Systematic evaluation of a strontium-specific extraction chromatographic resin for obtaining a purified Sr fraction with quantitative recovery from complex and Ca-rich matrices

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This paper presents a systematic evaluation of a commercially available strontium-specific extraction chromatographic resin based on a crown ether (Sr spec™), for use in applications of Sr isotope ratio analysis dealing with samples displaying a complex and/or Ca-rich matrix composition. A protocol, consisting of (i) loading a sample digest in 7 M HNO_3 onto the resin, (ii) rinsing the resin with 7 M HNO_3 to remove concomitant matrix elements and (iii) rinsing the resin with 0.05 M HNO_3 to strip off the purified Sr fraction, was found to provide the best results. The performance in terms of (i) the purity of the Sr fraction obtained, (ii) the efficiency of Rb/Sr and Ca/Sr separation, (iii) the Sr recovery from samples with a complex and Ca-rich matrix composition and (iv) the Sr isotope ratios obtained using multi-collector ICP-MS, was evaluated for various amounts (250, 500, 750 and 2000 μL) of resin using digests of bone and soil certified reference materials, dental tissues, fluorite and glass samples. Further, it was investigated whether or not the isolation protocol introduces Sr isotopic fractionation. Also the possibility of regenerating the resin after use, allowing multiple use of the resin, was assessed. Finally, the Sr isotopic composition of 2 bone (NIST SRM 1400 Bone Ash and NIST SRM 1486 Bone Meal) and 2 soil (BCR CRM 141 Calcareous Loam Soil and BCR CRM 142 Light Sandy Soil) certified reference materials was determined. The method was shown to be fit-for-purpose for population migration studies and provenancing of archaeological artefacts, and is expected to be suited for a broad range of Sr isotope ratio applications.

1. Introduction

Isotope ratio measurements aim at resolving (very) small differences in isotopic composition and hence, they are particularly vulnerable to spectral interferences. In inductively coupled plasma-mass spectrometry (ICP-MS), spectrally interfering ions derive from the plasma, the surrounding air, the solvent and the sample matrix, and occur mainly below 81 u.[1,2] In the context of isotope ratio determination *via* ICP-MS, also mass discrimination—a systematic error that arises when an instrument produces a different response for ions of different mass—has to be accurately corrected for. A number of studies conducted with both quadrupole-based and multi-collector ICP-MS have shown that the instrumental mass discrimination can vary considerably with the sample matrix and that the response of two elements of similar mass to a different matrix may not be sufficiently correlated.[2–6] The matrix-related occurrence of spectral interferences and mass discrimination indicate that accurate and precise measurements of small differences in isotopic composition should preferably be conducted on target elements that have been chemically isolated from the sample matrix.

Strontium has four naturally occurring isotopes, with the corresponding isotopic abundances: ^{84}Sr (0.55–0.58%), ^{86}Sr (9.75–9.99%), ^{87}Sr (6.94–7.14%) and ^{88}Sr (82.29–82.75%).[7] Since ^{87}Sr is additionally formed by the beta-decay of ^{87}Rb, rubidium and strontium are often co-present, leading to an isobaric ($^{87}Rb^+$) interference on the $^{87}Sr^+$ signal. The mass resolution of $\sim$ 300 000, that is required to resolve these isobaric ions, is beyond the capabilities of all present-day ICP-mass spectrometers. Further, also signals from Ca-dimer ions ($^{40}Ca^{44}Ca^+$, $^{42}Ca_2^+$, $^{40}Ca^{46}Ca^+$, $^{42}Ca^{44}Ca^+$, $^{43}Ca_2^+$, $^{40}Ca^{48}Ca^+$, $^{42}Ca^{46}Ca^+$, $^{44}Ca_2^+$) and $ArCa^+$ molecular ions ($^{36}Ar^{48}Ca^+$, $^{38}Ar^{46}Ca^+$, $^{40}Ar^{44}Ca^+$, $^{38}Ar^{48}Ca^+$, $^{40}Ar^{46}Ca^+$, $^{40}Ar^{48}Ca^+$) result in isobaric interferences on Sr ($^{84}Sr^+$, $^{86}Sr^+$ and $^{88}Sr^+$) signals.[8] The high isotope ratio precision attainable with multi-collector ICP-MS implies that a purified Sr fraction (*i.e.*, free from Rb, Ca and other matrix elements) needs to be obtained. Also when thermal ionization-mass spectrometry (TI-MS) is used for Sr isotope ratio determination, separation of Sr from Ca is mandatory since it has been recognized that the ionization efficiency of Sr is substantially reduced in the presence of large amounts of Ca.

The approach most commonly used to isolate strontium from rubidium and the concomitant sample matrix, involves cation exchange chromatography in HCl medium using the AG50W-X8

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ion exchange resin.[9–13] On this strongly acidic resin, strontium is retained strongly in 2 M HCl medium. Ideally, all rubidium will elute from the ion exchange column before the strontium fraction is collected, but in practice, and especially when working with high rubidium concentrations, a complete separation of Rb and Sr may be difficult to achieve.[14] The Sr fraction can be recovered using 8 M HCl medium, but this procedure does not lead to a quantitative Sr recovery,[12] implying the risk of introducing isotopic fractionation. Moreover, this 'traditional' cation exchange method results in an incomplete separation of Sr from other elements, *e.g.*, Ca.[15] Extraction chromatography was later described as a tool for Rb/Sr separation, that at the same time provides a satisfactory separation of Ca from Sr.[15–19] In this technique, a solution of a crown ether in octanol, sorbed onto an inert substrate, accomplishes the extraction of Sr from HNO_3 media. The strontium-specific resin, commercially available as Sr spec™ (TrisKem International, formerly Eichrom Environment), is often used in microquantities packed onto microcolumns ($\leq$ 300 μL resin) to purify Sr prior to Sr isotope ratio analysis.[20–23] Besides these manual separation techniques, also automated chromatographic procedures have been developed[24–27] and even coupled on-line to (MC-)ICP-MS for subsequent Sr isotope ratio analysis,[13,28,29] although quantitative Sr recoveries were not in all cases obtained.

In the work presented here, the capabilities of Sr spec™ resin for isolation of Sr from digests of samples displaying a complex and Ca-rich matrix composition (bone and dental tissues, soils, fluorite, glass) were systematically evaluated. Although the Sr spec™ resin is commonly used for Sr isolation in geological, geochemical and environmental applications, some variability in the use of this resin can be noted when comparing papers of different authors/groups. First, various resin bed volumes, ranging from 50 μL to 2 mL, are used. When working with samples that display a matrix composition that is not too complex, miniaturized methods are preferable. However, these methods are likely to fail in the cases where the Sr concentration is low and the matrix is complex (as is the case for, *e.g.*, bone and dental tissues). Second, HNO_3 media with a concentration ranging from 2 to 8 M are used for sample loading and matrix removal, although there is a difference in Sr retention amounting to a factor of 2 at these respective HNO_3 concentrations. Third, there is no uniform value for the Sr recovery after the extraction chromatographic separation, *i.e.*, the recovery is not reported, stated as not quantitative or reported to vary according to the amount of strontium and matrix loaded onto the resin. When Sr isotope ratios need to be determined, and especially when MC-ICP-MS is used to this purpose, a quantitative Sr recovery is preferred as in this way no Sr isotopic fractionation is introduced by the isolation procedure. When a quantitative recovery cannot be attained, it needs to be verified that on-column Sr isotopic fractionation does not occur on Sr spec™ resin, an aspect that has not been addressed so far.

In view of the three arguments given above, we have thoroughly compared the performance of Sr spec™ resin packed onto columns with a resin bed of 250, 500, 750 and 2000 μL, as the use of such larger resin beds allows the loading of (i) a relatively large amount of liquid sample with a complex matrix composition and (ii) higher amounts of Sr, while at the same time increasing the separation efficiency. The following aspects of resin performance were addressed: (i) concentration and volume of HNO_3 medium needed for efficient matrix removal and Sr elution, (ii) purity of the Sr fractions obtained with special attention to the separation of Sr and Ca that is hard to accomplish with other Sr isolation methods, (iii) efficiency of the Rb/Sr separation and (iv) Sr recovery. Further, (v) the potential occurrence of on-column Sr isotopic fractionation was investigated and finally, also (vi) the possibility of regenerating the resin after use, allowing multiple use of the same extraction chromatographic column, was evaluated.

2. Experimental

2.1. Reagents and materials

Pro analysi nitric acid (14 M) and hydrochloric acid (12 M) (Panreac, Spain) were further purified by sub-boiling distillation in quartz equipment. Hydrofluoric acid (22 M, instra-analyzed) and perchloric acid (10 M, instra-analyzed) were bought from J.T. Baker Chemicals N.V., The Netherlands. Ultrapure water with a resistivity >18 MΩ cm was obtained from a Milli-Q Element system (Millipore, USA) and used throughout this work for diluting concentrated acids. Standard solutions for elemental assay were prepared by diluting commercially available single element 1 g L^{-1} stock solutions (Alfa Johnson-Matthey, Germany). Certified reference materials used for method validation were available from the National Institute for Standards and Technology, USA (NIST SRM 987 $SrCO_3$ isotopic standard, NIST SRM 1400 Bone Ash and NIST SRM 1486 Bone Meal) and from the Community Bureau of Reference, Belgium (BCR CRM 141 Calcareous Loam Soil and BCR CRM 142 Light Sandy Soil). Argon for ICP-MS measurements had a purity >99.999% and was supplied by Air Liquide, Belgium.

