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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1039/C3AY00028A>

Analytical Methods, 5, 7, pp. 1687-1694, 2013-02-18

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Determination of Strontium Isotope Ratios in Biological Tissue Using MC-ICMS

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Abstract- A protocol is described for the accurate and precise determination of Sr isotope amount ratios in TORT-3 candidate certified lobster hepatopancreas reference material (CRM) from the National Research Council Canada. Separation of Sr and elimination of Rb interference was achieved based on a double pass of the dissolved sample matrix through a column packed with Eichrom Sr Spec resin. Parameters affecting the efficiency of separation were investigated in detail. Matrix elements were removed and Rb concentration was reduced to below 0.002% (expressed as the $^{85}\text{Rb}/^{88}\text{Sr}$ intensity ratio) in the purified solutions of TORT-3. Quantitative recovery ($98 \pm 4\%$ mean and 1SD, $n=12$) of strontium was obtained.

A modified method of standard-sample bracketing with internal normalization for mass bias correction was employed using natural Zr, added at a concentration of $2\text{ }\mu\text{g g}^{-1}$, to both sample and the bracketing Sr standard solution of NIST SRM 987. Instead of using only the $^{88}\text{Sr}/^{86}\text{Sr}$ ratio in SRM 987 to calibrate the $^{91}\text{Zr}/^{90}\text{Zr}$ ratio, all three $^{88}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$ ratios were used to separately calibrate a corresponding $^{91}\text{Zr}/^{90}\text{Zr}$ ratio, which were then used to calibrate the $^{88}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$ ratios in the sample. Interference from ^{87}Rb on ^{87}Sr arising from residual Rb in the purified TORT-3 solutions was corrected for by simultaneous measurement of ^{85}Rb and use of the IUPAC $^{87}\text{Rb}/^{85}\text{Rb}$ ratio of 0.385706, which was itself mass bias corrected assuming the same mass bias for $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{85}\text{Rb}$.

SRM 987 standard solutions containing $10\text{ }\mu\text{g g}^{-1}$ Sr and spiked with $2\text{ }\mu\text{g g}^{-1}$ Rb were used for method validation by subjecting them to the separation processes. Resulting Sr ratios were in good agreement with their certified values, confirming the accuracy of the approach. Absolute isotope amount ratios of 0.0565262 ± 0.0000048 , 0.70945 ± 0.00011 and 8.3824 ± 0.0012 (U, $k=2$) for $^{84}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{88}\text{Sr}/^{86}\text{Sr}$, respectively, were obtained in TORT-3. Analysis of the measurement uncertainty reveals that the certified values in SRM 987 (used for mass bias

calibration) are the main contributors to the uncertainty of Sr isotope ratios determined in TORT-

3. Values of -0.442 ± 0.071 , -1.254 ± 0.044 and 0.454 ± 0.030 (mean and 1SD, $n=18$) obtained for $\delta^{84/86}\text{Sr}$, $\delta^{87/86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$, respectively, are in a range similar to these reported previously for natural samples.

INTRODUCTION

Strontium isotopes have received increasing attention in the last decade due to their numerous significant applications in various scientific fields. Radiogenic ^{87}Sr is an important isotope used for Rb-Sr chronology. As new geochemical tracers, Sr isotope ratios are used for studying various processes occurring in nature¹⁻⁴. Apart from its geoscience applications, $^{87}\text{Sr}/^{86}\text{Sr}$ has also been used for provenance studies to facilitate identification of origin of environmental⁵ and food⁶⁻¹¹ samples, as well as for the study of fish¹², animal¹³ and human¹⁴⁻¹⁶ migration.

Compared to traditional thermal ionization mass spectrometry, the inherently high throughput, simple sample introduction process and ability to ionize nearly all elements in the periodic table that characterizes multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has made it a powerful tool for Sr isotope ratio determinations²⁻²⁷. Unfortunately, compared to TIMS, MC-ICP-MS suffers much larger mass bias²⁸. Consequently, correction for this effect is of paramount importance when the latter is used for the determination of absolute isotope amount ratios. Moreover, in addition to instrumental mass bias, matrix-dependent mass discrimination caused by changes in sample composition and temporal fluctuations in mass bias within the ICP also present a significant hindrance and require utmost attention.

With MC-ICP-MS, mass bias is generally treated as mass-dependent fractionation (MDF) and corrected for through use of various mathematical models, such as the most commonly used Russell's law:²

$$R^{i/j} = r^{i/j} \cdot \left(\frac{m_i}{m_j}\right)^f \quad (1)$$

where r and R are the measured and true isotope amount ratios, respectively, m_i and m_j are nuclide masses of the isotopes of interest, and f is the mass bias factor.

