Application of NOBIAS Chelate-PA 1 Resin to the Determination of Zirconium, Niobium, Hafnium, and Tantalum in Seawater

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Zirconium, niobium, hafnium, and tantalum are dissolved in seawater as hydroxide complexes at a concentration as low as 0.01 – 370 pmol kg^{-1} and are expected to be potential tracers for water masses in the ocean. Herein, we report a new analytical method for the multielemental determination of the four elements on the basis of column extraction, using a NOBIAS Chelate-PA 1 resin that contains ethylenediaminetriacetic acid groups. The elements were collected on the resin from seawater that had been added with 3.8 mM HF at pH 6.0, and were eluted with 5 M HF. After the evaporation of 5 M HF, the elements were dissolved in 0.5 M HNO_3–6 mM H_2SO_4–1 mM HF and were determined by a high resolution ICP-MS, using a calibration curve method. We optimized the procedure to achieve quantitative recoveries and low backgrounds for the elements, although the complex formation between the metal ions and NOBIAS Chelate-PA 1 was decelerated by the seawater matrix. The method was tested by investigating the seawater samples of reference material and those collected from the depths at a station in the western North Pacific Ocean.

Keywords Zirconium, niobium, hafnium, tantalum, seawater, chelating resin, high resolution ICP-MS, GEOTRACES

(Received March 8, 2018; Accepted May 15, 2019; Advance Publication Released Online by J-STAGE May 24, 2019)

Introduction

Zirconium (Zr) and hafnium (Hf) are Group 4 elements and usually exist in a tetravalent state on the Earth's surface. Niobium (Nb) and tantalum (Ta) belong to Group 5 and have a pentavalent state. Due to such high valencies, these elements are classified as high-field strength elements, and they form hydroxide complexes, such as $Zr(OH)_5^-$, $Hf(OH)_5^-$, $Nb(OH)_6^-$, and $Ta(OH)_5$ in seawater.[1,2] Since these species are strongly adsorbed on metal oxides, particularly the slightly positively charged surface of amorphous FeOOH,[3] they are scavenged from a water column. This process highly fractionates the Zr/Hf and Nb/Ta ratios in the ocean and makes them potential tracers of ocean circulation.[4]

The determination of Zr, Hf, Nb, and Ta is, however, challenging. First, the concentrations of the four elements in seawater are very low: 11 – 370 pmol kg^{-1} for dissolved Zr (dZr),[4-13] 0.1 – 2.4 pmol kg^{-1} for dHf,[4-9,11,13,14] 1.2 – 7.2 pmol kg^{-1} for dNb,[4-7,12,13] and 0.01 – 0.3 pmol kg^{-1} for dTa.[4-7,13] Second, the metal species are not stable enough in acidified seawater without HF and are adsorbed on the walls of the bottles, especially those made of fluorocarbon polymer. Third, special care is necessary for a conventional concentration procedure of evaporation–redissolution, because it is difficult to dissolve the oxides of the metals in diluted HNO_3.

Column extraction with a chelating resin is promising for the preconcentration of trace metals in seawater.[15] In a previous study, we used a TSK-8-hydroxyquinoline (TSK-8HQ) resin (Fig. S1a, Supporting Information) for the preconcentration of Zr, Hf, Nb, Ta, and W.[16] The homemade TSK-8HQ resin was prepared *via* a reaction between 5-amino-8HQ and Toyopearl AF-Epoxy-650M (40 – 90 µm bead size; Tosoh Corporation, Japan).[17] The complex formation between the metal ions and 8HQ on the resin is so fast that this method is considered powerful enough for the preconcentration of the metal ions from seawater. However, the chemical bond between 8HQ and the TSK resin is sometimes broken during the preconcentration, resulting in "bleeding"; namely, the effluent is contaminated by 8HQ and turns red. The bleeding gradually reduces the performance of the chelating resin column and causes interference with the measurement. Recently, Firdaus *et al.*[5] used a UTEVA resin (Eichrom Technologies, USA) for the preconcentration of Zr, Hf, Nb, and Ta from seawater. The extractant in the UTEVA resin is diamyl amylphosphonate, which is retained on the resin by hydrophobic interaction. Herein, we focused on the NOBIAS Chelate-PA 1 resin (Hitachi High-Technologies, Japan).[18] This resin consists of hydrophilic poly(hydroxy methacrylate) beads, functionalized with ethylenediaminetriacetic acid and iminodiacetic acid (Fig. S1b, Supporting Information). Ethylenediaminetriacetate is an analogue of ethylenediaminetetraacetate and a strong ligand for metal ions. In addition, the NOBIAS Chelate-PA 1 resin has advantages, including the effective separation of alkali metal and alkaline earth metal ions, low blanks of trace metals, and chemical and physical stability of the resin. Thus far, the NOBIAS Chelate-PA 1 resin has been widely applied to the preconcentration of divalent species, such as manganese, cobalt, nickel, copper, zinc, cadmium, and lead; and trivalent species, such as aluminum, iron, and rare earth elements.[18-21] Poehle and Koschinsky[12] applied NOBIAS Chelate-PA 1 to an online-preconcentration method to determine Zr and Nb. In this study, we applied the NOBIAS Chelate-PA 1 resin to the

