Journal of Nuclear and Radiochemical Sciences, Vol. 16, pp. 15-21, 2016

Articles

Rapid isolation method for radioactive strontium using Empore^{TM} Strontium Rad Disk

Zijian Zhang[a,*], Kazuhiko Ninomiya[a], Naruto Takahashi[a], Takashi Saito[b], Kazuyuki Kita[c], Yoshiaki Yamaguchi[d], Atsushi Shinohara[a]

[a]*Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan*
[b]*Shokei Gakuin University, 4-10-1 Yurigaoka, Natori, Miyagi, 981-1295, Japan*
[c]*College of Science, Ibaraki University, 2-1-1 Bunkyo, Mito, Ibaraki, 310-8512, Japan*
[d]*Radioisotope Research Center, Osaka University, 2-4 Yamadaoka, Suita, Osaka, 565-0871, Japan*

Received October 3, 2016; Accepted November 3, 2016, Published online

A rapid and convenient chemical separation method for determining ^{90}Sr activity in aerosol samples using Empore^{TM} Strontium Rad Disks was established. The method employed solid-phase extraction and ion-exchange chromatography, and achieved a Sr yield of > 80%. Furthermore, it completely eliminated ^{210}Pb, which interferes with ^{90}Sr radiation counting. Sample pretreatment, chemical separation and Cherenkov light measurement required approximately 4 h, 2.5 h, and 14 days, respectively, to achieve a detection limit of 0.004 Bq. Using the developed method, the ^{90}Sr concentration and $^{90}Sr/^{137}Cs$ activity ratio in aerosol samples collected after the Fukushima nuclear accident were determined.

1. Introduction

A serious accident occurred at the Fukushima Daiichi nuclear power plants (FDNPP) in March 2011, resulting in the discharge of large amounts of radionuclides into the environment. Of these nuclides, artificial ^{90}Sr has a particularly long half-life ($T_{1/2}$ = 28.6 years) and high radiotoxicity. Therefore, its measurement is a priority in environmental assessment and response.

As a fission product from nuclear weapons testing, ^{90}Sr had already been widely distributed over the Northern hemisphere before the FDNPP accident. It has been measured in atmospheric fallouts worldwide [1-4], and it was also detected in milk following the Chernobyl accident [5]. Several studies have indicated that the mobility of ^{90}Sr in the environment is higher than that of ^{137}Cs [6-7]. Thus, ^{90}Sr is one of the most important radionuclides in nuclear plant accidents in terms of impact on human health.

Following the FDNPP accident, many environmental samples from eastern Japan have been examined to investigate the circumstances of the accident and to assess the resultant contamination distribution. In a previous study, we used gamma-ray spectroscopy to determine the radioactivities of ^{131}I, ^{134}Cs, and ^{137}Cs in such samples. Aerosol samples were collected by high-volume air samplers and the time variation of radiocesium activity concentrations was observed [8]. In contrast, only a few studies have investigated ^{90}Sr in soils and seawater [9-10]. Consequently, data on the ^{90}Sr activity concentration in the atmosphere and its time variation are needed to fully evaluate the internal radiation exposure and evaluate the amount of radionuclides discharged during the accident.

Because ^{90}Sr and its daughter nuclide ^{90}Y are pure β emitters, the activity determination of ^{90}Sr in environmental samples requires chemical separation. Classical separation methods including multi-stage operations are time consuming and produce large amounts of chemical waste[11]. In recent years, new chemical separation techniques for strontium using solid-phase extraction have been developed [12-13]. However, these new methods have only been applied to soil, milk, and surface and ground water samples. A simple and rapid solid-phase extraction method for ^{90}Sr in aerosol samples would offer the advantage of exchange capacity, as no matrix interference (e.g, from calcium or strontium) would be present. However, such an approach has not been reported to date.

In this study, we developed a new chemical separation strategy for measuring ^{90}Sr in aerosol samples based on solid-phase extraction. The method consists of three steps: a selective Sr extraction using a Strontium Rad Disk^{TM} (3M Inc.), an ion-exchange separation to eliminate naturally occurring ^{210}Pb, and finally Cherenkov light measurements for the determination of ^{90}Sr by detecting ^{90}Y growth. The Strontium Rad Disk^{TM} can extract Sr selectively but it also extracts Ba, Ra, and Pb simultaneously [14]. We used cation-exchange chromatography with ethylenediaminetetraacetic acid (EDTA) elution after the extraction to eliminate the naturally occurring radionuclide ^{210}Pb, which is found in aerosol samples. However, Ba and Ra could not be eliminated. For low-background measurements, ^{90}Sr radioactivity was determined by counting the Cherenkov light emitted from ^{90}Y with a liquid scintillation counter [15]. Performance indicators of this technique, including Sr yields, Pb elimination rates, total operation time, and detection efficiency of Cherenkov light measurement, were determined using standard radioactive and/or stable isotope samples. Finally, the developed method was applied to aerosol samples collected in Mito City, Japan in April 2011. Thereby, we determined the ^{90}Sr activity concentration and $^{90}Sr/^{137}Cs$ activity ratio in the atmosphere following the FDNPP accident.