In the case of Sr isotopes, the $^{88}\text{Sr}/^{86}\text{Sr}$ ratio is widely employed for mass bias correction of $^{87}\text{Sr}/^{86}\text{Sr}$ through use of Eq. 1 and an assumption that $f^{88/86} = f^{87/86}$. Additionally, the $^{86}\text{Sr}/^{88}\text{Sr}$ ratio has frequently been assumed to be constant in nature and a value of 0.1194 (absolute and no associated uncertainty) is commonly used. However, recent studies have revealed that this is not the case. Fietzke and Eisenhauer³⁰ reported a $\delta^{88/86}\text{Sr}$ of 0.381 ± 0.010 ‰ (2SD) relative to SRM 987 for IAPSO standard seawater and values up to 0.3 ‰ for natural coral samples. Likewise, Halicz *et al.*³¹ determined that $\delta^{88/86}\text{Sr}$ in sedimentary terrestrial samples was 0.01 ± 0.03 ‰ (1SD) and values reached 0.28 ± 0.07 ‰ (1SD) for those of marine origin. Yang *et al.*³² reported a $\delta^{88/86}\text{Sr}$ of 0.207 ± 0.012 ‰ (1SD) in a fish liver DOLT-3. Clearly, with such variation it is not suitable for internal mass bias correction when absolute values of Sr isotope ratios are of interest. Moreover, recent studies have shown that mass-independent fractionation (MIF) is observed with MC-ICP-MS³³⁻³⁹ for many isotope systems, including Sr, highlighting that the mass bias factor f differs even for various isotope pairs of the same element. Consequently, biased ratio results may occur when traditional mass-dependent models, such as the Russell's law, are used to correct MIF in MC-ICP-MS.

Standard-sample bracketing (SSB) mass bias correction techniques are capable of correcting for both MDF and MIF⁴⁰ by using two adjacent standard solutions to correct for mass bias in the sample provided the standard is available with known isotopic composition. Although the SSB procedure cannot fully correct for drift during measurement cycles³⁰⁻³¹, a recent variation of the technique involves the use of an internal standard (e.g., Zr) added to both sample and standard to improve the quality of mass bias correction and consequently the precision of isotope ratio measurements^{32, 41}. This approach is based on the use of the known $^{88}\text{Sr}/^{86}\text{Sr}$ isotope ratio in the standard (e.g., SRM 987) to calibrate the “true” isotope amount ratio for $^{92}\text{Zr}/^{90}\text{Zr}$ or $^{91}\text{Zr}/^{90}\text{Zr}$ through Eq. 1. The resultant corrected ratio(s) is then used to calibrate the

$^{88}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$ ratios in the sample. The main advantage of this approach is that temporal changes in instrumental mass bias during the measurement sequence are corrected for³².⁴¹. In this study, we refer to this as being a combined SSB and internal normalization method (C-SSBIN). Since matrix-induced mass bias cannot be fully compensated for using C-SSBIN, as the corrected isotope amount ratios exhibit dependence on the sample concentration³², a near-perfect matrix separation and close matching of analyte and internal standard concentrations are required. However, the recent findings of MIF in MC-ICP-MS for Sr isotopes³⁹ has required revision of the C-SSBIN model because of $f^{88/86} \neq f^{87/86}$, wherein absolute determination of all three Sr isotope ratios is of interest. To eliminate any possible bias in the results, a modified C-SSBIN (mC-SSBIN) approach is undertaken here. Instead of using only the $^{88}\text{Sr}/^{86}\text{Sr}$ ratio in SRM 987 to calibrate the $^{91}\text{Zr}/^{90}\text{Zr}$ ratio, all three $^{88}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$ ratios are used to separately calibrate corresponding $^{91}\text{Zr}/^{90}\text{Zr}$ ratios, which are then used to calibrate the $^{88}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$ ratios, respectively, in the sample.

Apart from the issue of mass bias correction, accurate determination of Sr isotope ratios in real sample matrices requires correction for polyatomic and isobaric interferences (e.g., ^{84}Kr , ^{86}Kr , $^{44}\text{Ca}^{40}\text{Ar}$, $^{46}\text{Ca}^{40}\text{Ar}$, $^{44}\text{Ca}^{44}\text{Ca}$, $^{43}\text{Ca}^{44}\text{Ca}$ and ^{87}Rb), some of which is achieved through physical separation of concomitant interfering elements (e.g., Ca and Rb). Due to its complexity, validation of the entire procedure is of paramount importance. There is a paucity of isotope certified reference materials (iCRMs) available for this purpose⁴², especially matrix iCRMs. In the case of Sr, only one iCRM is currently available, i.e., SRM 987 (as highly purified SrCO_3)⁴³. As there is clearly a global need for matrix iCRMs for validation of many measurement processes, one of the objectives of this study was to provide a lobster hepatopancreas tissue, TORT-3, characterized for absolute Sr isotope ratios as well as δ -values relative to SRM 987.