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preconcentration of Zr, Hf, Nb, and Ta. We also applied an off-line automated preconcentration system, SPE-100 (Hiranuma Sangyo, Japan), to reduce labor and to improve the performance of the preconcentration. We report here the optimized procedure and performance of the method. We discuss the characteristics of NOBIAS Chelate-PA 1 in comparison to those of conventional resins, and also report the application of this method to the evaluation of reference seawater samples, and to the observation of vertical profiles of the elements in a water column in the western North Pacific Ocean.

Experimental

Reagents and materials

Deionized water (MQW) purified with a Milli-Q Gradient-A-10 system (Merck Millipore, USA) was used to prepare all the solutions. Ultra-high purity reagents including HCl, HF, HNO_3, H_2SO_4, acetic acid (HOAc), and aqueous ammonia (Optima Acids, Fisher Scientific, USA; TAMAPURE, Tama Chemicals, Japan; or Ultrapur-100, Kanto Chemical, Japan), were used for the analysis. The concentrated solutions were treated within a fume hood. Standard solutions of Zr, Nb, Hf, and Ta were prepared from 1000 mg L^{-1} standard solutions (Merck Millipore). All the solutions were prepared on a weight basis in a clean room (class 1000). A concentrated buffer of 2.5 M HOAc–NH_4OAc, at pH 6, was prepared with 25 g of HOAc (Optima, 17.3 M), 34 g of MQW, and 55 g of NH_4 (TAMAPURE AA-10, 6.3 M). For serial dilution of the metal standards, a diluted HF (Ultrapur-100) solution was used. Working standard and blank solutions were prepared in 0.5 M HNO_3 (Ultrapur-100)–6 mM H_2SO_4 (TAMAPURE AA-10)–1 mM HF (Ultrapur-100).

Low-density polyethylene (LDPE) bottles (Nalge Nunc, USA) were used for the solution storage and analysis. The bottles and caps were soaked overnight in an alkaline detergent (5% Scat 20-X, Nacalai Tesque, Japan), rinsed with tap water, soaked overnight in 4 M HCl (reagent grade, FUJIFILM Wako Pure Chemical, Japan), and rinsed with MQW. The bottles were then filled with 1 M HF (Ultrapur-100), loosely caped, sealed in a polyethylene bag, heated to ~80°C in a microwave oven, and left to stand on a bench overnight. The bottles were heated again, tightly capped, placed upside down on a bench overnight, and subsequently rinsed with MQW. Plastic tubings and micropipette tips were cleaned in a similar fashion as the bottles.

The chelating resin column used in this study was Nobias Chelate-PA 1L (Hitachi High-Technologies, Japan; Fig. S1c, Supporting Information). In the column, about 300 mg of the resin was sandwiched with frits of high-density polyethylene and sealed in a cartridge of polypropylene. Prior to use, the column was successively cleaned with 25 mL each of acetone (reagent grade), methanol (reagent grade), MQW, 1 M HCl-0.01 M H_2O_2 (reagent grade), MQW, 2 M HNO_3 (Ultrapur-100), MQW, 5 M HF (Ultrapur-100) × 2, and MQW, by injecting the solutions *via* the column at a flow rate of ~5 mL min^{-1} using a polypropylene syringe.

