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ORIGINAL PAPER

Development of the Isotope Analysis Technique for Inorganic Trace Elements Using Laser Ablation Assisted Resonance Ionization Mass Spectrometry (LA-RIMS)

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We have developed and assessed LA-RIMS as the isotope analysis method for trace inorganic elements in agricultural products. We used magnesium isotope analysis to verify that LA-RIMS had the capability to identify the production areas with the required precision of 0.3 %. We demonstrated direct measurements of trace strontium (sub ppm level) in brown rice and confirmed that the isotope analysis precision was improved through the signal intensity enhancement by increasing the ablation power and expanding the laser spot. For the present system, we estimated the strontium isotope ratio of $^{87}Sr/^{86}Sr$ to be 0.69 ± 0.10 (14 %). We concluded that the direct isotope analysis for trace inorganic elements such as strontium in brown rice using LA-RIMS had an advantage under the serious situation of isobaric interference and had sufficient capability to identify agricultural production areas.

KEYWORDS: *Isotope analysis, Trace Analysis, Resonance Ionization Mass Spectrometry, Laser Ablation,*

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Origin Determination, Brown Rice, Strontium Isotope

I. Introduction

The development of table-top size and highly sensitive mass spectrometers, such as the inductively coupled plasma mass spectrometer (ICP-MS), has made possible determination of material origin using isotope analysis, which is based on differences of natural isotope transfer processes. In Japan, agricultural products are obligated to carry labels telling their production areas. Since the price depends on production areas, there are consequently many cases of false labeling. Therefore, it is desirable to establish reliable methods to determine the origin of agricultural products. As one promising candidate, an origin determination method based on the isotope analysis for strontium in brown rice was suggested by Oda et al. 1). This method uses the fact that strontium isotope ratio (^{87}Sr/^{86}Sr) depends on the geological age of the production area. They adopted ICP-MS for the isotope analysis, but this has a problem of isobaric interference. Consequently, they had to chemically prepare samples to suppress the isobaric interference of the parent nuclide ^{87}Rb, which required much time and work.

As a highly sensitive trace element analysis method without isobaric interference, resonance ionization mass spectrometry (RIMS) has is available 2, 3). Since this method is based on the resonant transition between energy levels unique to each element and/or isotope, it can offer high sensitivity and selectivity. As a solid sample analysis method based on RIMS, laser ablation assisted RIMS (LA-RIMS) has a great advantage in simplicity 4, 5). A target element in a solid sample can be selectively and directly measured without isobaric interference in LA-RIMS.

We have proposed to apply LA-RIMS to agricultural product origin determination instead of ICP-MS. In this paper, we developed this application and assessed it for trace inorganic elements in agricultural products. Strontium is quite useful as described above, so we focused on trace strontium isotope measurement.

The origin determination mainly requires precision for the isotope analysis, because the difference in the isotope ratio is 0.3 % or less, *e.g.* we have to distinguish 0.710 from 0.712 for ^{87}Sr/^{86}Sr to determine brown rice origins. In addition, since the target element content for the isotope analysis is generally quite low, *e.g.* the strontium content in brown rice is sub ppm level, high sensitivity is also required. Therefore, we estimated the precision of the isotope ratio measured by LA-RIMS for inorganic elements and demonstrated the direct measurement of trace strontium with sub ppm level content in agricultural products. Additionally, we discussed enhancing the signal intensity to improve the sensitivity and the precision.

II. Experimental Setup

Figure 1 shows a schematic of the experimental setup consisting of a pulsed Nd: YAG laser, a tunable dye laser and a time-of-flight mass spectrometer (TOF-MS). The second (532nm) or third (355nm) harmonic of the Nd: YAG laser was used for laser ablation of solid samples. The tunable dye laser was pumped by the Nd: YAG or excimer laser and was tuned at the wavelength for resonant excitation of each element. The bandwidth of the dye laser was 5 GHz and generally much broader than an isotope shift. The repetition rate and the pulse width of the laser were 10Hz and 10 nsec, respectively. As an ionization scheme, the two-photon excitation followed by one photon ionization at the same wavelength, that is, the “2+1” transition, was adopted because it was quite simple to use and suitable for a single tunable laser system. The TOF-MS had a laser ionization chamber, a field-free drift region approximately 150 cm long, reflectron electrodes for energy focusing and a microchannel plate (MCP) ion detector; pressure in the chamber was less than 10^{-7} Torr. The signals obtained from the MCP detector were transferred to a personal computer through the digital oscilloscope. For high S/N measurements, we adopted the off-line pulse counting mode, in which the signals exceeding threshold intensity were counted in each time bin.

