



Determination of Zr, Nb, Mo, Sn, Hf, Ta, and W in seawater by N-benzoyl-N-phenylhydroxylamine extraction chromatographic resin and inductively coupled plasma-mass spectrometry



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ABSTRACT

A method has been developed for the determination of zirconium (Zr), hafnium (Hf), niobium (Nb), tantalum (Ta), molybdenum (Mo), tungsten (W), and tin (Sn) in seawater by quadrupole inductively coupled plasma-mass spectrometry (Q-ICP-MS). The method is based on separation of the seven elements by extraction chromatography using N-benzoyl-N-phenylhydroxylamine (BPHA) supported on a microporous acrylic ester polymeric resin. The optimized procedure indicates that the BPHA resin has high selective adsorption for Zr, Nb, Mo, Sn, Hf, Ta, and W (known as fluoride soluble elements), whereas other interference and matrix elements are minimally adsorbed. The optimized eluent mixture with their molarity gives satisfactory recoveries for all analytes. The recovery can be achieved 99% for Zr, 97% for Nb, 97% for Mo, 99% for Sn, 99% for Hf, 95% for Ta, and 98% for W, respectively, by eluting with 6 mL of 6 mol L⁻¹ HF/1 mol L⁻¹ HCl. Furthermore, the technique for separation and enrichment of these elements provides a low total method blank. The detection limits for this method are 0.5 ppt for Zr, 0.2 ppt for Nb, 1.7 ppt for Mo, 1.0 ppt for Sn, 0.1 ppt for Hf, 0.1 ppt for Ta, and 0.3 ppt for W, respectively. The validity of the method is evaluated by replicate analyses of seawater reference materials; the precision of the results is better than 3% (RSD, *n* = 4), and the results are in good agreement with certified values. The established procedure has proved to be both practical and effective for seawater sample analyses.

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1. Introduction

In seawater, Mo and W are dominated by the oxyacid species, MoO₄²⁻ and WO₄²⁻, which are more soluble than hydroxide species and have the potential to be used as indicators of hydrothermal activity on the seafloor [1–3]. Zr, Hf, Nb, and Ta are classified as refractory metals and are dominated by the hydroxide species, Zr(OH)₅⁻, Hf(OH)₅⁻, Nb(OH)₆⁻, and Ta(OH)₆⁻ [1,2]. They are not readily dissolved in seawater, and can be rapidly removed from solution by interaction with the surfaces of sinking particles, a process referred to as scavenging. Both of these factors result in very low concentrations of refractory metals in seawater. The refractory nature and low concentrations have limited the study of these elements in the hydrological cycle. Nevertheless, these metals are thought to have potential as oceanographic tracers [4]. Sn is one of the three most highly enriched metals (along with lead and tellurium) in atmospheric particulate matter compared with the earth's crust [5]. Transport of Sn from the continents to the oceans also appears to take place via the atmosphere. The distribution of Sn in the ocean is a function of geographic location and water depth, as well as other parameters. Therefore, it is interesting and useful for

marine geochemistry to compare the behaviors of these metals in the ocean. In addition, the analysis of seawater is an important field in analytical chemistry.

Determination of these metals in seawater faces two major difficulties: (1) the ultra-low concentrations require a sensitive instrument with a low detection limit, in addition to an appropriate preconcentration, and (2) a high matrix concentration (35 g kg⁻¹ of major ions in seawater at salinity = 35) can severely interfere with analysis of these metals.

Due to some improvements to the sample introduction system, such as an additional gas and high matrix tolerant cones, inductively coupled plasma-mass spectrometry (ICP-MS) offers many advantages. These include simultaneous analyses of all elements, and their quantitative determination at both high and low resolution with detection limits of the order of picograms per milliliter. However, for ultra-trace analytes, the matrix effects on detection limits are still a serious issue; therefore, suppression of these effects should be considered [6]. The simplest way to reduce the matrix and salt effects in ICP-MS measurements is by using large dilution factors or by matrix matching the standards. However, the large dilution approach is not applicable for low level high field strength elements (HFSE) content.

Undoubtedly, it is necessary to separate the analytes from the matrix elements of alkali and alkaline-earth metals in seawater prior to measurement, and this remains the most efficient way to avoid matrix

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effects, polyatomic and isobaric overlap interference, and clogging problems. In turn, this improves detection limits, and increases the concentrations of analytes to levels at which they can be quantitatively detected. Separation techniques to pre-concentrate trace elements in seawater have been developed, including co-precipitation [7–9], solvent extraction [10] and solid phase extraction [2,4,11–13]. Consequently, the complexity and time-consuming nature of the separation procedure has become a major disadvantage for routine analyses. So far, solid phase extraction is one of the fastest and cleanest preconcentration methods to separate and concentrate trace elements in seawater. Mckelvey and Orians [4] found that Chelex-100 was suitable for extraction of Zr and Hf from 1 L of seawater using isotope dilution analysis [4]. MAF-8HQ was used to concentrate Zr, Hf, Nb, Ta, and W from seawater [11]; however it was difficult to reduce the analyte blank concentrations and to elute the metals quantitatively. The use of TSK-8HQ resin solved this problem, when accompanied by large seawater samples [13].

