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Determination of ^{232}Th in seawater by ICP-MS after preconcentration and separation using a chelating resin

Hyoe Takata*, Jian Zheng, Keiko Tagami, Tatsuo Aono, Shigeo Uchida

Office of Biospheric Assessment for Waste Disposal, National Institute of Radiological Sciences, Anagawa 4-9-1, Inage-ku, Chiba 263-8555, Japan

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ABSTRACT

This article describes an analytical method for the separation, preconcentration and determination of ^{232}Th in seawater samples at sub-ng/L levels using a NOBIAS CHELATE PA1 resin and a sector field (SF) inductively coupled plasma mass spectrometer (ICP-MS). The resin showed excellent adsorption of ^{232}Th at a low pH of 2.4 ± 0.4 in a relatively small volume (200 mL) of seawater. ^{232}Th adsorbed on the resin was easily eluted using 5 mL of 0.8 M HNO_3. An enrichment factor of 40 was achieved for ^{232}Th analysis. Ethylenediamine–tetraacetic acid disodium salt dehydrate (EDTA) was used to investigate the effect of ^{232}Th-binding organic ligand on the retention of ^{232}Th on the chelating resin. Results obtained using acidified samples (pH of 2.4 ± 0.4) showed EDTA had no significant effect on ^{232}Th recovery, indicating that at this low pH, ^{232}Th was dissociated from the ^{232}Th-binding organic ligand and quantitatively retained on the NOBIAS CHELATE PA1 resin. The developed analytical method was characterized by a separation and preconcentration taking approximately 4 h and a low detection limit of 0.0038 ng/L for ^{232}Th, and was successfully applied to the determination of ^{232}Th in seawater samples collected from coastal areas, Japan.

1. Introduction

In marine systems, thorium (Th) has proven to be a very useful tracer of a wide range of oceanographic processes ranging from particle cycling and carbon export flux [1–6] to boundary scavenging [7,8]. Although a number of Th isotopes exist in seawater, Th consists almost entirely of primordial ^{232}Th ($t_{1/2} = 1.4 \times 10^{10}$ years), due to its extremely long half-life relative to the other Th isotopes. When chemical equilibrium is established, ^{232}Th can determine the chemical fate and speciation of all Th isotopes because they have the same chemical properties: Th has only one stable oxidation state, IV, under the oxidative condition in seawater, and Th (IV) ions are extremely reactive towards particles and organic matter. In addition, the radiogenic Th isotopes (^{234}Th, ^{230}Th, ^{228}Th) are produced *in situ* in seawater from their progenitors (^{238}U, ^{234}U and ^{228}Ra), but ^{232}Th is non-radiogenic and enters the seawater primarily as lithogenous materials, so the fate and the distribution of Th delivered to the seawater by fluvial and aeolian pathways can be understood.

Since ^{232}Th introduced into seawater is rapidly adsorbed on settling particles and removed to sediment, concentrations of ^{232}Th in seawater are so low (sub-ng/L levels) that its determination becomes a great challenge. The most sensitive techniques for the determination of ^{232}Th are α-counting, thermal ionization (TI) mass spectrometry (MS), secondary ion (SI)-MS, and inductively coupled plasma (ICP)-MS, but preconcentration and separation are often unavoidable. The high concentrations of Mg^{2+}, Ca^{2+}, Na^+, and K^+ in seawater ([Mg] = 1200 mg/L, [Ca] = 400 mg/L, [Na] = 10,000 mg/L, [K] = 400 mg/L) can cause a variety of problems and make direct analysis of ^{232}Th in seawater difficult, if not impossible, by TIMS, SI-MS and ICP-MS. The high salt concentrations in samples can lead to instable instrument performance due to clogging of the nebulizer, injector, and/or cones. Determination of ^{232}Th in a matrix of major ions that are present at concentrations 10^{11}–10^{12} times greater is a difficult analytical task. In order to increase sensitivity of the overall method, a pre-analysis step that entails both the separation of ^{232}Th from the seawater matrix and the concentration of the analyte is generally necessary.

Conventional separation and preconcentration techniques include a sequence of co-precipitation of ^{232}Th with $Fe(OH)_3$ and anion-exchange procedures, or anion–cation exchange and solvent extraction following the adsorption on MnO_2 coated filters [9–13]. These procedures are tedious and time consuming; they take a few days. For the preconcentration step, a sample that is acidified and stored at a low pH will have to be neutralized before it can be run through the MnO_2 coated filters or co-precipitated with $Fe(OH)_3$. During these tedious operations, there is a possibility for ^{232}Th to be adsorbed onto container surfaces and it

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* Corresponding author. Tel.: +81 43 206 4605; fax: +81 43 206 4601.
E-mail address: takata@nirs.go.jp (H. Takata).

