

Regular Article

# Rapid Chemical Separation Protocol for Optimized $^{90}\text{Sr}$ Determination by ICP-MS in Water Samples for Radiological Incident

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Received 15 September 2021; revised 24 November 2021; accepted 6 December 2021

Research has been conducted to speed up and simplify the  $^{90}\text{Sr}$  analysis method in water samples based on the importance of  $^{90}\text{Sr}$  measurement for environmental monitoring in the event of a radiological incident. To optimize the measurement with ICP-MS, which enables rapid analysis, we examined the pre-treatment conditions when cation exchange resin chromatography and Sr Resin solid-phase extraction were used. Sr was quantitatively recovered by cation exchange resin from 1 L synthetic water samples, and anionic components such as Ge and Se were efficiently removed. In addition, under the elution condition using 3 M  $\text{HNO}_3$ , it is possible to suppress the elution of Zr with a small volume of eluent. The eluate from cation exchange chromatography can be used for successive solid-phase extraction of Sr-Resin directly, which provides further Sr purification and concentration sufficient for  $^{90}\text{Sr}$  determination by ICP-MS. Verification was performed on real samples including high hardness bottled water. We confirmed that the results of the synthetic sample analysis were reproduced, and that Sr was quantitatively recovered (96–100%) and coexisting elements were removed sufficiently so as not to interfere with the measurement of  $^{90}\text{Sr}$ .  $^{90}\text{Sr}$  was concentrated by a factor of 100 during chemical separation procedure without any evaporation step. Processing time for more than 10 samples was 3 hours, which is fast enough for emergency response in the case of radiological incident.

**Key words:**  $^{90}\text{Sr}$ , chemical separation, ICP-MS, water, radiological incident

## 1. Introduction

Radioactive strontium ( $^{90}\text{Sr}$ ) is one of the major fission products produced by thermal neutron fission of  $^{235}\text{U}$  and  $^{239}\text{Pu}$ . Its chemical similarity to Ca causes the radionuclide to accumulate in hard tissue of biota. In

addition,  $^{90}\text{Sr}$  can impact aquatic ecosystems via ground water and river water due to its high solubility in the water phase. Historically, radioactive contaminations of the Techa River in the South Urals of Russia<sup>1,3)</sup> and the Columbia River around the Hanford site in the USA<sup>4)</sup> have occurred. These facts have led researchers to recognize the importance of establishing rapid and routine radiological monitoring of  $^{90}\text{Sr}$  in water for detecting accidental releases to the environment and avoiding ingestion by the public. In the event of a nuclear emergency, the WHO Codex guideline levels specifies

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that the activity concentration might not be greater than 100 Bq/kg for  $^{90}\text{Sr}$  for infant food and 100 Bq/kg for  $^{90}\text{Sr}$  for food other than infant food.

The governments of some Asian and African countries are promoting nuclear power generation, meaning the number of power plants are likely to increase and therefore simple, rapid and efficient analytical methods for radionuclides are in high and increasing demand. Radionuclide release accidents can affect widespread areas and present issues of trans-border contamination for neighboring countries that cannot be ignored. To respond to emergency radiological incident, it is important to develop procedures that are compatible with the equipment that individual laboratories commonly have.

Inductively coupled plasma mass spectrometry (ICP-MS) is a promising analytical method to replace radiation measurements from the viewpoint of high sample throughput for long-lived radionuclides<sup>5-7</sup>. Progress in ICP-MS for  $^{90}\text{Sr}$  analysis has been notable since the 2011 severe accident at the Fukushima Daiichi Nuclear Power station<sup>8</sup>. ICP-MS equipped with collision reaction cell (CRC) technology can significantly remove spectral interference from  $^{90}\text{Zr}$ <sup>9-11</sup>. In addition, various options such as a desolvating introduction system and an automated separation system can be adopted to enhance analyte sensitivity and sample throughput, respectively. Takagai *et al.*<sup>12</sup> used ICP-MS combined with the automated separation system for  $^{90}\text{Sr}$  analysis of contaminated soil by the accident of the Fukushima Daiichi Nuclear station and showed it to be an indispensable analytical tool. However, instrumental limit of detection (LOD) of ICP-MS in our laboratory is 500 Bq/L, which is higher than the WHO Codex guideline levels. There is still a need to improve procedures for pre-concentration and chemical separation to optimize ICP-MS and to reduce the sample preparation time.