These methods offer a great advantage in terms of simplicity, but they lack low blank concentrations or adequate sensitivity to measure very low levels of metals in seawater precisely. Furthermore, these methods have been reported for Zr, Hf, Nb, and Ta, whereas detailed analytical methods for the fluoride soluble elements, Zr, Hf, Nb, Ta, Mo, W, and Sn, have not been reported. The chemical similarity of these seven elements is key to understanding the fundamental nature of the geochemical processes that control trace metal distribution in the oceans.

In this study, a method is developed for the preconcentration of Zr, Nb, Mo, Sn, Hf, Ta, and W in seawater by *N*-benzoyl-*N*-phenylhydroxylamine (BPHA) extraction chromatographic resin, and concomitant determination by ICP-MS. Actually, BPHA has been used extensively for extraction of Ta, Nb, Zr, and Hf in geological samples [14–16]. Yang and Pin developed an extraction chromatographic method using BPHA [14] for the separation of HFSE from Ti-rich geological materials prior to ICP-AES measurement. The methods are simple, rapid and effective in the separation of Zr, Hf, Nb and Ta [14]. However, due to low sensitivity of ICP-AES for Ta and low abundance of Ta, the method was unable to determine low levels of Ta. Thus, they evaluated the validity of the BPHA method in conjunction with ICP-MS by analyzing international standards spanning the range of concentration from depleted (BIR-1) to relatively rich (BHVO-1) basaltic rocks [15]. However, so far the BPHA method has not been used in the separation of very low concentrations of these trace elements (picogram per milliliter or sub-picogram per milliliter levels) from the high salinity matrix in seawater. Thus, on the basis of our previous work [16], the robustness of the method in this study was examined by investigating the separation conditions, blank issues, and compatibility with sample preparation procedures. The validity of the method was evaluated by analyzing international standards of seawater spanning a range of concentrations, including Atlantic Ocean seawater and coastal seawater, as well as actual seawater samples collected from the Pacific Ocean. The methodology described here could potentially be applied to the analysis of various kinds of seawater, and geological and environmental samples.

2. Experimental

2.1. Reagents and geological samples

BPHA (Analytical grade, Aladdin Reagents Inc., China) and Amberchrom CG-71 (50–100 μm , Supelco Inc., USA) were used without further purification. Working standards in the range of micrograms per gram to nanograms per gram, ready for loading standard solutions and optimizing the column separation parameters, were prepared by dilution on a weight basis from 100 $\mu\text{g mL}^{-1}$ of fluoride soluble elements (MISA 05-1), alkali and alkaline earth metals (MISA 04-1), transition metals (MISA 06-1) and rare earth elements (REEs, MISA 01-1) (Accustandard Inc., USA). Ultra-pure water was purified with a Milli-Q

system (Millipore) and employed throughout the experimental preparations. The applied reagents, HCl, HF, and HNO_3 , were purified by DST-1000 Sub-Boiling Stills (Saville Corporation, USA).

The international standards for Atlantic seawater (salinity = $35.0 \pm 0.2\%$) and Atlantic coastal seawater reference materials for trace metals (CASS-5, NASS-6) were purchased from OSIL (UK) and the National Research Council Canada, respectively. National standard coastal seawater GBW080040 was provided by the Second Institute of Oceanography. In the course of this work, all preparation was carried out in an ultra-clean laboratory. The PFA bottles were boiled in 30% HNO_3 for 30 minutes, kept for 48 h at sub-boiling temperatures, and finally rinsed with pure water.

2.2. Preparation of BPHA resin

BPHA chelated resin was prepared by following the procedures described by Li et al. [17]. Five grams of Amberchrom CG-71 resin was soaked in 40 mL of 3% BPHA solution in ethanol instead of chloroform, and shaking for 2 h at room temperature (25 °C) up to saturation, to achieve the BPHA resin.

2.3. Procedure of column separation and preconcentration

BPHA resin (0.5 mL, about 0.2 g dry weight) was packed in a Bio-Spin Chromatography column (Bio-Rad Laboratories, Inc.), and was washed with 6 mol L^{-1} HF (4 mL) and Milli-Q water (8 mL, 18.25 $\text{M}\Omega\text{ cm}$ of the resistivity). A loading standard solution was ready for column separation. The standard working solution (2 μg) was diluted in 2 mL of 0.5 mol L^{-1} HCl, 1 mol L^{-1} HCl, and 3 mol L^{-1} HCl, respectively, and loaded onto respective BPHA resin columns. Prior to loading the sample, the columns were conditioned with respective concentration of HCl (4 mL) corresponding to 0.5 mol L^{-1} , 1 mol L^{-1} and 3 mol L^{-1} HCl.

The loaded columns were then eluted with respective concentration of HCl (6 mL) to remove the major elements, and the eluting solution was collected in 1 mL subsamples that were diluted to appropriate concentration for ICP-MS measurement.

Samples containing seawater (10–50 mL) were acidified with concentrated HCl to about 1 mol L^{-1} . The chemical separation steps were undertaken as follows: the seawater sample was loaded onto the BPHA resin; after loading, the column was washed with 1 mol L^{-1} HCl (6 mL), which would effectively remove matrix elements and interference (Fe, Mn, Cu, Zn, Ni, REEs etc.) from the sample.