Sr spec™ resin was purchased from TrisKem International (formerly Eichrom Environment), France. The resin consists of a crown ether (4,4′(5′)-di-*tert*-butylcyclohexane-18-crown-6) in octanol, sorbed onto an inert chromatographic support (particle diameter: 50–100 μm). Fresh Sr spec™ resin was dispersed in milli-Q water, the supernatant was replaced by fresh milli-Q H_2O (twice) and the resin was then loaded into pre-cleaned Biorad polypropylene 1 mL columns to obtain a resin bed of 250, 500 or 750 μL. After filling the columns, the resin was consecutively rinsed with 2 mL of milli-Q H_2O and 1 mL of 6 M HCl to clean the resin and assure the absence of traces of Sr and Pb, respectively. Besides these in-house made columns, also pre-packed columns filled with 2 mL Sr spec™ resin (particle diameter: 100–150 μm) and purchased from TrisKem International, were used.

2.2. Instrumentation

2.2.1. Elemental assay and semi-quantitative analyses. Elemental assays and semi-quantitative analyses were carried out using a quadrupole-based Perkin-Elmer SCIEX Elan 5000 ICP-MS instrument. The instrument settings and data acquisition parameters for this instrument are summarized in Table 1. The sample introduction system consisted of a multi-channel peristaltic pump (Minipuls-3), a GemTip cross-flow nebulizer, a Perkin-Elmer Type II spray chamber made of Ryton, and a Perkin-Elmer corrosion-resistant torch with alumina injector.

Table 1 Instrument settings and data acquisition parameters for the quadrupole-based Perkin-Elmer SCIEX Elan 5000 ICP-mass spectrometer

instrument settings	
RF power	1000 W
plasma gas flow rate	15 L min^{-1}
auxiliary gas flow rate	0.8 L min^{-1}
nebulizer gas flow rate	0.80–0.85 L min^{-1} [a]
sampling cone	Ni, aperture diameter 1.1 mm
skimmer	Ni, aperture diameter 0.9 mm
sample delivery	peristaltic pump
sample uptake rate	1 mL min^{-1}

[a] optimized daily for (i) maximum sensitivity for $^{9}Be^{+}$, $^{59}Co^{+}$, $^{103}Rh^{+}$, $^{115}In^{+}$, $^{208}Pb^{+}$ and (ii) minimal oxide formation ($^{232}Th^{16}O^{+}/^{232}Th^{+} < 3\%$).

data acquisition parameters	
scanning mode	peak hopping
dwell time	50 ms
settling time	5 ms
number of acquisition points per spectral peak	1
number of sweeps	20
number of readings	3
number of replicates	5
replicate time	~ 17 s per isotope
detector dead time	69 ns

2.2.2. Multi-collector ICP-MS for Sr isotopic analysis. Strontium isotope ratio determinations were carried out using a Thermo Scientific Neptune multi-collector ICP-MS instrument. This instrument provides double-focusing with a Nier-Johnson geometry and was operated in low-resolution mode ($m/\Delta m = 400$). The instrument settings, cup configuration and data acquisition parameters used for Sr isotope ratio determination are summarized in Table 2, in which also the accuracy and external precision obtained during a typical Sr MC-ICP-MS measurement session is given. Sample delivery was accomplished *via* an auto-aspirating low-flow (50 μL min^{-1}) PFA nebulizer, mounted onto a combined cyclonic/double-pass spray chamber made from quartz.

The purified Sr fractions obtained after extraction chromatographic isolation of Sr (see further) were diluted with 0.14 M HNO_3, adjusting the Sr concentration to ~ 200 μg L^{-1} for Sr isotope ratio measurements. Sr, Rb and Kr intensities were measured in static multi-collection mode (Table 2). Outliers were removed on the basis of a 2s-test (95% confidence interval). A solution of 200 μg L^{-1} Sr typically resulted in an $^{88}Sr^{+}$ ion current of 100–120 pA. All samples were run in a sample-standard bracketing sequence with a 200 μg L^{-1} Sr isotopic standard solution of NIST SRM 987 $SrCO_3$, that was previously conducted through the extraction chromatographic isolation procedure. Blank Sr signals were always negligible compared to the Sr intensities encountered for standards and samples (<0.1%). After measurement of every sample or standard solution, the sample introduction system was rinsed for a few minutes with 0.14 M HNO_3 in order to minimize memory effects.

Russell's law was used for mass discrimination correction *via* internal normalization to the invariant $^{86}Sr/^{88}Sr$ ratio of 0.1194. The intensities obtained for $^{83}Kr^{+}$ and $^{85}Rb^{+}$ were used to correct for the corresponding contributions at *m/z* 84 and 86 (Kr), and *m/z* 87 (Rb), respectively, using the numerical $^{84}Kr/^{83}Kr$, $^{86}Kr/^{83}Kr$ and $^{87}Rb/^{85}Rb$ ratios of 4.95652, 1.50435 and 0.38565, respectively, and taking into account the effect of mass discrimination on these experimental ratios. Hereby, it was assumed that Kr and Rb display the same mass discrimination behavior as Sr.

Table 2 Instrument settings, cup configuration and data acquisition parameters for the Thermo Scientific Neptune multi-collector ICP-mass spectrometer and accuracy and external precision obtained for a solution of NIST SRM 987 $SrCO_3$ (200 μg L^{-1} Sr) in a typical Sr measurement session

instrument settings	
RF power	1200 W
plasma gas flow rate	13 L min^{-1}
auxiliary gas flow rate	0.7 L min^{-1}
nebulizer gas flow rate	1.0 L min^{-1} [a]
sampling cone	Ni, aperture diameter 1.1 mm
skimmer	Ni, aperture diameter 0.9 mm
extraction lens voltage	4 V[a]
mass resolution	400
sample delivery	auto-aspiration
sample uptake rate	50 μL min^{-1}

[a] optimized daily for maximum $^{88}Sr^{+}$ sensitivity.

cup configuration					
L3	L2	L1	Ax	H1	H2
$^{83}Kr^{+}$	$^{84}Sr^{+}$ $^{84}Kr^{+}$	$^{85}Rb^{+}$	$^{86}Sr^{+}$ $^{86}Kr^{+}$	$^{87}Sr^{+}$ $^{87}Rb^{+}$	$^{88}Sr^{+}$

data acquisition parameters	
magnet delay time	3 s
integration time	4 s
number of cycles	10 per block
number of blocks	5
measurement time	~ 200 s

accuracy and external precision for Sr isotope ratios of NIST SRM 987 $SrCO_3$

ratio	experimental	2s	RSD (%)	accepted[30]
$^{87}Sr/^{86}Sr$	0.710260	0.000067	0.005	0.710248
$^{84}Sr/^{86}Sr$	0.05642	0.00014	0.12	0.05649
$^{84}Sr/^{88}Sr$	0.006739	0.000016	0.12	0.006748

The external precision of the measurement protocol was calculated on the basis of the mass discrimination corrected values retrieved for the NIST SRM 987 $SrCO_3$ isotopic standard throughout a measurement session. Throughout a timespan of a few months, an external precision of 50 ppm (0.005% RSD) was established for the $^{87}Sr/^{86}Sr$ ratio, and of 1200 ppm (0.12% RSD) on the $^{84}Sr/^{86}Sr$ and $^{84}Sr/^{88}Sr$ ratios (Table 2). Within the external precision of the measurements, the experimental values retrieved for NIST SRM 987 $SrCO_3$ are in excellent agreement with the accepted literature values for this isotopic standard[30] (Table 2).

2.3. Samples and sample digestion

The samples investigated in the context of this work consist of the bone certified reference materials NIST SRM 1400 Bone Ash and NIST SRM 1486 Bone Meal, the soil certified

reference materials BCR CRM 141 Calcareous Loam Soil and BCR CRM 142 Light Sandy Soil, and a number of dental tissues (enamel and dentine), fluorite and glass samples, all of archaeological interest.

The dentine and enamel fractions of the teeth available for investigation were mechanically separated from one another, followed by subsequent rinsing with ethanol to remove potential contamination originating from the cutting process, and dried in a drying stove. Digestion of the dental tissues was accomplished by means of a hotplate digestion using a HNO_3–HCl mixture (2:1) in a closed Savillex vial. After digestion was completed, the sample was evaporated to nearly dry and the residue was taken up in 14 M HNO_3 and diluted with milli-Q H_2O. This procedure was validated by applying the protocol to $\sim$ 0.1 g of the bone certified reference materials NIST SRM 1400 Bone Ash and NIST SRM 1486 Bone Meal, selected in view of the similar matrix composition of bone and dental tissues. After sample digestion, strontium concentrations were determined using quadrupole-based ICP-MS (Elan 5000, Table 1) *via* standard addition, and the Sr recovery was calculated. The average Sr recovery with corresponding 2s uncertainty interval for digestion of bone certified reference materials (Table 3a) was established as quantitative: 99.0 $\pm$ 3.9% (n = 7) for NIST SRM 1400 Bone Ash and 99.6 $\pm$ 2.8% (n = 7) for NIST SRM 1486 Bone Meal.

