Rapid Quantification of Radioactive Strontium-90 in Fresh Foods via Online Solid-Phase Extraction—Inductively Coupled Plasma—Dynamic Reaction Cell-Mass Spectrometry and Its Comparative Evaluation with Conventional Radiometry

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ABSTRACT: This paper describes a rapid quantification method for radioactive strontium (90Sr) in fresh foods (perishable foods) and has been comparatively evaluated with the common classical radiometric quantification method. Inductively coupled plasma—dynamic reaction cell-mass spectrometry with online solid-phase extraction (cascade-ICP—MS) rapidly determines 90Sr in a pure water-based sample. Despite its advantages, its application to fresh foods (perishable foods) has not yet been reported; however, the analytical potential of this method for fresh foods must be evaluated. In this study, 90Sr was determined in 12 fresh foods via improved cascade-ICP—MS (Icas-ICP—MS). Addition and recovery tests were demonstrated using real samples of grape, apple, peach, Japanese pear, rice, buckwheat, soybean, spinach, shiitake mushroom, grass, sea squirt, andounder. With a decomposed solution of Japanese pear, the measurement value coincided with the amount of spiked 90Sr. The reproducibility of the measurements was represented by relative standard deviations of 14.2 and 5.0% for spiked amounts of 20 and 200 Bq/kg, respectively (n = 10), and the recovery rates were 93.7 ± 7.1%. In this case, the limit of detection (LOD) was 2.2 Bq/kg (=0.43 pg/kg). These results were compared with the data obtained using a common classical radiometric quantification method (nitrate precipitation-low background gas flow counter (LBC) method) in the same samples. Both the methods showed equivalent performances with regard to reproducibility, precision, and LODs but different analysis times. Icas-ICP—MS required ~22 min for analysis, whereas the nitrate precipitation-LBC method required 20 days, confirming that Icas-ICP—MS is the suitable method for analyzing 90Sr in fresh foods.

INTRODUCTION

Radioactive strontium-90 (90Sr) is a typical fission product of uranium with a half-life of 28.74 years, and it is a pure β-ray emitter (100% β−-decay).1 90Sr behaves similar to the homologous element Ca because of their similar chemical properties; therefore, osteogenic sarcomas can potentially arise because of the incorporation and accumulation of 90Sr in the growing bone and tissues when humans absorb 90Sr from food.2 Several reports3−5 have reported the transfer of 90Sr into foods such as seafood as well as animal,6 agricultural,8−11 and dairy products,12−15 which were contaminated by past nuclear incidents. The harmful influence on human health by ingesting such contaminated food has also been reported.16−20 Thus, 90Sr analysis, in particular, the rapid analysis of 90Sr, in fresh foods was performed.21,22

Radiometric methods23 are commonly used for determining 90Sr concentration by employing a low background gas flow counter (LBC),24 a liquid scintillation counter (LSC),9 or a Cherenkov radiation counter.10 In radiometric analysis, coexisting radionuclides interfere with radiation from an analytical target; therefore, chemical separation is essential for removing coexisting radionuclides. In Japan, the Ministry of
**RESULTS AND DISCUSSION**

**Evaluation of Analytical Performance of Icas-ICP−MS for 90Sr Analysis.** The components of Icas-ICP−MS are based on previous reports.

Figure 1 shows the outline and flow design. The detailed measurement protocol is described in the “Measurements” part of the Experimental section. The Icas-ICP−MS system for 90Sr analysis comprised [I] the cascade-ICP−MS method (i.e., online SPE−O2 reaction in the DRC−quadrupole mass filter), [II] a single-channel data acquisition system quantifying both 90Sr and R% of Sr (split system), [III] an internal standard corrected signal integration method, and [IV] a sensitivity improvement system using a N2−Ar mixed gas effect. The experimental details of this system are included in the “Measurements” section.

Figure 2 shows a 5 Bq/L 90Sr peak profile of the reference material solution (black line). As a reference, a blank peak (0 Bq/L of 90Sr, gray line) is also shown in Figure 2. The peak area depends on the 90Sr concentration, as shown in the inset of Figure 2.
Figure 2. Quantifying the signal profile of $^{90}$Sr using the proposed method. Black peak line: the injection sample was a 50 mL solution containing 5 Bq/L radioactive $^{90}$Sr and 80 ppb natural isotope of Sr. Gray peak line: the sample was a 50 mL solution containing 80 ppb natural isotope of Sr. The intensities are a linear function of the $^{90}$Sr concentration vs the peak area (inset). The volume ratio between samples before and after preconcentration ($50 \rightarrow 0.6$ mL) was 83.3 times. Eluate flow rate: 5 mL/min. The LOD was 0.35 Bq/L. Total measurement time was 22 min. The 5 Bq/L is equal to 1 pg/L.

