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Characterization of Group 5 Dubnium Homologs on Diglycolamide Extraction Chromatography Resins from Nitric and Hydrofluoric Acid Matrices

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Summary. A diglycolamide-based resin was characterized for Group 5 (Ta, Nb and pseudo-homolog Pa) separation from Group 4 (Hf and Zr) and tri-valent actinides (Am). The batch uptake of the radionuclides of interest were determined for HNO₃/HF matrices and the results were used to develop a column separation method that could be used for Element 105 (Db) purification chemistry. Tantalum is significantly retained by the TODGA resin, while Pa/Nb show little to no retention. The affinity for Ta decreases as a function of increased [HNO₃], while Zr/Hf (and Am) affinities increase under the same conditions. Adsorption of Ta to polypropylene vials and column frits became a significant focus of this work following several observations made during the course of the column separation method development. All of the Group 5 elements were separated from Group 4 and Am while Ta may be completely isolated from Nb/Pa with the TODGA resin with improvements in column parameters: column height and bed volume.

1. INTRODUCTION

Studies of the chemical properties of the heaviest elements have traditionally been a challenging endeavor due to the short half-lives and low production rates of the nuclides of interest. Chemical systems must offer fast kinetics, such that the properties being studied can be achieved before the nuclide decays into another species. The system must also be rapidly repeatable over a sustained period of time to gain statistically valid results; therefore automation is a key focus. Prior to designing and constructing an automated system, a suitable chemical separation method must be developed and tested.

Various extraction techniques have been employed to predict the fundamental chemistry of element 105, dubnium (Db), based on its chemical homologs (Group 5 elements) and pseudohomolog, Pa. Ion-exchange

and solvent-extraction studies have shown that the chemical behavior of Db is highly dependent on the matrix conditions and extraction media [1-7]. In some cases, Db behaved most similarly to Ta, its closest chemical homolog [8-10] and in others, Db extraction behavior fell between those of Pa and Nb [11,12]. Predicting the behavior of Db and its homologs is complicated by the tendency of the Group 5 metal ions to hydrolyze, forming both non-neutral and neutral polyatomic species that may be less extractable for a given chemical system [10,13]. Initial Db chemistry studies focused on complexes formed in strong halide or mixed halide acid matrices [9,11,12,14]. In more recent studies, the chemical properties of Db [1,2,15], Rf [16-18] and their homologs have been characterized in HNO₃/HF and pure HF matrices. The results of these studies suggest that Rf forms weaker fluoro- complexes than those formed by its homologs whereas Db forms complexes similar to those of Pa.

In addition to characterizing the fundamental chemistry of Db, it is important to have a high degree of separation between the Group 4 and 5 species. Work performed at the Lawrence Berkeley Laboratory in Berkeley, CA provided evidence of an electron capture (EC) decay branch for the ²⁶³Db (*t*_{1/2} ~ 27-s half-life) produced in the reaction ²⁴⁹Bk(¹⁸O, 4n) using cation exchange columns and α -hydroxy isobutyric (α -HIB) acid [6]. Subsequent studies performed at the Paul Scherrer Institute in Villigen, Switzerland, combined α -HIB column elution and solvent extraction by tributyl phosphate (TBP)/cyclohexane further isolated ²⁶³Rf (EC daughter of ²⁶³Db), establishing a decay branch of approximately 3% [7]. Isolation of the Group 4 and 5 species is also necessary for distinguishing the terminus of the Element 115 decay chain [19]. In experiments performed at the Flerov Laboratory for Nuclear Reactions, Joint Institute for Nuclear Research, in Dubna, Russia an isotope of Element 115 with a mass number of 288 was produced by bombardment of a ²⁴³Am target with ⁴⁸Ca ions, ²⁴³Am(⁴⁸Ca, 3n)²⁸⁸115 [20, 21]. Five alpha transitions were observed prior to the terminating spontaneous fission event which was assigned to ²⁶⁸Db (*t*_{1/2} ~ 23.1 h); however, electron capture decay of the odd-odd ²⁶⁸Db nucleus followed by the spontaneous fission of ²⁶⁸Rf (*t*_{1/2} ~ 1.5 s) could not be excluded. The experiments in 2004 [20] suggested that the chemical properties of the terminating nucleus were similar to either Group 4 or Group 5 species, while those conducted in 2005 [21] provided evidence of Ta-like behavior (Group 5).

The combined Group 4 and 5 chemical separation methods performed in [6] and [7] are suitable for determining the terminus of Element 115 – however, the added step of liquid-liquid extraction adds a level of complexity to the automated system when compared with a single- or dual-stage column procedure. The goal of this work was to determine if a single-stage column procedure could be developed for Group 4 and 5 chemical

separations. A commercially available extraction chromatography (EXC) resin was evaluated as a potential candidate for the separation of Db homolog/pseudohomologs from each other as well as from potential interfering elements and matrix constituents, such as the Group 4 Rf homologs, actinides and lanthanides. The resins (50-100 μm diameter) are coated with N,N,N',N'-tetra-n-octyldiglycolamide (TODGA) which separates analytes based on size and charge characteristics of the solvated metal species [22]. Initial TODGA characterization studies reported a high degree of selectivity for tri-, tetra- and hexavalent metal ions in various acidic media with fast kinetics, and extractant-resin stability in nitric and hydrochloric acid matrices [22-25]. These resins have been used to separate short-lived activation products from light-ion irradiated lanthanide target material [26]. For heavy-element experiments where a target is bombarded with a heavy-ion beam, the dominant material collected on a catcher foil will be actinide transfer and fission products. In previous work the high affinity of TODGA for the +3, +4, and +6 actinides was demonstrated [22,23,27]; therefore, this resin could also be used to effectively remove the actinides from the initial sample matrix if loaded from a solution of high HNO_3 concentration. The Group 5 elements could then be further isolated using sequential elutions from an anion exchange resin which is capable of separating Nb and Zr in HNO_3 matrices.

