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Article

Determination of $^{87}Sr/^{86}Sr$ Ratios in Food Grains Characterized by Low Concentration Sr Using MC-ICP-MS

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ABSTRACT: This study presents a method for the reliable determination of $^{87}Sr/^{86}Sr$ in food grains, which are characterized by low Sr concentrations but high concentration ratios of Rb/Sr and K/Sr using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The Sr/matrix separation procedure using Sr resin was optimized for a standard reference material of wheat flour (NIST SRM 1567b). Consequently, a high Sr recovery (97.0 % ± 1.2 %, mean ± 1 SD, n = 7) and effective Sr/matrix separation (e.g., $^{85}Rb/^{88}Sr$ intensity ratio at MC-ICP-MS measurements × 100 of 0.00014 % ± 0.00003 %, mean ± 1 SD, n = 7) were achieved. Furthermore, potential spectroscopic interferences caused by matrix ions were estimated by analyzing NIST SRM 987 solutions spiked with varying amounts of Rb or Ca using MC-ICP-MS. The proposed method was validated by analyzing eight standard reference materials of vegetal, animal, and geological origins studied previously, yielding $^{87}Sr/^{86}Sr$ ratios consistent with literature values, which demonstrates the applicability of the method across diverse sample matrices. Finally, the proposed method was applied to standard reference materials for which $^{87}Sr/^{86}Sr$ ratios are not reported to our knowledge (NIST SRM 1567a and b wheat flour). The $^{87}Sr/^{86}Sr$ ratios of NIST SRM 1567a and b were estimated to be 0.70895 ± 0.00005 (2 SD, n = 34), and 0.70898 ± 0.00003 (2 SD, n = 25), respectively.

INTRODUCTION

Strontium (Sr) has four naturally occurring isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr. Sr-87 is a radiogenic isotope arising from rubisium-87 (^{87}Rb) through β-decay ($t_{1/2} = 4.88 \times 10^{10}$ a) [1]. Hence, the $^{87}Sr/^{86}Sr$ ratio has been widely used for geochronological dating. The geological ages of bedrock vary from region to region on the Earth's surface. The $^{87}Sr/^{86}Sr$ ratio in agricultural products is determined by the isotopic composition of the bioavailable Sr fraction in soil, which is itself influenced by the isotopic signature of the geographical provenance;[2-5] thus, the potential of the $^{87}Sr/^{86}Sr$ ratio in foods as a tracer of geographical origin is suggested (for example, rice,[6] wine,[7] honey,[8] olive oil,[9] coffee bean,[10] Chinese cabbage,[11] and beef [12]). Food grains play important roles in the human diet as staple foods in many regions, and a considerable amount of food grains is globally produced, traded, and consumed. Accordingly, the safety of food grains, including their geographical origin traceability, is gaining attention among consumers. Food grains have become one of the important targets of the $^{87}Sr/^{86}Sr$ ratio measurements.

Multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) is used for isotope ratio measurements, including

$^{87}Sr/^{86}Sr$, because of its high precision in measurements, high sample throughput, and simple sample introduction system. The biggest challenge for realizing accurate and precise $^{87}Sr/^{86}Sr$ ratio measurements using MC-ICP-MS is spectral interferences, including isobaric interference from krypton-86 ($^{86}Kr^+$) or $^{87}Rb^+$ and polyatomic interference caused by calcium (Ca), iron (Fe), or zinc (Zn) (e.g., $^{40}Ca^{46}Ca^+$, $^{43}Ca^{2+}$, $^{43}Ca^{44}Ca^+$, $^{48}Ca^{40}Ar^+$, $^{44}Ca_2^+$, $^{54}Fe^{16}O_2^+$, $^{54}Fe^{16}O^{17}O^+$, $^{56}Fe^{16}O_2^+$, $^{68}Zn^{18}O^+$, $^{70}Zn^{17}O^+$, and $^{70}Zn^{18}O^+$). In the $^{87}Sr/^{86}Sr$ ratio measurements, the most severe spectral interference is the isobaric interference from $^{86}Kr^+$ and $^{87}Rb^+$. Kr primarily originates from an impurity in argon (Ar) gas, and a certain amount of Kr is inevitably introduced into an ICP along with Ar gas; therefore, the isobaric interference from Kr must be numerically corrected. By contrast, because Rb, Ca, Fe, and Zn originate from sample matrices, the Sr/matrix separation using chemical separation techniques prior to the $^{87}Sr/^{86}Sr$ ratio measurements is essential, and the quality of the Sr/matrix separation is one of the factors determining the accuracy and precision of the $^{87}Sr/^{86}Sr$ ratio measurements using MC-ICP-MS. Special attention should be paid to residual Rb and Ca in purified Sr fractions because the presence of even a slight amount of Rb can cause serious isobaric interferences. Moreover, Ca, which is generally contained in natural samples in high concentration, can cause polyatomic interferences from Ca dimers and Ca argides when Sr/matrix separation is inadequate.

Ion-extraction chromatography using Sr spec™ resin (Eichrom Technologies, LLC, IL, USA; hereinafter called Sr resin) is a chemical separation technique applied to the Sr/matrix separation in various geological and environmental samples.[13] The separation procedure using Sr resin generally comprises the following steps:

Step 1: Resin cleaning with water and diluted HNO_3;

Step 2: Resin conditioning with HNO_3 having the same concentration as that used in the following sample loading step;

Step 3: Loading the sample dissolved in HNO_3 onto the Sr resin to retain Sr on the resin;

Step 4: Rinsing Sr resin with HNO_3 to remove the matrix elements; and

Step 5: Sr elution with diluted HNO_3 to recover Sr.

Compared to animal and geological matrices, vegetal matrices, including food grains, contain much more matrix elements (e.g., Mg, K, and Ca) relative to Sr. The notable characteristics of the elemental composition of vegetal matrices are the high concentration ratios of Rb/Sr and K/Sr (Table 1). A high Rb/Sr concentration ratio in vegetal matrices complicates the attainment of a sufficiently effective Sr/Rb separation because even a slight amount of Rb can cause severe isobaric interference during $^{87}Sr/^{86}Sr$ measurements. A high K concentration can cause a significant reduction of the Sr retention in Sr resin,[16] which will possibly make it difficult to obtain a high Sr recovery at the Sr/matrix separation of vegetal matrices. Among various vegetal reference materials, NIST SRM 1567b wheat flour has a significantly lower Sr concentration, resulting in much higher Rb/Sr and K/Sr concentration ratios compared to other matrices (Table 1). These characteristics are common to all food grains and complicate the effective Sr/matrix separation.