For example, the material should find use in studies of fractionation induced by laser ablation sampling of tissues

EXPERIMENTAL SECTION

Instrumentation. A Thermo Fisher Scientific Neptune (Bremen, Germany) MC-ICP-MS equipped with 9 Faraday cups and a combination of cyclonic and Scott-type spray chambers with a MCN50 PFA self-aspirating nebulizer (Elemental Scientific, Omaha, NE, USA) operating at $50 \mu\text{l min}^{-1}$ were used for all Sr isotope ratio measurements. The plug-in quartz torch with sapphire injector was fitted with a platinum guard electrode. Optimization of the Neptune was performed as recommended by the manufacturer; typical operating conditions are summarized in Table 1. The gain on each Faraday cup was monitored daily to ensure normalization of its efficiency. In addition, the “Virtual Amplifier” design was employed for all measurements in order to eliminate any bias caused by uncertainties in the gain calibration of the amplifiers.⁴⁴

A sector field ICP-MS Element2 from Thermo Fisher Scientific (Bremen, Germany) was used for a semi-quantitative analysis. A Digiprep Jr block heater and 50 mL volume Teflon tubes (SCP Science, Quebec, Canada) were used for evaporation of sample solutions. An Anton Paar Multiwave 3000 microwave oven (PerkinElmer, Woodbridge, Ontario, Canada) was used for microwave assisted sample digestion. Empty 2 mL columns (part number: AC-141-AL) and 25 mL extension funnels (part number: AC-120) were purchased from Eichrom Technologies LLC (Darien, IL, USA).

Reagents and Solutions. Nitric acid was purified in-house prior to use by subboiling distillation of reagent grade feedstock in a quartz still. High-purity (18 M Ω cm) de-ionized water (DIW) was obtained from a NanoPure mixed bed ion exchange system fed with reverse osmosis domestic feed water (Barnstead/Thermolyne Corp, Iowa, USA). High-purity hydrogen peroxide

was purchased from Seastar Chemical Inc. (Sidney, BC, Canada). Eichrom Sr Spec resin of particle size 50-100 μm was sourced from Eichrom Technologies Inc. (Darien, IL, USA). Zirconium stock solution ($1000\text{ }\mu\text{g g}^{-1}$) was obtained from SCP Science (Baie D'Urfé, Quebec, Canada).

Stock solutions containing $1000\text{ }\mu\text{g g}^{-1}$ Sr prepared in 5 % HNO_3 by dissolution of SRM 987 strontium carbonate and SRM 984 rubidium chloride (National Institute of Standards and Technology, Gaithersburg, MD, USA).. Stock solutions containing $1000\text{ }\mu\text{g g}^{-1}$ Ca were prepared in 5 % HNO_3 by dissolution of high purity Puratronic CaCO_3 purchased from the Alfa Aesar (Ward Hill, MA, USA) and NIST 915b CaCO_3 , respectively. A candidate lobster tissue CRM, prepared by the National Research Council Canada (Ottawa, Ontario, Canada), consisted of lobster tissue which had been ground, heated to remove the oils, solvent extracted to yield a near oil-free protein fraction, dried, sieved through a 610 micron screen, homogenized and bottled.

Sample Digestion. Sample preparation was undertaken in a class-100 clean room. Sub-samples of TORT-3 were accurately weighed (0.25 g) into individual pre-cleaned Teflon digestion vessels. Seven mls of HNO_3 and $0.5\text{ ml H}_2\text{O}_2$ were added to each vessel. Two procedural blanks were also prepared concurrently. The sealed vessels were heated in the oven using a 15 min ramp and 25 minute hold at 1400 W . After cooling, the caps were removed and rinsed, and contents transferred to pre-cleaned 50 ml Teflon vessels. The solutions were evaporated to dryness on a hot block at $95\text{ }^\circ\text{C}$ and the residues redissolved in 2.1 mls of 8 M HNO_3 with heating at $95\text{ }^\circ\text{C}$ for 30 min. An aliquot of $100\text{ }\mu\text{l}$ of each digest was stored in a 15 ml pre-cleaned plastic bottle for recovery measurements. The remaining 2 ml of sample digest was loaded onto a resin column for matrix separation.