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would not be recovered. In addition, these methods require a large seawater sample volume ($\geq$1 L) in order to minimize blank contribution to ^{232}Th from the adsorbents, ion-exchange resins, reagents, and all handling and procedural contaminations. Grinberg et al. [14,15] developed a method involving co-precipitation of ^{232}Th with $Ca_3(PO_4)_2$ and ICP-MS detection. Their method uses a relatively small volume of sample solution (50 mL), but precision for ^{232}Th determination in reference nearshore seawater material (CASS-4, National Research Council Canada) is greater than 20% at sub-ng/L levels.

Chelating resins (i.e. Chelex-100 resin, Bio-Rad Laboratories Tokyo, Japan; NOBIAS CHELATE resin PA1, Hitachi High-Tech., Hitachinaka, Japan) have been applied to the separation and preconcentration of a variety of trace elements from seawater samples before determination by ICP-MS [16–18]. Zhu et al. [16] reported a study using the Chelex-100 resin with a good recovery of 83% for ^{232}Th from spiked seawater; however, two steps as a preconcentration procedure are required. In addition, during the preconcentration procedure, a change in temperature and pH adjustment for the sample solution after the first preconcentration (pH 6.0, 55 °C) are necessary for the second preconcentration (pH 4.0, 20 °C). Since the NOBIAS CHELATE PA1 resin has two functional groups, ethylenediaminetriacetic and iminodiacetic acids, that are immobilized on a porous hydrophilic methacrylate polymer, the resin has excellent affinity for trace elements [17]. For the preconcentration, only one step is necessary which uses NH_4OH, CH_3COOH, HNO_3 and/or HCl as reagents, and the recovery is quantitative for many trace elements. The binding of trace elements to NOBIAS CHELATE PA1 resin is pH-dependent and previous studies using this resin have shown high recoveries of several trace elements from weakly acidified seawater samples (pH < 6) [17,18]. This resin can also effectively remove major elements, such as alkali and alkaline earth elements, under acidic and neutral conditions [17–19]. The total blanks contributed < 7% to the concentrations of most trace elements in seawater samples [17]. Sohrin et al. [17] used NOBIAS CHELATE PA1 resin to demonstrate that ^{232}Th was quantitatively recovered in a pH range of 1.5–9. In their detailed characterizations of the resin, they determined the pH dependency of ^{232}Th by using de-ionized water. At ambient pH in seawater with high ionic strength (i.e. 0.7 N), however, ^{232}Th can also exist as colloids of oxyhydroxides, carbonates, or organic matter in nature. In addition, the natural seawater matrix is not organic matter free. Naturally occurring organic ligands and micro-organisms [20,21], which have binding sites, have conditional stability constants around $10^{6.7}$ M^{-1} [20]. Furthermore, the total concentration of organic ligands range from 2 to 3 nM in surface waters [20]; therefore, sample acidification can also be used to release Th from complexes and to keep the element stabilized as labile inorganic forms. If an acidified sample is neutralized or adjusted to pH of 5–6 [17] prior to passing it through the NOBIAS CHELATE PA1 resin, Th can complex with natural organic ligands or form colloids of oxyhydroxides or carbonates, again and exist as kinetically inert complexes or colloids. In this way, adsorption of the analyte by the chelate resins can be inhibited.

This paper studies the determination of ^{232}Th in seawater using the NOBIAS CHELATE PA1 resin for the preconcentration and separation of ^{232}Th from natural seawater samples at an appropriate sample pH. We report the importance of sample pH on recovery of ^{232}Th from seawater and the effect of ^{232}Th-binding organic ligands on the resin, sample volume, and optimized volume of eluent. Recovery experiments were done using filtered (<0.2 μm) seawater samples collected from a Japanese coastal area by adding a yield tracer of ^{229}Th. We demonstrate that this resin can be utilized for preconcentration prior to detection by ICP-MS for the determination of low concentrations of ^{232}Th in seawater.

2. Experimental

2.1. Materials and chemicals

All laboratory materials, including bottles and pipette tips were cleaned in 1 M HNO_3 (analytical grade) and in de-ionized water (18 MΩ cm^{-1}) from a Milli-Q water (MQW) purification system (Millipore Corporation, Tokyo, Japan). All solutions were prepared with MQW. Super-pure grade HNO_3, NH_4OH, and CH_3COOH (Tama Chemicals Co., Tokyo, Japan) were used to prepare buffers, rinse solutions, eluent, and sample solutions. The HNO_3 was diluted with MQW to make up 0.8 M HNO_3 eluent. In addition, although no seawater reference material with a certified value of ^{232}Th is available, a certified reference material for other trace metals (e.g., heavy metals) in nearshore seawater, CASS-4, was obtained from the National Research Council, Canada.

