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Development of the rapid preconcentration method for determination of actinides in large volume seawater sample using Actinide resin

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Abstract: A simple and rapid preconcentration method of actinide from seawater using Actinide resin was developed and tested with the seawater spiked with a known U and Th. The developed method of Actinide resin based on column chromatography is less time-consuming and requires less labor compared with a typical co-precipitation technique for preconcentration of actinides. U and Th, which are relatively weak-bonded with Actinide resin among actinides, were used to determine the optimum flow rate of seawater sample and evaluate the capacity of Actinide resin to concentrate actinides from seawater. A flow rate of 50 mL min^{-1} was available with Actinide resin 2 mL (BV, bed volume). When 5 or 10 L of seawater containing U were loaded on Actinide resin (2 mL, BV) at 50 mL min^{-1}, the recovery of U was 93 % and 86 %, respectively. For extraction of actinides bound with Actinide resin, we compared three methods: solvent extraction, ashing-acid digestion, and ashing-microwave digestion. Ashing-microwave digestion method shows the best performance of which is the recovery of 100 % for U and 81 % for Th. For the preconcentration of actinides in 200 L of seawater, a typical co-precipitation method requires 2-3 days, but the developed method in this study is achieved the high recovery of actinides within 12 h.

Key words: actinide resin, actinides, concentration, seawater, ICP-MS, microwave digestion

1. Introduction

Radionuclides found in the environment are categorized into natural and artificial radionuclides. Artificial radionuclides were released into the environment due to the nuclear experiments in the 1940s to 1960s, in accidents at nuclear facilities such as the Chernobyl nuclear power plant and the Fukushima nuclear power plant, and through the operation of nuclear fuel reprocessing facilities.[1] The accident at the Fukushima nuclear power plant in Japan in 2011 resulted in the release of a substantial quantity of radioactive materials into the marine environment. These radioactive materials are moving on the sea current and causing radioactive contamination globally as well as around the accident site.[2] At

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present, the Japanese Government is discussing to marine discharge as a way of treating radioactive water caused by leaks from the damaged power plant.[3] Monitoring of the radioactive level in the marine environment is essential for the surveillance of national and international radiation accidents and for evaluating their impact on public health. A method that allows rapid radioactivity analysis should be developed for continuous monitoring of marine radioactivity and to facilitate immediate emergency response.

During the period between 1966 and 1991, the Russian Government dumped radioactive waste (liquid: 456 TBq, solid: 225 TBq) into the East Sea and the Sea of Okhotsk.[4] For this reason, radioactivity monitoring of the marine environment began in South Korea in 1994. The Korea Institute of Nuclear Safety is responsible for monitoring radioactivity in the marine environment in South Korea, according to the Nuclear Safety Act (Article 105, Monitoring of Nationwide Radioactive Environment). The levels of ^{137}Cs, ^{90}Sr, ^{3}H, $^{239+240}$Pu, and ^{240}Pu/^{239}Pu in marine organisms, sediments, and seawater, are evaluated twice a year.[4] The concentration of radioactive materials in seawater is extremely low; thus, the analysis requires 60 kg of seawater for the detection of ^{137}Cs and ^{90}Sr and 20 kg of seawater for Pu analysis. Notably, Pu analysis requires concentrating Pu from 20 kg seawater using several repetitions of iron co-precipitation, and the preparation for the measurement takes over two days. To analyze extremely low levels of Pu in seawater, 100-200 L of seawater is also used, and the concentration of Pu in seawater is determined using iron co-precipitation or MnO_2 co-precipitation.[5-7] According to recent studies, a higher rate of recovery can be achieved for the analysis of Pu in seawater by combining iron co-precipitation with CaF_2/LaF_3 precipitation than by repeating iron co-precipitation alone.[8,9] The pretreatment of actinides in seawater through the use of co-precipitation is the traditional and effective method, and has been applied in the field for monitoring marine environments. The pretreatment of a large volume of seawater, however, requires a long time (>24 h) with the disadvantage that several repetitions of the precipitation-dissolution process are necessary.

