Chapter 20
90Sr Analysis Using Inductively Coupled Plasma Mass Spectrometry with Split-Flow Injection and Online Solid-Phase Extraction for Multiple Concentration and Separation Steps

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Abstract We aimed to develop a rapid and sensitive method to analyze the radioactivity of 90Sr by combining multiple techniques, including online solid-phase extraction (SPE) and inductively coupled plasma mass spectrometry (ICP-MS). An automatic analytical system was designed to execute the proposed process from sample injection to measurement. The analysis time is approximately 20 min and the limit of detection is 0.3 Bq/L (equivalent to 0.06 pg/L) with 50 mL of the sample. Although several challenges were encountered with the ICP-MS measurements of 90Sr, several techniques were leveraged to overcome them. Online solid-phase extraction (SPE) was used to concentrate the sample automatically; the interference from polyatomic ions and isobars was removed by an oxidation, and the extraction and recovery ratio of solid phase were measured by split-flow injection with internal standard correction during the transient signal measurement. These improvements were shown to allow measurements of 90Sr in various kinds of samples to be conducted more quickly than by alternative conventional radiometric methods.

Keywords Strontium-90 · ICP-MS · Online solid phase extraction · Split-flow injection

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20.1 Introduction

Measurements of pure-beta-emitting radioactive $^{90}\text{Sr}$ require that it be isolated from other beta nuclides. The standard analysis process is milking, and low-back-gas-flow counting requires multi-step chemical separation; this process is complex, and takes a lot of time and human handling. Moreover, radioactive $^{90}\text{Y}$ production is required to conduct highly sensitive $^{90}\text{Sr}$ radiometric measurements and the entire analysis takes 1–2 weeks. However, there is a need for a simple and rapid analysis method, particularly for emergency situations such as the Fukushima Daiichi nuclear accident. In this chapter, we introduce a rapid method conducted in a fully automated analysis system for $^{90}\text{Sr}$ analysis using inductively coupled plasma mass spectrometry (ICP-MS) and online solid-phase extraction (online SPE) with a flow-injection system (Takagai et al. 2014, 2017). This method requires only nitric acid and water as reagents. The use of automation mitigates the radioactive hazards to human health and improves the precision of the analysis. The mass spectrometer includes a system to separate the elements in aqueous samples by mass (more precisely, the ratio between an element’s mass and its electric charge (m/z)). The mass resolution depends on the type of device used; the quadrupole-type mass spectrometer used in ICP-MS has an integral resolution. Therefore, this technique suffers from poor sensitivity and interference from isobars since there are several elements with masses of 90 such as the stable isotope $^{90}\text{Zn}$, naturally occurring in the environment. Though ICP-MS can be used to analyze inorganic elements with very high sensitivity, this analysis alone cannot be used to detect low concentrations of $^{90}\text{Sr}$ on the order of a few Bq/L such as the environmental $^{90}\text{Sr}$ level. The half-life of $^{90}\text{Sr}$ is 28.9 years and 1 Bq/L of $^{90}\text{Sr}$ is equivalent to a mass concentration of almost 0.2 pg/L. The limit of detection of the stable isotope $^{88}\text{Sr}$, by ICP-MS in an ordinary laboratory environment is approximately 500 pg/L because of contamination from the environment and the insufficient sensitivity. Our research team has previously developed a method of concentration and separation to improve the sensitivity and prevent the interference from other nuclides. In addition, as explained herein, several additional techniques are leveraged for this analysis. The proposed system measures $^{90}\text{Sr}$ based on a working curve determined using a standard solution of a stable isotope of Sr based on the correlation between the detection intensity of the stable isotope of Sr and $^{90}\text{Sr}$. This feature removes the need for a radioactive standard solution, which is difficult to obtain and handle.

