Tandem ICP – Mass Spectrometry for Sr Isotopic Analysis without Prior Rb/Sr Separation

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ABSTRACT

The use of a mixture of 10% of CH_3F and 90% of He as a reaction gas in tandem ICP – mass spectrometry (ICP-MS/MS) enables the accurate determination of the $^{87}Sr/^{86}Sr$ isotope ratio in geological materials, provided that mass discrimination is corrected for by using a combination of internal (Russell law, assuming a constant $^{88}Sr/^{86}Sr$ isotope ratio) and external correction (using the isotopic reference material NIST SRM 987 $SrCO_3$) in a sample-standard bracketing approach. No prior Rb/Sr separation is required as the isobaric overlap at a mass-to-charge ratio of 87 is avoided by monitoring the SrF^+ reaction product ions instead of the Sr^+ ions. Rb shows no reactivity towards CH_3F. The double mass selection (MS/MS mode) prevents both spectral overlap from atomic ions at the mass-to-charge ratios of the SrF^+ reaction product ions, but also a measurable effect from the matrix on the $^{87}Sr/^{86}Sr$ result. This aspect is critical, as it enables accurate results to be obtained without the need of using a matrix-matched standard to correct for mass discrimination, in contrast to previous work with a quadrupole ICP-MS instrument with a CH_3F/Ne-pressurized cell, in which the use of a matrix-matched standard was compulsory. The precision attainable – 0.05 % RSD external precision – suffices for making the newly developed method of use in a variety of applications.

1. INTRODUCTION

In comparison to elements with a similar atomic number, Sr shows a relatively pronounced natural variation in its isotopic composition as a result of one of its isotopes – ^{87}Sr – being radiogenic. The consequence is a wide variety of applications for which Sr isotopic analysis is of relevance (e.g., Rb/Sr geochronological dating and other geochemical applications, provenance determination of agricultural products of plant and animal origin and migration studies).[1-4]

Although like for every other element with ≥ 2 isotopes, also the isotopic composition of Sr shows natural variation as a result of isotope fractionation,[3,5,6] the main responsible for the natural variation in the isotopic composition of Sr[7,8] is the β^- decay of ^{87}Rb into ^{87}Sr ($T_{1/2} = 4.88 \times 10^{10}$ years[9]). This means that, in a closed system, sub-samples containing Rb and Sr will be enriched in ^{87}Sr, and the degree of enrichment depends on the time during which the two elements have resided together and their elemental ratio Rb/Sr.[10-12]

However, accurate determination of the ^{87}Sr/^{86}Sr isotope ratio by means of inductively coupled plasma-mass spectrometry (ICP-MS) is not free from challenges. One of the most important problems is the spectral overlap of the signals of the isobaric ions ^{87}Rb$^+$ and ^{87}Sr$^+$, which need a mass resolution of ~ 300,000 to be resolved, which is beyond the capabilities of present-day commercially available ICP-MS instruments.[13,14] Additional spectral interference due to the presence of polyatomic ions, such as ArCa$^+$ and Ca$_2^+$ dimers, can also jeopardize the accuracy of the isotope ratio results. The use of high mass resolution,[15] which furthermore results in a significant drop in signal intensity and deterioration in isotope ratio precision,[16] is not feasible for overcoming the spectral overlap. Sr has to be isolated from the matrix, or at least separated from Rb, prior to analysis.[17-19] Obviously, these isolation steps negatively affect the sample throughput and make Sr isotopic analysis labor-intensive.

It has been demonstrated that chemical resolution using a quadrupole-based ICP-MS (ICP-QMS) instrument equipped with a collision/reaction cell can be an elegant option to resolve spectral overlap,[20] thus extending the application range of ICP-QMS to the isotopic analysis of elements that otherwise suffer from spectral interference. The use of a collision/reaction cell allows to remove spectral overlap relying on physical processes (e.g., a combination of collisions with a non-reactive gas to slow down polyatomic ions more than atomic ions, thus enabling the former to be selectively discriminated against *via* kinetic energy discrimination),[21] or by selective ion/molecule reaction between an interfering ion,[22-24] or the target ion,[25-27] and a reactive gas. The latter approach is sometimes referred to as chemical resolution and allows interference-free measurement at either the original mass-to-charge (m/z) ratio of the target nuclide or at the m/z ratio of the reaction product ion formed. In this way, the sample pretreatment can be reduced or even eliminated, also facilitating the direct analysis of solid samples *via* laser ablation – ICP-MS (LA-ICP-MS).