Apparatus

The automated preconcentration system used, was a modified SPE-100 (Hiranuma Sangyo, Japan; Fig. S2, Supporting Information), which was set in a clean hood. The original system utilized alumina and zirconia parts in an 8-way valve, which were replaced with polychlorotrifluoroethylene parts. These parts were initially cleaned with an alkaline detergent and 4 M HCl, and were installed in the system. The flow line of the preconcentration system was initially cleaned without attaching a chelating resin column, using 25 mL of the following fluids at 5 mL min^{-1} successively from six ports of the 8-way valve: (1) methanol (reagent grade), (2) air, (3) 1 M HCl–0.01 M H_2O_2 (reagent grade), (4) air, (5) 1 M HNO_3 (Ultrapur-100), (6) air, (7) 5 mM HF (Ultrapur-100), (8) air, and (9) MQW × 2. A precleaned Nobias Chelate-PA 1 L column was then attached to the line with TYGON SE-200 tubes (Saint-Gobain, France).

Table 1 Operating conditions of HR-ICP-MS ELEMENT2

RF power	1.1 – 1.2 kW
Sampler cone	Nickel
Skimmer cone	Nickel
Nebulizer	PFA-100 MicroFlow
Sample take-up rate	100 μL min^{-1}
Desolvating system	Apex HF, Elemental Scientific
Plasma gas flow rate	16 L min^{-1}
Auxiliary gas flow rate	0.84 L min^{-1}
Nebulizer gas flow rate	Daily optimized for ^{90}Zr and ^{178}Hf
Touch position	Daily optimized for ^{90}Zr and ^{178}Hf
Lenses	Daily optimized for ^{90}Zr and ^{178}Hf
Resolution	Low
Search window	150%
Integration window	80%
Sample time	0.02 s
Sample per peak	20
Pass	3
Run	3
Scan (Pass × Run)	3 × 3 = 9

The column that had collected the elements was detached from the SPE-100 and attached to a manual elution system (Fig. S3, Supporting Information) because the SPE-100 could not use HF solution as an eluent. The elution system was constructed with the column, LDPE bottles, and PFA tubes (2 mm i.d.), and was set in a clean hood. The flow line was cleaned with an alkaline detergent, 4 M HCl, and hot 5 M HF prior to use. The eluent was sent by air pressure. The air was supplied by a peristaltic pump, *via* a cartridge filter with a pore size of 0.2 μm, and then introduced into the eluent bottle.

A semi-closed evaporation system was used to evaporate the HF sample solution and to recover HF (Fig. S4, Supporting Information). The flow line of the evaporation system was constructed with LDPE bottles and PFA tubes (1 mm i.d.), and was cleaned in a similar manner as the elution system. Sample solutions in 60 mL LDPE bottles were mounted in six aluminum sleeves and heated on a hot plate (dry stirring bath, AS ONE, Japan) at ~100°C in a fume hood. A silent air compressor AR-200 (IAC, Japan) was used to send air to the sample bottles. The air was passed through cartridge filters with a pore size of 0.2 and 0.01 μm, and then introduced into the sample bottles. The evaporated HF was collected with a water trap containing alkaline solution and cooled in ice and water.

A high-resolution ICP mass spectrometer (HR-ICP-MS) equipped with a magnetic sector mass analyzer (ELEMENT2, Thermo Fisher Scientific, USA) was used for the determination of the four elements. The solutions were introduced into ELEMENT2 using an apex HF Desolvating Nebulizer (Elemental Scientific, USA). The major operating conditions of HR-ICP-MS are listed in Table 1. Six isotopes, ^{90}Zr, ^{91}Zr, ^{93}Nb, ^{177}Hf, ^{178}Hf, and ^{181}Ta, that occur at a relatively high natural abundance and have no isobars were measured during each run. A calibration curve method was used for the determination. The working standard and blank solutions were measured after every 4 – 9 samples, to correct the drift of background and sensitivity.