To evaluate the ability of the NOBIAS CHELATE PA1 resin to extract ^{232}Th from the water sample at different pH values from 1.5 to 6.0, we used buffer and rinse solutions with various pH values. To prepare water samples in a pH range of 4.0–6.0, an ammonium/acetate buffer solution (2.5 M) was prepared by diluting NH_4OH and CH_3COOH in 100 mL of MQW. The pH was adjusted to pH 4.0, 5.0 and 6.0 with ammonium/acetate buffer solution, NH_4OH or HCl. A pH 4.0, 5.0 and 6.0 rinse solution was prepared by a 10-fold dilution of the above buffer solutions. For water samples in a pH range of 1.5–3.0, the pH was adjusted with HCl or NH_4OH. Rinse solutions in a pH range of 1.5–3.0 were prepared by adding HCl into MQW. All handling of samples was done in a clean booth, although the actual measurements by a ICP-MS were performed in a regular laboratory environment. Standard solutions were prepared by adding ^{229}Th, which served as the yield tracer, or an ICP calibration standard solution containing ^{232}Th and heavy metals, XSTC-355 (SpexCertiPrep Inc., Metuchen, NJ, USA) into 0.8 M HNO_3.

For the investigation of ^{232}Th recovery from natural seawater, coastal seawater with salinity of 33 was collected from the Pacific Ocean off the city Hitachinaka, Ibaraki Prefecture, Japan and filtered (<0.2 μm). The established analytical method was applied to filtered seawater samples collected from other Japanese coastal areas. The filtered seawater sample was immediately acidified with 10 M HCl to pH < 1.5 and left to stand for longer than a few months before analysis. After that, acidified filtered seawater sample was spiked with a ^{229}Th yield tracer. The amount of ^{229}Th spike was chosen to give ^{229}Th/^{232}Th ratios close to 1.

2.2. Instrumentation

To determine Th isotopes in 0.8 M HNO_3 elution, a sector field (SF)-ICP-MS (Element 2, Thermo Fisher Scientific Inc., Tokyo, Japan) was used in the low resolution mode in order to utilize the maximum instrument sensitivity. An APEX-Q high-efficiency sample introduction system (Elemental Scientific Inc., Omaha, NE, USA) with membrane desolvation unit (ACM) and a conical concentric nebulizer were used as sample introduction systems. Additionally, the normal skimmer cone was replaced by a high-efficiency cone (X-cone, Thermo Fisher Scientific Inc., Tokyo, Japan) to further increase SF-ICP-MS sensitivity. All the measurements were made in the self-aspirating mode to reduce the risk of contamination by the peristaltic pump tubing. The SF-ICP-MS was optimized daily using 0.1 ng/mL U standard solution with respect to maximum uranium sensitivity and low UO^+/U^+ and UH^+/U^+ ratios. For our APEX-Q/SF-ICP-MS system, the sensitivity was approximately 1.0×10^7 cps for 1 ng/g ^{238}U, and UO^+/U^+ and UH^+/U^+ ratios were less than 3% and 2×10^{-5} [22], respectively. Optimized instrument conditions for the determination of Th isotopes are listed in Table 1. Concentrations

Table 1
Optimized instrument and data acquisition parameters.

Instrument settings	
Forward power	1300 W
Nebulizer	Conical concentric
Sample cone	Nickel, 1.1 mm orifice diameter
Skimmer cone	Nickel, X-cone
Cooling gas	16 L/min
Auxiliary gas	0.8 mL/min
Sample gas	0.97–0.99 L/min
Data acquisition	
Low resolution	$m/\Delta m = 300$
Acquisition mode	E-Scan
Monitored isotopes	^{229}Th, ^{232}Th
Runs × passes	10 × 5
Mass windows (%)	10
Samples per peak	100
Integration type	Average
Total time of analysis	1 min
APEX-Q system	
Sample uptake rate	0.2 mL/min
Spray chamber temperature	140 °C
Condenser temperature	2 °C
Sweep gas (Ar)	3 L/min
Additional gas	0.11–0.13 L/min
N_2 gas	ca. 10 mL/min

of ^{232}Th were calculated from the results of isotopic ratios relative to the ^{229}Th spike according to the isotope dilution method.

