Development of Online Dilution System for quantification of $^{90}$Sr Using Automatic Solid-phase Extraction Inductively Coupled Plasma Mass Spectrometry

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Abstract

In this paper, we propose an online dilution system for rapid quantification of radioactive strontium-90 (\(^{90}\)Sr) with inductively coupled plasma mass spectrometry coupled solid-phase extraction and \(O_2\) dynamic reaction (cascade ICP–MS). The proposed system automatically provides a higher dilution ratio, which is at most \(3.3 \pm 0.2\) times the ratio obtained by the previous method, without increasing the analysis time (<15 min). A detection limit of 2.7 Bq/kg wet (0.54 pg/kg wet) was achieved. The recovery test results were consistent with two different spiked values.
Introduction

The radioactive isotope, strontium-90 (\(^{90}\text{Sr}\)), \((T_{1/2} = 28.80\ \text{y})\) is formed via nuclear fission of uranium or plutonium and represents one of the pure beta emitters that are difficult to measure. \(^{90}\text{Sr}\) has similarities with calcium in terms of chemical and biochemical behaviors, and therefore, it accumulates in bones for prolonged periods upon intake. The concentration factors (CFs) for most marine products are greater than 1. In particular, a CF of \(>10^3\) has been reported for fishbone.\(^1,2\)

The demand for a rapid quantification method for \(^{90}\text{Sr}\) in environmental samples and fresh foods collected near nuclear facilities is growing because of the difficulty in measuring it as well as its hazardous nature, as evidenced by the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident. Radiometric methods involving a liquid scintillation counter (LSC) or a low-background gas flow counter (LBC) are conventionally utilized to determine the concentration of \(^{90}\text{Sr}\). However, the LBC method, which is a Japanese standard analytical method for \(^{90}\text{Sr}\) quantification (otherwise, LSC are used as global standard), is time-consuming (more than 2 weeks) and has complicated pretreatment processes.\(^3\) It requires the purification of \(^{90}\text{Sr}\) and its daughter nuclide, \(^{90}\text{Y}\), from other interfering nuclides by ion-exchange chromatography. Recently, an automated analysis system for \(^{90}\text{Sr}\) quantification, based on inductively coupled plasma–mass spectrometry (ICP–MS), was developed.\(^4\) By combining the quadrupole ICP–MS system with an O\(_2\) dynamic reaction cell (DRC) and online solid-phase extraction (SPE), the system can be utilized for the rapid quantification of \(^{90}\text{Sr}\) within 15–30 min to accommodate various demands such as environmental monitoring. This system is called “cascade ICP–MS” due to above mentioned multi-step continuous separation process of \(^{90}\text{Sr}\) in an ICP-MS system. Additional functions have been reported, which enhance the performance of the cascade ICP–MS. For example,
the internal standard corrected signal integration (ISCSI) system was applied to correct the mass chromatogram obtained from the cascade ICP–MS system for matrix effects by comparing the signal intensities of the analytical targets and the internal standard during elution, followed by the integration of the corrected intensities.\(^5\) The split method facilitated the acquisition of the \(^{90}\text{Sr}\) concentration and recovery percentage (R\%) of Sr simultaneously with a split-flow line, which provided reference signal intensities of stable isotopes before the SPE column pretreatment.\(^6\) In the split method, the sample solution was divided into two line flows: the main-line flow passing through the SPE column, and the split-line flow directly introduced into the ICP–MS system. The introduction of the N\(_2\)–Ar mixed gas into the nebulizer enhanced sensitivities by more than 3.7 fold for \(^{90}\text{Sr}\) measurement.\(^7\) A limit of detection (LOD) of 0.3 Bq/L (0.059 pg/L) within 30 min was obtained by the composite use of these techniques.\(^5–7\) Previous reports have demonstrated the applications of the cascade ICP–MS system for \(^{90}\text{Sr}\) quantification in groundwater, rainwater, and solid samples.\(^5–9\) However, the introduction of a large amount of the matrix material into the ICP–MS system, due to multiple measurements of the samples containing the matrix material, causes considerable loss of sensitivity and necessitates the cleaning of the inner parts such as cones and DRC. This problem, which has been actually faced, should be easily observed in analysis with several grams of marine products because the allowable limit of salt concentration in the samples is <1000 mg/L. Therefore, maintaining the required sensitivity of \(^{90}\text{Sr}\) and suppressing the effects of the matrix material introduced into the cascade ICP–MS system during the measurement of the signals from the split line are necessary.