Unfortunately, the isotope ratio precision typically offered by ICP-QMS is rather modest, with values around 0.1% RSD internal precision. Pressurizing the collision/reaction cell of a ICP-QMS instrument with an inert collision gas can lead to a slight improvement in the isotope ratio precision, by damping the fluctuations in signal intensity, through the mixing ions sampled from the plasma ion source at slightly different moments in time.[28,29] However, the isotope ratio precision thus attainable is still considerably worse than that achievable with thermal ionization mass spectrometry (TIMS) or multi-collector ICP-MS (MC-ICP-MS), with an internal precision down to 0.001% RSD. Therefore, the use of ICP-QMS for the determination of isotope ratios has often been restricted to the study of induced changes in the isotopic composition of target elements in the context of tracer experiments with enriched stable isotopes,[30,31] or of elemental assay using isotope dilution for calibration.[32] However, it has to be stressed that, the use of the more expensive MC-ICP-MS or TIMS instrumentation is not always required when natural variation in the isotopic composition of a target element needs to be studied, as for some applications, particularly those dealing with radiogenic nuclides, the precision attainable with a ICP-QMS instrument can be fit-for-purpose.[11,33-35]

Additionally to the difficulties with spectral overlap mentioned above, every type of ICP-MS instrumentation suffers from mass discrimination,[36] a term referring to the differences in the efficiencies of ion extraction, transmission and/or detection as a function of the analyte mass. This effect results in a bias between the measured isotope ratio and the corresponding true value that needs to be adequately corrected for. Different approaches have been described in the literature for this purpose (e.g., internal correction, external correction and the combination of both).[37] Also, it has been demonstrated that mass discrimination effects become more pronounced in ICP-QMS when the collision/reaction cell is pressurized with a gas, as a result of slight differences in the collisional and/or chemical behavior of the isotopes as a function of their mass.[26,38]

In earlier work, the use of methyl fluoride (CH_3F) as a selective reaction gas (in combination with Ne as a non-reactive collision gas) in a ICP-QMS instrument equipped with a dynamic reaction cell (DRC) for the direct determination of Sr isotope ratios has been described.[25] In this approach, the selective reaction between CH_3F and Sr^+ (Rb^+ does not react with CH_3F) allows for circumventing the isobaric overlap at m/z = 87 by measuring the relative signal intensities of the Sr isotopes *via* the intensities of the corresponding SrF^+ ions. Owing to the mono-isotopic character of F, the SrF^+ ions show the same isotopic pattern as do the Sr^+ ions themselves. Despite the achievements shown in the work referred to, this did not result in a general breakthrough for Sr isotopic analysis, as it was noted that (i) interfering nuclides occurring at the m/z ratio of the selected reaction product ions (e.g., ^{103}Rh, ^{106}Cd, $^{105,106}Pd$ and ^{107}Ag) could not be removed, and (ii) that the matrix composition affects the mass discrimination to a large extent, such that the use of a matrix-matched isotopic standard for external mass bias correction was required. These important drawbacks have hindered routine application of this approach in real-life applications.

Recently, a new type of ICP-MS device was introduced onto the market. The so-called triple quadrupole ICP-MS instrumentation is equipped with a tandem mass spectrometry configuration (ICP-MS/MS), with an octopole collision/reaction cell located in-between two quadrupole analyzers. This set-up opens new possibilities for interference-free determination of ultra-trace concentrations of elements that otherwise suffer from strong spectral overlap.[39,40] In MS/MS-mode, only those ions with the original m/z-ratio of the analyte element pass the first quadrupole and enter the reaction cell. This results in an enhanced control over the reactions taking place in the cell and a strong reduction in matrix effects. Because of this, highly reactive gases (e.g., NH_3 and CH_3F) can be used without the risk of obtaining complex mass spectra that are difficult to interpret.[41] ICP-MS/MS with a CH_3F/He (10% CH_3F and 90 % He) mixture[42] as a reaction gas has recently been successfully used by the authors for the purpose of ultra-trace determination of several elements (Al, As, Co, Cr, Mn, Ni, Se, Ti and V),[43,44] but the possibilities of ICP-MS/MS for isotope ratio determinations have not been fully explored yet,[45-49] and no work to date has reported on the use of this technique for Sr isotopic analysis.

In this work, the capabilities of tandem ICP - mass spectrometry with CH_3F as a reaction gas were evaluated, with the aim to develop a method that enables the straightforward determination of the $^{87}Sr/^{86}Sr$ isotope ratio in geological materials, without previous Sr isolation or Rb/Sr separation.