Table 2 Programs of the preconcentration system

Column conditioning

Step	Fluid	Port	Amount /mL	Flow rate /mL min^{-1}	Time /min
1	MQW	1	60	10	6
2	Air	7	20	30	0.7
3	Buffer	2	40	2	20
	(Wait)	—	—	—	5
4	Air	7	10	6	1.7
Total time/min					33.4

Sample loading

Step	Fluid	Port	Amount /mL	Flow rate /mL min^{-1}	Time /min
1	Sample	3	280	1	280
2	Air	7	10	6	4.7
3	Buffer	2	20	2	10
4	Air	7	20	30	0.7
Total time/min					295.4

The detection limit was determined as three times the standard deviation (SD) for a blank solution of 0.5 M HNO_3–6 mM H_2SO_4–1 mM HF: 6 pmol kg^{-1}, 0.2 pmol kg^{-1}, 0.05 pmol kg^{-1}, and 0.02 pmol kg^{-1} for Zr, Nb, Hf, and Ta, respectively.

Optimized procedure for seawater samples

For an acidified seawater sample (pH 1.6 – 2.2), HF was added to achieve a final concentration of 3.8 mM HF. A 250-g portion of the seawater sample was weighed in an LDPE bottle, added with 1 mL of 2.5 M HOAc–NH_4OAc buffer, adjusted to pH 6.00 ± 0.05, and immediately processed using the preconcentration system. Table 2 shows the programs of the preconcentration system for the column conditioning and sample loading. For the seawater analysis, we used two Nobias Chelate-PA 1L columns that were serially connected. The columns were conditioned by passing 0.01 M HOAc–NH_4OAc buffer at pH 6.00 ± 0.05 just before the analysis. The seawater sample was loaded at a flow rate of 1 mL min^{-1}. After the sample loading, 0.01 M HOAc–NH_4OAc buffer was sent again to remove the seawater matrix. Subsequently, the columns were detached from the preconcentration system and attached to the elution system. The analyte metal ions were eluted with 60 mL of 5 M HF, at a flow rate of 0.17 mL min^{-1}.

The eluate was added with 0.1 mL of 0.3 M H_2SO_4 and gently dried using the evaporation system for ~7 h. After cooling, a droplet of the remaining solution was added with 5 mL of 0.5 M HNO_3–1 mM HF and mixed with a mechanical shaker at a speed of 270 r min^{-1}, at 50°C, for 30 min. The final solution was weighed and then introduced into HR-ICP-MS. The exact concentration factor was calculated on the weights of seawater and the final solution.

For the automated preconcentration system, the flow line was cleaned by sending 50 mL of MQW from port 3. For the columns, they were cleaned by flowing 40 mL of 5 M HF and 60 mL of MQW, and then detached from the elution system and attached to the preconcentration system. The columns were repeatedly used for this procedure at least 50 times without efficiency deterioration.

Results and Discussion

Optimization of the chelating resin column extraction

First, we explored the optimum condition for an MQW sample. When an MQW sample to which had been added Zr, Nb, Hf, and Ta, and of which the pH was adjusted with HNO_3, NH_3, and/or HOAc–NH_4OAc buffer, was loaded on a Nobias Chelate-PA 1L column, we found that a fraction of the four elements was adsorbed on the wall of the bottle, resulting in low recovery (Fig. S5, Supporting Information). The results suggest that the hydroxy complexes of the four elements are not stable in solution, especially at a higher pH. When we added 2 mM HF to the sample, the four elements were recovered with a recovery higher than 90%. This suggests that the fluoride complexes of the elements are stable in the sample solution and were collected on the chelating resin. We found that the percentage recovery of the elements decreased at a low pH as the loading flow rate increased (*e.g.* the recovery of Nb at pH 1.7 was 94 and 90% at a flow rate of 2 and 6 mL min^{-1}, respectively). We also found that the mixture solution of HF and HNO_3 quantitatively eluted the four elements from the chelating resin column. Based on these experiments, the following conditions were determined as the optimum conditions for freshwater analysis: the HF concentration in a sample is 2 mM; the pH of the sample is 4 – 6; the flow rate during the sample loading is 6 mL min^{-1}; elution, with 20 mL of 5 M HF–2 M HNO_3 at a flow rate of 0.17 mL min^{-1}. The four elements added in an MQW sample were quantitatively recovered under the optimum condition (Table S1, Supporting Information).