2. Materials and Methods

2.1. Reagents. Empore^{TM} Strontium Rad Disks (47 mm in diameter) were employed to extract Sr from aerosol samples. These disks contain a proprietary multi-cyclic macromolecule covalently bound to a solid silica support embedded in a stable, inert matrix of polytetrafluoroethylene fibrils. When 2–4 M HNO_3 or HCl solution is passed through the disk, up to 3 mg of Sr in the solution could be selectively extracted [14]. Dowex 50W-X8 cation-exchange resin (100-200 mesh, Wako

*Corresponding author. E-mail: chous11@chem.sci.osaka-u.ac.jp, TEL: +81-668505417

© 2016 The Japan Society of Nuclear and Radiochemical Sciences
Published on Web 11/17/2016

Inc.) was used for cation-exchange chromatography to eliminate ^{210}Pb.

Standard solutions of ^{89}Sr (serial number: ST010, radioactivity: 100 kBq) and ^{90}Sr (serial number: SR010, radioactivity: 100 kBq) were obtained from the Japan Radioisotope Association. Lead-210 solution was separated from the ^{226}Ra standard solution (serial number; RAB65, radioactivity: 185 kBq) obtained from the Czech Metrology Institute. An Ultima Gold™ uLLT scintillation cocktail (Perkin Elmer Inc.) was used for beta-ray measurement of these nuclidesin test experimental steps for developing new chemical separation method. Strontium-85 was generated by proton irradiation of a Rb target using the Azimuthally Varying Field (AVF) cyclotron of at the Research Center for Nuclear Physics at Osaka University. The ^{85}Sr radioactivity was 1.4 MBq in October, 2011. A standard stable Sr solutions of $Sr(NO_3)_2$ in 0.5 M HNO_3 (1000 mg L^{-1}) was used as a Sr carrier and for external calibration of the inductively coupled plasma-mass spectrometry (ICP-MS) measurements.

Concentrated solutions of ultrapure analytical grade HNO_3 and HCl were purchased from Kishida Inc. Diluted acid solutions were obtained by mixing the concentrated regents with Milli-Q water. All water used in this study was obtained from a Milli-Q™ water purification system. All other chemicals were of Japanese Industrial Standards special grade.

2.2. Instruments. All gamma-ray measurement was performed with a coaxial-type high-purity germanium detector (GEM40, ORTEC). The detector was connected to a multichannel analysis system (MCA7600, Seiko EG&G).

In the experiments to develop new chemical separation methods, an LS 6500 liquid scintillation counter (Beckman Inc.) was used to measure beta-rays. For the determination of ^{90}Sr activities in aerosol samples by the Cherenkov lights measurement of ^{90}Y, we used a 1220 QUANTULUS™ Ultra Low Level Liquid Scintillation Spectrometer (PerkinElmer Inc.) with 20 mL Teflon™ vials (PerkinElmer Inc.) The detection efficiency for ^{90}Sr counting was determined by measuring of the ^{90}Sr standard solution.

An Agilent/HP 4500 ICP-MS (Agilent Technologies Inc.) was used for determining chemical yields of Sr, after the chemical separation and sequential Cherenkov light measurement.

2.3. Aerosol samples. A series of aerosol samples were collected in April 2011 at Mito City (N36.40, E140.44) in Ibaraki Prefecture of eastern Japan. In each sample, aerosols were collected on PaLL Tissuquartz™ filters, 2500 QAT-UP (Sigma-Aldrich Inc.), with a Kimoto-121FT high-volume air sampler (Kimoto Texh Inc.). The size of the filter was 10 × 8 cm^2. The air-flow of the sampler was approximately 700 L min^{-1}. Cesium-137 activity was directly determined for each sample with the germanium semiconductor detector. A standard filter was used to determine the efficiency of the germanium semiconductor detectors. The standard filter spotted radioactive standard solution uniformly was folded into the same shape of the measurement samples [8].

We chose four filter samples from the samples collected in April for determining the ^{90}Sr activity concentrations in the aerosols using our new method. The details of the samples are shown in Table 1. These four samples had relatively high ^{137}Cs activities, and thus we expected that these samples would have ^{90}Sr high activities above that of the liquid scintillation counter detection limit. We analyzed a half or quarter portion of each aerosol filter sample.

2.4. Strontium separation procedure.

2.4.1. Sample pretreatment. First, each separated filter sample was cut into pieces (approximately 5 × 2 cm^2), which were then put into a 500-mL Teflon beaker. Next, 100 mL of 12 M HCl, 30 mL of 13 M HNO_3, and 1.0 mg of stable Sr carrier were added to the beaker. The acid solution was then heated on a hot plate to 150 °C for 3 h to extract Sr into the solution. After cooling to room temperature for 1 h, the solution was filtered with a 0.45-µm membrane cellulose filter (φ47, Advantec no.7) after decantation to roughly separate the solution and residues. The solution was then placed into a 300 mL-polyethylene container. The residues on the filters were washed with 30 mL of 3.25 M HCl twice followed by 30 mL Milli-Q water once. The washing solutions were also added to the polyethylene container. The mixed sample solution was weighed, and then 3 mL of the solution was removed to obtain the initial Sr concentration by ICP-MS for the chemical yield determination. The remaining solution was transferred to a 500-mL measuring flask. Milli-Q water was added into the acid to adjust the concentration to 3.25 M HCl, which is suitable for Sr extraction by the disk [14].

In this study, the extraction yield of ^{90}Sr from each aerosol filter was obtained by comparing its activity with those of ^{137}Cs from the same sample before and after chemical treatment. We presumed that the Sr and Cs in the aerosol sample had similar chemical extractability into the acid solution. The filter residues after extraction were dried in a desiccator at room temperature, and then formed into approximately the same geometric shape as the intact filter for gamma-ray measurement.