2.3. Preconcentration and separation procedure

The protocol for preconcentration and separation of ^{232}Th is shown in Fig. 1. All handling of samples was done in a clean booth, although the actual measurements by the ICP-MS were performed in a regular laboratory environment. The NOBIAS CHELATE PA1 resin, which was packed in a polypropylene syringe, was preconditioned prior to preconcentration and separation step. The resin columns were mounted in a column stand (Muromachi Technos Co. Ltd., Tokyo, Japan) and then washed with 5 mL of 95% ethanol solution (Kanto Chemicals Co. Ltd., Tokyo, Japan). To remove any metals, decrease the blank level and improve the limit of detection (LOD), the resin columns were washed with 20 mL of 3 M HNO_3 and then with 30 mL of MQW. This washing process was repeated three times. The resin column was treated with 5 mL of rinse solution at a gravity flow rate (1 mL/min). The capacity of the resin was determined to be 0.16 ± 0.01 mmol/g using Cu^{2+} [17].

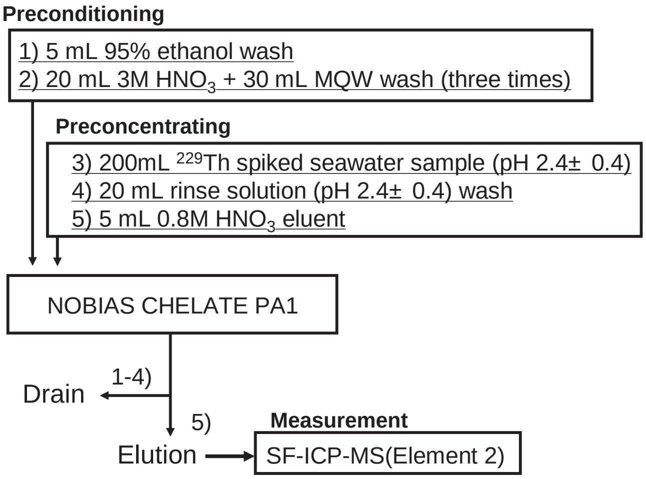

Fig. 1. Analytical procedure for the determination of ^{232}Th in seawater samples by SF-ICP-MS.

During the preconcentration step, two resin columns were mounted in tandem in the stand. Acidified filtered seawater samples were spiked with a ^{229}Th yield tracer. The amount of ^{229}Th spike was chosen to give ^{229}Th/^{232}Th ratios close to 1. After spike-equilibration for a few days, the pH of each aliquot of sample was adjusted with NH_4OH to a pH of 2.4 ± 0.4. The pH of a 200 mL aliquot of acidified filtered seawater sample was adjusted with NH_4OH to a pH of 2.4 ± 0.4. Immediately after the pH adjustment, the sample solution was passed through the conditioned resin columns, and then 10 mL of the rinse solution with the same pH as that of seawater samples was passed though the columns. ^{229}Th and ^{232}Th adsorbed on the column were removed from the resin with 5 mL of 0.8 M HNO_3 and collected in a 6-mL high density polyethylene vial. The concentrations of ^{229}Th and ^{232}Th were determined with the APEX-Q/SF-ICP-MS.

3. Results and discussion

3.1. Optimum pH for Th uptake

To investigate the effect of sample pH on the adsorption of Th on the resin, the pH was adjusted using a buffer solution, HCl, or NH_4OH to yield a sample pH range of 1.5–6.0 prior to loading onto the resin. In addition, to accurately define where the recovery of Th decreases with lower and higher pH values, we carried out a series of experiments on a smaller range of pH values (1.5–3.0). After the columns were conditioned using a rinse solution with the same pH as the sample solution, 200 mL of the sample solution was passed through the columns at a gravity flow rate (1 mL/min) to avoid the loss of efficiency on the recovery. Then, the rinse solution was passed through them to remove any remaining sample solution including alkaline earth metals on the column walls. The concentrations of ^{229}Th and ^{232}Th in the effluent were determined by SF-ICP-MS.

The recovery of ^{229}Th from NOBIAS CHELATE PA1 resin as a function of pH for seawater samples is shown in Fig. 2A. The yield tracer, ^{229}Th, was quantitatively recovered at pH values of 2.0–2.8. The signal intensities of ^{232}Th in sample solutions plotted against sample pH showed a similar variation to that of the ^{229}Th recovery (Fig. 2B). In this study, we quantified the ^{232}Th in seawater samples according to the isotope dilution method by measuring ^{229}Th/^{232}Th isotope ratio. We added ^{229}Th to seawater samples to a concentration of 0.1 ng/L. The isotope ratio showed a similar value along the pH gradient (mean ^{229}Th/^{232}Th isotope ratio: 0.72 ± 0.09). Thus, ^{229}Th works well for isotope dilution analysis, suggesting that ^{232}Th is quantitatively recovered at sample pH values from 2.0 to 2.8.

