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Measurement of strontium isotope ratio in nitric acid extract of peanut testa by ICP-Q-MS after removal of Rb by extraction with pure water

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ABSTRACT

The difference in the distributions of Sr and Rb in peanut seeds was utilized to develop a precise method for Sr isotope ratio measurement by inductively coupled plasma quadruple mass spectrometry (ICP-Q-MS). The testa instead of the whole peanut seed was selected as the sample because apparent enrichment of Sr in comparison to Rb was found in the testa. Furthermore, Rb in the testa was removed by pure water extraction with the aid of sonication to remove the isobaric interference in Sr isotope ratio measurement. The testa taken from one peanut seed was treated as one sample for the analysis. After optimization of the operating conditions, pure water (10 mL for each sample) extraction in 30 min with sonication was able to remove over 95% of Rb in the testa, while after the Rb removal Sr could be completely extracted using 10 mL of 0.3 mol L^{-1} HNO_3 for each sample. The integration time in ICP-Q-MS measurement was optimized to achieve a lower measurement uncertainty in a shorter time; the results showed that 1 s was required and enough for the precise measurement of Sr isotope ratios giving a relative standard uncertainty ($n=10$) of *ca.* 0.1%. The present method was applied to peanut seeds grown in Japan, China, USA, India, and South Africa.

1. Introduction

Strontium has four stable and naturally occurring isotopes, *i.e.* ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr [1]. In these isotopes, ^{87}Sr is the unique radiogenic isotope whose concentration gradually increases due to the radioactive decay of ^{87}Rb isotope with a half-life of *ca.* 49 billion years [2].The concentration of ^{87}Sr and its ratio to other Sr isotopes vary with geological ages and consequently geographical locations. Based on this property, Sr isotope ratio has been measured as a tracer of geographical origin of food samples [3–13] and drinks [14,15] as well as a tracer of ecosystem processes [16].

Because ^{87}Sr is the radiogenic daughter of ^{87}Rb, they often occur together in natural samples. The atomic masses of ^{87}Rb and ^{87}Sr are respectively 86.9091858(28) and 86.9088816(25) [17], where the number in each bracket is the expanded uncertainty following the last significant figure. This fact indicates that if a mass spectrometer could completely separate ^{87}Rb from ^{87}Sr, the resolution of the mass spectrometer will reach at least 286 000. Such a high resolution mass spectrometer is impracticable and pretreatments of natural samples are often required to separate ^{87}Rb from the samples prior to the measurement of ^{87}Sr.The separation of Rb from Sr could be achieved with solid phase extraction using cation exchange resin [3,6] or Sr–resin [5] as well as with chromatographic separation [13,14].

Peanut, *Arachis hypogaea L.*, is one of popular food materials in many countries of the world. The world peanut total production is *ca.*29 million metric tons per year, with China, India, and USA as the top three leading countries [18]. Commerce of peanut is active among various countries and proper information on the geographical origin will be valuable for fair trade of peanut. However, there are few reports on this topic up to date. Therefore, the authors are trying to provide a measurement method for Sr isotope ratio in peanut, which could be a candidate factor for tracing the graphic origin.

The present authors had done a research on the distribution of various elements in different parts of peanut seed, *i.e.*, the testa, the embryonic axis, and the cotyledon [19]. In that work, distribution of 18 elements, including Sr, was obtained in the parts of peanut seed after completely digestion using HNO_3, H_2O_2, and HF with the assist of microwave irradiation. The results showed that Sr was relatively enriched in the testa. By contrast, Rb was at the same level to the other parts or relatively depleted. These facts indicate that testa might be an ideal sample for testing the Sr isotope ratios in peanut seed.

In the present work, a simple extraction method, instead of the complete acid digestion adopted in the previous work [19], was investigated to obtain the sample for measuring Sr isotope ratios in the testa of peanut seed, along with the removal effect of Rb

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prior to the extraction of Sr. The present method requires only pure water and diluted nitric acid for pretreatment of the sample, which is much simpler than the separation methods using cation exchange resins, Sr-resins, or chromatographs. Pure water extraction with the assist of sonication was investigated and applied to the removal of Rb from the testa sample. After the removal, extraction of Sr was carried out with diluted nitric acid and sonication. The present method was applied to the analysis of Sr isotope ratios in peanut seed samples grown in Japan, China, USA, India, and South Africa.