Batch experiments were conducted to determine the extraction efficiency of TODGA for Group 4 and Group 5 species in a mixed HNO_3/HF system. Addition of the F^- ion hinders formation of polyatomic species that may be less extractable [1]. We used the results of the batch experiments to design a series of column experiments to test the chemical system for its effectiveness of separating Group 5 elements in a configuration that can be automated. The ultimate goal of this research is to establish an effective separation scheme for Db that removes all other interfering elements while providing key information as to the chemical behavior of Db in the given chemical system.

2. EXPERIMENTAL

2.1 Reagents and Materials

The TODGA resin (50-100 μm , 40% w:w, Eichrom Industries, Inc.) was used for both batch and column separation experiments. All acid solutions were prepared from reagent grade acids and de-ionized water (18 $\text{M}\Omega\text{-cm}$). Tracer solutions of ^{182}Ta , ^{177}Ta , ^{233}Pa , ^{175}Hf , ^{95}Zr , ^{95}Nb , and ^{243}Am were prepared with activity concentrations ranging from 0.5 to 25 counts per second (cps) per mL of solution. All tracers, with the exception of ^{182}Ta were carrier free and purified by the authors. The ^{182}Ta tracer solution (Isotope Products) contained 30 μg of stable Ta / g of solution. A 1 mL aliquot of the tracer solution was diluted to 100 mL (volumetrically) in 2

M HNO₃/0.1 M HF acid, which was used for experiments. Actinide tracers were taken from laboratory certified stock solutions. Carrier-free ¹⁷⁵Hf and ¹⁷⁷Ta tracers were produced separately at the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory. The ¹⁷⁵Hf was produced from the (p,n) reaction on a natural Lu metal foil (99.9 %, < 10 ppm Hf) and the ¹⁷⁷Ta was produced from the (p,n) reaction on a natural Hf metal foil (97.0 %, < 100 ppm Ta). The foils were dissolved and the isotopes of interest were purified using sequential anion-exchange columns. Zirconium and Nb were isolated from the mixed fission products arising in the thermal-neutron irradiation of ²³⁵U and were also purified with sequential anion-exchange columns. All tracers were converted to HNO₃/HF matrix solutions prior to use.

2.2 Activity Measurements

Activity measurements were performed on a high purity Ge (HPGe) gamma-ray spectrometry system coupled with a multi-channel analyzer (DSPEC, Ortec). The detection efficiency was between 0.05% and 11% for the 75 to 1600 keV photon range. Spectral files were analyzed using Maestro spectral software (Ortec) or Genie2000 interactive peak fit software (Canberra Industries). The gamma photons with the highest relative yield and no potential spectral interferences were selected for determining the activity of each radionuclide of interest (Table 1). All gamma energy and relative yield data were taken from the Brookhaven National Laboratory, National Nuclear Data Center Chart of Nuclides. Systematic counting error was minimized by using a consistent sample volume (1 mL), vial type (15 mL polypropylene centrifuge tube) and source-detector geometry. A fixture was used for reproducible sample placement on top of the detector surface. The decay schemes of the observed nuclides and the count rate of the detector were such that there was no need to correct for photon summing.

Table 1 Photon energies selected for activity determination.

Radionuclide (half-life)	Energy (Intensity,%)
¹⁸² Ta (t _{1/2} = 114.43 d)	1121.3 keV (34.9%)
	1221.3 keV (27.0%)
¹⁷⁷ Ta (t _{1/2} = 2.356 d)	112.9 (22%)
²³³ Pa (t _{1/2} = 26.967 d)	311.9 keV (38.5%)
¹⁷⁵ Hf (t _{1/2} =70 d)	343.4 keV (84%)
⁹⁵ Zr (t _{1/2} = 64.02 d)	724.2 keV (44.3%)
⁹⁵ Nb (t _{1/2} = 34.975 d)	765.8 keV (99.81%)
²⁴³ Am (t _{1/2} = 7.37E3 y)	74.7 keV (67.2%)

2.3 Batch Uptake Experiments

The uptake parameters for Hf, Zr, Nb, Ta, and Pa on TODGA resin in HNO₃/HF solutions were determined by batch extraction experiments as described in [22]. The initial activity of a given radionuclide stock solution

aliquot was determined by gamma-ray spectrometry. The aliquot was then evaporated to dryness using a warm water bath equipped with air-jets. Dry TODGA resin, 10 – 20 mg, was added to each sample along with 1 mL of a mixed HNO₃/HF solution. The HNO₃/HF concentrations ranged from 0.1 M – 8.0 M HNO₃ and 0.001 M – 1.0 M HF. The sample slurry was equilibrated for 1 hour on a rotary mixer and then filtered through a 0.45 µm polytetrafluoroethylene (PTFE) filter for complete removal of the resin from the solution. The filtered supernatant liquid was placed in a centrifuge tube and counted for 1 hour on the gamma-ray spectrometry system.