2. EXPERIMENTAL

2.1. *Reagents and standards*

Only high-purity reagents were used throughout the work. Ultra-pure water (resistivity > 18.2 MΩ cm) was obtained from a Milli-Q Element water purification system (Millipore, France). Ultra-pure 28 M HF (Fisher Chemicals, Great Britain) and pro-analysis 14 M HNO_3 (ChemLab, Belgium), further purified by sub-boiling distillation, were used for acid digestion. Appropriate dilutions from 1 g L^{-1} single-elemental standard solutions (Ag, Ca, Cd, Pd, Rb and Sr – Instrument Solutions, The Netherlands) were made for obtaining solutions used in the context of method development. The isotopic reference material NIST SRM 987 Strontium Carbonate with a certified Sr isotopic composition ($^{87}Sr/^{86}Sr = 0.71034 \pm 0.00026$) and an in-house standard solution of Sr (Instrument solutions, The Netherlands), previously characterized via MC-ICP-MS ($^{87}Sr/^{86}Sr = 0.70753 \pm 0.00006$), were used for optimization, method development and validation purposes.

2.2. *Samples*

Five geological reference materials – USGS AGV1 Andesite and USGS G-2 Granite, USGS BHVO-1 Basalt, BCR CRM 141 Calcareous Loam Soil and BCR CRM 142 Light Sandy Soil – were analyzed for their $^{87}Sr/^{86}Sr$ isotope ratio and the results obtained were compared to values reported in the literature for the purpose of validation.

2.3. *Sample preparation*

Sample digestion was carried out in Savillex® beakers, that had been previously submitted to a cleaning procedure with both HNO_3 and HCl and subsequent rinsing with Milli-Q water.

Approximately 0.2 g of each reference material was accurately weighed and dissolved in 3 mL of 14 M HNO_3 and 10 mL of 28 M HF. The mixture was heated in an open beaker on a hot plate (90 °C) until dryness. For the reference materials USGS AGV1 (Andesite) and USGS G-2 (Granite), the residue was taken up in 1.4 M HNO_3. In the case of USGS BHVO-1 (Basalt), BCR CRM 141 (Calcareous Loam Soil) and BCR CRM 142 (Light Sandy Soil), an additional digestion was required to obtain a clear solution. Therefore, 5 mL of 14 M HNO_3 was added to the residue and the resulting mixture heated at 110°C in a closed beaker overnight. After digestion, the solutions thus obtained were appropriately diluted for subsequent analysis. To avoid possible contamination, only "metal-free" tubes were used to prepare all dilutions (15 or 50 mL polypropylene centrifuge tubes, VWR, Belgium).

2.4. *Instrumentation*

All measurements were performed using an Agilent 8800 tandem ICP-MS instrument (ICP-QQQ, Agilent Technologies, Japan), equipped with a MicroMist nebulizer (400 µL min^{-1}) fitted onto a Peltier-cooled Scott-type spray chamber (2 °C). The octopole collision/reaction cell was pressurized with a mixture of CH_3F/He (10% CH_3F and 90% He, "Certified Master Class", Air Liquide, Belgium). The CH_3F/He mixture was introduced *via* the 4th inlet (operation range of the mass flow controller, 0 – 100 %, corresponding to gas flow rates of 0 – 1 mL min^{-1}, calibrated for O_2)

3. RESULTS AND DISCUSSION

3.1. Method development for interference-free determination of Sr

An important prerequisite for successful direct Sr isotopic analysis is the ability of the analytical method to monitor the signals of (at least) ^{86}Sr, ^{87}Sr and ^{88}Sr free from spectral overlap. The actual isotope ratio of interest is ^{87}Sr/^{86}Sr, while ^{88}Sr/^{86}Sr is used for internal correction for mass discrimination. As measuring ^{84}Sr provides no added value, while increasing the measurement time and potentially deteriorating the isotope ratio precision, this nuclide was not monitored. In this work, CH_3F (a mixture of 10 % CH_3F and 90 % He) was evaluated as a reaction gas in ICP-MS/MS. *Via* product ion scanning, with the cell pressurized with 1 mL min^{-1} of CH_3F/He, the mass-to-charge (m/z) ratio of each of the target nuclides ($^{86,87,88}Sr^+$) was selected in the first quadrupole, and the entire mass spectrum was scanned using the second quadrupole for identifying the reaction product ions formed. The main reaction product ions were identified as $^{86,87,88}SrF^+$. In MS/MS mode, the CH_3F/He flow rate setting was evaluated in the range of 0 - 1.0 mL min^{-1}, and a maximum signal-to-background ratio was found at 0.90 mL min^{-1}. The optimum instrument settings are summarized in Table 1.