To analyze radionuclides in a large water sample, previous studies have employed pretreatment using extraction chromatography, which is more rapid and simpler than precipitation.[11-18] The studies introduced techniques such as analysis of gross alpha in water samples using Actinide resin,[13,14] ^{137}Cs in seawater using Cs-resin^{TM},[15] and ^{90}Sr in seawater using DGA resin.[16-18] The Actinide resin^{TM} is well known for binding strongly with actinides (Am(III), Pu(IV), U(VI), Th(IV), and Np(IV)).[10] According to previous studies, approximately 1 g of Actinide resin allows to pre-concentrate above 99 % of actinides in 3-5 L of water sample.[11,12] Batch or column-type chromatography can be applied, and the actinides can be pre-concentrated to Actinide resin by using a peristaltic pump at a flow rate of 16 mL min^{-1}.

Alpha spectrometry and inductively coupled-plasma mass spectrometry (ICP-MS) are frequently used in the analysis of alpha nuclides, where appropriate sample pretreatment and chemical separation are required to obtain accurate radioactivity data. However, alpha spectrometry require substantial counting-time for determination of an extremely low level environmental samples, while allowing the analysis of ^{238}Pu radioactivity, which is difficult to measure using ICP-MS due to the short half-life of the nuclide.[19] On the other hand, for long-lived alpha nuclides, ICP-MS is more advantageous for measuring the mass than activity. ICP-MS is considerably more useful than α-spectrometry for analyzing alpha nuclides that are present at extremely low levels in the environment, as the time taken for the analysis is markedly short and the detection limit is low so that the method allows the measurement of mass from μg kg^{-1} to pg kg^{-1}.[16,20,21] The number of studies analyzing the mass concentration of alpha nuclides using ICP-MS has continuously increased, with a recent notable impro- vement in the sensitivity, and this method is currently being used for environmental radioactivity monitoring.[4,8,9,22,23]

In this study, a pretreatment method based on pre-concentrating actinides in seawater using an Actinide resin and subsequent conversion to a medium suitable for chemical separation is investigated. In previous studies where the Actinide resin used for the pretreatment of actinides in seawater was decomposed by applying the alkaline fusion method followed by extraction of the target nuclide,[12] the method of alkaline fusion was found not to be appropriate. This study thus evaluates the efficiency of concentrating actinides in a large volume seawater using an Actinide resin based on the flow rate, and compares the following three methods for the extraction of actinides by binding with the Actinide resin: organic solvent extraction, ashing-acid digestion, and ashing-microwave digestion. The applicability of the Actinide resin is assessed using U and Th that bind relatively weakly compared to other actinides on the Actinide resin. In the case of Pu, Np, and Am that bind more strongly with the Actinide resin than U, the rate of recovery is expected to be higher than that of U.

2. Materials and Methods

2.1. Samples and reagents

The seawater sample (salinity 34-35 %) used in this study was collected from the East Sea (close to Busan) in Korea. The collected sample was acidified to pH 2 using concentrated HCl solution, and the suspended materials were removed using a 47 mm GF/F filter (0.7 μm pore size, Whatman).

All reagents were analytical grade and the used reagents were 30 % hydrogen peroxide solution, 2-propanol, sodium metavanadate, calcium nitrate tetra-hydrate (Sigma Aldrich, Germany), 65 % nitric acid, and 32 % hydrochloric acid (Merck Emsure® KGaA, Germany). The de-ionized water (18.2 MΩ·Cm) used in all experiments was from Cascada (PALL Life Sciences, USA), and the Actinide resin (50-100 μm, Eichrom Technologies Inc., USA) was purchased from Eichrom. The standard solution for the ICP-MS calibration curve was prepared by diluting the ^{238}U and ^{232}Th single-element standard solutions (MSU-10PPM, MSTH-10PPM, Inorganic ventures, USA) with 2 % HNO_3. Thirty types of multi-element standard solutions (Plasma Emission Standard (ICP), AccuStandard®, USA) were diluted with 2 % HNO_3 for analysis of the inorganic elements.

2.2. Apparatus

An automated nuclide separation device KXT-H (KAERI eXtraction Technique-Hybrid) was used to concentrate the actinides in seawater using the Actinide resin.[16] The applied flow rate was 1-50 mL min^{-1} with KXT-H, and it had 8 channels. For one sample, 8 columns filled with the resin could be used simultaneously. When treating 5 L of sample to each column; thus, the KXT-H allowed the treatment of 40 L at once.

