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Analytical Methods

Determination of the strontium isotope ratio by ICP-MS ginseng as a tracer of regional origin

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Abstract

This study presents the inductively coupled plasma mass spectrometry (ICP-MS) as a method for tracing the regional origin of ginseng. The results of the analysis of 15 Korean ginsengs from three different regions and of 15 Chinese ginsengs from three different regions reveal that the Sr isotope ratios $^{87}Sr/^{86}Sr$ of the ginsengs differed according to their origin. For pretreatment, the ginseng samples were dried, and were dissolved through microwave digestion, then were each made to amount to 6 ml with 11.9 M HCl. Rb was then separated from Sr to enable an interference-free measurement through cation exchange chromatography. Six millilitres of the ginseng sample were injected in the column, and 60 ml of 11.9 M HCl was passed through the column at a 1 ml min^{-1} flow rate to separate Rb from Sr. After Rb was eluted completely, 60 ml of 5.0 M HCl was passed at a 1 ml min^{-1} flow rate to collect Sr. In the Sr collection step, the first 10 ml portion of 30 ml eluate was discarded, and the next 10 ml portion was taken and was diluted with de-ionized water at a ratio of 1:3, for analysis purposes. The results of the analysis of 30 ginseng samples revealed that the Chinese ginsengs have an $^{87}Sr/^{86}Sr$ ratio range of 0.672–0.701, and the Korean ginsengs 0.705–0.714. The Korean ginsengs, therefore, have a higher $^{87}Sr/^{86}Sr$ ratio range than the Chinese ginsengs. Of the Korean ginsengs, $^{87}Sr/^{86}Sr$ ratio range of ginsengs from Punggi, Geumsan and Hongcheon are about 0.706–0.709, 0.705–0.706, and 0.710–0.714, respectively.

Keywords: ICP-MS; Sr; Ginseng; Isotope ratio

1. Introduction

Ginseng is a well-known herb widely used as a health food and as medicine. It is the root of the ginseng that is mainly used for these purposes. There are two types of ginseng: *Panax ginseng*, which originates from Korea or China, and *Panax quinquefolium*, which has US origins (Wu, Lin, & Chau, 2001). The medicinal efficacy of ginseng is largely affected by the soil and the climate of the place where it grows. Korean ginsengs are well known among *P. ginsengs* for their high efficacy. Korean ginseng is favored worldwide as a health food or medicine, and is registered as a Korean specialty. The regional origin tracing of ginseng, therefore, is necessary to protect Korean ginseng, which is different from the ginsengs of other countries.

Wine's origin tracing study through the determination of the strontium (Almeida & Vasconcelos, 2004; Barbaste, Robinson, Guilfoyle, Medina, & Lobinski, 2001) and lead (Almeida & Vasconcelos, 1999; Barbaste et al., 2001; Mihaljevič, Ettler, Šebek, Strnad, & Chrastný, 2006) as well as carbon, oxygen, and hydrogen (Bréas, Reniero, Serrini, Martin, & Rossmann, 1994) isotope ratio in wine has been reported. In addition, a study on stable isotope ratios is under way to trace material's origin by measuring isotopes such as neodymium (Reynolds, Frank, & Burton, 2006) and uranium (Durand, Chabaux, Rihs, Duringer, & Elsass, 2005) in water. Sr and Pb elements concentration in the ginseng is closely affected by the soil in which it grows, which is formed by the weathering of parent rock

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(Balcaen, Schrijver, Moens, & Vanhaecke, 2005; Kreissig, Nägler, Kramers, van Reenen, & Smit, 2000) the growth environment (e.g., fertilizer and moisture), environmental contamination, etc. (Baranowska, Barchańska, & Pyrsz, 2005; Baxter, Crews, Dennis, Goodall, & Anderson, 1997; Durand, Ahmad, Hamelin, Gunnell, & Curmi, 2006; Fernandes et al., 2005; Šperková & Suchánek, 2005; Stocker, Schramel, Kettrup, & Bengsch, 2005). Specifically, the soil where the ginseng grows is expected to significantly affect the ginseng, which is preserved for more than five years to ensure its merchantability. The seven contents of ginsenosides in five-year-old *P. ginseng* show the highest values compared with *P. ginseng* from one year to five years of age (Shi, Wang, Li, Zhang, & Ding, 2007).