This method was slightly modified for the short-lived Ta isotope analysis. The dry down step was omitted to reduce the processing time and minimize sorption issues that were observed with the ¹⁸²Ta batch experiments (discussed in the Results section). Smaller aliquot volumes (15-100 µL) of radionuclide stock solution were directly mixed with the HNO₃/HF solution. Dry resin (10-20 mg) was added to each sample vial followed by the HNO₃/HF solution. The mixture was placed on a vortex mixer on the lowest setting for 1 hour to allow for wetting of the resin. The Ta solution was added to each of the resin slurries and counted by gamma spectrometry for 5 minutes (approximately 10,000 accumulated counts). The samples were equilibrated for 1 hour with continuous mixing (except during the 5-minute counting interval), then filtered and recounted as described above. This procedure was only performed with the carrier-free ¹⁷⁷Ta and the ¹⁸²Ta solutions to determine if there was a mass effect on the adsorption of Ta.

The TODGA column capacity factor (k'), or the number of free column volumes to peak maximum, can be inferred from the batch extraction distribution ratio using the method described in [22] and [24].

2.4 Kinetics of Uptake

The half-lives of Db isotopes range from seconds to hours and the on-line chemical system may have to run continuously at rates of ~1-2 mL min⁻¹. The kinetics of uptake of Eu(III) on TODGA in HNO₃ are relatively fast, with equilibrium achieved within 10 minutes [26], however, Eu(III) is extracted as the charge neutral species. The mechanism of Ta uptake on TODGA in the mixed HNO₃/HF is unknown, therefore the kinetics of uptake, must be evaluated. The standards were made, in triplicates, by placing 1 mL of 0.4 M HNO₃/0.1 M HF in a 1.5 mL centrifuge tube and 100 µL of a stock ¹⁷⁷Ta solution. The preconditioned samples were made by mixing 1 mL of 0.4 M HNO₃/0.1 M HF in a 1.5 mL centrifuge vial containing 10-20 mg TODGA resin on a rotary mixer for 4 hours [26]. A 100 µl spike of ¹⁷⁷Ta was added to the samples and each sample was mixed for a desired time interval before quickly filtering to isolate the solution from the resin. A 900 µL spike of each

filtered solution was added to 200 μL of de-ionized water (to maintain original counting geometry) and the samples were counted on the gamma-ray spectrometry system.

2.5 Ta Adsorption Experiments

During the course of the experiments, adsorption of Ta to the polypropylene (PP) vials and column frits was observed. It is known that Group 5 elements can sorb to glass, Teflon, perfluoro alkoxy (PFA) and PP containers at $\text{HF} \leq 10^{-4} \text{ M}$ [14,15]. The $[\text{HF}]$ for this work is between 10^{-3} and 5×10^{-1} , therefore, adsorption over the course of the experiments was not expected. The Ta batch study was repeated without resin (i.e. the sample with a known amount of activity was dried down, reconstituted with HNO_3/HF , equilibrated for 1 hr, filtered and recounted by gamma spectrometry) to determine sorption losses to the PP centrifuge tube and PTFE filter.

2.6 Column Experiments

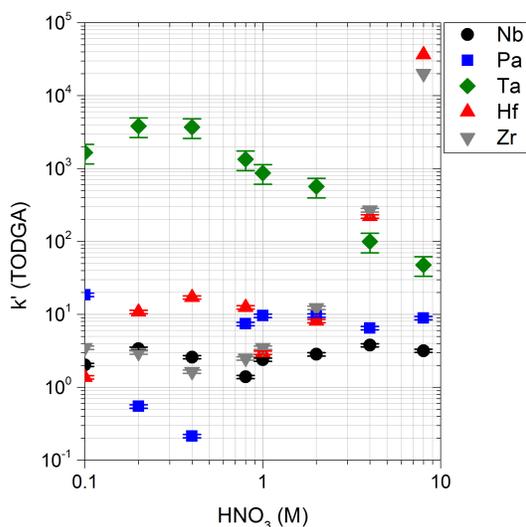
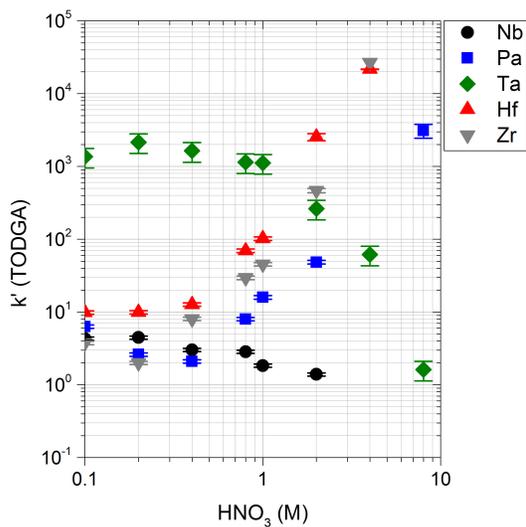
Column extraction of mixed radionuclides was performed with pre-packed 2 mL cartridges containing dry TODGA resin. Aliquots of each tracer solution were combined and evaporated to dryness in a warm water bath with a forced air stream, then reconstituted in 1 mL of the appropriate HNO_3/HF acid solution. Initial sample activity was determined for the mixed radionuclide solution using the gamma-ray spectrometry system. For the sequential extraction experiments, a 24-hole polycarbonate vacuum box (Eichrom, Darien, IL, USA) with a pressure regulator was used to accelerate the elution process and maintain an eluent flow rate of 0.5 to 1 mL min^{-1} . This flow rate was chosen based on the recommendations of the manufacturer. The resin cartridge was conditioned with 2.5-5 bed volumes (5-10 mL) of the appropriate HNO_3/HF sample matrix solution immediately prior to sample loading. Sequential elutions were performed with various acid matrices and volumes based on the results of the batch experiments. A final elution fraction of 0.1 M ammonium bioxalate, was used to remove Am from the resin [28-30]. Each collected fraction was evaporated to dryness in a warm water bath, reconstituted in 1 mL of the given matrix fraction and counted on the gamma-ray spectrometry system.