With the aim of demonstrating the capabilities of the MS/MS approach to avoid spectral overlap, two standard solutions were analyzed, the first one containing 10 µg L^{-1} of Sr and the second one containing the same concentration of Sr and 10 µg L^{-1} of Ag, Cd, Pd and Rb. These elements can give rise to spectral interference at the original m/z ratio of one of the target nuclides (^{87}Rb) or at the m/z ratio of the selected reaction product ions ($^{105,106}Pd$, ^{106}Cd, ^{107}Ag). Both standard solutions were measured in both single quadrupole mode (SQ, where the first quadrupole is not operating as a mass filter, but only as an ion guide) and MS/MS mode. The results are given in Figure 1. In both modes, the isotopic pattern observed for the pure Sr solution was the same without and with reaction, as a consequence of the mono-isotopic character of F, enabling the determination of the isotopic composition of Sr *via* measurement of the intensities of the SrF^+ ions. A comparison between the results for both standard solutions (without and with admixed elements) shows the effect of the overlap of the signals of ^{87}Sr and ^{87}Rb, which was resolved in both modes owing to reaction of the Sr^+ ions with CH_3F, while Rb^+ shows no reactivity towards this gas. Although a better sensitivity was achieved in SQ mode, the spectral interferences occurring in the presence of Ag, Cd and Pd ions at the m/z ratio of the selected reaction product ions prevent accurate Sr isotopic analysis in this mode. For samples containing those elements, Sr isotopic analysis without previous Sr isolation can only be successfully accomplished in MS/MS mode.

In MS/MS mode, some figures of merit (e.g., sensitivity or limits of detection and of quantification) were characterized and the corresponding results are given in Table 2.

3.2. Optimization of instrument settings and data acquisition parameters for the accurate and precise isotope ratio determination of Sr via SrF^+ monitoring

With the objective of achieving accurate and precise ^{87}Sr/^{86}Sr isotope ratio results *via* conversion of Sr^{+} into the corresponding SrF^{+} ions using CH$_3$F/He as a reaction gas in ICP-MS/MS, the detector dead time was experimentally determined and the effect of the data acquisition parameters was checked.

The detector dead time was determined according to the method proposed by Russ.[50] Standard solutions of Sr with concentrations of 2.5, 5.0 and 10 µg L^{-1} were measured at different detector dead times in the range of 0 to 70 ns. The ^{88}SrF^{+}/^{86}SrF^{+} ratios were plotted *versus* the dead time for each concentration. According to this approach, the point where the lines intersect corresponds with the correct value, which was 32.6 ± 0.3 ns in this case. The experimentally determined detector dead time was inserted into the software and used throughout all further work.

In addition, data acquisition parameters were optimized. The best performance is typically obtained when combining a sufficiently long acquisition time (*cf.* the role of the total number of ions detected in Poisson counting statistics) with fast scanning (to counteract the noisy character of the ICP ion source).[29] Different experiments were conducted with the aim of evaluating the effect of the data acquisition parameters on the accuracy and precision of the isotope ratio results. ^{87}SrF^{+}/^{86}SrF^{+} ratios and internal precision values, expressed as RSD (%), were determined using 10 replicates for each measurement and 100 sweeps per replicate. The results thus obtained are presented in Figure 2 as a function of the total acquisition time per replicate, for both the raw data and the results after the use of an internal correction (*vide infra*). As expected, the RSD (%) decreases for longer acquisition times, down to a minimum at a total acquisition time of 90 s, corresponding with an acquisition time of 30 s for each of the isotopes selected (RSD = 0.12 and 0.09 % for the raw data and the internally corrected data, respectively). It can be seen that the ^{87}SrF^{+}/^{86}SrF^{+} ratio itself also changes with increasing total acquisition time, until a constant ratio is obtained for the highest values (Figure 2). This tendency can most probably be explained as a result of the use of chemical reactions, where the reaction product ions typically require more time to actually reach the second quadrupole and detector and give rise to a stable ion beam. More evidence for this hypothesis was found in additional experiments, where – for measurements with a short total acquisition time - a wait time offset (WTO) was used. This WTO is an additional time on top of the quadrupole settling time, allowing the slowdown of the ions in the cell to be compensated for and giving the system time to arrive at steady state conditions. A WTO in the order of a few milliseconds (~5 ms) was sufficient to compensate for the effect seen at low acquisition times. Additionally to the experiments explained above, also the number of sweeps per replicate was evaluated as a possible parameter affecting the precision in the isotope ratio measurements. However, although a wide range of number of sweeps was tested (50 - 1000), no reproducible effect on the accuracy or precision was noticed, probably, because longer dwell times (expressed as the acquisition time per nuclide / number of sweeps) are required when dealing with isotope ratio measurement after chemical reaction in the cell. Based on the results of these experiments, 100 sweeps and a total acquisition time of 90 s were selected as the optimum parameters, as they provide the best possible precision and stable isotope ratio results. When using these longer acquisition times, no additional measurement time was needed to obtain a constant isotope ratio result, and thus, the WTO was set at 0 ms. The optimized instrument settings and data acquisition parameters used in all further experiments are shown in Table 1.