Sr, which is used as a tracer of geological age and topography, has four isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr. Among these isotopes, ^{87}Sr is radiogenic, and its concentration gradually increases through the radioactive decay of the ^{87}Rb isotopes. The absolute percent difference of ^{87}Sr is proportional to the geological age. The stable isotope ratio $^{88}Sr/^{86}Sr$, therefore, can be used as an internal standard for the classification of a ginseng sample. Studies on Strontium isotope determination using inductively coupled plasma mass spectrometry (ICP-MS) have been conducted only for the purpose of determining the optimal measurement conditions of the archaeological or geological ginseng samples. No study has yet been conducted on the origin tracing of ginseng.

In this study, the $^{87}Sr/^{86}Sr$ isotope ratio was determined, using Quadrupole ICP-MS, for 30 ginseng samples from six different regions, to investigate the traceability of the origin of ginseng. The optimum condition of cation exchange chromatography was set to avoid isobaric overlap between ^{87}Sr and ^{87}Rb, and the correlation between the $^{87}Sr/^{86}Sr$ ratio and the origin of the ginseng was determined.

2. Experimental procedure

2.1. Materials and reagents

HNO_3 (Dongwoo fine chem, 69.0–71.0%, electronic grade) and HCl (Dongwoo fine chem, 36.0–38.0%, electronic grade) were used as they are not purified. 1000 mg l^{-1} of a stock strontium carbonate (isotopic) standard reference solution (Sr, SRM 987, NIST) was prepared by dissolving 1 g of powder in 1% (v/v) HNO_3. An Rb stock standard solution was prepared by dissolving 0.1 g of powdered $RbNO_3$ (p.a., Aldrich) in 3% (v/v) HNO_3. Standard solutions were prepared daily from the stock solution by weight, with de-ionized water (resistance $\geqslant$ 18.2 MΩ) or a 0.5% HNO_3 solution.

2.2. Ginseng samples

Experiments were carried out for a total of 30 ginseng samples, which includes five-year-old Korean ginsengs directly sampled from three different regions (five from Punggi, five from Geumsan, and five from Hongcheon) and 15 Chinese dry ginsengs bought from Chengdu, Xi'an, and Beijing, the representative ginseng markets in China (Fig. 1). The roots were removed from the fresh Korean ginsengs, and only the bodies of the ginsengs were dried in the oven and were powdered for the experiment because only the bodies of the dry Chinese ginsengs are sold, without the roots. With respect to the confidence level of the ginseng samples, it is thought that in no case would Korean ginseng be sold in China as Chinese ginseng since Korean

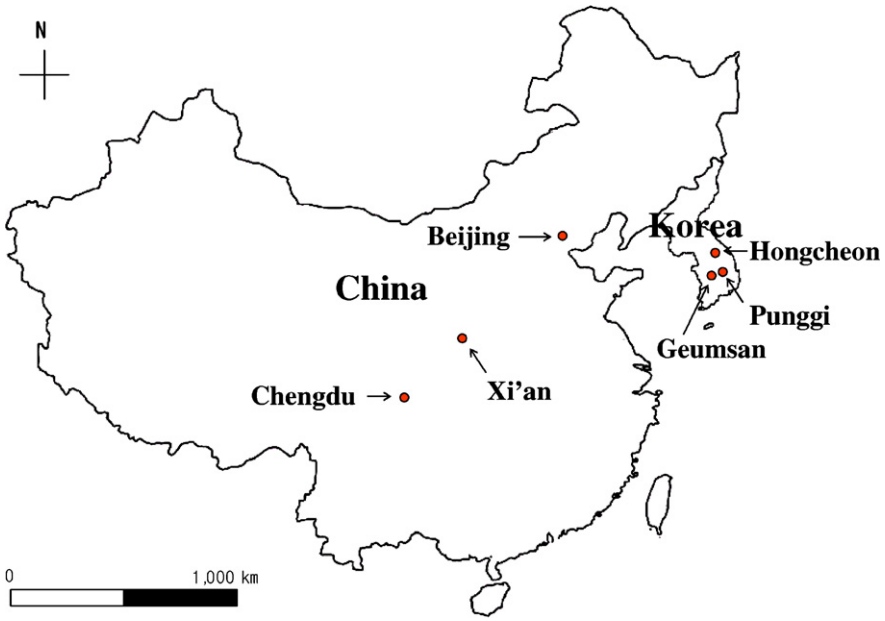

Fig. 1. The site map showing ginseng sampling station.

ginseng is more expensive than Chinese ginseng in the world ginseng market. Furthermore, treatment and distribution costs must be added to make fresh Korean ginseng into dry ginseng.