20.2 Materials and Methods

Figure 20.1 explains the online the SPE/ICP-MS method. This system combines several techniques. A FIAS400 flow injection device, which has an eight-direction switching valve and two peristaltic pumps, was used. Either a NexION300S or ELAN DRC II (PerkinElmer) ICP-MS instrument, which have collisions and
reaction cells to remove the spectrum interference, were also used. As Fig. 20.1 shows, the system incorporates several techniques: (A) a mechanism to remove the interference from isobars with the $^{90}$Sr measurements using the collisions and reaction cells in the ICP-MS instrument. (B) PEEK columns (PerkinElmer Japan, $\phi 4 \times L50$ mm) filled with Sr resin (Eichrom Technology, Particle size 50–100 $\mu$m) were used with the flow-injection system for online concentration and separation. Because the adsorption capacity of the Sr resin is limited, one or two columns may be connected alternatively based on the Sr concentration of the sample (not only $^{90}$Sr but also stable Sr). (C) To monitor the fluctuation in the ICP-MS measurement sensitivity and the measurement intensity due to the sample matrix (several interference matters) over the long term, internal standard elements are introduced at a fixed speed at a point below the columns and before the nebulizer; this is expected to minimize the error in the measurements. (D) To measure the relative recovery ratio, a novel technique based on split-flow injection was developed; this mechanism allows the sample to be split online and analyzed in parallel both before and after the column concentration step. These strategies are seamlessly integrated into a single system to enable rapid analysis.
20.3 Results and Discussion

20.3.1 Addressing the Interference from Isobars that Affects the ICP-MS Measurements

Sources of interference for the measurement of $^{90}\text{Sr}$ include other isobars and polyatomic ions with mass numbers of 90 (including $^{90}\text{Zr}$, $^{90}\text{Y}$, and $^{89}\text{Y}^1\text{H}$, and $^{54}\text{Fe}^{36}\text{Ar}$, and $^{74}\text{Ge}^{16}\text{O}$) or the plasma involved in ICP-MS. The multi-step column separation process can remove most of these components before they are introduced to ICP-MS. However, traces of these components remain, affecting the quantitative values obtained because the $^{90}\text{Sr}$ concentration is also low. Figure 20.2 shows the mass spectrum with and without oxygen in the reaction cells. A certified radioactive reference material (DAMRI, 51.7 kBq/g, 01.04.1993) was diluted as an RI standard solution for the measurement. Figure 20.2 shows that the device converted the Zr and Y in the RI standard solution to ZrO and YO, resulting in higher mass numbers. On the other hand, only a portion of the Sr was converted to SrO. Figure 20.3 shows the relationship between the introduced oxygen gas flow causing a reaction with oxygen and the differences between the intensities of the detected ions. Sr, Zr, and Y were converted to plasma ions and exposed to collisions in the reaction cells, resulting in oxidation. The susceptibility of an ion to oxidization depends on the

![Fig. 20.2 Mass spectra of a radioactively certified $^{90}\text{Sr}$ solution containing stable Sr, Y, and Zr without the oxygen reaction (white line) and with the oxygen reaction (solid black line) in the dynamic reaction cell (Takagai et al. 2014). In the spectrum in the absence of oxygen, the peak attributed to $^{90}\text{Zr}$ overlapped with that associated with $^{90}\text{Sr}$. In the presence of oxygen, the Zr peak was shifted to a higher mass number as it existed as ZrO while some of the Sr remained as $^{90}\text{Sr}$ in the position of m/z = 90. In the oxygen reaction in the dynamic reaction cell, only a small portion of the Sr was converted to SrO. The spectra showed that 25 ppt was present in the $^{90}\text{Sr}$ certificated solution (equivalent to 127 Bq/g) when the sample was directly injected through a concentric nebulizer into the ICP-MS instrument without online column preconcentration.](image-url)
element. The detected ion Zr and Y intensities decreased proportionally as the oxygen gas flow increased, indicating that most of the Zr and Y were oxidized. However, the detected Sr intensity remained approximately fixed, meaning that Sr is relatively resistant to oxidization. This confirms that Sr can be physically separated from Zr and Y on the basis of the susceptibility to oxidization. Thus, combining this technique with column separation removes the interference from isobars and polyatomic ions completely such that the detection counts of m/z = 90 is approximately the same as background level in the blank sample. Thus, it is possible to measure lower concentrations over the relatively low background signal.

20.3.2 Addressing the Sr Selectivity of the Resin Based on Its Adsorption Characteristics

As shown in Fig. 20.4, the adsorption characteristics of the Sr resin were evaluated in terms of the recovery ratios for 53 kinds of elements. The results show that Sr was adsorbed selectively by the resin. However, Ba and Pb, whose mass numbers are 138 and 208 respectively, were also adsorbed. Therefore, for the measurement of...
beta rays, it is necessary to separate Sr and Pb. However, ICP-MS separates nuclides based on their masses for detection and, thus, Pb in an eluate from the columns does not affect the detection of m/z = 90.