In the case of ICP-MS measurement,  $^{90}\text{Sr}^+$  can be affected by isobaric interfere from  $^{90}\text{Zr}^+$  and polyatomic interference from  $^{74}\text{Ge}^{16}\text{O}^+$  and  $^{74}\text{Se}^{16}\text{O}^+$ <sup>13</sup>. Attention should also be paid to the peak tailing effect from  $^{88}\text{Sr}^+$ . An abundant amount of stable Sr can suppress ICP-MS sensitivity<sup>14</sup>. CRC using oxygen gas is effective to lower  $^{90}\text{Zr}^+$  interference through the formation of  $^{90}\text{Zr}^{16}\text{O}^+$ , whilst the reaction of  $\text{O}_2$  with  $^{90}\text{Sr}^+$  does not proceed. Ohno *et al.* reported that  $^{90}\text{Zr}^+$  interfering ions in a test solution containing 1  $\mu\text{g/L}$  Zr were removed by the reaction using oxygen gas and they had a contribution of about 2 counts per second<sup>14</sup>.

High Sr content samples could lead to underestimation by suppressing sensitivity and overestimation of  $^{90}\text{Sr}$  due to the peak tailing effect. The degree of the significance for the peak tailing effect is evaluated using the interference signal at  $m/z = 90$  and  $^{90}\text{Sr}^+ / ^{88}\text{Sr}^+$  signal ratio. Abundance sensitivity for quadrupole ICP-MS and

sector field ICP-MS are on the orders of  $10^{-9-14}$  and  $10^{-7-10}$ , respectively. The stable Sr concentrations in river water and groundwater analyzed in this study are in the range of 1–100  $\mu\text{g/L}$ . One study has found that the concentrations of Sr varied from ~6 to 800  $\mu\text{g/L}$ , and averaged ~60  $\mu\text{g/L}$  in a river water system<sup>15</sup>, whereas another study has found that the global river average was 78  $\mu\text{g/L}$ <sup>16</sup>.

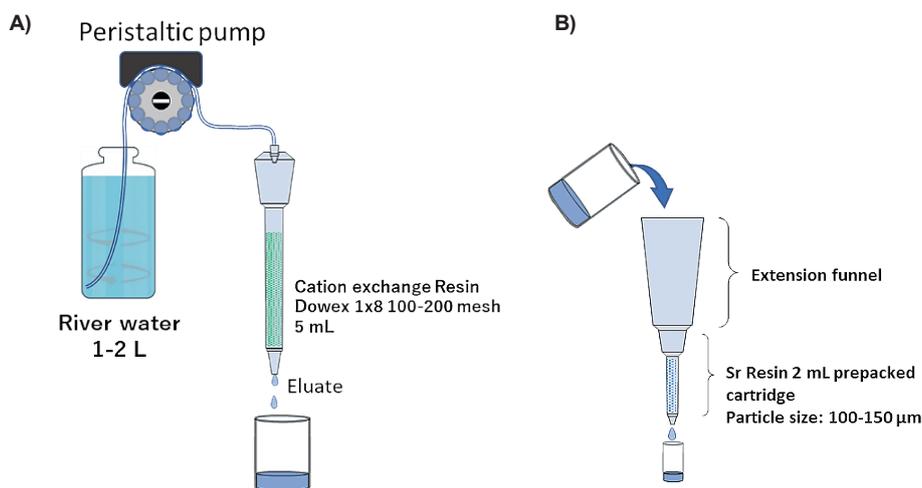
The Sr separation method has been well studied within the context of radiometric Sr detection through isolation from other beta emitting radionuclides. For radiogenic Sr isotope ratio analysis ( $^{86}\text{Sr}/^{87}\text{Sr}$ ) used for geological dating, the separation focus has been focused on the removal of major components including Ca, which is a homologous element, and the removal of Rb, which is an interfering element during isotope analysis. Chemical separation methods suitable for radiochemical measurements have been summarized by Vadja and Kim<sup>17</sup> and Shao *et al.*<sup>18</sup>. Several methods have been investigated, including precipitation<sup>19, 20</sup>, ion exchange<sup>19</sup> and solid phase extraction chromatography<sup>21-24</sup>. The application of extraction chelating Sr-resin (Triskem International) over the last decade has shown excellent Sr selective affinity. While radiometric measurements require attention to interference from other beta nuclides, mass spectrometry is different as it removes interference from stable isotopes such as  $^{90}\text{Zr}$ .

We investigated a rapid and simple analytical method for monitoring drinking water in radiological incidents. The method was optimized for rapid ICP-MS and therefore eliminated evaporation step, which is time-consuming and can introduce contamination. For this purpose, we developed a two-stage chemical separation method using cation exchange chromatography for preconcentration and Sr-resin extraction chromatography for further Sr purification. The method was designed so that the sample could be introduced directly into the column and the resulting Sr solution could be measured directly by ICP-MS.