Figure 3. Signal profiles of Sr in the proposed method. The sample was a 50 mL solution containing 100 Bq/L radioactive $^{90}$Sr and 5 µg/L stable Sr. Panel [A] indicates the $^{88}$Sr signal from the bypass line. Panel [B] presents the signal of preconcentrated $^{88}$Sr and $^{90}$Sr from the online column.

Figure 4. Relation between the $^{88}$Sr intensity flowing in the split line and the peak area of the preconcentrated $^{88}$Sr eluted from the column line. The sample volume was 10 mL.

Figure 5. Analytical performance of the proposed method. Panel [A] indicates the concordance of the $^{90}$Sr concentrations between the spiked certified reference material and the quantitative values obtained by the proposed method. Panel [B] presents the variation in the quantitative values with the proposed method. The RSD represents the relative standard deviation of the measurement ($n = 3$).

The measured and spiked concentrations obtained using the proposed method were sufficiently consistent, as shown in Figure 5A. Additionally, the reproducibility was improved by increasing the $^{90}$Sr concentration in the sample, as shown in Figure 5B (i.e., RSD was 14.1 and 3.1% for 4 and 10 Bq/L of $^{90}$Sr, respectively). R % showed stable values (R %; $97 \pm 5.8\%$ ($n = 18$) regardless of the $^{90}$Sr concentration in the calibration range).

Otherwise, to obtain LOD values for each food samples, certain different concentrations of certificated $^{90}$Sr were added to the food sample. The LOD values were obtained from these lines. The average LOD ($n = 12$, 3σ) was $0.35 \pm 0.14$ Bq/L, which was equal to 1.7 Bq/kg as a solid sample (=0.33 pg/kg as a mass concentration).

Analytical Performance Evaluation: Comparison of $^{90}$Sr Analysis via Nitrate Precipitation-LBC with Icas-ICP-MS. Samples [50 mL standard solution ($n = 5$ samples)] identical to those for Icas-ICP-MS measurement were subjected to analysis via nitrate precipitation-LBC, which is commonly used for official analysis. When 2 or 10 Bq/L of $^{90}$Sr was added, the measured values were 2.66 Bq/L (RSD 5.7%) and 12.6 Bq/L (RSD 2.6%), respectively. During this time, the LODs of $^{90}$Sr were 0.18 and 0.20 Bq/L ($n = 5$), respectively. A total of 20 days was required for the analysis.

Table 1 lists a comparison of the analytical values obtained via Icas-ICP-MS and nitrate precipitation-LBC when analyzing 50 mL of standard solution containing 4 or 10 Bq/L of $^{90}$Sr. Results revealed that in the Icas-ICP-MS analysis, compared with nitrate precipitation-LBC analysis, the LOD, the coincidence of interfering components such as $^{90}$Zr and $^{74}$Ge, which were essentially contained in the concentration range of ppt—sub ppb as ingredients of the natural solution (note: isobar ($m/z = 90$; $^{74}$Ge$^{16}$O) was produced by reaction of $^{74}$Ge and oxygen). During this time, the final volume introduced into the ICP-MS after online SPE was 0.6 mL ($\pm 1.1\%$). This result was calculated from the eluate flow rate (5.0 mL/min), detected peak width (14.4 s ($\pm 1.1\%$) × 0.50 = 0.6 mL). Based on these values, the volume ratio between the initial solution (50 mL) and after preconcentration was 83.3 times.

Stable $^{88}$Sr peaks before and after SPE were simultaneously obtained using a split method during one sample injection into this system. Figure 3A shows the $^{88}$Sr peak before SPE, that is, the original solution flowed into the split line (bypass line). Figure 3B shows a peak of preconcentrated $^{88}$Sr eluted from the SPE column. Linearity is observed between the $^{88}$Sr intensity measured in the split line (i.e., $^{88}$Sr original concentration before SPE) and the preconcentrated $^{88}$Sr peak area (i.e., $^{88}$Sr concentration after SPE), as shown in Figure 4. The published cascade-ICP-MS method also shows almost complete R % (99%, RSD 1.2%) in measuring water-based reference material solutions. Based on this property, the proposed method gave the actual R % using the data in Figure 4 (i.e., the actual R % values were obtained by calculating the ratio between the actual and theoretical preconcentrated concentrations).

Figure 4. Relation between the $^{88}$Sr intensity flowing in the split line and the peak area of the preconcentrated $^{88}$Sr eluted from the column line. The sample volume was 10 mL. 

Figure 5. Analytical performance of the proposed method. Panel [A] indicates the concordance of the $^{90}$Sr concentrations between the spiked certified reference material and the quantitative values obtained by the proposed method. Panel [B] presents the variation in the quantitative values with the proposed method. The RSD represents the relative standard deviation of the measurement ($n = 3$).
The ratio in relation to the added amount, the dispersion (precision) of the measured value, the reproducibility, and the recovery rate were essentially comparable. However, the Icas-ICP-MA method is much more rapid, requiring only 22 min relative to 20 days for the nitrate precipitation–LBC method. In contrast, the recovery rate in Icas-ICP-MS analysis gradually decreases with increase of sample injection exceeding 60 mL (3); however, with nitrate precipitation-LBC analysis, the sample volume can be higher.