3.2. Effect of organic ligands on adsorption of Th on NOBIAS CHELATE PA1 resin

The signal intensities of ^{232}Th decreased (Fig. 2B) for the water samples at a pH of $\geq$3. Th-binding organic ligands could inhibit Th adsorption on the resin. The effect of organic ligands on the preconcentration of ^{232}Th with NOBIAS CHELATE PA1 resin was studied using ethylenediamine–tetraacetic acid disodium salt dehydrate (EDTA) which has an affinity to Th (a conditional stability constant of $10^{23.2}$ M^{-1} at an ionic strength of 0.1 N [23]). The working solution of EDTA (16 mM) was prepared with MQW. Sample solutions were prepared by adding ^{232}Th to HCl–acidified MQW at a pH of <1.5 to get a concentration of 100 ng/L. After EDTA was added to the sample solutions to get a concentration range of 16–16,000 nM, the sample solutions, adjusted to a pH of 2.4 ± 0.4, were stored for > 6 h in a dark place at room temperature. This period was sufficiently long enough to allow evaluation of the effect of organic ligands on the adsorption of ^{232}Th by the resin during the preconcentration

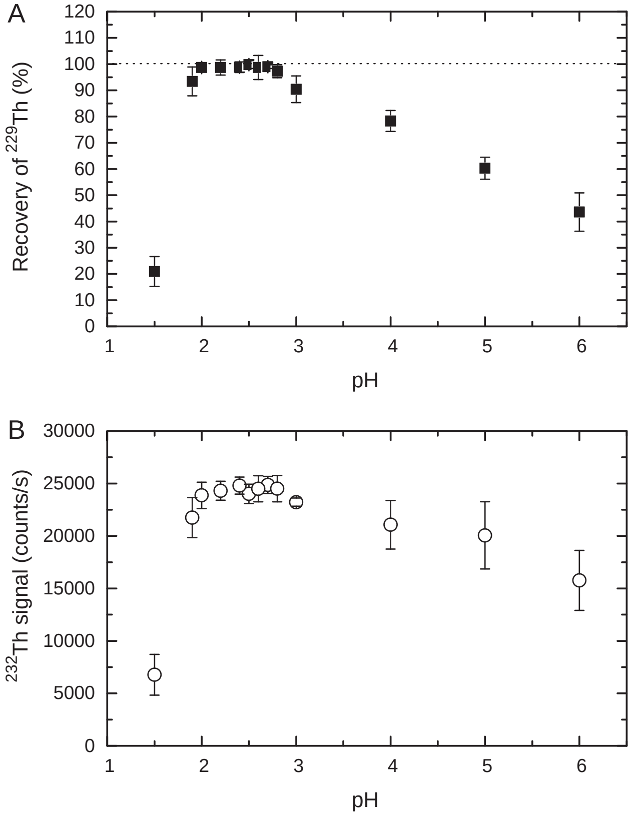

Fig. 2. Relationship between pH and (A) recovery of ^{229}Th in seawater and (B) ^{232}Th signal intensities when using NOBIAS CHELATE PA1 resin columns. Error bars indicate the standard deviation of three replicate samples.

procedure (approximately 4 h). These samples were analyzed by quadrupol ICP-MS (Agilent 7500c, Yokogawa Analytical Systems, Inc., Japan) following preconcentration with NOBIAS CHELATE PA1 resin.

Fig. 3 shows the effect of organic ligands on the recovery of ^{232}Th in the EDTA spiked solutions. Even though a large excess of EDTA was present (40–40,000 times more than that of ^{232}Th) with a relatively high stability constant of $10^{23.2}$ M^{-1} [23] compared to that of $10^{6.7}$ M^{-1} for naturally occurring organic ligands in seawater [20], at a pH of 2.4 ± 0.4 EDTA had no significant effect on ^{232}Th recovery. This result indicates that ^{232}Th is dissociated from its organic complexes and retained on the resin. In this study, recovery experiments were made for seawater samples with dissolved organic carbon concentrations of approximately 100 μM (data not shown) by adding ^{229}Th tracer to a concentration of 0.1 ng/L. This value is similar to that of naturally occurring ^{232}Th in ocean waters [13,24,25]. In addition, it has been reported that the concentrations of naturally occurring organic ligands are 2–3 nM [20], suggesting that these ligands are present in excess of ambient Th concentrations in seawater. As shown in Fig. 2A, however, at a pH of 2.4 ± 0.4 organic complexes of Th as well as colloids of oxyhydroxides can be disassociated, and quantitative recovery of ^{232}Th can be obtained under this low pH condition.