Soil certified reference materials were digested according to a procedure that consists of a combination of a microwave-assisted acid digestion and a hotplate digestion using HNO_3, HCl, HF and $HClO_4$, that leads to a complete dissolution of the soil sample.[31] The average Sr concentration and recovery with a corresponding 2s uncertainty interval for each of the soil certified reference materials BCR CRM 141 Calcareous Loam Soil and BCR CRM 142 Light Sandy Soil determined *via* standard addition (Elan 5000, Table 1) are summarized in Table 3b. Within experimental uncertainty, a good agreement is found between the experimental Sr concentration and the indicative value for the Sr concentration in both of these soil certified reference materials.

Table 3 Experimental strontium recoveries upon digestion of (a) bone and (b) soil certified reference materials. The experimental Sr concentrations and recoveries reported are the average of the results obtained for 7 separate digestions, with corresponding 2s uncertainty interval

(a) bone certified reference materials

	$[Sr]_{experimental}$ ($\mu g\ g^{-1}$)	$[Sr]_{certified}$ ($\mu g\ g^{-1}$)	recovery (%)
NIST SRM 1400 Bone Ash	246 $\pm$ 10	249 $\pm$ 7	99.0 $\pm$ 3.9
NIST SRM 1486 Bone Meal	263 $\pm$ 7	264 $\pm$ 7	99.6 $\pm$ 2.8

(b) soil certified reference materials

	$[Sr]_{experimental}$ ($\mu g\ g^{-1}$)	$[Sr]_{indicative}$ ($\mu g\ g^{-1}$)	recovery (%)
BCR CRM 141 Calcareous Loam Soil	485 $\pm$ 12	490 $\pm$ 120	99.0 $\pm$ 2.5
BCR CRM 142 Light Sandy Soil	186 $\pm$ 6	164 $\pm$ 20	113.8 $\pm$ 3.6

Fluorite and glass samples were dissolved in a closed Savillex vial on a hotplate. Strontium was leached from the fluorite samples using 6 M HCl,[32] while for the dissolution of glass samples, a HF–HNO_3 mixture (3:1) was used in a first step, followed by evaporation and redissolution in aqua regia (HCl–HNO_3 3:1) in a second step.[33] After the digestion step, both sample types were evaporated to nearly dry, the residue was taken up in 14 M HNO_3 and diluted with milli-Q H_2O.

2.4. Element retention on Sr spec™ resin

The binding properties, expressed as the capacity factor k', of Sr and other elements (Na, K, Ca, Rb, Cs, Ba and Pb) on Sr spec™ resin as a function of the HNO_3 concentration are available from the literature (Fig. 1 and Fig. 2 in ref. 17). The elements that should be considered in the context of the study presented here comprise (i) the target element Sr, (ii) Rb, giving rise to the isobaric $^{87}Rb^+$ interference on $^{87}Sr^+$, (iii) Ca, that is present in a high concentration in every sample type investigated and (iv) the other major constituents of these sample types, such as Na, Mg, Al, Si, K, Fe, Zn and Ba. It is noteworthy that Pb is retained even stronger than Sr on Sr spec™ resin (Fig. 2 in ref. 17), but the samples investigated in the context of this study display very low Pb concentrations.

3. Results and discussion

3.1. Selection of the HNO_3 concentration best suited for Sr purification and elution

A first aim of the optimization was to establish which HNO_3 concentration is the most efficient for sample loading and subsequent removal of Rb, Ca and the other concomitant matrix elements. The capacity factor for Sr reaches its maximum value in the HNO_3 concentration range of 3 to 7 M.[17] On the one hand, the use of 3 M HNO_3 is preferred over 7 M HNO_3 since at HNO_3 concentrations above 3 M, increasing amounts of nitric acid are competing with Sr to be extracted by the crown ether, resulting in a slightly lower capacity factor for Sr (range 70–90).[15] On the other hand, the capacity factor for Rb is lower at 7 M HNO_3 than at 3 M HNO_3,[17] so that a more efficient separation of Rb and Sr can be accomplished at 7 M HNO_3. As both HNO_3 concentrations provide some benefits, it was investigated whether or not a difference in Sr recovery could be established depending on the HNO_3 concentration used. Hereto, a digest of NIST SRM 1400 Bone Ash was split into two aliquots, where one was diluted to 3 M HNO_3, and the other to 7 M HNO_3. An amount of these aliquots, equivalent to 10 μg Sr, was loaded onto a pre-packed (2 mL resin) extraction chromatographic column. The column loaded with the aliquot in 3 M HNO_3 was subsequently rinsed with 20 mL 3 M HNO_3, while the column loaded with the 7 M HNO_3 aliquot was rinsed with 20 mL 7 M HNO_3, after which Sr was eluted using 20 mL 0.05 M HNO_3 in both cases. After elution, the Sr recovery was determined by comparing the Sr concentrations retrieved in the original digest and in the eluted fraction (Elan 5000, Table 1). This entire experiment was repeated 3 times. The experimental Sr recovery in the 3 M HNO_3 setup appeared to be never higher than $\sim$ 50%. Although 3 M HNO_3 has been used in previous studies for sample loading and matrix removal on Sr spec™, the

recovery was not reported, or was indeed stated as not quantitative.[18,21,28] The use of 7 M HNO_3 for sample loading and column rinsing, on the contrary, resulted in a quantitative Sr recovery for the 3 repetitions (average recovery with corresponding 2s uncertainty interval of 99.5 ± 1.6%). When non-quantitative recoveries are established, there is an increased risk of isotopic fractionation being introduced, so that 7 M HNO_3 was selected as the optimum medium for sample loading onto and matrix removal from the Sr spec™ resin in the context of this work.

3.2. Separation of rubidium and strontium

The selectivity of Sr spec™ resin for Sr allows an efficient separation of Rb and Sr. An experiment was set up in order to evaluate if the Rb/Sr separation efficiency depends on the relative amounts of Rb and Sr present. Hereto, standard solutions containing Rb and Sr in 7 M HNO_3, with a Sr/Rb ratio of 0.1, 1 and 10, were prepared. An amount equivalent to 10 μg Sr from each of these three standard solutions was loaded onto three separate pre-packed (2 mL resin) columns. The solution that passed through the column after sample loading (effluent) was collected. Next, the resin was rinsed with 20 mL (arbitrary volume) 7 M HNO_3, divided into 1 mL aliquots with every aliquot collected separately, followed by Sr elution with 20 mL (arbitrary volume) 0.05 M HNO_3, where again every 1 mL aliquot was collected separately. The resulting 41 aliquots (1 effluent, 20 rinse and 20 elution) were analysed for the presence of Rb and Sr (Elan 5000, Table 1). In this way, the elution profile shown in Fig. 1 was obtained. In the case of a 10-fold excess of Rb over Sr (Sr/Rb = 0.1), all the Rb is removed from the resin after rinsing with 5 mL of 7 M HNO_3, while no Sr is released from the resin during the rinse with 7 M HNO_3. The Sr fraction is subsequently recovered after rinsing the resin with 6 mL of 0.05 M HNO_3 (Fig. 1). The same observations are noted from the elution profiles obtained for the standard solutions with a Sr/Rb ratio of 1 (Fig. 1) and 10. The amount of rubidium present in the purified strontium fractions of the three standard solutions was always below 40 pg, which is similar to blank level, implying that the separation of Rb and Sr is complete.

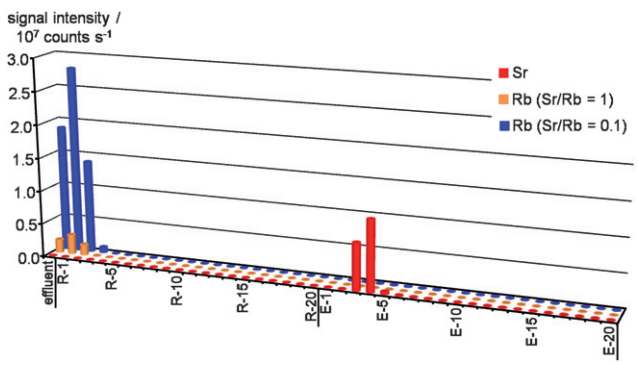

Fig. 1 Elution profile obtained for a standard solution with a Sr/Rb ratio of 0.1 and 1 loaded onto a pre-packed column containing 2 mL Sr spec™ resin. An amount of each standard solution equivalent to 10 μg Sr was loaded onto the resin. R-x = 1 mL 7 M HNO_3 rinse fraction x; E-x = 1 mL 0.05 M HNO_3 elution fraction x.