3. RESULTS AND DISCUSSION

3.1 Batch Experiments

The effect of the HNO_3 concentration on the uptake of Ta, Nb, Pa, Hf, and Zr on the TODGA resin at 0.001 M, 0.02 M and 0.1 M HF are provided (Fig. 1). Protactinium and Nb undergo little to no retention on the TODGA resin with most of the HNO_3 - HF mixtures tested. Both radionuclides were significantly retained at high

[HNO₃] in the presence of 0.001 M HF. Tantalum is sufficiently retained by the TODGA resin with $k'_{Ta} > 100$ at HNO₃ < 6 M and HF > 0.001 M. The k' for Ta decreases significantly as the HNO₃ > 1 M. Group 5 transition metals and Pa undergo partial hydrolysis forming both neutral and non-neutral hydroxo- nitrato and fluoro species in mixed HNO₃/HF matrices [1,8]. Currently, there is no data relating complexation of these species with TODGA; however, it is likely that the oxygen donor groups of the TODGA extractant will show less affinity for the fluoro- species than the nitrato- species. Tantalum undergoes hydrolysis more quickly than Nb or Pa, and is the last to form fluoro- complexes [8,10]. This may explain the high k'_{Ta} for the TODGA resin in low HNO₃/HF matrices. In the presence of 0.001M HF, Pa is extracted by the TODGA resin at higher [HNO₃] (Fig. 1a). The charge-neutral hydroxo- nitrato Pa species is more dominant than the cationic or anionic species at high [HNO₃] (> 6 M); however, the addition of HF can significantly reduce the nitrato- species in solution [31].



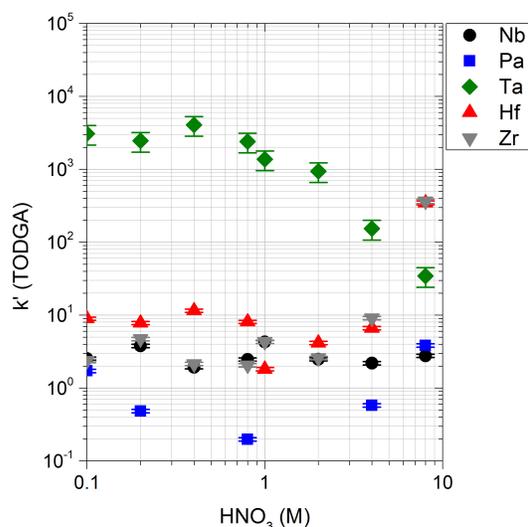


Fig. 1 Uptake (k') of Pa, Nb, Ta, Hf, and Zr on TODGA resin (50-100 μm) vs. $[\text{HNO}_3]$ at 0.001 M HF (a - top), 0.02 M HF (b - middle) and 0.1 M HF (c - bottom) 22(2) $^\circ$, 1 hour equilibration in batch mode. Errors are from the standard deviation of replicates.

Zirconium and Hf predominantly form cationic species at low HNO_3/HF [32,33] and are only slightly retained by the TODGA resin at $\text{HNO}_3 < 1 \text{ M}$ (Fig. 1). The highest k' values for these elements occurred in the 8 M HNO_3 with $\text{HF} < 0.1 \text{ M}$ solution matrices. The four-fold increase in nitrate vs. fluoride ion concentration may promote the formation of more charge neutral nitrate species. The k' values for the extraction of Zr are similar to those determined in pure HNO_3 matrices [34,35].

Isolation of the Group 5 from Group 4 homologs using TODGA with higher HNO_3 concentrations and $\text{HF} > 0.02 \text{ M}$ is achievable. Separation of Ta from Nb/Pa is possible given the results of the batch experiments; however, the ^{182}Ta tracer used for these studies was not carrier-free (150 ng/sample), and may have influenced the adsorption of Ta on the resin. To determine if there was a mass effect, the batch studies were repeated with carrier-free ^{177}Ta solution in HNO_3 and 0.1 M HF (Fig. 2).