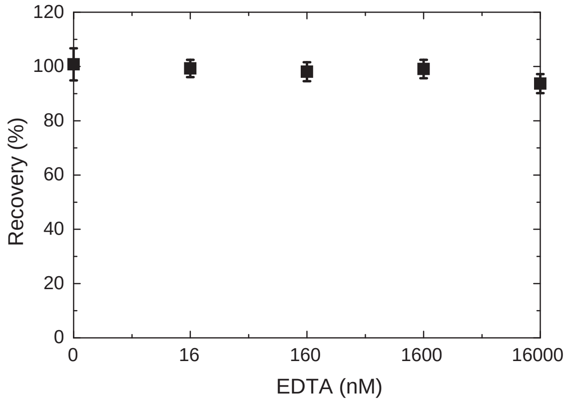

Fig. 3. Effect of organic ligands on the preconcentration of ^{232}Th in seawater when using NOBIAS CHELATE PA1 resin columns for 100 ng/L ^{232}Th. Error bars indicate the standard deviation of three replicate samples.

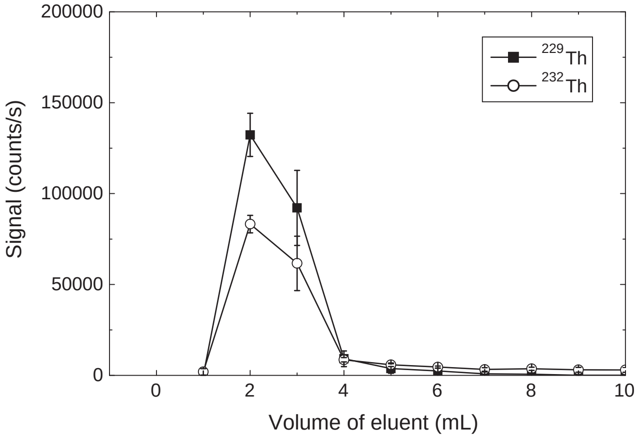

Fig. 4. The elution profiles of ^{229}Th and ^{232}Th from NOBIAS CHELATE PA1 resin columns using 10 mL of 0.8 M HNO_3. Error bars indicate the standard deviation of three replicate samples.

3.3. Volume of elution

To evaluate the elution efficiency of Th, a 200 mL aliquot of ^{229}Th spiked seawater sample, resulting in a total of 0.2 ng/L of ^{229}Th, was preconcentrated with NOBIAS CHELATE PA1 resin. With the NOBIAS CHELATE PA1 resin and a flow rate of 1.0 mL/min, the time used for preconcentration from a small volume of seawater sample (200 mL) takes about 4 h. The ^{229}Th was eluted from the resin column using 10 × 1.0 mL of 0.8 M HNO_3, and each fraction was analyzed by SF-ICP-MS. The signal intensity profiles for two isotopes of Th were compared in each fraction. Fig. 4 shows the elution profiles for ^{229}Th and ^{232}Th from the ^{229}Th tracer spiked seawater sample. The profile of ^{232}Th observed in each fraction was similar to that of ^{229}Th, so that 5 mL of 0.8 M HNO_3 was sufficient to elute ^{232}Th from the resin. Recovery of ^{229}Th was obtained as 'total amount of the element in the fraction' divided by 'initially added amount'. The recovery at each fraction is plotted in Fig. 5. More than about 98% of ^{229}Th was eluted in the first 5 mL fractions.

3.4. Blank value, LOD and precision

The LOD of ^{232}Th for SF-ICP-MS was 0.15 ng/L, evaluated from three times the standard deviation of 0.8 M HNO_3 ($n = 10$) (by direct measurement). We also evaluated a procedural blank value based on the NOBIAS CHELATE PA1 resin preconcentration and separation of 200 mL of MQW sample ($n = 13$) and detected by APEX-Q/SF-ICP-MS. For the procedural blank, an aliquot containing 200 mL of HCl–acidified MQW, the pH of which was adjusted to 2.4 ± 0.4 just before the column pretreatment by adding small amounts of NH_4OH, was processed in the same manner as the seawater sample solutions. Although conventional methods [25–29] require a large

Table 2
Comparison of sample volume, procedural blank, limit of detection, and separation and preconcentration method obtained with different techniques for ^{232}Th analysis reports.