## 2. Experimental

### 2.1 Materials and Chemicals

Ultra-pure water was obtained using a Milli-Q Reference system (Merck Millipore, USA). Laboratory materials, including bottles and tubing were soaked in 1 M HCl and then rinsed in the ultra-pure water. The ultra-pure water was also used to prepare all solutions. Nitric acid was commercially obtained electro-industry grade acid (Kanto Chemical, Japan). XSTC-622 multi-elemental standard solution (SPEX CertiPrep, USA) was used to obtain the column chromatograms for Na, Ca, Mg, Sr, among other elements. Atomic adsorption analysis grade Zr, Se and Ge standard solutions were also used.



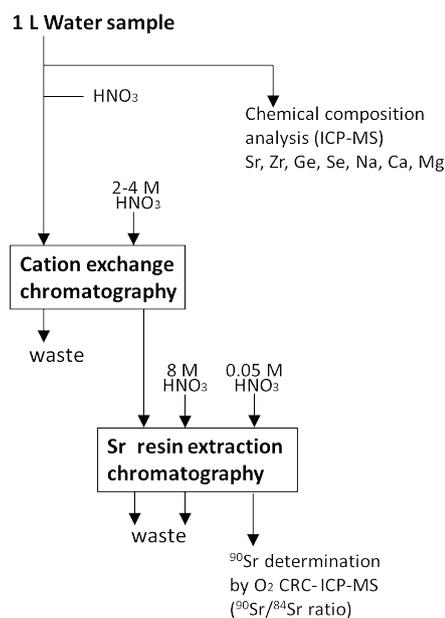
**Fig. 1.** Schematic illustration of chromatography processes. A) Cation exchange chromatography column is consisted of 5 mL of cation exchange resin, DOWEX1X8, and polypropylene empty column. Water sample is loaded to the column by peristaltic pump. B) Sr resin extraction chromatography column is prepacked 2 mL, connected to extension funnel to increase in loading volume up to 30 mL.

Cation exchange resin (5 mL, AG50W-X8, 100-200 mesh, Bio-Rad, USA) was filled into a polyethylene column (Muromac mini-column M) (Fig. 1A). The cation exchange column was cleaned by rinsing with 30 mL of 8 M HNO<sub>3</sub> and 30 mL of 0.05 M HNO<sub>3</sub>. Then, 20 mL of 4 M HNO<sub>3</sub> was added to the column prior to introducing sample solution.

Extraction chelating resin, 2 mL Sr Resin column (100-150 μm particle size, Part No. SR-C20-A), was purchased from Eichrom Technology (USA). Sr Resin is functionalized by 4,4(5′)-di-*t*-butylcyclohexano 18-crown-6 (crown ether) in 1-octanol, which specifically adsorb Sr<sup>2+</sup> ion in HNO<sub>3</sub> medium by recognizing the ionic radius. An extension funnel was connected to the Sr Resin column to increase in the sample reservoir volume to about 30 mL (Fig. 1B). Sr Resin column was rinsed with 10 mL of 0.05 M HNO<sub>3</sub> and 10 mL of 4 M HNO<sub>3</sub> prior to use.

To examine the separation procedure, synthetic standard samples were prepared from SPEX XSTC-622 multi-elemental standard solution (10 mg/L). All analyte elements were present in a 5 μg amount of a 1 L water sample. 2.5 μg of Sr, Na, Ca, Mg, and Rb from XSTC-622 multi-elemental standard solution and 100 μg of Zr were doped and adjusted to a volume of 30 mL in 3 M HNO<sub>3</sub> to the standard sample for cation exchange resin chromatography and Sr Resin chromatography.

Real water samples were used to validate developed method. The river water samples were collected in the Ukedo River of Fukushima Prefecture on 9<sup>th</sup> July 2019 and stored in plastic bottles after filtration with 0.45 μm pore membrane and acidification (pH < 2). The tap water sample was collected in Hirosaki City, Aomori, Japan.