2.3. Pretreatment and cation exchange separation of Sr in the ginseng samples

Pretreatment is necessary to separate Rb from Sr, using a Dowex AG50WX-8/400 mesh column (10 cm bed length, 1.0 cm internal diameter, corresponding to a bed volume of 49 ml). In the case of ginseng, direct pretreatment with HCl is impossible, and therefore 6 ml HNO_3 was added to 0.2 g ginseng samples for pretreatment by microwave digestion procedure (Etos, Milestone, Italy). The pre-treated samples then evaporated and each of them were made to amount to 6 ml with 11.9 M HCl in order to satisfy the conditions for distribution coefficients (Dv) with strong-acid cation exchange resin (Sr adsorption condition: 11.9 M HCl, Sr desorption condition: 5.0 M HCl). Hundred millilitres of 11.9 M HCl were passed through the column at a 1 ml min^{-1} flow rate for the initial cleaning of the column. In the first Rb separation step, a 6 ml ginseng sample was injected in the column, and 60 ml of 11.9 M HCl was passed through the column at a 1 ml min^{-1} flow rate. In this step, Rb was removed from the column while Sr was maintained within the column. In the second Sr collection step, 60 ml of 5.0 M HCl was passed through the column at a 1 ml min^{-1} flow rate. The first 10 ml portion of the 30 ml eluate was discarded, and the next 10 ml portion was taken and diluted with de-ionized water at a ratio of 1:3, for analysis purposes. Then, 30 ml of 11.9 M HCl was passed as a regeneration step since no Sr remained in the column after the 30 ml elution volume was passed. The same procedure was applied to 6 ml of the blank solution (11.9 M HCl), under the same conditions (Nelson, Murase, & Kraus, 1964).

2.4. Pump flow rate

Linearity was confirmed, since perfect separation cannot be ensured if the swelling effect of the cation exchange occurs in the experiment. As the R^2 was determined to be 0.9999, it was confirmed that no swelling effect was involved in the experiment. Based on this value, it was also determined that 11.9 rpm corresponds to 1 ml min^{-1}.

2.5. ICP-MS analysis

Element analysis was performed through ICP-MS with the use of a concentric nebulizer and nickel cones (X-7 series, Thermo, UK). In order to maintain the optimum operation condition of ICP-MS, a tuning solution made up of 1 μg l^{-1} Co, In, Pb, U, Ce, Ba, etc. was used. ^{59}Co, ^{115}In, ^{208}Pb, ^{238}U, ^{140}Ce, ^{138}Ba, $^{140}Ce^{16}O+$, and mass 69's $^{138}Ba^{2+}$ isotope intensity in the solution was measured. The optimum condition was determined by compromising the highest ^{115}In ion intensity and the lowest ratio between Ba^{2+}/Ba^{+} (⩽2%) and CeO^{+}/Ce^{+} (⩽3%). Operating conditions used were as follows: rf power of 1300 W; sample uptake rate of 24 rpm; cooling gas flow rate of 13 l min^{-1}; nebulizer gas flow rate between 0.94 and 0.97 l min^{-1} and auxiliary gas flow rate of 0.7 l min^{-1}.

For the optimization of the data collection process, the $^{87}Sr/^{86}Sr$ and $^{88}Sr/^{86}Sr$ ratios were determined using 10 μg l^{-1} of the Sr isotopic standard solution, and the effect of the equipment depending on the mass bias correction and relative standard deviations (RSD) was studied. In order to obtain the best precision (lowest RSD) 500 sweeps per reading and a dwell time 10 ms were used. Three replicates for each measurement were carried out.

