

Determination of radiostrontium released from Fukushima Daiichi Nuclear Power Plant through extraction chromatography and liquid scintillation counting

Akihiro MAEKAWA^{1)*}, Noriyuki MOMOSHIMA²⁾, Shinji SUGIHARA²⁾
and Toshiya TAMARI³⁾

- 1) Graduate School of Sciences, Kyushu University, 6-10-1, Hakozaki, Higasi-ku, Fukuoka 812-8581, Japan
2) Radioisotope Center, Kyushu University, 6-10-1, Hakozaki, Higasi-ku, Fukuoka 812-8581, Japan
3) Kyushu Environmental Evaluation Association, 1-10-1, Matsukadai, Higashi-ku, Fukuoka 813-0004, Japan
*2sc12060w@s.kyushu-u.ac.jp

Two soil samples were collected on April 18–20, 2011 at Namie town and Tomioka town, which are located 26 km northwest and 11 km south of the Fukushima Daiichi Nuclear Power Plant, respectively. A 0–1 cm soil layer was used for analysis to determine the presence of radiostrontium. The soil was ashed, acid-digested, and strontium was separated from interference with use of an extraction chromatography resin (Sr resin, Eichrom Technologies). The isolation and purification of strontium from matrix components can be completed in 12 h. After 2 weeks for ingrowth of ⁹⁰Y, measurements of a beta-ray of ⁹⁰Y and ⁸⁹⁺⁹⁰Sr were conducted with a low-background liquid-scintillation counter for 1200 min. The concentration of ⁹⁰Sr was determined to be 57.4 ± 1.0 and 10.1 ± 0.4 Bq kg⁻¹ for Namie town and Tomioka town, respectively. ⁸⁹Sr was not detected in either sample. The extraction chromatography method was successfully applied to determine the level of radiostrontium in the contaminated soil. When 2 g of soil is used, the detection limit of ⁹⁰Sr is evaluated to be 2.7 Bq kg⁻¹ under a chemical yield of strontium of 70 %

Key Words: Radiostrontium, soil, Sr resin

1. Introduction

Various kinds of radionuclides were released from the Fukushima Daiichi Nuclear Power Plant (FDNPP) due to the accident that occurred in March of 2011. ⁸⁹Sr (half-life: 50.5 days) and ⁹⁰Sr (half-life: 28.8 years) are hazardous because they accumulate in bone. However, due to the time-consuming analytical steps required for a determination of radiostrontium, there have been less reports done on the level of radiostrontium than those of radiocesium. Because both ⁸⁹Sr and ⁹⁰Sr only emit a beta-

ray, which does not have a line energy spectrum, a laborious chemical separation of radiostrontium from other radionuclides is required to determine radioactivity. For example, the ion exchange method and the oxalate precipitation method, which are both accepted as official methods for measuring radiostrontium, require about 25 and 30 hours, respectively, to isolate strontium¹⁾. In emergency situations such as a nuclear accident, a rapid method for radiostrontium analysis is needed to analyze many samples. We adopted extraction chromatography, which utilizes crown ether as the extractant, to simplify

the analysis of radiostrontium. One of the characteristics of crown ethers is that they form a stable complex with specific metal ions by choosing the appropriate cavity size and substituents. The purpose of this study is to establish extraction chromatography as a viable method to analyze radiostrontium and to apply this method to a determination of radiostrontium in the soil at Fukushima.

2. Materials and methods

(1) Soil samples

In this study, two soil samples were used for the experiments. Fig. 1 shows the locations of the sampling sites. Surface soil samples of 5 cm length were collected on April 18, 2011 at Namie town and on April 20, 2011 at Tomioka town. The air radiation dose rates at the sampling points were measured with a NaI scintillation survey meter (TCS-171B, ALOKA) 1 m above the ground surface. The soil samples were cut into 1 cm sub samples at a laboratory. The radioactivity of ^{137}Cs in the sub soil samples was determined with a Ge detector (GMX, EG&G ORTEC Ltd.). After air-drying, the 0–1 cm soil sub sample was used for radiostrontium analysis.