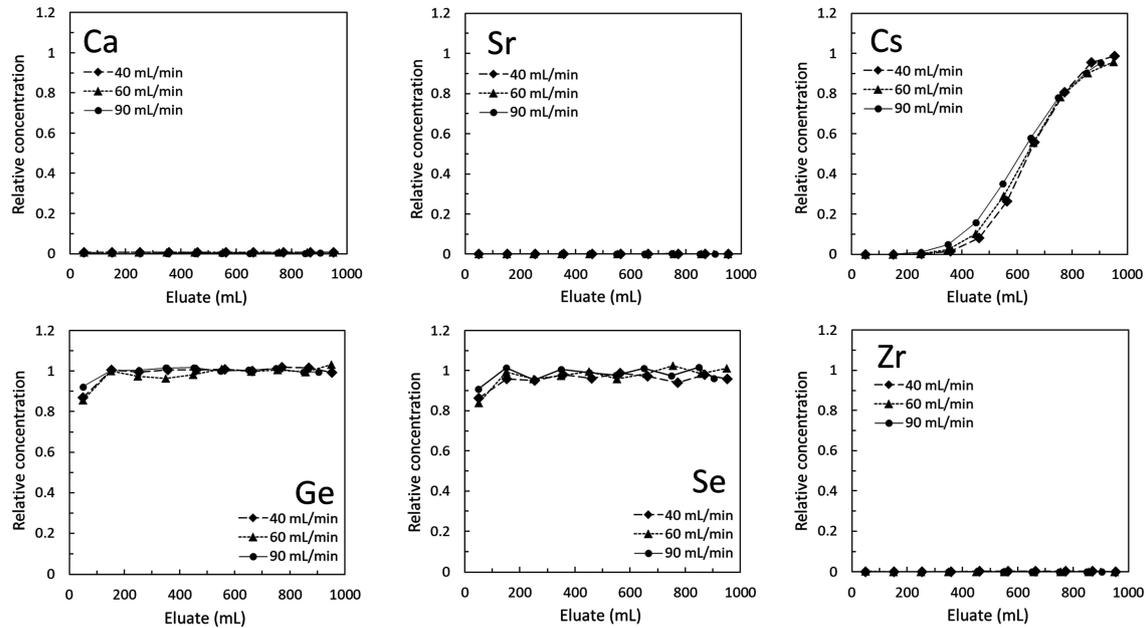


**Fig. 2.** Chemical procedure for <sup>90</sup>Sr in water sample by two-stage chromatography using cation exchange and Sr resins prior to ICP-MS determination.

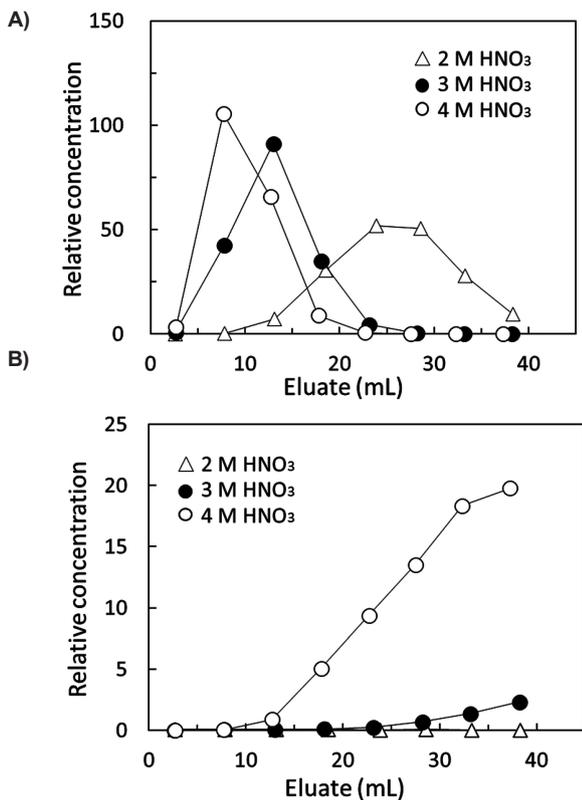
Two kinds of bottled water (BW) were purchased from the market and acidified.

## 2.2 Equipment

To analyze the effectiveness of chemical separation, concentrations of Sr and other elements were measured using a tandem quadrupole ICP-MS (Agilent 8800 ICP-QQQ, Agilent, USA) installed at Hirosaki University.



**Fig. 3.** Elution profile of Ca, Sr, Cs, Ge, Se, and Zr during sample loading step in cation exchange resin chromatography. Flow rates were 40, 60, and 90 mL/min.



**Fig. 4.** Elution profiles of A) Sr and B) Zr obtained using various concentration of HNO<sub>3</sub> in cation exchange resin chromatography.

### 2.3 Cation exchange chromatography

Figure 2 summarizes the two-stage chemical separation method we followed for <sup>90</sup>Sr in water sample by chromatography using cation exchange and Sr selective resins. Figure 1 offers schematic drawings of the columns and pump used in the chromatographic processes. Measured volume of concentrated HNO<sub>3</sub> was added to the 1 L water sample solution to make a solution concentration of 0.1 M HNO<sub>3</sub>. This was introduced into the cation exchange resin column using a peristaltic pump (Masterflex L/S Precision Pump). Flow rates were adjusted to 10, 20, 30, 40, 60, 90 mL/min; slowest flow required up to 100 minutes for this pre-concentration with the 1 L water sample. Retained cations including Sr<sup>2+</sup> were eluted by 2, 3 and 4 HNO<sub>3</sub> by gravity flow to optimize Sr elution and to minimize Zr concentration. Eluates were collected in 100 mL fractions during the sample loading step and 5 mL fractions during the elution step.