2.4.2 Solid-phase extraction. The complete separation procedure, including a solid-phase separation and a cation

TABLE 1: Details of the four FDNPP aerosol samples and chemical analysis results

Aerosol sample name	MIT4	MIT9	MIT12	MIT13
Air volume (m^3)	2070	1572	3085	2139
Sampling start date	2011/4/9	2011/4/14	2011/4/19	2011/4/21
Measurement date	2015/7/17	2015/8/1	2015/7/18	2015/7/13
Effective air-volume (m^3)	497	770	771	1069
^{137}Cs yield	99±2%	99±5%	98±3%	98±4%
Stable Sr yield	83±6%	87±6%	86±6%	85±6%
^{90}Sr concentration ($mBqm^{-3}$)	1.5±0.1	0.79±0.6	0.50±0.04	0.055±0.005
^{137}Cs concentration (Bqm^{-3})	0.82±0.08	0.057±0.006	0.11±0.01	0.041±0.004
^{90}Sr/^{137}Cs activity ratio (×10^{-3})	1.9±0.2	14±1	4.6±0.6	1.3±0.2

Notes: ^{90}Sr and ^{137}Cs activity concentrations were calculated from the equation provided in the "Measurement instruments" subsection. Effective air-volume was calculated from the mass of aerosol sample analyzed. All activities were decay collected to 11 March, 2011. The confidence interval was 95%.

exchange chromatography, is illustrated in Figure 1. For solid-phase extraction, an Empore™ Strontium Rad Disk was set in a φ47-mm diameter funnel and preconditioned by the addition of 10 mL methanol, waiting 20 min, and then rinsing with 30 mL of 3.25 M HCl by vacuum filtration with a flow rate of approximately 50 mL min^{-1}. The sample acid solution in the 500-mL flask was then passed through the disk to extract Sr ions into the solid-phase. The disk was then washed with 15 mL of Milli-Q water to remove residual acids. To elute Sr ion from the disk, 10 mL of 0.02 M EDTA solution was passed through at a flow rate of 2 mL min^{-1} [16]. Another 10 mL of this EDTA solution was passed through the disk at 10 mL min^{-1} as the final rinse. These two solutions were combined and used for cation-exchange separation.

2.4.3 Cation-exchange separation. The cation-exchange process is illustrated in the lower-right portion of Figure 1. First, 0.25 g of Dowex 50W-X8 (100-200 mesh) ion-exchange resin was placed into an S-size Muromac™ mini-column (Φ8 × 50 mm). Then, 10 mL Milli-Q water and 10 mL of 0.01M HCl were passed through the column consecutively to condition the ion-exchange resin. To the 20 mL EDTA sample solution, 0.75 mL of 13 M HNO_3 was added to adjust its pH, and the solution was passed through the preconditioned column. Under these conditions, both Sr and Pb ions were adsorbed onto the cation-exchange resin. Then, 10 mL of 10^{-5} M HCl solution was passed through the column to wash out the residual EDTA, followed by 15 mL of 2% (w/v) EDTA solution to remove Pb ions from the resin. Finally, 15 mL of 3.25 M HCl was passed through the column for Sr ion elution. The final solution was placed into a 20 mL Teflon vial to be measured by a low-background liquid scintillation counter.

2.5. Radioactivity calculation. Beta-rays from ^{90}Y, a daughter nuclide of ^{90}Sr, were measured to determine the amount of ^{90}Sr in the aerosol samples. The beta rays emitted from ^{90}Y have an endpoint energy of 2.2 MeV and can effectively emit Cherenkov light in water. The Cherenkov light counting efficiency for ^{90}Sr is much lower than that for ^{90}Y, therefore we can measure ^{90}Y activity selectively. We can identify the activity of ^{90}Sr from the growth of ^{90}Y over time. Owing to the large difference between the half-lives of ^{90}Sr and ^{90}Y, radioactive equilibrium was reached within 2 weeks. The ^{90}Sr activity approximately coincides with the ^{90}Y activity after 2 weeks from ^{90}Sr isolation.

The ^{90}Sr activity concentration (Bq m^{-3}) in air, A, was determined from the ^{90}Y activity as

$$A = \frac{C - C_b}{\varepsilon R V}$$

where C is the count rate after ^{90}Sr-^{90}Y radioactive equilibration, C_b is the background count rate, and ε is the counting efficiency of Cherenkov light for ^{90}Y. In our measurement system, the background counting rate was approximately 0.028 count per second (CPS), and the detection efficiency of Cherenkov light from ^{90}Y was 68.7 ± 0.1 %. R is the yield of Sr chemical separation determined by ICP-MS, and V is the collected air volume (m^3) of the aerosol samples. In the ICP-MS measurement, the chemical yield was determined by measuring the amount of stable Sr carrier ions in the measurement sample after a sequential Cherenkov light measurement. A 1 mL aliquot of each measurement sample was diluted 1000 times with water and HNO_3, and adjusted to a final concentration of 5% w/v HNO_3. Four external calibration solutions were prepared with the 5% w/v HNO_3 to 0, 10, 20, 50, and 100 ng mL^{-1}. The calibration curve for the Sr was found to be linear ($R^2 \geq 0.9999$). In each measurement, we performed at least six analytical runs and used the averaged value. The chemical yields were determined from the ratio of the Sr mass in the measurement sample to that of the Sr added initially.