The thermal decomposition characteristics of the Actinide resin were evaluated by thermogravimetric analysis (TGA, TA Instruments, USA). To compare the Actinide resin decomposition methods, an electric muffle furnace, a microwave digester (ETHOS EASY, Milestone, Italy), and fusion fluxer (K2 Prime, Kantanax™, Canada) were used. The crucible used

Table 1. Analytical conditions of ICP-MS and ICP-OES

	ICP-MS	ICP-OES
Parameter	Value	
Plasma power (W)	1550	1200
Plasma torch	Quartz	Quartz
Spray chamber	Quartz, cyclonic	Quartz, Scott
Nebulizer	PFA 400 μL min^{-1}	Teflon 1.5 mL min^{-1}, Burgner
Nebulizer gas flow (L min^{-1})	1.00	0.80
Coolant gas flow (L min^{-1})	14	13
Auxiliary gas flow (L min^{-1})	0.80	0.80
Uptake time (s)	60	30
Wash time (s)	60	30
Internal standard	^{187}Re	-

in the alkaline fusion was a Pt crucible (Pt 95 %-Au 5 %) with high resistance to alkaline molten flux and borate flux. $LiBO_2$ and LiBr (XRF Science Limited, Australia) were used as a fusion flux.

For the quantification of U and Th to evaluate the performance at each step of the pre-treatment, a quadrupole-type ICP-MS (iCAP-RQ, Thermo Fisher Scientific, Germany) was used. Component analyses of the Actinide resin and the inorganic salts in seawater were performed using ICP-OES (SPECTRO BLUE, SPECTRO, Germany). The analytical conditions used for the ICP-MS and ICP-OES analyses are presented in *Table* 1. ^{187}Re single-element standard solution (CGRE1-5, Inorganic ventures, USA) was used as the internal standard for the ICP-MS measurements; prior to use, the solution was diluted to 5 μg kg^{-1} for all samples.

2.3. Experimental procedures

This study is broadly divided into the determination of the optimum flow rate, development of the method to extract actinides from the Actinide resin, and evaluation of Actinide resin's capacity to treat the seawater sample (*Fig.* 1). Because the binding capacity between the Actinide resin and actinides is extremely high, the concentration process is relatively easy, while extraction of the concentrated nuclides is difficult.[10] In this study, to develop and optimize the method of extracting the concentrated actinides in Actinide resin, the following three methods were comparatively analyzed: organic solvent extraction, ashing-acid digestion, and ashing-microwave digestion. Under the same conditions (pH 1, HCl medium), the binding affinity between Actinide resin and actinides follows the order: Am(III) > Pu(IV) > Th(IV) > Np(IV) > U(VI).[10] U and Th that have comparatively low binding capacity for the Actinide resin were selected for evaluating the applicability of the Actinide resin.

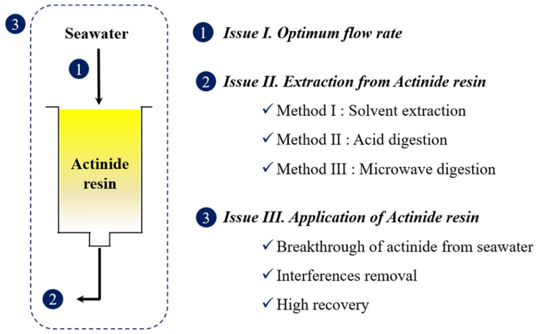

Fig. 1. Schematic diagram of experiment and main issues in this study.

2.3.1. Determination of the optimum flow rate

KXT-H was used to appear various flow rates. The 0.7 g of Actinide resin (2 mL, Bed Volume) was filled in 2 mL column. Samples that made of 1 L of de-ionized water containing 10 μg each of ^{238}U and ^{232}Th were passed through the Actinide resin at a flow rate of 5, 20, 35, and 50 mL min^{-1}. The concentration of ^{238}U and ^{232}Th in the solution through the Actinide resin was measured using ICP-MS to determine the optimum flow rate.

2.3.2. Comparative analysis of methods of extracting target nuclide from Actinide resin

A solution containing 1 μg each of ^{238}U and ^{232}Th was passed through Actinide resin (2 mL, BV) to prepare the sample for comparative analysis of the extraction methods. The extraction methods were evaluated by comparing the following methods: 1) organic solvent extraction using 2-propanol (Method I)[10,12,24]; 2) acid digestion after thermal decomposition of the resin (Method II); 3) microwave digestion (Method III).