Fig. 1

As agricultural product samples, rice grains produced in Aichi Prefecture, Japan, were used. The rice hull was peeled off by using forceps in order to prevent surface contamination. The bare brown rice sample was directly placed into the vacuum chamber with no preparation and then irradiated by the ablation laser as shown in **Fig. 2**. Subsequently, the dye laser with the resonant excitation wavelength was passed through above the ablation spot after the diffusion time for the ablated vapor had passed. Electrode 2 in Fig. 2 worked as a suppressor of ions produced by the thermal ionization process in the laser ablation. **Table 1** shows the contents of inorganic elements in brown rice [6].

Fig. 2

Table 1

III. Results and Discussion

1. Verifying the Precision of the Isotope Ratio Measured by LA-RIMS

Since the precision of the measured isotope ratio is quite important for the origin determination of agricultural products, we estimated the precision of the isotope ratio measured by LA-RIMS. As an agricultural product sample, we adopted brown rice. For the origin determination, strontium is a promising candidate as the target element but its concentration is generally quite low. To estimate the isotope ratio precision, we alternatively adopted magnesium which has a four orders larger concentration than strontium in brown rice. Magnesium has the same outer shell electron configuration as strontium because both are alkali-earth metals. Both can transit through the levels with similar properties in the resonant ionization process. Therefore, magnesium is suitable for verifying the precision.

The resonance absorption wavelength differs between not only each element but also each isotope, where its difference is called the isotope shift. Therefore, we have to precisely control the laser wavelength to obtain a uniform isotope ratio. Since the laser wavelength control is generally complicated, we adopted a broad-band laser with a bandwidth much broader than the isotope shift. We additionally used a high enough laser power to saturate the resonant ionization. Consequently, we can achieve highly stable isotope ratio measurements without precisely controlling the laser wavelength.

In LA-RIMS, thermal ionization in the laser ablation process is a serious problem. We suppressed the thermal ionization component by using the positional difference between the resonant ionization and the laser ablation. Here, since we passed the dye laser for the resonant ionization through a little above the ablation spot and applied a higher voltage to electrode 1 than electrode 2 in Fig.2, the ions produced by the laser ablation were accelerated upward more than the resonant ionization component. Consequently, both components had different flight paths and could be separated from each other. **Figure 3** shows the LA-RIMS spectrum directly obtained from brown rice, when the laser wavelength was tuned at 459.735 nm, corresponding to the two-photon resonant excitation from $3s^2\ ^1S_0$ to $3s4s\ ^1S_0$ for magnesium 7). In this excitation scheme, since the transition between the two states with the zero total angular momentum (J = 0) was applied, there was no difference for each isotope in the transition probability caused by hyperfine structure. As the ablation laser, the second harmonic (532 nm) of the Nd: YAG laser was used. Sodium has a low ionization potential and often thermally ionized by laser ablation, but its signal was suppressed and only the magnesium signal was detected.

Fig. 3

We checked the long-term stability of the LA-RIMS spectra, because the signals have to be accumulated for a large number of laser shots to obtain high precision. **Figure 4** shows the temporal variation in magnesium isotope ratio (^{25}Mg/^{26}Mg) measured by LA-RIMS, where horizontal axis represents laser shot number and the average values for 500 shots, *i.e.* 50 sec, are plotted. Results showed good stability of the measured isotope ratio and its fluctuation was within 1.8 %. Finally, we accumulated data for 34,000 laser shot (3,400 sec), so that the isotope ratio ^{25}Mg/^{26}Mg was estimated to be 0.871 ± 0.003 (0.3 %), which achieved the required precision. This ratio had a systematic discrepancy with the value (0.908) evaluated by the Subcommittee for Isotopic Abundance Measurements (SIAM) 8). This indicated that the analysis system might have an isotope effect *e.g.* in its ion detector, an ion transport process, etc. However, since the system could analyze the isotope ratio with high stability, it could determine the correct isotope ratio through comparison with a standard sample. From these results, we demonstrated that isotope analysis for an inorganic element using LA-RIMS had the capability for agricultural product origin determination.