20.3.3 Radioactive $^{90}\text{Sr}$ Measurements Using a Standard Solution of the Stable Isotope, $^{88}\text{Sr}$

In general, ICP-MS measures analytical targets by comparing the detected intensity of a sample with that of a standard solution with a known concentration. Therefore, it is necessary to measure an $^{90}\text{Sr}$ solution with a known concentration for the subsequent analysis of $^{90}\text{Sr}$. However, radioactive $^{90}\text{Sr}$ has to be handled carefully in a specialized facility for radioactive materials. Thus, to allow easier and safer measurement, it is better to avoid the use of radioactive standard materials. We hypothesized that a $^{90}\text{Sr}$ calibration curve of a stable isotope of Sr could be used to measure Sr because the detected intensities of $^{90}\text{Sr}$ and the stable Sr isotope are correlated. However, ICP-MS exhibits a mass bias, a phenomenon where the efficiency varies for different ions depending on the mass. Several methods can be used to correct the mass bias such as the relative standardization method to derive a correction factor by measuring the certified standard materials whose isotopic ratio is guaranteed before and after the sample measurement and the internal correction method to correct the results using the measured values of two stable isotopes when an element has multiple stable isotopes. Both of the methods are used to correct the mass bias in the measured values and to calculate their true isotopic ratios.

In this study, we conducted $^{90}\text{Sr}$ measurements using $^{88}\text{Sr}$ as the target as the ratio of $^{88}\text{Sr}/^{86}\text{Sr}$ is the same as the natural isotope abundance ratio. This ratio can be controlled by changing the cell entrance voltage, one of the voltage parameters related to the ion vitrification in ICP-MS. Figure 20.5 shows the changes in the measured ratio of $^{88}\text{Sr}/^{86}\text{Sr}$ as the cell-entrance voltage was varied. In one condition,
the ratio was close to the natural isotope abundance ratio of 8.375. In Fig. 20.6, the measured intensities of $^{88}\text{Sr}$ and $^{90}\text{Sr}$ at each concentration are plotted on the same graph. The abundance of $^{88}\text{Sr}$ (82.58%) was converted to 100% and the detected intensity at each concentration was plotted; the resulting data demonstrated a good correlation coefficient of 0.9996. This suggests that it is possible to measure $^{90}\text{Sr}$ by using a calibration curve of $^{88}\text{Sr}$. Although the measurement of the isotopic ratio using ICP-MS contains errors due to the calculation of the $^{90}\text{Sr}$ values using a calibration curve for $^{88}\text{Sr}$, these errors are smaller than the measured signal errors.

**20.3.4 Analysis of $^{90}\text{Sr}$ Using Online SPE/ICP-MS**

Online SPE can be used to automatically concentrate Sr in a sample in the column, elute it in an eluent, and introduce it to ICP-MS. The process from concentration to measurement is described as follows. The column was first conditioned in 20 vol% nitric acid. Then, the sample was introduced to the column. It took about 10 min to concentrate a 50 mL sample. The split-flow method was used to measure the recovery ratio at the columns during this process (explained below). Other substances present in the columns were washed out with the 20 vol% nitric acid. The
concentrated Sr in the resin was eluted by switching a value position (in flow injection system). Figure 20.7 shows an eluted chromatogram when 5 Bq/L of 90Sr was introduced and measured. Moreover, in the proposed online SPE method, transient signal (= peak) can be observed. It takes about 20 min to analyze a 50 mL sample and about 10 min to analyze a 10 mL sample. It takes only 20 s to identify the peak. Figure 20.8 shows the linearity of the measured 90Sr intensity as a function of its concentration between 5 and 20 Bq/L. The measured 90Sr concentrations were compared with the values measured using an accepted method for radiation measurement—the pico-beta-measurement method. Figure 20.9 shows that the results obtained by the proposed method correlated closely with those obtained by the pico-beta-measurement method in the concentration range from 2 to 100 Bq/L.

The precision of the measurements obtained by ICP-MS analysis also depends on the sample concentration. Figure 20.10 shows the analysis results for samples with 2 and 10 Bq/L (0.4 and 2 pg/L, respectively) of 90Sr in 10 replicates. Even though the 0.4 pg/L concentration is relatively low for ICP-MS, an RSD of 12.6% was achieved, demonstrating the reproducibility of this technique. The measurement of 2 pg/L also showed good reproducibility (RSD of 5.2%). Thus, it can be concluded that, in terms of the method’s sensitivity, reproducibility, and consistency with the conventional method, it is a practical analysis technique.

