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Large volume injection in ion chromatography Separation of rubidium and strontium for on-line inductively coupled plasma mass spectrometry determination of strontium isotope ratios

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Abstract

Large volume injection, up to 5 mL, was evaluated and optimised for the on-line ion chromatographic separation of Rb and Sr before ICP-MS measurement of Sr isotope ratios. Flat-topped chromatographic peaks, ideally suited for multicollector ICP-MS isotope ratio measurements, could be obtained when the composition of the mobile phase (nitric acid and 18-crown-6 ether) was identical to the matrix of the sample. Under those conditions rubidium eluted at the dead volume of the column while strontium produced a flat-topped transient signal with several minutes of stable plateau. On-line data acquisition during several minutes at the plateau of Sr signal allowed high precision Sr isotope ratio measurement. The developed procedure was evaluated for Sr isotope ratio measurements on different types of samples, including cider, apples, apple leaves, and soil extracts, in the frame of a long-term project aiming at origin authentication using strontium isotope ratio measurements. It was observed that sample matrix caused broadening of the strontium chromatographic peak and loss of flat-topped peak profile. Under those circumstances the addition of the complexing crown-ether 18-crown-6 both to samples and chromatographic eluent provided two distinct advantages. First, a drastic increase in the retention of strontium was observed which could be modulated by increasing the concentration of nitric acid in the eluent up to 900 mM. This increase in the eluent HNO_3 concentration allowed the application of the method to acid soil digests and other high acidity samples. Second, the matrix of the sample did not affect any more the chromatographic peak profile and similar chromatographic separations could be obtained for samples and standards maintaining the flat-topped Sr peak profile. Sample preparation consisted of a simple 1:10 dilution of the cider or pre-treated solid samples by adding HNO_3 (900 mM) and 18-crown-6 ether (5 mM) to obtain similar composition in the sample solution and the HPLC eluent.

Keywords: Large volume injection; Ion chromatography; Flat-topped peak profile; Strontium isotope ratios; MC-ICP-MS

1. Introduction

Strontium has four naturally occurring stable isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr. Isotopes ^{84}Sr, ^{86}Sr and ^{88}Sr occur in constant ratios in nature, while ^{87}Sr is radiogenic being the product of the radioactive decay of ^{87}Rb. Consequently, the ^{87}Sr/^{86}Sr isotope ratio in rocks and soils varies according to their age and Rb/Sr ratio [1]. Moreover, ^{87}Sr/^{86}Sr isotope ratio provides a fingerprint for different rock types and has been employed as a tracer in provenance studies of archaeological [2], environmental [3], and food samples [4,5].

High precision isotope ratio measurements are required for the determination of strontium isotope variations in nature. Such precision has been routinely achieved with thermal ionisation mass spectrometry (TIMS) as the reference technique with reported RSD values of 0.002% for ^{87}Sr/^{86}Sr isotope ratio [6–8] However, for TIMS analysis the analyte has to be completely isolated from the matrix and, therefore sample pretreatment is tedious and time consuming. In recent years multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) has also shown to provide high precision strontium isotope ratio measurements (typically 0.002% RSD) [9–11] as a result of the simultaneous isotope detection, and allows a higher sample throughput in comparison to TIMS and the possibility of continuous liquid and gaseous sample introduction. Nevertheless, for the accurate determination of Sr isotope ratios

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by MC-ICP-MS, an effective separation of Rb from Sr before isotope ratio measurement is mandatory in order to eliminate the isobaric interference of ^{87}Rb on ^{87}Sr.

Elemental isolation for radiogenic isotope systems has been traditionally performed off-line using ion-exchange or chelating resins, where the element of interest is separated from the sample matrix and isobaric elements in acid media based on procedures previously developed for TIMS. Thus, the cation-exchange resin Dowex AG 50W-X8 has been extensively employed to isolate Sr from geological [12] and wine samples [13] in HCl medium although high volumes of eluents were required, and a complete separation of Sr from Rb was difficult to achieve for samples with high rubidium concentration. Additionally, the strontium-selective extraction chromatographic resin Sr.Spec, consisting of a crown ether (bis-*t*-butyl-*cis*-dicyclohexano-18-crown-6) adsorbed on an inert substrate and loaded in micro-columns, provides high strontium selectivity and recoveries in HNO_3 medium with very small reagent volumes [14,15]. However, all these off-line separation procedures are tedious, time-consuming, and suffer from contamination risks during sample pre-treatment which could affect blank levels and offset the advantages of MC-ICP-MS over TIMS determinations.