A 1 mol L^{-1} HCl/0.4% H_2O_2 solution was passed through the column to elute Ti (the volume used depended on the Ti content of the sample). Finally, the adsorbed Zr, Nb, Mo, Sn, Hf, Ta, and W were eluted with a 6 mol L^{-1} HF/1 mol L^{-1} HCl solution (6 mL). (HF has strong corrosive effect on the skin. Pay attention to wear acid resistant gloves and operate in a fume cupboard in the laboratory. If unfortunately contact with skin, immediately wash with plenty of water flow for at least 15 minutes. Hydrofluoric acid burn treatment liquid (20 mL of 5% calcium chloride, 20 mL of 2% lidocaine, 5 mg of dexamethasone) used by soaking or wet compress in wound can relieve the pain effectively.) The effluent was collected in a 10 mL PFA vessel and evaporated on a hot plate to near dryness (about 0.05 mL) at 110 °C. Then, three drops of 30% H_2O_2 and concentrated HNO_3 were added in turn to decompose the organic residue and to effectively remove residue of hydrofluoric acid or hydrochloric acid. Finally, 2 mL of 2% HNO_3 containing Rh and Ir as internal standards was added to the PFA vessel, eventually becoming the nitric acid medium, so that the residual chloride ion is not enough to generate obvious polyatomic interference. This solution was then ready for elemental concentration measurement by ICP-MS.

2.4. Instrumentation and measurement

During the method setup, a quadrupole ICP-MS (Thermo-Scientific X series-2) was used in the conventional mode for semi-quantitative and

quantitative measurements of multi-elements. Calibration of ICP-MS is carried out with artificial solutions, using internal standardization with ^{103}Rh for ^{90}Zr , ^{93}Nb , ^{95}Mo and ^{118}Sn , ^{193}Ir for ^{176}Hf , ^{181}Ta , and ^{182}W . The concentration range of the calibration standards used is from 1 ng g^{-1} to 50 ng g^{-1} . Typical operating conditions for this instrument are given in Table 1.

For seawater analysis, samples and standards were introduced into the plasma through an Aridus II desolvating sample introduction system (CETAC Technologies, Omaha, NE, USA). This system removes water in the sample solutions by passing them through a desolvating membrane at $160\text{ }^\circ\text{C}$, thus providing a “dry” sample to the plasma. This increases introduction efficiency by a factor of 5–10 over the conventional sample introduction system. After each analysis, the sample was washed from the system over 10 minutes using a 2% HNO_3 solution, resulting in a negligible residual signal.

3. Results and discussion

3.1. Optimization of preconcentration conditions

ICP-MS performances in analyses of geological materials are often affected by interface effects, matrix effects (suppression or enhancement), polyatomic and isobaric interference, signal drift, and the memory effect. When bulk seawater samples are analyzed, high levels of salt content not only cause plugging of the sampling orifice, with a concomitant decrease in signal intensities, but they also cause severe matrix effects and potential spectral interference. The polyatomic species $^{56}\text{Fe}^{37}\text{Cl}^+$ and $^{56}\text{Fe}^{35}\text{Cl}^+$ can cause serious isobaric interference with $^{93}\text{Nb}^+$ (monoisotopic) and ^{91}Zr , respectively. Other sources of polyatomic interference include oxide species such as $^{74}\text{Ge}^{16}\text{O}^+$ and $^{74}\text{Se}^{16}\text{O}^+$ with $^{90}\text{Zr}^+$, $^{77}\text{Se}^{16}\text{O}^+$ with $^{93}\text{Nb}^+$, $^{162}\text{Dy}^{16}\text{O}^+$ with $^{178}\text{Hf}^+$, and $^{165}\text{Ho}^{16}\text{O}^+$ with $^{181}\text{Ta}^+$ [18]. Polyatomic ions such as $^{52}\text{Cr}^{40}\text{Ar}^+$, $^{55}\text{Mn}^{40}\text{Ar}^+$, $^{56}\text{Fe}^{40}\text{Ar}^+$, $^{60}\text{Ni}^{40}\text{Ar}^+$, and $^{80}\text{Se}^{16}\text{O}^+$ can also possibly interfere with Mo. Therefore, the separation procedure for Zr, Hf, Nb, Ta, Mo, W, and Sn from multi-elements solution by BPHA resin is discussed below.

3.1.1. Effect of different concentration of HCl on the removal of the matrix elements

The effects of HCl concentration on the removal of matrix elements, and the subsequent collection of Zr, Nb, Mo, Sn, Hf, Ta, and W by a BPHA resin column, were investigated in this study. When a higher concentration of HCl was employed to extract and elute the major elements, degradation of the resin and retention of part of the Fe, V, and Cr was observed on the column. Therefore, the concentration of HCl selected was between 0.5 and 3 mol L^{-1} .

Table 1
ICP-MS instrumentation and operating conditions.