Column Separation. TORT-3 contains higher Sr and Rb concentrations ($36 \mu\text{g g}^{-1}$ and $5 \mu\text{g g}^{-1}$, respectively) than an earlier characterized biotissue³², and should provide a good candidate Sr isotope CRM. A 50-100 μm mesh Eichrom Sr Spec resin was used instead of a 100-150 μm mesh for better selective separation of Sr from Rb in the sample matrix. The separation procedure was based on previously developed methodology^{9, 32} with minor modification required to more efficiently eliminate Rb and other matrix elements. Prior to packing the columns, the resin, empty columns (2 ml) equipped with frits and column extensions (25 ml) were soaked in 0.2 M HNO_3 for several hours and rinsed with DIW. Columns containing 0.65 ml (1.5 cm resin bed depth) of resin were cleaned and preconditioned using acidic solutions as detailed in Table 2.

After the sample loading, the columns were rinsed with 2x3 mls 8 M HNO_3 and finally eluted with 3x5 mls of DIW into clean 50 ml Teflon vessels. The eluents were evaporated to dryness in the hot block at 95°C overnight and redissolved in 2 mls of 8 M HNO_3 prior to subjecting them to a second separation identical to the above. The final eluents were evaporated to dryness at 95°C and reconstituted to 3.1 mls 2 % HNO_3 . An aliquot of 100 μl from each of the purified solutions was removed for recovery measurements and determination of Rb and Ca concentrations. The remaining 3 mls of purified solutions were each spiked with 0.24 g of $25 \mu\text{g g}^{-1}$ zirconium standard solution, yielding a concentration of $2 \mu\text{g g}^{-1}$, prior to determination of isotope ratios by MC-ICP-MS. A solution of SRM 987 in 2 % HNO_3 containing a similar concentration of Sr as that in the purified TORT-3 solutions was prepared and spiked to a concentration of $2 \mu\text{g g}^{-1}$ Zr. This solution served as the transfer standard for mass bias correction.

Analysis Procedure and Data Processing. Samples and standards were introduced into the plasma in the sequence: SRM 987_{std} -sample-SRM 987_{std} . Intensities of Sr, Zr and all interfering isotopes obtained from a blank solution of 2 % HNO_3 were subtracted from all samples and

standards. A static run was employed to collect ^{83}Kr (L4), ^{84}Sr (L3), ^{85}Rb (L2), ^{86}Sr (L1), ^{87}Sr (C), ^{88}Sr (H3), ^{90}Zr (H2) and ^{91}Zr (H3). Data acquisition parameters are summarized in Table 1. Three measurements were made on each sample solution. Minor isobaric interferences from ^{84}Kr on ^{84}Sr and ^{86}Kr on ^{86}Sr were corrected through subtraction of intensities generated from a 2 % HNO_3 blank. Raw intensity data were exported to Excel for calculation of final Sr ratios. Interference of ^{87}Rb on ^{87}Sr arising from residual Rb ($<0.002\%$, expressed as $^{85}\text{Rb}/^{88}\text{Sr}$) in the purified TORT-3 solution was corrected based on the intensity of simultaneously measured ^{85}Rb . The IUPAC value of $^{85}\text{Rb}/^{87}\text{Rb}$ was used for this purpose and mass bias correction was applied to the ratio assuming the same mass bias for $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{85}\text{Rb}$.

Mass Bias Correction. To correct both MDF and MIF, an alternative mC-SSBIN method was applied based on the strategy depicted in Figure 1. Certified values of 8.37861 ± 0.00325 , 0.71034 ± 0.00026 and 0.05655 ± 0.00014 (U, 95% confidence interval) for $^{88}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$, respectively, were used to calculate their corresponding mass bias corrected ratios of $^{90}\text{Zr}/^{91}\text{Zr}$ in accordance with Eq. 1. Three resultant mean values of $^{90}\text{Zr}/^{91}\text{Zr}$ were then used to normalize $^{88}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$ ratios in the lobster CRM TORT-3. Note that the Zr internal standard element serves as the mass-bias correction proxy. For example, even though the value obtained for the Zr isotope ratio may itself be biased due to the limitations of the employed mass-bias correction models (e.g., assumption $f^{\text{Sr}} = f^{\text{Zr}}$), this bias is largely negated in the second step of the calibration ($\text{Zr} \rightarrow \text{Sr}$). This cancellation of bias, however, occurs only when matrix separation and concentration matching is fully attained. Additionally, δ values for the Sr isotope ratios in TORT-3 were calculated relative to those in SRM 987:

$$\delta^{86}\text{Sr} = \left(\frac{R_{\text{sample}}^{86}}{R_{\text{NIST987}}^{86}} - 1 \right) \cdot 1000 \text{ ‰} \quad (2)$$

where $R_{\text{sample}}^{i/86}$ and $R_{\text{NIST987}}^{i/86}$ are mass bias corrected ("true") ratios in the sample and the standard, respectively.