The uncertainties of the ^{137}Cs radioactivity concentrations were the combined uncertainties of the efficiency and counting statistics in the gamma-ray measurement. The uncertainties of the stable Sr yield resulted from errors in the ICP-MS measurement. The total uncertainties in the ^{90}Sr radioactivities were the combined uncertainties of ^{137}Cs yields, stable Sr yield, counting statistics in the ^{90}Sr measurement, and uncertainty in the efficiency of the Cherenkov light measurement. When reporting the results, 95% confidence intervals were used in this study.

3. Results and Discussion

3.1. Optimization of ^{210}Pb cation-exchange separation conditions. Cation exchange was applied after extraction by the Rad Disk method to eliminate ^{210}Pb, because contamination by naturally occurring ^{210}Pb causes considerable background signals during ^{90}Sr detection. Pb ions in solution are usually separated by precipitation in a chromate form at pH

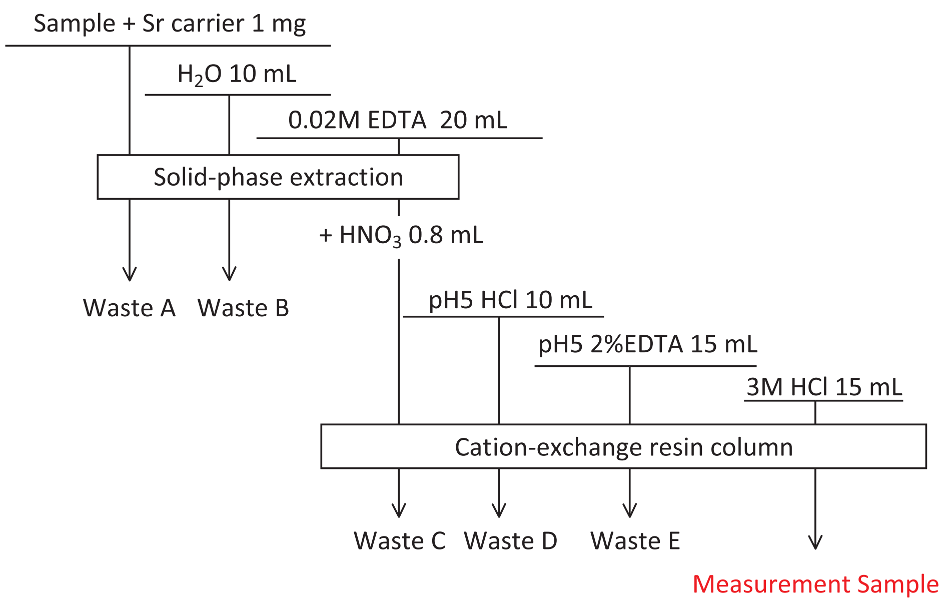

Figure 1. Schematic of the chemical separation procedure for the isolation of ^{90}Sr from aerosol samples by solid-phase extraction

5.5 [17]. However, this method does not eliminate Pb in the presence of EDTA solution, which forms a stable complex with Pb ions at this pH. Instead, we employed cation-exchange chromatography for Pb ion elimination. Thus, optimization of the conditions for the separation of ^{90}Sr from ^{210}Pb was necessary.

In our separation method (illustrated in Figure 1), Sr ions in 0.02 M EDTA solution eluted from the solid-phase extraction disk were adsorbed onto the cation-exchange resin and separated from the Pb ions. To estimate the separation efficiency and determine the elution curves of Pb and Sr ions, a ^{210}Pb solution was passed through the cation-exchange column under conditions comparable to those in Figure 1. After passing 10^{-5} M HCl solution through the column to adjust the pH conditions, 2% (w/v) EDTA solution at pH = 5 was passed through the column and each 1 mL fraction of the elute was stored in a plastic vial. Then, 6 mL scintillation cocktail was added to each vial and the activities were measured by a liquid scintillation counter. The resulting ^{210}Pb elution curve is shown in Figure 2. Elution of ^{210}Pb from the column starts after 7 mL EDTA solution is eluted, and ^{210}Pb elimination is completed with 12 mL of EDTA solution. From this result, we conclude that ^{210}Pb separation is achieved by 15 mL of EDTA solution (Figure 1).

The elution behavior of Sr ions from the column was investigated using the ^{89}Sr isotope. To obtain an elution curve, 3.25 M HCl was passed through the column and collected in 2 mL fractions. We added 6 mL scintillation cocktail to each fraction and the ^{89}Sr activities were measured with a liquid scintillation counter. The resulting Sr elution curve (Figure 3) shows that 95% Sr is recovered from the column with 12 mL HCl solution. We adopted 15 mL as the optimized volume of the HCl solution for the elution of Sr ions from the resin, as shown in Figure 1.

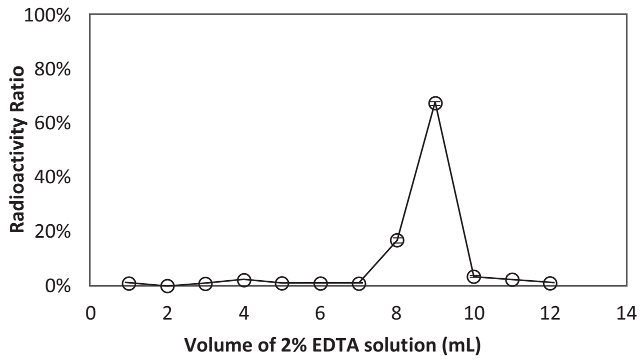

Figure 2. Elution curve of ^{210}Pb from the cation-exchange column by 2% EDTA solution at pH = 5. The elution profile was determined using 1 mL aliquots. The y-axis is the activity ratio of eluted ^{210}Pb to initially added ^{210}Pb.