Nebulizer	Micro-concentric MCN-100 (or CETAC)
Nebulizer pressure	1.5 mbar
Analyzer pressure	1.1×10^{-7} mbar
Expansion pressure	2.0 mbar
Ni sampling cone orifice	1.0 mm
Ni skimmer cone orifice	0.7 mm
Ar Auxiliary gas flow rate	0.8 L min^{-1}
Ar nebulizer gas flow rate	0.67 L min^{-1}
Ar cooling gas flow rate	14 L min^{-1}
Solution uptake rate	0.4 mL min^{-1}
Acquisition mode	Peak jumping
Channel per mass	3
Channel spacing and dwell time per sweep	0.02 ms and per point 30 ms
Detection mode	Pulse counting
Number of sweeps	150
Repeat integrations	5
Isotopes measured	^{90}Zr , ^{93}Nb , ^{95}Mo , ^{118}Sn , ^{176}Hf , ^{181}Ta , ^{182}W , ^{103}Rh and ^{193}Ir

Fig. 1a, b, and c showed the column effluent curves, corresponding to 0.5 mol L^{-1} HCl, 1 mol L^{-1} HCl, and 3 mol L^{-1} HCl as loading solution. As shown in Fig. 1a, c, and a large number of the major elements (e.g., Al,

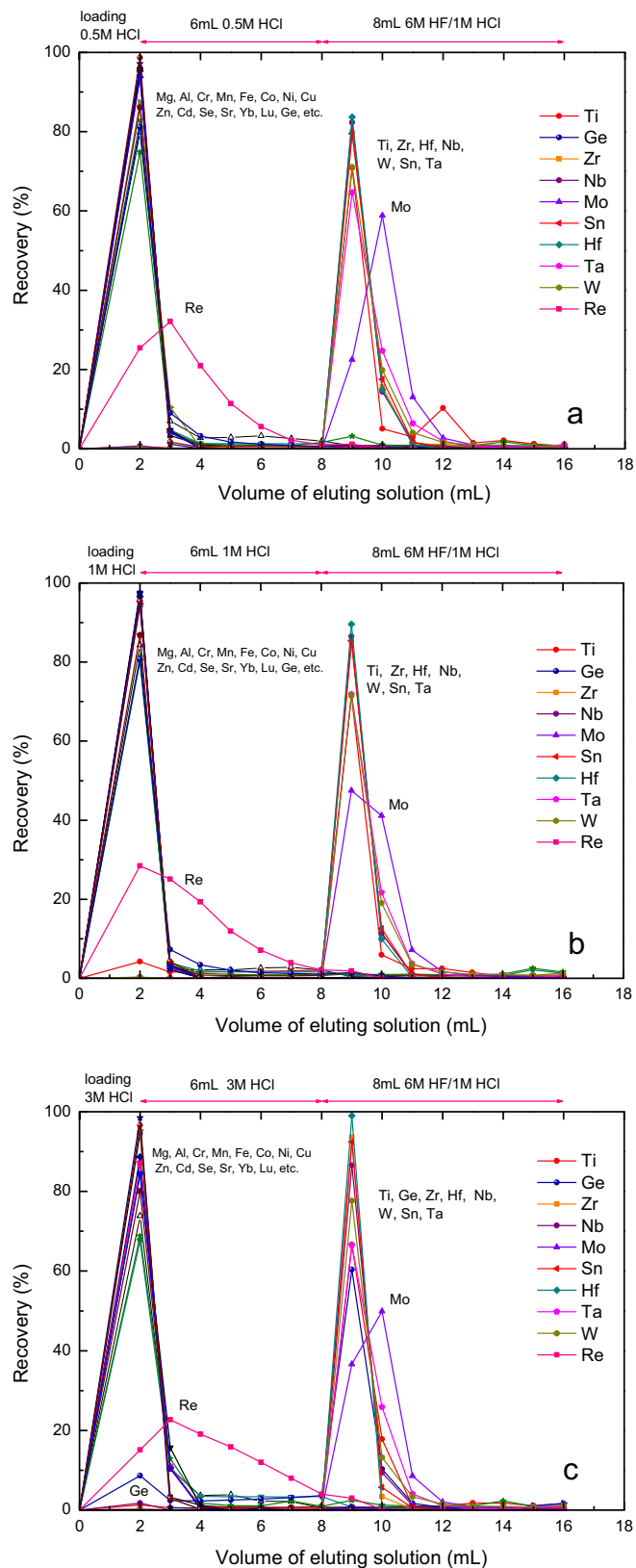


Fig. 1. The effect of different HCl concentrations in the loading solution on the removal of interference elements. a) 0.5 M HCl , b) 1 M HCl and c) 3 M HCl .

Table 2
Recoveries of the seven elements eluted by different concentrations of the HF/1 mol L⁻¹ HCl solution.