Table 1. Comparison of Analytical Performance between This Method and Conventional Radiometry

|                     | Icas-ICP-MS | nitrate precipitation-LBC (radiometry) |
|---------------------|-------------|----------------------------------------|
| quantitative value (concordance rate) in 2.00 Bq/L measurement | 2.06 (+3%) | 2.66 (+33%) |
| quantitative value (concordance rate) in 10.0 Bq/L measurement | 11.1 (+11%) | 12.6 (+26%) |
| detection limit (Bq/L) | 0.35 | 0.20 |
| recovery (R (%)) | 97.0 ± 5.8% | 94.7 ± 0.48% |
| reproducibility of 4.0 Bq/L measurements, (RSD (%), n = 3) | 14.1% | 5.7% |
| reproducibility of 10.0 Bq/L measurements, (RSD (%), n = 3) | 3.1% | 5.6% |
| analytical time to measure | 22 min | 20 days |

“Sample was 50 mL of aqueous solution containing the certified reference radioactive 90Sr (4.0 and 10.0 Bq/L).” Concordance rates were calculated using the following equation: concordance rate (%) = \[\frac{\text{quantified concentration} - \text{precise spiked concentration}}{\text{precise spiked concentration}}\] × 100. “The reproducibility (n = 18).”

Table 2. 90Sr Concentrations in Agricultural and Marine Products as per the Icas-ICP-MS

| no. | product | spiked 90Sr (Bq/kg) | measurement value of 90Sr and the RSD (%) | recovery rate (%) | LOD* (Bq/kg) |
|-----|---------|---------------------|------------------------------------------|------------------|--------------|
| 1   | grape   | 0 <LOD              | 24.7 ± 3.2 (13.1)                         | 96.6 ± 8.0       | 2.52         |
|     |         | 20                  | 195.7 ± 1.7 (0.9)                         |                  |              |
| 2   | apple   | 0 <LOD              | 22.2 ± 4.9 (22.1)                         | 97.4 ± 3.9       | 2.05         |
|     |         | 20                  | 214.2 ± 12.6 (5.9)                        |                  |              |
| 3   | peach   | 0 ND                | 19.2 ± 1.9 (10.1)                         | 93.7 ± 7.1       | 2.95         |
|     |         | 20                  | 209.9 ± 13.0 (6.2)                        |                  |              |
| 4   | Japanese pear | 0 <LOD         | 20.0 ± 2.8 (14.1)                         | 85.4 ± 5.3       | 2.21         |
|     |         | 20                  | 208.9 ± 10.4 (5.0)                        |                  |              |
| 5   | rice    | 0 <LOD              | 20.6 ± 1.8 (8.6)                          | 51.8 ± 2.7       | 0.99         |
|     |         | 20                  | 208.7 ± 15.4 (7.4)                        |                  |              |
| 6   | buckwheat | 0 <LOD            | 23.0 ± 2.6 (11.1)                         | 91.1 ± 3.2       | 1.88         |
|     |         | 20                  | 185.5 ± 8.4 (4.5)                         |                  |              |
| 7   | soybean | 0 <LOD              | 24.6 ± 7.4 (30.3)                         | 22.7 ± 1.4       | 1.45         |
|     |         | 20                  | 211.3 ± 20.4 (9.7)                        |                  |              |
| 8   | spinach | 0 <LOD              | 20.2 ± 1.6 (7.8)                          | 34.2 ± 1.9       | 1.15         |
|     |         | 20                  | 209.7 ± 14.7 (7.0)                        |                  |              |
| 9   | shiitake mushroom | 0 <LOD         | 21.5 ± 7.6 (35.4)                         | 52.6 ± 4.0       | 2.21         |
|     |         | 20                  | 203.0 ± 12.1 (5.9)                        |                  |              |
| 10  | grass   | 0 <LOD              | 14.2 ± 3.1 (22.2)                         | 37.3 ± 1.5       | 1.58         |
|     |         | 20                  | 202.7 ± 15.7 (7.8)                        |                  |              |
| 11  | sea squint | 0 <LOD           | 18.5 ± 3.2 (17.4)                         | 43.8 ± 4.8       | 1.52         |
|     |         | 20                  | 193.3 ± 8.5 (4.4)                         |                  |              |
| 12  | flounder | 0 <LOD            | 21.4 ± 1.2 (5.5)                          | 47.0 ± 4.6       | 0.43         |
|     |         | 20                  | 198.2 ± 12.6 (6.3)                        |                  |              |

“Sample was 50 mL of aqueous solution containing the certified reference radioactive 90Sr (4.0 and 10.0 Bq/L).” Concordance rates were calculated using the following equation: concordance rate (%) = \[\frac{\text{quantified concentration} - \text{precise spiked concentration}}{\text{precise spiked concentration}}\] × 100. “The reproducibility (n = 18).”