2. Experimental

2.1. Instrumentation

The measurements of Rb and Sr isotopes were carried out using an inductively coupled plasma quadruple mass spectrometer (ICP-Q-MS) of Agilent 7700x (Agilent Technologies, Tokyo, Japan). The typical operating conditions are summarized in Table 1, and these conditions were checked and optimized daily prior to the experiment. The measurement operation was carried out with the assist of an auto-sampler (ASX 520, CETAC Technologies, Omaha, USA). Pure water extraction of Rb and nitric acid extraction of Sr were carried out using an ultrasonic cleaner (*VS*-100III, As One Co. Ltd, Osaka, Japan) working at 28 kHz and 100 W. A microwave digestion instrument (ETHOS 1, Milestone General K.K., Kawasaki, Japan) and TFM® digestion vessels were utilized for acid digestion of the testa residual after extraction to check the extraction efficiencies of Rb and Sr. Pure water used throughout the present experiment was prepared using a Millipore purification system (Element, Nihon Millipore Kogyo, Tokyo, Japan).

2.2. Chemicals and materials

Single-element standards of Rb and Sr (guaranteed by the Japan Calibration Service System, JCSS) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). An isotope standard of Sr, NIST SRM 987, was purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, USA). Ultrapur® grade of HNO_3, H_2O_2, and HF for extraction and digestion of the samples and making sample solutions were also purchased from Kanto Chemical Co., Inc. The raw peanut seeds (without the husk) grown in Japan (4 brands), China (3 brands), USA (1 brand), India (1 brand), and South Africa (1 brand) were purchased from the market in Japan. All the tests were carried out using peanut seeds from a brand grown in Japan. Extraction of Rb and Sr from the peanut testa was carried out using 15-mL polypropylene centrifuge tubes with high density polyethylene caps purchased from As One Co. Ltd. The initial centrifuge tubes and caps were clean enough for the analysis of Rb and Sr, which were confirmed in a preliminary test. Therefore, the centrifuge tubes and caps were applied in the present experiment without prewashing using acid solutions.

Table 1
Typical operating conditions of ICP-MS.

ICP-MS (Agilent 7700x)		
Plasma conditions:		
	Incident power	1.55 kW
	Coolant gas flow rate	Ar 15.0 L min^{-1}
	Auxiliary gas flow rate	Ar 0.90 L min^{-1}
	Sample gas flow rate	Ar 0.80 L min^{-1}
	Make-up gas flow rate	Ar 0.40 L min^{-1}
	Dilution gas mode	Off
	Collision gas flow rate	He 4.00 L min^{-1}
Sampling conditions		
	Sampling depth	8 mm from load coil
Nebulizer: MicroMist		
	Sample uptake rate	0.4 mL min^{-1}
Spray chamber: Scott double path		
	Wall temperature	2 °C
Data acquisition		
	Peak pattern	isotope analysis
	Data points	3 points per peak
	Integration time	1 s
	Replicates	10

2.3. Optimized pretreatment of the sample for measurement

The peanut seeds were randomly taken from the stock of each brand. Peanut seeds were heated in an oven at 105 °C for 1 h prior to separating the testa from the peanut seed. The testa from each peanut seed was rinsed with pure water and then put into a centrifuge tube, into which 10 mL pure water was added. The centrifuge tube was caped and subjected to sonication for 30 min. After that, the testa was washed with pure water. And then, the testa was put into the centrifuge tube and 10 mL of 0.3 mol L^{-1} HNO_3 was added. After sonication for 30 min, the HNO_3 extract was properly diluted for measurement by ICP-Q-MS.

3. Results and discussion

3.1. Rb and Sr in different parts of peanut seed

From the data in a previous research on the distribution of the elements in different parts of peanut seeds from Japan and China [19], the present authors found that Sr in peanut seed was enriched in the testa while Rb was depleted in the testa. For example, the Sr/Rb ratios in the testa and the total peanut seed grown in China were 6.8 and 0.57, respectively. This fact indicates that the testa has relatively lower Rb content and is fit for Sr isotope analysis instead of the total peanut seed. Therefore, the testa was selected as the target part for analysis.