However, the four elements added in the seawater sample were not quantitatively recovered under the optimum condition for freshwater (Table S2, Supporting Information). Through experiments, we attributed the incomplete recovery to the following two causes. First, 2 mM HF was not enough to stably dissolve the four elements in the seawater sample. It is probable that major cations in seawater, such as calcium, form complexes with fluoride ions to reduce the activity of free fluoride ions in seawater. We found that about 4 mM HF is necessary to keep the four elements stable in a seawater sample. Second, we found that the seawater matrix reduces the reaction rate of the complex formation between the four metal ions and the chelating groups on the Nobias Chelate-PA 1 resin. This resulted in a much wider band of the adsorbed elements, and finally, breakthrough of a portion of the four elements in the seawater sample, when the sample was loaded on a column under the optimum condition for freshwater. To overcome this problem, we used two columns that were connected in series, reduced the sample flow rate to 1 mL min^{-1}, and increased the volume of eluent. We found no significant difference in the elution efficiency between the HF solution and the mixed solution of HF and HNO_3, when an increased amount of eluent was used. We decided to use the HF solution as the eluent for the seawater analysis, to reduce environmental burden. Figure 1 shows the percentage recoveries of the four elements in 20 mL each fractions of eluate, when the four elements had been collected from a seawater sample. Although a significant amount of Ta is observed in eluent 3, cumulative recoveries reach more than 95% for each element in eluents 1 – 3. Thus, we decided the optimum conditions for seawater analysis as follows: the HF concentration in a sample is 3.8 mM; the pH of the sample is 6; the flow rate during the sample loading is 1 mL min^{-1}; and elution, with 60 mL of 5 M HF at a flow rate of 0.17 mL min^{-1}. Table 3 shows the results of the recovery experiments of the four elements at a natural concentration level from the seawater

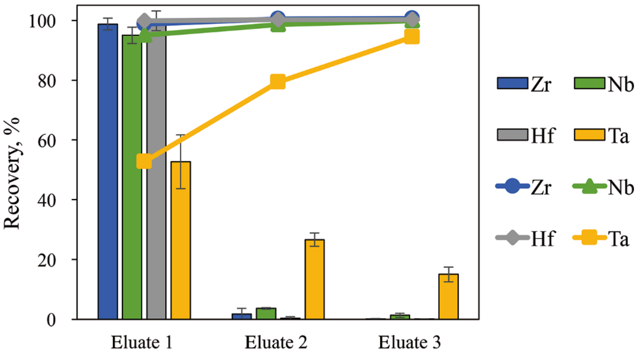

Fig. 1 Recovery of Zr, Nb, Hf, and Ta from a seawater sample (3.8 mM HF–0.01 M HCl) using serial columns.

Table 3 Recovery of Zr, Hf, Nb, and Ta from a seawater sample

Element	Concentration/pmol kg^{-1}		Recovery, %[a]
	Spiked	Found[a]	
Zr	0	129 ± 14	102 ± 5
	158	291 ± 8	
Nb	0	1.50 ± 0.40	99.0 ± 6.1
	3.02	4.49 ± 0.16	
Hf	0	0.28 ± 0.03	101 ± 4
	0.835	1.11 ± 0.03	
Ta	0	0.015 ± 0.003	90.6 ± 8.5
	0.106	0.111 ± 0.009	

a. Average ± SD for seven replicate analyses.

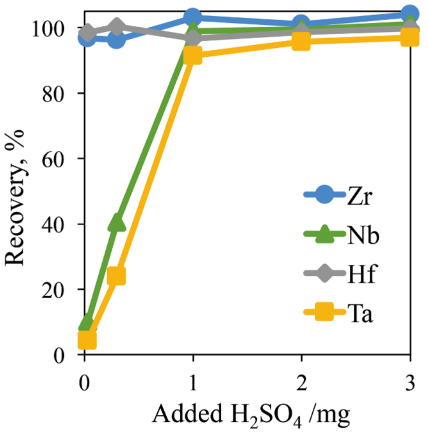

Fig. 2 Effect of added H_2SO_4 on the recovery of Zr, Nb, Hf, and Ta for evaporation–redissolution.

sample. The seawater sample was prepared by mixing seawater samples that had been collected from different depths in the North Pacific Ocean, filtered and acidified immediately after sampling, and stored for years. The recoveries were calculated on the basis of the measured concentrations of the elements in the seawater samples with and without elemental spike. The percentage recoveries for Zr, Nb, and Hf were from 99 to 102%, with SD less than 6%. The recovery for Ta was slightly lower, and the SD was slightly higher, probably because the concentration of Ta was close to the detection limit.