3.3. Isolation of Sr from concomitant matrix elements

In order to evaluate the capability of Sr spec™ resin to result in a purified Sr fraction from a digest with a high Ca content and complex matrix composition (*e.g.*, bone and dental tissue, soil), an amount of a NIST SRM 1400 Bone Ash digest equivalent to approximately 10 μg Sr, was loaded onto a pre-packed (2 mL resin) column. Since nearly no Rb is present in NIST SRM 1400 Bone Ash, also 50 μg Rb, under the form of a standard solution in 7 M HNO_3, was added. The 41 1 mL-aliquots, obtained after following the same matrix removal and Sr elution protocol as described in § 3.2, were analysed for their Sr and Rb content and the presence of bone matrix elements (Elan 5000, Table 1). The elution profile thus obtained is displayed in Fig. 2. All the elements determined are retained by the resin to some extent, but are subsequently removed during the rinse with 7 M HNO_3. A very intense Ca peak is noted during the first 4 mL of the rinsing process, leaving a quasi Ca-free Sr fraction on the resin, showing that Sr and Ca are efficiently separated. It can be seen from Fig. 2 that also the separation of Rb and Sr is successfully accomplished in the presence of a heavy bone matrix. From these observations, it can be concluded that the removal of all the bone matrix elements determined is complete after rinsing the resin with 10 mL of 7 M HNO_3, and that the entire Sr fraction is recovered after elution with 6–10 mL of 0.05 M HNO_3 when using 2 mL of Sr spec™ resin.

The same experiment was performed on a 2 mL resin bed using (i) a digest of NIST SRM 1486 Bone Meal in 7 M HNO_3, and (ii) digests of the soil certified reference materials BCR CRM 141 Calcareous Loam Soil and BCR CRM 142 Light Sandy Soil in 7 M HNO_3. Exactly the same conclusions as these from Fig. 2 were drawn from the elution profile of NIST SRM 1486 Bone Meal. The elution profiles obtained for both soil certified reference materials are similar, and that obtained for a digest of BCR

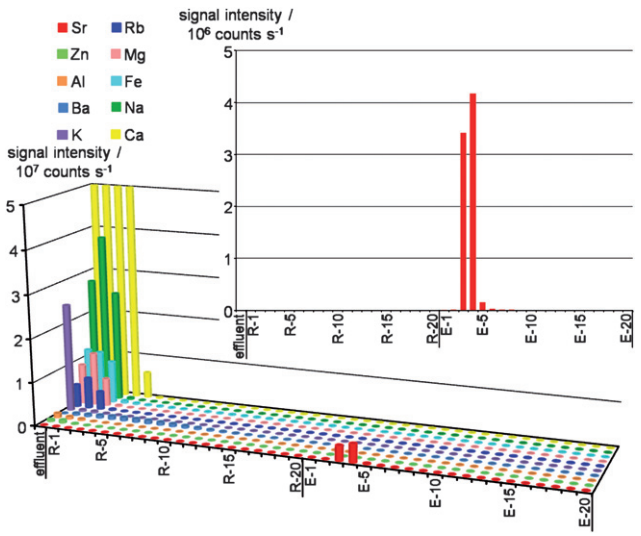

Fig. 2 Elution profile obtained for a NIST SRM 1400 Bone Ash digest loaded onto a pre-packed column containing 2 mL Sr spec™ resin. An amount of digest equivalent to 10 μg Sr was loaded and 50 μg Rb was additionally spiked onto the resin. A zoom on the Sr elution profile is also displayed (upper right). R-x = 1 mL 7 M HNO_3 rinse fraction x; E-x = 1 mL 0.05 M HNO_3 elution fraction x.

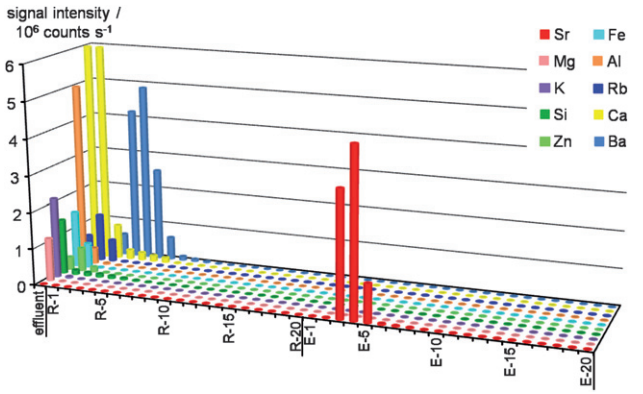

Fig. 3 Elution profile obtained for a BCR CRM 142 Light Sandy Soil digest loaded onto a pre-packed column containing 2 mL Sr spec™ resin. An amount of digest equivalent to 10 μg Sr was loaded onto the resin. R-x = 1 mL 7 M HNO_3 rinse fraction x; E-x = 1 mL 0.05 M HNO_3 elution fraction x.

CRM 142 Light Sandy Soil is displayed in Fig. 3. In the case of soil digests, it is clear that also soil matrix elements, such as Al, Si and Ba, are efficiently removed during the rinsing process, allowing a purified Sr fraction to be obtained (Fig. 3). As the elution profile obtained for bone certified reference materials (Fig. 2) is analogous to that obtained for soil certified reference materials (Fig. 3), it can be stated that the proper use of pre-packed columns with 2 mL Sr spec™ resin allows quasi-pure Sr fractions to be obtained, even when working with samples displaying a complex matrix composition and/or a (very) high Ca content.

3.4. Protocol for the use of pre-packed columns with 2 mL resin bed

The separation protocol developed, consisting of (i) conditioning the resin with 3 mL 7 M HNO_3, followed by loading such an amount of sample digest in 7 M HNO_3 onto the resin that results in 5 up to 35 μg Sr, (ii) removal of slightly retained matrix elements by rinsing the resin with 10 mL 7 M HNO_3 and (iii) elution of the purified Sr fraction with 10 mL 0.05 M HNO_3, was applied to digests of the bone certified reference materials used throughout this work (Table 4) and a set of soils and teeth of archaeological interest. A Sr recovery with corresponding 2s uncertainty interval of 99.7 ± 2.0% for bone certified reference materials (n = 13, Table 4), 97.6 ± 3.8% for dental tissues (n = 34) and 99.6 ± 3.9% (n = 3) for soil samples, was obtained, resulting in an average Sr recovery of 98.3 ± 3.9% (n = 50) on Sr spec™ resin with a resin volume of 2 mL, confirming that Sr can be quantitatively isolated from heavy matrices *via* the separation protocol proposed.

3.5. Protocol for the use of columns with a 250, 500 and 750 μL resin bed

It was expected that the use of smaller beds of Sr spec™ resin would permit the use of smaller amounts of HNO_3 solution for removal of concomitant matrix elements and elution of the purified Sr fraction. To investigate this, Biorad polypropylene columns were packed with 250, 500 and 750 μL of Sr spec™ resin followed by rinsing the resin consecutively with 2 mL of milli-Q H_2O and 1 mL of 6 M HCl. On a column packed with 500 μL resin, an amount of standard solution in 7 M HNO_3, containing Rb and Sr with a Rb/Sr ratio of 10, was loaded, so that 10 μg of Sr, and thus 100 μg of Rb, were present. The effluent coming from the column upon loading was collected. Subsequently, the effluent was also collected with every 500 μL aliquot being collected separately while rinsing the resin with 5 mL of 7 M HNO_3. Then, 5 mL of 0.05 M HNO_3 was used for elution of the Sr fraction, where again every 500 μL aliquot was collected separately. The resulting 21 (1 effluent, 10 rinse and 10 eluent) fractions were analyzed for the presence of Rb and Sr (Elan 5000, Table 1). From the elution profile thus obtained, displayed in Fig. 4, it is clear that an efficient separation of Rb and Sr is accomplished. The Rb is removed from the resin after rinsing with 2 mL of 7 M HNO_3. After switching from 7 M HNO_3 (matrix removal) to 0.05 M HNO_3 (Sr elution), the Sr elution from the resin only starts after passing ~ 1 mL of 0.05 M HNO_3. The Sr fraction is quantitatively recovered after elution with a subsequent 3.5–4 mL of 0.05 M HNO_3, while already more than 95% of the Sr amount loaded is recovered in the first 3 mL of 0.05 M HNO_3 (Fig. 4 and Fig. 5).

A separation protocol, consisting of (i) conditioning the resin with 1 mL of 7 M HNO_3, followed by loading an amount of Sr from a sample digest in 7 M HNO_3 onto the resin, (ii) rinsing the resin with 5 mL of 7 M HNO_3 in a first step and 1 mL of 0.05 M HNO_3 in a second step, and (iii) elution of the Sr fraction with 5 mL of 0.05 M HNO_3, was applied to a solution of NIST SRM 987 $SrCO_3$ and digests of NIST SRM 1400 Bone Ash, BCR CRM 141 Calcareous Loam Soil and BCR CRM 142 Light Sandy Soil. As is summarized in Table 4a, such an amount of NIST SRM 987 $SrCO_3$ solution in 7 M HNO_3 was loaded onto a column packed with 250, 500 and 750 μL of Sr spec™ resin, such that approximately 6, 12 and 25 μg of Sr was present on each resin volume. An analogous experiment was set up using 2 replicate digests of NIST SRM 1400 Bone Ash that were each split into 3 equal aliquots and loaded onto columns packed with 250, 500 and 750 μL Sr spec™ resin (Table 4b). Three replicate digests of both BCR CRM 141 Calcareous Loam Soil and BCR CRM 142 Light Sandy Soil were also loaded onto columns packed with 500 and 750 μL Sr spec™ resin (Table 4d,e). After application of the separation protocol, the rinse fraction (5 mL of 7 M HNO_3 + 1 mL of 0.05 M HNO_3) and the purified Sr fraction (5 mL of 0.05 M HNO_3) obtained from every column involved, were analyzed for the presence of Sr, Rb and/or bone or soil matrix elements. No detectable amounts of Sr were retrieved in the rinse (7 M HNO_3) solutions, while no significant amounts of Rb and bone/soil matrix elements were retrieved in the purified Sr (0.05 M HNO_3) fractions.