Fig. 4

2. Direct Detection of Trace Strontium in the Brown Rice

Next, we demonstrated the direct detection of trace strontium in brown rice by LA-RIMS. Here, a dye laser tuned to the wavelength of 538.209 nm, corresponding to the two-photon resonant excitation from $5s^2\ ^1S_0$ to $5p^2\ ^1S_0$ for strontium9), was passed through a little above the ablation spot after the vapor diffusion time (100 nsec) had passed. As with magnesium, we also adopted the scheme between the zero total angular momentum states. The dye laser power was 24 μJ with the spot size of 80 μm, corresponding to the power density of 5×10^7 W/cm^2. As the ablation laser, the second harmonic (532 nm) of the Nd: YAG laser was also used and its power was 0.16 mJ with the spot size of 100 μm, corresponding to the power density of 2×10^8 W/cm^2. **Figure 5** shows the LA-RIMS spectrum directly obtained from brown rice by accumulating signals for 2,000 laser shots (200 sec) in the off-line pulse counting mode. Since only the strontium signal was enhanced by the resonant ionization laser, we concluded that trace strontium with sub ppm level concentration was directly detected. However, organic polymer fragments mainly produced by the laser ablation process were also observed and interfered with the strontium spectrum. From the viewpoint of high precision measurements, we should suppress this component. We considered that the fragment component could be suppressed by blocking the thermal ionization component.

Fig. 5

We estimated the strontium isotope ratio ^{87}Sr/^{86}Sr to be 0.53 ± 0.22 (40 %), which agreed with the reported value 0.71 8) within the experimental uncertainty. However, the precision of our isotope ratio measurement was quite low and inadequate to identify the production areas because of the small signals *i.e.* poor statistics. To improve the statistics, we had to increase the strontium signal level. If the strontium signal could be obtained at the same level as magnesium, the required precision for the origin determination could be achieved as described in the previous section. Consequently, we had to enhance the strontium signal by four orders of magnitude.

3. Enhancement of Signal Intensity

We can enhance the strontium signal obtained in a finite time period by using a high-repetition-rate laser, increasing ablation power, expanding the laser spot and improving ion transport efficiency. In this paper, we attempted to enhance the signal by increasing the ablation power and expanding the laser spot.

Here, the dye laser for the resonant ionization passed through 4 mm above the ablation spot, *i.e.* above the ion suppressor (electrode 2 in Fig. 2), and was delayed 5 μsec from ablation laser due to diffusion of ablated vapor. In this configuration, a large region for the resonant laser ionization can be reserved and ions produced by the ablation process can be easily rejected. As a laser for the ablation, the third harmonic (355 nm) of the Nd: YAG laser was used and its power was 1.8 mJ with the spot size of 1.7 mm, corresponding to the power density of 8×10^6 W/cm^2. The laser wavelength for the resonant ionization was tuned at 459.637 nm, corresponding to the two-photon resonant excitation from $5s^2\ {}^1S_0$ to $5s10s\ {}^1S_0$ for strontium [9)] and its power was 0.42 mJ with the spot size of 800 μm, corresponding to the power density of 8×10^6 W/cm^2.