(2) Methods

The analytical procedure was based on a standard method for the separation and measurement of ^{89}Sr and ^{90}Sr in soil (SRS01, Eichrom Technologies, Inc.)²⁾ and we modified it to ensure that a sufficient amount of removal of radiocesium in the sample sufficiently. Fig. 2 shows the modified procedure schematically. A soil sample of about 10 g of soil sample was collected in a porcelain boat and ashed at 400°C for 4 h using a tubular furnace. After homogenization of the ashed soil, 2 g of the sample were subjected to analysis. A total of 5 mg of Sr carrier and 10 mg of Cs carrier, as well as 20 mL of concentrated HNO_3 , was added to the sample. It was then heated on a hot plate for 3 h, to extract radiostrontium into the solution. In the original method of Eichrom, the

solution was used for subsequent steps without further treatment. However, the present surface soil samples, which were collected in a contaminated area, contained a large amount of radiocesium (^{134}Cs , ^{137}Cs). We applied the original method first, and then confirmed that a certain amount of radiocesium remained in the solution, which would interfere with the process of beta-ray counting. To ensure the removal of radiocesium from the solution, Sr was coprecipitated with CaCO_3 and the supernatant was discarded. The CaCO_3 precipitate was dissolved in 0.1 M of HNO_3 and used for subsequent purification steps. The preconcentration of Sr with a cation exchange column and the isolation of Sr with Sr resin were carried out according to Eichrom's standard method. After 2 weeks of ingrowth of ^{90}Y , the isolated Sr fraction was reloaded on the Sr resin and the ^{90}Y was separated from the Sr. After drying the separated ^{90}Y , it was dissolved in HNO_3 and mixed with a scintillator.

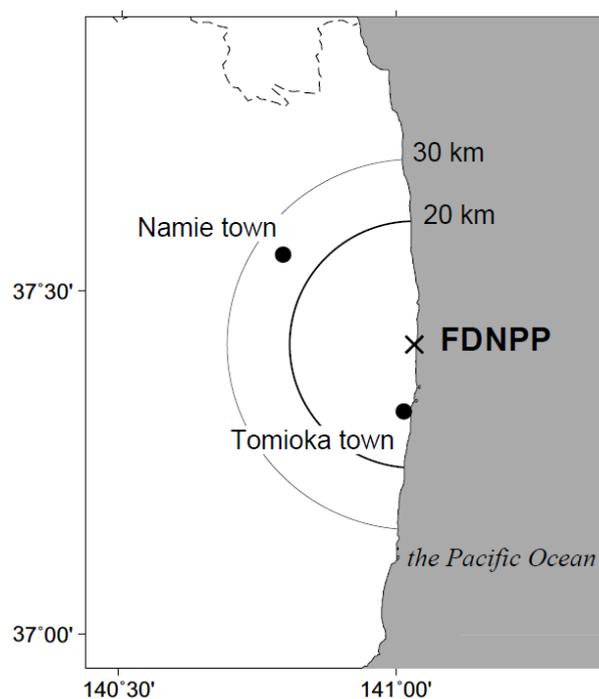


Fig. 1. Sampling locations.

Table 1. Radioactivity concentrations of the soil samples and air dose rate at the sampling points.

Sample	Radioactivity concentration (Bq kg^{-1})			$^{90}\text{Sr}/^{137}\text{Cs}$ ratio	Air dose rate ($\mu\text{Sv h}^{-1}$)	Sampling date	Measurement date
	^{89}Sr	^{90}Sr	^{137}Cs				
Namie	Not detected	57.4 ± 1.0	2.57×10^5	2.2×10^{-4}	19.0	2011/04/18	2012/01/07
Tomioka	Not detected	10.1 ± 0.4	4.17×10^4	2.4×10^{-4}	5.0	2011/04/20	2012/02/25