The product information is described in the Supporting Information. RSD: relative standard deviation; n = 3 except for Japanese pears (n = 10). <LOD: lower limit of detection. The average recovery percentages (n = 8–23). LOD: limit of detection. 3σ.
be increased. Thus, when the sample size is large, lower concentrations can be measured via nitrate precipitation–LBC analysis than Icas-ICP–MS.

Otherwise, this Icas-ICP–MS basically uses Eichrom Sr resin in the SPE prior to ICP–MS analysis. Alternatively, Eichrom Sr resin with LBC may give rise to an interference of Sr analysis. The Eichrom Sr resin can trap not only Sr but also Ba and Pb.\textsuperscript{26} Pb exists in \textsuperscript{210}Pb which emits radiation, and the nuclide interferes Sr analysis in radiometric analysis such as the LBC method. Therefore, when the Eichrom Sr resin is used in the radiometric analysis, the spectrophotometric separations using LSC\textsuperscript{32} or beta-ray spectrometers\textsuperscript{33} will be needed.

**Analysis of Actual Samples Containing \textsuperscript{90}Sr.** The measurement results (recovery; detection limits) obtained from the analysis, the decomposition solutions of 12 agricultural and marine commercial products (obtained from markets in Fukushima Prefecture) via the Icas-ICP–MS method are summarized in Table 2. Samples were prepared by the addition of 0 (no addition), 20, or 200 Bq/kg \textsuperscript{90}Sr to the decomposition solutions. Results reveal that all of the samples with any added \textsuperscript{90}Sr were below the LOD and that \textsuperscript{90}Sr was not detected by any method. LOD was within 0.43–2.95 Bq/kg (=0.08–0.59 Bq/L) in each sample, and there was no remarkable difference in the variety of samples. Furthermore, the quantitative values almost coincided with the samples with the addition of 20 or 200 Bq/kg. As a reference, Figure S1 in the Supporting Information shows the peak profile when 200 Bq/kg of \textsuperscript{90}Sr was added to grapes. The shape of the peak showed the same as in the case of the standard solution. Japanese pear (84–109%) showed a high recovery rate, but soy beans (21–25%), spinach (31–37%), and sea squirt (35–51%) produced low recovery rates (note: the recovery rate means whole recovery rate for the total analytical system as ICP–MS. Those are not only resin recovery). This can be attributed to the fact that the presence of excess stable Sr isotope inhibits plasma ionization and disturbance occurs during ICP–MS measurements (cf. Table S1 in the Supporting Information). When excess concentration of the solute in sample solution is injected into ICP–MS, it is well known that the quantification of the target is typically interfered by the space charge effect. The quantitative values were consistent with the addition amounts obtained by correcting with these recovery rates and a correction method.\textsuperscript{29} Most of the repeated reproducibility (n = 3) of the measured values for the samples under the same conditions was within 10%, but the relative standard deviation (RSD) of the measured value tended to improve as the \textsuperscript{90}Sr amount increased (200 Bq/kg was added in this case).

Reproducibility tests (n = 10) were conducted on Japanese pears via the use of the Icas-ICP–MS method by measuring samples under the same conditions consecutively. As a result, for the samples with the addition of 20 or 200 Bq/kg, RSDs of the measured values were 14.2 and 5.0%, respectively, and stable measurement values were obtained (cf. Figure S2 in the Supporting Information). Results showed the same extent of dispersion as in the analysis of standard \textsuperscript{90}Sr solutions, and the quantitative values were consistent with the added amounts at all times. During this time, the analyses of all 10 samples were concluded in a total of approx. 220 min. This result indicated that Icas-ICP–MS is faster when compared to the radiological analysis.

Table 3 shows the results obtained via nitrate precipitation–LBC and their comparison with Icas-ICP–MS. Similar to nitrate