In this study, we developed an online dilution system for diluting a sample solution passing through the split-flow line. This study shows that the proposed system
suppresses the analytical interference caused by the large amount of the matrix material in the sample by automated water infusion into the sample solution. Using sea fish samples collected within 20 km of FDNPPs, we also performed $^{90}$Sr-spiked tests to evaluate performance parameters such as analysis time, LOD, concordance ratio between the spiked and measured values, relative standard deviation (RSD), and R% of Sr.

**Experimental**

**Reagents and apparatus**

The $^{90}$Sr standard solution (3.7 kBq in 5 mL) obtained from the Japan Radioisotope Association (Tokyo, Japan) was diluted to the required concentration. All the sample solutions were adjusted to 20% HNO$_3$ by ultrapure water and high purity 68 v/v% nitric acid (Tama Chemicals Co., Ltd., Kanagawa, Japan). The other reagents used, which were of analytical grade, were obtained from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan) and were used without further purification unless otherwise noted. A NexION 350S ICP–MS instrument (PerkinElmer, Inc., Shelton, CT, USA) and other components were the same as those adopted in our previous studies. Table S1 in Supporting Information (S.I.) shows the measurement parameters and conditions. The flow rate in the tube was monitored using a TruFlo sample monitor (Glass Expansion, Melbourne, Australia). A Freeze dryer (Tokyo Rikakikai Co., Ltd., Tokyo, Japan) and an ETHOS One microwave digestion system (Milestone Stl, Sorisole, Italy) were used for the pretreatment of the fish sample. SPE powders (250 mg) of an Eichrom Sr resin (particle diameter 50–100 μm; chemical composition 4,4'(5')-di-(t-butylcyclohexano)-18-crown-6, purchased from Eichrom Technologies,
LLC (IL, USA)) were packed into original empty polytetrafluoroethylene (PTFE) columns (PerkinElmer Japan, ID 4.0 mm, length 50 mm), and these were used as special SPE columns for installing into this system.

**Flow design of the proposed method**

Figure 1 shows the flow design of the proposed system. Table S2 in S.I. presents the program for the components of the flow-injection system. The injected sample solution was divided into main and split-line flows by a splitter, as shown in Fig. 1[A]. The ratio of the main line to the split line was 33:1. The split ratio and flow rate were adjusted by the internal diameters (IDs) of the peristaltic pump tubes for Pump 2 behind the splitter. The IDs of the main and split tubes were 1.14 and 0.13 mm, respectively. The maximum injection volume of the sample solution was 50 mL. The SPE column was placed on the downstream side of Port #7. The injected sample solution was prepared to be 20 v/v% (4.4 M) HNO₃. Sr-resin has a specific affinity to Sr ion in concentrated HNO₃ (1 to 7M); thence Sr ion can be separated from coexistent elements.¹¹ Low concentrations of HNO₃ solution (less than 0.05M) or water can elute trapped Sr ion from the column. In the main line, most of the injected samples flowed from Port #8 to #7 for the preconcentration of Sr in an SPE column after column conditioning with 20 v/v% HNO₃ via an injector of S10 Autosampler (PerkinElmer). Subsequently, the solutes, except the analytical targets, were drained from Port #4 to #3. Conversely, the solution in the split line was not concentrated, and the signal indicative of stable Sr was measured by the ICP–MS system for Sr quantification and calculation of R%. Ultrapure water joined the split line from Port #2 to #1 through a 3rd mixer and from Port #6 to #5 through a 2nd mixer to suppress the signals corresponding to an
excessive amount of stable Sr and other coexistent elements. After the flow lines were merged, the internal standard solution (ISTD; 0.1 μg/L of indium solution in 3 v/v% HNO₃) was introduced into the ICP–MS system for measurement. Polyvinyl chloride (PVC) tubes with IDs of 1.14 and 0.19 mm were used for the online dilution line and ISTD line, respectively.