The HNO_3 concentration used in the sample loading process (Step 3) will considerably affect the Sr recovery and the Sr/matrix separation efficiency. Horwitz et al. (1992) [16] showed that the uptake of Sr by the Sr resin increases with increasing the HNO_3 concentration in the HNO_3 concentration range of 0.02–8 mol L^{-1}. The uptake of Rb by the Sr resin reaches the maximum at 3 mol L^{-1} HNO_3 and then decreases with increasing the HNO_3 concentration.[16] These results suggested that the higher Sr recovery and a more effective Sr/Rb separation may be possibly achieved when HNO_3 of a higher concentration is used. Some of the previous reports chose 6–8 mol L^{-1} HNO_3 for the sample loading.[7, 15, 17–20] Horwitz et al. (1991) also showed that a high HNO_3 concentration >3 mol L^{-1} will result in a competition of Sr with HNO_3 for retention on

Table 1. Concentration ratios of Sr and major matrix elements contained in the vegetal, animal, and geological reference materials

Reference materials		Concentration (mg kg^{-1})	Concentration ratio			
		Sr	Rb/Sr	Ca/Sr	K/Sr	Mg/Sr
Vegetal	NIST SRM 1515 (apple leaves)	25.1 ± 1.1[a)]	0.41[d)]	608[d)]	641[d)]	108[d)]
	NIST SRM 1567b (wheat flour)	<0.8[b)]	0.89[e)]	251[e)]	1761[e)]	526[e)]
	NIST SRM 1570a (spinach)	55.54 ± 0.50[a)]	0.23[d)]	275[d)]	522[a)]	162[d)]
Animal	NIST SRM 1400 (bone ash)	249 ± 7[a)]	0.0029[f)]	1533[d)]	0.75[a)]	27[d)]
	NIST SRM 1486 (bone meal)	264 ± 7[a)]	0.0017[f)]	1007[d)]	1.56[a)]	18[d)]
	GSJ JCp-1 (coral)	7240 ± 70[a)]	0.000011[f)]	52[d)]	0.026[a)]	0.13[d)]
	NRC FEBS-1 (otolith)	- [h)]	- [h)]	186[d)]	- [h)]	0.011[d)]
Geological	GSJ JA1 (andesite)	263[c)]	0.047[g)]	159[g)]	24[g)]	36[g)]
	GSJ JB2 (basalt)	178[c)]	0.041[g)]	405[g)]	20[g)]	156[g)]

[a)] Certified value (mean ± expanded uncertainty). [b)]Measured value in this study. [c)]Recommended value reported by Imai *et al.* (1995).[14] [d)] Value estimated from a certified value for the concentration of each element. [e)]Value estimated from the certified values for the Rb, Ca, K, and Mg concentrations and a measured value of the Sr concentration in this study. [f)]Value calculated from a certified value for the Sr concentration and a literature value of the Rb concentration presented by Galler *et al.* (2007).[15] [g)]Value calculated from the recommended value for the concentration of each element depicted by Imai *et al.* (1995).[14] [h)]Value that is neither certified nor measured in previous literature.

crown ether contained in Sr resin and a slight decrease in the extraction efficiency of Sr.[21] In addition, the retention of Ca on Sr resin increases with increasing HNO_3 concentration in the HNO_3 concentration range 0.02–8 mol L^{-1}, suggesting that a more effective Sr/Ca separation may be achieved when a lower HNO_3 concentration is used. This was why HNO_3 of a relatively low concentration (1–3 mol L^{-1}) was also chosen by other studies. [9, 22–30] Although the influence of the HNO_3 concentration on the Sr recovery and Sr/matrix separation efficiency must be carefully evaluated based on the characteristics of the chemical compositions of the target samples, a study conducted by De Muynck *et al.* (2009), [18] which examined the optimal HNO_3 concentration in the Sr/matrix separation of Ca-rich samples (bone tissues) is the only example to our knowledge. The Sr concentration in the bone tissues (≈250 mg kg^{-1}) is much higher than that in food grains, and the sample matrices of the bone and food grains greatly differ from each other; thus, conditions must be optimized based on the food grain characteristics for reliable $^{87}Sr/^{86}Sr$ ratio measurements.

This study aims to provide a Sr/matrix separation protocol for the accurate and precise determination of $^{87}Sr/^{86}Sr$ ratios in food grains and apply it to determine $^{87}Sr/^{86}Sr$ ratios in reference materials of wheat flour: NIST SRM 1567a and b. First, HNO_3 concentration used in Step 3 of the separation procedure is optimized for achieving high Sr recovery and effective Sr/matrix separation, using digested NIST SRM 1567b. The following conditions are also addressed: the volume of Milli-Q water and diluted HNO_3 to sufficiently reduce the Sr blank resulting from the Sr resin (Step 1); the volume of HNO_3 required for attaining effective Sr/matrix separation (Step 4); and volume of HNO_3 to be collected as the Sr fraction (Step 5). The optimizations are conducted using two resin bed volumes (0.4 and 2.0 mL). Although small resin bed volumes are generally preferred for samples characterized by high Sr concentrations, the evaluation of the effects of resin volumes on the efficiency of the Sr/matrix separation is essential, considering the characteristics of food grains. Next, the effects of residual Rb and Ca in a purified Sr fractions on $^{87}Sr/^{86}Sr$ ratios measured using MC-ICP-MS were evaluated by analyzing NIST SRM 987 solutions spiked with different Rb or Ca concentrations to confirm whether the achieved Sr/matrix separation was sufficiently effective. Furthermore, the proposed procedure was validated by analyzing various sample matrix types: vegetal matrices (NIST SRM 1515 apple leaves and NIST SRM 1570a spinach), animal matrices (NIST SRM 1400 bone ash, NIST SRM 1486 bone meal, JCp-1 coral, and FEBS-1 otolith), and geological matrices (JA-1 andesite and JB-2 basalt), which have been already analyzed in previous studies.[17–18, 27, 31–66] Finally, the proposed method was applied to standard reference materials for which $^{87}Sr/^{86}Sr$ ratios are not reported, i.e., NIST SRM 1567a and b wheat flour. Although method validation using literature values of reference materials with similar sample matrices is essential for the accurate and precise determination of the $^{87}Sr/^{86}Sr$ ratio, to the best of our knowledge, the values for food grain reference materials have not been reported in literature.

EXPERIMENTAL

Reagents and materials. The standard reference material of the Sr isotope ratio, NIST SRM 987 (strontium carbonate powder), was purchased from the National Institute of Standards and Technology (NIST; MD, USA). NIST SRM 1515, NIST SRM 1567a, NIST SRM 1567b, NIST SRM 1570a, NIST SRM 1400, and NIST SRM 1486 were purchased from the NIST. NMIJ CRM 7502-a rice flour was purchased from the National Metrology Institute of Japan (Ibaraki, Japan). JCp-1, JA1, and JB2 were acquired from the Geological Survey of Japan (Ibaraki, Japan). FEBS-1 was procured from the National Research Council of Canada (Ottawa, Canada). For details regarding reagents and labwares used in this study, refer to the Supporting Information.