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Table 3. Comparison of Classical Nitrate Precipitation LBC Method and Icas-ICP–MS

| no. | product          | spiked \textsuperscript{90}Sr\textsuperscript{a} | nitrate precipitation-LBC measured value\textsuperscript{b} (counting error) | LOD\textsuperscript{b} | recovery rate\textsuperscript{c} (%) | Icas-ICP–MS measured value\textsuperscript{b} | LOD\textsuperscript{d} | recovery rate\textsuperscript{d} (%) |
|-----|------------------|-----------------------------------------------|--------------------------------------------------------------------------------|------------------------|---------------------------------------|-----------------------------------------------|------------------------|---------------------------------------|
| 1   | grape            | 0                                             | <LOD                                                                           | 3.3                    | 63.8                                  | >LOD                                           | 2.52                   | 96.6                                  |
| 2   | apple            | 19.7                                          | 21.2 (±1.49)                                                                  | 2.6                    | 69.8                                  | >LOD                                           | 24.7                   | 97.4                                  |
| 3   | peach            | 19.7                                          | 19.3 (±1.53)                                                                  | 2.9                    | 62.8                                  | >LOD                                           | 22.2                   | 93.7                                  |
| 4   | Japanese pear    | 0                                             | <LOD                                                                           | 2.9                    | 72.6                                  | <LOD                                           | 2.95                   | 93.7                                  |
| 5   | rice             | 19.5                                          | 19.1 (±1.39)                                                                  | 2.5                    | 74.6                                  | >LOD                                           | 19.2                   | 92.9                                  |
| 6   | buckwheat        | 19.7                                          | 22.8 (±1.64)                                                                  | 2.9                    | 64.5                                  | >LOD                                           | 20.0                   | 95.4                                  |
| 7   | soybean          | 19.7                                          | 19.8 (±1.44)                                                                  | 2.6                    | 73.0                                  | <LOD                                           | 19.0                   | 97.9                                  |
| 8   | spinach          | 19.6                                          | 18.0 (±1.39)                                                                  | 2.6                    | 69.7                                  | >LOD                                           | 20.6                   | 95.5                                  |
| 9   | shiitake mushroom| 19.7                                          | 19.2 (±1.40)                                                                  | 2.4                    | 73.3                                  | <LOD                                           | 20.2                   | 93.6                                  |
| 10  | grass            | 19.6                                          | 19.7 (±1.44)                                                                  | 2.5                    | 72.2                                  | <LOD                                           | 21.5                   | 94.5                                  |
| 11  | sea squirt       | 19.6                                          | 20.5 (±1.40)                                                                  | 2.3                    | 78.5                                  | <LOD                                           | 14.2                   | 94.2                                  |
| 12  | flounder         | 19.6                                          | 18.6 (±1.41)                                                                  | 2.5                    | 73.0                                  | >LOD                                           | 18.5                   | 93.5                                  |

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\textsuperscript{a}Precise concentration. \textsuperscript{b}LOD: lower limit of detection. \textsuperscript{c}Error of LBC counting rate. \textsuperscript{d}LOD: limit of detection. \textsuperscript{e}n = 1. Recovery was calculated from stable Sr concentration obtained by ICP–AES measurement. \textsuperscript{f}The data are the same as in Table 2.
preparation-LBC, all the samples with no $^{90}\text{Sr}$ addition (12 samples in total) showed results below the LOD. When $^{90}\text{Sr}$-added samples (20 Bq/kg) were measured, the quantitative value obtained via nitrate precipitation-LBC substantially agreed with the added amount. Moreover, the results almost coincided with the results of Icas-ICP−MS (Table 2). The LOD of nitrate precipitation-LBC tended to be slightly higher than that of Icas-ICP−MS. In other words, if the amount of the solid sample used for the measurement was 10 g, the analytical sensitivity of Icas-ICP−MS was slightly better than that of nitrate precipitation-LBC.

Table 4 shows the difference of trueness between the Icas-ICP−MS method and nitrate precipitation LBC analysis. The values were obtained from the ratio of the (measurement value of $^{90}\text{Sr}$)/(spiked $^{90}\text{Sr}$). From the comparison of the average values and RSDs, there are almost no differences between two methods.

**Evaluation of $^{90}\text{Sr}$ Analysis Performance of Icas-ICP−MS in Various Samples.** To confirm the quantitative character in real sample analysis, representative samples were selected and $^{90}\text{Sr}$ was added in various concentrations and analyzed. We selected peach, brown rice, and flounder as the model sample for fruit, grain, and fish, respectively. To each of these samples, 20, 50, 100, 200, and 500 Bq/kg of $^{90}\text{Sr}$ was added and measurements were performed using $n = 3$. Results are shown in Figure 6. Good linearity was obtained over a wide range from all samples, with good agreement between the addition amount and the measured value. All samples showed good reproducibility. These results verified that with Icas-ICP−MS, quantitative values could be adequately obtained in fresh food samples of different composition at various concentration levels.

| no. | product | Icas-ICP−MS ratio | nitrate precipitation-LBC |
|-----|---------|------------------|---------------------------|
| 1   | grape   | 1.24             | 1.08                      |
| 2   | apple   | 1.11             | 0.98                      |
| 3   | peach   | 0.96             | 0.98                      |
| 4   | Japanese pear | 1.00 | 1.16                  |
| 5   | rice    | 1.03             | 1.09                      |
| 6   | buckwheat | 1.15 | 1.01                  |
| 7   | soybean | 1.23             | 0.92                      |
| 8   | spinach | 1.01             | 0.97                      |
| 9   | shiitake mushroom | 1.08 | 1.01                  |
| 10  | grass   | 0.71             | 1.05                      |
| 11  | sea squirt | 0.93 | 0.94                 |
| 12  | flounder | 1.07 | 1.13                 |
| 13  | average | 1.04             | 1.03                      |
| 14  | RSD     | 0.14             | 0.07                      |

*The product information is described in the Supporting Information.

bConcordance ratio were calculated using the following equation: ratio = quantified concentration/spiked concentration. The data of approx. 20 Bq/kg spiked were used in the calculation. *The data for calculation are used from Table 3.