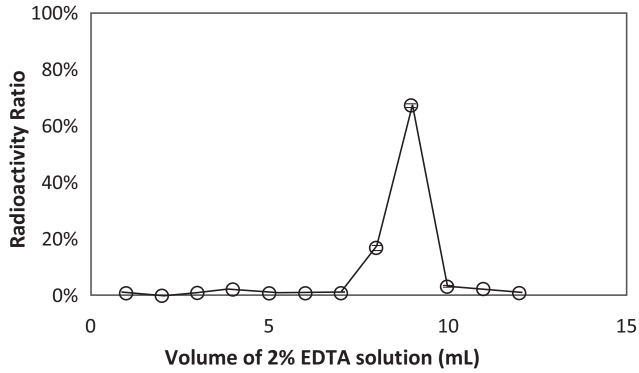

Figure 3. Elution curve of ^{89}Sr from the cation-exchange column by 3.25 M HCl. The elution profile was determined using 2 mL aliquots. The y-axis is the activity ratio of eluted ^{89}Sr to initially added ^{89}Sr.

3.2. Estimation of Sr losses in each chemical separation step. The Sr yield in each step of the optimized method was investigated by measuring the gamma-rays from ^{85}Sr (0.514 MeV) using a germanium semiconductor detector, and/or the amount of stable Sr carrier in the sample solution by ICP-MS. The Sr yield by the solid-phase extraction method is determined to be more than 95%, which is consistent with the disk extraction performance (Waste A) [14]. Cations other than Sr do not cause serious interference in this step. In our method, to remove any residual acid from the disk that may disrupt EDTA complex formation, the disk was washed with 10 mL water before Sr ion elution. With this washing step, the loss of Sr ions in Waste B (see Figure 1) is suppressed to within 2–3%. In the cation-exchange operation, Sr-containing EDTA eluate from the disk was mixed with 0.75 mL of 13 M HNO_3, and then passed through the cation-exchange resin. The Sr ion losses during passage through the column, pH conditioning, and elution of ^{210}Pb from the column are contained in Wastes C, D, and E, respectively. We measured the activity of ^{85}Sr in these wastes by gamma-ray counting and the amount of stable Sr in these wastes by ICP-MS. The Sr losses in these wastes are less than 1%. Hence, we conclude that no significant loss of Sr occurs in these steps.

TABLE 2: Yields of stable Sr after chemical separation and loss of Sr in each separation step

Sample name	MIT4	MIT9	MIT12	MIT13
Waste A	1%	3%	1%	2%
Waste B	2%	3%	1%	5%
Waste C	1%	1%	2%	1%
Waste D	<1%	<1%	<1%	<1%
Waste E	<1%	<1%	<1%	<1%
Stable Sr yield	83±6%	87±6%	86±6%	85±6%

Notes: See Figure 1 for detailed separation procedure. The confidence interval was 95%.

3.3. Extraction yields of ^{90}Sr from aerosol samples. Cesium-137 yields in acid pretreatment step were measured for alternative evaluating ^{90}Sr leaching yields from aerosol samples. Stable Sr yields of the chemical separation were measured by ICP-MS. From the Cherenkov light counting result, the ^{137}Cs yields and the stable Sr yields, the activities of ^{90}Sr in the aerosol samples were determined and are summarized in Table 2.

The activities of ^{90}Sr in the atmosphere are in the range of 0.055–1.5 mBq m^{-3}, which is consistent with previous measurement results [2].

For the four analyzed aerosol samples, the ^{137}Cs is perfectly leached during acid pretreatment. Cesium-134 and -137 are transported through the atmosphere in sulfate aerosol form [18], and sulfate aerosols dissolve in HCl solution easily. Strontium is also transported through the atmosphere in soluble aerosol form, as, unlike iodine, Sr does not exist in gaseous form. Therefore, we conclude that the ^{90}Sr in the filter is completely removed by the acAfter the pretreatment, five waste solutions (A-E) were collected during chemical separation, and the chemical separation yield and Sr loss were estimated by stable Sr ion measurement using ICP-MS. The Sr yields and losses in the waste solutions are summarized in Table 2. The Sr chemical yields in all four samples are more than 80%. The sum of the Sr yields and losses in each waste are less than

100% because of the margin of error in the ICP-MS measurement, and the retention of Sr ions on the disk and/or cation-exchange resin.

3.4. Backgrounds in measurement of ^{90}Sr for aerosol samples. There are three major background interferences for ^{90}Sr (^{90}Y) in the four aerosol samples in this study, i.e., ^{89}Sr from the FDNPP accident, ^{90}Sr from global fallout, ^{210}Pb, and ^{226}Ra and its daughter nuclides. Each of their effects on the ^{90}Sr determination are discussed in details as follows.