Optimization of evaporation–redissolution

Evaporation–redissolution is necessary to change the solution matrix from that suitable for elution to that suitable for measurement with ICP-MS, and to concentrate the analytes for precise measurement. When a sample solution of Zr, Nb, Hf, and Ta is completely dried in a bottle heated on a hot plate, a portion of the elements is transformed into oxides, which causes the incomplete redissolution of the elements in the diluted acid solution that is suitable for measurement with ICP-MS.[22] In our previous method, we used a water bath for evaporation.[16] In this case, the sample solution was not completely dried, and the four elements were quantitatively recovered. However, the procedure consumed time and energy. In this study, we used a hot plate for evaporation. Although it shortened the evaporation time, it was difficult to stop the heating process just before complete dryness, particularly when plural samples were processed concurrently. We decided to add a small amount of H_2SO_4 before heating to prevent the complete evaporation of the sample solution. Figure 2 shows that the addition of about 2 mg of H_2SO_4 is enough to attain the quantitative recovery of the four elements *via* evaporation–redissolution. We found that the effects of this amount of H_2SO_4 on the determination of the four elements with HR-ICP-MS were insignificant.

At an early stage of this study, we used a conventional diaphragm pump to send air to the sample bottles during evaporation. It took about 10 h to evaporate 60 mL of 5 M HF. The four elements were contaminated during this procedure; the contamination corresponded to a concentration of 0.50 pmol kg^{-1} for Zr and 0.015 pmol kg^{-1} for Ta in seawater. Possible sources of the contamination are dust and aerosol in ambient air. Another possible source is the diaphragm pump, because some parts in the pump are made of cast iron that contains Nb and Ta. To prevent the contamination, we adopted a silent air compressor, which supplies clean air, instead of the diaphragm pump, and passed the compressed air through filters. The evaporation time was shortened to about 7 h because of the relatively high pressure of air that was supplied by the silent air compressor. For the optimized evaporation–redissolution procedure, the blank corresponded to 0.13 ± 0.14, 0.018 ± 0.012, 0.0005 ± 0.0007, and 0.003 ± 0.001 pmol kg^{-1} for Zr, Nb, Hf, and Ta (average ± SD, $n = 4$), respectively.

Procedure blank and detection limit

The procedure blank of the method was estimated by analyzing 250 g of MQW using the optimized procedure for seawater. We assumed that the concentrations of Zr, Nb, Hf, and Ta are negligible in MQW. The observations for the procedure blank were attributed to reagents and surrounding conditions, which will be applicable to the seawater samples as well. The detection limit of the method was determined as three times the SD of the procedure blank. The results are listed in Table 4, indicating that the procedure blank and detection limit are sufficiently low for the determination of the four elements in seawater.

Analysis of reference seawater samples

There are no reference seawater samples established for Zr, Nb, Hf, and Ta. We expect that the reference seawater samples, CASS and NASS, supplied by the National Research Council of Canada will be useful for the community of marine chemistry when we determine the concentrations of the four elements. CASS-5 was collected from Halifax Harbour, and NASS-6 was collected from Sandy Cove, Nova Scotia. We added 3.8 mM HF prior to the analysis. The analytical results are presented in Table 5, in comparison with literature data on previous lots of

CASS-3 and NASS-5. It is apparent that the concentrations of the four elements are substantially different among the reference samples, although they had been collected from a small area within a distance of a few hundred kilometers. The results suggest that the concentrations of the four elements vary largely near shore conditions. The concentrations of Ta in CASS-5 and NASS-6 are close to those observed at pelagic stations in the Atlantic Ocean.[6]