The first measurement are the same as those shown in Table 2. After 18 measurements, a slight decrease in recovery rate was confirmed for all samples. It is considered that slight decrease in recovery rates arise from the deterioration of efficiency of Sr-reins. However, because the recovery rates can be always monitored at the same time as quantification using the split method, the quantitative value was consistent with the addition amount. These results indicated that Icas-ICP−MS is useful in the repeated analysis of fresh food samples containing various matrix components.

Figure 8 shows the results of the reproducibility tests ($n = 3$ or more) with various concentrations of $^{90}\text{Sr}$ added to the 12 fresh samples. Results confirmed that the RSD value drastically increased below a certain $^{90}\text{Sr}$ concentration. Thus, it was verified. Pear, peach, brown rice, and flounder were selected as typical samples for fruit, grain, and seafood, respectively. For comparison, the standard solution was measured. To each of these samples, 200 Bq/kg (40 Bq/L = 8 pg/L) of $^{90}\text{Sr}$ was added and maximum of 18 continuous measurements were performed. The results are shown in Figure 7. Specific recovery rate is shown for each sample. The results of
confirmed that a stable quantitative value of RSD ≤ 10% could be obtained by measuring 50 mL of solution that contains 90Sr of 20 Bq/kg (=5 Bq/L) or more. This result was similar to that obtained from measuring the standard solution (Figure 5B).

**CONCLUSIONS**

Because the official radiometric analysis for a small amount of 90Sr in the order of several Bq requires time for pretreatment, it was difficult to analyze a large number of specimens in short time. Therefore, it was difficult to apply food analysis to foods that quickly perish, such as fresh food. In this study, a rapid 90Sr analysis with 12 types of fresh food was conducted using Icas-ICP−MS that employs online solid-phase extraction with ICP−DRC-MS; comparative evaluation was performed using classical radiometric measurement. For comparison with the Icas-ICP−MS analysis, the nitrate precipitation-LBC method, which is a radiometric analysis method, was conducted. Samples were tested by adding and recovering 90Sr to Japanese fresh foods. For the sample, the dissolved sample was divided for Icas-ICP−MS and nitrate precipitation-LBC analyses; results were compared for samples analyzed under the same condition, which revealed that the quantitative values of 90Sr substantially agreed with the addition amount in both the methods. The LOD was 0.4–3.0 Bq/kg and the time required for the measurement was about 22 min. Meanwhile, with this method, the nitrate precipitation-LBC analysis matched the quantitative values well. Furthermore, for each LOD, both the methods indicated an almost equal analytical sensitivity. Icas-ICP−MS proved to be useful for the analysis of fresh foods because it shortened the analysis time from 20 days (nitrate precipitation-LBC) to 22 min (Icas-ICP−MS).

**METHODS AND EXPERIMENTS**

**Apparatus.** Icap-ICP−MS: as an analytical system for 90Sr, we adopted online solid-phase extraction coupled to ICP−MS,39 and this system comprised the following instruments: a NexION 350S instrument (PerkinElmer, Inc., Shelton, CT, USA) with ultrapure O2 as a reaction gas (>99.99995%) in a collision-reaction cell (DRC). A make-up gas mass flow upgrade kit was installed in ICP−MS to pass N2 gas to improve sensitivity.31 An US5000AT+ ultrasonic nebulizer (Teledyne CETAC Technology, NE, USA), a FIAS 400 flow-injection system (PerkinElmer) with specially fabricated double eight-way switching valves, and an S10 autosampler for ICP−MS (PerkinElmer) were attached to an ICP−MS. The experimental parameters and conditions for ICP−DRC-MS are shown in Table S2 in the Supporting Information.

The splitter and microvolume mixer components of the split line were obtained from GL Science Co. Ltd, Tokyo, Japan. The velocity of the solution in the tube was measured using a Trullo flowmeter (Glass Expansion, Melbourne, Australia). The velocity was controlled by varying the tube diameters as follows.

For the split ratio, main/split ratio = 23:1 as well as the internal diameters (IDs) of the solution feeder (main tube), split line, and internal standard solution feeder were 0.76, 0.13, and 0.19 mm, respectively. All these tubes were peristaltic pump tubes made from polyvinyl chloride. Other flow tubes were constructed from fluorophenylalanine tubing with an ID of 0.8 mm. Under these conditions, the volume ratio between the main and split flows was 100:4.

