

Characterization of the homologs of flerovium with crown ether based extraction chromatography resins: studies in hydrochloric acid

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Abstract A crown-ether-based extraction chromatography resin, Eichrom Pb resin, was characterized for separations of flerovium (Fl) homologs, specifically Pb and Sn. The batch uptake of Pb(II) and Sn(IV) radionuclides was determined from an HCl matrix. Both Pb(II) and Sn(IV) are strongly retained on the resin at different HCl concentrations. The affinity for Pb(II) decreases with increasing HCl concentration while Sn(IV) uptake increases. Extraction kinetics for Pb(II) and Sn(IV) were examined and show suitable uptake on the second time scale. Separation methods for the isolation of individual homologs, Pb(II) and Sn(IV), have been established using 2 mL pre-packed vacuum flow Pb resin columns.

Keywords Macrocycles · Crown ethers · Extraction chromatography · Flerovium · Homologs · Heavy element

Introduction

Chemical investigations of the transactinide elements ($Z \geq 104$) present many challenges. The short half-lives and small cross sections at the nano- or picobarn levels result in low production rates, which means that transactinides need to be studied one atom-at-a-time. As a result,

an individual atom is unable to interact with another atom of the same element, and can only interact with its surroundings. Therefore, studies of the homologs of the transactinides (elements in the same chemical group) must be carried out either on-line, by producing individual atoms at an accelerator and performing rapid chemical extractions immediately after their production, or with carrier-free, ultratrace radionuclides. To obtain reliable results it is necessary that the chemical system chosen allows the single atom to undergo many exchanges with the extractant molecule so that it mimics an equilibrium state over the short time-scale of the experiment [1]. Extraction chromatography gives the selectivity of a liquid–liquid extraction system with the ease of running a column, along with the benefits of a large number of metal–ligand interactions [2].

Reaction kinetics are important in the selection of a chemical system. The short half-life of Fl (^{289}Fl , $t_{1/2} = 1.9_{-0.4}^{+0.7}$ s [3]) means that the chemical system will never reach a true equilibrium state. Therefore, the atom of interest must undergo enough exchanges so that it reaches a pseudo-equilibrium state allowing for extrapolation of its chemical properties from the behavior of its homolog elements from the same chemical group in the same system. Each chemical system must be tested to ensure that it can operate on the time scales encountered during an on-line experiment (typically seconds to minutes). Initial studies presented here focus on finding an extractant with suitable kinetics for an on-line Fl chemistry experiment, with possible implementation once an automated chemical system that is capable of being run on the second time scale has been established.

The primary motivation for the study of transactinide elements is to investigate the role of relativistic effects on the chemical properties within a group of the Periodic

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Table. These effects lead to vastly differing predictions between the established trends of the lighter homologs within a group and the corresponding transactinide elements [4, 5]. Based on classical predictions, Fl appears in Group 14 of the Periodic Table and its chemistry should be similar to that of Pb and Sn. Considering the trend in Groups 13–17 of the Periodic Table, where as the atomic number Z increases down a group the elements attain more of a metallic character, Fl should therefore be more metallic than its nearest homolog, Pb. Relativistic calculations on Fl suggest an increased stability of the ground state, compared to that of Pb, with a configuration of $[\text{Rn}] 5f^{14}6d^{10}7s^27p_{1/2}^2$ [6]. Some predictions have indicated a higher volatility and inertness leading to Fl behaving somewhat similarly to Hg or a noble gas [7–10]. Other more recent predictions expect Fl to be more volatile than Pb but still metallic in character [11]. Recent gas phase experiments have been performed on Fl with differing results as to its behavior [12, 13]. In order to investigate these deviations, the chemical properties of the transactinides must be compared to the properties of their lighter homologs. Therefore, extractants of interest for future chemical studies must have high selectivity for the homologs of Fl as well.

Crown ethers are macrocyclic ligands that exhibit highly selective extraction behavior for various metal atoms. The coordination chemistry of crown ethers has been studied in a variety of separations with a large number of different metals [14–16]. The high selectivity of crown ethers is attributed to their extraction ability, which is based on their charge density and ionic radius as determined by the ring size. In solution, the free crown ether has flexibility in its cavity size, but this can be inhibited by adding steric hindrances to the sides of the crown [15–17].