Fig. 20.6 Correlation between the intensity of stable isotope, 88Sr, and the radioactive isotope, 90Sr, at different concentrations. 88Sr (n = 3) measurements are shown as white circles (○) and 88Sr (n = 3) measurements are shown as black crosses (×). When the abundances of 88Sr and 90Sr are the same, the slopes of the calibration corresponded closely. In addition, the background of the artificial 90Sr isotope was almost zero. Therefore, the 90Sr can be indirectly derived from the measurements of the 88Sr stable isotope using the calibration curve. The detection limit of standard ICP-QMS (with a concentric nebulizer and without any accessories or attachments) was 0.055 ng/L (equivalent to 280 Bq/L)
Fig. 20.7 Chromatograms of $^{90}\text{Sr}$ and a blank sample (pure water) purified by online solid extraction. When a blank sample (50 mL of pure water) was injected, no peaks were detected on the chromatogram. When 50 mL of $^{90}\text{Sr}$ was injected, an obvious peak with a width of 20 s was detected. When the elution flow rate was 5 mL/min, the preconcentrated phase volume was approximately 0.8 mL. When 50 mL of the sample was injected, the preconcentration factor (volume ratio) was approximately 63 times.

Fig. 20.8 Linear calibration curve for $^{90}\text{Sr}$. The peak area is used for the quantification of $^{90}\text{Sr}$. The detection limit was approximately 0.5 Bq/L when 50 mL of the sample was injected. The measurement time was 20 min.
**Fig. 20.9** Correlation between the quantitative values obtained by the beta-spectrometer (radiometry) and the proposed ICP-MS method. Sufficient linearity was obtained in the concentration range of 2–100 Bq/L.

![Graph showing correlation between beta-spectrometer and ICP-MS methods.](image)

**Fig. 20.10** Repeatability of the $^{90}$Sr measurements. The measurement repeatability was confirmed over ten replicates of the samples with $^{90}$Sr concentrations of 2 and 10 Bq/L (50 mL of the sample were injected each time).

![Graph showing repeatability of $^{90}$Sr measurements.](image)

AVE. 10.03 Bq/L
RSD 5.2%

AVE. 2.06 Bq/L
RSD 12.6%
20.3.5 Addressing the Peaks Associated with the Enriched Stable Sr Isotope

It is known that the measured intensity of the detected elements decreases when a large quantity of the ion is introduced with ICP-MS. The decrease in the temperature of the plasma and the space-charge effect are considered to be the causes of this phenomenon. Basically, coexisting elements are separated while being concentrated and separated in the columns; therefore, the decrease in the measured intensity does not matter when judging the concentrations of minor elements. However, the coexisting stable isotope of Sr is highly concentrated and eluted when measuring $^{90}$Sr. This may cause the decrease in the measured intensity. We established an internal standard correction and a signal integration method to solve this problem (Furukawa et al. 2017). Internal standard elements were introduced after the column to obtain a fixed signal intensity. Figure 20.11 shows a variation of the internal standard signals when a high concentration of the stable isotope of Sr was introduced. As the peak of the eluted Sr became larger, the internal standard signal decreased. The ratio of two things between the increased intensity of Sr peak and the decreased intensity of the internal standard signal was calculated as a correction factor for the measured Sr intensity. ICP-MS detects each ion and records its intensity per unit time because each element number is measured continuously using the instrument’s peak-hopping mode. The internal standard correction and signal integration can be used to correct the intensity of the Sr measurements over time to control for the decrease in the whole peak intensity.

20.3.6 Split-Flow Injection System to Simultaneously Measure the Concentration and Recovery Ratio from a Single Sample (Furukawa and Takagai 2016)

The recovery ratio is defined as the proportion of the elements that are eluted and measured to those that are introduced and concentrated in the resin. The recovery ratio of the column is affected by the other elements coexisting in the sample, physical obstructions (such as the velocity of flow and viscosity), volume differences between samples, and the deterioration of the resin. Thus, to monitor the changes in the recovery ratio, an experiment was designed to introduce a sample and measure its concentration before and after passing through the columns. In other words, more than two measurements must be conducted. The split-flow injection system developed in this study splits samples online before they are injected into the resin such that one portion can be measured directly and the other portion is first concentrated before being analyzed. Thus, the intensity before and after passing through
the resin is measured automatically. Because the measured intensities before and after passing through the resin are proportional to the amount of the substance present, the recovery ratio relative to its absolute quantity can be calculated by integrating the measured intensity. In addition, the split-flow injection method can provide a relative recovery ratio without concentrating the sample based on the correlation between the intensities measured before and after passing through the columns.