Eluting solution	Mean of recovery ± SD (%) (n = 3)						
	Zr	Nb	Mo	Sn	Hf	Ta	W
0.1 mol L ⁻¹ HF/1 mol L ⁻¹ HCl	97.32 ± 0.91	90.25 ± 0.91	1.04 ± 1.13	91.89 ± 2.13	97.77 ± 0.57	7.57 ± 1.51	90.19 ± 1.89
1 mol L ⁻¹ HF/1 mol L ⁻¹ HCl	98.11 ± 0.91	93.16 ± 1.35	20.12 ± 2.12	95.46 ± 0.50	99.35 ± 1.01	31.54 ± 1.11	91.13 ± 1.01
3 mol L ⁻¹ HF/1 mol L ⁻¹ HCl	98.31 ± 0.91	95.18 ± 0.68	31.11 ± 1.23	97.13 ± 2.10	99.50 ± 0.85	48.91 ± 0.51	93.95 ± 0.43
6 mol L ⁻¹ HF/1 mol L ⁻¹ HCl	99.06 ± 0.91	97.20 ± 1.53	97.56 ± 0.56	99.21 ± 0.73	99.93 ± 0.34	95.67 ± 0.89	98.24 ± 0.98

Fe, Mg, Li, Be, Co, Ni, Zn, Mn, Cu, Se, Rb, Sr, Y, Cd, Sb, Cs) and REEs did not adsorb onto the BPHA resin and could be eluted with 6 mL of 0.5–3 mol L⁻¹ HCl. More than 99% of Zr, Hf, Nb, Ta, Mo, W, and Sn were adsorbed on the BPHA resin. The results indicate that the alkali metals, alkaline earth metals, transition metals, and rare earth metals from MISA are not adsorbed by the BPHA resin, whereas the fluoride soluble group elements (e.g., Zr, Hf, Mo, Nb, Ta, Sn, W, Ti) are adsorbed on the BPHA resin. This is due to the chelation of BPHA to the elements of groups IVB (such as Ti, Zr, and Hf), VB (such as Nb and Ta) and VIB (such as Mo and W).

BPHA is relatively small size and stable at high acid concentrations, has π electrons abundantly and acts as a superior ligand for solvent extraction of IVB, VB and VIB elements on periodic table. Amberchrom CG-71 resin can adsorb or accept more BPHA, because it possesses excellent chemical and physical stability and contains relatively large number of active aromatic sites that allow π - π interactions. Thus, theoretically, this BPHA extraction chromatographic resin can adsorb tetra-, penta- and hexavalent elements such as Nb, Ta, Zr, Hf, Ti, Mo and W, while the alkali metals, alkaline earth metals, transition metals, and rare earth metals hardly adsorbed on the BPHA resin because of no chelation with BPHA. Actually, as expected, the results of loading column experiments reveal that the BPHA resin has high selective adsorption for Zr, Hf, Mo, W, Nb, Ta, and Sn.

These seven elements retained on the column could be stripped with a 6 mol L⁻¹ HF/1 mol L⁻¹ HCl solution (8 mL). For the three cases (0.5 mol L⁻¹ HCl, 1 mol L⁻¹ HCl, and 3 mol L⁻¹ HCl), stripped with a 6 mol L⁻¹ HF/1 mol L⁻¹ HCl, the residual concentrations of the major elements (such as Mn, Fe, Ni, etc.) in the analyte solution were very low ($\sim 10^{-1}$ ppt), and REEs were not detected in the analyte solution by Q-ICP-MS. The element Ge was detected in the analyte solution when 3 mol L⁻¹ HCl was used as the eluent, probably due to a chelated complex being adsorbed on the BPHA resin. Ge was recovered in the collection solution by eluting with a 6 mol L⁻¹ HF/1 mol L⁻¹ HCl solution. To avoid this problem, as well as the polyatomic interference of chloride species, and taking into account reagent contamination, a concentration of 0.5–1 mol L⁻¹ of HCl was deemed suitable for the separation procedure.

3.1.2. Effect of different concentration of HF on the recoveries of Zr, Nb, Mo, Sn, Hf, Ta and W

The effect of HF concentration on the stripping efficiency of Zr, Hf, Mo, W, Nb, Ta, and Sn from the column was investigated using a MISA 05-1 solution containing Zr, Nb, Mo, Sn, Hf, Ta, and W (2 μ g each, replicate 3 experiments). The results obtained by Q-ICP-MS are shown in Table 2. As shown in Table 2, the recoveries of Zr, Hf, Nb, Ta, Sn, Mo and W increased with the increase of the eluent concentration of HF. The recoveries of Zr, Hf, Nb, Sn, and W were achieved more than 90%, when eluted with 4 mL of 0.1 mol L⁻¹ HF/1 mol L⁻¹ HCl solution, even up to 99.9% eluted with 6 mol L⁻¹ HF/1 mol L⁻¹ HCl.

Obviously, elution with more diluted HF molar concentrations led into poor recovery of these elements. A lower concentration of HF was insufficient elute Mo and Ta, but Mo and Ta were gradually eluted from the column if the concentration of HF was above 1 mol L⁻¹, and mostly obtained by using a 6 mol L⁻¹ HF/1 mol L⁻¹ HCl solution (4 mL). These phenomena indicate that Zr, Hf, Nb, Sn, and W would be hardly retained on BPHA resin at low concentrations of HF

(0.1 mol L⁻¹), whereas Ta and Mo would remain largely unaffected. On the one hand, these are probably because that HF can form very stable fluoride complexes with Zr, Hf, Nb, Sn, W, Mo and Ta ions. 0.1 mol L⁻¹ of fluoride ion can disrupt binding between BPHA with Zr, Hf, Nb, Sn and W, while it is not enough to compete with the BPHA and to form fluoride complexes of Mo and Ta. In addition, these phenomena indicate that the complex stability constants of Zr, Hf, Nb, Sn and W with the fluoride ion are much higher than those of Mo and Ta. Thus, only higher concentration of fluoride ion in high acidity can form molybdenum fluoride complexes and tantalum fluoride complexes. The concentration of fluoride ion in the exchange column increased with the increase of the concentration of HF as eluent, resulting in competition between fluoride ion and BPHA with Mo or Ta, and destroyed the chelation of BPHA resin for Mo and Ta. Thus, Mo and Ta (maybe as the form of MoF₈²⁻ and TaF₆⁻) were washed down into the solution, and flowed out the BPHA resin column.