Nitrate precipitation-low background gas flow counting system (nitrate precipitation-LBC): a LBC-4202B LBC (Hitachi Aloka Medical Co., Ltd, Tokyo, Japan) was employed by applying 1750 V (in the Geiger–Müller region). Measurement was conducted using a 10% methane–90% argon mixed gas (PR gas). Additionally, an Optima 7300 DV ICP−atomic emission spectrometer (ICP−AES) was employed for measuring the stable Sr recovery efficiency.

**Reagents.** Sr stock solution (single element; stable isotopes; concentration 1000 ppm) and the other single-element stock solutions were obtained from Nacalai Tesque (Kyoto, Japan). Working solutions (20% HNO3) and all injected samples (20% HNO3) were prepared by appropriate serial dilution of the metal ion solutions in water or ultrapure nitric acid. The radioactive 90Sr stock solution (1.005 × 105 Bq/g) was obtained from the public interest incorporated association, Japan Radioisotope Association (JRA, Tokyo, Japan) with a calibration certificate. It was serially diluted to the appropriate concentration in water or ultrapure nitric acid (20% HNO3 sol.). Water obtained from a DIRECT-Q3 UV Ultrapure water supply system (Merck Millipore SAS, Molsheim, France) was used. The concentrated HNO3 (high-purity electronic grade, 61 w/w %) was obtained from Kanto Chemical Co., Inc. (Tokyo, Japan).

SPE powders (250 mg) of an Eichrom Sr resin [particle diameter 50–100 µm; chemical composition 4,4-(S′)-di(f-butylcyclohexano)-18-crown-6, purchased from Eichrom Technologies, LLC (IL, USA)] were packed into original empty polytetrafluoroethylene columns (PerkinElmer Japan, ID 4.0 mm, length 50 mm), and these were used as special SPE columns for installing into Icas-ICP−MS. In use, the two special SPE columns were connected in series. All other required reagents and organic solvents (analytical grade materials) were purchased from Wako Chemical Co., Ltd. and used without further purification.

**Sample Collection and Pretreatment.** Agricultural, forestry, and fishery products from the vicinity of Fukushima Prefecture were selected as model samples; 2–10 kg of 12 items, which were fruits (grapes, apples, peaches, and Japanese pears); cereals (rice, buckwheat, and soybeans); farm products (spinach, shiitake mushrooms, and grass); and marine products (flounder and sea squirt) were obtained from a wholesale market or fishermen’s cooperative. Details of the samples are given in the Supporting Information (photos, breeds, states, collection data, and locations of the samples are provided).

The samples were treated according to the literature,24,34 and these procedures (carbonization and solubilization) are described in Figure S3 in the Supporting Information, that is, the samples were sorted into waste and edible parts, whereby 1 kg or more of edible parts were obtained. The edible parts were homogenized using a mixer (such as a food mixer). Three hundred grams of aliquot were placed on a porcelain evaporating dish and dried to constant weight. After drying, the sample was carbonized with an electric heater and heated in an electric furnace at 500 °C for 48 h. Aqua regia was added to the incinerated sample, which was then evaporated to dryness on a hot plate. Then, nitric acid was added and the sample was evaporated to dryness again. One to three hundred milliliters of nitric acid (1 + 4) was then added. The sample was heated on the hot plate for 1 h and then suction-filtered using a Buchner funnel and filter paper (no. SC). The residue was rinsed with nitric acid (1 + 4). The filtrate and washed residue were combined and transferred to a 2 L measuring cylinder. The volume was then adjusted to 1500 mL with nitric acid (1 + 4). Fifty milliliter aliquots of the solubilized sample were distributed; then, an appropriate amount of certified reference solution of 90Sr was
spiked into these distributed samples. These samples were then subjected to the nitrate precipitation-LBC and Icas-ICP−MS methods for analysis.

**Measurements.** Quantification of $^{90}\text{Sr}$ Using Icas-ICP−MS. As shown in Figure 1A, 50 mL of sample solution containing $^{90}\text{Sr}$ (20% HNO$_3$ aq. sol.) was injected into the Icas-ICP−MS system via an autosampler. After injection, the sample was split two ways and a major volume of the sample was passed through the main flow line powered by the pump#1 (5 mL/min). The sample was then introduced into the SPE column. Strontium in the sample was adsorbed on resin in the column, and other materials that did not adsorb on the resin were discharged to drain. The minor part of the sample was passed through the split flow line powered by the pump#2. The split ratio of the sample volume was main-line/split line = 23:1. A solution of elute and internal standard (ISTD) material solution containing indium (In) was added to the divided sample in the split line on the flow line and thoroughly mixed with the mixer. The solution was nebulized by an ultrasonic nebulizer (USN) and introduced into the ICP−MS. N$_2$−Ar mixed gas (1%) [1% ultrapure N$_2$ gas (>99.9995%) was added to ultrapure Ar gas (>99.9999%)] was used as plasma gas because of sensitivity improvement. Mixed gas was generated prior to USN using a T-connector; thus, the mixed gas was used for sample nebulization via USN.