### 2.4 Sr Resin extraction chromatography

The eluted Sr fraction from cation exchange chromatography was directly introduced into the Sr Resin column because Sr is strongly associated at 2–4 M HNO<sub>3</sub> ( $k' > 40^{25}$ ). On the other hand, Zr is not adsorbed by Sr Resin. Kavasi *et al.*<sup>22)</sup> reported that decontamination factor for Zr was more than 10<sup>4</sup> with 87% Sr yield.

The flow rate tested ranged from 0.2 mL/min to 0.9 mL/min, which reflected sample volume remaining in column reservoir due to gravity flow. After the column was rinsed with 10 mL of 8 M HNO<sub>3</sub> to remove interfering elements, Sr was eluted by 0.05 M HNO<sub>3</sub>.

**Table 1.** Chemical yields, concentration factor (*CF*) for Sr and Decontamination factor (*DF*) for other elements during chemical separation processes

Element	Cation exchange resin chromatography			Sr Resin chromatography			Total			
	Chemical yield		<i>CF</i>	Chemical yield		<i>CF</i>	<i>DF</i>	Chemical yield		<i>CF</i>
	Sample load	Elution	<i>DF</i>	Sample load	Rinse			Elution	<i>DF</i>	
Sr	0.1%	97.6%	33	0.1%	0.2%	97.9%	2.9	95.6%	96	
Na	87.0%	13%	0.23	88%	10%	<0.1%	> 300	< 0.01%	>160	
Mg	5.4%	93%	0.03	85%	5.5%	0.4%	92	0.3%	3	
K	82.6%	17%	0.17	69%	27%	<2%	>17	< 0.4%	>3	
Ca	0.3%	100%	0.03	78%	20%	0.6%	55	0.6%	2	
Ge	99.1%	<3%	>1	94%	5%	0.07%	470	< 0.002%	>470	
Se	98.1%	<6%	>0.5	94%	5%	0.17%	200	< 0.01%	>100	
Rb	53.2%	44%	0.07	92%	8%	0.04%	770	0.02%	52	
Zr	0.2%	0.6%	5	73%	4%	0.04%	870	0.0002%	4100	
Cs	36.4%	60%	0.05	93%	5%	0.05%	680	0.03%	34	
Ba	0.6%	100%	0.03	14%	68%	19%	2	19%	0.05	

### 3. Results and discussion

#### 3.1 Cation exchange chromatography

Monovalent cations such as Cs<sup>+</sup>, and Rb<sup>+</sup> were not detected in the initial sample loading, while relative concentrations increased above the loaded volume of 300 mL (Fig. 3 and Supplementary Fig. S1). Relative concentrations for Ge, Se and W were close to 1, which indicated they did not associate with cation exchange resin due to presence of anionic species in 0.1 M HNO<sub>3</sub> medium. Sr and Zr elutions were not observed during the sample loading step, which indicated they were retained in the cation exchange column. Divalent cations (e.g., Ca<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>), and U showed similar profiles.

For the 90 mL/min flow rate as the sample loading condition, attention should be paid to the connection between the tubing and resin column; it can be released accidentally by the increased pressure. Therefore, we choose 60 mL/min flow rate for sample loading.

Sr yields in 40 mL of 2 M HNO<sub>3</sub> for elution were in the range of 94–97% (Fig. 4A). Additional elution was needed for quantitative collection. Sr elutions by 3 M and 4 M HNO<sub>3</sub> had similar profiles and these elutions were completed by 30 mL of eluate as could be seen from Figure. 4A. Sr yield increased to 97–98% and 98–99%, respectively, at the 3 M and 4 M HNO<sub>3</sub> concentration.

The relative concentration of Zr gradually increased with eluate volume in 3 M and 4 M HNO<sub>3</sub> elution conditions (Fig. 4B). The Zr residual rate was 0.6% by 30 mL of eluate for the 3 M HNO<sub>3</sub> condition (Table 1). The relative concentration of Zr for the 4 M HNO<sub>3</sub> condition was about 10 times larger than that in 3 M HNO<sub>3</sub> condition. The Zr chemical yield reached 10–15% by 30 mL of eluate. The distribution coefficient of Sr using a Sr Resin is more than 50 in 3 M HNO<sub>3</sub> <sup>25</sup>. 3 M HNO<sub>3</sub> was selected for Sr elution from the viewpoint of getting a low Zr residual rate of the initial amount and reducing

the sample volume of load solution for the subsequent Sr Resin extraction chromatography.