For the development of a suitable chemical system for Fl homologs, a commercially available extraction chromatography resin was evaluated for the separation of Pb and Sn. The resin, Eichrom Pb resin (50–100 μm particle diameter), is coated with 4',4''(5'')-di-tert-butyl-dicyclohexano-18-crown-6 (DtBuC18C6) (Fig. 1), which as mentioned above separates analytes based on their size as well as their charge and complexation [14, 15, 17, 18]. This

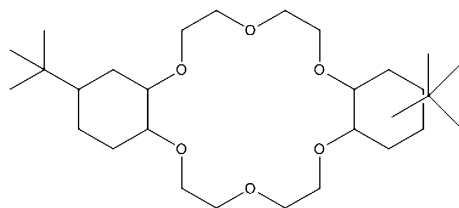


Fig. 1 Pb resin extractant 4',4''(5'')-di-tert-butyl-dicyclohexano-18-crown-6 (DtBuC18C6)

resin was developed for the specific application of separating Pb from other analytes; however, no research into the behavior of Sn has been performed previously.

Batch experiments were conducted to determine the extraction efficiency of the Pb resin for both Pb(II) and Sn(IV) from HCl. In acidic solution, Pb tends to stay in the +2 oxidation state, while Sn is stable as the +4 [19–21]. The extraction kinetics were investigated, and column separation schemes were developed for the separation of Pb(II) and Sn(IV) with different elution orders. To assess the speciation of Pb(II) and Sn(IV), liquid–liquid extraction experiments were performed with varying DtBuC18C6 concentrations. The primary focus of this work was to establish a suitable separation scheme for Fl, that gives direct insight into the chemical form of the extracted homologs with appropriate kinetics for potential future application to a Fl chemistry experiment.

Experimental

Reagents and materials

The Pb resin (50–100 μm , 40 % w:w, Eichrom Industries, Inc.) was used for both batch and column studies [18]. The extractant 4',4''(5'')-di-tert-butyl-dicyclohexano-18-crown-6 (90 %) was purchased from Sigma Aldrich and used in liquid–liquid extraction experiments as received. Dichloromethane (99.9 %, un-stabilized, Fisher) was used without further purification. Acids were prepared from trace-metal grade acids and de-ionized water (18 M Ω cm). The tracer solutions of ^{212}Pb and ^{113}Sn were prepared with activity concentrations ranging from 2 to 10 cps per 20 μL . The ^{232}U (legacy material, Lawrence Livermore National Laboratory (LLNL)) decay chain was used to obtain ^{212}Pb as a tracer for all studies by milking the ^{212}Pb from a generator [22]. The ^{113}Sn tracer was produced at the Center for Accelerator Mass Spectrometry (CAMS) at LLNL via the $^{\text{nat}}\text{In}(p,n)^{113}\text{Sn}$ reaction. The $^{\text{nat}}\text{In}$ foil (99.9 %, Goodfellow Inc.) was dissolved in 1 M HCl and the ^{113}Sn was separated by passing the solution through an AG 1 \times 8 anion exchange column (removing In) and eluting ^{113}Sn with 3 M HNO_3 as in Refs. [23, 24].

Activity measurements

Activity measurements were performed on a high purity germanium (HPGe) gamma-ray spectrometer coupled with a multi-channel analyzer (DSPEC, Ortec). The detector efficiency was between 0.05 and 11 % for the 75–1600 keV energy range. Spectral files were analyzed with Maestro spectral software (Ortec). The spectral lines

with the highest relative yield were chosen for determining the activity of each radionuclide (Table 1) [25].

All post-extraction ^{113}Sn counting was performed 24 h after conclusion of the experiment to allow the ^{113}In daughter (which the activity is derived from) to reach secular equilibrium.

Batch uptake experiments

The uptake parameters for Pb(II) and Sn(IV) on Pb resin in HCl solutions were determined by batch extraction experiments. To a 1.5 mL centrifuge vial, 10–20 mg Pb resin were added along with 1 mL of HCl ranging in concentration from 0.001 M to concentrated. The resin was placed on a rotary mixer for 1 h to precondition the resin. A 20 μL spike containing either ^{212}Pb (eluted from the generator with 2.0 M HCl) or ^{113}Sn (oxidized to Sn(IV) with a drop of H_2O_2) in 2.0 M HCl was added to the wet resin. The solutions were equilibrated for 3 h on a rotary mixer, each sample was counted with a HPGe detector for 120–900 s (≥ 1000 counts under the desired photo-peak), and then filtered through a 0.45 μm polytetrafluoroethylene (PTFE) filter to completely separate the resin from the solution. A 700 μL aliquot of each filtered solution was added to 320 μL de-ionized water in a 1.5 mL centrifuge vial (to maintain initial counting geometry) and counted for 300–900 s (depending on activity) with the same HPGe detector used in initial counts. All experiments were performed in triplicate and the reported errors are based on the standard deviation of the replicates. The Pb resin 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 the references [18, 26].