For signal stabilization, a sample read delay of 75 s was chosen. In-between the loading of solution of both samples and standards, the sampling system was rinsed with 2% HNO_3 for 75 s.

The mass bias of the measured data was corrected to determine the correct isotope ratio. For correction, both the internal correction, which uses a naturally occurring isotope ratio = 8.37521, and the external correction, which uses the Sr isotopic standard solution NIST SRM 987, were applied. The corrected isotope ratio was obtained using power laws (Wasserburg, Jacobsen, DePaolo, McCulloch, & Wen, 1981).

$$(^{87}Sr/^{86}Sr)_c = (^{87}Sr/^{86}Sr)_m \times [8.37521/(^{88}Sr/^{86}Sr)_m]^{0.5} \quad (1)$$

where c and m denote the corrected and measured data, respectively.

3. Results and discussion

3.1. Optimum chromatography condition for the separation of Sr

To satisfy the optimum condition for the chromatography separation, 10 ml of the Sr and Rb mixing standard solution (Sr 10 mg l^{-1}, Rb 10 mg l^{-1}) in an 11.9 M HCl solution matrix was injected in the column. Then, 100 ml of the 11.9 M HCl eluent was passed through the column as the first Rb separation step, and 100 ml of the 5.0 M HCl eluent was then passed through the column as the second Sr collection step. Ten millilitres of the eluates were collected, respectively, and their ^{84}Sr, ^{85}Rb, ^{86}Sr, ^{87}Sr, ^{87}Rb, and ^{88}Sr ions were analyzed using ICP-MS. As shown in Fig. 2, the intensity of the ^{85}Rb and ^{87}Rb ions, which correspond to Rb, was rapidly decreased in 0–20 ml, and was not detected at all after 30 ml, when the 11.9 M HCl eluent was passed through the column. This result shows that Rb was completely separated in the first 20 ml of the eluate. Moreover, the intensity of the ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr ions, which correspond to Sr, was rapidly increased in the 100–130 ml (0–30 ml for 5 M HCl) section when the 5 M HCl eluent was passed through the column. This result shows that the desorption of Sr in

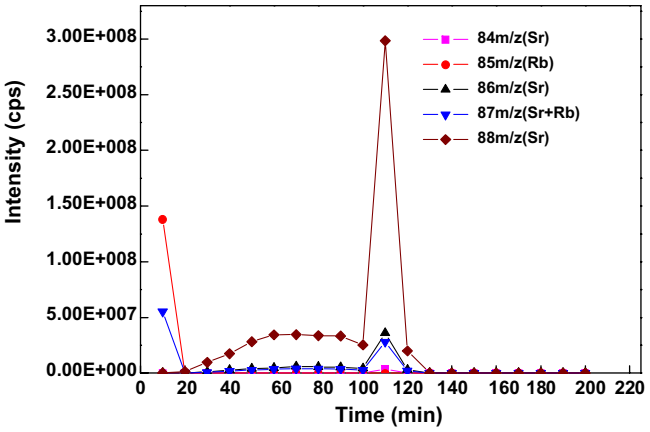

Fig. 2. Comparison of the ion intensities obtained for the different Sr isotopes and for the Rb isotope in column pre-treated as the standard solution (Sr 10 mg l^{-1}, Rb 10 mg l^{-1}).

the column occurred completely in the first 30 ml of the eluate.

Considering the retention time and the reagent consumption, the ginseng samples were separated under the conditions. That is the Sr collection step, only the second 10 ml of the eluate, which had the highest Sr concentration in the initial 30 ml eluate, was taken and diluted with deionized water at a ratio of 1:3. This is to decrease the matrix effect due to high HCl concentration, and to optimize the intensity.

Table 1 shows the results of the analysis of the ^{88}Sr and ^{85}Rb ion concentration and the ^{85}Rb ion intensity before and after the chromatography separation of the blank solution and the 30 ginseng samples. According to the intensity of mass 85 after the extraction, the ^{85}Rb ion intensity of the 30 ginseng samples was 382 ± 69, and the blank intensity was 399.8 ± 55, showing no significant difference. This was because Rb was completed separated from Sr.