Vertical profiles of Zr, Nb, Hf, and Ta in the western North Pacific Ocean

GEOTRACES is an international program that aims to improve the understanding of biogeochemical cycles and large-scale distribution of trace elements and their isotopes in the marine environment (http://www.geotraces.org). In this program, a crossover station is a location where the track of one cruise overlaps with that of another cruise although the research vessels need not be simultaneously present at the same location. The comparison of the results from the crossover stations provides a measure of internal consistency. In a previous study, we revealed the vertical profiles of Zr, Nb, Hf, and Ta in a water column at station K2 (160.005°E, 47.023°N, bottom depth 5189 m) during the MR05-01 cruise of R/V Mirai, JAMSTEC in March 2005.[7] The seawater samples were collected from each depth using a clean sampling system, passed through a Nuclepore filter with a pore size of 0.2 μm (Coaster, USA), and analyzed with the MAF-8HQ preconcentration method.[16] Station BD07 (160.086°E, 47.000°N, bottom depth 5238 m) was occupied during the KH-12-4 cruise of R/V Hakuho Maru in August 2012. The seawater samples were collected from each depth using a clean sampling system, filtered with an

Table 4 Procedure blank and detection limit of the method

Element	Procedure blank /pmol kg^{-1} [a]	Detection limit /pmol kg^{-1}	Concentration in seawater /pmol kg^{-1}
Zr	0.60 ± 0.31	0.9	11 - 366
Nb	0.075 ± 0.004	0.013	1.2 - 7.2
Hf	0.0029 ± 0.0024	0.007	0.1 - 2.4
Ta	0.0052 ± 0.0003	0.0008	0.02 - 0.3

a. Average ± SD for five replicate analyses.

Table 5 Analytical results on reference seawater

Element	Concentration/pmol kg^{-1}			
	CASS-5[a,b]	CASS-3[c]	NASS-6[a,b]	NASS-5[a,d]
Zr	218 ± 6	90	247 ± 6	183 ± 9
Nb	4.0 ± 0.3	6.7	4.2 ± 0.2	7.8 ± 0.9
Hf	1.49 ± 0.04	0.49	1.68 ± 0.05	1.24 ± 0.24
Ta	0.022 ± 0.002	0.21	0.023 ± 0.001	0.25 ± 0.15

a. Average ± SD for two replicate analyses.
b. This study.
c. Data taken from Ref. 7.
d. Data taken from Ref. 16.