In this way, the stable isotope $^{88}\text{Sr}$ was detected (this time, O$_2$ gas was introduced to DRC). As a result, $^{88}\text{Sr}$ contained in the split sample, that is, $^{88}\text{Sr}$ concentration before condensation (SPE) was quantified by preparing a calibration curve based on the concentration versus intensity of the $^{88}\text{Sr}$ standard solution in advance.

After all of the samples were passed through the column, the column was cleaned with a nitric acid solution after the adsorption of Sr by passing 20% nitric acid (flow rate 5 mL/min). Thereafter, the state shown in Figure 1B occurs when the automatic valve is switched. In this state, ultrapure water was made to flow as the eluent (=cleaning solution) in the main channel and the concentrated Sr was eluted from the column on the main channel. This concentrated Sr was mixed with In solution as ISTD, nebulized by USN, and introduced into the ICP−MS. The sample was nebulized by USN and plasma-ionized with mixed gas of ultrapure Ar gas (>99.9995%) obtained by mixing 1% of ultrapure N$_2$ gas (>99.9999%) [note: gas mixing was performed by using a T connector immediately before USN. Therefore, atomization by USN was also performed with mixed gas]. Subsequently, O$_2$ reaction was conducted in DRC and isotopes, such as $^{90}\text{Sr}$ and $^{88}\text{Sr}$, after concentration was detected by the QMS filter. Quantitation was calculated by preparing a calibration curve based on the standard solution concentration versus peak area of $^{88}\text{Sr}$ in advance. In this way, the $^{90}\text{Sr}$ and $^{88}\text{Sr}$ concentrations were determined after concentration (SPE).

While performing these measurements, the flow path was cleaned up by passing the eluent (=ultrapure water as cleaning solution) through the split channel (flow rate of 5 mL/min).

The operation and step contents of FI used for online SPE are shown in Table S3 in the Supporting Information. The time required for one sample measurement was 22 min. The method for quantitative determination of $^{90}\text{Sr}$ by Icas-ICP−MS and conversion to radioactivity concentration.

By adjusting the MS bias, measurement could be performed using the method that quantifies $^{90}\text{Sr}$ using the stable isotope as a standard substance, the Sr recovery rate obtained by the split method, and the online internal standard correction method.

The $^{90}\text{Sr}$ weight concentration was converted to the radioactivity concentration Bq/L using the following equation.

$$A = \left( \frac{\ln \frac{A}{A_{1/2}} \times \frac{m}{M}}{N_s} \right) \times \frac{1}{L}$$

where A, $t_{1/2}$, m, M, and N$_s$ indicate the radioactivity concentration (Bq/L), half-life (s), weight (g) of the analyte to be analyzed per liter (in this instance $^{90}\text{Sr}$), mass number of the measured isotope, and Avogadro’s number (cf. in the sample amount of this study $^{90}\text{Sr}$ was 5 Bq/kg = 1 Bq/L = 0.2 pg/L respectively.

**Nitrate Precipitation-LBC.** Samples were analyzed using the Ministry of Education, Culture, Sports, Science and Technology (MEXT) oxalate method. The samples were the same as those measured with Icas-ICP−MS. The flowchart of the analysis process is shown in Figure S4 in the Supporting Information. The time required for one sample measurement was 20 days. The recovery rate was obtained by measuring stable Sr (carrier) with solutions before and after precipitation with ICP−AES. The $^{90}\text{Sr}$ radioactivity concentration was corrected on the date of sample preparation using the decay curve.

**Analysis of the Major Components in the Sample.** With the $^{90}\text{Sr}$ measurement, the major components in the samples were analyzed. The water content, ash percentage, and concentrations of potassium, calcium, and stable strontium were measured. The analytical procedure obtained from the Japan Consumer Affairs Agency is shown in Figure S5 in the Supporting Information.

The water and ash contents were calculated from the weight after the sample reached constant weight and the weight after incineration, respectively. The results are shown in Table S1 in the Supporting Information.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01381.

Signal profile of the actual fruit sample (grape) containing 20 Bq/kg of $^{90}\text{Sr}$; quantitative results for major components in the sample; reproducibility of the quantitative value in sequential sample injection; ICP−DRC-MS instrumental parameters and conditions; sample information (no. 1−12); solubilization process for samples; flow chart of the nitrate precipitation-LBC method; and flow chart of major component analysis of the sample (PDF)

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**Notes**

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