In the organic solvent extraction method (Method I), the target nuclide was extracted from the Actinide resin by using 10 mL of 2-propanol solution. To prepare a suitable sample condition for chemical separation, 0.1 mL of 0.1 M $NaVO_3$ and 3 mL of 1.25 M $Ca(NO_3)_2$ were added to the extraction solution of 2-propanol, and followed by evaporation at 80 °C. A 1-2 mL aliquot of 30 % H_2O_2 was added to the evaporated solution, followed by evaporation at 150 °C; this process was repeated four times. To completely destroy the extraction solution and remove H_3PO_4, 20 mL of concentrated HNO_3 solution was used, followed by refluxing at 200 °C. After completely drying the remaining solution at 250 °C, it was diluted to a concentration of 2 % HNO_3.

For acid digestion (Method II) and microwave digestion (Method III), the Actinide resin with bound U and Th was placed into a Pyrex beaker, and ashing for thermal decomposition was carried out in an electric muffle furnace at 600 °C for 2 h (temperature rise: 1 h; temperature retention: 1 h). Here, Actinide resin was ashed without separation resin from column. To the ashed sample, 40 mL of aqua regia ($HCl:HNO_3 = 3:1$, v/v) was added, followed by 1 h reflux at 200 °C to decompose the residual materials. Afterwards, the solution was completely dried at 250 °C, then dissolved and diluted to the concentration of 2 % HNO_3.

For microwave digestion (Method III), the ashed sample was placed in a microwave vessel to which 10 mL of strong HNO_3 solution was added for decomposition of the sample. To compare the effects of the decomposition temperature, sample decomposition was carried out at 200 °C and at 220 °C. The temperature was then increased to the pre-determined level for 15 min, where the decomposition was carried out once again for 15 min at the temperature. When the microwave digestion was complete, the sample was cooled, then diluted to the concentration of 2 % HNO_3.

2.3.3. Evaluation of loading capacity of Actinide resin for seawater

To evaluate the volume of seawater sample that can be treated by the Actinide resin, 1, 3, 5, and 10 L of seawater was applied to 2 mL (BV) of Actinide resin. It is generally known that approximately 3-4 µg L^{-1} of ^{238}U is found in seawater.[8] ^{238}U was injected into the prepared seawater sample until a level 100-fold higher than the typical seawater level of ^{238}U (500 µg L^{-1}) was reached. The efficiency of the concentration process in different media was compared by injecting ^{238}U (500 µg L^{-1}) into equal amounts of seawater and de-ionized water. The prepared sample was passed through the Actinide resin at 50 mL min^{-1} using the KXT-H. Following complete decomposition of Actinide resin with the concentrated U through ashing-microwave digestion, the solution was diluted to the concentration of 2 % HNO_3.

The effect of the high-concentration inorganic salts in seawater on Actinide resin was examined. For this, 3-10 L of seawater was passed through 2 mL (BV) of Actinide resin and the resin was decomposed using the ashing-microwave digestion method. The Actinide resin digestion solution and the initial seawater sample were diluted, and the levels of inorganic elements (Na, K, Mg, Ca, and Sr) were measured using ICP-OES; the decontamination factor (DF) was then determined.

3. Results and Discussion

3.1. Determination of optimum flow rate for seawater treatment

In general, the sample flow rate for extraction chromatography influences the efficiency of the concentration of the target nuclide. As the flow rate will increase, the sample treatment time will decrease. Thus, a suitable flow rate should be selected, as a minimum reaction time is necessary for binding between the target nuclide and the resin. The efficiency of concentrating U and Th based on the sample flow rate for the treatment (5-50 mL min^{-1}), was evaluated. For 1 L of sample passing through the resin at 5-35 mL min^{-1}, the levels of injected U and Th were below the detection limit of ICP-MS and thus could not be measured. For the sample separated at 50 mL min^{-1}, the injected U and Th were passed through the Actinide resin about 0.1 % and 0.3 %, respectively. In comparison to a previous study[12] where a maximum flow rate of 16 mL min^{-1} was applied, the results of this study show that ≥ 99 % concentration was possible at 50 mL min^{-1} to reduce the seawater pre-treatment time.