RESULTS and DISCUSSION

Matrix Separation. As noted earlier, the mC-SSBIN mass bias correction model requires matrix matching between the sample and the standard to ensure accuracy. Since it is practically impossible to match all matrix elements between a sample and a standard solution, separation of the matrix elements is performed. It is widely recognized that non-quantitative recovery of analyte during such a process may result in isotope fractionation⁴⁵⁻⁴⁶, and quantitative (above 95 %) recovery of analyte is thus required to ensure accurate results.

During preliminary studies, low recoveries (<85%) were obtained when a digest of TORT-3 was diluted to 15 mls in 8 M HNO₃ and loaded onto a Sr Spec column comprising 100-150 µm size resin, similar to previous studies^{9,32}. Subsequent investigation determined that both volumes for sample loading and rinsing in 8 M HNO₃ had a significant effect on recovery.

Based on measurements of all collected fractions characterizing loading of a 1 ml sample (a standard containing 10 µg g⁻¹ SRM 987 Sr and 2 µg g⁻¹ Rb) in 8 M HNO₃ (L1), 5x2 mls of 8 M HNO₃ rinsing (R1-R5), and 5x2 mls of DIW eluting (E1-E5), loss of Sr was found in fraction R3 and increased as the volume of 8 M HNO₃ used for rinsing increased, as shown in Figure 2a.

The smaller particle size of 50-100 µm mesh Sr Spec resin was tested and better separation of Sr and Rb was achieved. As shown in Figure 2b, no washout of Sr was evident during rinsing, even in R5, for a total of 10 mls of 8 M HNO₃, and close to 100 % of the Rb was removed with 4 mls 8 M HNO₃. However, it was found that a larger volume of 12 mls DIW was needed to completely elute Sr with the smaller 50-100 µm mesh Sr Spec resin, compared to 8 mls DIW needed with the 100-150 µm size resin. It was also found that sample loading volume should be

limited to 2 mls or less, since an excess amount of 8 M HNO_3 used during loading and rinsing would lead to the loss of Sr. Thus a volume of 2 mls sample in 8 M HNO_3 for loading, 3x2 mls 8 M HNO_3 for rinsing, 3x5 mls DIW for eluting and 50-100 μm sized Sr Spec resin were used for all subsequent experiments to obtain efficient separation of Rb and quantitative recovery of Sr $[100 \pm 3 \text{ \% (1SD, n=3)}]$.

Initially, the collected DIW eluent (15 mls) was examined for determination of Sr isotope ratios and for semi-quantitative analysis to check the efficiency of matrix separation using a single column pass. Concentrations of concomitants were significantly reduced for the majority of elements but a few matrix elements (i.e., Na, Al, Ca, Zn, Ba and Pb) remained at levels greater than 0.2 %, expressed as a ratio of individual matrix element concentration to Sr concentration, in the purified digests. A small amount of Rb (0.005 %, expressed as $^{85}\text{Rb}/^{88}\text{Sr}$) was found in the eluent. Therefore, a second pass of the digest through the column was performed in order to achieve the desired low level of Rb ($<0.002 \text{ \%}$) and other matrix elements in the purified TORT-3 solutions. No further improvement in the reduction of matrix elements was noted when a third pass through the column was performed. Thus, a double pass column separation was used for all subsequent experiments. The collected 15 mls DIW effluent was evaporated to dryness and reconstituted to 3.1 mls in 2% HNO_3 , prior to determination of isotope ratios by MC-ICP-MS. Recovery of Sr using this procedure was $98 \pm 4 \text{ \%}$ ($n=12$), based on the concentration of Sr measured in the purified solution of TORT-3 compared to that of the original digest.