On the other hand, this observation reveals that the affinity of BPHA resin for Mo and Ta is much larger than that for Zr, Hf, Nb, Sn and W, and BPHA deserves to be called a tantalum specific reagent. Certainly, it also reflects that the presence of fluoride ion has a negative effect on the extraction of Zr, Hf, Nb, Ta, Sn, Mo, and W by BPHA resin. Interestingly, this investigation provides a potential method for separation of Zr, Hf, Nb, W, and Sn from Mo and Ta.

3.1.3. Elution curve of Zr, Nb, Mo, Sn, Hf, Ta and W

The separation and elution profile for Fe, Mn, Cr, Ti, Rb, Sr, La, Zr, Hf, Nb, Ta, Sn, Mo, and W in the MISA standard is shown in Fig. 2. By using 1 mol L⁻¹ HCl as an eluent, major elements (e.g., Al, Mg, Fe, Mn, Cu, Co, Ni, Zn) and REEs were completely removed. Although the isobaric interference caused by Ti was insignificant, Ti could cause matrix effects and lead to clogging of the sampling cone. Thus, Ti was subsequently eluted with a 1 mol L⁻¹ HCl/0.4% H₂O₂ solution, which further resulted in the

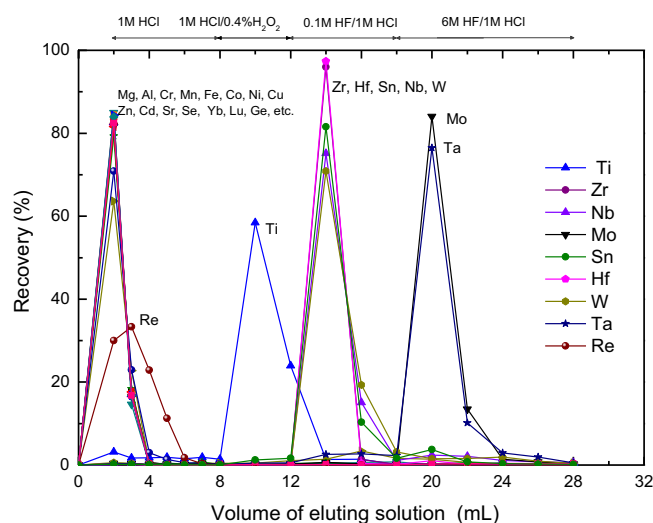


Fig. 2. Elution curves of selected elements for the BPHA resin preconcentration procedure described in this study.

Table 3
Recovery of elements from spiked seawater.

Mean \pm SD ($n = 4$)	Samples	Zr	Nb	Mo	Sn	Hf	Ta	W
Concentrations (pg g ⁻¹)	Unspiked Atlantic seawater	26.3 \pm 0.7	1.8 \pm 0.2	10144 \pm 171	87.34 \pm 5.9	1.1 \pm 0.3	1.3 \pm 0.3	19.0 \pm 0.5
	Unspiked GBW(E) 080040	30.6 \pm 0.1	3.0 \pm 0.2	9550 \pm 88	20.64 \pm 0.7	1.5 \pm 0.2	1.0 \pm 0.1	24.6 \pm 0.3
Recovery (%) = $(C_{\text{spiked seawater value}} - C_{\text{unspiked seawater value}}) \times V/20 \times 100\%$	Spiked Atlantic seawater	99.9 \pm 2.8	98.2 \pm 1.1	98.4 \pm 2.4	103.0 \pm 0.8	100.8 \pm 0.9	95.2 \pm 0.6	101.5 \pm 0.8
	Spiked GBW(E) 080040	99.4 \pm 2.7	101.1 \pm 2.8	98.7 \pm 1.2	102.7 \pm 1.8	102.9 \pm 2.2	96.4 \pm 1.3	100.6 \pm 0.9

separation of the seven elements Zr, Hf, Mo, W, Nb, Ta, and Sn from the interference elements. Finally, these seven elements were stripped with a 0.1 mol L⁻¹ HF/1 mol L⁻¹ HCl solution and a 6 mol L⁻¹ HF/1 mol L⁻¹ HCl solution. As shown in Fig. 2, the concentrations of the interference and matrix elements associated with the analytes after separation were reduced to trace levels, thereby eliminating the possibility of significant interference and matrix effects.