3.2. Compositional analysis of Actinide resin and thermal decomposition properties

Croudace *et al.* (2006) used the alkaline fusion method to extract actinides concentrated by an Actinide resin.[12] The alkaline fusion method is a powerful pre-treatment technique for the complete dissolution of a solid sample. The applicability of this method to the Actinide resin was assessed herein, where 0.7 g of Actinide resin was placed into a Pt crucible with a $LiBO_2$ flux agent and LiBr

Fig. 2. Status of Pt crucible before (left)/after (right) $LiBO_2$ fusion of Actinide resin.

releasing agent for complete decomposition. The decomposed sample was diluted to the concentration of 2 % HNO_3, then the main components were analyzed using ICP-OES. The compositional analysis confirmed the presence of approximately 97 mg g^{-1} of P, mostly as a component of the DIPEX (*bis*(2-ethylhexyl)methane diphosphonic acid) functional group of the Actinide resin.[10] In using the fusion method, Pt would react with a high level of P, as well as C, another main component of the resin, at high temperature, both of which would cause serious damage to the crucible.[25] The inside of the Pt crucible used in this study for Actinide resin fusion was in fact severely damaged after the fusion process, where the damage was visible even to the naked eye, as shown in *Fig.* 2. The damage is presumed to be due to P and C. Thus, the fusion method, among the methods of Actinide resin extraction, is thought to be undesirable due to the significant drawback of damage to the expensive crucible and the complexity of the sample medium by injected $LiBO_2$ and LiBr, which outweigh the merit of complete sample decomposition.

In this study, thermal decomposition of the Actinide resin was evaluated using TGA. The changes in the weight of the Actinide resin with increasing temperature are shown in *Fig.* 3. The Actinide resin mostly comprises a scaffold composed of organic polymers, and contains the DIPEX functional group that binds with the actinides.[10] From *Fig.* 3, it is presumed that the two peaks that suddenly appeared around 500 °C correspond to decomposition of the organic polymer inert support and the functional group constituting most of the resin, whereas at 500-800 °C, the weight change was negligible and ~20 % of the initial sample weight remained in the form of ash. Most of the resin components were decomposed by simply providing heat above a certain level; thus, the ashing process used herein was carried out at the maximum temperature of 600 °C.

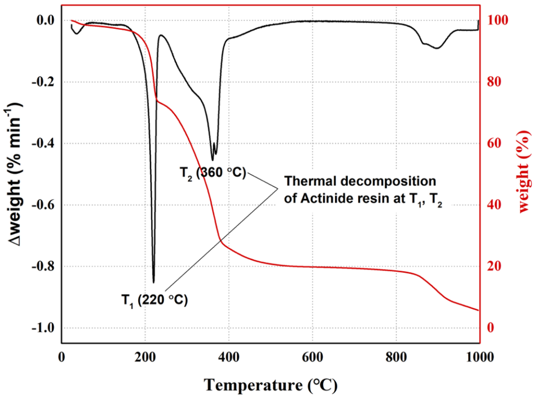

Fig. 3. Thermal properties of Actinide resin (4 °C min^{-1} in air).

3.3. Comparison of the extraction method

To extract the concentrated nuclide from the Actinide resin in a form suitable for chemical separation, this study compared the rate of recovery and the required time for the following methods: 1) organic solvent extraction, 2) ashing-acid digestion, and 3) ashing-microwave digestion. The results are presented in *Table* 2.

3.3.1. Method Ⅰ: Solvent extraction

The actinides concentrated through the Actinide resin can be extracted using 2-propanol. This extraction method leads to the simultaneous extraction of all nuclides rather than allowing selective extraction of individual nuclides.[10] The method can thus be used for gross alpha radioactivity measurement by mixing all extracted actinides with the scintillation liquid to utilize the liquid scintillation counter (LSC), while it is unsuitable for analyzing the levels of individual nuclides.[13,14] To analyze individual nuclides in the extraction solution, the complete decomposition of 2-propanol is crucial. Such decomposition of 2-propanol requires a process of repeated addition of concentrated HNO_3 and H_2O_2 to the sample solution

Table 2. Comparison of extraction method of actinide resin

Method		Recovery[1] (%)		Elapsed time (h)	No. of samples
		^{238}U	^{232}Th		
Method I. Solvent extraction		62.4 ± 8.7	62.0 ± 14.1	5	5
Method II. Acid digestion	220 °C	96.4 ± 2.2	70.2 ± 3.7	6	4
Method III. Microwave digestion	200 °C	90.6 ± 2.9	73.0 ± 14.1	3.5	10
	220 °C	101.6 ± 4.6	81.4 ± 3.8		7

[1]Average ± standard deviation

containing the $NaVO_3$ catalyst, with subsequent evaporation. The process, however, necessitates a considerable amount of time and effort.[10,12,24] As shown in *Table* 2, the process for decomposition of the 2-propanol extraction solution took ~5 h, and the rate of recovery of U and Th as identified through repeated experiments ($n = 5$) was 62.4 ± 8.7 % (mean ± standard deviation, SD, the same hereinafter) and 62.0 ± 14.1 %, respectively. The recovery level may be attributed to incomplete extraction of the actinides from the resin or to their loss during the decomposition of the 2-propanol process.