In the purified Sr fractions obtained, the Sr recovery was determined (Table 4). Recoveries ≥ 97% are established for all amounts of Sr (~ 6, 12 and 25 μg) originating from a NIST SRM 987 $SrCO_3$ solution on every resin volume (250, 500 and 750 μL) used (Table 4a). Although statistically insignificant, the Sr recovery evolves from 100.3 ± 2.5% (n = 3) for 6 μg Sr to 97.9 ± 2.7% (n = 3) for 12 μg Sr and even 96.6 ± 1.6% (n = 3) for 25 μg Sr. This mild trend, however, is most outspoken for the lowest resin volume (250 μL) used (Table 4a), what might indicate that the amount of resin to be used is depending on the amount of Sr

Table 4 Resin volume, mass of Sr loaded (μg), mass of Sr retrieved (μg) in the purified Sr fraction after the isolation process, experimental recovery and $^{87}Sr/^{86}Sr$ isotope ratio obtained for replicate analyses of the certified reference materials used throughout this work: (a) NIST SRM 987 $SrCO_3$, (b) NIST SRM 1400 Bone Ash, (c) NIST SRM 1486 Bone Meal, (d) BCR CRM 141 Calcareous Loam Soil and (e) BCR CRM 142 Light Sandy Soil. The 2s uncertainty interval on the $^{87}Sr/^{86}Sr$ ratio is typically 0.00008. Columns that were used multiple times in the resin regeneration experiment are labeled as column x - pass y, where x denotes the column number and y indicates the y-th time that column x was used

resin volume used (μL)	column - pass	Sr mass loaded (μg)	Sr mass found (μg)	recovery (%)	$^{87}Sr/^{86}Sr$
(a) NIST SRM 987 $SrCO_3$					
2000	column 1 - pass 1	10.0	10.0	99.9	0.71026
750	—	6.4	6.5	101.6	0.71027
750	—	12.5	12.2	97.4	0.71026
750	—	25.0	24.3	97.2	0.71026
500	—	6.4	6.4	100.2	0.71029
500	column 6 - pass 1	12.5	12.4	99.5	0.71024
500	—	25.0	24.2	97.0	0.71025
250	column 7 - pass 1	6.4	6.3	99.0	0.71029
250	column 8 - pass 1	12.5	12.1	96.9	0.71032
250	—	25.0	23.9	95.7	0.71023
(b) NIST SRM 1400 Bone Ash					
2000	column 1 - pass 2	11.3	11.2	99.1	0.71310
2000	column 2 - pass 1	20.2	20.0	99.0	0.71316
2000	column 3 - pass 2	31.7	30.9	97.5	0.71312
2000	column 4 - pass 1	35.0	34.9	99.7	0.71311
2000	column 4 - pass 3	16.8	17.0	101.2	0.71314
2000	column 5 - pass 1	20.2	20.1	99.5	0.71313
2000	column 5 - pass 3	23.5	23.6	100.5	0.71314
2000	—	10.0	10.0	100.3	0.71314
750	—	6.5	6.5	99.3	0.71313
750	—	6.4	6.3	98.7	0.71311
500	column 9 - pass 1	6.5	6.3	97.0	0.71312
500	column 9 - pass 3	6.4	6.3	97.9	0.71312
500	column 10 - pass 1	6.4	6.3	98.8	0.71310
250	—	6.5	6.0	91.3[a]	0.71312
250	column 11 - pass 1	6.4	5.8	90.3[a]	0.71309
(c) NIST SRM 1486 Bone Meal					
2000	column 2 - pass 2	11.6	11.6	99.9	0.70931
2000	column 3 - pass 1	7.5	7.4	98.7	0.70930
2000	column 3 - pass 3	5.2	5.2	100.8	0.70927
2000	column 4 - pass 2	16.2	16.2	100.2	0.70931
2000	column 5 - pass 2	32.0	32.0	99.8	0.70931
500	column 6 - pass 3	8.3	8.1	98.0	0.70929
(d) BCR CRM 141 Calcareous Loam Soil					
500	column 6 - pass 2	4.6	4.6	100.9	0.70927
500	column 10 - pass 2	6.4	6.3	98.2	0.70923
250	column 7 - pass 2	6.1	6.2	102.4	0.70920
(e) BCR CRM 142 Light Sandy Soil					
500	column 9 - pass 2	1.3	1.3	98.1	0.71501
250	column 11 - pass 2	2.3	2.3	101.6	0.71508
250	column 8 - pass 2	0.1	0.1	101.3	0.71234[b]

[a] result not taken into account to determine the average recovery for Sr isolation from NIST SRM 1400 Bone Ash digests (see text). [b] result not taken into account to determine the $^{87}Sr/^{86}Sr$ ratio for BCR CRM 142 Light Sandy Soil (see text).

to be loaded onto the resin and the complexity of the concomitant matrix. When 250 μL of Sr spec™ resin is used for isolating Sr from a NIST SRM 1400 Bone Ash digest, the recovery is indeed limited to ~ 90% (Table 4b). This can be attributed to (i) the lower amount of resin used and/or (ii) the complex matrix composition of bone tissue, and confirms the assumption that miniaturized methods are more likely to fail when working with samples displaying a complex matrix composition. On the contrary, higher volumes of Sr spec™ resin (500 and 750 μL) indeed allow a quantitative recovery of 98.4 ± 1.8% (n = 5) for NIST SRM 1400 Bone Ash and of 98.0% (n = 1) for NIST SRM 1486 Bone Meal (Table 4c) to be obtained. Further, also lower amounts of Sr (0.1–6 μg) were loaded onto columns with 250 and 500 μL resin in the form of digests of soil certified reference materials (Table 4d,e). Quantitative Sr recoveries are obtained for every Sr amount and resin volume evaluated, equal to 100.5 ± 4.3% (n = 3) for BCR CRM 141 Calcareous Loam Soil and 100.4 ± 3.9% (n = 3) for BCR CRM 142 Light Sandy Soil. It is important to note that even when only ~ 100 ng Sr is loaded onto 250 μL resin, a quantitative recovery is established.

From the experiments above, it can be concluded that the performance of columns packed with resin beds of 250, 500 and 750 μL display a performance very similar to that of larger prepacked 2 mL resin columns. When no heavy matrices are involved and the absolute Sr mass to be loaded does not exceed a few μg, 250 μL of Sr spec™ resin is sufficient to obtain quantitative Sr recoveries. When the samples display a complex matrix composition and/or an absolute Sr mass higher than ~ 10 μg needs to be

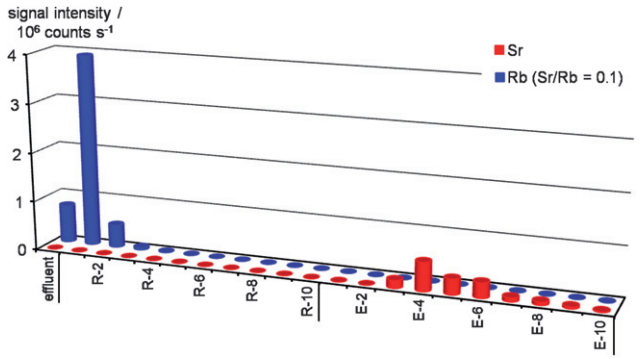

Fig. 4 Elution profile obtained for a standard solution with a Sr/Rb ratio of 0.1 loaded onto a column containing 500 μL Sr spec™ resin. An amount of standard solution equivalent to 10 μg Sr was loaded onto the resin. R-x = 500 μL 7 M HNO_3 rinse fraction x; E-x = 500 μL 0.05 M HNO_3 elution fraction x.

loaded, the use of larger resin volumes (500 and 750 μL, and even 2 mL) can be beneficial in order to reach a quantitative Sr recovery. Although a few μg of Sr is a large amount from the point of view of the MC-ICP-MS analysis itself, the use of larger resin volumes (250 μL and more) resulting in a quantitative Sr recovery is beneficial as this approach allows to conduct the entire digest of a sample displaying a Sr concentration of several 10's to 100's μg g^{-1} (*e.g.*, bone and dental tissues and many types of geochemical samples) through the isolation process without the need of a preliminary determination of the Sr concentration.

3.6. Isotopic fractionation introduced by the isolation process

Recently, it has been demonstrated that Sr isotopic fractionation occurs in geochemical environments.[34,35] Further, it has been demonstrated that on-column isotopic fractionation can occur for certain elements, *e.g.*, Cu and Zn,[36] and such fractionation effects have also been reported on for Sr when using cation-exchange chromatography in HCl medium.[34] Thus, obtaining a quantitative analyte recovery is required to prevent an isotopic bias introduced during the isolation process. In this work, first, a slightly decreasing trend in Sr recovery was noted with increasing Sr amounts and increasing complexity of the sample matrix, especially when using 250 μL of Sr spec™ resin (Table 4b). Second, the resin volumes used in this study are larger than the microcolumns used in previously reported Sr isolation methods using Sr spec™ resin.[20–23] Third, in this work, a rather large sample amount, ranging from 0.1 to 10 mL of digest depending on the Sr concentration present, was loaded onto the resin. These three arguments imply the need to evaluate the extent to which on-column Sr isotopic fractionation occurs on Sr spec™ resin, and this was investigated for 2 resin volumes, *i.e.*, 500 μL and 2 mL.