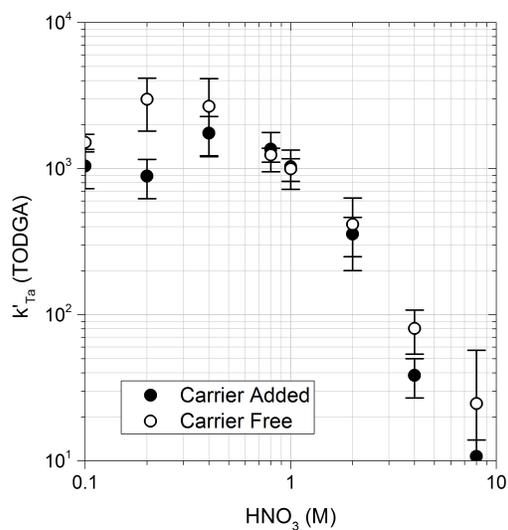


Fig. 2 Uptake (k') of carrier added (^{182}Ta) vs. carrier free (^{177}Ta) on TODGA resin (50-100 μm) vs. $[\text{HNO}_3]$ at 0.1 M HF, 22(2) $^\circ$, 1 hour equilibration. Errors presented are counting errors.

Tantalum adsorption to the original sample vial was observed during some of the column studies using 0.001 to 0.1 M HF with 2 and 4 M HNO_3 loading solutions. This effect was not observed with other radionuclides. Batch studies for Ta were repeated at higher $[\text{HF}]$ to determine uptake parameters. The k'_{Ta} values for TODGA are provided (Fig. 3) for 0.6 - 8 M HNO_3 with 0.1 to 0.5 M HF.

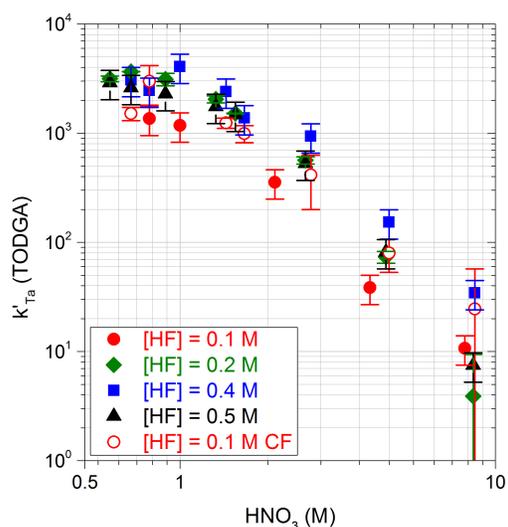


Fig. 3 Uptake (k') of ^{182}Ta on TODGA resin (50-100 μm) vs. $[\text{HNO}_3]$ at various $[\text{HF}]$, 22(2) $^\circ$, 1 hour equilibration. "CF" denotes carrier-free ^{177}Ta data. Errors presented are counting errors.

The front end sample vial, PTFE filter and final sample vial were counted after equilibration to ensure that the activity was loaded on to the resin (for all batch studies). The k'_{Ta} for TODGA is independent of the $[\text{HF}]$ in

$\text{HNO}_3 < 1 \text{ M}$ matrices (Fig. 4). At $\text{HNO}_3 > 1 \text{ M}$, the k_{Ta} initially increases between 0.1 and 0.2 M HF, and then decreases at higher [HF]. The behavior of Ta in low HF/ HNO_3 matrices is unpredictable, especially when the sample is evaporated in a polypropylene vessel (discussed in the next section). The mechanism of Ta extraction by TODGA (i.e. hydrolysis, complexation, polynucleation, or colloid aggregates with PP) remains unclear; therefore, $\text{HF} < 0.1 \text{ M}$ is not recommended in the current system.

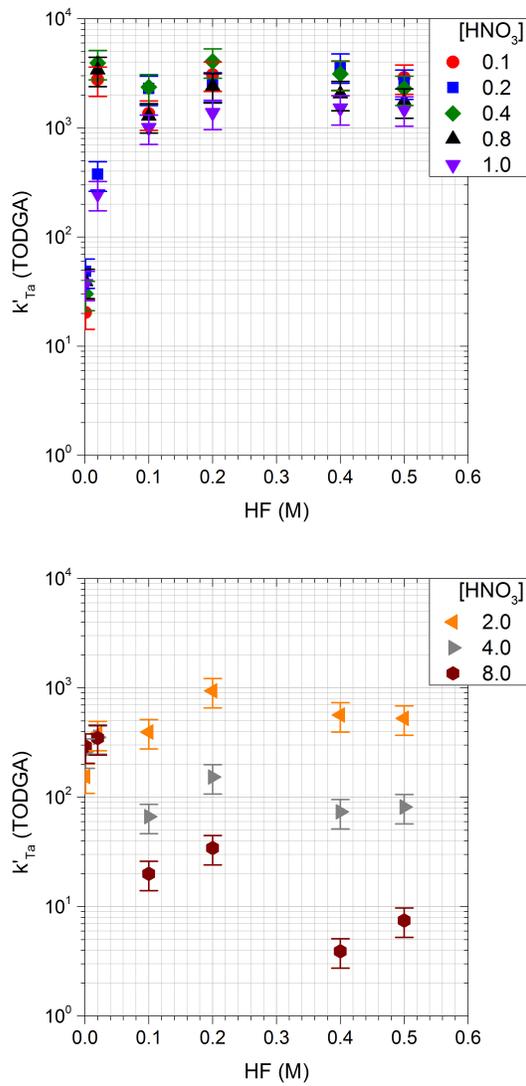


Fig. 4 Uptake (k') of ^{182}Ta on TODGA resin (50-100 μm) vs. [HF] at 0.1 – 1 M HNO_3 (a - top) and 2.0-8.0 M HNO_3 (b - bottom), 22(2) $^\circ$, 1 hour equilibration in batch mode. Errors presented are counting errors.

