



# 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<sup>-1</sup> HF/1 mol L<sup>-1</sup> 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, MoO<sub>4</sub><sup>2-</sup> and WO<sub>4</sub><sup>2-</sup>, 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)<sub>5</sub><sup>-</sup>, Hf(OH)<sub>5</sub><sup>-</sup>, Nb(OH)<sub>6</sub><sup>-</sup>, and Ta(OH)<sub>6</sub><sup>-</sup> [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<sup>-1</sup> 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  $\mu\text{m}$ , 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  $\text{HNO}_3$ , were purified by DST-1000 Sub-Boiling Stills (Savillex 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%  $\text{HNO}_3$  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  $\text{L}^{-1}$  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  $\mu\text{g}$ ) was diluted in 2 mL of 0.5 mol  $\text{L}^{-1}$  HCl, 1 mol  $\text{L}^{-1}$  HCl, and 3 mol  $\text{L}^{-1}$  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  $\text{L}^{-1}$ , 1 mol  $\text{L}^{-1}$  and 3 mol  $\text{L}^{-1}$  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  $\text{L}^{-1}$ . 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  $\text{L}^{-1}$  HCl (6 mL), which would effectively remove matrix elements and interference (Fe, Mn, Cu, Zn, Ni, REEs etc.) from the sample.

A 1 mol  $\text{L}^{-1}$  HCl/0.4%  $\text{H}_2\text{O}_2$  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  $\text{L}^{-1}$  HF/1 mol  $\text{L}^{-1}$  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%  $\text{H}_2\text{O}_2$  and concentrated  $\text{HNO}_3$  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%  $\text{HNO}_3$  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

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