In addition, most of the elements (Zr, Nb, Sn, Hf, and W) were hardly retained on BPHA resin stripped with a 0.1 mol L⁻¹ HF/1 mol L⁻¹ HCl solution, as expected, whereas Mo and Ta still remained on the column and were eluted with a 6 mol L⁻¹ HF/1 mol L⁻¹ HCl solution (10 mL). None of the matrix elements, REEs, or Ti, Zr, Hf, Sn, Nb, and W were detected in the 6 mol L⁻¹ HF/1 mol L⁻¹ HCl effluent liquid from the BPHA resin, whereas quantities of Ta (95.67%) and Mo (97.56%) were extracted and detected.

According to the recovery data of the seven elements (Zr, Nb, Sn, Hf, W, Ta, and Mo) and the interference elements shown in Fig. 1b and Fig. 2, it should be noted that 5 mL of 1 mol L⁻¹ HCl is enough to remove interference elements from the analyte. The eluting volume of 6 mol L⁻¹ HF/1 mol L⁻¹ HCl solution to extract Zr, Nb, Sn, Hf, W, Ta and Mo, can be reduced to 6 mL or even 4 mL. Combined with the results of Table 2, the recoveries can be achieved more than 99% for Zr, Sn and Hf, 98% for W, 97% for Nb and Mo, and 95% for Ta, respectively.

3.2. Recovery of the separation procedure

To test the recovery of the procedure, the standard addition technique was adopted to evaluate the degree of accuracy of this proposed method. Samples of coastal or Atlantic Ocean seawater (20 mL) with concentrated HCl (2 mL) added were spiked with MISA 05-1 standard solution (20 ng; replicate four experiments), and directly loaded on BPHA chelated resin. The above procedure was repeated with the same seawater samples (20 mL) unspiked, and results of the spiked and unspiked seawater were compared. Seawater was separated and preconcentrated by BPHA resin and eluted with a 6 mol L⁻¹ HF/1 mol L⁻¹ HCl solution. The procedural recovery was evaluated, and

the mean values were from 95.2% to 103.0% as shown in Table 3. The results show that the seven metals were quantitatively recovered with good precision (<3%) and good repeatability.

3.3. Detection limits

The ICP-MS instrumental detection limits for each analyte (Zr, Hf, Nb, Ta, Mo, W, and Sn) were calculated based on three times the standard deviation of 10 determinations of 2% HNO₃ blank solution. The results obtained before (a) and after (b) installing an Aridus II desolvating sample introduction system are compared in Table 4. The new interface enhances the performance significantly; the measured detection limits are in the range of 0.04–0.35 ppt, compared with 0.5 ppt for Zr, 0.2 ppt for Nb, 1.7 ppt for Mo, 1.0 ppt for Sn, 0.1 ppt for Hf, 0.1 ppt for Ta, and 0.3 ppt for W when using the conventional interface. In this work, the high sensitivity method was used for Zr, Hf, Nb, Ta, Sn, and W of blank measurements and seawater samples only.

3.4. Total method blanks

For the enrichment and separation method, a low total method blank is crucial in the determination of ultra-trace metals in seawater. Therefore, further work is required to assess blank levels for the method. The total method blank was obtained through the acidification of concentrated HCl, column extraction, evaporation and determination using the same procedure and same volume of solution as those used for the seawater samples. The results are shown in Table 5, together with the method detection limit (MDL), which was calculated from three times the standard deviation of four replicate experiments. Total method blanks ($n = 4$, 2 mL of solution) were varied from 1.2 to 2.9 pg, 0.8 to 1.8 pg, 1.5 to 2.9 pg, 3.4 to 6.1 pg, 0.2 to 0.6 pg, 1.9 to 2.6 pg, and 6.1 to 9.7 pg, for Zr, Nb, Mo, Sn, Hf, Ta, and W, respectively. The range of the total method blanks is much lower than that of the other chemical procedures [15], due to the relatively small volume of resin, HCl, and HF used. The total method blanks of Sn and W were comparatively high, although the total blank contribution was consequently

Table 4
Instrumental detection limits.

Elements	Zr	Nb	Mo	Sn	Hf	Ta	W
Isotope	91	93	95	118	178	181	182
Abundance	11.22%	100%	15.92%	24.22%	27.28%	99.99%	26.5%
Detection limit (pg mL ⁻¹)	a						
	b						
	0.5	0.2	1.7	1.0	0.1	0.1	0.3
	0.12	0.06	0.35	0.19	0.04	0.04	0.09

Table 5
Method blank and method detection limits.

Replicates	Method blank (pg mL ⁻¹)						
	Zr	Nb	Mo	Sn	Hf	Ta	W
No. 1	1.2	0.8	2.9	3.4	0.6	2.4	6.1
No. 2	1.9	1.8	2.0	6.1	0.2	2.1	9.0
No. 3	2.9	1.2	1.5	5.0	0.6	2.6	9.7
No. 4	1.3	1.0	2.1	3.9	0.5	1.9	6.1
Mean \pm SD	1.8 \pm 0.8	1.2 \pm 0.4	2.1 \pm 0.6	4.6 \pm 1.2	0.5 \pm 0.2	2.3 \pm 0.3	7.7 \pm 1.9
MDL	2.4	1.3	1.7	3.6	0.6	0.9	5.7

Table 6
Concentrations of Zr, Hf, Mo, W, Nb, Ta, and Sn in seawater samples.