3.2. Optimization of integration time for isotope analysis

The integration time of ICP-Q-MS was optimized to measure Sr isotope ratios with a better precision. Optimization of the integration time was carried out using a 5 ng mL^{-1} Sr standard solution in 0.3 mol L^{-1} HNO_3. The relative standard uncertainties of measured $^{87}Sr/^{86}Sr$ ratio were investigated with the integration time of 0.1, 0.3, 0.5, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.5, and 2 s. The observed relative standard uncertainties are plotted in Fig. 1 against the integration time, where the value for each relative expanded uncertainty was calculated from the standard deviation of 10 replicates: *i.e.*, the standard deviation was divided by the positive square root of 10 and multiplied by the coverage factor $k(=2)$. It can be seen that the relative expanded uncertainty decreased gradually from *ca.* 0.5% to *ca.* 0.15% with the increase of integration time from 0.1 s to 1.0 s. However, when the integration time was over 1 s, decrease of the relative expanded uncertainty was insignificant even by increasing the integration time to 2 s. Therefore, the measurements in the following experiments were performed with an integration time of 1 s.

3.3. The influence of Rb concentration on the accuracy and the precision of Sr isotope measurement

The interference of remaining ^{87}Rb with the measurement of ^{87}Sr could be corrected mathematically based on the isotopic composition of Rb. However, the precision of measured $^{87}Sr/^{86}Sr$ isotope ratio depended on the measurand/interference ratio. The dependence of

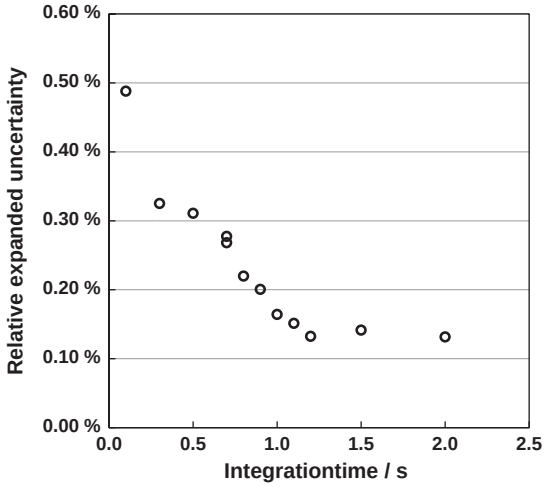

Fig. 1. Dependence of the relative expanded uncertainty of $^{87}Sr/^{86}Sr$ measurement on the integration time.

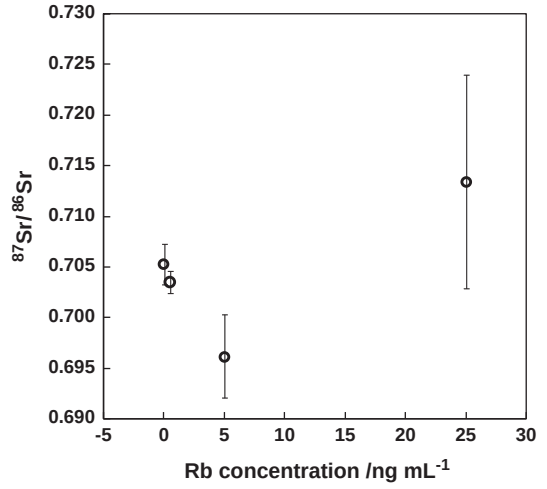

Fig. 2. Dependence of the accuracy and the precision of $^{87}Sr/^{86}Sr$ measurement on the concentration of Rb. The concentration of Sr in each solution was 5 ng mL^{-1}. The bar corresponding to each data point indicates the standard uncertainty of measurement.

the precision of measured $^{87}Sr/^{86}Sr$ isotope ratio on the relative concentration of Rb in the solution was investigated. Measurements of the $^{87}Sr/^{86}Sr$ isotope ratio were carried out for test solutions containing 5 ng mL^{-1} of Sr in 0.3 mol L^{-1} HNO_3 with various concentrations of Rb, *i.e.* 0, 0.5, 5, and 25 ng mL^{-1}. The results are illustrated in Fig. 2, for which the signal intensities of ^{87}Sr was obtained after subtracting the ^{87}Rb signal intensities based on the observed $^{85}Rb/^{87}Rb$ ratio in a Rb standard solution. It can be seen that the result obtained using the test solution with 0.5 ng mL^{-1} of Rb agreed with that without Rb. By contrast, the results obtained using the test solutions with 5 ng mL^{-1} and 25 ng mL^{-1} Rb were obviously different from that without Rb and were much more imprecise. These results could be attributed to the fact that the intensity ratios of $^{87}Rb/^{87}Sr$ in the test solutions (Sr, 5 ng mL^{-1}) with 0, 0.5, 5, and 25 ng $mL^{-1}$of Rb were *ca.* 0, 0.4, 4, and 20, respectively.

