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Extraction chromatographic separations of tantalum and tungsten from hafnium and complex matrix constituents

Mathew S. Snow[a,*], Martha R. Finck[a], Kevin P. Carney[a], Samuel S. Morrison[b]

[a] Idaho National Laboratory, PO Box 1625, Idaho Falls, ID, 83415-2805, USA
[b] Pacific Northwest National Laboratory, PO Box 999, MSIN J4-80, 902 Battelle Blvd, Richland, WA, 99352, USA

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ABSTRACT

Tantalum (Ta), hafnium (Hf), and tungsten (W) analyses from complex matrices require high purification of these analytes from each other and major/trace matrix constituents, however, current state-of-the-art Ta/Hf/W separations rely on traditional anion exchange approaches that show relatively similar distribution coefficient (Kd) values for each element. This work reports an assessment of three commercially available extraction chromatographic resins (TEVA, TRU, and UTEVA) for Ta/Hf/W separations. Batch contact studies show differences in Ta/Hf and Ta/W Kd values of up to 10^6 and 10^4 (respectively), representing an improvement of a factor of 100 and 300 in Ta/Hf and Ta/W Kd values (respectively) over AG1 × 4 resin. Variations in the Kd values as a function of HCl concentration for TRU resin show that this resin is well suited for Ta/Hf/W separations, with Ta/Hf, Ta/W, and W/Hf Kd value improvements of 10, 200, and 30 (respectively) over AG1 × 4 resin. Analyses of digested soil samples (NIST 2710a) using TRU resin and tandem TEVA-TRU columns demonstrate the ability to achieve extremely high purification (>99%) of Ta and W from each other and Hf, as well as enabling very high purification of Ta and W from the major and trace elemental constituents present in soils using a single chromatographic step.

1. Introduction

Tantalum isotope analyses are a valuable analytical tool for geochemical and cosmochemical studies [1,2]. Tantalum contains two stable isotopes, with ^{181}Ta being the most abundant form of tantalum (99.988% abundant) and ^{180}Ta being much less abundant (0.012% abundant). ^{180}Ta is an important isotope as it is the rarest stable isotope found in nature and is the only naturally occurring isotope that exists in a stable isomeric state; ^{180}Ta's formation pathways in supernovas are currently under investigation via modeling and high precision mass spectrometry studies [1,2]. Tantalum concentration analyses are also of value to geological studies, where Ta concentrations in samples are frequently compared to concentrations of chemically similar Nb for studying mantle derived melts and chrondritic samples [3,4], and to mineral exploration/industrial studies, where tantalum recovery from mineral deposits for electronics, optics, aerospace, nuclear and other industrial uses represents a growing industry [5,6].

High precision elemental and isotopic analyses of tantalum require high purification from any potential isobaric interferences. While ^{181}Ta has no atomic isobars, the separation of neighboring elements Hf and W are essential for analyses of the minor isotope ^{180}Ta as both Hf and W have stable isotopes that interfere with ^{180}Ta analysis (with ^{180}Hf representing 30.08% of natural Hf and ^{180}W representing 0.12% of naturally occuring tungsten). Conversely, analyses of the isotopic composition of Hf and W samples, which form a basis for age dating and neutron flux estimates from meteors and extrasolar particles, also benefit from complete separation of Ta, Hf, and W prior to analysis by mass spectrometry [7,8].

Current state-of-the-art Ta analytical separation techniques rely on purification of Ta from Hf, W and from the bulk matrix using anion exchange chromatography [9–13]. Ta/Hf/W separations are facilitated by differences in the expected oxidation state of each element, where in aqueous solutions Ta prefers the pentavalent oxidation state, Hf the tetravalent state, and W the hexavalent state. Although anion exchange techniques have been proven to be very robust, traditional anion exchange chromatography separations for Hf, Ta, and W show relatively similar distribution coefficient values (defined as the concentration of analyte in the solid phase divided by the concentration in the aqueous phase) [10,11]. These inefficient separations often result in the requirement for multiple separation columns in order to achieve high degrees of purification of each analyte required for the abovementioned applications.

* Corresponding author.
E-mail address: mathew.snow@inl.gov (M.S. Snow).

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Extraction chromatographic resins (such as TEVA, UTEVA, and TRU resins from Eichrom Technologies) provide a potential alternative to traditional anion exchange techniques. Since the active sites on extraction chromatographic resins are in a liquid form (bound to a stationary phase via hydrophobic interactions) these sites have more flexibility to coordinate around ions in solution. This feature potentially enables much higher affinities and faster kinetics for binding ions than traditional ion exchange resins, resulting in improved separation efficiencies [14]. Surprisingly, despite the promise of these techniques, to our knowledge no studies on the separation of Ta, Hf, and W using these resins have been reported in the literature to date.

This work reports a systematic analysis of several chromatographic resins (TEVA, TRU, and UTEVA) for separating W, Hf, and Ta. Initial batch contact studies with varying concentrations of HCl, HNO_3, and HF were performed as a precursor to designing targeted chemical separation approaches for each element. Column separation studies based upon the batch contact studies and using pure Ta/Hf/W solutions were performed to demonstrate the potential separation capabilities of each resin, with results from extraction chromatography being compared directly to those obtained using traditional anion exchange techniques under the same chromatographic conditions. Finally, the effectiveness of TEVA and TRU resins for purifying Ta and W from Hf and major/minor elements in complex matrices was evaluated via separations from soil digestate samples (NIST SRM 2710a).

2. Materials and methods

All acids utilized in this work were Trace Metals Grade or better. TEVA, TRU, and UTEVA resins were obtained from Eichrom Technologies, while analytical grade anion exchange resin (AG 1 × 4, Cl^-, 100–200 mesh) obtained from Bio-Rad was utilized to represent the general behavior expected for typical strong anion exchange resins.