3.3. Mass bias correction

As mentioned in the introduction, ICP-MS is affected by mass discrimination, such that a measured isotope ratio differs from the corresponding true value. Several approaches have been described to correct for the mass bias thus caused. The use of internal correction, external correction and the combination of both, were evaluated with the aim of obtaining better accuracy and precision. For the internal correction approach, the ^{88}Sr/^{86}Sr ratio is assumed to be (sufficiently) constant in nature and used to correct the ^{87}Sr/^{86}Sr ratio by means of the Russell law, with the assumption that $f^{88/86} = f^{87/86}$ (see equation 1). Alternately, the raw data were externally corrected for the mass bias using the NIST SRM 987 as an external standard, used in a sample - standard bracketing approach (SSB). Finally, also the combination of both correction methods was tested. Figure 3 and Table 3 show the results for a sequence of 10 measurements of an in-house standard solution of Sr with an isotopic composition that was previously characterized via MC-ICP-MS (^{87}Sr/^{86}Sr = 0.70753 ± 0.00003). As can be seen, the raw data are biased high, and the use of internal correction using the Russell law (equation 1), based on an ^{88}Sr/^{86}Sr isotope ratio of 8.3752 does not allow to properly correct for mass discrimination. Although internal correction leads to a significant improvement in both, internal and external precision, the results are still biased high. The bias remaining after applying internal correction most probably results from additional mass discrimination produced by collisions and reactions in the cell (not all isotopes react to exactly the same extent with the reaction gas (CH_3F), neither are they equally affected by collisions with the inert He gas). Therefore, external correction with NIST SRM 987 in a SSB approach (equation 2) was tested. Good agreement was found between the externally corrected data and the true value, but with this correction method, the external precision was not improved beyond that of the raw data. Finally, the combination of internal and external correction was seen to provide the best results in terms of both accuracy and precision, without any significant difference between the experimentally determined isotope ratios and the true value, and with an external precision of 0.035 % RSD (n = 10). Additionally, as shown in Figure 3, also an improved internal precision (the standard deviation on 10 replicates for each measurement) was achieved when the isotope ratios were internally corrected.

In order to better assess the capabilities of the last approach for the determination of isotope ratios of Sr using CH_3F in ICP-MS/MS, longer-term studies were performed. $^{87}SrF^+/^{86}SrF^+$ isotope ratio results were collected during a period of one month and provided an average of 0.70756 ± 0.00028 and an external precision of 0.039 % RSD (n = 50). Thus, the combination of internal and external correction was used in all further work.

$$\left(\frac{^{87}\mathbf{Sr}}{^{86}\mathbf{Sr}}\right)_{\text{sample, corrected}} = \left(\frac{^{87}\mathbf{Sr}}{^{86}\mathbf{Sr}}\right)_{\text{sample, measured}} \text{x} \left(\frac{\mathbf{m}_{^{87}\mathrm{Sr}}}{\mathbf{m}_{^{86}\mathrm{Sr}}}\right)^{\mathbf{f}} \;;\; \mathbf{f} = \ln\left[\frac{\left(^{88}\mathbf{Sr}/^{86}\mathbf{Sr}\right)_{\text{measured}}}{\left(^{88}\mathbf{Sr}/^{86}\mathbf{Sr}\right)_{\text{true}}}\right] / \ln\left[\frac{\mathbf{m}_{^{88}\mathrm{Sr}}}{\mathbf{m}_{^{86}\mathrm{Sr}}}\right] \tag{1}$$

$$\left(\frac{^{87}\mathbf{Sr}}{^{86}\mathbf{Sr}}\right)_{\text{sample, corrected}} = \left(\frac{\left(\frac{^{87}\mathbf{Sr}}{^{86}\mathbf{Sr}}\right)_{\text{sample, measured}}}{\frac{\left(\frac{^{87}\mathbf{Sr}}{^{86}\mathbf{Sr}}\right)_{\text{std}-1,\text{measured}} + \left(\frac{^{87}\mathbf{Sr}}{^{86}\mathbf{Sr}}\right)_{std+1,measured}}{2}}\right) x \left(\frac{^{87}\mathbf{Sr}}{^{86}\mathbf{Sr}}\right)_{\text{std,true}} \tag{2}$$

3.4. Influence of sample matrix on isotope ratio results in SQ and MS/MS mode

In previous work,[25] it was shown that – even when the Sr isotopes can be measured interference-free – a good accuracy and precision of the $^{87}Sr/^{86}Sr$ isotope ratio results could not be guaranteed for geological reference materials, unless matrix-matched isotopic standards were used for external mass bias correction. This leads to the conclusion that matrix effects are responsible for the deviations obtained.