Based on our previous results [19], the Rb/Sr ratios in the testa of peanut seeds grown in China and Japan were *ca.* 0.1 and *ca.*1, respectively. These results indicate that the $^{87}Sr/^{86}Sr$ isotope ratio in the testa of peanut seed grown in China might be measured in good accuracy and good precision without any removal of Rb. However, removal of Rb is required for peanut seed grown in Japan for precise measurement of $^{87}Sr/^{86}Sr$ isotope ratio.

3.4. Optimization of pure water extraction for Rb removal

Because Rb is one of the alkali metals, it is easily soluble in water. The present authors tried a preliminary check on pure water extraction of Rb from the testa of peanut seed, for which the results showed that Rb could be extracted with pure water and Sr was almost not extracted (extraction rate less than 1%). Therefore, further investigation of the extraction condition was carried out for optimization. The extraction rates of Rb in two individual samples with a sonication time of 10 to 60 min were plotted in Fig. 3. It can be seen that the extraction rate of Rb for both samples were over 90% after a sonication time of 30 min, which permitted the precise measurement of $^{87}Sr/^{86}Sr$ isotope ratios. Therefore, sonication time was set to 30 min for the following experiment.

In the present experiment, the testa was separated from the peanut seed after heating in an oven (dry separation). The testa could also be separated from the peanut seed after sonication in pure water for 10 min (wet separation). A test was carried out for the testa obtained with wet separation, where two halves of one peanut seed were subjected to dry separation and wet separation, respectively, prior to the extraction of Rb and Sr. The test was carried out for six peanut seeds, the relation between the Rb/Sr ratio in the nitric acid extracts obtained by dry separation and those obtained by wet separation gave a correlation factor of approximately 0.98.The results of $^{87}Sr/^{86}Sr$ isotope ratios obtained after wet separation and those obtained after dry separation agreed with each other. These results indicate that the extraction of Rb and Sr did not depend on the separation condition, either wet or dry.

3.5. Optimization of nitric acid extraction for extracting Sr

The extraction of Sr was carried out using HNO_3, while the concentrations of HNO_3 at 0.1, 0.3, and 2.0 mol L^{-1} were investigated for the extraction rate of Sr. The sonication time was fixed to 30 min for extraction. The results of Sr extraction rates are illustrated as bar-graph in Fig. 4. It can be seen that an extraction rate of *ca.* 93% could be achieved using 0.1 mol L^{-1} HNO_3. When 0.3 mol L^{-1} HNO_3 was used, the extraction rate exceeded 99%. Further increase of the concentration of HNO_3up to 2 mol L^{-1} did not significantly improve the extraction rate of Sr. Furthermore, Sr in the residual after HNO_3 extraction was analyzed after acid digestion using HNO_3, H_2O_2, and HF. The results indicated that Sr in the residual was negligible (less than 0.2%). In order to process

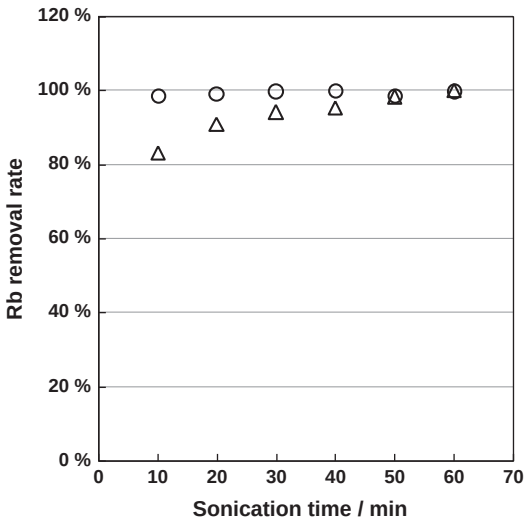

Fig. 3. Dependence of Rb removal rate on extraction time using pure water. ○, Sample 1; △, Sample 2.

the extraction in a relatively weaker acid solution without significant deterioration of Sr extraction rate, 0.3 mol L^{-1} HNO_3 was chosen as the extraction solution for Sr from the testa of peanut seed.

