

NOTE

Novel method for low level Sr-90 activity detection in seawater by combining oxalate precipitation and chelating resin extraction

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⁹⁰Sr released into seawater from nuclear bomb testing and nuclear facility accident sites requires long-term monitoring. However, measuring ⁹⁰Sr in seawater is still difficult and time-consuming. This study is aimed at improving the preconcentration method for successive purification using DGA Resin chromatography, which is applied to ⁹⁰Sr analysis in seawater. At natural pH, the oxalate coprecipitation technique effectively collected Sr (84% in Sr yield) from seawater without Mg or Na. For ⁹⁰Sr determination, ⁹⁰Y in secular equilibrium with ⁹⁰Sr was directly extracted using Fe coprecipitation and DGA Resin chromatography. The proposed method simplifies the analytical processes associated with the conventional method. Analytical results for surface seawater in the western North Pacific (0.81 ± 0.06 Bq m⁻³, $n = 5$) were consistent with those obtained using the conventional method (0.81 ± 0.07 Bq m⁻³, $n = 5$).

Keywords: strontium-90, nuclear power plant, seawater monitoring, preconcentration, oxalate precipitation

INTRODUCTION

Strontium-90 concentrations of around 1.0 Bq m⁻³, originating from atomic bomb testing (UNSCEAR, 2000), were detected in surface seawater in the western North Pacific in 2011 (Povinec *et al.*, 2012). The accident at the Fukushima Daiichi Nuclear Power Plant (Japan) resulted in the release of ⁹⁰Sr into the ocean in early April 2011 (Casacuberta *et al.*, 2013), and continuous leakage from the power plant in 2013 was also pointed out (Castrillejo *et al.*, 2015). In order to assess the impact of this leakage on the marine environment, it is necessary to detect low levels of ⁹⁰Sr in seawater and to distinguish it from the background level. Here, we aimed to establish a method to determine ⁹⁰Sr concentrations as low as 0.2 Bq m⁻³, which is one order of magnitude lower than the average background level in the Pacific surface water.

Preconcentration of Sr from large-volume seawater samples (e.g., 20–40 L) and purification of Sr and/or Y are necessary to measure the ⁹⁰Sr concentration in open-ocean seawater.

For the preconcentration of ⁹⁰Sr in seawater, carbonate coprecipitation (Noshkin and Mott, 1967; Sugihara *et al.*, 1959), oxalate precipitation (Bojanowski and Knapinska-Skiba, 1990), and cation exchange chromatography (Grahek and Rožmarić Mačefat, 2005) were applied. Carbonate precipitation is the most widely used method for preconcentration because it allows Sr to be collected quantitatively. However, the disadvantage of this method is Mg precipitation with both Sr and Ca. Conversely, the oxalate precipitation method, which uses oxalic acid and a base, produces less Sr recovery (*ca.* 80–90%, Bojanowski and Knapinska-Skiba, 1990), but can avoid Mg incorporation.

The Sr purification procedure includes several treatment steps, is time-consuming, and requires a huge amount of time and a specialized technique. DGA Resin separation is a new approach to directly separate a prog-