Figure 6 shows the improved LA-RIMS spectrum of strontium in brown rice, where the signals were accumulated for 10,000 laser shots (1,000 sec). Although the whole signal intensity was enhanced, the polymer fragment component was suppressed. Additionally, ^{84}Sr with low isotopic abundance (0.56 %) was also detected. We considered that the sample was not strongly ablated due to the relatively low power density but the large total energy pulse caused a large amount of sample vapor as a whole. We estimated the strontium isotope ratio of ^{87}Sr/^{86}Sr to be 0.69 ± 0.10 (14 %). The precision of the measured isotope ratio was improved by increasing the ablation power and expanding the laser spot but it was still inadequate to identify production areas. We considered that the laser spot could possibly be at least doubled with the same ionization efficiency if a more effective ionization scheme or higher laser power (about 8 mJ) was used. Since a laser with the repetition rate of 10 kHz is available commercially, a signal per unit time three orders larger than that obtained by the present 10 Hz laser system is possible. Consequently, we considered that the signal intensity was able to be enhanced at least 4,000 times, so that the required precision 0.3% could be achieved.

From these results, we concluded that the direct isotope analysis for trace inorganic elements such as strontium in brown rice using LA-RIMS had an advantage under the serious situation of isobaric interference and it might have sufficient capability to identify agricultural production areas with sensitivity and precision.

Fig. 6

IV. Conclusion

We assessed LA-RIMS as the isotope analysis method for trace inorganic elements in agricultural products. We estimated the precision of magnesium isotope analysis to verify that LA-RIMS had the capability to identify the production areas with required precision of 0.3 %. Direct measurements of trace strontium (sub ppm level) in brown rice were done and the isotope analysis precision was improved through the signal intensity enhancement by increasing the ablation power and expanding the laser spot. Consequently, ^{84}Sr with low isotopic abundance (0.56 %) was also detected. For the present system, we estimated the strontium isotope ratio of ^{87}Sr/^{86}Sr to be 0.69 ± 0.10 (14 %). This precision was inadequate to identify agricultural production areas but the required precision should be able to be achieved sufficiently by using a high-repetition-rate laser, which are presently commercially available. We concluded that the direct isotope analysis for trace inorganic elements such as strontium in brown rice using LA-RIMS had an advantage under the serious situation of isobaric interference and might have capability to identify agricultural production areas with sensitivity and precision.

As future work, we will try to actually use the high-repetition-rate laser and redesign the ion extraction electrodes to improve the ion transport efficiency and demonstrate the origin determination of agricultural products using LA-RIMS.

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Figure captions

Fig.1 Schematic of the experimental setup.

Fig.2 Configuration of sample holder and ion extraction electrodes. Electrode 1 also worked as a sample holder. Ions or neutral atoms transferred upward through electrode 2 and then ions were extracted toward TOF-MS.

Fig.3 LA-RIMS spectrum of magnesium obtained from brown race. This spectrum is the measured raw time spectrum triggered by the resonant ionization laser.

Fig.4 Temporal variation in magnesium isotope ratio (^{25}Mg/^{26}Mg) measured by LA-RIMS. Horizontal axis represents laser shot number and average values for 500 shots (50 sec), are plotted

Fig.5 LA-RIMS spectrum of strontium obtained from brown rice by accumulating signals for 2,000 laser shots (200 sec) in the off-line pulse counting mode. The mass spectrum using only the ablation laser is also drawn for comparison. The horizontal axis is converted from ion flight time to mass number.

Fig.6 Improved LA-RIMS spectrum of strontium obtained from brown rice. The signals were accumulated for 10,000 laser shots (1,000 sec) in the off-line pulse counting mode. The mass spectrum obtained at off-resonance wavelength is also drawn. The horizontal axis is converted from ion flight time to mass number.

Table 1 Inorganic elements in brown rice

Element	Content (ppm)
Na	10
K	2300
Ca	90
Mg	1100
P	2900
Fe	21
Zn	18
Cu	2.7
Mn	21
Sr	0.2