Effect of Residual Ca and Rb on Sr Isotope Ratio Determinations. Following a double pass column separation, the only noticeable impurity was found to be Ca at a $2 \mu\text{g g}^{-1}$ level in the purified 3 mls TORT-3 solution. Residual Ca most likely arose from reagents as a similar amount was found in sample blanks. The residual Rb content was in the range 0.0010-0.0015 % (expressed as an intensity ratio of $^{85}\text{Rb}/^{88}\text{Sr}$) in the purified solutions. Polyatomic or isobaric

interferences comprising $^{44}\text{Ca}^{40}\text{Ar}$, $^{46}\text{Ca}^{40}\text{Ar}$, $^{44}\text{Ca}^{44}\text{Ca}$, $^{43}\text{Ca}^{44}\text{Ca}$ and ^{87}Rb need to be corrected for and thus the effects of Ca and Rb were investigated by examining standard solutions of $1\text{ }\mu\text{g g}^{-1}\text{ Sr}$ prepared from SRM 987 in the presence of varying amounts of Ca and Rb. Samples were spiked with $2\text{ }\mu\text{g g}^{-1}\text{ Zr}$ as internal standard and the mC-SSBIN method used for mass bias correction. Results are summarized in Table 3. For comparison purposes, $\delta^{i/86}\text{Sr}$ (i=84, 87 and 88) values were used. Clearly, $\delta^{i/86}\text{Sr}$ values were not significantly affected by the spiked Ca concentrations at levels of $2\text{ }\mu\text{g g}^{-1}$ and below, but the effect of Ca became evident when its concentration increased to $10\text{ }\mu\text{g g}^{-1}$. This observation confirms that the $2\text{ }\mu\text{g g}^{-1}$ residual Ca at in the purified 3 mls TORT-3 has no significant effect on determined Sr ratios. In addition, contributions from Ca polyatomic interferences were corrected through subtraction of intensities of measured isotopes using sample blank containing the same amount of Ca. On the other hand, Rb has a significant effect on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, even at concentrations as low as 1 ng g^{-1} (about 0.0015 % of the intensity ratio of $^{85}\text{Rb}/^{88}\text{Sr}$), as shown in Table 3. Further experiments demonstrated that Rb led to increased Sr ratios even at a much lower level of 0.0001 %. Since the residual Rb content in the purified TORT-3 solutions is about an order of magnitude higher (0.0010-0.0015%), its correction is essential.

Correction for ^{87}Rb Interference. The minor interference from ^{87}Rb on ^{88}Sr arising from the residual Rb in the purified TORT-3 solution was corrected for on the basis of the simultaneously measured ^{85}Rb signal ($I^{85\text{Rb}}$) using the IUPAC value for $^{87}\text{Rb}/^{85}\text{Rb}$ ($R^{87/85}=0.385706=0.278346/0.721654$)⁴⁷, which was mass bias corrected assuming the same mass bias for $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{85}\text{Rb}$ according to the following equations:

$$r^{87/88\text{Sr}} = \frac{I^{87\text{Sr}}}{I^{88\text{Sr}}} \quad (3)$$

$$I^{88\text{Sr}} = I^{88} - I^{85\text{Rb}} \cdot r^{87/85\text{Rb}}$$

(4)

$$r^{87/85\text{Rb}} = R^{87/85\text{Rb}} \cdot \left(\frac{m_{87}}{m_{85}} \right)^f = 0.385706 \cdot \left(\frac{m_{87}}{m_{85}} \right)^f$$

(5)

$$f = \ln \left(\frac{R^{88/86\text{Sr}}_{\text{NIST987}}}{r^{88/86\text{Sr}}_{\text{NIST987}}} \right) \cdot \ln \left(\frac{m_{86}}{m_{88}} \right)$$

(6)

To validate this correction, 1 $\mu\text{g g}^{-1}$ standard solutions of Sr were prepared from SRM 987 and Rb added in the range 0.0001-0.002 % (expressed as an intensity ratio of $^{85}\text{Rb}/^{88}\text{Sr}$) to encompass that found in the purified TORT-3 solutions. Samples were spiked with 2 $\mu\text{g g}^{-1}$ Zr as internal standard and of the mC-SSBIN model used for mass bias correction. Results are summarized in Figure 3a. It is evident that this Rb correction strategy works well within the tested concentration range. However, when Rb levels were increased above 0.005 %, a biased $^{87}\text{Sr}/^{86}\text{Sr}$ ratio occurred even with use of this correction protocol. This could be attributed to the imperfect correction of ^{87}Rb at high levels because of the assumption of identical mass bias for $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{85}\text{Rb}$ used in the calculation. Fortunately, accurate results can be obtained with the use of double pass column separation to achieve the needed low residual levels of Rb (<0.002 %, expressed as an intensity ratio of $^{85}\text{Rb}/^{88}\text{Sr}$) and Ca at 2 $\mu\text{g g}^{-1}$ in the purified TORT-3 solutions, as demonstrated in Figure 3b.