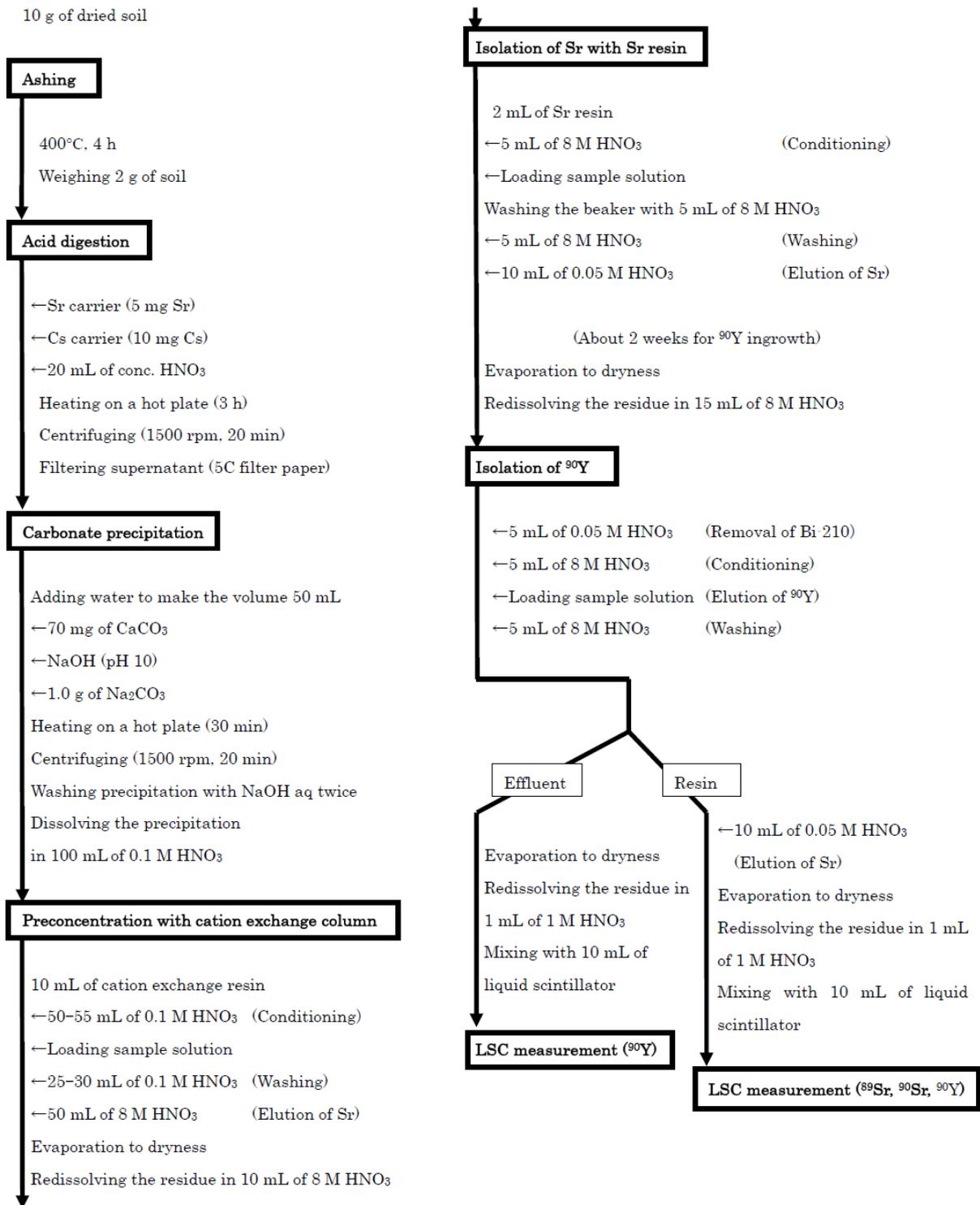


Fig. 2. Experimental procedure

The radioactivity of ⁹⁰Y was measured with a low-background liquid-scintillation counter (LSC-LB5, ALOKA) for 1200 min. ⁸⁹Sr and ⁹⁰Sr, which were retained in the Sr resin, were stripped by 0.05 M HNO₃. Their activities were also measured by a LSC in the same manner as ⁹⁰Y. The chemical yield of strontium was determined by atomic absorption spectrometry. The counting efficiency of ⁹⁰Sr and ⁹⁰Y was determined using

a ⁹⁰Sr standard solution

3. Results and discussion

(1) Radiostrontium concentration

Fig. 3 shows the beta-ray spectra obtained in this study. The maximum beta energies of ⁹⁰Sr, ⁸⁹Sr, and ⁹⁰Y

were 546, 1495, and 2280 keV, respectively. The standard ^{90}Sr spectrum, which is in radioactive equilibrium between ^{90}Sr and ^{90}Y , exhibited two distinct beta peaks: ^{90}Y in the higher channel and ^{90}Sr in the lower channel. The ^{90}Y spectrum of the Namie sample revealed one peak in the higher channel only, suggesting a successful separation from matrix components including Sr isotopes. The ^{90}Sr spectrum of the Namie sample exhibited a peak in the lower channel region and a weak scattered peak of ^{90}Y which grew during the period of the measurement. If ^{89}Sr was present in the sample, the peak would appear around the 500 channel between ^{90}Sr and ^{90}Y in the spectrum considering the beta energy of ^{89}Sr . Table 1 presents the results of the measurements. The concentration of ^{90}Sr was 57.4 and 10.1 Bq kg⁻¹ (ash weight basis) for Namie town and Tomioka town, respectively. ^{89}Sr was not identified in the spectrum of ^{90}Sr . An identification of ^{89}Sr in the spectrum was carried out by subtracting the ^{90}Y grown during the measurement and subtracting ^{90}Sr corresponding to that of the ^{90}Y spectrum. If ^{89}Sr existed, then the source should be FDNPP, thus the subtracted spectrum with positive values in the channel region for ^{89}Sr would be observed. However, no positive ^{89}Sr spectrum was confirmed in either sample. It is likely that it decayed out because of its short half-life (50.5 days). Even before the accident, ^{90}Sr was deposited on the soil surface as a result of atmospheric nuclear testing. According to research conducted in 2009, the maximum concentration of ^{90}Sr in Japanese soil was 14 Bq kg⁻¹, and it varied depending on the location³⁾. At Namie town, there is a strong possibility that ^{90}Sr was newly deposited after the FDNPP accident; the impact of the accident is unclear at Tomioka town. The $^{90}\text{Sr}/^{137}\text{Cs}$ ratio was 2.2×10^{-4} at Namie town and 2.4×10^{-4} at Tomioka town. Both of these values fall within the range reported by MEXT (Ministry of Education, Culture, Sports, Science and Technology, Japan)⁴⁾.