In this work, we assessed whether also with the newly developed ICP-MS/MS approach matrix effects necessitate the use of a matrix-matched standard. Therefore, the accuracy and precision of Sr isotopic analysis was assessed for pure Sr standard solutions, Sr standards with increasing concentrations of some matrix elements added (up to 1000 µg L^{-1} Ca and 200 µg L^{-1} Rb) and geological reference materials, both in SQ and MS/MS mode. The standards were measured on 3 different days in order to assess the robustness of the method under such conditions. No significant differences were found between the Sr standard solution and the different Rb- and Ca-containing solutions, neither between the results obtained in SQ and MS/MS-mode, which indicates that for these rather simple matrices, matrix effects can be neglected. For the geological reference materials, however, the situation is clearly different. For one of the reference materials, USGS AGV-1 Andesite, isotopic analysis in SQ mode (where all matrix ions are passing the first quadrupole and enter the collision/reaction cell) resulted in a $^{87}Sr/^{86}Sr$ isotope ratio of 0.65432 ± 0.00085 (after mass bias correction, based on a combination of both internal and external correction using NIST SRM 987). This result deviates strongly from the corresponding reference value of 0.70406 ± 0.00005. In MS/MS mode, however, where only a very limited selection of ions enters the cell, a good agreement was found between the results obtained and the corresponding reference value (see next section). This leads to the conclusion that for samples with a heavy matrix, matrix effects do have an influence on the final results. However, these effects can be overcome by operating the tandem mass spectrometer in the MS/MS mode, which is an additional proof of the strength of the method developed in this work.

3.5. Determination of the isotopic composition of Sr in geological reference materials using ICP-MS/MS

This novel method using CH_3F as a reaction gas in ICP-MS/MS for the determination of the isotopic composition of Sr without prior Sr isolation from the matrix, was used for the analysis of five reference materials of geological origin. The results are shown in Table 4. No significant differences were established between the experimental results and the corresponding reference values. In addition, the precision expressed as standard deviation for n = 5 was not significantly different ($F < F_{critical}$) from that obtained for an in-house standard solution of Sr (n=10, Table 3), except for BCR CRM 142, for which a very slight difference was found (3.66 > 3.63). Therefore, it can be stated that the approach for Sr isotopic analysis developed in this work allows accurate and precise isotope ratio results to be obtained, without the requirement of using a matrix-matched isotopic standard for mass bias correction, as was required in a similar context (CH_3F/Ne-pressurized reaction cell) with a Perkin Elmer Sciex Elan DRC ICP-MS instrument [25].

4. CONCLUSION

In this work, the capabilities of a novel approach for Sr isotopic analysis using CH_3F as a reaction gas in ICP-MS/MS were demonstrated. The method developed was able to remove all interfering species that could hinder Sr isotopic analysis. The removal of matrix elements, before they enter into the reaction cell provided by the MS/MS-mode, diminishes the influence of matrix effects on the final results, thus avoiding the necessity of using a matrix-matched standard, in contrast to the SQ-mode where the use of a matrix-matched standard is compulsory. The method developed enables accurate and precise (external precision better than 0.05% RSD) determination of the $^{87}Sr/^{86}Sr$ isotope ratio. It was shown that this approach can be successfully applied to the Sr isotopic analysis of reference materials of geological origin, without prior Rb/Sr separation. The robustness of the results obtained for these complex materials suggest that such method could also be deployed for the analysis of other types of samples for which Sr isotopic analysis could be of scientific interest.

ACKNOWLEDGMENT

The UGent authors acknowledge Agilent Technologies for providing them with an ACT-UR research project grant. MR acknowledges the funding from the Spanish Ministry of Economy and

Competitiveness (Project CTQ2012-33494) and from the Aragón Government (Fondo Social Europeo).

