On-line separation of strontium from a matrix and determination of the $^{87}$Sr/$^{86}$Sr ratio by Ion Chromatography/Multicollector-ICPMS

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In this work a high throughput, robust and sensitive method for the precise isotopic analysis of $^{87}$Sr/$^{86}$Sr by coupling Ion Chromatography (IC) and Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) is presented. The effective separation of Sr from a sample matrix by IC enables on-line isotopic determination of the $^{87}$Sr/$^{86}$Sr ratio in transient signals by MC-ICPMS, without laborious off-line and time consuming sample preparation step and the need for clean room facilities. Mass discrimination and instrument drift were corrected by using the natural constant $^{86}$Sr/$^{88}$Sr ratio as an internal standard. A precision ($2\sigma$) of the $^{87}$Sr/$^{86}$Sr ratio of 0.003% was achieved in natural fresh water and high salinity samples, e.g. Dead Sea water, as well as carbonate and silicate rocks. Robustness, relatively high precision and accuracy, as well as minimum possibility of sample contamination of the developed analytical method have been demonstrated in complex natural samples of water and rocks as well. This method for the first time reports a possibility of isotopic analysis of cations by on-line IC separation with precision close to that obtained by an off-line technique.

Introduction

The strontium isotopic composition is an important geochemical tracer. It is used in a wide range of applications, including paleoceanography, isotope stratigraphy and sedimentology, tracing water sources,1 mantle processes2 and in the geochronological Rb-Sr system.3 The natural variation in the $^{87}$Sr/$^{86}$Sr ratio is derived from the radioactive decay of $^{87}$Rb to $^{87}$Sr. In rocks, the ratio is a function of their age and composition, while in marine carbonate rocks it reflects the isotopic composition of seawater from which it had precipitated. The isotopic composition of Sr in rocks is a useful tool in the reconstruction of geological history. The isotopic composition of strontium plays an important role in hydrogeology, enabling tracing the source of groundwater flows and water mixing. However, reliable use of this isotopic tracer requires a high precision isotopic analysis.

Multicollector thermal ionization mass spectrometry (TIMS) is a common method for the precise analysis of the strontium isotope ratio, with the best internal and external precisions ($2\sigma$) of 0.002% and 0.001%, respectively.4,5 The method entails the chemical separation of Sr in clean room facilities and is a time consuming procedure even using chromatographic purification of Sr.6

The introduction of an inductively coupled plasma (ICP) ion source into multicollector mass spectrometry (MC-ICPMS) for isotope ratio analysis has considerably simplified the analytical procedures for a number of isotopic systems by reducing the collection time of the measurements.

The objective of the present study was to develop a method for on-line precise and accurate determination of the $^{87}$Sr/$^{86}$Sr ratio. Considering the advantages of hyphenated techniques like gas chromatography (GC)-MC-ICPMS, IC sector field (SF) ICPMS,7 and IC-MC-ICPMS for the direct determination of isotope ratios in anions (Cl, Br and S) 8 – this approach was based on interfacing an ion chromatograph with MC-ICPMS to determine strontium isotope ratios. The instrumental setup enables isotopic analysis of strontium, which occurs mainly as a trace element in natural samples, after on-line separation and purification by ion chromatography. The technique was proposed few years ago9 but the precision and accuracy achieved were relatively poor ($2\sigma > 2 \times 10^{-4}$).

Experimental

Sample preparation

Natural water samples were filtered with a 0.45 μm filter and acidified with concentrated nitric acid (Baker, Instra-AnalyzedPlus) to pH ≈ 1. Carbonate samples, including standard strontium carbonate (isotopic standard NIST SRM 987), BCS 393, coral sample (MBL-1) and phosphate rock (BCR-32) were dissolved in 3 mol L$^{-1}$ nitric acid. Basalt (BR) and andesite...
(AGV-1) silicate rocks were decomposed using microwave assisted digestion (Milestone UltraWAVE, Sorisole (BG) Italy) in a mixture (7:1 v/v) of nitric acid and hydrofluoric acid (Suprapur, Merck, Germany). All samples and standards were diluted with deionized water (Milli-Q Integral 3 Q-POD Water Purification System, Merck Millipore, Darmstadt, Germany) to a strontium concentration of a few mg L⁻¹ in order to obtain high counting statistics for mass spectrometric measurements. Natural water samples with low Sr concentrations (0.05–0.2 mg L⁻¹) were introduced into the IC by using a 200 μL sample loop. Samples and standards were introduced from the IC into the Ar-plasma ion source of the MC-ICPMS at a flow rate of 1.0 mL min⁻¹ using a glass Meinhard nebulizer and a cyclonic spray chamber cooled to 7 °C.