In a first experiment, the 500 μL aliquots of the Sr fraction, obtained after separation of Rb and Sr from a standard solution of Rb and Sr (10 μg Sr + 100 μg Rb loaded onto the resin) using 500 μL Sr spec™ resin (§ 3.5) were 2-fold diluted and analyzed for their Sr isotopic composition (Neptune, Table 2). In this way, the evolution of the Sr isotopic composition during the elution could be monitored (Fig. 5). In Fig. 5a, the Sr elution profile

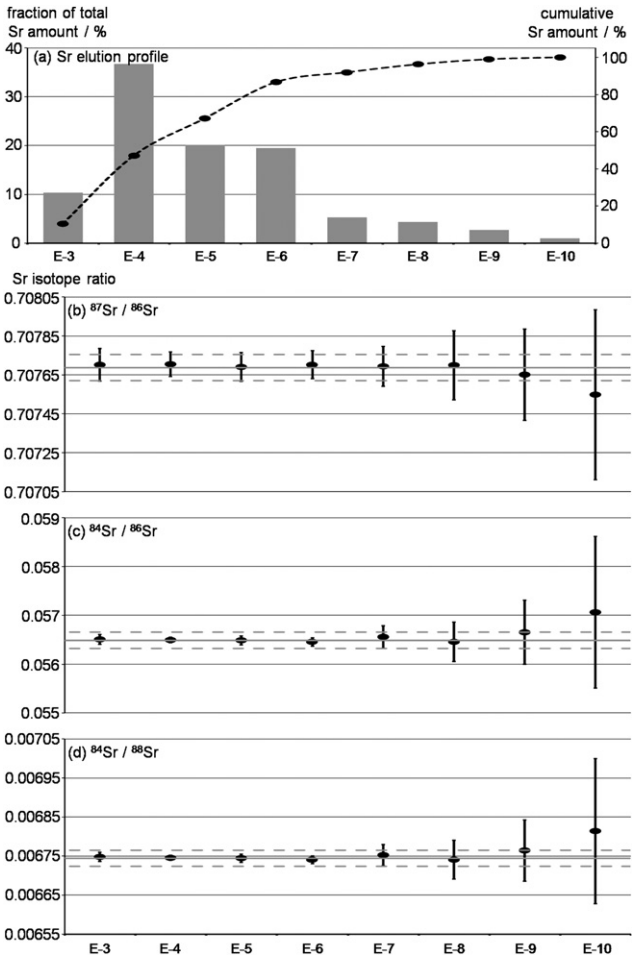

Fig. 5 (a) Sr elution profile (500 μL 0.05 M HNO_3 elution fractions E-3 to E-10 from Fig. 4), displayed as the Sr mass present in every 500 μL fraction relative to the total Sr mass of 10 μg loaded onto the resin (grey bars), and cumulative Sr mass recovered during the elution process (dotted line). Evolution of the (b) $^{87}Sr/^{86}Sr$, (c) $^{84}Sr/^{86}Sr$ and (d) $^{84}Sr/^{88}Sr$ ratio of an Alfa Johnson-Matthey Sr standard solution during the elution process. Error bars represent 2s uncertainty intervals. Grey solid and dotted lines respectively represent the experimental Sr isotope ratio and corresponding 2s uncertainty interval previously determined for the Sr standard solution.

(500 μL 0.05 M HNO_3 fractions E-3 to E-10 from Fig. 4) is presented as the procentual and cumulative Sr amount in every fraction, while in Fig. 5b–d, the experimental $^{87}Sr/^{86}Sr$, $^{84}Sr/^{86}Sr$ and $^{84}Sr/^{88}Sr$ ratios for these individual fractions are displayed. It can be seen from Fig. 5b–d that for the 6 first 500 μL aliquots (E-3 to E-8, cumulatively representing 96.3% of the total Sr amount loaded), an excellent agreement is found between the Sr isotope ratios of every individual aliquot and the experimentally determined Sr isotope ratios of the standard solution (Alfa Johnson-Matthey natural Sr, Table 5a). A bias relative to the experimental Sr isotope ratios of the natural Sr standard solution is observed for the aliquots E-9 and E-10, although only for the last fraction (E-10), a value outside of the experimental Sr isotope ratio range for the Sr standard solution, is observed. This considerable bias amounts to 0.2 ‰ for the $^{87}Sr/^{86}Sr$ ratio, and to 10 ‰ for the

Table 5 Experimental Sr isotope ratios and corresponding 2s uncertainty interval obtained for (a) a 200 μg L^{-1} Alfa Johnson-Matthey Sr standard solution and (b) a NIST SRM 987 $SrCO_3$ solution (200 μg L^{-1} Sr) before and after the extraction chromatographic Sr isolation process

	$^{84}Sr/^{86}Sr$		$^{84}Sr/^{88}Sr$		$^{87}Sr/^{86}Sr$	
	R	2s	R	2s	R	2s
(a) experimental Sr isotope ratios obtained for a Merck Sr standard solution (natural Sr)						
	0.05649	0.00017	0.006745	0.000020	0.70769	0.00007
(b) experimental Sr isotope ratios obtained for NIST SRM 987 $SrCO_3$						
before isolation process	0.05645	0.00008	0.006740	0.000009	0.71025	0.00007
after isolation process	0.05647	0.00009	0.006743	0.000010	0.71026	0.00008

$^{84}Sr/^{86}Sr$ and $^{84}Sr/^{88}Sr$ ratios. Despite this bias, the experimental isotope ratios for fraction E-10 are still in agreement with the experimental isotope ratios for the natural Sr standard solution due to the large experimental uncertainty on the former. This deteriorating isotope ratio precision, observed from aliquot E-7 onwards, can be attributed to the low Sr amounts (5.3, 4.3, 2.7 and 1.0%, respectively) present in these last fractions, and thus the decreasing Sr concentrations (<100 μg L^{-1}) available for multi-collector ICP-MS measurement. It appears that not only the precision is negatively affected by these low Sr concentrations, but also the accuracy, as is observed for a replicate of BCR CRM 142 Light Sandy Soil (Table 4e), where only 100 ng of Sr was loaded onto the resin and thus a Sr concentration of only 25 μg L^{-1} was available for Sr isotope ratio measurement. Hence, the deviating isotope ratios observed for elution fraction E-10 can be a consequence of (i) the low Sr concentration and/or (ii) actual Sr isotopic fractionation of the last 1% of Sr. The first option seems the most likely, as is supported by the deviating $^{87}Sr/^{86}Sr$ ratio for the third replicate of BCR CRM 142 Light Sandy Soil and the very good agreement of experimental $^{87}Sr/^{86}Sr$ isotope ratios with the corresponding reference values for the various certified reference materials analyzed throughout this work (Table 4). From the observation that 7 individual 500 μL 0.05 M HNO_3 fractions, together representing 99.0% of the Sr amount loaded, do not display a detectable extent of Sr isotopic fractionation, it can be derived that the cumulative Sr isotope ratio matches that of the sample loaded, and it can be concluded that no Sr isotopic fractionation is introduced by the Sr isolation process using Sr spec™ resin.

In a second experiment, 10 μg of Sr under the form of a solution of NIST SRM 987 $SrCO_3$ was conducted through the isolation process using a pre-packed column with 2 mL resin, followed by Sr isotope ratio determination of the entire purified Sr fraction obtained. Also the isotopic composition of the NIST SRM 987 $SrCO_3$ standard solution (200 μg L^{-1} Sr) without preliminary column chemistry, was determined. The experimental Sr isotope ratios thus obtained are summarized in Table 5b. A good agreement, within experimental error, between the Sr isotope ratios obtained for NIST SRM 987 $SrCO_3$ before and after the isolation process is established. Further, the experimental values before and after the isolation process are in very good agreement with the accepted values for NIST SRM 987 $SrCO_3$[30] (Table 2), allowing the conclusion that no detectable Sr isotopic fractionation is introduced by the extraction chromatographic isolation procedure *via* Sr spec™ resin.

3.7. Regeneration of the Sr spec™ extraction chromatographic resin

An experiment was set up to assess the performance of Sr spec™ resin after being regenerated, so when it is used multiple times to isolate strontium from a sample digest displaying an evenly complex matrix composition as that of the sample digest loaded onto the column upon its first use. This approach can be dangerous in view of potential cross-contamination between samples when the sample matrix is not completely removed and/or the isolation process does not lead to a quantitative Sr recovery. However, as both an efficient matrix removal and a quantitative Sr recovery were established, the possibility of using a regenerated resin was evaluated. The regeneration procedure put forward consisted of rinsing the resin with milli-Q H_2O after use, followed by rinsing the resin with 6 M HCl, the same procedure as was used in this work to pre-clean the resin before use. Milli-Q H_2O has been suggested and found successful to regenerate Pb spec™ resin,[31,37] a lead-specific resin similar to Sr spec™. However, since Sr spec™ resin is slightly different from Pb spec™ resin,[17,37] it was not taken for granted that this regeneration step would be efficient. Hence, the effect of this regeneration step with milli-Q H_2O and 6 M HCl on the Sr recovery, the separation of Rb and Sr, and the $^{87}Sr/^{86}Sr$ isotope ratio obtained, was experimentally evaluated.