3.6. Application of the present method to peanut seeds grown in various countries

After the optimization mentioned above, the present method was applied to peanut seeds grown in Japan (4 brands), China (3 brands), USA (1 brand), India (1 brand), and South Africa (1 brand). Twenty peanut seeds were randomly taken from the stock of each brand and each seed was individually subjected to the removal of Rb by pure water extraction and the extraction of Sr by 0.3 mol L^{-1} HNO_3. The concentration of Sr in the 0.3 mol L^{-1} HNO_3 extract of each peanut seed was preliminarily determined. After that, dilution of the extract was carried out to obtain an analysis solution containing *ca.* 5 ng mL^{-1} Sr in 0.3 mol L^{-1} HNO_3. The measurements of ^{85}Rb and ^{87}Rb were also carried out to correct the interference of ^{87}Rb with ^{87}Sr. A solution made from NIST SRM 987 was analyzed to correct the mass-discrimination effect in ICP-Q-MS. The analytical results of the NIST SRM 987 solution before and after the measurements of the samples were agreed with each other considering the uncertainty of measurement.

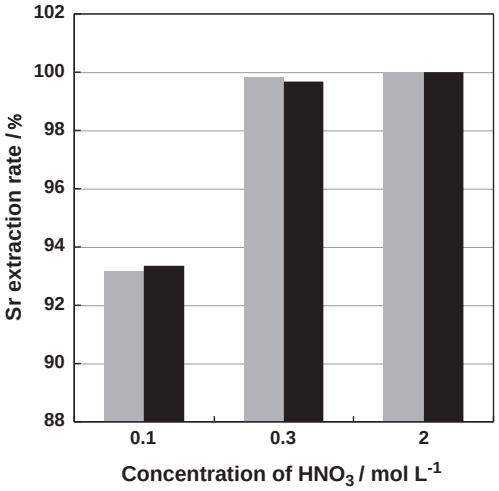

Fig. 4. Dependence of Sr extraction rate on the concentration of HNO_3. Gray bar, Sample 1; Black bar, Sample 2.

The results of $^{87}Sr/^{86}Sr$ isotope ratios for peanut seed of each brand are illustrated in Fig. 5(a–j). The maximum and minimum of Y-axis scale, *i.e.* $^{87}Sr/^{86}Sr$ ratio, in Fig. 5(a–j) were set to the 0.730 and 0.695, respectively. Each bar in the plots shows the expanded uncertainty of measurement with coverage factor k (=2).

Furthermore, the average value of $^{87}Sr/^{86}Sr$ in peanut seeds of each brand and the expanded uncertainty are plotted in Fig. 6. The expanded uncertainty of the average value was calculated from the positive square root of the sum-square value of the sample-to-sample uncertainty, *i.e.* standard deviation divided by the positive square root of 20, and the measurement uncertainty, *i.e.* a half value of the bar in Fig. 5. It can be seen that the brands grown in Japan gave the lowest $^{87}Sr/^{86}Sr$ isotope ratio with the average values close to 0.705. The brands grown in China gave the average values around 0.710, which is similar to the brand grown in the USA. The brand grown in India and South Africa gave an average value of 0.715 and 0.718, respectively. The present results might help to differentiate the brands grown in Japan and those grown in other countries investigated. However, it is impossible to differentiate the brands grown in China and the USA, both of which could be differentiated from the brand grown in South Africa. It is difficult to differentiate the brand grown in India and those grown in China, the USA, and South Africa.