**Instrumental setup**

A schematic of the IC-MC-ICPMS system is shown in Fig. 1.

**Ion chromatography**

An ion chromatograph (Dionex ICS-5000⁺, Thermo Scientific) which included an autosampler (AS-DV), an inorganic cation exchange column (IonPac CS16, 5 x 250 mm, 5 μm) with a guard column (IonPac CG16, 5 x 50 mm), a self-regenerating suppressor (CSRS 500), and a conductivity detector was used. The CSRS 500 was operated at a temperature of 20 °C during the separation of cations. At a column temperature of 30 °C, the separation of the Rb and Sr peaks was not sufficient. Therefore, the temperature of the column was optimized and it was found that Rb and Sr peaks were separated at a temperature of 60 °C (Fig. 2a). Samples were injected via a 25 μL loop (or 200 μL), mixed in situ with the eluent-46 mmol L⁻¹ methanesulfonic acid (isocratic elution), and transported through the guard column into the analytical ion chromatography column. After that, the sample passed through the suppressor, where exchange of anions with OH⁻ was accomplished. Having passed the ion conductivity detector, the eluent was nebulized into the MC-ICPMS. The suppressor unit was continuously rinsed with deionized water. An IC eluent flow rate of 1.0 mL min⁻¹ was found to be optimal for chromatographic separation. A wet plasma mode was used as the dry plasma conditions (Aridus II desolvation nebulizer) require a flow rate of 0.2 mL min⁻¹. Taking into account the parameters of the applied column (the length, the diameter and the particle diameter), the time of chromatographic separation would be much longer and also the analytical signals would undergo or suffer significant peak broadening. When a flow rate of 1.0 mL min⁻¹ was employed, the entire time of analysis was about 14 min. The applied flow rate was typical for the type of chromatographic column used in this study. According to the Van Deemter equation, a lower flow rate (e.g. 0.2 mL min⁻¹) can cause peak broadening, because of sample ion diffusion into the mobile phase.

**Mass spectrometry**

Strontium isotopic compositions were measured at the Biological and Chemical Research Centre at the University of Warsaw using an MC-ICPMS instrument “Nu Plasma II” (Nu Instruments, Wrexham, UK) equipped with 16 Faraday cup detectors.

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Fig. 1 A schematic of the IC-MC-ICPMS system.

Fig. 2 Isotope analysis of strontium in sea water: (a) IC-MC-ICPMS chromatograms; (b) ⁸⁷Sr/⁸⁶Sr isotope ratio during peak elution.
Five of these were used for the measurement of masses 83, 85–88 for the isotopes of Kr (83), Rb (85) and strontium (86, 87 and 88). The amplifier boards of the collectors were calibrated on a weekly basis, using an internal 40 V reference signal. The introduction of the analytes into the MC-ICPMS after IC separation resulted in transient signals for each isotope, which was eluted from the IC column. Therefore, the whole area of the transient signal peak was integrated for the calculation of isotope ratios. The background baseline level was estimated by averaging 20–30 points of the signal between the end of the Rb signal and the beginning of the Sr signal. This averaged baseline signal was subtracted from the integrated peak on a point by point basis.

To provide reference solutions of strontium for instrumental tuning, a six-way syringe loading injector with a 200 μL loop was connected to enable the introduction of the reference standards into the eluent flow. Fine-tuning of the MC-ICPMS instrument was performed by maximizing the signal intensity of 88Sr. Signals of 87Sr, 86Sr, 85Rb (85Rb was measured for correcting an isobaric interference of 86Kr) and 83Kr (83Kr was measured for correcting an isobaric interference of 86Kr and on 86Sr) were simultaneously measured by using the Faraday cup detectors. Operating parameters for the IC-MC-ICPMS system are listed in Table 1.