Effectiveness of removal for interference elements can be expressed by the decontamination factor. The decontamination factor (*DF*) of a coexisting element is given in Equation 1:

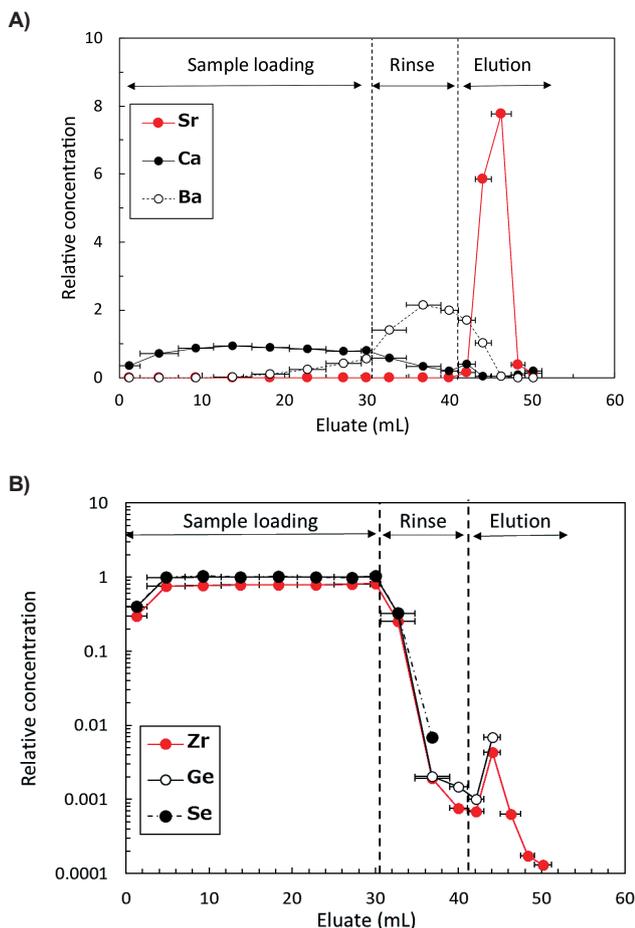
$$DF = \frac{C_o}{C_s} \quad \text{Equation 1}$$

where *C<sub>o</sub>* is the concentration in the sample before the separation and *C<sub>s</sub>* is the concentration in the sample after the separation. The chemical yield for Zr was 0.6 %, which corresponded to a *DF<sub>Zr</sub>* of 5. If Zr concentration in a water sample is low, the separated Sr fraction from the cation exchange resin can potentially be used for <sup>90</sup>Sr determination by ICP-MS. However, evaporation and dissolution processes are required to adjust the HNO<sub>3</sub> concentration for ICP-MS measurements. In addition, attention must be paid to contamination of interference elements from the laboratory environment during any evaporation process.

Despite the limited Zr decontamination, the sample volume could be reduced from 1 L to 30 mL through cation exchange chromatography, which corresponded to a concentration factor (*CF*) of 33 (Table 1). The decontamination factors of Zr (*DF<sub>Zr</sub>*), Ge (*DF<sub>Ge</sub>*), Se (*DF<sub>Se</sub>*) during cation exchange chromatography were 5, > 1, and > 0.5, respectively.

#### 3.2 Sr Resin extraction chromatography

The eluate from cation exchange resin chromatography could be introduced into the Sr Resin column directly. No elution of Sr during sample loading and rinse steps indicated that Sr was adsorbed on Sr Resin (Fig. 5A). Sr was then eluted in 0.05 M HNO<sub>3</sub>. The relative concentration of Sr rose to 8 at 6 mL of eluate. 10 mL of 0.05 M HNO<sub>3</sub> yielded 98% Sr recovery.



**Fig. 5.** Elution profiles of A) Sr, Ca and Ba and B) Zr, Ge, and Se in Sr Resin extraction chromatography.

Zr, Ge and Se flowed through the Sr Resin column due to their weak affinity to Sr Resin (Fig. 5B). The relative Zr concentration sharply decreased to 4 orders of magnitude lower than that of the loaded sample for the rinsing step by 8 M HNO<sub>3</sub>. In the early elution step, a small Zr peak and Ge and Se peaks were observed. But Zr chemical yield was only 0.04% in the Sr fraction. The *DF*s were 870 for Zr, 470 for Ge and 200 for Se.

The combined chemical separation of cation exchange resin and Sr Resin chromatography achieve *DF*<sub>Zr</sub> of 4100. CRC-ICP-MS operated in the oxygen reaction mode could provide Zr<sup>+</sup> removal efficiency 10<sup>4</sup> relative to the sensitivity for the no oxygen gas condition. If the Zr concentration can be reduced to 1 ppt by chemical separation, CRC-ICP-MS is enough to reduce interference at *m/z* = 90 less than 0.01 cps and avoid interfering with the <sup>90</sup>Sr determination. Under the oxygen reaction mode of ICP-MS, a sensitivity of 100 cps/ppt for Sr is obtained in this study. Instrumental LOD is 0.1 ppt (500 Bq/kg) with 10 sec of integration time. After the developed 2 stage chemical separation procedure with 97 times

preconcentration for <sup>90</sup>Sr, the method LOD is 5 Bq/kg, which is enough low relative to the WHO Codex guideline level (100 Bq/kg).