Sample preparation

Acid digestion of reference materials. The vegetal (NIST SRM 1515, NIST SRM 1567a, NIST SRM 1567b, and NIST SRM 1570a) and animal reference materials (NIST SRM 1400, NIST SRM 1486, JCp-1, and FEBS-1) were digested using a microwave-assisted acid digestion system, UltraWAVE (Milestone S.r.l, BG, Italy). The geological reference materials (JA1 and JB2) were digested via the hotplate digestion method. Each digested sample solution was evaporated prior to Sr/matrix separation. Evaporation was performed on a hot plate at 130 °C until the volume of each solution was reduced to almost a single drop. Each drop from reference materials was redissolved in 2.5 mL 8 mol L^{-1} HNO_3 and subjected to Sr/matrix separation. To optimize the HNO_3 concentration used in the sample loading (Step 3) and rinsing (Step 4) processes in the Sr/matrix separation, the digested solution of 6 g NIST SRM 1567b was split into six aliquots and individually evaporated. Two from each were redissolved in 2.5 mL of 1, 3, and 8 mol L^{-1} HNO_3. One set of digested NIST SRM 1567b redissolved in 1, 3, and 8 mol L^{-1} of HNO_3 was used to optimize the Sr/matrix separation procedure with 0.4 and 2.0 mL of Sr resin. For details regarding acid digestion, refer to the Supporting Information section.

Sr/matrix separation. The Sr/matrix separation was performed using the Sr resin with a particle diameter of 100–150 μm, which is purchased from Eichrom Technologies Inc. This Sr resin contained a crown ether (4,4'(5')-di-t-butylcyclohexano 18-crown-6) in octanol sorbed onto an inert polymeric support. Herein, two resin bed volumes (0.4 and 2.0 mL) were tested. In addition to prepacked columns containing the Sr resin of 2.0 mL bed volume purchased from Eichrom Technologies Inc., in-house-made columns containing the Sr resin of 0.4 mL bed volume were

prepared by loading Sr resins onto a Bio-Spin® chromatography column purchased from Bio-Rad Laboratories, Inc. (CA, USA). Before the preparation of the in-house made columns, Sr resins were washed according to the following procedure: fresh Sr resins were dispersed in Milli-Q water; the supernatant was removed after 30 min resting; and fresh Milli-Q water was added again. This procedure was repeated four to five times. The washed Sr resins were then stored in Milli-Q water until use.

Milli-Q water and 0.05 mol L^{-1} HNO_3 were used in the resin cleaning process (Step 1). The HNO_3 concentration used in the column conditioning (Step 2) was set as equal to that of HNO_3 used in the sample loading (Step 3) and rinsing (Step 4) processes. In the Sr elution process (Step 5), 0.05 mol L^{-1} HNO_3 was used. The HNO_3 concentration used in the sample loading (Step 3) and rinsing (Step 4) processes was optimized using the digested NIST SRM 1567b redissolved in 1, 3, or 8 mol L^{-1} of HNO_3 for 0.4 and 2.0 mL of the Sr resin. The following points were also assessed using columns containing 0.4 or 2.0 mL of Sr resin, which were loaded with the digested NIST SRM 1567b redissolved in 8 mol L^{-1} HNO_3: the HNO_3 volume used in the rinsing process (Step 4) and the volume of 0.05 mol L^{-1} HNO_3 used in the Sr elution process (Step 5).

Sample preparation for $^{87}Sr/^{86}Sr$ ratio measurements. A stock solution of NIST SRM 987 (≈10 mg kg^{-1} in 5 % HNO_3) was diluted with an appropriate amount of 3 % HNO_3 to adjust the Sr concentration to 200 μg kg^{-1} and then used as an isotopic reference material during $^{87}Sr/^{86}Sr$ ratio measurements. To evaluate the influences of Rb and Ca in analyte solutions on $^{87}Sr/^{86}Sr$ ratio measurements, 200 μg kg^{-1} NIST SRM 987 solutions were prepared with final concentrations of 0.001, 0.002, 0.004, 0.01, and 0.1 μg kg^{-1} of Rb or 1, 2, and 10 mg kg^{-1} of Ca by adding appropriate amounts of the diluted single elemental standard solutions of Rb or Ca to the NIST SRM 987 stock solution and diluting it with an appropriate amount of 3 % HNO_3. Before the $^{87}Sr/^{86}Sr$ ratio measurements of reference materials, all purified Sr fractions were diluted with 3 % HNO_3 to achieve Sr concentrations of ≈200 μg kg^{-1}. For detailed sample preparation for elemental analyses, refer to the Supporting Information section.

Instrumentation

ICP-MS for elemental analyses. Quantitative analyses of Sr, Rb, Ca, Fe, and Zn were conducted using ICP-MS (7700x, Agilent Technologies Japan, Ltd., Tokyo, Japan) equipped with a MicroMist™ nebulizer (flow rate: 100 μL min^{-1}), a Scott-type spray chamber, a Pt sampling cone (orifice diameter: 1 mm), and a Pt skimmer cone (orifice diameter: 0.4 mm). Table S1 summarizes detailed operating conditions for ICP-MS.

MC-ICP-MS for $^{87}Sr/^{86}Sr$ ratio analyses. The $^{87}Sr/^{86}Sr$ values were determined using a Neptune plus MC-ICP-MS (Thermo Fisher Scientific, Germany) equipped with a nebulizer for the ESI SC-micro autosampler made with PFA (flow rate: 100 μL min^{-1}, Elemental Scientific Inc., NE, USA) and a dual cyclonic double-pass spray chamber made of quartz. The operating conditions were optimized daily for the maximum ^{88}Sr signal intensity and stability. The ^{88}Sr intensity for 200 μg kg^{-1} Sr was typically 7–10 V. Table 2 presents the typical operating conditions of MC-ICP-MS. Before measuring NIST SRM 987 solutions or purified Sr fractions, 3 % (*v*/*v*) HNO_3 blank solution was first measured each time for blank correction. After measuring all solutions, except for blank solutions, the sample introduction system of MC-ICP-MS was rinsed with 5 % (*v*/*v*) HNO_3 solution for 20 min. Outliers from the measured values of each block (50 cycles) were removed based on a 2-s test (95 % confidence interval).