All volumes of resin bed used in this work (250, 500, 750 and 2000 μL) were submitted to regeneration and subsequent evaluation *via* certified reference materials (NIST SRM 987 $SrCO_3$, NIST SRM 1400 Bone Ash, NIST SRM 1486 Bone Meal, BCR CRM 141 Calcareous Loam Soil and BCR CRM 142 Light Sandy Soil). The results of this resin regeneration experiment are summarized in Table 4. In a first column regeneration study, bone certified reference materials (NIST SRM 1400 Bone Ash and NIST SRM 1486 Bone Meal) were processed using pre-packed columns with 2 mL Sr spec™ resin after regeneration. In a first batch (fresh resin, pass 1), an amount of NIST SRM 987 $SrCO_3$ or a digest of NIST SRM 1400 Bone Ash or NIST SRM 1486 Bone Meal in 7 M HNO_3 was loaded onto a new column. After the Sr isolation procedure, the column was washed with 20 mL milli-Q H_2O in order to regenerate the resin. In a second batch (pass 2), digests of the bone certified reference materials were loaded onto the regenerated resins. A column that had been loaded with a digest of NIST SRM 1400 Bone Ash in the first batch, was loaded with a digest of NIST SRM 1486 Bone Meal in the second batch, and vice versa. The column that processed an amount of NIST SRM 987 $SrCO_3$ was loaded with a digest of

NIST SRM 1400 Bone Ash. A second regeneration step using 20 mL milli-Q H_2O was applied, and in a third batch (pass 3), digests of NIST SRM 1400 Bone Ash were loaded onto the regenerated resins. After the isolation procedure for the three batches, the Sr recovery was determined (Elan 5000, Table 1), and found to be quantitative, even when using a regenerated resin (Table 4). Further, the amount of Rb retrieved in the purified Sr fractions did not exceed 40 pg, which is similar to blank level. The $^{87}Sr/^{86}Sr$ ratio obtained for the bone certified reference materials is also summarized in Table 4. No systematic difference is observed between the isotope ratio results obtained for a digest of a certain certified reference material after the use of a new column on the one hand, and one that was used once or twice before, on the other hand. Further, the isotope ratio results obtained for a digest of a certain certified reference material processed by a column that was previously used to process a digest of another certified reference material, are not significantly different from that obtained upon use of a fresh column. Moreover, the $^{87}Sr/^{86}Sr$ ratio obtained for every NIST SRM 1400 Bone Ash and NIST SRM 1486 Bone Meal digest is, within experimental uncertainty, in excellent agreement with the previously reported $^{87}Sr/^{86}Sr$ ratio for these bone certified reference materials[28] (Table 7b,c).

A second, similar, column regeneration study was carried out using columns packed with 250 and 500 μL Sr spec™ resin. In a first batch (pass 1), a solution of NIST SRM 987 $SrCO_3$ and digests of NIST SRM 1400 Bone Ash, were used. After the separation procedure, the resin was cleaned using 10 mL milli-Q H_2O and 1 mL 6 M HCl, and subsequently used for Sr isolation from a second batch of samples (pass 2), consisting of digests of the soil certified reference materials BCR CRM 141 Calcareous Loam Soil and BCR CRM 142 Light Sandy Soil. Then, after a second regeneration step using milli-Q H_2O and 6 M HCl, digests of bone certified reference materials were processed in a third batch (pass 3). The Sr recoveries and $^{87}Sr/^{86}Sr$ ratios retrieved, are summarized in Table 4. The Sr recovery established for the soil certified reference materials is quantitative, demonstrating that the regeneration step is efficient even after processing bone tissue digests in a first batch. Further, within experimental uncertainty, the same $^{87}Sr/^{86}Sr$ ratio is found for every replicate of each soil certified reference material, except replicate 3 of BCR CRM 142 Light Sandy Soil, due to a very low Sr concentration (Table 4d,e), irrespective of the reference material (NIST SRM 987 $SrCO_3$ or NIST SRM 1400 Bone Ash) processed by these columns in the first batch. The Sr recoveries obtained for the bone certified reference materials in the third batch also are found as quantitative, while the $^{87}Sr/^{86}Sr$ ratios retrieved are in good agreement with previously retrieved $^{87}Sr/^{86}Sr$ ratios for these materials.

In a third resin regeneration experiment, dental tissues and also samples with a different but also complex and Ca-rich matrix composition, were processed. Columns packed with 2 mL Sr spec™ resin were used to process digests of dental tissue (enamel and dentine), fluorite and glass samples, while other digests of fluorite samples were processed using columns with 500 μL Sr spec™ resin. The $^{87}Sr/^{86}Sr$ ratios obtained for a selection of dental tissue, fluorite and glass samples are summarized in Table 6. The dental tissues (Table 6a) were digested in duplicate, followed by Sr isolation from each of the digests. A pre-packed column with 2 mL Sr spec™ resin that was loaded with a digest of dentine in the first batch, was loaded with a digest of enamel of a different tooth in the second batch after resin regeneration. The Sr recovery appeared to be quantitative after column regeneration, and the amount of Rb retrieved in the purified Sr fractions was limited to blank level (<40 pg). Further, a very good agreement is observed between the duplicate $^{87}Sr/^{86}Sr$ isotope ratios obtained for the dental tissues (Table 6a). No systematic trend in $^{87}Sr/^{86}Sr$ ratios is established according to the use of new or regenerated resin, according to the fact if first a dentine or an enamel sample was processed in the first batch, or according to the $^{87}Sr/^{86}Sr$ ratio displayed by the sample processed by the column in the first batch. Analogous conclusions can be drawn from the results obtained for the fluorite samples investigated (Table 6b), where also no difference in performance after regeneration is observed between 500 μL and 2 mL resin beds. Further, some of the fluorite and glass samples have also been investigated *via* thermal ionization-mass spectrometry (TI-MS) according to an analogous and previously described procedure.[33] Within experimental uncertainty, an excellent agreement is observed between the MC-ICP-MS results obtained *via* new and regenerated resin on the one hand, and the previously determined TI-MS values, on the other hand (Table 6b,c), which allows concluding that accurate results are obtained with both new and regenerated Sr spec™ resin.

From the excellent performance observed for a regenerated resin and the agreement of results obtained (i) *via* new and regenerated resin for various certified reference materials, and (ii) *via* MC-ICP-MS on the one hand and TI-MS on the other hand, it can be concluded that the regeneration of Sr spec™ resin using milli-Q H_2O and 6 M HCl is efficient. The regeneration approach validated here allows to use the resin at least 3 times (*i.e.*, 2 regeneration steps) without detectably affecting the resin characteristics (*e.g.*, Sr recovery, separation of Rb and Sr, and $^{87}Sr/^{86}Sr$ ratio retrieved), even in the case of samples displaying a complex matrix composition and/or a high Ca content.

3.8. Sr isotopic analysis of certified reference materials

The average $^{87}Sr/^{86}Sr$ ratios of the certified reference materials used throughout this work are summarized in Table 7. For NIST SRM 987 $SrCO_3$, an average $^{87}Sr/^{86}Sr$ ratio with corresponding 2s uncertainty interval of 0.710266 ± 0.000052 (n = 10) was obtained (Table 7a), in excellent agreement with the average value found in this work over a timespan of a few months (0.710260 ± 0.000067, Table 2), and the accepted literature value for this reference material ($^{87}Sr/^{86}Sr$ = 0.710248[30]).