In 3 M HNO<sub>3</sub>, Ba was well retained in the resin. The reason for this is that Ba tends to have a relatively high *Kd* value in HNO<sub>3</sub> solutions, behavior similar to that of Sr. In 8 M HNO<sub>3</sub>, Ba was gradually eluted, although the residual rate of Ba was 19%, which corresponded *DF*<sub>Ba</sub> of 2. Pb has also a higher *Kd* than Sr in HNO<sub>3</sub> solutions<sup>23</sup>. Because Pb is retained in the column, it was efficiently removed (*DF*<sub>Pb</sub> > 10000). In mass spectrometry, <sup>140</sup>Ba and <sup>210</sup>Pb does not interfere with <sup>90</sup>Sr, but removal of such radioisotopes is important in radiochemical analysis as it is a naturally occurring beta emitter.

### 3.3 Application of the combined chromatography method to real water samples

The combination of cation exchange chromatography and Sr Resin chromatography can provide a 96-fold concentration factor for Sr and *DF*<sub>Zr</sub> of 4.1 × 10<sup>3</sup> according to experiment adopted to synthetic water samples. Processing times for cation exchange resin and Sr Resin chromatography were 60 min and 120 min, respectively. Sample throughput depends on laboratory equipment, especially peristaltic pump availability for cation exchange. We used a 4-channel peristaltic pump and we were able to process 4 batches in a day with a single Sr Resin processing and ICP-MS determination, which meant 16 samples could be analyzed per day.

Ometakova and Dulanska<sup>26</sup>) reported that 89% of Sr was recovered from a 50 mL water sample by carbonate coprecipitation followed by separation with Sr Resin, which lost 11% of Sr. Combined method among phosphate coprecipitation, TRU + Sr Resins, and ICP-MS/MS for urine sample showed approximately 10 h of the processing time (6.5 h for chemical separation and 3.5 h for ICP-MS/MS measurement)<sup>13</sup>. The developed method is more rapid and achieve quantitative Sr recovery. Maxwell *et al.*<sup>27</sup>) reported rapid analytical method using Sr Resin and vacuum box system and gas flow proportional counter. Rapidness of the procedure is comparable to that of developed method in this study. Radiation measurement provides total activity of radioactive Sr (<sup>89</sup>Sr + <sup>90</sup>Sr), and then, <sup>90</sup>Sr needs to be evaluated by <sup>90</sup>Y growth and separation. Combination of the analysis of <sup>90</sup>Sr by ICPMS and <sup>89</sup>Sr + <sup>90</sup>Sr by radiation measurement can provide both <sup>89</sup>Sr and <sup>90</sup>Sr results in radiological incident situation.

The method was applied to real water samples (Table 2): river water, tap water and two kinds of commercially marketed bottled water (BW). BW-1 was categorized as very hard water (318 mg/L as CaCO<sub>3</sub>) and BW-2 was soft water (36 mg/L as CaCO<sub>3</sub>). The concentration of major components and trace elements including Zr were determined by ICP-MS for the four sample types. Sr

**Table 2.** Chemical composition of real water samples

Element	River water	Tap water	BW-1	BW-2
Na /ppm	4.7	8.1	6.5	10.0
Mg /ppm	0.9	1.9	25.5	5.0
K /ppm	0.5	0.8	1.0	1.3
Ca /ppm	4.5	6.1	85.6	6.2
Sr /ppb	25	24	342	58
Ba /ppb	3	8	110	3
Ge /ppt	1	18	3	12
Se /ppt	43	102	203	52
Rb /ppt	484	1122	201	4780
Zr /ppt	0.7	<0.3	<0.3	3.5
Cs /ppt	2	62	1	320

**Table 3.** Chemical yield and concentration factor (*CF*) for Sr, and decontamination factor (*DF*) for major components and possible interference elements