3.2. Sr isotope ratio measurements and mass bias correction

Fig. 3 shows the results of the 10 time measurements of the $^{87}Sr/^{86}Sr$ ratio of the Sr isotope standard (NIST SRM 987), which were carried out within a one month period in order to determine the measurement precision of ICP-MS depending on time. As for the long-term measurement, which was carried out for one month, the mean $^{87}Sr/^{86}Sr$ ratio obtained was 0.719, and the RSD was 0.30%. As for the short-term measurement, which was carried out for one day, the RSD obtained was 0.27%. This means

Table 1
Comparison of the ion concentrations and ion intensity for the ^{88}Sr isotope and for the ^{85}Rb isotope in untreated and pre-treated as the sample blank solution, and in a ginseng samples

Sample name	Without extraction		Extraction	
	Mass 88 ion concentration (μg l^{-1})	Mass 85 ion concentration (μg l^{-1})	Mass 88 ion concentration (μg l^{-1})	Mass 85 ion intensity/ion (s^{-1})
Blank	Non-detection	Non-detection	Non-detection	399.8
China 1 (Beijing)	28017.1	8156.6	23.7	384.2
China 2 (Beijing)	26035.5	14554.2	55.6	395.4
China 3 (Beijing)	18237.5	5342.0	61.0	258.6
China 4 (Beijing)	26634.1	8316.2	6.1	412.3
China 5 (Beijing)	26765.1	8876.6	6.5	455.6
China 6 (Chengdu)	29917.8	8814.6	9.0	322.5
China 7 (Chengdu)	28464.2	2768.5	6.1	424.5
China 8 (Chengdu)	17436.7	9719.3	4.6	358.4
China 9 (Chengdu)	27557.1	3193.5	5.0	210.2
China 10 (Chengdu)	29528.4	9224.4	6.2	419.5
China 11 (Xi'an)	21672.1	4914.1	6.9	385.2
China 12 (Xi'an)	23804.6	7932.5	8.3	333.5
China 13 (Xi'an)	19653.3	11282.0	8.8	299.5
China 14 (Xi'an)	28262.2	6392.1	10.7	488.6
China 15 (Xi'an)	28593.3	8248.1	17.2	457.6
Korea 1 (Punggi)	57063.8	26907.0	13.1	355.4
Korea 2 (Punggi)	28345.8	6138.6	8.2	438.9
Korea 3 (Punggi)	23125.2	25102.3	5.1	334.5
Korea 4 (Punggi)	29776.0	6819.0	5.0	429.6
Korea 5 (Punggi)	56911.0	7580.7	3.7	455.6
Korea 6 (Geumsan)	19306.8	17.5	7.5	398.2
Korea 7 (Geumsan)	22079.5	20643.3	23.5	421.6
Korea 8 (Geumsan)	14001.4	4835.4	6.9	458.6
Korea 9 (Geumsan)	25042.9	15856.6	7.3	263.3
Korea 10 (Geumsan)	76588.7	16258.5	13.2	368.4
Korea 11 (Hongcheon)	44614.3	9705.7	24.6	410.6
Korea 12 (Hongcheon)	36825.0	2997.4	17.6	446.2
Korea 13 (Hongcheon)	18488.6	6419.6	9.3	289.4
Korea 14 (Hongcheon)	49106.2	3063.3	19.6	458.6
Korea 15 (Hongcheon)	34118.3	6312.7	19.3	333.8

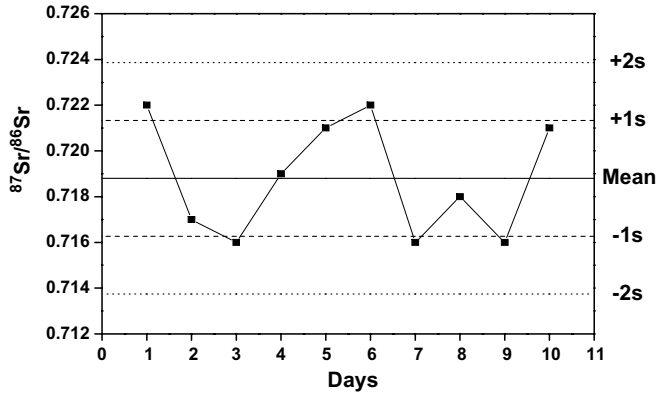

Fig. 3. Variation of the isotope ratio of the Sr isotopic standard NIST SRM-987, observed a period of one month (s = standard deviation of the mean). The certified value for $^{87}Sr/^{86}Sr$ is 0.71034 ± 0.00026.