Method Validation and Final Results. Standard solutions prepared from SRM 987 containing 10 $\mu\text{g g}^{-1}$ Sr and spiked with 2 $\mu\text{g g}^{-1}$ Rb was subjected to the matrix separation procedure to validate the proposed method. Isotope ratios of 0.0565495 ± 0.0000010 , 0.7103350 ± 0.000034 and 8.378847 ± 0.000061 (mean and 1SD, n=3) were obtained for $^{84}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$, respectively, in good agreement with their certified values of 0.05655 ± 0.00014 ,

0.71034 ± 0.00026 and 8.37861 ± 0.00325 (as 95 % confidence interval).

For the final determination of Sr isotope ratios in the biological TORT-3 samples, 18 matrix separated solutions were prepared and each was measured three times under the optimized experimental conditions. Results are presented in Table 4. For comparison purposes, $\delta^{86/86}\text{Sr}$ values relative to SRM 987 were also calculated in accordance with Eq. 2. Values of -0.442 ± 0.071 , -1.254 ± 0.044 and 0.454 ± 0.030 (mean and 1SD, n=18) obtained for $\delta^{84/86}\text{Sr}$, $\delta^{87/86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$, respectively, are in a range similar to these reported previously for natural samples³⁰⁻³².

Uncertainty estimations for Sr ratios were made in accordance with JCGM 100:28 Evaluation of Measurement Data-Guide to the Expression of Uncertainty in Measurement⁴⁸, using the following law of propagation of uncertainty:

$$u_{R_i}^2(y) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) + 2 \cdot \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left(\frac{\partial f}{\partial x_i} \right) \cdot \left(\frac{\partial f}{\partial x_j} \right) \cdot u(x_i) \cdot u(x_j) \cdot r_{(i,j)} \quad (7)$$

where $y = f(x_1, x_2, \dots, x_N)$. The partial derivatives $\partial f / \partial x_i$ are often referred to as sensitivity coefficients, $u(x_i)$ and $u(x_j)$ are the standard uncertainties associated with the input x_i and x_j , and $r_{(i,j)}$ is the correlation coefficient ($-1 \leq r_{(i,j)} \leq 1$). The combined uncertainty of the grand mean, u_R^- , was obtained by combining the uncertainties of the individual estimates and the variations between these means as per recent guidelines from NIST⁴⁹. The following equation was used:

$$u_R^2 = SD^2 + \frac{1}{n^2} \sum u_{R_i}^2 \quad (8)$$

where SD is the standard deviation of the n means and u_{R_i} is the uncertainty of the individual estimates of the measurand, $i = [1..n]$. As expected, those for Sr isotope ratios in the sample are larger than the simple standard deviations calculated from their replicate measurements. The

uncertainties associated with the certificate values of $^{88}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$ in SRM 987 are the principal sources contributing to the final combined standard uncertainties.

Based on results presented in Table 4 from five different bottles, ANOVA was performed. A value of 1.29 was found for an F factor, smaller than the critical value of 3.18, indicating the material is homogeneous at the level of a 0.25 g sub-sample.

CONCLUSION

An accurate and precise method has been developed for the determination of Sr isotope ratios (traceable to NIST SRM 987 *via* $^{88}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$) by MC-ICP-MS using a modified mass bias correction approach comprising a combined standard-sample bracketing and internal normalization with Zr. A double pass column separation was necessary to reduce Rb to a requisite low level in the purified sample solutions. Evaluation of the combined uncertainty reveals that components arising from the uncertainties in the certificate values of the Sr ratios in SRM 987 used for mass bias correction are the main contributors to the uncertainties in all derived absolute Sr isotope ratios.

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Table 1. MC-ICP-MS operating conditions

Instrument settings	
Rf power	1280 W
Plasma Ar gas flow rate	16.0 L min ⁻¹
Auxiliary Ar gas flow rate	1.00 L min ⁻¹
Ar carrier gas flow rate	1.04 L min ⁻¹
Sampler cone (nickel)	1.1 mm
Skimmer cone (nickel)	0.8 mm
Sample uptake rate	50 µL min ⁻¹
Sample uptake time	130 seconds
Wash time	120 seconds
Lens settings	Optimized for maximum analyte signal intensity and stability
Data acquisition parameters	
Scan type	Static measurements
Cup configuration	⁸³ Kr (L4), ⁸⁴ Sr (L3), ⁸⁵ Rb (L2), ⁸⁶ Sr (L1), ⁸⁷ Sr (C), ⁸⁸ Sr (H3), ⁹⁰ Zr (H2) and ⁹¹ Zr (H3)
Zoom Optics	Focus Quad: 0 V and Dispersion Quad: 0 V
Resolution	~300
Sensitivity	25 V/ppm for ⁸⁸ Sr
Integration time	4.194 s
Number of Integrations	1
Cycles/Blocks	7/4