Strontium-89 with a half-life of 50.5 days is one of the most important radionuclides from the FDNPP nuclear accident. The activity of ^{89}Sr can be detected by Cherenkov light counting, owing to its high-energy beta-rays. However, the Day 0 counting rate in Figure 4 is approximately 0.02–0.03 CPS, which agrees well with that of a blank sample (0.028 CPS). Thus, we conclude that ^{89}Sr activity is not detected in our measurements. The ^{89}Sr/^{90}Sr activity ratio of the FDNPP fuel was calculated as 0.43 by ORIGEN 2 code [19]. We began our measurement in 2015 (approximately 1500 days after the accident), and the ^{89}Sr/^{90}Sr activity ratio was estimated as 1.6×10^{-10}.

The global background of ^{90}Sr in the atmosphere is negligible in our study. The background ^{90}Sr atmospheric concentration was 1×10^{-6} Bq m^{-3} in the Northern hemisphere in 1983 [20]. A sharp increase in the atmospheric concentration of ^{90}Sr was observed in Europe after the Chernobyl nuclear accident. However, the ^{90}Sr activity concentration of the global fallout returned to its pre-accident level [2] and has continued to decrease to date. The atmospheric concentration of ^{90}Sr follows the fallout behavior and its level should be lower than 1×10^{-6} Bq m^{-3}. However, in our data, the lowest ^{90}Sr atmospheric concentration is 55×10^{-6} Bq m^{-3}. Thus, we can conclude that the ^{90}Sr activity detected in our study originates from the FDNPP accident release event.

Naturally occurring ^{210}Pb provide severe background signals for ^{90}Sr counting by Cherenkov lights measurements. The ^{90}Sr activity concentrations obtained in the present study are 0.055–1.5 mBq m^{-3}. Conversely, Tanahara et al. reported that the ^{210}Pb activity concentrations in Okinawa Islands, Japan, were 0.06 to 1.98 mBq m^{-3} from 2004 to 2011 [21]. Lead-210 only emits low-energy end-point beta-rays (0.06 MeV), but its daughter nuclide ^{210}Bi emits relatively high-energy beta-rays (1.2 MeV). The beta-rays of ^{210}Bi emit Cherenkov light in water, and its efficiency is approximately 30% that of ^{90}Y. As we discussed above, our method eliminates the ^{210}Pb contribution completely. In addition, we also confirm the possibility of ^{210}Pb existence owing to radioactive equilibrium. If ^{210}Pb contamination was present, more time would be required to achieve radioactive equilibrium relative to that required for the pure ^{90}Sr-^{90}Y equilibrium, because ^{210}Bi has a longer half-live than ^{90}Y. However, all of our sequential measurement results show good agreement with the calculated ^{90}Sr-^{90}Y radioactive equilibrium. Thus, we conclude that complete ^{210}Pb elimination is achieved and thus does affected our determination of ^{90}Sr in the aerosol samples.

Radium-226 and its daughter nuclides of ^{222}Rn, ^{214}Bi and ^{214}Pb may cause background signals in the beta-ray measurements [22], because ^{226}Ra is not eliminated by our method. However, the atmospheric concentration of ^{226}Ra is approximately 1.5 µBq m^{-3} [23], and the low-activity ^{226}Ra and its daughters compared with that of ^{90}Sr allow it to be ignored in the Cherenkov light measurements.

3.5. Activities of ^{90}Sr in four aerosol samples collected after the FDNPP accident. The activities of ^{90}Sr in the aerosol samples collected after the FDNPP accident were determined using the optimized separation method described above. The chemical separation method with solid-phase extraction was performed on each aerosol sample, and 15-mL 3.25 M HCl measurement samples were obtained. Cherenkov counting was performed over more than 2 weeks for each measurement sample. The ^{90}Y growth curves for the aerosol samples are shown in Figure 4.

As shown in Table 2, the ^{90}Sr activity concentrations are approximately 1/1000 those of ^{137}Cs. Comparing the ^{90}Sr/^{137}Cs