Table 2. Instrument settings and data acquisition parameters for MC-ICP-MS

Instrument settings	Parameters
RF power	1200 W
Guard electrode	On
Plasma gas flow rate	15.0 L min^{-1}
Auxiliary gas flow rate	0.60–0.70 L min^{-1}
Sample gas flow rate	0.93–0.96 L min^{-1}
Sampler cone	Nickel (orifice diameter: 1.1 mm)
Skimmer cone	Nickel (orifice diameter: 0.8 mm)
Nebulizer	PFA nebulizer for SC-micro (sample uptake rate: 100 μL min^{-1})
Sampling uptake time	90 s
Wash time	20 min
Data acquisition parameters	
Scan type	Static mode
Cycles/blocks	50
Zoom optics	Focus quad, −3.00 V Dispersion quad, 0.00 V
Resolution	≈300
Integration time	8.389 s
Cup setting	L4: ^{2}Kr, L3: ^{83}Kr, L2: ^{84}Sr, L1: ^{85}Rb, C: ^{86}Sr, H1: ^{87}Sr, H2: ^{88}Sr

Blank correction, isobaric interference correction, and mass bias correction. Before all the data processing, the signal intensities at *m/z* 85, 86, 87, and 88 obtained from the blank solution measurement were subtracted from those obtained from the subsequent sample solution measurement for blank correction. The isobaric interferences of ^{86}Kr and ^{87}Rb were corrected by subtracting theoretical signal intensity of ^{86}Kr and ^{87}Rb from the signal intensities at *m/z* 86 and 87, respectively. The theoretical signal intensities of ^{86}Kr and ^{87}Rb were estimated from the measured signal intensities at *m/z* 83 and 85 using the isotope ratios of Kr and Rb (*i.e.*, $^{86}Kr/^{83}Kr$ = 0.150257 and $^{87}Rb/^{85}Rb$ = 0.385706), respectively.[40] The mass bias was corrected using the conventional internal correction technique based on the exponential law [67] using the stable Sr isotope amount ratio of $^{86}Sr/^{88}Sr$ = 0.1194 [68] (for details, refer to the Supporting Information section).

RESULTS AND DISCUSSION

Optimization of the Sr/matrix separation procedure using Sr resin and results of the NIST SRM 1567b separation

(1) Optimization of the Sr/matrix separation procedure using Sr resin

Step 1: Resin cleaning. The amounts of Milli-Q water and 0.05 mol L^{-1} HNO_3 used for the column cleaning were evaluated to keep the procedural blanks of Sr sufficiently low. The elution profile of Sr during the resin cleaning step for 0.4 and 2.0 mL Sr resin was obtained by determining the Sr amount in each fraction that passed through each column after Milli-Q water and 0.05 mol L^{-1} HNO_3 loading (Fig. S1a and b). The results showed that Milli-Q water which was ≈10 times the resin bed volume reduced the Sr blank level to a sufficiently low value of 0.1 pg for 0.4 mL Sr resins and 0.7 pg for 2.0 mL Sr resins. The trace amounts of Sr were eluted again by the subsequent loading of 0.05 mol L^{-1} HNO_3 (Fig. S1a and b insets). However, further washing with 0.05 mol L^{-1} HNO_3 using ≈10 times the resin bed volume considerably reduced the Sr blank level to 0.1 pg for 0.4 mL Sr resin and 0.4 pg for 2.0 mL Sr resin. These results implied that using 5 and 20 mL of Milli-Q water and 0.05 mol L^{-1} HNO_3 was sufficient for cleaning 0.4 and 2.0 mL Sr resin, respectively.

Step 2: Conditioning. Using 3 mL 8 mol L^{-1} HNO_3 for both 0.4 and 2.0 mL Sr resins.

Step 3*: *Sample loading. For the optimization of the HNO_3 concentration, one set of the digested NIST SRM 1567b redissolved in 1, 3, and 8 mol L^{-1} of HNO_3 was loaded onto individual columns containing 0.4 or 2.0 mL Sr resin. The Sr mass loaded onto each column was ≈0.8 μg. Subsequently, 0.4 or 2.0 mL Sr resin loaded with samples redissolved in 1, 3, and 8 mol L^{-1} HNO_3 was rinsed with 4 or 20 mL of 1, 3, and 8 mol L^{-1} HNO_3, respectively. Sr was eluted with 1 mL of 0.05 mol L^{-1} HNO_3 for 0.4 mL Sr resin and 5 mL of 0.05 mol L^{-1} HNO_3 for 2.0 mL Sr resin. The Sr recovery was determined for each experiment based on the mass of the loaded sample, mass of the purified Sr fraction, and Sr concentration in the loaded sample and the purified Sr fraction determined using ICP-MS. The experiments were repeated thrice.

Figures 1a and 1b shows the Sr recovery percentages (mean ± 1 SD) and concentration ratios of Rb/Sr and Ca/Sr for the 1, 3, and 8 mol L^{-1} HNO_3 setups. The 2.0 mL Sr resin achieved Sr recoveries

Fig. 1 Influence of the HNO_3 concentration on Sr/matrix separation during the sample loading and matrix elution steps, demonstrating its influence on Sr recoveries (a-1 and b-1) and the residual Rb/Sr (a-2 and b-2) and Ca/Sr (a-3 and b-3) concentration ratios in the purified Sr fraction. The digested solution of 6 g NIST SRM 1567b wheat flour was divided into six aliquots, with two aliquots each being redissolved in 1, 3, and 8 mol L^{-1} HNO_3 after evaporation, respectively. One set of digested NIST SRM 1567b, redissolved in 1, 3, and 8 mol L^{-1} HNO_3, was loaded onto three individual columns containing 0.4 mL Sr resin, while the other set was loaded onto three individual columns containing 2.0 mL Sr resin. Each aliquot contained ≈0.8 μg of Sr. Sr recoveries are presented as mean ± 1 SD (n = 3).

of more than 90 % at all HNO_3 setups (Fig. 1b-1). The highest recovery (97.7 % ± 1.2 %) was obtained with the 8 mol L^{-1} HNO_3 setup (Fig. 1b-1). This result was consistent with that of Horwitz et al. (1992), which showed that the capacity factor of Sr resin for Sr increases with the increasing HNO_3 concentration in the HNO_3 concentration range of 0.02 to 8 mol L^{-1}. Although 0.4 mL Sr resin achieved a high Sr recovery (96.3 % ± 0.5 %) at the 8 mol L^{-1} HNO_3 setup, the Sr recoveries with both 1 and 3 mol L^{-1} HNO_3 setups were appreciably low (Fig. 1a-1). This result suggests that using low HNO_3 concentration did not achieve sufficient retention of 0.8 µg Sr, despite the recommended working capacity of the 0.4 mL resin being 1.6 mg Sr[14], which is much larger than 0.8 µg. This discrepancy may result from the characteristic of wheat flour, i.e., the high concentration ratio of K/Sr: Sr retention on the Sr resin, already reduced by the low HNO_3 concentration, was further reduced by the high concentrations of coexisting K. In case of animal and vegetal reference materials (i.e, NIST SRM 1400, NIST SRM 1486, JCp-1, and NIST SRM 1515), which show lower concentration ratios of K/Sr than food grains, high Sr recovery (> 95 %) was previously reported in the 3 mol L^{-1} HNO_3 setup using Sr resins of small bed volumes (i.e., 0.25 and 0.3 mL) [29–31]. The concentration ratio of Rb/Sr in the purified Sr fraction in the 8 mol L^{-1} HNO_3 setup was substantially lower than those in the 1 and 3 mol L^{-1} HNO_3 setups with 0.4 and 2.0 mL Sr resins (Fig. 1a-2 and 1b-2). In contrast, the concentration ratio of Ca/Sr was highest in the 8 mol L^{-1} HNO_3 setup (Fig. 1a-3 and 1b-3). These results align with those reported by Horwitz et al. (1992), which showed that the capacity of Sr resin to retain Rb decreases, while its capacity to retain Ca increases with the increasing HNO_3 concentration. No significant difference of Sr recovery, and concentration ratios of Rb/Sr and Ca/Sr were observed between 0.4 and 2.0 mL Sr resins in the 8 mol L^{-1} HNO_3 setup (Fig. 1a and 1b).