3.2 Kinetics of Ta Uptake on TODGA Resin

Data obtained from batch studies suggest that Ta can be separated from other Db homologs (Nb/Pa) and Rf homologs (Zr, Hf) using a mixed HNO_3/HF matrix with TODGA resin during a 1 hour equilibration time. The

short-lived isotopes of Db and the goal of an on-line chemical separation system require flow rates of mL min^{-1} . The kinetics of Ta uptake on TODGA resin in a 0.4 M HNO_3 /0.1 M HF matrix was determined (Fig. 5). The sorption of Ta to the TODGA resin as a function of time is slow, with the maximum (based on batch studies) reached at ≥ 1 hour. It is unclear if this is a kinetic effect or a speciation effect. However, after 30 seconds of equilibration, the k_{Ta} is > 100 , which is sufficient for separating Ta from Pa, Nb, Zr and Hf in 0.4 M HNO_3 /0.1 M HF.

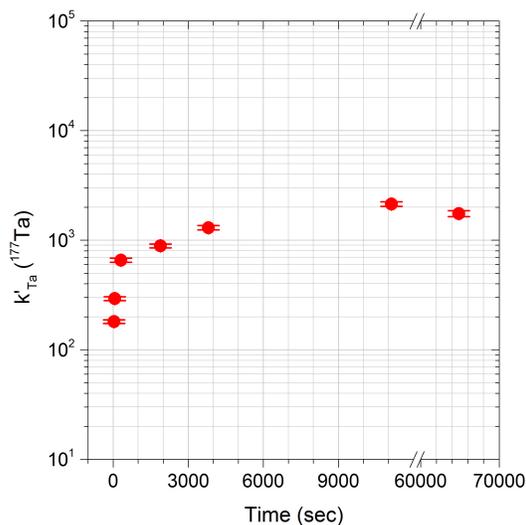


Fig. 5 Uptake parameter, k' , vs. time on TODGA from 0.4 M HNO_3 /0.1 M HF on TODGA resin (50-100 μm), 22(2) $^\circ$, 18 hour total equilibration. Errors are from the standard deviation of replicates.

3.3 Column Experiments and Ta Adsorption

Column experiments were conducted to determine if a sequential separation of Group 4/5 homologs and Am could be achieved by varying only the HNO_3 /HF concentrations. Sequential extractions were performed with pre-packed TODGA resin cartridges (2 mL bed volume) with procedures constructed from the HNO_3 /HF matrices used for batch experiments. A final elution fraction of 0.1 M ammonium bioxalate, was used to remove Am and any other remaining activity from the resin [28-30]. In the first experiment, the evaporated sample was reconstituted in 2 M HNO_3 /0.001 M HF, shaken vigorously and loaded onto the column within 5 minutes of reconstitution. Under these conditions, Nb was expected to move through the column with minimal retention with the other radionuclides remaining on the resin bed. The average elution efficiency over two separate trials is provided (Table 2).

Table 2 Initial column experiments for Group 5 separation from Group 4 and Am on TODGA resin. Values are reported as the average relative activity percent observed in each fraction for 2 separate trials.

Load/Elution Matrix	Nb	Am	Pa	Ta	Hf	Zr
2 M HNO ₃ /0.001 M HF (1 mL load, 2 mL rinse)	66 ± 12	5 ± 7	5 ± 5	24 ± 16	0	0
0.4 M HNO ₃ /0.02 M HF (2 mL)	20 ± 7	0	77 ± 7	9 ± 6	32 ± 20	21 ± 20
8 M HNO ₃ /1 M HF (15 mL)	8 ± 3	0 ± 11	11 ± 14	8 ± 6	33 ± 16	60 ± 17
0.1 M Bioxalate (15 mL)	0	84 ± 2	3 ± 1	0	13 ± 1	8 ± 0
Residual in Sample Vial	5 ± 4	0	1 ± 2	53 ± 25	0	0 ± 1