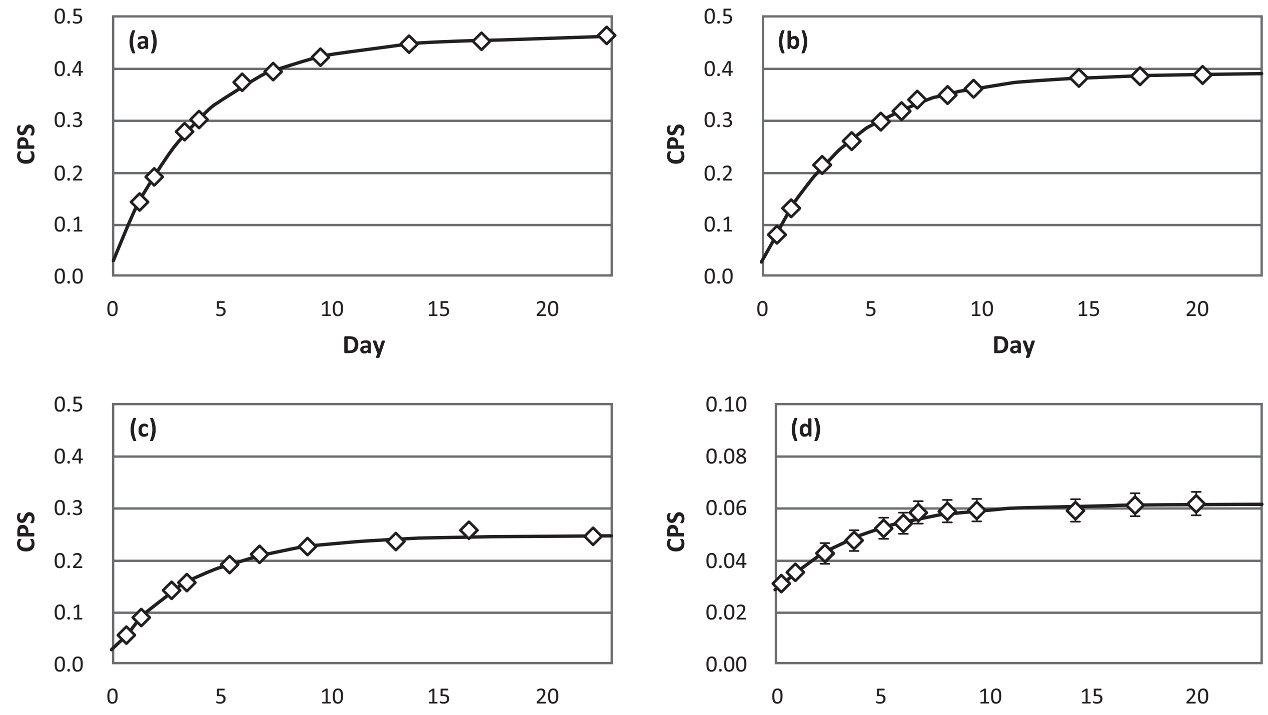

Figure 4. Yittrium-90 growth curves from ^{90}Sr in (a) MIT4, (b) MIT9, (c) MIT12, and (d) MIT13 aerosol samples. The data points were obtained by the 1220 QUANTULUS™ counter. The solid lines are the ^{90}Y growth, calculated by fitting the counting data to the equation for radioactive equilibrium.

activity ratio in aerosols with those from soil and seawater samples provides us with a better understanding of the radioactivity discharge conditions in the FDNPP event. Soil samples collected in eastern Japan had the $^{90}Sr/^{137}Cs$ ratio of 1/10-1/10000 [10]. The Ministry of Education, Culture, Sports, Science & Technology in Japan (MEXT) reported that $^{90}Sr/^{137}Cs$ ratios in soils were approximately 1/1000 at many survey points in Fukushima Prefecture, including some points with ratios as high as 1/10-1/100 [24]. The soil $^{90}Sr/^{137}Cs$ ratios are comparable to our aerosol values; however, our data exhibit large variation. The $^{90}Sr/^{137}Cs$ ratio for seawater samples collected at 30-600 km offshore in June 2011 was reported to be 0.0265±0.006 [25]. Povinec et al. reported that the $^{90}Sr/^{137}Cs$ ratio at the coast near the FDNPP varied between 0.006 and 64.5 from April 2011 to February 2012 [26]. The ratio is higher than that from our aerosol samples, probably because of the direct discharge of ^{90}Sr from the FDNPP site to the sea [27]. Because ^{90}Sr is less volatile than ^{137}Cs, the $^{90}Sr/^{137}Cs$ ratio in aerosols would be lower. Water can contain additional ^{90}Sr in soluble chemical forms, which may also contribute to a higher $^{90}Sr/^{137}Cs$ ratio in seawater than in aerosols.

4. Conclusions

A rapid isolation method for ^{90}Sr in aerosol samples has been developed using Empore™ Sr Rad Disk. The problem of contamination by ^{210}Pb during solid extraction was resolved by cation exchange. The yield of Sr in this scheme was > 80% and ^{210}Pb was completely eliminated. Because the separation method consists of only two steps, the ^{90}Sr chemical separation from the pretreated sample solution is achieved much faster (approximately 2.5 h) than in conventional methods. Aerosol samples collected in Mito City after the FDNPP accident were analyzed by the developed method, and the activities of ^{90}Sr were determined for the first time. The $^{90}Sr/^{137}Cs$ activity ratio in aerosol samples collected at Mito about 130 km south from the FDNPP site following the accident were found experimentally to be in the order of 1/1000.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number JP16K45678 and a Grant-in-Aid for Scientific Research (KAKENHI) on Innovative Areas under the A04-08 research teams (grant number 24110009).

References

(1) H. Higuchi, H. Fukatsu, T. Hahimoto, N. Nonaka, K. Yoshimizu, M. Omine, N. Takano, T. Abe, Radioactivity in surface air and precipitation in Japan after the Chernobyl Accident. J. Environ.6, 131-144 (1988).

(2) Y. Igarashi, M. Kajino, Y. Zaizen, K. Adachi, M. Mikami, Atmospheric radioactivity over Tsukuba, Japan : A summary of three years of observations after the FDNPP accident, PEPS, 2, 44 (2015).

(3) K. Irlweck, B. Khademi, $^{239(240),\,238}Pu$, ^{90}Sr, ^{103}Ru and ^{137}Cs concentrations in surface air in Austria due to dispersion of Chernobyl releases over Europe, J. Environ., Radioact. 20, 133-148 (1993).

(4) V. A. Kashparov, S. M. Lundin, S. I. Zvarich, V. I. Ioshchenko, S. E. Levchuk, Y. V. Khomutinin, I. M. Maloshtan, V. P. Protsak, E. M. Pazukhin, Soil contamination with fuel component of Chernobyl radioactive fallout, Radiochemistry 45 189-200 (2003).

(5) K. Južnič, Š. Fedina, Distribution of ^{89}Sr and ^{90}Sr in Slovenia, Yugoslavia, after the Chernobyl accident. J. Environ. Radioact, 5, 159-163 (1987).