Based on these results, 8 mol L^{-1} HNO_3 was selected as the optimum HNO_3 concentration for use in the sample loading and rinsing to achieve high Sr recovery and effective Rb removal as Rb causes more severe spectral interference than Ca at much lower concentrations in $^{87}Sr/^{86}Sr$ ratio measurements. Although relatively low HNO_3 concentrations (1–3 mol L^{-1}) have been used for Sr/matrix separation in food grains,[24,28] the results of this study suggest that low HNO_3 concentrations are not recommended for food grains, especially with small Sr resin bed volumes. The low HNO_3 concentration with small Sr resin bed volume may markedly reduce Sr recovery, and even with large Sr resin bed volumes, insufficient Sr/Rb separation may cause nonnegligible isobaric interferences from Rb under some conditions in $^{87}Sr/^{86}Sr$ ratio measurements.

Step 4: Rinsing. The volume of 8 mol L^{-1} HNO_3 used for the rinsing step was evaluated for the 0.4 and 2.0 mL of Sr resin to achieve a complete removal of the matrix elements. After loading the digested 2.5 g of NIST SRM 1567b, which was redissolved in 8 mol L^{-1} HNO_3, onto columns containing 0.4 or 2.0 mL of Sr resin, the columns were rinsed using 4 or 20 mL of 8 mol L^{-1} HNO_3, respectively. Each rinsing fraction was collected by 1 mL. The recovery percentages of the matrix elements, which possibly caused the spectroscopic interferences toward the Sr isotopes (Rb, Ca, Fe, and Zn) in each fraction, were determined based on the total amount of each element loaded onto the columns (≈1.7 µg Rb, 480 µg Ca, 35 µg Fe, and 29 µg Zn) and the amount of each element contained in each fraction. In the case of the 0.4 mL Sr resin, the matrix element recoveries reached 100 % by an R-2 fraction (Fig. 2a). The total recovery of each element by an R-2 fraction was as follows: Rb: 100 %; Ca: 104 %; Fe: 100 %; and Zn: 100 %. In the case of the 2.0 mL Sr resin, the matrix element recoveries reached 100% by an R-4 fraction (Fig. 2b). The total recovery of each element by an R-4 fraction was as follows: Rb: 100 %; Ca: 103 %; Fe: 100 %; and Zn: 101%. In consideration of the significantly high concentration of these matrix elements

Fig. 2 Elution profiles of Sr and matrices obtained from the digested 2.5 g NIST SRM 1567b wheat flour being redissolved in 8 mol L^{-1} HNO_3. These profiles were obtained during sample loading and rinsing steps with 8 mol L^{-1} HNO_3 and subsequent Sr elution step with 0.05 mol L^{-1} HNO_3 for 0.4 mL (a) and 2.0 mL (b) Sr resins. The digested 2.5 g of NIST SRM 1567b loaded onto each column contained approximately 2 µg Sr, 1.7 µg Rb, 480 µg Ca, 35 µg Fe, and 29 µg Zn. A fraction of the 0 mL elution volume corresponds to a loading effluent.

relative to Sr, we decided to rinse 0.4 and 2.0 mL Sr resins using 4 and 20 mL 8 mol L^{-1} HNO_3, respectively. The total recoveries of Sr eluted in rinse fractions were less than 1 % with both 0.4 and 2.0 mL Sr resins.

Step 5: Sr elution. The volume of 0.05 mol L^{-1} HNO_3 collected as the purified Sr fraction was evaluated to achieve a high Sr recovery for the 0.4 and 2.0 mL Sr resin. After the abovementioned rinsing step of Sr resin loaded with the digested NIST SRM 1567b, 2.5 and 14 mL of 0.05 mol L^{-1} HNO_3 were loaded onto the columns containing 0.4 and 2.0 mL Sr resins, respectively. The effluents were collected with every 0.25 mL of aliquot with 0.4 mL Sr resin and 1 mL of aliquot with 2.0 mL Sr resin. For simplicity, each fraction will be referred to herein as E-1, -2, -3, and so on in the order of their collection. The Sr amount in each fraction was determined using ICP-MS. Based on the results, the Sr recovery of each fraction relative to the total Sr amount loaded onto the column (2.0 μg) was plotted for the 0.4 mL (Fig. 2a) and 2.0 mL (Fig. 2b) Sr resin. With the 0.4 and 2.0 mL Sr resin, Sr had not yet eluted in E-1 and began eluting from E-2 onward. More than 98 % of the loaded Sr was recovered between E-2 and E-5 and between E-2 and E-6 for the 0.4 and 2.0 mL Sr resin, respectively. Therefore, fractions E-2 to E-5 (total volume, 1 mL) for the 0.4 mL Sr resin and E-2 to E-6 (total volume, 5 mL) for the 2.0 mL Sr resin were collected as purified Sr fractions. Table 3 presents the Sr/matrix separation procedures for the 0.4 and 2.0 mL Sr resin employed in this study.

(2) Results of the Sr/matrix separation of NIST SRM 1567a and b. The optimized Sr/matrix separation procedure was applied to NIST SRM 1567a in addition to NIST SRM 1567b. These two reference materials had the same sample matrix of wheat flour, but different production lots. Prior to the Sr/matrix separation, the sample digestion was performed for seven and six replicates of 1567a and b, respectively. Each digestion was processed for Sr/matrix separation using individual columns containing 0.4 or 2.0 mL Sr resin. For simplicity, each column was named based on its resin bed volume and sequential serial number. For example, "C0.4-10" refers to a 10th column containing 0.4 mL Sr resin.