Figure 1[B] shows the flow map after switching the valve position. The preconcentrated Sr was liquated into an eluent from the SPE column by flowing ultrapure water from Port #6 to #7 using Pump 1. Subsequently, the elution liquid that flowed from Port #4 to #5 was merged with the ISTD solution using a 1st mixer, while Pump 2 was temporarily stopped. Finally, the signals of ⁹⁰Sr and stable Sr were measured using the ICP–MS system for determining the ⁹⁰Sr concentration and R% of Sr. The data obtained by the sequence of analytical steps were calculated using the same method previously reported.⁶

Pretreatment of an actual fish sample

A recovery test was performed using whitebait collected in the Fukushima offshore within 20 km of FDNPPs. A 6 kg portion of the fresh sample was freeze-dried by a freeze dryer and homogenized. The water content (Water%) was obtained as a difference between the wet and dry weights. An 8 mL portion of a 68 v/v% HNO₃ solution was added to the freeze-dried sample (0.5 and 1.0 g of the dry weight), and it was digested in a microwave at 180°C for 35 min. After cooling to room temperature, the digested sample was filtered using a 0.45-μm pore-size filter membrane made of polyvinylidene difluoride (PVDF). HNO₃ (68 v/v%) was added, so that the final concentration became 20% after adding 0.5 Bq of ⁹⁰Sr. The sample solution, diluted to
10 mL with ultrapure water, was injected for measurement into the cascade ICP–MS system. The LOD of $^{90}$Sr was converted from Bq per liter into Bq per kg wet weight using the following equation.

$$\text{LOD}_w = \text{LOD}_r \times \frac{V}{m} \times \frac{(100-\text{Water\%})}{100}$$

where $\text{LOD}_w$, $\text{LOD}_r$, $V$, $m$, and Water\% indicate the LOD (Bq/kg wet), LOD (Bq/L), sample volume (L), weight of the digested sample (kg), and water content (%), respectively.

### Results and Discussion

**Volume ratio and flow rate into the ICP–MS system with and without an online dilution system**

As mentioned above, the volume ratio between the main and split-line flows was 33:1 in the proposed online dilution system, and it indicated that the flow rate of the sample solution in the main flow was higher than that in the previous system (main:split ratio = 27:1). The final flow rate of the sample solution in the split-flow line was 6.6 mL/min with this system. The flow rate in the split-flow line was 2.0 mL/min before the online dilution line joined the split line at a 3rd mixer; subsequently, it finally increased to 6.6 mL/min in this system, i.e., the final dilution ratio increased by up to 3.3 times. Moreover, the flow rate without online dilution was also 2.0 mL/min. The conditions were optimized by changing the internal diameter (I.D.) of the peristaltic pump tubes (1.14, 1.52, 2.06, 3.18 mm) for Pump 2 (for the use of online dilution line). As a result, there was little difference (< 3%) in Sr signal intensities by changing any tube as shown in Fig. S1 in S.I. In this case, we selected reasonable 1.14 mm ID tube. Otherwise, a
0.13 mm ID tube was employed in split-flow line to reduce the sample split ratio. When 10 mL of the sample solution was injected, the volume passing through the split-flow line was 0.17 mL, and 1.7% of the injected sample was introduced into the ICP–MS system without preconcentration by the SPE column. In other words, 98.3% of the injected sample flowed into the column. The process of injection into this system was completed in approximately 100 s. The total volume introduced into the ICP–MS system was 11 mL with the online dilution system.