3.3.2. Method II: Ashing-acid digestion

Based on the TGA data for the Actinide resin, the column filled with the resin was ashed at 600 °C. The residue recovered after ashing was subjected to acid digestion using aqua regia. The time taken for the ashing-acid digestion was 6 h. From replicate experiments ($n = 4$), the rate of recovery of the extracted U and Th was determined to be 96.4 ± 2.2 % and 70.2 ± 3.7 %, respectively, indicating that the reproducibility of the analysis was ≤ 5 %. The mean rate of recovery was considerably high for U, whereas that for Th was relatively low. Even after the wet acid digestion process, residual materials were still visible on the sample. The low rate of recovery of Th is attributed to incomplete decomposition of the residual materials that are produced after the dry ashing, during the wet process of acid digestion. Th, in general, shows extremely low solubility due to its significantly strong ability to adhere to the surface of materials.[26] This is in agreement with the low rate of recovery for the extraction of Th compared to U, as reported in a previous study,[27] where U and Th were extracted from a source material or soil using the acid digestion method.

3.3.3. Method III: Ashing-microwave digestion

Microwave digestion was applied to ensure complete decomposition of the residue from ashing of the Actinide resin with concentrated actinides . The method allows high-temperature, high-pressure decomposition of the sample using a concentrated acid. The amount of sample is limited to 0.5 g or below, and it is difficult to apply the method if the sample contains an abundance of carbon compounds or volatile compounds.[23] However, because such compounds in the sample were removed through the primary thermal decomposition process, microwave digestion could be applied. In replicate experiments ($n = 10$) employing microwave digestion at 200 °C, the residue produced after the dry ashing process was incompletely decomposed in some cases, indicating a low level of reproducibility. The rate of recovery of U and Th was 90.6 ± 2.9 % and 73.0 ± 14.1 %, respectively, with ≤ 5 % reproducibility for the analysis of U; on the other hand, the reproducibility for Th through repeated experiments was approximately 14 %, indicating comparatively low reproducibility. With respect to the rate of recovery, the result was similar to that of ashing-acid digestion (Method II). It is seeemed to be due to incomplete decomposition of the reside from the incineration process.

The decomposition of the residue from the incineration process was not highly reproducible using microwave digestion at 200 °C; thus, the temperature was increased to 220 °C for the microwave digestion. The results of replicate experiments ($n = 7$) showed that all residual materials were decomposed after ashing, while the rate of recovery of U and Th was 101.6 ± 4.6 % and 81.4 ± 3.8 %, respectively, with ≤ 5 % reproducibility. Among the extraction methods, ashing-microwave digestion for 3.5 h was the most rapid process for extraction of the actinides, with high levels of both recovery and reproducibility; thus, this method was selected as the optimum extraction method from Actinide resin.

3.4. Application of Actinide resin to the concentration of actinides in seawater

The efficiency of concentrating the actinides based on the volume of de-ionized water and the seawater samples is shown in *Fig.* 4. Analysis of the concentration of U in 1-10 L of de-ionized water sample that was passed through 2 mL of the Actinide resin (BV) showed that the rate of recovery of U was 95.6-101.3 % in 1-5 L of sample. The rate decreased to 93.4 ± 4.8 % for 10 L of sample, but the recovery was still high. Analysis of the concentration of U in 10 L of seawater sample showed a relatively low level of recovery compared to that for de-ionized water. In the treatment of 1 L and 3 L seawater samples, the rate of recovery was 96.3 ± 5.6 % and 95.9 ± 4.2 %, respectively, while the rate of recovery gradually decreased to 92.9 ± 6.1 % and 86.3 ± 9.0 %, respectively, in moving from 5 to 10 L seawater samples. Notably, the increased amount of seawater sample to be treated in turn increased the SD through repeated experiments. The low levels of recovery and reproducibility are presumably attributed to the high concentration of salts in seawater, which interferes with the binding between U and the Actinide resin.