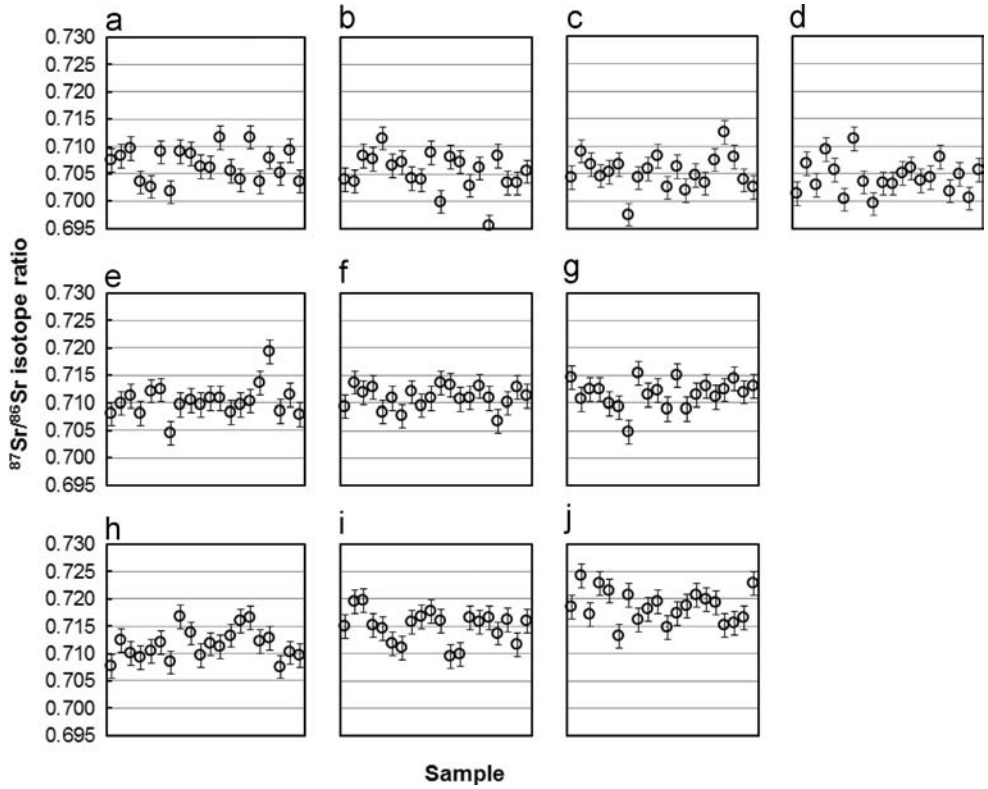

Fig. 5. Analytical results of $^{87}Sr/^{86}Sr$ isotope ratio in the testa of peanut seeds grown in various countries. (a) to (d), four brands grown in Japan; (e) to (g), three brands grown in China; (h) to (j), one brand each grown in the USA, India, and South Africa. Bar, expanded uncertainty of measurements, k=2.

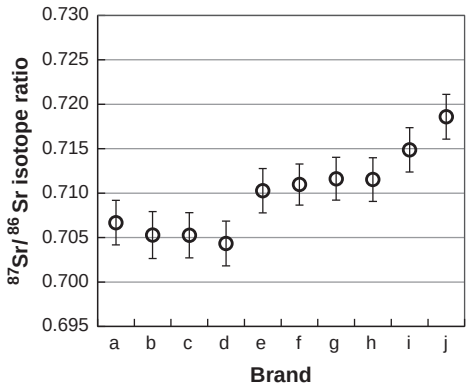

Fig. 6. Comparison of the results for different brands of peanut seeds. (a) to (d), four brands grown in Japan; (e) to (g), three brands grown in China; (h) to (j), one brand each grown in the USA, India, and South Africa.Bar, expanded uncertainty, $k=2$.

4. Conclusion

A simple and effective method was suggested for Sr isotope ratios analysis of peanut seed. Choice of the testa instead of the whole peanut seed could significantly decrease the relative concentration of Rb in the sample. Rb and Sr in the testa could be effectively extracted using pure water and 0.3 mol L^{-1} HNO_3 with sonication, respectively. The concentration of Rb in the HNO_3 extracts was low enough for the precise measurement of Sr isotope ratios. Based on the average value of $^{87}Sr/^{86}Sr$ isotope ratio of each brand, peanut seeds grown in Japan might be differentiated from those grown in other countries investigated in the present experiment. Further differentiation of peanut seeds grown in various countries might be achieved combing the results of $^{87}Sr/^{86}Sr$ isotope ratio with the concentrations or isotope ratios of other elements.

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