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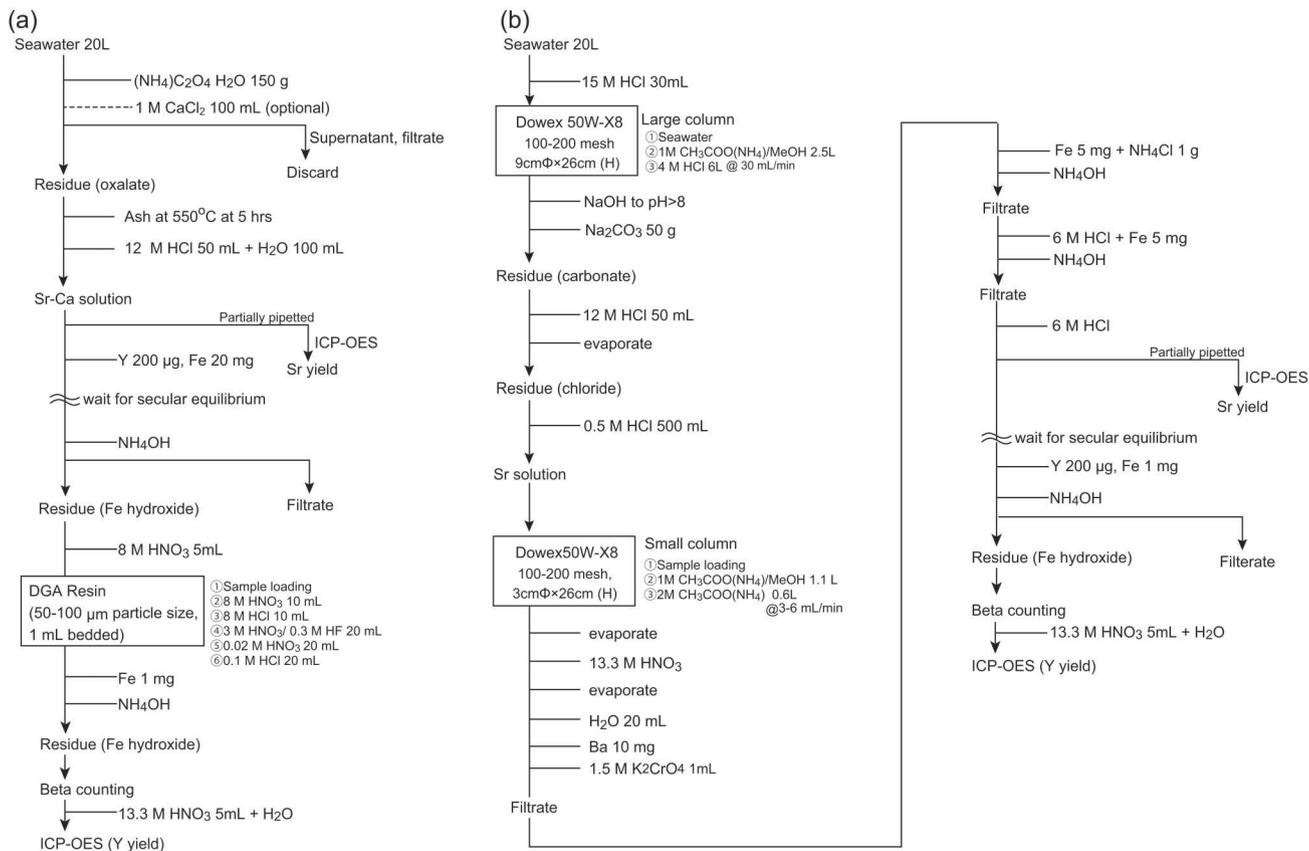


Fig. 1 Schematic charts of ^{90}Sr analytical procedures using oxalate precipitation and DGA Resin separation (a) and the conventional cation exchange chromatography and chromate coprecipitation (b).

eny radionuclide, ^{90}Y , from a seawater sample (Maxwell *et al.*, 2013; Tazoe *et al.*, 2016). Adopting highly efficient DGA Resin separation as a purification process can achieve to simplify preconcentration step, which improves analytical throughput and reliability.

In this study, the preconcentration method and successive DGA Resin separation are improved (Fig. 1a) to analyze the background level of ^{90}Sr in a large-volume seawater sample. Direct separation of ^{90}Y using DGA Resin in combination with preconcentration using Ca-oxalate coprecipitation is applied to determine the ^{90}Sr concentration of the background level surface seawater.

EXPERIMENTAL

Seawater sample

In this study, 200 L of seawater was obtained from Station A11 (36°00.0' N, 146°00.0' E) during an R/V Hakuho-Maru KH-15-1 cruise conducted on March 6–26, 2015. Seawater was collected from about 5 meters below the surface using an underway sampler. Unfiltered seawater was stored in a 20 L polyethylene container. 5

mL of seawater was distributed to determine the stable Sr concentration by ICP-OES.

Analytical procedure for large-volume seawater sample Sr preconcentration by oxalate coprecipitation and Y separation using DGA Resin Aqueous nitric acid, hydrochloric acid, and ammonium were prepared from electro-industry grade chemicals (Kanto Chemicals). Other chemical reagents (JIS special grade) were obtained from Wako Chemical. 150 g of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was added to 20 L of seawater and shaken vigorously (Fig. 1a). After 20 hours, most of the supernatant was discarded by decantation, and then, the precipitate was filtrated using a 5C quantitative filter (Advantec Toyo). The oxalate precipitate was decomposed in a furnace for 5 hours at 550°C . Then, the residue was dissolved in 50 mL of 12 M HCl , and the remaining ash was filtered out. The sample solution was diluted to 150 mL using Milli-Q water. Small portions of the sample solution were separated for determination of the stable Sr yield by ICP-OES (SPECTROBLUE TI, SPECTRO Analytical Instruments). 200 μg of Y (1,000 mg L^{-1} standard solution for AAS,