Table 2. Column separation procedure

Eichrom Sr Spec column	Step
2x3 mls 8 M HNO ₃	Clean
1x3 mls 8 M HNO ₃	Condition
Sample in 2 mls 8 M HNO ₃	Load
3x2 mls 8 M HNO ₃	Rinse
3x5 mls DIW	Elute

Table 3. Effect of Ca and Rb on Sr isotope ratios

Sample	$^{84}\text{Sr}/^{86}\text{Sr}$ (1SD, n=3)	$^{87}\text{Sr}/^{86}\text{Sr}$ (1SD, n=3)	$^{88}\text{Sr}/^{86}\text{Sr}$ (1SD, n=3)
SRM 987	0.01±0.01	-0.01±0.02	-0.06±0.04
SRM 987+0.5 $\mu\text{g g}^{-1}$ Ca	0.02±0.01	0.00±0.02	0.03±0.04
SRM 987+1 $\mu\text{g g}^{-1}$ Ca	0.00±0.01	-0.02±0.02	-0.06±0.04
SRM 987+2 $\mu\text{g g}^{-1}$ Ca	0.00±0.01	0.01±0.02	-0.06±0.04
SRM 987+10 $\mu\text{g g}^{-1}$ Ca	-0.05±0.01	-0.16±0.02	0.03±0.04
SRM 987	0.00±0.01	-0.01±0.01	0.00±0.04
SRM 987+1 ng g^{-1} Rb	0.00±0.01	6.47±0.01	0.00±0.04
SRM 987+2 ng g^{-1} Rb	0.00±0.01	12.73±0.02	-0.00±0.04
SRM 987+10 ng g^{-1} Rb	0.01±0.01	64.39±0.05	0.00±0.04
SRM 987+50 ng g^{-1} Rb	-0.01±0.01	319.65±0.06	0.06±0.04

Table 4. Sr isotope ratios for TORT -3 lobster hepatopancreas CRM

Sample	$^{84}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{88}\text{Sr}/^{86}\text{Sr}$
Lobster digest 1-1	0.0565238	0.709481	8.382661
Lobster digest 1-2	0.0565238	0.709416	8.381994
Lobster digest 1-3	0.0565253	0.709493	8.382759
Lobster digest 1-4	0.0565347	0.709465	8.382289
Lobster digest 2-1	0.0565232	0.709453	8.382276
Lobster digest 2-2	0.0565185	0.709480	8.383001
Lobster digest 2-3	0.0565202	0.709475	8.382671
Lobster digest 2-4	0.0565302	0.709474	8.382597
Lobster digest 3-1	0.0565244	0.709441	8.382303
Lobster digest 3-2	0.0565294	0.709438	8.382177
Lobster digest 4-1	0.0565273	0.709392	8.382367
Lobster digest 4-2	0.0565301	0.709413	8.382254
Lobster digest 4-3	0.0565275	0.709430	8.382387
Lobster digest 4-4	0.0565209	0.709445	8.382392
Lobster digest 4-5	0.0565269	0.709433	8.382282
Lobster digest 5-1	0.0565293	0.709476	8.382461
Lobster digest 5-2	0.0565276	0.709488	8.382496
Lobster digest 5-3	0.0565277	0.709398	8.382115
$\bar{x} \pm \text{SD (n=18)}$	0.0565262±0.0000040	0.709449±0.000032	8.38242±0.00025
Recommended value (U, k=2)	0.0565262±0.0000048	0.70945±0.00011	8.3824±0.0012

Figure 1. Flow chart for mass bias correction

Figure 2. Column separation profiles for standard solutions. Normalized analyte signals in % plotted against collected fractions. (a): 10 µg g⁻¹ SRM 987 Sr and 2 µg g⁻¹ Rb with use of 100-150 µm size Sr Spec resin; (b): 10 µg g⁻¹ SRM 987 Sr and 2 µg g⁻¹ Rb with use of 50-100 µm size Sr Spec resin.

Figure 3. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained using different correction strategies. (a): $\blacktriangle$: raw measured ratio, $\blacklozenge$: mass bias corrected ratio, $\bullet$: mass bias and Rb corrected ratio, error bar is 1SD, $n=3$; (b): $\blacklozenge$: mass bias corrected ratio, $\bullet$: mass bias and Rb corrected ratio, error bar is 1SD, $n=3$.