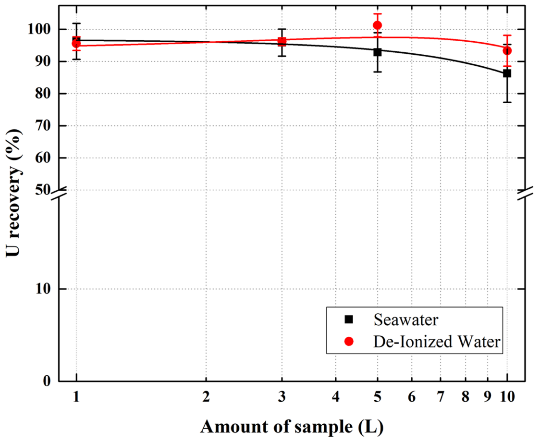

Fig. 4. Behavior fo U from seawater and de-ionized water on Actinide resin (2 mL BV) at 50 mL min^{-1} (U: 500 μg L^{-1}).

Most of the +1 or +2 oxidation state inorganic salts found in high concentration in seawater are known not to bind with the Actinide resin.[10] For the process of actinides separation using the Actinide resin, the efficiency of removing Na, K, Mg, Ca, and Sr (among the inorganic salts in seawater) was evaluated; the results are presented in *Table* 3. The decomposition factor (DF) for all target elements was ≥ 1,000, indicating ≥ 99.9 % removal efficiency through the use of the Actinide resin. For quantification of the actinides subsequent to concentration using the Actinide resin, a process of chemical separation is essential. The high concentration of salts in seawater interferes with the separation of the target nuclide during the process of chemical separation. The Actinide resin improves the recovery of actinides during the separation process by sufficiently removing the inorganic salts present in high concentrations in seawater.

Table 3. Decontamination factor for selected elements

Seawater (L)	Decontamination Factor				
	Na	K	Mg	Ca	Sr
3	15674	1590	7270	1276	5145
5	14554	1290	7532	1436	5921
10	13766	1267	7502	1614	5594
Mean ± SD	14665 ± 959	1382 ± 180	7435 ± 143	1442 ± 169	5553 ± 390

The analysis of alpha nuclides requires a purification process involving chemical separation after pre-treatment, although this process is outside the scope of this study. For alpha nuclides(U, Th, Am, Pu and Np), an ion exchange resin or TEVA® (Eicrhom), UTEVA® (Eicrhom), or TRU® (Eicrhom) resin may be used to carry out the chemical separation.[4,8,20,28] For sample purification through chemical separation using such resins, the sample is often prepared in HNO_3 medium. The ashing-microwave digestion method suggested in this study does not add any acid other than nitric acid; thus, the final sample is in a concentrated HNO_3 solution. Thus, the sample can be subjected to chemical separation without an additional post-treatment process. However, if alpha nuclides are extracted using a method involving the decomposition of the Actinide resin, the high concentration of H_3PO_4 present in the sample may interfere with the extraction chromatography used for chemical separation. In the case of U, the separation efficiency may fall as U binds with H_3PO_4 rather than with the separation resin, such as the UTEVA resin, and thus passes through the column.[19] However, by adding excess Al to fix H_3PO_4 as $AlPO_4$, the influence of H_3PO_4 on the chemical separation can be minimized.

The results of seawater pre-treatment using the Actinide resin suggest that the method would prove useful in the concentration of Pu, Am, and Np that show higher binding affinity than U. The proposed method for pre-treatment of actinides in a large volume of seawater sample is illustrated in *Fig.* 5. The seawater is acidified to pH 1, then passed through a 2 mL Actinide resin (BV) column at a flow rate of 50 mL min^{-1}. Depending on the amount of seawater to be analyzed, the amount of Actinide resin or the number of columns may be increased for more rapid pre-treatment. Using the KXT-H suggested in this study will allow a maximum of 8 columns, corresponding to a flow rate of 400 mL min^{-1}. The conventional method of co-precipitation used for the pre-treatment of actinides in seawater requires two days for the pre-treatment of 20 L seawater. By applying four Actinide resin columns (2 mL, BV) at