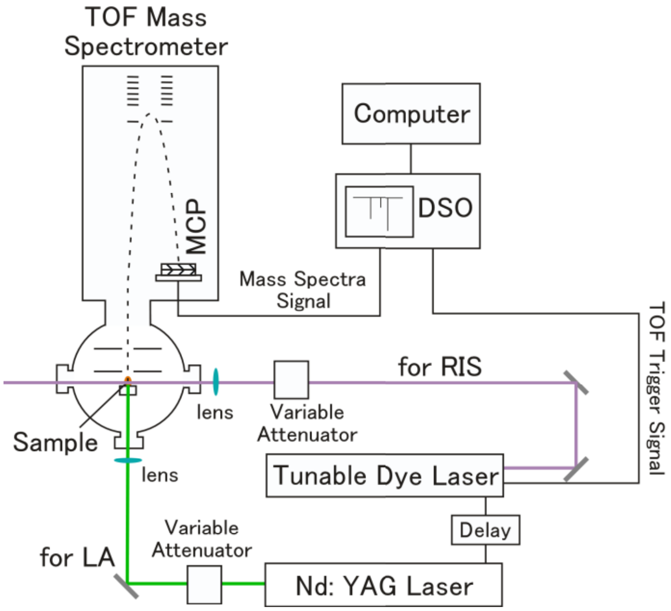

Fig. 1

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”Development of the Brown Rice Origin Determination Technique Based on Isotope Analysis Using Laser Ablation Assisted Resonance Ionization Mass Spectrometry”

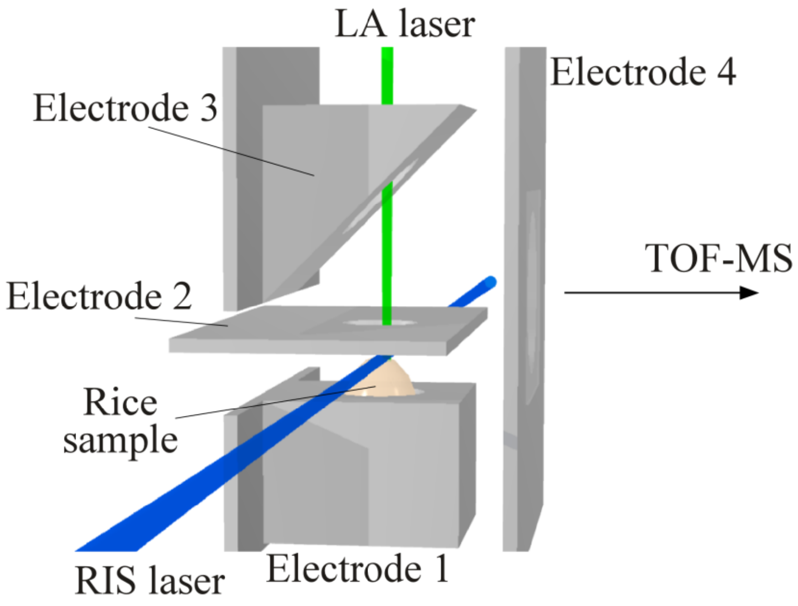

Fig. 2

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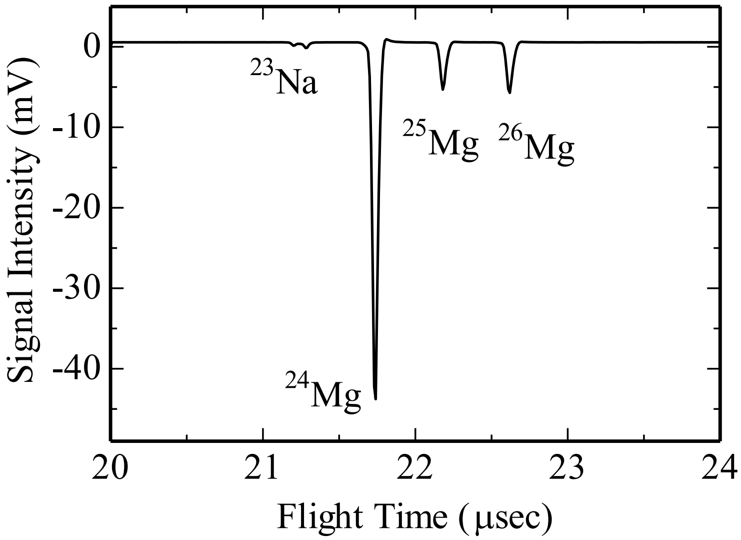