The developed method is based on the on-line separation of strontium from the matrix, prior to its isotope counting by MC-ICPMS. As shown in the chromatogram of IC separation (see Fig. 2b), significant isotope fractionation was observed during peak elution from the chromatography column. Therefore, in IC-MC-ICPMS analysis the whole peak area should be integrated for the isotope ratio calculations and unlike the GC-MC-ICPMS, where 95% of peak area was integrated for the best precision.

### Mass discrimination correction

The isotopic mass discrimination of the mass spectrometer was corrected by the use of an 86Sr/88Sr internal standard, which is assumed to be constant in nature. The use of internal normalization for mass discrimination correction is a common practice in TIMS and in MC-ICPMS employing the exponential law:

\[
F = \log(R_{\text{true}}/R_{\text{obs}}) \log(m_{86}/m_{88})
\]

where \(R_{\text{obs}}\) is the measured \(^{86}\text{Sr}/^{88}\text{Sr}\) ratio, \(m_{86}\) and \(m_{88}\) are the exact masses of \(^{86}\text{Sr}\) and \(^{88}\text{Sr}\) isotopes, respectively, \(F\) is the correction factor per atomic mass unit and \(R_{\text{true}}\) is the certified \(^{86}\text{Sr}/^{88}\text{Sr}\) ratio value. The latter is taken as 0.1194 according to the convention of the International Union of Geological Sciences (IUGS) Subcommission on Geochronology, which enables inter-laboratory standardization.

The exponential law for correction of mass bias is a common practice; however, the model should be validated before being used. This is due to the fact that this model relies on the assumption of identical mass bias for different isotope pairs of \(^{88}\text{Sr}/^{86}\text{Sr}\). As reported in recent publications, a mass independent fraction was observed for Sr isotopes using MC-ICPMS, meaning that \(F_{88/86} \neq F_{87/86}\). In the present work, the exponential law mass bias correction was used as it corresponded to all the certified and recommended values.

### Results and discussion

#### Isotopic measurements of standard NIST SRM 987

As mentioned above, introduction of the analytes into the MC-ICPMS after IC separation produces a transient signal. Due to isotope fractionation (Fig. 2b) that occurs on the column, the entire area of this transient signal was integrated for the calculation of isotope ratios of the elements. The background was measured before the transient signal and was subtracted from the average measured counting.

The measurement of Sr isotopes using argon ICP ion source mass spectrometers may be erroneous due to the presence of Kr in argon gas. Thus, the measured \(^{86}\text{Sr}\) ion beam was corrected for isobaric interferences from \(^{86}\text{Kr}\). For this purpose, the ion beam of \(^{83}\text{Kr}\) was monitored and the measured intensity at mass 86 was corrected for the \(^{86}\text{Kr}\) contribution using the \(^{86}\text{Kr}/^{83}\text{Kr}\) ratio of 1.52. Typically, this correction was less than \(10^{-5}\) of the \(^{86}\text{Sr}\) beam. However, no mass discrimination correction was needed, because of the low level of Kr ion beam.