Table 3. Sr/matrix separation procedures for a column containing 0.4 and 2.0 mL Sr resins employed in this study

Steps	Reagent	Reagent volume (mL)	
		0.4 mL Sr resin	2.0 mL Sr resin
Step 1: Column cleaning	Milli-Q water	5	20
	0.05 mol L^{-1} HNO_3	5	20
Step 2: Conditioning	8 mol L^{-1} HNO_3	3	3
Step 3: Sample loading	8 mol L^{-1} HNO_3	2.5	2.5
Step 4: Rinsing	8 mol L^{-1} HNO_3	4	20
Step 5: Sr elution	0.05 mol L^{-1} HNO_3	1	5

The mean values of the Sr recoveries and the associated 1 SD were 97.0 % ± 1.3 % (n = 7) for NIST SRM 1567a and 97.0 % ± 1.2 % (n = 7) for NIST SRM 1567b (Table S3). The elemental analyses of the residual Rb and Ca in the Sr fractions were performed using ICP-MS to confirm that the Sr/matrix separation of NIST SRM 1567a and b was successfully conducted. The mean values for the concentration ratios of Rb/Sr × 100 in the purified Sr fractions were 0.0006 % ± 0.00003 % (n = 7) for NIST SRM 1567a and 0.0005 % ± 0.00004 % (n = 7) for NIST SRM 1567b. The $^{85}Rb/^{88}Sr$ intensity ratio × 100 in MC-ICP-MS measurements was also obtained (Table S2) for comparison with the other reference materials described below. The mean values of the $^{85}Rb/^{88}Sr$ intensity ratio × 100 were 0.00017 % ± 0.00007% (SD, n = 7) for NIST SRM 1567a and 0.00014 % ± 0.00003% (n = 7) for NIST SRM 1567b. The mean values of the concentration ratio of Ca/Sr in the purified Sr fractions of NIST SRM 1567a and b were 1.3 ± 0.1 (n = 7), and 1.5 ± 0.2 (n = 7), respectively. Based on these results, the effect of the residual Ca and Rb in the purified Sr fractions is discussed in detail in the subsequent section.

Influence of the residual Rb and Ca on the measured $^{87}Sr/^{86}Sr$ ratios

Long-term reproducibility of the $^{87}Sr/^{86}Sr$ ratios for NIST SRM 987. The long-term reproducibility of $^{87}Sr/^{86}Sr$ for NIST SRM 987 was determined by repeatedly analyzing the NIST SRM 987 solution over a 29-month period from February 2021 to June 2023. The reproducibility was calculated as 0.710255 ± 0.000022 (mean ± 2 SD, n = 100, Fig. 3a). The reproducibility was in good agreement with the data available in the literature for NIST SRM 987 determined by TIMS techniques, such as 0.710248 ± 0.000011 (mean ± 2 SD, n = 427) [69] and 0.710263 ± 0.000016 (mean ± 2 SD, n = 43).[70] The result was also in good agreement with the literature values determined by the MC-ICP-MS instruments, such as 0.710245 ± 0.000037 (mean ± 2 SD, n = 16),[71] 0.710273 ± 0.000033 (mean ± 2 SD, n = 97),[72] and 0.71025 ± 0.00002 (mean ± 1 SD, n = 41).[73]

Spectral interferences caused by the residual Rb and Ca in the Sr fraction. Although the effects of the residual Rb and Ca were evaluated by Irrgeher *et al.* (2013),[19] Liu *et al.* (2016),[31] and Fortunato *et al.* (2004),[74] a comparison of their results showed that the effects of the residual Rb and Ca vary to a large extent depending on the instrumental settings and equipment. As for the range of the residual Rb without substantial effect on the measured values of the $^{87}Sr/^{86}Sr$ ratio, Irrgeher *et al.* (2013) [19] showed a range of $^{85}Rb/^{88}Sr < 0.002$ % (expressed as an intensity ratio × 100 at the MC-ICP-MS measurements), while Liu et al. (2016) demonstrated $^{85}Rb/^{88}Sr < 1$ % (expressed as an intensity ratio × 100 at the MC-ICP-MS measurements and corresponding to the concentration ratio of Rb/Sr < 0.013 %).[31] As for the range of the residual Ca that cannot make a significant effect on the measured values of the $^{87}Sr/^{86}Sr$ ratio, Irrgeher *et al.* (2013) [19] reported a

spiked with various amounts of Rb or Ca were measured to investigate the influences of Rb and Ca in analyte solutions. In Fig. 3b, the $^{87}Sr/^{86}Sr$ ratios deviated from the long-term reproducibility range when the Rb concentrations in the analyte solutions exceeded 0.1 μg kg^{-1} (0.04 % expressed as the intensity ratio of the $^{85}Rb/^{88}Sr$ × 100 at MC-ICP-MS measurements or 0.05 % expressed as the concentration ratio of Rb/Sr × 100). By contrast, the $^{87}Sr/^{86}Sr$ ratios were in the long-term reproducibility range when the Rb concentrations in the analyte solutions did not exceed 0.01 μg kg^{-1} (0.004 % expressed as the intensity ratio of $^{85}Rb/^{88}Sr$ × 100 at the MC-ICP-MS measurements or 0.005 % expressed as the concentration ratio of Rb/Sr × 100). These results indicated that the isobaric interference correction method of Rb described in the "EXPERIMENTAL" section works efficiently when the Rb concentration is sufficiently low. Fig. 3c shows that the $^{87}Sr/^{86}Sr$ ratios deviated from the long-term reproducibility range when the Ca concentrations in the analyte solutions exceeded 10 mg kg^{-1} (50 expressed as the concentration ratio of Ca/Sr). In contrast, no detectable deviation of the $^{87}Sr/^{86}Sr$ ratios from the range of long-term reproducibility was observed when the Ca concentrations in the analyte solutions did not exceed 5 mg kg^{-1} (25 expressed as the concentration ratio of Ca/Sr). This result indicated that the influence of the polyatomic interference caused by Ca on the $^{87}Sr/^{86}Sr$ ratios of the 200 μg kg^{-1} Sr solutions is negligible when the Ca concentrations are not exceeding 5 mg kg^{-1}.

As mentioned in the "Results of the Sr/matrix separation of NIST SRM 1567a and b" section, the mean values and associated 1 SD of the $^{85}Rb/^{88}Sr$ intensity ratio × 100 in MC-ICP-MS measurements were 0.00017 % ± 0.00007 % (n = 7) for NIST SRM 1567a and 0.00014 % ± 0.00003 % (n = 7) for NIST SRM 1567b. Both values were sufficiently lower than 0.004 %. The mean values of the concentration ratio of Ca/Sr in the purified Sr fractions of NIST SRM 1567a and b were 1.3 ± 0.1 (n = 7) and 1.5 ± 0.2 (n = 7), respectively, which were sufficiently lower than 25. These results showed that an effective Sr/matrix separation can be achieved for a reliable $^{87}Sr/^{86}Sr$ ratio determination of the food grain matrix when the optimized condition is employed.