Uptake kinetics

The HCl concentration at which the maximum uptake (4 M HCl for ^{113}Sn (IV) and 1 M HCl for ^{212}Pb (II)) occurs in the batch experiments was the concentration of choice for kinetics studies. The standards were prepared by placing 1 mL of HCl at the desired concentration (depending on whether ^{212}Pb or ^{113}Sn was used) in a 1.5 mL centrifuge tube and adding 100 μL of a stock radionuclide solution. The standards were made in triplicate and counted with a HPGe detector for 120 s in the case of ^{212}Pb and 3600 s in

the case of ^{113}Sn . The preconditioned samples were prepared (in triplicate) by adding 1 mL of the desired concentration of HCl to a 1.5 mL centrifuge vial containing 10–20 mg Pb resin and placing on a rotary mixer for 1 h. A 100 μL spike of either ^{212}Pb (II) or ^{113}Sn (IV) in the above mentioned HCl concentration was added to the samples, and each sample was mixed for a specific time interval before quickly filtering to isolate the solution from the resin. A 700 μL spike of each filtered solution was added to 400 μL of de-ionized water (to maintain original counting geometry) and the samples were counted with a HPGe detector for 240–300 s (^{212}Pb) or 6300 s (^{113}Sn).

Column experiments

The column extraction of mixed ^{212}Pb (II) and ^{113}Sn (IV) was performed with pre-packed 2 mL cartridges containing dry Pb resin. Aliquots of each tracer were combined and evaporated to dryness in a warm water bath with a forced air stream, then reconstituted in 1 mL of the appropriate HCl solution. The initial sample activity was determined by HPGe counting. For the extraction experiments, a 24-hole polycarbonate vacuum box (Eichrom, Darien, IL, USA) with a pressure regulator was used to accelerate the elution process to maintain an eluent flow rate of ~ 2 mL/min (~ 4 mmHg gauge reading). The resin cartridge was conditioned with 10 bed volumes (20 mL) of the appropriate HCl solution. Extractions were performed with HCl concentrations based on the results from the batch experiments. The radionuclides were loaded on the column in 3 M HCl, where both are retained, and 0.4 M HCl was used to elute ^{113}Sn (IV) and 8 M HCl to elute ^{212}Pb (II). Separate experiments were performed to reverse the elution order. Three rinse fractions at 3 M HCl were collected followed by 1 mL elution fractions ($\times 10$) of the desired HCl concentration. Care was taken to stop the column flow just as liquid was about to reach the top-frit so the column never ran dry and each elution fraction was a consistent 1 mL. Fractions were counted on a HPGe.

Speciation experiments

Solutions containing different concentrations of DtBuC18C6 in un-stabilized dichloromethane were prepared in volumetric flasks with volumes and masses as described for Pb and Sn speciation in Tables 2 and 3 respectively.

Stock solutions of ^{212}Pb (II) were prepared by evaporating the generator eluted ^{212}Pb (II) solution and reconstituting it in 0.4 M HCl (peak of the ^{212}Pb (II) extraction from batch results). A ^{113}Sn (IV) stock solution was prepared in 4 M HCl (peak of the ^{113}Sn (IV) extraction from batch results). To a 1.5 mL centrifuge tube, 480 μL of

Table 1 Photon energies selected for activity determination [25]

Radionuclide (half-life)	Energy (intensity %)
^{212}Pb ($t_{1/2} = 10.64$ h)	238.6 keV (43.6)
^{113}Sn ($t_{1/2} = 115.1$ d)	391.7 keV (65.0)

Table 2 Sample masses and volumes for Pb speciation studies

[DtBuC18C6] (M)	Mass DtBuC18C6 (g)	Volume (mL)
0.00036	4.4	25
0.0025	12.0	10
0.0090	43.6	10
0.065	313.7	10
0.12	563.9	10

Table 3 Sample masses and volumes for Sn speciation studies

[DtBuC18C6] (M)	Mass DtBuC18C6 (g)	Volume (mL)
0.00064	7.8	25
0.0057	27.4	10
0.017	82.9	10
0.067	322.4	10
0.13	651.7	10

either 0.4 or 4 M HCl was added along with 500 μL of crown ether solution (each DtBuC18C6 concentration was studied in triplicate for both Sn(IV) and Pb(II)). These were allowed to mix for one hour on a rotary mixer to ensure pre-conditioning of the organic phase. To each tube a 20 μL spike of the desired $^{212}\text{Pb(II)}$ or $^{113}\text{Sn(IV)}$ activity was added, and the phases were allowed to mix for one hour on a rotary mixer. A 300 μL aliquot from each phase was taken and counted with a HPGe detector to determine the distribution ratios for Sn(IV) and Pb(II) at each concentration of DtBuC18C6.