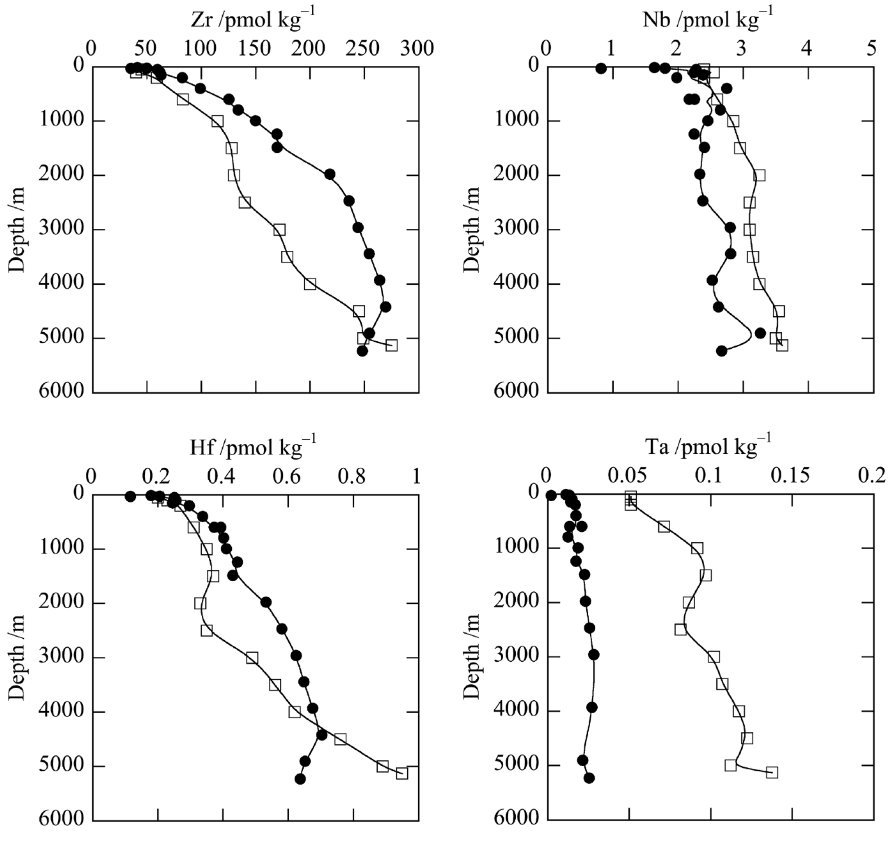

Fig. 3 Vertical profiles of dissolved Zr, Nb, Hf, and Ta in a water column at stations BD07 (closed circles; 160.086°E, 47.000°N, bottom depth 5238 m; this study) and K2 (open squares; 160.005°E, 47.023°N, bottom depth 5189 m; Ref. 7).

AcroPak capsule filter with a pore size of 0.2 µm (Pall, USA), added with mixed acid to a final concentration of 0.01 M HCl–2 mM HF, and stored at an ambient temperature for six years until the determination of the four elements. Thus, the stations K2 and BD07 would serve as a crossover station to verify the analytical methods.

Figure 3 shows the vertical profiles of Zr, Nb, Hf, and Ta at BD07 and K2. At BD07, the concentrations of dissolved Zr (dZr) and dHf are low in surface water and gradually increase with depth down to 4400 m. The two elements showed a strong correlation: dHf = 0.00214 dZr + 0.10, $r = 0.992$, $n = 22$. Although the concentrations of dZr and dHf at K2 are similar to those at BD07, they increase more steeply at the bottom. The dNb and dTa at BD07 show a slight increase with depth. Although dNb and dTa at K2 have similar vertical profiles with those at BD07, their concentrations at K2 are significantly higher than those at BD07. We found that a fraction of Ta had been adsorbed during the storage of the BD07 samples. After preconcentration, we added HF solution to the empty bottle used for storage to dissolve the elements that had been adsorbed on the wall of the bottle. Although the adsorbed fraction was less than 5% against the preconcentrated amount for Zr, Nb, and Hf, it reached 34 ± 4% for Ta ($n = 4$). The results suggest that 0.01 M HCl–2 mM HF is not adequate to keep Ta stable in seawater for several years. An improved storage condition should be investigated in future work.

Conclusions

A multi-elemental determination method for Zr, Nb, Hf, and Ta in seawater has been developed. The four elements were concentrated 50-fold *via* column extraction with a chelating resin (NOBIAS Chelate-PA 1) and *via* evaporation–redissolution; subsequently, they were determined by HR-ICP-MS. The optimized procedure realized the quantitative recoveries and the low procedure blank of the four elements. The method was successfully applied to the analysis of the seawater samples. Compared to that of TSK-8HQ, the best merit of NOBIAS Chelate-PA 1 is robustness. NOBIAS Chelate-PA 1 is resistant to 5 M HF and can be used for more than 50 cycles of the preconcentration without a significant change in performance. The demerit of NOBIAS Chelate-PA 1 is that the reaction rate of the complex formation is decreased by the seawater matrix. To overcome this fault, we used two columns connected in series, a slow flow rate of sample loading, and a large amount of eluent to recover the four elements from a wide adsorbed band. Future investigations, such as that on the mechanism controlling the reaction rate and on the optimization of the column design and the storage condition, would further improve the method.

Acknowledgements

This research was supported by The Japan Society for the Promotion of Science (JSPS) KAKENHI grants (Grant Nos. JP24241004, JP15H0127, and 19H01148) and by Mitsumasa Ito Memorial Research Grant from the Research Institute for Oceanochemistry Foundation. The authors thank the crew, technicians, students, and scientists onboard the KH-12-4 cruise for their assistance with the seawater sampling. We express our appreciation regarding the preliminary experiments carried out by graduate student Hiroaki Fujisaka. We would like to thank Editage (www.editage.jp) for English language editing.

Supporting Information

Figures and tables that are not included in the main body are presented in Supporting Information. This is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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