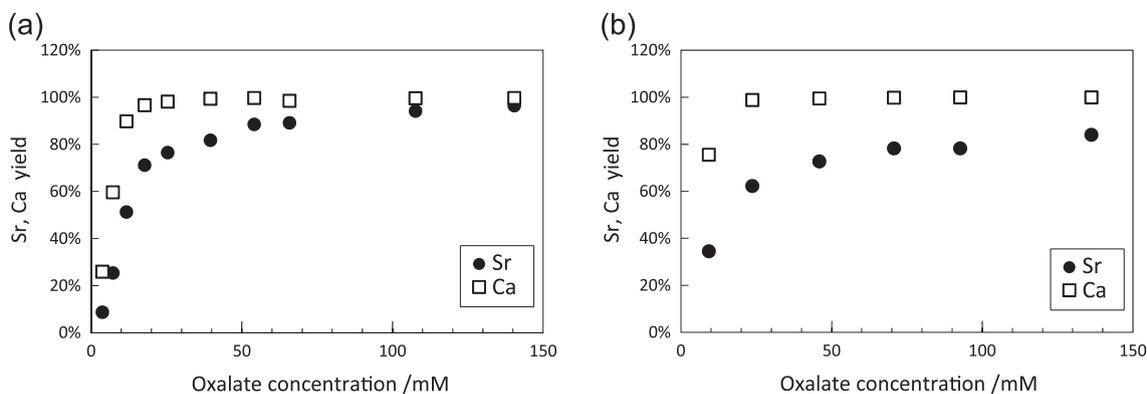


Fig. 2 Sr and Ca yields by oxalate precipitation using (a) ammonium oxalate monohydride and (b) oxalic acid with NaOH.

Wako) and 20 mg of Fe purified from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were added as carriers. ^{90}Y was allowed to grow into secular equilibrium with ^{90}Sr for more than 2 weeks. ^{90}Y was then coprecipitated with Fe hydroxide by the addition of aqueous NH_4OH . The precipitate was filtered with a GF/F filter and dissolved in 5 mL of 8 M HNO_3 . The ^{90}Y separation method using DGA Resin, beta counting, and data processing are described in Tazoe *et al.* (2016). After beta counting, the sample was dissolved in HNO_3 and diluted for the determination of the Y yield using ICP-OES.

Conventional separation procedure using large-volume cation exchange resin columns The conventional method (MEXT, 2003) adopted in this study mainly included ion exchange and multiple coprecipitation (Fig. 1b). A 20 L seawater sample was preconcentrated using a large-volume column bedded cation exchange resin (Dowex 50W-X8, 100–200 mesh, 9 cm in diameter, 26 cm in height). Samples were passed through the column at flow rate of 30 mL/min. After Mg and Ca were removed with 2.5 L of a 2 M $\text{CH}_3\text{COO}(\text{NH}_4)$ solution and methanol mixture, Sr was recovered from 6 L of 4 M HCl. NaOH was added to the sample to adjust the pH to >8 , and then, 50 g of Na_2CO_3 was added while stirring to effect carbonate precipitation. After discarding the supernatant, the precipitate was filtered and dissolved in 500 mL of 0.5 M HCl. The sample was loaded onto the second cation exchange column (Dowex 50W-X8, 100–200 mesh, 3 cm in diameter, 26 cm in height). The remaining Ca, Bi, and Pb were removed using a 1.1 L mixture of 2 M $\text{CH}_3\text{COO}(\text{NH}_4)$ solution and methanol, after which Sr was eluted in 600 mL of 2 M $\text{CH}_3\text{COO}(\text{NH}_4)$. The eluent was evaporated to dryness and then dissolved in HNO_3 . The solution was again evaporated to, and the residue was dissolved in 20 mL of water. Coprecipitation with Ba chromate and Fe hydroxide was performed to remove Pb, Ba, and the initial ^{90}Y . After secular equilibrium was reached, ^{90}Y was precipitated with Fe hydroxide and counted using a gas flow proportional counter.

RESULTS AND DISCUSSION

Optimization of coprecipitation protocol

The precipitation rates of Sr and Ca were examined using a small volume of seawater. Potassium oxalate was added to 200 mL of seawater, and the precipitate was filtered using a 0.45 μm pore membrane filter. Precipitates were ashed, and the Na, Mg, Ca, and Sr contents were determined by inductively coupled plasma optical emission spectrometer (ICP-OES). The precipitation rates of both Ca and Sr increased with oxalate concentration and reached 98% and 76%, respectively, at an oxalate concentration of 25 mM (Fig. 2a). At higher oxalate concentrations, Ca was sufficiently precipitated, and the amount of Sr precipitate gradually increased with the oxalate concentration, indicating that Sr was mainly incorporated with the initial Ca precipitation. The Sr yield reached 88% at an oxalate concentration of 54 mM.