(2) Evaluation of the extraction chromatography method

When using the extraction chromatography method, it is necessary to ensure that other radionuclides are not present in the final solution by checking the beta-ray spectrum or measuring the gamma spectrum. Table 2 presents a comparison of the extraction chromatography

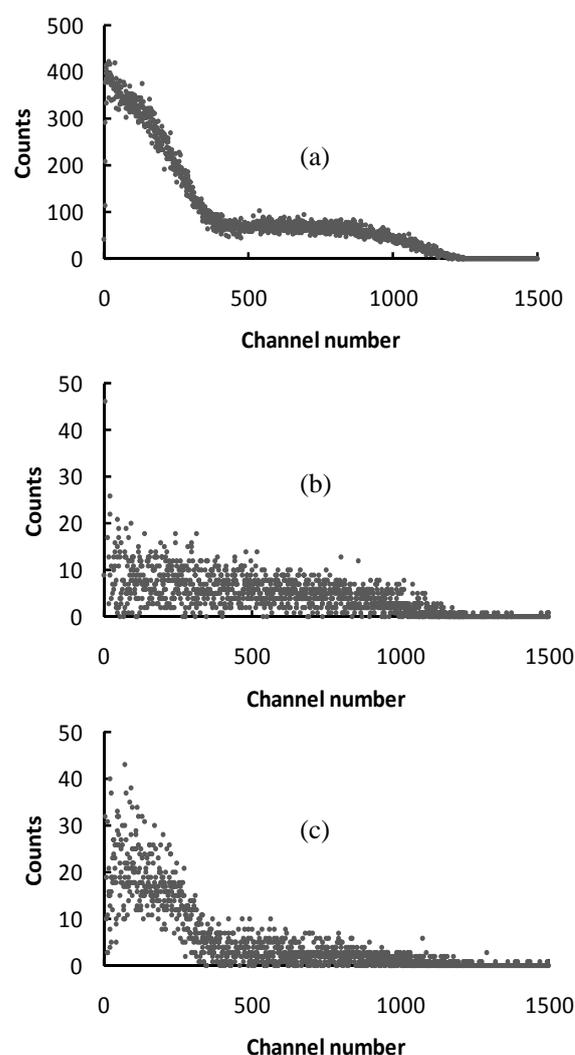


Fig. 3. Beta-ray spectrum obtained by liquid-scintillation counting. (a) ^{90}Sr standard solution (activity: 3.6 Bq, counting time: 300 min). (b) ^{90}Y isolated from Namie town soil (counting time: 1200 min). (c) ^{90}Sr isolated from Namie town soil (counting time: 1200 min). All spectra do not include background.

Table 2. Comparison of the extraction chromatography method and the official methods

	Extraction chromatography	Official methods
Detection limit	2.7 Bq kg ⁻¹	0.2 Bq kg ⁻¹
Sample weight	2 g	100 g
Chemical yield	70–74%	90%
Required time for strontium separation	12 h	25–30 h

method and the official methods of MEXT. The detection limit of ^{90}Sr was 2.7 Bq kg^{-1} with 2 g of soil and 1200 min counting time. A larger amount of soil is needed to lower the detection limit. The chemical yield of strontium was 70–74%, which was lower than that in the official methods. Vajda et al. (1992) also reported that the chemical yield was about 80%⁵⁾. An additional preconcentration step before loading the sample solution into Sr resin would improve the chemical yield. In addition, the volume of the washing and eluting solution in the Sr resin step should be optimized. The isolation and purification of strontium from matrix components can be completed in 12 h using the extraction chromatography method. It was demonstrated that this method was definitely faster than the official methods. In conclusion, the extraction chromatography method is a rapid and simple method that can be used for the determination of radiostrontium. This method was successfully applied to determine radiostrontium in contaminated soil.

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