Table 2
Uncorrected and mass bias corrected results obtained for the Sr isotope ratio in a NIST SRM-987[a] (10 μg l^{-1} Sr concentration)

Measurement	$^{87}Sr/^{86}Sr$		$^{88}Sr/^{86}Sr$
	Uncorrected	Corrected	
1	0.722 ± 0.0015	0.711 ± 0.0021	8.619 ± 0.0175
2	0.716 ± 0.0012	0.707 ± 0.0013	8.595 ± 0.0064
3	0.716 ± 0.0010	0.709 ± 0.0023	8.546 ± 0.0255
4	0.718 ± 0.0040	0.710 ± 0.0044	8.589 ± 0.0255
5	0.721 ± 0.0017	0.712 ± 0.0020	8.587 ± 0.0122
6	0.721 ± 0.0010	0.718 ± 0.0027	8.601 ± 0.0304
7	0.716 ± 0.0006	0.708 ± 0.0024	8.582 ± 0.0280
8	0.718 ± 0.0021	0.712 ± 0.0028	8.536 ± 0.0232
9	0.716 ± 0.0006	0.708 ± 0.0026	8.575 ± 0.0310
10	0.721 ± 0.0006	0.709 ± 0.0009	8.667 ± 0.0081

[a] Certified values: 0.71034 ± 0.0026 for $^{87}Sr/^{86}Sr$ and 8.37681 ± 0.00325 for $^{87}Sr/^{86}Sr$.

that, with respect to measurement accuracy depending on time, long-term measurement was slightly more accurate than short-term measurement.

The instrument-induced bias and the sample-induced bias significantly influenced the ICP-MS measurement. Therefore, the correction of the mass bias is essential in the determination of the correct isotope ratio. In this study, the mass bias was corrected through external correction and using ICP-MS to enhance the accuracy of the Sr measurement. Table 2 shows the values obtained through internal correction and the values that did not undergo mass bias correction. The accuracy is shown to increase in the values obtained through internal correction. The ginseng samples were analyzed through external correction because internal mass bias correction has a particular disadvantage: the detector is saturated when the concentration difference between two samples is significant because the count rate of ^{88}Sr is high in the internal mass bias correction, which requires an additional measurement of the ^{88}Sr isotope concentration. However, it is believed that both correction methods can be used in the determination of the Sr isotope ratio in ginseng.

3.3. Sr isotope ratio measurements in the ginseng samples

The ginseng samples were analyzed using the external mass bias correction method. Fig. 4 shows the $^{87}Sr/^{86}Sr$ ratio of the 30 ginseng samples. The results of the analysis show that there was a significant difference between the 15 Chinese ginsengs and the 15 Korean ginsengs. The $^{87}Sr/^{86}Sr$ ratio range in the Chinese ginsengs was 0.672–0.701, and 0.705–0.714 in the Korean ginsengs, showing a higher $^{87}Sr/^{86}Sr$ ratio range in the Korean ginsengs than in the