Sr signal profiles of the proposed method

Figure 2 shows the signal profiles obtained via measurements of the split-line flow and main-line flow when 10 mL of 100 Bq/L 90Sr standard solution in 20 v/v% HNO3 was injected. The dotted and solid lines indicate the signal profiles provided by the previous method (without online dilution) and the proposed method (with online dilution), respectively. The measurement results indicated that the split-line flow had a trapezoidal-shape of stable Sr, as shown in Fig. 2[A]. The online dilution system decreased the average intensities of 88Sr (m/z = 88) from 15 × 10^4 ± 1.4 × 10^4 to 4.6 × 10^4 ± 0.5 × 10^4 cps. In the different concentration, same behavior was observed. For instance, when the 0.1 μg/L of the stable Sr solution was injected, the average intensities of 88Sr decreased from 182 ± 23 to 55 ± 9 cps (the profile is not shown here). Therefore, the intensity ratio between the previous method and the proposed method was 1:3.3, indicating that the flow rates in the respective lines were correlated with the volume ratio. Figure 2[B] shows the chromatogram-like signal profiles of 88Sr and 90Sr obtained from the main-line flow. Table 1 shows the integrated intensities of 90Sr when 10 Bq/L and 100 Bq/L of the 90Sr standard solution were measured using the two methods. No
considerable difference was observed between the proposed and previous method, namely, water infusion via the online dilution line did not affect the intensity obtained for the concentrated Sr solution. In addition, the LOD of $^{90}\text{Sr}$ in this method was 2.0 Bq/L (0.4 pg/L) when 10 mL of the sample was injected. The value is the same as that in the previous method, obtained as a sensitivity per unit volume indicator. Basically, the proposed method was equally sensitive for an analytical target compared with the previous method (note: 50 mL of the sample was injected in previous reports).

Recovery test by using the digested fish sample solution

A recovery test was performed to evaluate the quantitative determination performance of the proposed system using $^{90}\text{Sr}$-spiked whitebait (0, 82.5, 165 Bq/kg wet). The Water% of whitebait was 83.5 ± 0.4%. Table shows the results obtained via the recovery test. The $^{90}\text{Sr}$ concentrations in the non-spiked samples were below the LOD. The measured values were consistent with the spiked values, i.e., 82.5 and 165 Bq/kg wet. The concordance ratios calculated between the measured and spiked values were 101.6 and 99.8%, respectively. Repeated measurements ($n = 3$) exhibited sufficient reproducibility, and the RSDs were below 15% at various concentrations of $^{90}\text{Sr}$. The R% of Sr tended to decrease as the amount of the dissolved sample increased. Horwitz reported that a K$^+$ concentration above 0.03 mol/L or Na$^+$ and Ca$^{2+}$ concentration above 0.4 mol/L exerted suppressing effects on the capacity factor (k’) for the Sr of Sr resin.11 When 0.5 g of the dried sample was digested in 10 mL of the solution, the contents of major coexistent elements and Sr in the sample solution were Na: 985 mg/L, Mg: 154 mg/L, K: 1115 mg/L, Ca: 374 mg/L, and Sr: 1.3 mg/L. The contents per gram of dried weight were Na: 19.7 mg/g dry, Mg: 3.1 mg/g dry, K: 22.3 mg/g dry, Ca: 7.5 mg/g dry,
and Sr: 0.03 mg/g dry, respectively. The concentration of K reached a level high enough to affect k’; therefore, the results indicated that the suppressed R% was caused by the high K concentration. The concentrations of Na and Ca were within acceptable levels. No influence of the decrease in R% was observed on the measured value because of the correction by the split-flow method. In the proposed method, 15 min per measurement was required when 10 mL of the sample was injected. The result showed that the analysis time needed by this method was the same as that needed by the previous method. In other words, because the intensity of the stable Sr in the split-line flow was measured to calculate R% during the column preparation and Sr elution in the online dilution system, sequential processing was performed without increasing the analysis time. The result also indicated that this method could quantify $^{90}\text{Sr}$ earlier than radiometric standard methods, even in the presence of a high salt concentration.

**Conclusions**

In this study, we developed an online dilution system that performed selective dilution of the sample solution to suppress the effects of a large number of coexistent elements by automated infusion of water via bypassed lines, combined with cascade ICP–MS for $^{90}\text{Sr}$ quantification. A LOD of 2.7 Bq/kg wet (0.54 pg/kg wet) was obtained when 10 mL of the digested sample was injected into this system. The required analysis time was 15 min. Recovery tests were performed using a $^{90}\text{Sr}$-spiked whitebait sample for demonstration, and the obtained values were consistent with the spiked values at different $^{90}\text{Sr}$ concentrations.
Acknowledgements

We acknowledge Mr. Kazuki Iijima and Mr. Kenso Fujiwara from Japan Atomic Energy Agency for providing insightful comments and suggestions. Additionally, we acknowledge members of Japan Nuclear Fuel Chemical Analysis Co., Ltd. (Aomori, Japan) for their help.