Results and discussion

Batch experiments

The effects of HCl concentration on the uptake of Sn(IV) and Pb(II) by the Pb resin are shown in Fig. 2. Lead shows a strong affinity to the resin from 0.04 to 2 M HCl and then it decreases significantly with increasing HCl concentration above 2 M, in good agreement with literature [18]. Tin shows a slight uptake from 0.04 to 1 M HCl and then the adsorption increases significantly to a peak extraction at around 4 M HCl. Currently there are no data available on the extraction of Sn(IV) with 18-crown-6 from hydrochloric acid media. It is expected that Sn(IV) in $[\text{HCl}] > 0.7 \text{ M}$ exists as the SnCl_6^{2-} anion [20, 27, 28]. Crown ethers are known to form positively charged hydronium ion complexes by coordinating with H_3O^+ ,

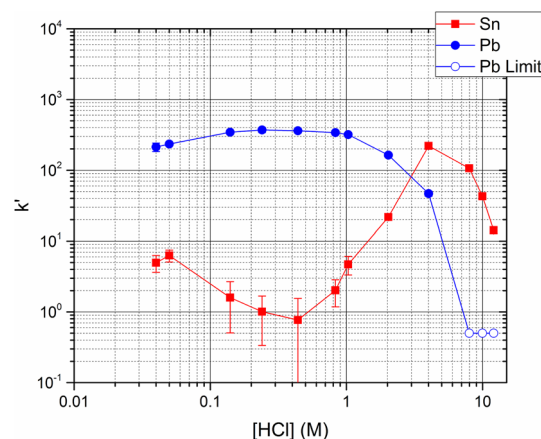


Fig. 2 The batch uptake (k') of $^{212}\text{Pb(II)}$ and $^{113}\text{Sn(IV)}$ as a function of hydrochloric acid media on Pb resin (50–100 μm) with a 3 h equilibration time. Error are from the standard deviation of replicates

where the hydronium ion fits perfectly into the ring [29, 30]. Therefore, the increasing k' for Sn(IV) above 1 M HCl suggests that hydronium activated crown ethers form an ion-association complex with the SnCl_6^{2-} anion (this conclusion is drawn from data presented in Fig. 2 and in Fig. 5 below).

Kinetics of Sn and Pb uptake on Pb Resin

The data obtained from the batch studies indicates that Sn(IV) can be separated from Pb(II) using a pure HCl matrix with the Pb resin at an equilibration time of three hours. The short-lived isotopes of Fl and the goal of an on-line chemical separation will require flow rates of mL min^{-1} . Therefore, the kinetics of the extraction must be suitable on the second time-scale versus hours. The kinetics of Pb and Sn on the Pb resin at 1 and 4 M HCl (maximum k' from batch studies), respectively, were investigated (Fig. 3a, b). The sorption of Pb(II) on the Pb resin was extremely fast with near immediate uptake and full equilibrium reached within five minutes. The sorption of Sn(IV) on the Pb resin was considerably slower than that of Pb(II), presumably from the participation of multiple crown ether/hydronium ion complexes (as discussed in Fig. 5) in the extraction of the negatively charged SnCl_6^{2-} complex; however, significant extraction was seen in seconds, with full equilibrium was reached after approximately an hour.

Column experiments

The column experiments were used to determine if a stepwise extraction of Pb(II) and Sn(IV) could be achieved by varying only the HCl concentration. Based on the batch