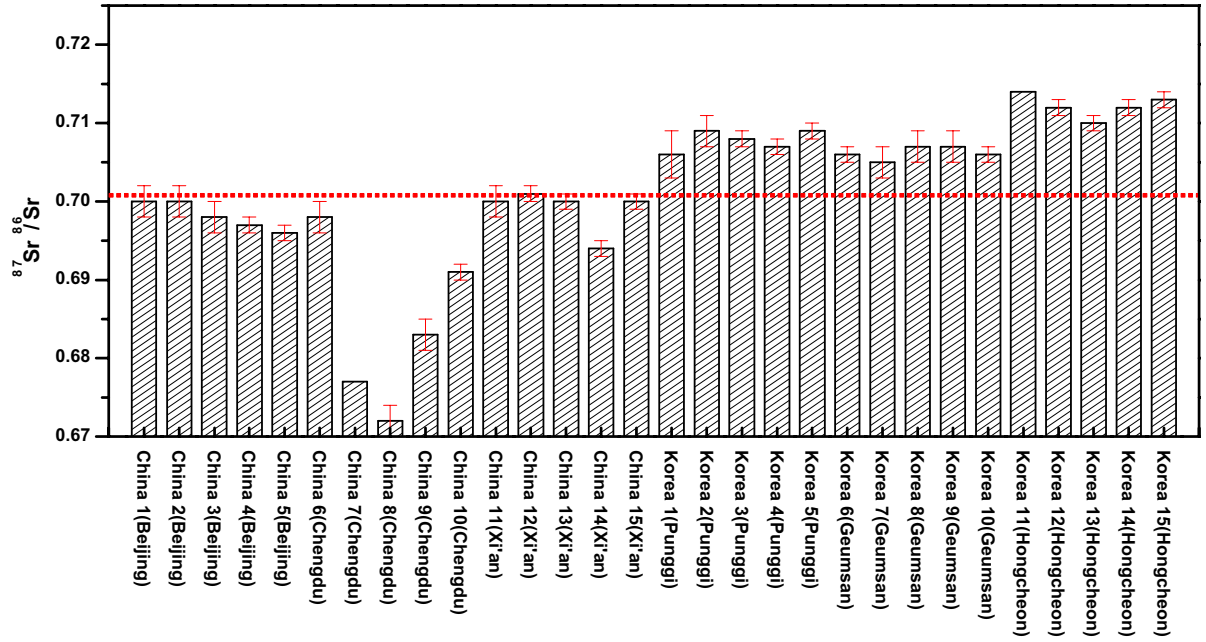

Fig. 4. Comparison of the means ginsengs samples. The straight lines indicate the respective standard deviation value.

Chinese ginsengs. Measurement was made three times for all the ginseng samples, and the standard deviation was less than 0.002. Of the Korean ginsengs, the $^{87}Sr/^{86}Sr$ ratio range was 0.705–0.707 in the Geumsan ginsengs, and 0.710–0.714 in the Hongcheon ginsengs, showing a higher $^{87}Sr/^{86}Sr$ ratio range in the ginsengs from Hongcheon than in the ginsengs from Geumsan. But $^{87}Sr/^{86}Sr$ ratio range of Geumsan slightly differs from that of Punggi.

The results of this study show that the determination of the $^{87}Sr/^{86}Sr$ ratio in ginseng had sufficient accuracy to distinguish the Korean ginsengs from the Chinese ginsengs.

4. Conclusions

In this work, an analytical procedure based on determination of the Sr isotope ratio $^{87}Sr/^{86}Sr$ in ginsengs by ICP-MS was developed and applied to 30 samples from three different Korea regions and three different regions in China. The accurate and precise analysis of Sr isotope ratios was carried out ICP-MS by controlling and correcting the factors such as the mass bias correction, internal correction, and short/long-term measurement. The isotope ratio of ginseng in different areas was strongly depended on the lithology and the growth environment conditions. The analysis results of 30 ginseng samples revealed that $^{87}Sr/^{86}Sr$ ratio range of Chinese and Korean ginsengs were about 0.672–0.701 and 0.705–0.714, respectively. The Korean ginsengs have a higher $^{87}Sr/^{86}Sr$ ratio range than the Chinese ginsengs. The determination of the $^{87}Sr/^{86}Sr$ ratio in ginseng had sufficient accuracy to distinguish the Korean ginsengs from the Chinese ginsengs. Therefore, strontium isotope ratio is one of the attractive methods for a tracer regional origin of ginseng.

References

Almeida, C. M., & Vasconcelos, M. T. (1999). Determination of lead isotope ratios in port wine by inductively coupled plasma mass spectrometry after pre-treatment by UV-irradiation. *Analytica Chimica Acta, 396*, 45–53.

Almeida, C. M., & Vasconcelos, M. T. (2004). Does the winemaking process influence the wine $^{87}Sr/^{86}Sr$? A case study. *Food Chemistry, 85*, 7–12.

Balcaen, L., Schrijver, I. D., Moens, L., & Vanhaecke, F. (2005). Determination of the $^{87}Sr/^{86}Sr$ isotope ratio in USGS silicate reference materials by multi-collector ICP-mass spectrometry. *International Journal of Mass Spectrometry, 242*, 251–255.