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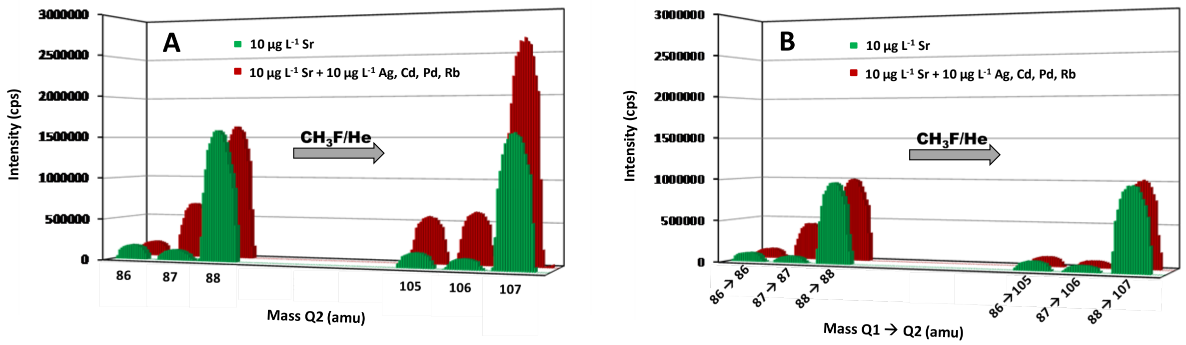

Figure 1. Mass spectrum, showing the isotopic composition of Sr at the original mass-to-charge ratio (m/z = 86, 87 and 88) and at the mass-to-charge ratios of the selected reaction product ion (SrF^+ m/z = 105, 106 and 107) for a standard solution of Sr (in green) and for a standard solution of Sr doped with Ag, Cd, Pd and Rb (in red) in both, single quadrupole or SQ (A) and MS/MS mode (B).

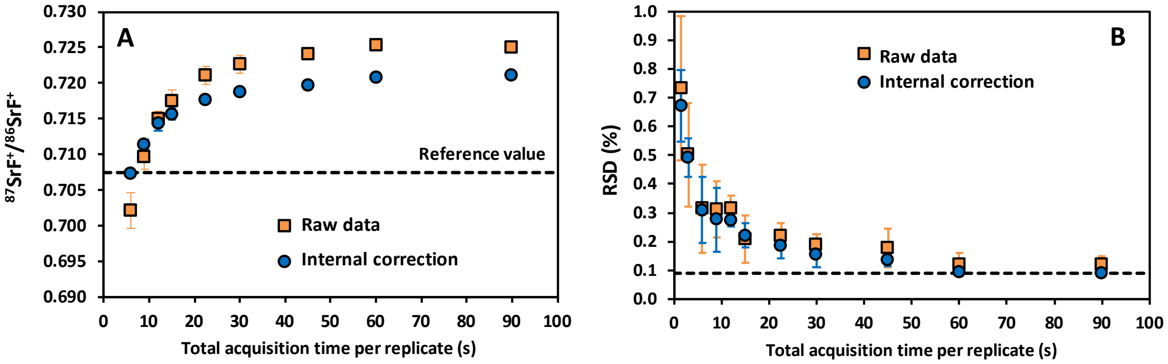

Figure 2. Raw and internally corrected ^{87}Sr/^{86}Sr isotope ratio as a function of the total acquisition time per replicate (A). Internal precision for the raw and internally corrected data expressed as RSD (%) for 10 replicate measurements as a function of the total acquisition time per replicate (B). The error bars indicate the standard deviation of 3 different analyses (each consisting of 10 replicate measurements) obtained on 3 different days.