	River water	Tap water	BW-1	BW-2
Yield	95.9% ± 2.3%	96.2% ± 2.5%	100.3% ± 1.2%	99.1% ± 2.9%
<i>CF</i>	95.9 ± 2.3	96.2 ± 2.5	100.3 ± 1.2	99.1 ± 2.9
<i>DF</i>				
Na	130 ± 48	290 ± 45	240 ± 72	220 ± 66
Mg	23 ± 12	45 ± 6	16 ± 5	24 ± 4
K	31 ± 19	87 ± 10	91 ± 27	81 ± 26
Ca	2.6 ± 0.2	3.7 ± 0.2	2.9 ± 0.3	1.5 ± 0.1
Ge	> 660	270 ± 240.0	> 480	> 810
Se	2,200 ± 1,100	1,500 ± 600	850 ± 311	4,900 ± 2,200
Rb	37 ± 14	101 ± 5	62 ± 25	76 ± 26
Zr	1,300 ± 325	2,850 ± 869	563 ± 138	650 ± 135
Cs	>25	160 ± 81	> 35	63 ± 25
Ba	0.070 ± 0.002	0.064 ± 0.003	0.081 ± 0.003	0.069 ± 0.003
Repetition ( <i>N</i> )	3	3	3	3

concentration ranged from 24 ppb to 342 ppb (Table 2). Zr, Se, and Ge concentrations were quite low for all samples. Standard solutions for these elements were added to all samples to determine the *DF* precisely. Concentrated HNO<sub>3</sub> was added to four types of samples to get 0.1 M HNO<sub>3</sub> and the two-stage chemical separation method was applied. The concentrations of Sr, and the major and interference components were determined by ICP-MS.

Sr chemical yield during cation exchange and Sr Resin chromatography ranged from 95.9% to 100.3%, which were consistent with our previously described experiment used synthetic standard water samples (Table 3). Our results also indicated that the major component causing water hardness (~300 mg/L as CaCO<sub>3</sub>) did not interfere with the Sr pre-concentration or recovery.

No difference was observed in the Ca chemical yield ranging from 93%-100% during cation exchange chromatography. The method provided sufficient adsorption for Ca, Sr and Ba. Ion-exchange capacity of AG 50W-8 cation exchange resin is 1.7 meq/mL. Ca content

in 1 L of BW-1 was equivalent to 45 % of the total capacity (190 mg-Ca) for the 5 mL cation exchange resin. Higher Ca concentrations and larger sample volumes might saturate the resin and reduce Sr recovery. Low *DF* for Ba (0.06-0.08) was attributed to their affinity to Sr Resin. As mentioned above, the level of Ca concentration for a separated sample was sufficiently low (< 30 ppm) for ICP-MS.

*DF* for Zr for the bottled water samples was approximately 600, which was slightly lower than those for synthetic standard water samples and other water samples. The major components in four types of water samples seemed to enhance the Zr elution during cation exchange chromatography, although Zr concentration in river water is generally low (< 5 ppt) to avoid interfering with <sup>90</sup>Sr analysis during ICP-MS determination. If a water sample contains 10 ppb Zr, our two-stage chemical separation method can reduce Zr concentration to 2 ppt (*DF*<sub>Zr</sub> = 500) and Zr interference with <sup>90</sup>Sr can be eliminated by using CRC-ICP-MS. *DF*s of Ge and Se were also consistent with synthetic standard water samples, and the

contents were reduced to negligible levels.

As a result, we confirmed that this method for determining  $^{90}\text{Sr}$  in water sample was also effective for actual hard water samples with up to 300 mg/L as  $\text{CaCO}_3$  of hard water.

#### 4. Conclusion

For  $^{90}\text{Sr}$ , which is an important target nuclide for environmental monitoring in the radiological incident, we conducted research on speeding up and simplifying the  $^{90}\text{Sr}$  analysis method using in monitoring water quality. To optimize the measurement with ICP-MS, we examined the sample pretreatment conditions using chemical separation by cation exchange resin and Sr Resin extraction chromatography.

1. Sr was quantitatively recovered by cation exchange resin chromatography from a 1 L synthetic water sample, and anionic components such as Ge and Se were efficiently removed. In addition, under the elution condition to 3 M  $\text{HNO}_3$ , it was possible to suppress the elution of Zr using a relatively small amount (30 mL) of eluent.
2. The eluate from cation exchange resin chromatography was used directly for subsequent solid-phase extraction by Sr Resin, which further purified Sr enough for  $^{90}\text{Sr}$  determination by ICP-MS.
3. Verification was performed on four types of actual samples that included a sample of high hardness bottled water. We confirmed that the results of the synthetic standard water samples could be reproduced, and that Sr was quantitatively recovered and interfering elements were sufficiently removed.
4.  $^{90}\text{Sr}$  can be concentrated by a factor of 100 during the chemical separation without any evaporation step. Processing time for 4 samples was 3 hours, which was sufficiently fast for planning responses to radiological incident.

#### Acknowledgement

This work was further supported by Environmental Radioactivity Research Network Center (E-21-09). In addition, this work was partially supported by a Grant-in-Aid for Scientific Research on Innovative Areas (Research in a proposed research area; #19H04245) from the Japan Society for the Promotion of Science.

#### Conflict of Interest Disclosure

The authors declare that they have no conflict of interest.

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