Baranowska, I., Barchańska, H., & Pyrsz, A. (2005). Distribution of pesticides and heavy metals in trophic chain. *Chemosphere, 60*, 1590–1599.

Barbaste, M., Halicz, L., Galy, A., Medina, B., Emteborg, H., Adams, F. C., et al. (2001). Evaluation of the accuracy of the determination of lead isotope ratios in wine by ICP MS using quadrupole, multicollector magnetic sector and time-of-flight analyzers. *Talanta, 54*, 307–317.

Barbaste, M., Robinson, K., Guilfoyle, S., Medina, B., & Lobinski, R. (2001). Precise determination of strontium isotope ratios in wine by inductively coupled plasma sector field multicollector mass spectrometry (ICP-SF-MC-MS). *Journal of analytical atomic spectrometry, 17*, 135–137.

Baxter, M. J., Crews, H. M., Dennis, M. J., Goodall, I., & Anderson, D. (1997). The determination of the authenticity of wine from its trace element composition. *Food chemistry, 60*, 443–450.

Bréas, O., Reniero, F., Serrini, G., Martin, G. J., & Rossmann, A. (1994). Isotope ratio mass spectrometry: Analysis of wines from different european countries. *Rapid Communications in Mass Spectrometry, 8*, 967–970.

Durand, N., Ahmad, S. M., Hamelin, B., Gunnell, Y., & Curmi, P. (2006). Origin of Ca in South Indian Calcretes developed on metamorphic rocks. *Journal of Geochemical Exploration, 88*, 275–278.

Durand, S., Chabaux, F., Rihs, S., Duringer, P., & Elsass, P. (2005). U isotope ratios as tracers of groundwater inputs into surface waters: Example of the upper Rhine hydrosystem. *Chemical Geology, 220*, 1–19.

Fernandes, A. P., Santos, M. C., Lemos, S. G., Ferrira, M. M., Nogueira, A. R., & Nóbrega, J. A. (2005). Pattern recognition applied to mineral characterization of Brazilian coffees and sugar-cane spirits. *Spectrochimica Acta Part B, 60*, 717–724.

Kreissig, K., Nägler, T. F., Kramers, J. D., van Reenen, D. D., & Smit, C. A. (2000). An isotopic and geochemical study of the northern Kaapvaal Craton and the Southern marginal zone of the Limpopo Belt: Are they juxtaposed terranes? *Lithos, 50*, 1–25.

Mihaljevič, M., Ettler, V., Šebek, O., Strnad, L., & Chrastný, V. (2006). Lead isotopic signatures of wine and vineyard soils-tracers of lead origin. *Journal of Geochemical Exploration, 88*, 130–133.

Nelson, F., Murase, T., & Kraus, K. A. (1964). Ion exchange procedures : I. Cation exchange in concentration HCl and $HClO_4$ solutions. *Journal of Chromatography A, 13*, 503–535.

Reynolds, B. C., Frank, M., & Burton, K. W. (2006). Constraining erosional input and deep-water formation in the North Atlantic using Nd isotopes. *Chemical Geology, 226*, 253–263.

Shi, W., Wang, Y., Li, J., Zhang, H., & Ding, L. (2007). Investigation of ginsenosides in different parts and ages of *Panax ginseng*. *Food chemistry, 102*, 664–668.

Šperková, J., & Suchánek, M. (2005). Multivariate classification of wines from different Bohemian regions (Czech Republic). *Food Chemistry, 93*, 659–663.

Stocker, A., Schramel, P., Kettrup, A., & Bengsch, E. (2005). Trace and mineral elements in royal jelly and homeostatic effects. *Journal of Trace Elements in Medicine and Biology, 19*, 183–189.

Wasserburg, G. J., Jacobsen, S. B., DePaolo, D. J., McCulloch, M. T., & Wen, T. (1981). Precise determination of Sm/Nd ratios, Sm and Nd isotopic abundances in standard solutions. *Geochimica et Cosmochimica Acta, 45*, 2311–2323.

Wu, J., Lin, L., & Chau, F.-T. (2001). Ultrasound-assisted extraction of ginseng saponins from ginseng roots and cultured ginseng cells. *Ultrasonics Sonochemistry, 8*, 347–352.