Stock solutions containing pure Ta, Hf, and W for distribution coefficient and initial chromatographic studies were prepared using high purity solid reagents (>99.99%, Aldrich). A small quantity of each metal was added to individual 30 mL Savillex vials. 2 mL concentrated HF and 1 mL concentrated HNO_3 were added to each vial following which vials were capped and heated on a hotplate at 130 °C for 45 min to achieve complete dissolution. While necessary for dissolving the initial solid samples, the later usage of low concentrations of HF (0.02 M) was also required to keep W stable as a dissolved analyte in solution. Appropriate aliquots of each solution were then obtained and diluted to create stock solutions containing 2 ppm of each metal in 0.01, 0.1, 1, 3, 6, and 9 M HCl and HNO_3 solutions (with 0.02 M HF in each) in preparation for distribution coefficient studies.

2.1. Distribution coefficient studies

Distribution coefficient values were calculated using the equation below:

$$K_d\left(g/g\right) = \frac{[X]_{solid}}{[X]_{aqueous}} \quad (1)$$

where Kd represents the distribution coefficient, $[X]_{solid}$ represents the concentration of analyte X bound to the solid phase, and $[X]_{aqueous}$ represents the concentration of analyte X present in the aqueous phase. All measurements were performed gravimetrically. Kd values were determined via batch contact experiments and were calculated as the mass of analyte in the solid phase (in units of ng analyte/g resin) divided by the mass in the aqueous phase (ng analyte/g solution). Prior to sorption experiments, the anion exchange resin was dried in an oven at 40 °C for 15 h; TEVA, TRU, and UTEVA resins were utilized directly without prior treatment. After drying, 0.1 g of each resin were weighed into 15 mL polyethylene centrifuge tubes (Corning), following which 5 mL of the 2 ppm metal solution was added to each centrifuge tube. Tubes were then capped, sealed with parafilm placed on an orbital mixer and mixed at a rate of ~45 rpm for 24 h. After 24 h, samples were centrifuged or filtered using a 0.45 μm filter, and 100 μL aliquots were obtained. Aliquots were then diluted with 2% HNO_3 + 0.02 M HF prior to mass spectrometric analysis.

2.2. Initial column separations

Optimal conditions for chromatographic separations were determined based on results from distribution coefficient studies. Side-by-side chromatographic comparisons were performed using 2 mL Bio-Rad poly-prep columns that were packed with 2 mL of the appropriate resin (either TEVA, TRU, or AG1 × 4). For extraction chromatographic studies, a top frit was utilized (Porex Technologies, 90–130 μm). Columns were preconditioned with 10 mL 6 M HNO_3 + 0.02 M HF followed by 10 mL of the matrix used as the load solution (3 M HCl + 0.02 M HF or 0.1 M HNO_3 + 0.02 M HF for TEVA separations, 6 M HCl + 0.02 M HF for optimized TRU separations, and 6 M HNO_3 + 0.02 M HF for AG1 × 4 separations).

5 mL solutions containing 2 ppm of each metal in the appropriate load solution matrix were loaded onto each column using three 1 mL rinses of the same matrix as the load solution (without the analytes present). 20 mL of the solution containing the same matrix as the load solution (without the analytes present) was then added to each column in 5 mL aliquots, followed by 50 mL of 6 M HNO_3 + 0.02 M HF. 100 μL of each elution fraction were extracted and diluted to 10 mL in 2% HNO_3 + 0.02 M HF prior to analysis by inductively couple plasma-mass spectrometry (ICP-MS).

2.3. Soil sample analyses

To test the performance of each separation procedure with complex matrices, samples of a highly refractory soil (NIST 2710a) were digested and subjected to the various separation schemes (Fig. 1). Soils samples were digested using a MARS 6 (CEM) microwave digestion system. 0.5 g of dried soils were added to individual CEM microwave digestion vessels containing 4 mL concentrated HNO_3 + 4 mL concentrated HF and digested using the microwave digestion protocol described elsewhere [15]. Following digestion, samples were evaporated to dryness, reconstituted in 5 mL of the appropriate matrix (6 M HCl + 0.02 M HF for TEVA/TRU, 6 M HCl + 0.02 M HF for TRU, and 6 M HNO_3 + 0.02 M HF for AG1 × 4) and remicrowaved. Samples were then filtered using a 0.45 μm filter and the mass of the resulting solution was quantified gravimetrically. A 100 μL aliquot of the filtrate was obtained for ICP-MS analysis and the remaining 4.9 mL of solution were split into two equal 2.45 mL fractions prior to transferring to columns for separations.

Three column separation schemes were tested using soil sample digestate solutions: 1) tandem TEVA/TRU separations using prepacked EICHROM TEVA/TRU cartridges, 2) 2 mL Bio-Rad columns packed with TRU resin, and 3) 2 mL Bio-Rad columns packed with AG 1 × 4 resin. For tandem TEVA/TRU separations, columns were preconditioned using 10 mL 6 M HNO_3 + 0.02 M HF followed by 10 mL 6 M HCl + 0.02 M HF. Soil digestate solutions were transferred to the columns with three 1 mL rinses followed by 10 mL of 6 M HCl + 0.02 M HF. TEVA/TRU columns were then separated and an additional 10 mL of 0.1 M HNO_3 + 0.02 M HF and 30 mL of 6 M HNO_3 + 0.02 M HF were added to the TEVA column, while 30 mL 1 M HCl + 0.02 M HF was added to the TRU column. For separations using a 2 mL Bio-Rad column packed with TRU resin, soil digestate solutions (in 6 M HCl + 0.02 M HF, as opposed to 9 M HCl + 0.02 M HF as used during initial TRU column experiments, see