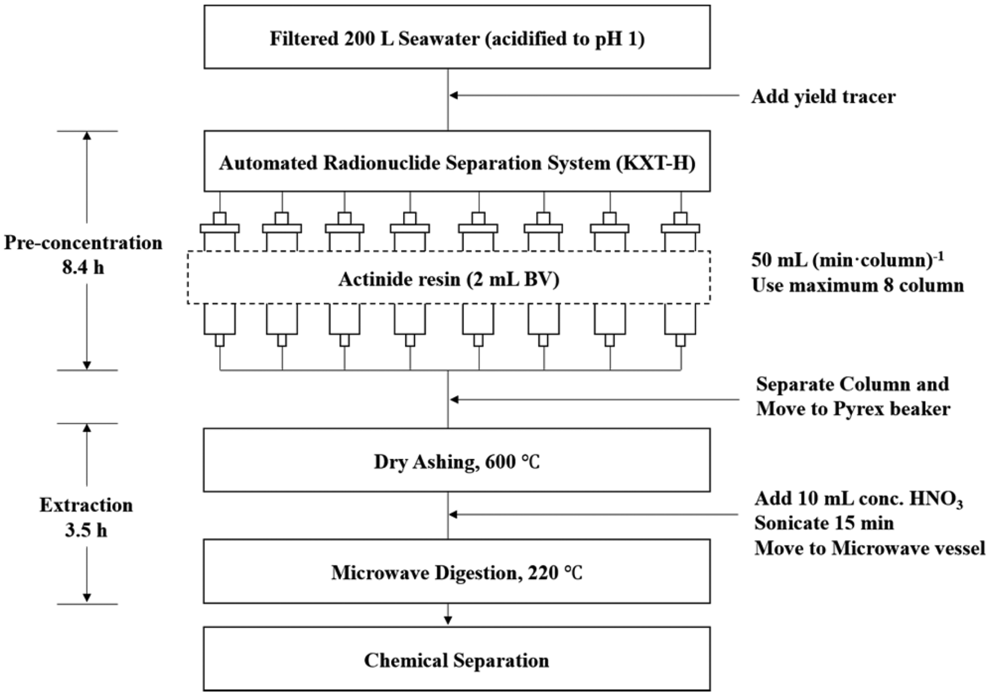

Fig. 5. Schematic diagram of pre-concentration of acitinide in 200 L seawater using Actinide resin and KXT-H.

50 mL min^{-1}, the pre-treatment of 20 L seawater will be complete within 6 h (1.7 h for concentration and 3.5 h for extraction using the resin). The co-precipitation method for the pre-treatment of 200 L seawater requires two or more days.[5] On the other hand, using the pre-treatment method and KXT-H suggested in this study, the 8 Actinide resin columns (2 mL, BV) will allow 8.4 h for concentration and 3.5 h for extraction using the resin. Therefore, by applying the pre-treatment method developed in this study, more rapid concentration of actinides in seawater is possible, compared to that achieved with the conventional co-precipitation method.

4. Conclusions

Determining the radioactivity level or the radionuclide isotopic ratio in the environment is crucial as the data may provide information regarding the nuclear safety or public health from accidents at nuclear facilities. However, the analysis of actinides present at extremely low levels in seawater is difficult due to the substantially large sample amount to be analyzed and the consequent need for a pre-treatment process, which prevents more immediate acquisition of the radiation information. Thus, pre-treatment method using an Actinide resin for more rapid analysis of actinides in seawater was evaluated herein.

The optimum flow rate and the maximum amount of seawater sample that can be treated with the Actinide resin were evaluated. Using 2 mL of Actinide resin (BV), the treatment of 5 L seawater at 50 mL min^{-1} led to 92.9 ± 6.1 % recovery of actinides. The ashing-microwave digestion method was developed for the extraction of actinides through the Actinide resin. After ashing of the Actinide resin column containing the concentrated actinides from seawater, microwave digestion allows complete decomposition. Compared to the conventional solvent extraction, ashing-microwave digestion is a more rapid method with excellent reproducibility that affords ≥ 80 % recovery of both U and Th with a SD within 5 %. Unlike other actinides (Pu, Am, and Np), U and Th bind weakly with the Actinide resin, and it is predicted that the rate of recovery for the pre-treatment of Pu, Am, and Np in seawater would be even higher.

While the conventional method requires two or more days for pre-treatment of the actinides in 200 L of seawater, the pre-treatment method developed in this study allows 12 h or less. The development of a rapid method for determination of radionuclides in the environment may improve the surveillance for unforeseen nuclear accidents, while enhancing the ability to monitor environmental radioactivity in abnormal situations. The pre-treatment of actinides in seawater, as developed in this study, is anticipated to initiate more rapid radiation analysis.

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