In order to fully exploit the advantages of MC-ICP-MS over TIMS, an on-line separation of Sr from the matrix and interfering elements would be the best alternative. The ICP ion source can be used as a chromatographic detector due to their low broadening effects and negligible memory effects for Rb and Sr. The only practical difficulty is the ability of the multicollector system to follow transient signals and measure isotope ratios on those transient signals with adequate precision and accuracy. The first studies on the hyphenation between liquid chromatography and MC-ICP-MS were described by Günther-Leopold et al. [16,17]. Short transient signals of ca. 60 s baseline peak width were evaluated, and the authors showed that the isotope ratio precision for the on-line coupling was reduced by a factor of 10 in comparison to continuous sample introduction and a drift on the isotope ratios during peak elution could be observed. Krupp and Donard [18] reported similar results using GC–MC-ICP-MS coupling. It seemed clear that actual multicollector ICP-MS instruments are not ready to handle fast changing signals [18].

The first attempt for the on-line separation of Rb and Sr prior to ICP-MS isotope ratio measurement was described by Latkoczy et al. [19] using ion chromatography (IC) coupled to a sector field (SF) ICP-MS instrument. In order to obtain a broad “global” Sr peak, 14 consecutive injections of 0.5 mL sample volume each were introduced into the system every 20 s. After Rb elution the flow rate was reduced from 3 to 0.5 mL min^{-1} generating a stable transient Sr signal of more than 16 min duration. No differences between the isotope ratios obtained by continuous sample introduction (steady-state signal) and on-line IC separation (transient signal) were observed with typical ^{87}Sr/^{86}Sr isotope ratio precision of 0.02 and 0.07% RSD, respectively for the SF-ICP-MS instrument. Unfortunately, matrix elements such as calcium coeluted with strontium and that could affect MC-ICP-MS isotope ratio measurements.

The aim of the present work was the evaluation and optimization of an on-line Rb–Sr ion chromatographic separation procedure in order to obtain flat-topped transient signals with several minutes of stable plateau. Such flat-topped peaks would be ideally suited for MC-ICP-MS strontium isotope ratio measurements on different types of samples, and they should provide similar isotope ratio precision in comparison to continuous measurement after an off-line separation. Also, for multicollector ICP-MS it is important to achieve a good separation of Sr from other matrix elements as mass bias can be affected by these elements.

2. Experimental

2.1. Instrumentation

2.1.1. Chromatographic details

The separation of Rb from Sr was performed using a Dionex DX-120 ion chromatograph (Sunnyvale, CA, USA). Two Dionex cation-exchange columns were tested, IonPac CG2 guard (4 mm × 50 mm) and CS2 analytical column (4 mm × 250 mm), with sulfonated substrate surface, and IonPac CG12A guard (4 mm × 50 mm) and CS12A analytical column (4 mm × 250 mm), with carboxylic acid groups. For both column types the short 50 mm length (guard column) and the long 250 mm length (analytical column) were evaluated. Different lengths of perfluoroalcoxy (PFA) sample loops (Omnifit, Cambridge, England) were checked to change the injection volume.

2.1.2. ICP-MS instrumentation

Two ICP-MS systems were used. Optimisation studies were performed on a quadrupole ICP-MS (HP 4500, Agilent Technologies, Manchester, UK) operating at a RF power of 1260 W and a nebulizer gas flow rate of 1.10 L min^{-1} Ar. The column effluent was connected using 0.3 mm id polyetheretherketone (PEEK) tubing (Supelco, Pennsylvania, USA) directly to a Meinhard nebulizer with a Scott double-pass quartz spray chamber cooled down to 2 °C. The torch position and ion lens voltage settings were optimised daily for optimum sensitivity with a 10 ng g^{-1} Li, Co, Y, Tl, Ce solution in HNO_3 1% (w/w). Data acquisition parameters were 1 point per peak and 0.5 s acquisition time/isotope using the time-resolved acquisition program. Monitored isotopes were ^{83}Kr, ^{84}Kr-Sr, ^{85}Rb, ^{86}Kr-Sr, ^{87}Rb–Sr and ^{88}Sr resulting in a total integration time of 3 s during the chromatographic separation.

On-line and off-line strontium isotope ratio determinations were performed on a MC-ICP-MS (Neptune, ThermoFinnigan, Bremen, Germany) equipped with nine Faraday collectors, eight movable and one fixed Faraday cups, operating at RF power of 1200 W and low resolution mode. HPLC coupling was made through a 0.3 mm id PFA tubing to the sample introduction system consisting of a PFA-100 microconcentric nebulizer and a cyclonic Scott double-pass spray chamber. Lens settings were optimised daily for maximum analyte sensitivity. Data acquisition was simultaneous for all measured masses: 83 (L3), 84 (L2), 85 (L1), 86 (C), 87 (H1) and 88 (H2) with a total integration time of 4.194 s per chromatographic data point.