The measurement of \(^{87}\text{Sr}\) isotope is interfered by the \(^{87}\text{Rb}\) isotope. This interference is very small in the NIST SRM 987 standard after Rb was removed from the matrix by IC separation. Nevertheless, \(^{87}\text{Sr}\) was corrected for \(^{87}\text{Rb}\) by simultaneous measurements of mass 85 (\(^{85}\text{Rb}\)) signals and using an \(^{87}\text{Rb}/^{85}\text{Rb}\) value of 0.385705 (ref. 16) corrected for mass discrimination by the exponential law and assuming that Rb mass discrimination is the same as that of Sr. The off-line Rb separations may be accompanied with a small amount of Rb and the correction must be applied. However, in cases where the rubidium signal is high, the correction should be based on the experimentally measured \(^{87}\text{Rb}/^{85}\text{Rb}\) ratio rather than on the IUPAC recommended natural abundance ratio, and therefore, it is not a trivial correction.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The IC-MC-ICPMS operational parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MC-ICPMS parameters</strong></td>
<td></td>
</tr>
<tr>
<td>RF power</td>
<td>1300 W</td>
</tr>
<tr>
<td>Coolant gas flow rate</td>
<td>13 L min(^{-1}) of Ar</td>
</tr>
<tr>
<td>Auxiliary gas flow rate</td>
<td>0.97 L min(^{-1}) of Ar</td>
</tr>
<tr>
<td>Nebulizer gas pressure</td>
<td>23.6 psi</td>
</tr>
<tr>
<td>Interface cones</td>
<td>Nickel</td>
</tr>
<tr>
<td><strong>Measurement parameters</strong></td>
<td></td>
</tr>
<tr>
<td>Resolution mode</td>
<td>~300</td>
</tr>
<tr>
<td>Faraday cup configuration</td>
<td>H7 – ^{88}\text{Sr}, H5 – ^{87}\text{Sr}, H3 – ^{86}\text{Sr}, H1 – ^{85}\text{Rb}, L3 – ^{83}\text{Kr}</td>
</tr>
<tr>
<td>Integration time</td>
<td>0.5 s</td>
</tr>
<tr>
<td><strong>IC parameters</strong></td>
<td></td>
</tr>
<tr>
<td>Column</td>
<td>Dionex IonPac CS16</td>
</tr>
<tr>
<td>Temperature of column</td>
<td>60 °C</td>
</tr>
<tr>
<td>Eluent</td>
<td>46 mmol L(^{-1}) methane-sulfonic acid</td>
</tr>
<tr>
<td>Eluent flow rate</td>
<td>1.0 mL min(^{-1}) [820 psi]</td>
</tr>
</tbody>
</table>
Table 2  The $^{87}$Sr/$^{86}$Sr isotope ratio values obtained for the analyzed samples in this work compared with reported values

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of matrix</th>
<th>Measured value</th>
<th>$\pm 2\sigma$ ($\times 10^{-5}$)</th>
<th>Reported value</th>
<th>$\pm 2\sigma$ ($\times 10^{-5}$)</th>
<th>Sr in sample (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST SRM 987</td>
<td>Strontium carbonate</td>
<td>0.70125</td>
<td>2.8</td>
<td>0.710203 (ref. 21)</td>
<td>3.4</td>
<td>60%</td>
</tr>
<tr>
<td>Sea of Galilee</td>
<td>Water</td>
<td>0.70752</td>
<td>4.6</td>
<td>0.70747 (ref. 5)</td>
<td>2.1</td>
<td>0.66</td>
</tr>
<tr>
<td>Sahina spring</td>
<td>Water</td>
<td>0.70772</td>
<td>8.6</td>
<td>0.70776 (ref. 22)</td>
<td>2.8</td>
<td>0.55</td>
</tr>
<tr>
<td>Dan river</td>
<td>Water</td>
<td>0.70760</td>
<td>30</td>
<td>0.70736 (ref. 23)</td>
<td>2</td>
<td>0.06</td>
</tr>
<tr>
<td>Banias river</td>
<td>Water</td>
<td>0.70700</td>
<td>30</td>
<td>0.70730 (ref. 23)</td>
<td>4</td>
<td>0.16</td>
</tr>
<tr>
<td>NASS-4</td>
<td>Ocean water</td>
<td>0.70930</td>
<td>10</td>
<td>0.70935 (ref. 22)</td>
<td>3.7</td>
<td>8</td>
</tr>
<tr>
<td>Dead Sea</td>
<td>Brine water</td>
<td>0.70797</td>
<td>6.6</td>
<td>0.70803 (ref. 5)</td>
<td>3</td>
<td>320</td>
</tr>
<tr>
<td>BR</td>
<td>Silicate rock, basalt</td>
<td>0.70389</td>
<td>5.2</td>
<td>0.70389 (ref. 24)</td>
<td>No data</td>
<td>1320</td>
</tr>
<tr>
<td>MBL-1</td>
<td>Coral (Red Sea)</td>
<td>0.70913</td>
<td>3.0</td>
<td>0.70919 (ref. 22)</td>
<td>2.2</td>
<td>7000</td>
</tr>
<tr>
<td>BCR-32</td>
<td>Phosphate rock</td>
<td>0.70796</td>
<td>10</td>
<td>0.70815 (ref. 25)</td>
<td>3.2</td>
<td>1150</td>
</tr>
<tr>
<td>AGV-1</td>
<td>Silicate rock, andesite</td>
<td>0.70379</td>
<td>10</td>
<td>0.70393 (ref. 21)</td>
<td>3.4</td>
<td>660</td>
</tr>
</tbody>
</table>