Technique	Sample volume (L)	Procedural blank (pg/sample)	LOD (pg/L)	Separation and preconcentration method	Reference
Alpha spectrometry	220–270	8000.0[a]		Iron co-precipitation	[26]
TIMS	1.00	6.5		Iron co-precipitation, anion-exchange	[27]
TIMS	200	1600.0		Iron co-precipitation or manganese-fiber, anion-exchange	[28]
TIMS	1–12	58–263		Iron co-precipitation, anion-exchange	[29]
Electrothermal vaporization ICP-MS	0.05		13.0	Calcium phosphate co-precipitation	[14]
Solution nebulization ICP-MS	0.05		130.0	Calcium phosphate co-precipitation	[15]
Laser ablation ICP-MS	0.05		51.0	Calcium phosphate co-precipitation	[15]
Electrothermal vaporization ICP-MS	0.05		13.0	Calcium phosphate co-precipitation	[15]
TIMS	1.00	1.2		Iron co-precipitation, anion-exchange	[25]
Q-ICP-MS (Agilent HP4500)	0.50	<400.0	50.0	Adsorption by a chelating resin	[16]
SF-ICP-MS (Element 2) (APEX-Q)	0.20	N.D.	3.8	Adsorption by a chelating resin	This study

LOD: limit of detection. N.D.: not detected.

[a] Concentrations of ^{232}Th were converted to g as follows: 2.5×10^5 dpm/g.

volume of seawater samples (≥1 L) to minimize the contribution of procedural blanks (Table 2), the procedural blank values in our method were less than the LOD of SF-ICP-MS. This result suggests that the contamination for the overall preconcentration procedure from any chemicals and instruments including pipettes, bottles, HNO_3, NH_4OH and HCl is negligible for the analysis of ^{232}Th in acidified samples. When contamination and interference are negligible, the LOD for 40-fold preconcentration (sample volume: 200 mL, elution volume: 5 mL) is one-fortieth of the LOD for SF-ICP-MS without preconcentration. The calculated value for ^{232}Th (0.0038 ng/L) is approximately one order of magnitude lower than the concentration range of ^{232}Th in seawater (0.024–0.377 ng/L) [24,27–30]. To our best knowledge, this LOD is among the lowest reported so far in the recent literature on ^{232}Th determination by ICP-MS (Table 2). In addition, although no seawater reference material with a certified value of ^{232}Th is available, several research groups have reported ^{232}Th concentration in the CASS-4 reference nearshore seawater material for trace metals, thus we analyzed ^{232}Th in this reference material by a comparison and method validation. The results are presented in Table 3. Grinberg et al. [14,15] reported ^{232}Th concentration ranged from 0.4 to 0.9 ng/L in CASS-4 with relatively low precision (RSD, 20–67%). Zhu et al. [16] provided a ^{232}Th concentration of 0.46 ng/L with a much better precision (RSD, 4.3%). Our result of 0.44 ng/L (RSD, 4.5%) for ^{232}Th in CASS-4 is in good agreement with literature values, indicating that the developed analytical method is suitable for the determination of low level ^{232}Th in seawater samples.

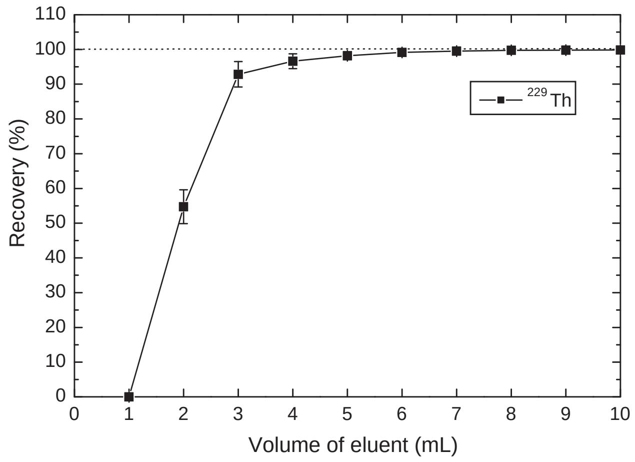

Fig. 5. The recovery of ^{229}Th from NOBIAS CHELATE PA1 resin columns using 10 mL of 0.8 M HNO_3. The dotted line and error bars indicate 100% recovery and the standard deviation of three replicate samples, respectively.

3.5. Analytical application

The established analytical method was applied to filtered (<0.2-μm) seawater samples collected from Japanese coastal areas. Considering previously reported data on ^{232}Th concentrations in filtered seawater samples in oceanic water (0.024–0.229 ng/L) [28–30] and the LOD of SF-ICP-MS (0.15 ng/L), at least a 40-fold enrichment factor is required to determine ^{232}Th in seawater samples. This was achieved with a sample volume of 200 mL and elution volume of 5 mL. The analytical results are shown in Table 4. The concentrations of ^{232}Th (mean value: 0.270 ± 0.040 ng/L) in the coastal water samples were comparable to those reported in filtered seawaters in the western Mediterranean Sea (mean value: 0.189 ± 0.025 ng/L) [29], but greater than those reported in waters in the central Pacific Ocean (mean value: 0.043 ± 0.012 ng/L) [30]. Because ^{232}Th enters seawater primarily as lithogenous materials

Table 3
^{232}Th concentrations in a reference material for nearshore seawater CASS-4 obtained in this study as compared with literature values.