Fig.3 $^{87}Sr/^{86}Sr$ ratios of NIST SRM 987 solutions, as measured in this study (a). Broken lines represent the range of long-term reproducibility. Close circles denote outliers beyond the reproducibility range. The $^{87}Sr/^{86}Sr$ ratios obtained for 200 μg kg^{-1} NIST SRM 987 solutions spiked with various amounts of Rb (b) and Ca (c). Error bars in each figure show the associated 2 SD values for individual measurements (n = 5).

concentration ratio of Ca/Sr ≤ 2, while Fortunato *et al.* (2004) demonstrated a concentration ratio of Ca/Sr ≤20.[74] These results suggested that it is essential to evaluate the effects of residual Rb and Ca according to the instrumental settings and equipment.

The $^{87}Sr/^{86}Sr$ ratios of the 200 μg kg^{-1} NIST SRM 987 solutions

Results of the Sr/matrix separation using the optimized procedure and the $^{87}Sr/^{86}Sr$ ratio measurements of the vegetal, animal, and geological reference materials

Method validation for sample acid digestion and evaluation of procedural blanks of Sr. The sample acid digestion method was validated via the quantitative analyses of Sr present in vegetal and animal standard reference materials using ICP-MS prior to $^{87}Sr/^{86}Sr$ ratio measurements. Three replicates of NIST SRM 1515, NIST SRM 1570a, NIST SRM 1400, NIST SRM 1486, NMIJ CRM 7502-a, and JCp-1 were digested. The Sr concentrations of NIST SRM 1567a and b were not certified; hence, the reference material of rice flour (NMIJ CRM 7502-a), which had a chemical composition similar to that of wheat flour, was used to substitute

Fig. 4 $^{87}Sr/^{86}Sr$ ratios of two vegetal reference materials (NIST SRM 1515 apple leaves and 1570a spinach) measured in this study and comparison with literature data. Each circle represents the measured value of an aliquot from each digested solution. The number of digestion (e.g., digestion 1 etc.) corresponded to that in Table S2. Closed and open circles denote the results obtained from Sr/matrix separation with 0.4 and 2.0 mL Sr resins, respectively. The mean value ± 2 SD obtained from each digested solution is represented by the same-colored broken line. Gray broken lines indicate the mean value of all measured values and their associated 2 SD. Open square denotes the published $^{87}Sr/^{86}Sr$ ratio and its associated 2 SD. Studies corresponding to each number are listed here, along with the measurement method for $^{87}Sr/^{86}Sr$ ratios used in each work, i.e., NIST SRM 1515 (1, MC-ICP-MS;[31] 2, MC-ICP-MS;[32] 3, TIMS;[33] 4, TIMS;[34] and 5, MC-ICP-MS [35]) and NIST SRM 1570a (1, MC-ICP-MS;[17] and 2, TIMS [36]).

NIST SRM 1567a and b. The Sr concentrations of the three aliquots from each digested solution were determined using ICP-MS. Each aliquot was analyzed thrice. The measured and certified values were in good agreement, showing that the acid digestion procedure was appropriately performed (Table S3). Additionally, the total procedural blank levels for Sr were evaluated. The total procedural blanks of Sr, including all experimental procedures (e.g., acid digestion and Sr/matrix separation), were 8.8 pg for 0.4 mL Sr resin and 9.5 pg for 2.0 mL Sr resin, which were sufficiently small compared with the mass amount of Sr loaded onto columns (0.9–29.5 μg).

Sr/matrix separation using the optimized procedure. The Sr/matrix separations of the two vegetal reference materials (NIST SRM 1515 and NIST SRM 1570a), four animal reference materials (NIST SRM 1400, NIST SRM 1486, JCp-1, and FEBS-1), and two geological reference materials (JA1 and JB2) were performed under the optimized condition. Two to five replicates of each reference material digestion were individually conducted prior to the Sr/matrix separation (Table S2). Each digest was processed for the Sr/matrix separation using individual columns containing 0.4 or 2.0 mL Sr resin. High Sr recoveries ≥95 % were established with all purified Sr fractions from all the vegetal and animal reference materials, regardless of Sr amounts loaded onto columns and Sr resin bed volumes (Table S2). The mean values and associated 1 SD of Sr recoveries were 97.4 % ± 2.4 % (n = 5) for NIST SRM 1515, 97.3 % ± 1.3 % (n = 5) for NIST SRM 1570a, 97.2 % ± 1.4 % (n = 5) for NIST SRM 1400, 97.7 % ± 1.6 % (n = 5) for NIST SRM 1486, 97.0 % ± 1.0 % (n = 5) for JCp-1, 97.4 % ± 1.1 % (n = 5) for FEBS-1, 94.5 % ± 1.5 % (n = 2) for JA1, and 91.0 % ± 0.3 % (n = 2) for JB2. The signal intensity ratios of $^{85}Rb/^{88}Sr \times 100$ in MC-ICP-MS measurements for all purified Sr fractions from all reference materials were <0.00100 % (much lower than 0.004 %), confirming that the interference correction method of Rb described in the "EXPERIMENTAL" section is sufficient (Table S2). In addition, the Ca concentration in each purified Sr fraction from each reference material was less than 300 μg kg^{-1} for 200 μg kg^{-1} Sr (much lower than 5 mg kg^{-1}). This corresponded to a Ca/Sr concentration ratio <1.5 (much lower than 25). These results implied that the Sr/matrix separation of every reference material was successfully performed with the optimized procedure. This procedure is applicable to a wide range of sample matrices.

$^{87}Sr/^{86}Sr$ ratio measurements of the vegetal, animal, and geological reference materials. The $^{87}Sr/^{86}Sr$ ratios of three to six aliquots from each purified Sr fraction were measured between February 2021 and June 2023 (Fig. 4–7 and Table S2). Each circle in Figures 4–7 represents the measured value of an aliquot from each digested solution, with closed and open circles indicating results obtained from Sr/matrix separation with 0.4 and 2.0 mL Sr resin, respectively. The mean value of the results from each digested