For the bone certified reference materials NIST SRM 1400 Bone Ash and NIST SRM 1486 Bone Meal, a very good agreement is observed, within experimental error, between the experimental Sr isotope ratios obtained for every replicate analysis (Table 4b,c). Further, an average $^{87}Sr/^{86}Sr$ ratio with corresponding 2s uncertainty interval of 0.71312 ± 0.00004 (n = 15) and 0.70930 ± 0.00003 (n = 6) is retrieved for the bone certified reference materials NIST SRM 1400 Bone Ash and NIST SRM 1486 Bone Meal, respectively (Table 7b,c). These experimental $^{87}Sr/^{86}Sr$ ratios are in agreement with the $^{87}Sr/^{86}Sr$ ratio obtained for these materials *via* MC-ICP-MS in an earlier study,[28] and agree even better with TI-MS reference values for these materials

Table 6 $^{87}Sr/^{86}Sr$ isotope ratio obtained for duplicate analyses of dental tissues, fluorite and glass samples using new and regenerated Sr spec™ resin in a volume of 500 or 2000 μL. new = resin not used before, reg. = regenerated resin. rep. 1 and rep. 2 indicate duplicate digestions. For the dental tissues, 4 columns (numbered 1–4) were used to process the 8 samples

				$^{87}Sr/^{86}Sr$	
sample code	technique	resin volume used (μL)	resin: new or regenerated	R	2s
(a) dental tissues					
1488-dentine-rep. 1	MC-ICP-MS	2000	1, new	0.71028	0.00007
1488-dentine-rep. 2	MC-ICP-MS	2000	4, reg.	0.71032	0.00007
	average			0.71030	0.00006
1488-enamel-rep. 1	MC-ICP-MS	2000	2, new	0.70997	0.00007
1488-enamel-rep. 2	MC-ICP-MS	2000	3, reg.	0.70991	0.00007
	average			0.70994	0.00008
1758-dentine-rep. 1	MC-ICP-MS	2000	3, new	0.71050	0.00007
1758-dentine-rep. 2	MC-ICP-MS	2000	2, reg.	0.71052	0.00007
	average			0.71051	0.00003
1758-enamel-rep. 1	MC-ICP-MS	2000	4, new	0.71028	0.00007
1758-enamel-rep. 2	MC-ICP-MS	2000	1, reg.	0.71022	0.00007
	average			0.71025	0.00008
(b) fluorite					
C-rep. 1	MC-ICP-MS	500	new	0.70933	0.00010
C-rep. 2	MC-ICP-MS	500	reg.	0.70928	0.00009
	average			0.70931	0.00008
S-rep. 1	MC-ICP-MS	500	new	0.71008	0.00014
S-rep. 2	MC-ICP-MS	500	reg.	0.71015	0.00009
	average			0.71012	0.00010
Archaeo-1-rep. 1	MC-ICP-MS	2000	new	0.70853	0.00021
Archaeo-1-rep. 2	MC-ICP-MS	2000	reg.	0.70857	0.00018
	average			0.70855	0.00006
	TI-MS			0.70853	0.00002
Litho-1	MC-ICP-MS	2000	reg.	0.70941	0.00020
	TI-MS			0.70934	0.00002
Litho-4	MC-ICP-MS	2000	reg.	0.70847	0.00016
	TI-MS			0.70841	0.00002
(c) glass					
Sag-589	MC-ICP-MS	2000	reg.	0.70890	0.00016
	TI-MS[33]			0.70896	0.00001
Sag-713-rep. 1	MC-ICP-MS	2000	new	0.70877	0.00018
Sag-713-rep. 2	MC-ICP-MS	2000	reg.	0.70873	0.00020
	average			0.70875	0.00006
	TI-MS[33]			0.70881	0.00001
Sag-714	MC-ICP-MS	2000	reg.	0.70877	0.00018
	TI-MS[33]			0.70887	0.00002

Table 7 Average $^{87}Sr/^{86}Sr$ isotope ratio obtained for the various certified reference materials investigated throughout this work with a comparison to literature values, whenever available

	$^{87}Sr/^{86}Sr$	
	R	2s
(a) NIST SRM 987 $SrCO_3$ isotopic standard		
MC-ICP-MS (this work, n = 10)	0.710266	0.000052
accepted value[30]	0.710248	
(b) NIST SRM 1400 Bone Ash		
MC-ICP-MS (n = 15), this work	0.71312	0.00004
MC-ICP-MS (n = 3)[28]	0.71332	0.00021
TI-MS (n = 20)[28]	0.71310	0.00001
(c) NIST SRM 1486 Bone Meal		
MC-ICP-MS (n = 6), this work	0.70930	0.00003
MC-ICP-MS (n = 3)[28]	0.70939	0.00014
TI-MS (n = 1)[28]	0.709307	0.000004
(d) BCR CRM 141 Calcareous Loam Soil		
MC-ICP-MS (n = 3), this work	0.70924	0.00007
(e) BCR CRM 142 Light Sandy Soil		
MC-ICP-MS (n = 2), this work	0.71505	0.00010

reported in the same study[28] (Table 7b,c). This observation can be taken as an argument that the separation protocol and resin regeneration used in this work can be applied successfully and that the multi-collector ICP-MS protocol for isotope ratio measurement and correction for Kr and Rb interferences and mass discrimination provides accurate Sr isotope ratio results.

As total sample dissolution was accomplished using a previously described method for the digestion of soil samples,[31] the $^{87}Sr/^{86}Sr$ isotope ratio retrieved for the soil certified reference materials BCR CRM 141 Calcareous Loam Soil (Table 4d) and BCR CRM 142 Light Sandy Soil (Table 4e) represents that of the total Sr content of the soil. To the best of the author's knowledge, the Sr isotopic composition of these materials has not been reported earlier. The replicate $^{87}Sr/^{86}Sr$ ratios obtained for BCR CRM 141 Calcareous Loam Soil (n = 3) are in very good agreement (Table 4d) and an average $^{87}Sr/^{86}Sr$ ratio with corresponding 2s uncertainty interval of 0.70924 ± 0.00007 was retrieved (Table 7d). One replicate of BCR CRM 142 Light Sandy Soil results in a significantly lower $^{87}Sr/^{86}Sr$ ratio than that

obtained for the other two replicates (Table 4e), due to a low Sr concentration. The other two replicate analyses of BCR CRM 142 Light Sandy Soil yield an average $^{87}Sr/^{86}Sr$ ratio with a corresponding 2s uncertainty interval of 0.71505 ± 0.00010 (Table 7e).

3.9. Sr isotopic analysis of samples of archaeological interest

The $^{87}Sr/^{86}Sr$ isotope ratios obtained for the dentine and enamel of a selection of teeth of archaeological interest are summarized in Table 6a. Comparing the $^{87}Sr/^{86}Sr$ ratio obtained for the dentine and the enamel of the same tooth sample learns that these tissues display a clearly different $^{87}Sr/^{86}Sr$ ratio relative to each other. On the basis of these results, it can be concluded that the separation method and measurement protocol presented here are fit-for-purpose in the case of, *e.g.*, population migration studies. In such type of studies, it is the intention to establish whether or not an individual spent his/her entire life in the same geological area. When a clearly different $^{87}Sr/^{86}Sr$ ratio is displayed by both dental tissues, this observation points towards the fact that the individual spent the last years of his/her life in an area that is geologically distinct from the area of birth/childhood, what implies that this individual has migrated during his/her life.[38–41] The results presented here can be an indication that the individuals investigated have migrated throughout their life history.

Besides for population migration studies, the $^{87}Sr/^{86}Sr$ ratio is also a powerful tool in provenance determination.[42–45] The results for selected fluorite samples (Table 6b) reveal that these samples all display a distinct $^{87}Sr/^{86}Sr$ ratio, implying a distinct geological provenance of these artefacts. This observation again underlines that the methodology developed in this work is fit-for-purpose, in this case for provenance studies.

4. Conclusions

The performance of a commercially available strontium-specific extraction chromatographic resin, Sr spec™, to be used in Sr isotope ratio applications involving samples displaying a complex and Ca-rich matrix composition, was systematically evaluated. It was shown that a protocol consisting of (i) loading a sample digest in 7 M HNO_3 onto the resin, (ii) rinsing the resin with 7 M HNO_3 to remove concomitant matrix elements and (iii) rinsing the resin with 0.05 M HNO_3 for elution of the Sr fraction, provides a pure Sr fraction that is free from Ca, Rb and other concomitant matrix elements in a quantitative way. This evaluation was performed using bone and soil certified reference materials (NIST SRM 1400 Bone Ash, NIST SRM 1486 Bone Meal, BCR CRM 141 Calcareous Loam Soil and BCR CRM 142 Light Sandy Soil), dental tissues, fluorite and glass samples, and a similar resin performance was observed for the different sample types. Various resin volumes (250, 500, 750 and 2000 μL), larger than the microquantities (<300 μL resin) often deployed, were used in this evaluation, and it was found that the optimum resin volume can be selected in view of the absolute Sr mass to be loaded onto the resin, as the characteristics of the isolation process do not display a significant variation according to the resin volume used. Moreover, the performance of these larger resin volumes is better compared to microquantities of resin, as for the latter it was observed in previous studies that the recovery is not quantitative and the Sr/matrix separation often not complete. Further, the absence of on-column Sr isotopic fractionation on Sr spec™ was demonstrated. A comparison of the $^{87}Sr/^{86}Sr$ ratio of the certified reference materials and samples investigated in this study obtained using the methodology developed and the previously determined $^{87}Sr/^{86}Sr$ ratio of some of these materials testifies that the methodology developed provides accurate results. It was also demonstrated that regenerating the resin after use, allowing it to be used multiple times, can be successfully accomplished using milli-Q H_2O and 6 M HCl without a detectable loss of performance or influence on the experimentally determined $^{87}Sr/^{86}Sr$ isotope ratio. Finally, $^{87}Sr/^{86}Sr$ isotope ratios are reported for the bone and soil certified reference materials used throughout this work. It can be concluded that the 'large' resin volumes used throughout this work (250–2000 μL) display an excellent performance (recovery, purity of the Sr fraction), that is in some cases even better than that of miniaturized methods, especially in the case where complex and/or Ca-rich sample matrices are involved. Taking into account that the resin can be successfully regenerated, the better performance obtained by the use of 'larger' volumes of resin might be preferred, as the miniaturized methods sometimes give rise to an incomplete separation of Sr from, *e.g.*, Rb and Ca, and/or a non-quantitative Sr recovery.

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