Study	Observed value[a] (ng/L)	RSD (%)
Grinberg et al. [14]	0.5 ± 0.1	20.0
Grinberg et al. [15]	0.7 ± 0.2[b]	28.6
Grinberg et al. [15]	0.9 ± 0.6[c]	66.7
Grinberg et al. [15]	0.4 ± 0.2[d]	50.0
Zhuetal. [16]	0.46 ± 0.02	4.3
This study	0.44 ± 0.02	4.5

RSD: relative standard deviation.

[a] Average ± standard deviation, $n = 3$.

[b] Determined with a solution nebulization unit coupled to ICP-MS.

[c] Determined with laser ablation unit coupled to ICP-MS.

[d] Determined with electrothermal vaporization unit coupled to ICP-MS.

Table 4
Analytical results for seawater samples collected from Japanese coastal areas during 2010.

Site	Station	Location		Distance to land (km)	Salinity	^{232}Th (ng/L)[a]
Off Yubetsu, Hokkaido (August 2010)	Stn HY-l	44°13′56″N	143°37′16″E	0.5	33.5	0.33 ± 0.01
	Stn HY-2	44°14′26″N	143°37′36″E	1.0	33.6	0.26 ± 0.01
	Stn HY-3	44°14′56″N	143°37′56″E	2.0	33.5	0.22 ± 0.01
Off Ishinomaki, Miyagi (September 2010)	Stn MI-1	38°34′39″N	141°28′6″E	0.8	27.3	0.34 ± 0.01
	Stn MI-2	38°34′39″N	141°28′27″E	1.2	33.5	0.30 ± 0.01
	Stn MI-3	38°34′39″N	141°29′8″E	1.5	33.6	0.18 ± 0.01
Off Kakogawa, Hyogo (October 2010)	Stn HK-1	38°34′39″N	141°28′6″E	0.5	31.3	0.29 ± 0.01
	Stn HK-2	38°34′39″N	141°28′27″E	1.5	31.3	0.29 ± 0.02
Off Onga, Fukuoka (July 2010)	Stn HO-1	33°54′31″N	130°39′14″E	0.5	32.8	0.31 ± 0.02
	Stn HO-2	33°54′53″N	130°38′48″E	1.0	32.8	0.24 ± 0.01
	Stn HO-3	33°55′10″N	130°38′48″E	2.0	32.8	0.26 ± 0.02
Off Onga, Fukuoka (September 2010)	Stn HO-1				32.2	0.30 ± 0.01
	Stn HO-2				32.3	0.27 ± 0.01
	Stn HO-3				32.3	0.26 ± 0.01
Off Onga, Fukuoka (November 2010)	Stn HO-1				33.5	0.33 ± 0.02
	Stn HO-2				33.5	0.28 ± 0.02
	Stn HO-3				33.5	0.23 ± 0.01

[a] Average ± standard deviation of measurement by SF-ICP-MS.

[31], concentration of ^{232}Th is influenced by sources, such as aeolian input, riverine input, and resuspension of marine sediments. In the open ocean, such as in the central Pacific Ocean, aeolian input dominates the ^{232}Th budget, while in coastal regions, besides the aeolian input, riverine input may be very important, thus, relatively high concentrations of ^{232}Th can be observed in coastal waters.

4. Conclusion

The use of a NOBIAS CHELATE resin for preconcentration and separation of ^{232}Th from seawater and sensitive determination by SF-ICP-MS have been described. Compared to traditional analytical techniques, the developed method uses a relatively small volume of seawater (200 mL). It takes about 4 h for the preconcentration step. ^{232}Th was quantitatively collected at a low sample pH of 2.4 ± 0.4 by the resin, thereby inhibiting adsorption on container walls, organic ligand complexation, and the formation of colloids. In addition, a low HNO_3 concentration (0.8 M) is used for the elution of ^{232}Th, so that the eluted ^{232}Th fraction can be directly introduced into SF-ICP-MS for analysis. Finally, the extremely low procedural blank for the developed preconcentration and separation method ensures an excellent LOD (0.0038 ng/L). The concentrations of ^{232}Th in coastal seawater samples determined by using this proposed method are comparable with those reported in other regions. This sensitive analytical method lends itself to a better understanding of the biogeochemistry of ^{232}Th in coastal marine environments.

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