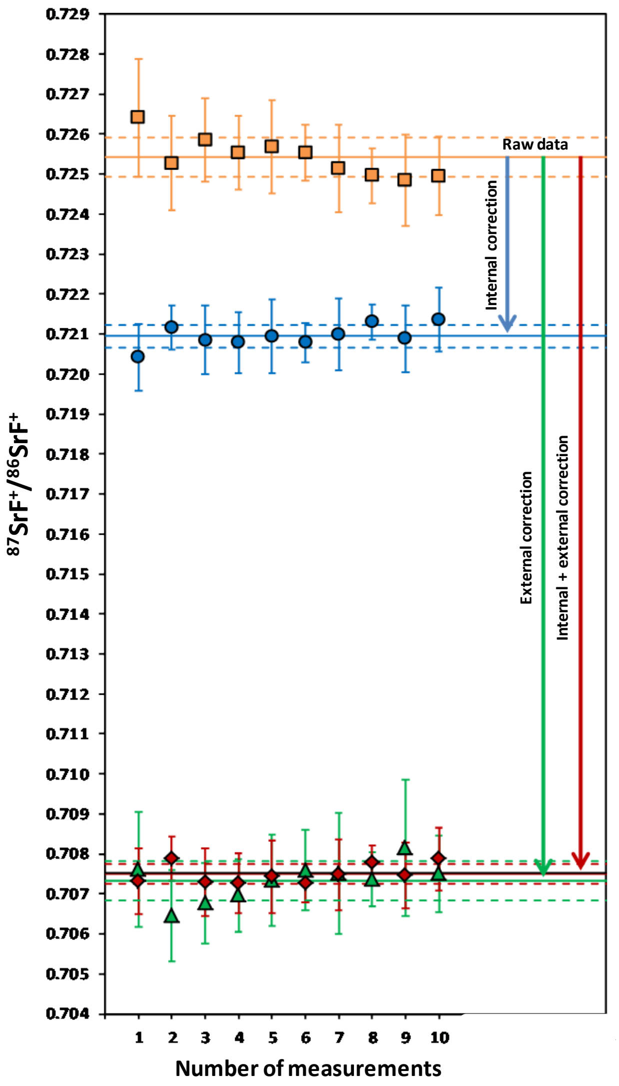

Figure 3. Results obtained using different mass bias correction approaches for an in-house standard solution of Sr measured in a sample-standard bracketing sequence (sample: n = 10). The error bars show the standard deviation on 10 replicates for each measurement.

Table 1. Optimum instrument settings and data acquisition parameters for the determination of the ^{87}Sr/^{86}Sr isotope ratio *via* the corresponding SrF^+ reaction product ions using CH_3F/He as a reaction gas in ICP-MS/MS

Agilent 8800	
Reaction Gas	CH_3F/He (10/90)
Scan type	MS/MS
Plasma mode	Low matrix
RF power (W)	1550
Extract 1 (V)	-3.0
Q1 bias (V)	0
Reaction gas flow rate setting (mL min^{-1})	0.90
Q1 → Q2	86 → 105 87 → 106 88 → 107
Octopole bias (V)	-4.7
Energy discrimination (V)	-8.4
Extract 2 (V)	-175.0
Q2 QP bias (V)	-13.1
Wait time offset (ms)	0
Sweeps / replicate	100
Acquisition time / mass (s) [1 acquisition point per spectral peak]	30
Number of replicates	10
Total analysis time / sample (s)	906

Table 2. Calibration data and instrumental limits of detection (LoD) and of quantification (LoQ) obtained for Sr using CH_3F as a reaction gas in ICP-MS/MS

Isotope	**Reaction product ion**	**CH_3F/He flow (mL min^{-1})**	**Q1 (amu)**	**Q2 (amu)**	**Sensitivity[a] (counts L µg^{-1} s^{-1})**	**Intercept[a] (counts s^{-1})**	**R^2**	**LoD[b] (ng L^{-1})**	**LoQ[b] (ng L^{-1})**
^{86}Sr	**^{86}SrF$^+$**	0.90	86	105	21660 ± 90	48 ± 310	0.999992	1	4
^{87}Sr	**^{87}SrF$^+$**		87	106	14690 ± 50	68 ± 210	0.999993	1	4
^{88}Sr	**^{88}SrF$^+$**		88	107	172000 ± 900	340 ± 600	0.999998	0.8	3

[a] Uncertainties expressed as standard deviation (n = 10)

[b] LoDs and LoQs calculated as 3 and 10 times the standard deviation on 10 consecutive measurements of a blank solution (0.14 M HNO_3), divided by the slope of the calibration curve, respectively.

Table 3. Sr isotope ratio results obtained using ICP-MS/MS with different mass bias correction approaches

Mass Bias Correction	**^{87}SrF$^+$/^{86}SrF$^+$ ± s**	**RSD (%)**
Raw Data	0.72542 ± 0.00049[a]	0.067[a]
Internal Correction	0.72095 ± 0.00028[a]	0.039[a]
External Correction	0.70733 ± 0.00048[a]	0.068[a]
Internal + External Correction (n=10)	0.70751 ± 0.00025[a]	0.035[a]
Internal + External Correction (n=50)	0.70756 ± 0.00028[b]	0.039[b]
	^{87}Sr/^{86}Sr	**RSD (%)**
Reference Value (MC-ICP-MS)	0.70753 ± 0.00003	0.0042

[a] Results obtained for n = 10

[b] Results obtained for n = 50 collected from different sequences during a period of one month.

Table 4. Results obtained using ICP-MS/MS for reference materials with geological origin

Sample description	Experimental result ± s[a]	Reference value ± uncertainty
USGS AGV-1 Andesite	0.70408 ± 0.00038	0.70406 ± 0.00005
USGS G-2 Granite	0.70968 ± 0.00021	0.70983 ± 0.00006
USGS BHVO-1 Basalt	0.70337 ± 0.00029	0.70347 ± 0.00001
BCR CRM 141 Calcareous Loam Soil	0.70909 ± 0.00030	0.70924 ± 0.00007
BCR CRM 142 Light Sandy Soil	0.71513 ± 0.00048	0.71505 ± 0.00010

[a] Standard deviation on 5 consecutive measurements.