(6) M. Herranz, L.M. Romero, R. Idoeta, C. Olondo, F. Valiño, F. Legarda, Inventory and vertical migration of ^{90}Sr fallout and $^{137}Cs/^{90}Sr$ ratio in Spanish mainland soils, J. Environ. Radioact, 102, 987-994 (2011).

(7) B. Luksiene, D. Marciulioniene, I. Gudeliene, F. Schönhofer, Accumulation and transfer of ^{137}Cs and ^{90}Sr in the plants of the forest ecosystem near the Ignalina Nuclear Power Plant, J. Environ. Radioact, 116, 1-9 (2013).

(8) Z. Zhang, K. Ninomiya, N. Takahashi, A. Shinohara, Daily variation of I-131, Cs-134 and Cs-137 activity concentrations in the atmosphere in Osaka during the early phase after the FDNPP accident, J Radioanal. Nucl. Chem. 303, 1527-1531 (2015).

(9) G. Steinhauser, V. Schauer, K. Shozugawa, Concentration of strontium-90 at selected hot spots in Japan, PLoS One, 8, e57760 (2013).

(10) Ministry of Education, Culture, Sports, Science and Technology (MEXT), Results of the nuclide analysis of plutonium and strontium by MEXT, http://radioactivity.nsr.go.jp/en/contents/5000/4167/24/1750_093014.pdf, (accessed 03 November 2015).

(11) Ministry of Education, Culture, Sports, Science and Technology (MEXT), Analysis method of radioactive strontium (in Japanese) http://www.kankyo-hoshano.go.jp/series/lib/No2.pdf (accessed 20 October 2016)

(12) S.K. Fiskum, R.G. Riley, C.J. Thompson, Preconcentration and analysis of strontium-90 and technetium-99 from Hanford groundwater using solid phase extraction, J. Radioanal. Nucl. Chem. 245, 261-272 (2000).

(13) J. J. Mateos, E. Gómez, F. Garcias, M. Casas, V. Cerdà, Rapid $^{90}Sr/^{90}Y$ determination in water samples using a sequential injection method. Appl. Radiat. Isot. 53 (1-2), 139-144 (2000).

(14) L. L. Smith, K. A. Orlandini, J. S. Alvarado, K. M. Hoffmann, D. C. Seely, R. T. Shannon, Application of Empore™ strontium rad disks to the analysis of radiostrontium in environmental water samples, Radiochim Acta 73, 165-170 (1996).

(15) K. Günther, S. Lange, M. Veit, A rapid method for determining ^{89}Sr and ^{90}Sr by Cerenkov counting. Appl. Radiat. Isot. 67 (5), 781-785 (2009).

(16) F. Heynen, E. Minne, S. Hallez, Empore™ strontium rad disks: Validation procedure for strontium-90 analysis in radioactive wastes, Radiochim. Acta 95, 529-534 (2007).

(17) B. Y. Lalit, T. V. Ramachandran, S. Rajan, Lead-210 content of food samples in India, Radiat. Environ. Biophys. 18, 13-17 (1980).

(18) N. Kaneyasu, H. Ohashi, F. Suzuki, T. Okuda, F. Ikemori, Sulfate aerosol as a potential transport medium of radiocesium from the Fukushima nuclear accident., Environ Sci Technol, 4, 5720-5726 (2012).

(19) K. Nishihara, H. Iwamoto, K. Suyama, Estimation of fuel compositions in Fukushima-Daiichi Nuclear Power Plant, JAEA-Data/Code 2012-018 (2012).

(20) United Nations Scientific Committee on the Effects of Atomic Radiation (UNSEAR), UNSCEAR 2000 Report to the General Assembly, with scientific annexes, http://www.unscear.org/unscear/en/publications/2000_1.html (accessed 05 July 2016).

(21) A. Tanahara, F. Nakaema, Y. Zamami, T. Arakaki, Atmospheric concentrations of ^{210}Pb and ^{7}Be observed in Okinawa Islands, Radioisotopes, 63, 175-181 (2014).

(22) M.Al-Mad, R. Blackburn. Application of Cerenkov radiation for the assay of ^{226}Ra in natural water, Sci. Total Environ., 173/174, 53-59 (1995).

(23) IAEA, The Environmental Behaviour of Radium: Revised Edition, Technical Reports Series No. 476, IAEA, Vienna (2014).

(24) Ministry of Education, Culture, Sports, Science and Technology (MEXT), Analysis results concerning (i)

gamma-emitting nuclides and (ii) Sr-89 and Sr-90 (Second Distribution Survey) by MEXT http://radioactivity.nsr.go.jp/en/contents/6000/5636/24/338_Sr_0912018_e.pdf (accessed 03 November 15).

(25) N. Casacuberta, P. Masqué, J. Garcia-Orellana, R. Garcia-Tenorio, K.O. Buesseler ^{90}Sr and ^{89}Sr in seawater off Japan as a consequence of the Fukushima Dai-ichi nuclear accident, Biogeosciences, 10, 3649-3659 (2013).

(26) P. P. Povinec, K. Hirose, M. Aoyama, Radiostrontium in the Western North Pacific: characteristics, behavior, and the Fukushima impact. Environ. Sci. Technol. 46, 10356-10363 (2012).

(27) P. P. Povinec, K. Hirose, Fukushima radionuclides in the NW Pacific, and assessment of doses for Japanese and world population from ingestion of seafood, Sci. Rep. 5, 9016 (2015).