Figure 20.1 shows a diagram of the split-flow injection. After the sample is input at valve #1, the splitter divides it into two column pathways. The rotational frequency of the peristaltic pump and the inside diameter of the pump tube control the division ratio. When the division ratio is 1:1, the volume of the sample that is concentrated is half that of the sample that is not. To attain greater preconcentration of the sample solution, the split ratio for the direct injection can be increased such that a larger amount of the sample is introduced into the column. Figure 20.12 shows the correlation between the measured intensity before passing through the columns and
after concentrating the sample for a standard solution when the division ratio (column injection volume: split volume) was 100:4.

The degree of correlation between the detected intensity of the split sample and the Sr measurement after concentration shows the difference between the recovery ratio of a sample compared to that in the standard solution. Taking the recovery ratio of a standard solution as 100%, the relative recovery ratio of each sample was measured. Figure 20.13 shows the relative recovery ratios of the stable isotope of Sr for which m/z = 88, 86, or 84 (as the signal of $^{90}$Sr is hardly detected in the split measurements). The relative recovery ratio of the stable Sr isotope was calculated as a correction factor for the $^{90}$Sr measurement to obtain the corrected $^{90}$Sr value.

Fig. 20.12  Relationship between the intensities of the split stable Sr isotope and the preconcentrated Sr used to calculate the relative recovery. For the calculation, a linear calibration curve for the split Sr intensity versus the preconcentrated Sr intensity was prepared for a stable Sr standard solution. Based on the line, the relative recovery, R, can be calculated by the following equation given that the split Sr intensity and the preconcentrated Sr peak area have an approximately linear relationship of the form $y = ax + b$

$$R = \frac{B}{C} \times 100 = \frac{B}{a(A) + b} \times 100$$

where $a$ and $b$ were the slope and intercept of the linear line, respectively, $A$ represents the intensity of the split Sr intensity, $B$ is the detected Sr area, and $C$ is the calculated Sr area after concentrating the sample for a standard solution when the division ratio (column injection volume: split volume) was 100:4.

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To evaluate the method of split-flow injection, an experiment was conducted with the addition of Ba, known to decrease the Sr recovery ratio. Figure 20.14 shows the measured Sr concentration and the concentration with the corrected relative recovery ratio in the presence of various amounts of Ba and a fixed concentration of Sr. Although the relative recovery ratio of Sr decreased by the addition of Ba, it was confirmed that for the correction of the relative recovery ratio, the use of the split-flow injection technique was effective.
injection method allows the correct concentration (i.e., that without the influence of Ba) to be derived. Therefore, the proposed method is an effective way to correct the recovery ratio. The split measurement does not affect the total measurement time and affects the measurement sensitivity only slightly as the division ratio between the columns and the direct introduction is changed.

### 20.4 Conclusion

Here, we demonstrated $^{90}$Sr analysis using online SPE/ICP-MS with a split-flow injection method. Several techniques were combined in a single automated system. By using split-flow injection to measure the recovery ratio, the drawback of SPE being affected by changes to the matrix over time was mitigated. This approach can complement the radiation measurement method as an alternative technique for $^{90}$Sr measurements and the user may select the proper method depending on the specific application (i.e. rapid measurement and the concentration of $^{90}$Sr and stable isotopes etc.). It takes 10–20 min only to complete the $^{90}$Sr analysis, requiring more than 2 weeks with the alternative technique. This analysis requires 50 mL of sample and the limit of detection is 0.3 Bq/L (equivalent to about 0.06 pg/L) with an argon-nitrogen mixed gas effect (Furukawa et al. 2018). This ability to measure concentrations as small as a few Bq/L in a small sample makes this technique suitable for a wide-area, multi-point sampling and analysis. Thus, this method can be readily used not only for environmental water analysis but also for applications requiring prompt measurements, such as the analysis of perishable foods.

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