The average value obtained for NIST SRM 987 using the IC-MC-ICPMS method for the $^{87}$Sr/$^{86}$Sr ratio was 0.71025 ± 0.00003 (2σ). In the present study, using the operation parameters listed in Table 1, a peak area of 4 V s (peak high of 2.2 V) was obtained for 1 nmol of the injected Sr.

Although the obtained precision by IC-MC-ICPMS was worse by a factor of two (as was expected), compared to TIMS or continuous MC-ICPMS, the results obtained here were still within the uncertainty of the certified value of 0.71034 ± 0.00026 (370 ppm) (NIST SRM 987, certificate issue 1/5/2000) and in agreement within the uncertainty of the value of 0.710263 ± 0.000016. It should be noted that all isotopic ratios were corrected for instrument discrimination using the fixed conventional $^{86}$Sr/$^{88}$Sr value of 0.119412. Variations of the $^{86}$Sr/$^{88}$Sr isotope ratio in different sample matrices were reported in some recent studies. In present work, these variations were not included because all recommended and certified values with which we compared our results were measured using the fixed value of $^{86}$Sr/$^{88}$Sr equal to 0.119412.

Isotopic measurements of natural water samples, carbonates and related materials

The accuracy and precision of the developed method has been evaluated using standard reference materials, internal-laboratory standards and natural water samples (varied from very fresh water through sea water up to brine water with 35% total dissolved salts), in which the isotopic composition was measured by other analytical methods. It was expected that due to the chromatographic separation, the elimination of matrix effect would be achieved. As shown in Table 2, there is a very good agreement between our results and the certified or recommended values. In all cases, the difference is smaller than the sum of errors and confirms that separation of strontium by the IC eliminated the matrix effect; in another case the results vary from those reference values.

The attained precisions, as expected, were worse by a factor of 2–3 than precisions obtained for the strontium isotope ratio, when measured as a continuous signal and not as a transient signal. In the case of a very low Sr concentration (lower than 0.5 mg L$^{-1}$ and a peak height of $^{86}$Sr less than 0.5 V), the precision degraded seriously by a factor of 3–4 (Table 2).

Conclusion

In this study coupling an ion chromatograph on-line to MC-ICPMS for a rapid, high precision and robust isotopic analysis of strontium was demonstrated. The performance of the IC-MC-ICPMS system for Sr isotope ratio measurements was evaluated and has shown good accuracy and reasonable precision. The uncertainty may still be 2–3 times worse than the high precession results obtained by TIMS and MC-ICPMS with an off-line Sr separation and continuous flow but the ease of sample preparation and the throughput more than compensate for that. The recovery of Sr was found to be ~100% and the Sr signal showed cleanliness without problems of over loading the column. The throughput of the new method is about 30 samples per day (one repetition per sample) compared to 4–5 samples by TIMS and 8–10 samples by MC-ICPMS (including time of column separation). A single complete analysis of the Sr isotope ratio determination using IC-MC-ICPMS takes about 14 min. The method does not require sample preparation and purification steps in a clean room and matrix effects are eliminated making this technique attractive for many applications. An additional significant advantage of the proposed analytical method is the possibility of following ion separation and recovery during the analytical run (Fig. 2a).

This innovative analytical technique opens the door for the analysis of additional cations by on-line IC-MC-ICPMS separation and determination of their isotope composition.

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