Supporting Information

Table S1 shows the measurement parameters of the proposed quadrupole ICP-MS system for $^{90}$Sr analysis. Table S2 shows the program for the valve and pumps. Figure S1 shows the variation of Sr intensity using different internal diameter of a tube. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.
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Table 1  Comparison of the intensities of $^{90}\text{Sr}$ in the main-flow line between the proposed method and previous method.

| $[^{90}\text{Sr}]_T$ / Bq L$^{-1}$ | Counting rate in the main-flow line $\pm$ standard deviation / cps | Previous method $^{10-11}$ | Proposed method |
|----------------------------------|-------------------------------------------------|-----------------------------|------------------|
| 0                               | 21 ± 11                                         | 12 ± 11                     |
| 10                              | 268 ± 14                                        | 231 ± 13                    |
| 100                             | 1767 ± 58                                       | 1697 ± 78                   |

Experimental condition: 20 v/v% HNO$_3$, 10 mL injection. Citation number was corresponding with the number of the reference section.
### Table 2  Recovery test results of a $^{90}\text{Sr}$-spiked actual fish sample

| ID | Fish sample $^a$ (dry weight) | Spike / Bq $^{-1}$ wet | Measured value / Bq $^{-1}$ wet | RSD $^c$, % | Sr recovery $^d$, % | Concordance ratio $^e$, % |
|----|-------------------------------|------------------------|---------------------------------|------------|------------------|---------------------|
| 1  | whitebait (0.5 g)             | 0                      | N.D., (<5.3 $^b$)               | –          | 28.5             | –                   |
| 2  |                               | 165.0                  | 164.7                           | 14.2       | 79.6             | 99.8                |
| 3  | whitebait (1.0 g)             | 0                      | N.D., (<2.7 $^b$)               | –          | 28.0             | –                   |
| 4  |                               | 82.5                   | 83.8                            | 9.1        | 40.9             | 101.6               |

a. Fish (whitebait) was collected within 20 km of FDNPP.
b. The limit of detection (3σ).
c. Relative standard deviation ($n = 3$).
d. Sr recovery (%) was given using the following equation: $I_{p(m)}/ I_{p(e)} \times 100$, where $I_{p(m)}$ is measured intensities from main line, and $I_{p(e)}$ is expected intensities from main line when Sr recovery is 100%. $I_{p(e)}$ was calculated as $I_{p(e)} = \alpha I_{s(m)} + \beta$, which was obtained by measuring the standard solution contained stable Sr and no coexisting elements. Here, $I_{s(m)}$ is measured intensities from split-flow line, $\alpha$ and $\beta$ are the slope and y-intercept, respectively.
e. Concordance ratio (%) was given using the following equation: (measured value/spiked value) $\times 100$

Experimental condition: 10 mL of the digested solution (20 v/v% HNO$_3$) was injected.
Figure Captions

Fig. 1  Schematic of the cascade ICP–MS system equipped with an online dilution system. The sample solution, water, and 20 v/v% HNO₃ are injected by an injector. ISTD, internal standard solution; USN, ultrasonic nebulizer.

Fig. 2  Selective reduction for the signal from the split line with online dilution. Panel [A] shows the signal from the split line, and panel [B] shows the signal from the main line. The injected sample solution was 10 mL of the 100 Bq/L ⁹⁰Sr standard solution. The dotted and solid lines indicate the signal profiles provided by the previous method (without online dilution) and the proposed method (with online dilution), respectively.
Fig. 1  Schematic of the cascade ICP–MS system equipped with an online dilution system. Abbreviation: ISTD, internal standard solution; USN, ultrasonic nebulizer.
Fig. 2  Selective reduction for the signal from the split line with online dilution. Panel [A] shows the signal from the split line, and panel [B] shows the signal from the main line. The injected sample solution was 10 mL of the 100 Bq/L $^{90}\text{Sr}$ standard solution. The dotted and solid lines indicate the signal profiles provided by the previous method (without online dilution) and the proposed method (with online dilution), respectively.
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