Niobium behaved as expected, with 66 ± 12% removed from the column using 1.5 bed volumes of the loading matrix (1 mL load volume, 2 mL rinse volume). Tailing of Nb to the second fraction was expected because of the small load/rinse volumes. From the batch experiments, k_{Nb} for the loading matrix is approximately 1.5 (Fig. 1a), which corresponds to a mobile phase volume of 2 mL to reach peak maximum on the 2 mL resin cartridge. Protactinium primarily eluted in the 0.4 M HNO₃/0.02 M HF fraction (77 ± 7%) along with significant amounts of Hf, Zr and the remaining Nb. This separation scheme is not adequate for complete isolation of Group 5 from Group 4 elements; however, there is sufficient separation from the trivalent actinides. A significant amount of Ta (24 ± 16%) was present in the first collected fraction, which was unexpected due to the high k_{Ta} factor determined in the batch experiment (Fig. 1a) and less than half of the original activity was collected from the column. After sequential elution, the original sample vial and resin cartridge were counted by gamma-ray spectrometry to determine if any residual activity remained. Most of the Ta was retained in the original sample vial. Adsorption of Ta to the original sample vial was not expected from 0.001 M HF. During batch experiments, the initial sample vials were counted to discover losses due to adsorption and no significant activity was found. The column study was repeated with a higher [HF] (0.1 M) in the load solution; however, 70% of the Ta remained sorbed to the original sample vial and no clear separation for Group 4 and 5 elements

was obtained. Several variations of the column experiment (matrix manipulation) were performed to prevent adsorption of Ta to the sample vial and none were successful.

Batch experiments without resin present were conducted to determine conditions under which Ta was adsorbed. Aliquots of the ^{182}Ta tracer were placed in PP vials, evaporated to dryness, and reconstituted in 4 M HNO_3 with various concentrations of HF ranging from 0 to 1 M. Each sample was shaken and equilibrated for 1 hour before the solution was removed from the tube. Tantalum was inconsistently removed from the PP vials in solutions containing 0 to 1 M HF in 4 M HNO_3 (Fig. 6). It is known that Group 5 elements can sorb to PP containers at $\text{HF} \leq 10^{-4}\text{ M}$ [14, 15]. Under the conditions tested, Ta adsorption was observed in all matrices with a high degree of variance between each batch study. The carrier-free Nb and Pa tracers did not exhibit the same adsorption issues. The increased concentration of Ta from stable ^{181}Ta in the tracer solution (150 ng mL^{-1}) may have promoted the formation of colloidal or polymerized aggregates; however, no effect was observed for the carrier-free vs. carrier-added batch study (Fig. 2).

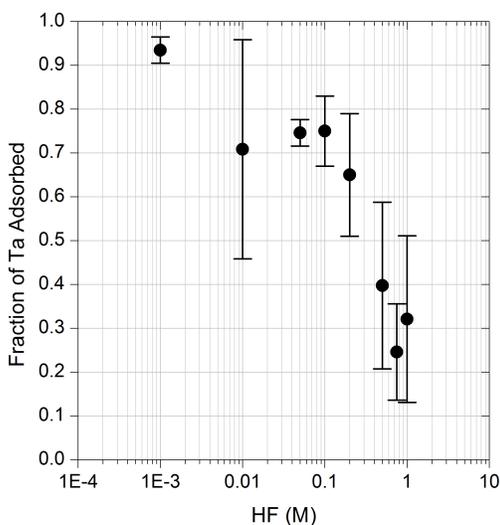


Fig. 6 Fraction of ^{182}Ta sorbed to the PP vials when the load matrix is 4 M HNO_3 at various $[\text{HF}]$, $22(2)^\circ$, 1 hour equilibration. The values reported are the average of three separate trials, with errors from standard deviation.

The differences between the original batch data (Fig. 1 and 2) and the sorption experiments (Fig. 6) were confounding. It was suggested that the sorption issue may be mechanically driven by the dry down process in the PP vial. For the original batch studies, the Ta solution was evaporated to dryness, reconstituted in either 0.001 M HF/0.1 M HNO_3 (Fig. 1) or 4 M HF/6 M HNO_3 (Fig. 2) and then added to the various HNO_3/HF matrices and counted for initial activity concentration. With the column studies, all of the radionuclides of interest were evaporated to dryness, reconstituted in the same vial, counted for initial activity concentration, and

then directly added to the column. This method was also used for the adsorption studies (Fig. 6). As the stock solution of Ta (HNO_3/HF) is evaporated to dryness, the majority of the HF is removed from solution (boiling point $67\text{ }^\circ\text{C}$) prior to the HNO_3 ($121\text{ }^\circ\text{C}$). Water vapor is removed from the sample, which concentrates the HNO_3 and causes the PP vial to etch and dissolve into solution. Samples dried down in Teflon also had some adsorption issues but were much less significant ($< 5\%$ sorbed after reconstitution and removal). Dubnium experiments conducted with the automated system should not be affected by this phenomenon, as the sample dry-down step would be associated with alpha counting-source preparation. If evaporation is required, PP vessels should not be used.

In the final experiment, a mixed radionuclide sample was prepared in a stock solution of $8\text{ M HNO}_3/0.1\text{ M HF}$. The sample was evaporated to dryness, reconstituted, placed in a clean polypropylene vial and counted prior to column loading. The vial was checked for residual activity after transferring the solution to the column reservoir and minimal activity was lost to adsorption. The column was rinsed with $8\text{ M HNO}_3/0.1\text{ M HF}$ (15 mL or 7.5 bed volumes). Under these conditions, Pa and Nb eluted within the first 1.5 bed volumes (3 mL). The Ta elution profile was much broader, requiring 7.5 bed volumes (15 mL) of the rinse matrix for 99% removal (Fig. 7). All of the Group 5 elements were removed from the column prior to the removal of Group 4 and Am. The isolation of Ta from Nb/Pa may be achievable with the TODGA resin under these conditions with a different column height and bed volume.