Fig. 5 $^{87}Sr/^{86}Sr$ ratios of four animal reference materials—NIST SRM 1400 bone ash, 1486 bone meal, GSJ JCp-1 coral, and NRC FEBS-1 otolith— measured in this study and comparison with literature data. Each circle represents the measured value of an aliquot from each digested solution. The number of digestion (e.g., digestion 1, digestion 2, etc.) corresponded to that in Table S2. Closed and open circles denote the results obtained from Sr/matrix separation with 0.4 and 2.0 mL Sr resins, respectively. The mean value ± 2 SD obtained from each digested solution is represented using the same-colored broken line. Gray broken lines represent the mean value of all measured values and their associated 2 SD. Open square denotes the published $^{87}Sr/^{86}Sr$ ratio and its associated 2 SD. Literatures corresponding to each number are listed here, along with the measurement method for the $^{87}Sr/^{86}Sr$ ratios employed in each work, i.e., NIST SRM 1400 (1, TIMS;[15] 2, MC-ICP-MS;[18] 3, MC-ICP-MS;[37] 4, MC-ICP-MS;[38] and 5, MC-ICP-MS [36]), NIST SRM 1486 (1, TIMS;[15] 2, MC-ICP-MS;[18] 3, TIMS;[39] 4, MC-ICP-MS;[40] 5, MC-ICP-MS;[38] and 6, MC-ICP-MS [36]), GSJ JCp-1 (1, MC-ICP-MS;[41] 2, NanoSIMS;[42] 3, TIMS;[43] 4,TIMS;[44] 5, MC-ICP-MS;[45] 6, TIMS;[46] 7, MC-ICP-MS;[38] 8, 9, LA-ICP-MS;[47] and 10, TIMS [36]), and FEBS-1 otolith (1, MC-ICP-MS;[48] and 2, LA-MC-ICP-MS [48]).

solution was in good agreement with each other within the 2 SD range for all reference materials (Figs. 4–7 and Table S2), indicating that successful sample digestion and Sr/matrix separation. No significant difference was observed between results obtained with 0.4 and 2.0 mL Sr resins, indicating that the difference in the resin bed volume did not affect the measured$^{87}Sr/^{86}Sr$ ratios when Sr/matrix separation was performed under appropriate conditions. In addition, mean values for these eight reference materials (NIST SRM 1515, NIST SRM 1570a, NIST SRM 1400, NIST SRM 1486, JCp-1, FEB-1, JA1, and JB2) were in good agreement with literature values within the 2 SD range (Fig. 4–6). The 2 SD value of $^{87}Sr/^{86}Sr$ ratios measured in this study was reasonable compared with literature values obtained via MC-ICP-MS, confirming the validity of the overall method for determining $^{87}Sr/^{86}Sr$ ratios.

Finally, the method was applied to standard reference materials, NIST SRM 1567a and b that appeared to have not been measured in the literature. The $^{87}Sr/^{86}Sr$ ratios of NIST SRM 1567a and b were determined as 0.70895 ± 0.00005 (mean ± 2 SD, n = 34) and

Fig. 6 $^{87}Sr/^{86}Sr$ ratios of two geological reference materials—GSJ JA1 andesite and JB2 basalt—measured in this study and comparison with literature data. Each circle represents the measured value of an aliquot from each digested solution. The number of digestion (e.g., digestion 1, digestion 2, etc.) corresponded to that in Table S2. The mean value ± 2 SD obtained from each digested solution is represented using a broken line of the same color. Gray broken lines represent the mean value of all measurements and their associated 2 SD. Open square denotes the published $^{87}Sr/^{86}Sr$ ratio and its associated 2 SD. Studies corresponding to each number are listed here, along with the method employed for measuring $^{87}Sr/^{86}Sr$ ratios in each work, i.e., JA1 (1, TIMS;[49] 2, TIMS;[50] 3, TIMS;[51] 4, TIMS;[52] 5, TIMS;[53] 6, TIMS;[54] and 7, 8, MC-ICP-MS [55]) and JB2 (1, TIMS;[54] 2 TIMS;[53] 3, TIMS;[56] 4, TIMS;[57] 5, TIMS;[58] 6, MC-ICP-MS;[59] 7, TIMS;[60] 8, TIMS;[61] 9, TIMS;[62] 10, TIMS;[63] 11-14, TIMS;[27, 52] 15, TIMS;[64] 16, MC-ICP-MS;[65] and 17, TIMS [66]).

Fig. 7 $^{87}Sr/^{86}Sr$ ratios of two vegetal reference materials newly measured in this study: NIST SRM 1567a and b wheat flour. Close circles represent the mean value of the measured values of three to six aliquots from each Sr fraction obtained by separating seven or six individual digested replicates of the reference material using individual columns and the associated 2 SD. The number of digestion (e.g., digestion 1, digestion 2, etc.) corresponds to that in Table S2. Closed and open circles denote the results obtained from Sr/matrix separation with 0.4 and 2.0 mL Sr resins, respectively. Solid and broken lines represent the mean value of all measured values and the associated 2 SD, respectively.

0.70898 ± 0.00003 (mean ± 2 SD, n = 25), respectively (Fig. 7). The relative 2 SD values on the $^{87}Sr/^{86}Sr$ ratio of these two reference materials were 0.0057 % and 0.0040 %, respectively. These values were reasonable compared to the relative 2 SD values of the other reference materials measured in this work, i.e., NIST SRM 987 (0.0032 %), NIST SRM 1515 (0.0034%), NIST SRM 1570a (0.0033 %), NIST SRM 1400 (0.0020 %), NIST SRM 1486 (0.0041 %), GSJ JCp-1 (0.0028 %), NRC FEB-1 (0.0022 %), GSJ JA1 (0.0030 %), and GSJ JB2 (0.0027 %)

CONCLUSION

The Sr/matrix separation protocol using the Sr resin was optimized for food grains. Food grains are characterized by noticeably low Sr concentration, and high concentration ratios of Rb/Sr and K/Sr, which complicate Sr/matrix separation. This study showed that this issue could be solved using a high concentration of HNO_3 (8 mol L^{-1}) during the sample loading step for Sr/matrix separation. High Sr recovery and sufficient Sr/Rb separation in the standard reference material of wheat flour (NIST SRM 1567b) were achieved with the 8 mol L^{-1} HNO_3 setup. Conversely, this study indicated that using low HNO_3 concentrations (1 and 3 mol L^{-1}) during this step is not recommended for food grains, especially with small resin bed volumes. For NIST SRM 1567b, Sr recoveries were appreciably low with the 1 and 3 mol L^{-1} HNO_3 setups when using the 0.4 mL Sr resin, and the concentration ratios of Rb/Sr in purified Sr fractions were considerably higher than that of the 8 mol L^{-1} HNO_3 setup, regardless of resin bed volumes.

Finally, the $^{87}Sr/^{86}Sr$ ratios of reference materials NIST SRM 1567a and b were determined. Although method validation using literature values of reference materials with similar sample matrices is essential for the accurate and precise determination of the $^{87}Sr/^{86}Sr$ ratio, to the best of our knowledge, the values for food grain reference materials, including NIST SRM 1567 a and b, have not been previously reported. Therefore, this study contributes to improving the reliability of $^{87}Sr/^{86}Sr$ ratio measurements for determining the geographical origin of foods, including food grains.

ASSOCIATED CONTENT

The supporting information (Table S1-S3 and Fig. S1) is available at www.at-spectrosc.com/as/home.

AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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