In this study, oxalate precipitation using oxalic acid and NaOH, which is a recommended procedure in the literature (MEXT, 2003), was also examined. With this method, the Sr yield was 15% lower (73% at a 46 mM oxalate concentration, Fig. 2b) than that of ammonium oxalate. The addition of ammonium oxalate to raw seawater (pH = 7.6–8.2) could effectively precipitate Sr by incorporating it into Ca oxalate (Fig. 2a). Therefore, we decided on the addition of ammonium oxalate monohydride, the final concentration of which was 50 mM (7.5 g L^{-1}), to seawater so that the Sr yield was increased by up to 90%. The actual Sr recoveries for large-volume seawater samples were about 80%, because some of the Sr oxalate forming suspended fine particles was lost by decantation.

A very small amount Na and Mg was incorporated with Ca oxalate precipitates in the initial stage (less than 0.3%, Supplementary Fig. S1). The supernatant needed to be discarded within 20 hours to reduce the Mg precipitates.

Table 1. Comparison of analytical result and performance between new and conventional procedures

	Oxalate coprecipitation and DGA Resin chromatography (new)	Cation exchange chromatography and chromate coprecipitation (conventional)
Number of process		
Preconcentration		
precipitation	1	1
chromatography	0	1
filtration	2	1
ashing	1	0
evaporation	0	1
Purification and milking		
precipitation	2	5
chromatography	1	1
filtration	2	4
evaporation	0	2
Typical handling time	8 hrs	34 hrs
Sr yield	80.0 ± 1.5	94.6 ± 2.9
Y yield	91.9 ± 1.9	88.1 ± 9.8
⁹⁰ Sr concentration/Bq m ⁻³	0.81 ± 0.06	0.81 ± 0.07
N	5	5

Decay is corrected to sampling date (11, March 2015).

Comparison with the conventional method

The proposed method in this study is simpler than the conventional method in terms of chromatography, coprecipitation, and evaporation. Scavenging processes involving precipitation are necessary in the conventional method to eliminate interfering radionuclides; however, in the proposed method are replaced by chromatography using DGA Resin (Table 1).

The conventional method is time-consuming (34 hours); in particular, large-volume cation exchange column chromatography in the conventional method requires a long separation time (16 hours). The sample handling time for the proposed method is 8 hours, which does not include the waiting time for oxalate precipitation and secular equilibrium. This handling time is one-third of that in the conventional method. The oxalate precipitation method is simple to handle and exhibits high throughput as compared to large-volume column chromatography. By simply adding weighed ammonium oxalate monohydrate to seawater under natural pH conditions, it is possible to perform preconcentration for more than ten samples in a day, even on the ship. The Sr yield obtained using oxalate precipitation (80.0 ± 1.6%, $n = 5$) is about 15% lower than that of the conventional method (94.6 ± 2.6%, $n = 5$). However, the Sr yield can be improved with the addition of Ca because the precipitation of Sr with oxalate is mainly controlled by the presence of Ca. The addition of Ca (e.g., 100 mL of a 1 M CaCl₂ solution for

20 L of seawater, with a final Ca concentration of 5 mM) can facilitate coprecipitation of the remaining Sr with excess oxalate ions and coagulate the suspended fine Sr oxalate after the first precipitation by ammonium oxalate (Supplementary Fig. S2). Furthermore, this process effectively reduces the remaining ash after thermal decomposition.

Analyses of ⁹⁰Sr using this method were performed on five aliquots of surface water in the western subarctic North Pacific (Table 1). The arithmetic mean and standard deviation of the ⁹⁰Sr concentration from five replicate analyses were 0.81 ± 0.06 Bq m⁻³. The respective values are shown in the supplementary material (Supplementary Table S1). The decay constant for the detected beta particles was well consistent with that of ⁹⁰Y. This averaged value is in good agreement with that obtained in the conventional method (0.81 ± 0.07 Bq m⁻³). The proposed method using 20 L of seawater achieved a lower limit of detection of 0.2 Bq m⁻³, and it could be an alternative to conventional large-scale ion chromatography and precipitation using harmful fuming nitric acid.

CONCLUSION

To determine the background level of ⁹⁰Sr concentrations in seawater, the preconcentration method using ammonium oxalate was optimized by successive DGA Resin chromatography. By adding 150 g of ammonium

oxalate monohydrate, Sr could be precipitated without the need for pH adjustment. The analysis results for ^{90}Sr in open-ocean seawater were in good agreement with those obtained by the conventional method. We suggest here a simplified method of ^{90}Sr determination in seawater as an alternative to the conventional method.

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SUPPLEMENTARY MATERIALS

URL (<http://www.terrapub.co.jp/journals/GJ/archives/data/51/MS441.pdf>)
Figures S1 and S2
Table S1