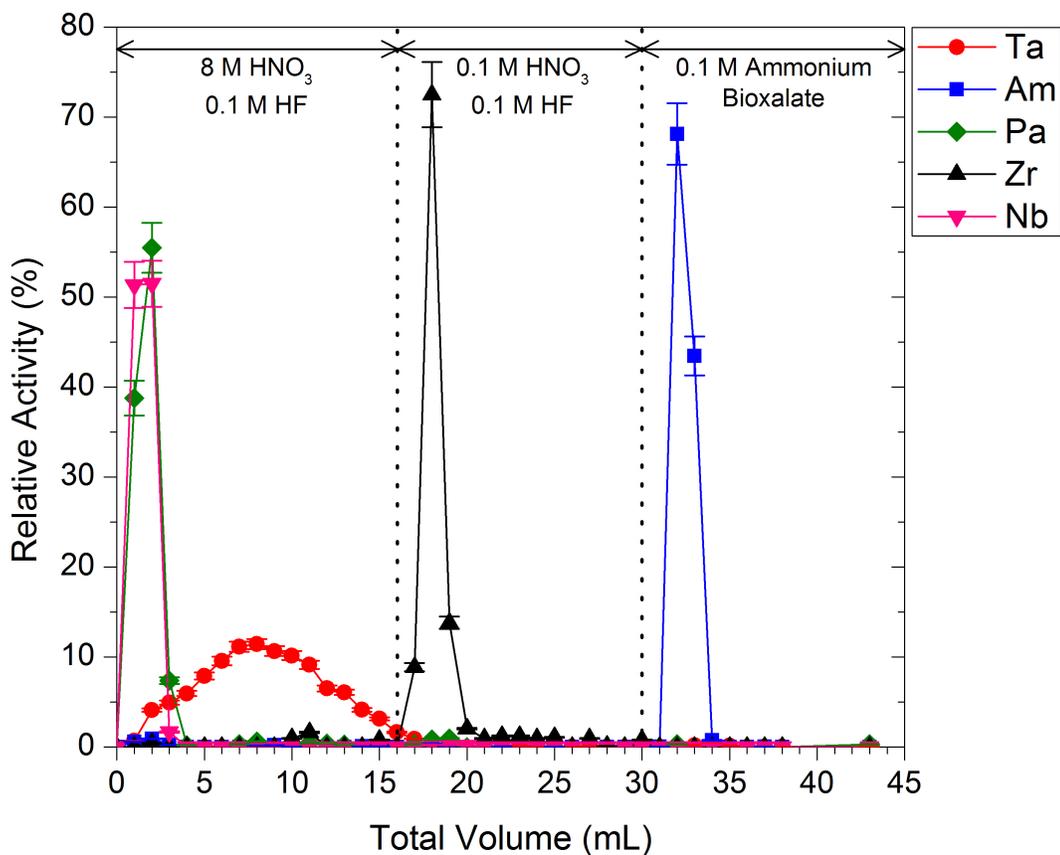


Fig. 7 Elution profile for Ta, Pa, Nb, Zr and Am with the indicated reagents from a 2 mL TODGA resin cartridge (50-100 μm particle size), 22(2) $^\circ$ at a flow rate of 0.5 – 1 mL min $^{-1}$. Errors presented are counting errors.

4. CONCLUSIONS

The sequential extraction of Ta, Nb and Pa from mixed HNO $_3$ /HF acid matrices in the presence of Group 4 elements and actinides using TODGA resin has been observed; however, the exact species and mechanism of complexation are unknown. Tantalum retention on TODGA in the presence of HNO $_3$ /HF is particularly strong, while Pa/Nb are only weakly retained under the same conditions. Under the current HNO $_3$ /HF matrix conditions, there are several competitive interaction processes that are governing speciation and extraction efficiency, i.e. hydrolysis, complexation (fluoro-, nitrate-, etc.), and polynucleation (at low HF concentrations). Determining what species are extracted by the TODGA can provide more insight into how Db will interact with TODGA under the same conditions.

In batch studies, no significant differences were observed for carrier-free versus carrier-added Ta (60 ng – 150 ng) in terms of uptake onto TODGA. A TODGA system may be favorable for Db chemistry in that inter-group separation of the Group 5 homologs is possible; however, further study is required for Ta elution

volume reduction, necessary for counting source preparation. The complete isolation of Group 4 and 5 homologs from Am negates the need for additional precipitation steps and separate columns to remove An^{3+}/Ln^{3+} .

This work provides a foundation for developing a radioanalytical method suitable for Db research, however, a much more in-depth study of the physico-chemical mechanisms of the TODGA extraction of the homolog/pseudohomolog species will be necessary to determine if the method is robust enough for ultra-trace analysis. Additional studies will be conducted to determine the kinetic limitations of the TODGA extraction method under the current matrix conditions with different bed volumes and column diameter. The ability to increase the flow rate and reduce elution volumes will provide a better window of opportunity for observing the chemical characteristics of the short-lived Db isotopes.

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