Seawater samples			Mean \pm σ ($n = 9$)						
			Zr (pg g ⁻¹)	Nb (pg g ⁻¹)	Mo (ng g ⁻¹)	Sn (pg g ⁻¹)	Hf (pg g ⁻¹)	Ta (pg g ⁻¹)	W (pg g ⁻¹)
NASS-6			35.0 \pm 6.0	2.5 \pm 1.0	8.18 \pm 0.04	97.3 \pm 4.1	0.7 \pm 0.2	2.0 \pm 1.0	15.7 \pm 2.2
CASS-5			37.1 \pm 6.3	1.9 \pm 0.6	8.05 \pm 0.03	105.1 \pm 3.2	0.9 \pm 0.2	1.9 \pm 1.2	18.5 \pm 1.0
Pacific Ocean seawater	10° 04' N 154° 24' W	5 m	19.5 \pm 5.4	1.4 \pm 0.3	8.57 \pm 0.17	146.5 \pm 2.9	0.5 \pm 0.1	1.3 \pm 0.8	37.3 \pm 2.5
		100 m	21.4 \pm 6.2	1.7 \pm 0.2	8.72 \pm 0.58	139.8 \pm 3.6	0.6 \pm 0.3	1.1 \pm 0.5	20.3 \pm 0.1
	200 m	18.5 \pm 5.1	2.0 \pm 0.2	9.20 \pm 0.08	101.2 \pm 6.4	0.4 \pm 0.2	0.8 \pm 0.4	18.8 \pm 3.8	
	5148 m	34.7 \pm 6.6	2.8 \pm 0.4	9.55 \pm 0.27	146.4 \pm 3.5	0.7 \pm 0.2	0.9 \pm 0.3	30.6 \pm 1.1	
	20° 02' N, 161° 32' E	0 m	22.7 \pm 3.5	1.6 \pm 0.2	9.13 \pm 0.11	180.0 \pm 0.20	0.5 \pm 0.2	1.5 \pm 0.3	66.9 \pm 3.7
	21° 19' N, 126° 33' E	0 m	37.3 \pm 9.9	3.1 \pm 0.1	8.68 \pm 0.11	138.8 \pm 2.5	1.2 \pm 0.1	1.3 \pm 0.3	138.7 \pm 9.0
NASS-5 reference [13]			16.69 \pm 0.82	0.72 \pm 0.08			0.22 \pm 0.04	0.05 \pm 0.03	6.80 \pm 0.74
CASS-3 reference [19]			8.21	0.62	8.15		0.09	0.04	7.90

no more than 1.5% and 3.2% of the quantity of Sn (0.020 ng g⁻¹) and W (0.015 ng g⁻¹), respectively, in 20 mL of seawater, and had no discernable effect on the measurement of Sn and W in the seawater samples. The MDL for this method was 2.4, 1.3, 1.7, 3.6, 0.6, 0.9, and 5.7 pg g⁻¹ for Zr, Nb, Mo, Sn, Hf, Ta, and W, respectively. Compared to the concentrations of these metals in seawater, the method blank and MDL are low enough to make it possible to analyze seawater samples successfully with this method.

3.5. Application of the analytical technique

To validate the applicability and suitability of this method to seawater, two filtered coastal seawater reference materials, CASS-5 and NASS-6, were employed. In addition, application assays of six filtered seawater samples were conducted (Table 6). Four samples were collected from water depths of 5 m, 100 m, 200 m and 5148 m at station 10° 04' N, 154° 24' W in the Pacific Ocean, one sample was collected in the middle of the Pacific Ocean surface (20° 02' N, 161° 32' E) and one sample was collected in the Philippine Sea surface (western Pacific) (21° 19' N, 126° 33' E). Because of the lack of information in the current literature on metal concentrations in certified and natural seawater, and to obtain accurate data, the experiments for these seawater samples were repeated nine times. As shown in Table 6, the values of the NASS-6 and CASS-5 were found to be consistent with the values of NASS-5 and CASS-3 reported by Firdaus et al. [13,19]. The values of the six seawater samples in Pacific Ocean are in agreement with the values in the Western North Pacific Ocean provided by Firdaus et al. [19]. These results indicate the practicability of the current method.

4. Conclusions

The detailed experimental data analyzed by ICP-MS indicate that BPHA chelated resin has high selective adsorption for Zr, Nb, Mo, Sn, Hf, Ta, and W. Elution curves indicate that the elements that form virtually all concomitant matrix species were separated with a single pass small volume of BPHA chelated resin (0.5 mL). A new separation

procedure and method, based on a BPHA chelated resin and ICP-MS analysis, was evaluated for the concomitant determination of Zr, Nb, Mo, Sn, Hf, Ta, and W at low levels in seawater using 6 mol L⁻¹ HF/1 mol L⁻¹ HCl solution as eluent. The method separates Zr, Nb, Mo, Sn, Hf, Ta, and W as a group from other matrix interference and has proved to be an ideal separation method compared with existing methods [4,9,11] due to its simplicity and separation efficiency. This method successfully analyses very low levels of Zr, Hf, Nb, Ta, W, and Sn, and Mo in seawater, and could become a routine method for determining these elements in seawater samples.

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