Fig. 3

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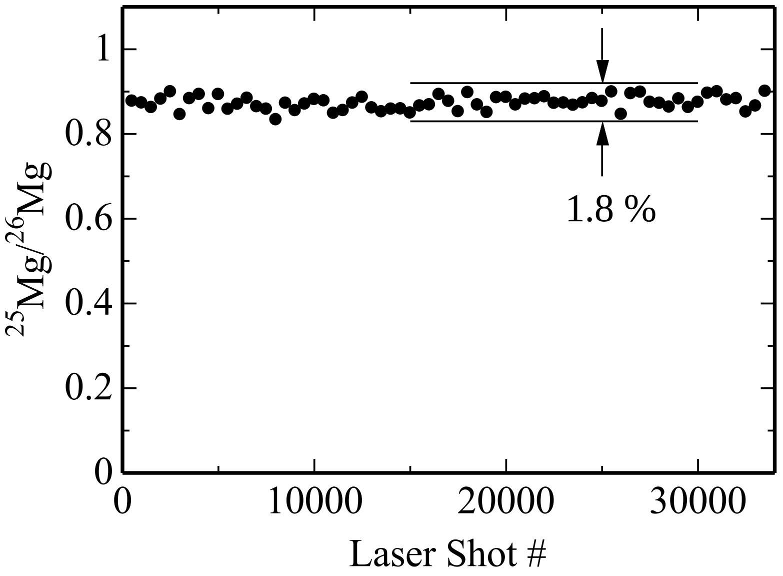

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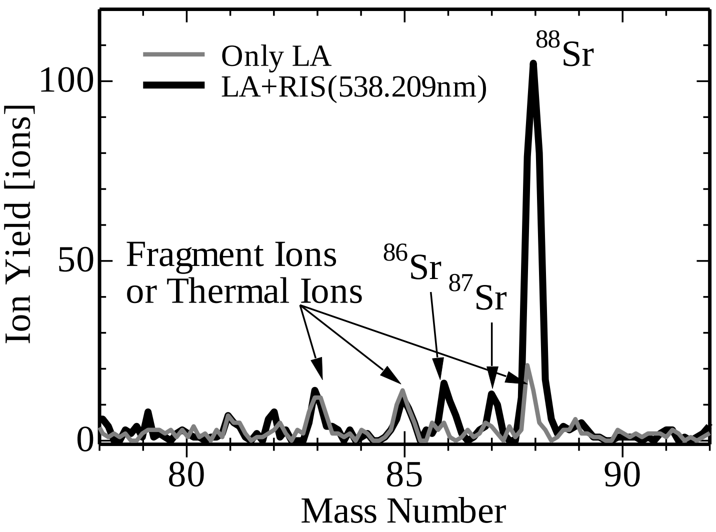

Fig. 5

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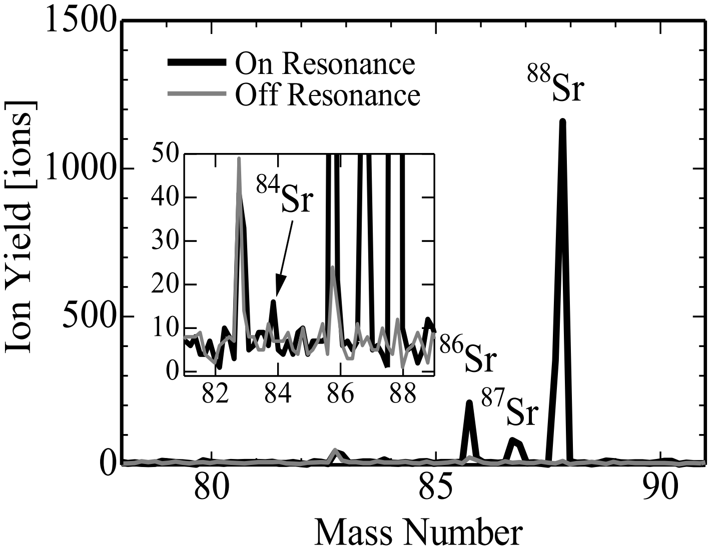

Fig. 6

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