered samples using IDMS. Results showed that RF-PGD-ToFMS, operated in RF pulsed mode, may offer a new analytical tool for isotope ratio measurements. However, it was found that a careful selection of the correct integration window in the pulse profile for each analyte is critical to ensure accurate isotope ratios. Despite the fact that the polyatomic interferences could be reduced at higher pressures (e.g. 450 Pa), using lower pressures (250 Pa) allows to obtain higher sensitivities. Moreover, selection of appropriate time-segments (measurement window) of the pulse profile (in which spectral interferences are minimized) is an additional parameter for selectivity control.

Traditional methods of analysis of geological samples are based on the decomposition of powders, typically through microwave-assisted acid digestions, and the subsequent analysis of the resulting liquid sample. Nevertheless, direct solid analysis techniques, such as RF-PGD-ToFMS and LA-ICP-MS, can be also used as alternative tools to avoid the required digestion procedures that are often the most time-consuming stage of the analysis and may be associated with the risk of sample contamination and analyte loss. The sample preparation procedure based on lithium borate fusion which produces 2 mm thick borate glasses (an approach widely used for other direct solid sample analysis techniques) was found to be suitable for RF-PGD-ToFMS measurements, being the precision and accuracy obtained similar to those reported for LA-ICP(IDMS) analysis of powdered samples.

Additionally, it should be stated that the use of IDMS combined to RF-PGD-ToFMS allows the quantification of representative non-conductive glasses, without requiring external calibrations with certified reference materials. In this case, the thickness and surface area of the samples and standards will not be a critical parameter to control as it is for traditional calibration procedures used in GD sources. Thus, the research carried out expands the applicability of RF-PGD-ToFMS not only to the quantitative analysis of solids but

also to powdered samples via isotope dilution analysis that can be extremely relevant to the analysis of geological and environmental samples.

#### 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.

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