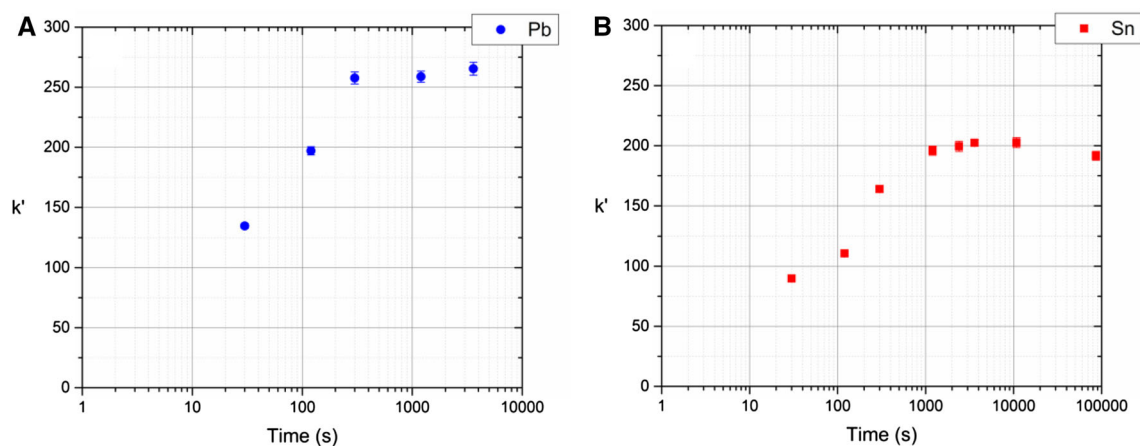


Fig. 3 **a** Kinetics of $^{212}\text{Pb}(\text{II})$ in 1 M HCl media and **b** $^{113}\text{Sn}(\text{IV})$ in 4 M HCl media on Pb resin (50–100 μm), varying equilibration times. Errors are from the standard deviation of replicates

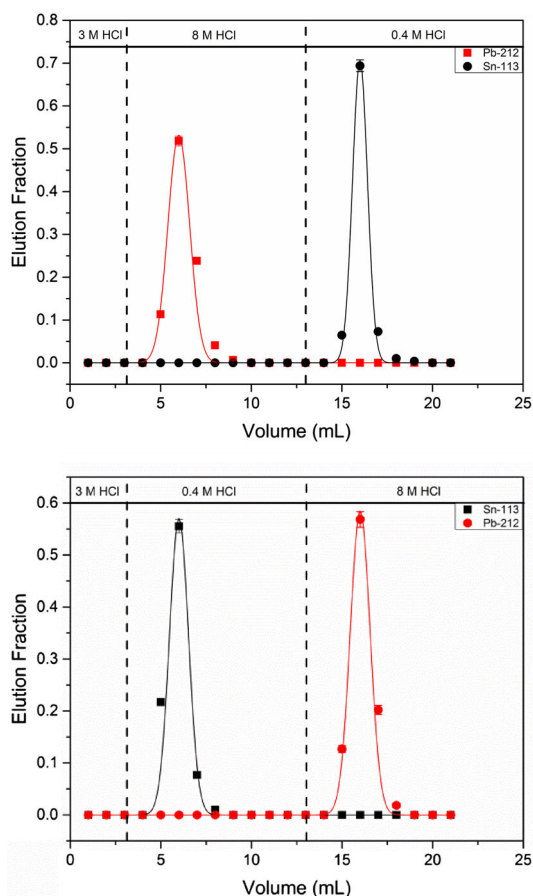


Fig. 4 Column elution of 2 mL pre-packed Eichrom Pb resin cartridges at ~ 2 mL/min flow rate for the separation of Pb(II) from Sn(IV) with (*top*) Pb eluted first and (*bottom*) Sn eluted first. Errors presented are counting errors

study results, a load solution of 3 M HCl was chosen due to the fact that both Pb(II) and Sn(IV) are retained on the Pb resin at this concentration. Two separate columns setups

were run, one with the goal of removing Pb(II) before Sn(IV) and the other with the reverse order. To remove Pb(II) 8 M HCl was used while 0.4 M HCl was used to strip Sn(IV) (Fig. 4).

Both analytes behaved as expected with virtually no breakthrough during column loading. Lead(II) was eluted completely with no Sn(IV) breakthrough and vice versa, usually within the first couple of free column volumes. These separation schemes are fast and yield an excellent separation between Pb(II) and Sn(IV) regardless of their elution order

Speciation experiments

Plotting the logarithm of the distribution ratios for $^{212}\text{Pb}(\text{II})$ and $^{113}\text{Sn}(\text{IV})$ as a function of the logarithm of the concentration of DtBuC18C6 yields a line where the slope of a linear fit to the line is equivalent to the number of DtBuC18C6 molecules required to extract each metal atom.

From the linear regressions in Fig. 5, the number of crown ligands coordinated to the Pb(II) metal ion is found to be 0.94 ± 0.02 . This indicates that one DtBuC18C6 molecule is required to extract each Pb(II) ion into the organic phase, supporting the notion that Pb(II) extracts into the cavity of the crown ether. Similarly, the number of crown ligands coordinated to the Sn(IV) metal ion is found to be 1.61 ± 0.05 . This suggests that a mixture of 1:1 and 1:2 (Sn(IV):DtBuC18C6) complexes are formed. This supports the idea that the highly stable SnCl_6^{2-} complex is either being extracted by two positively charged DtBuC18C6- H_3O^+ complexes or one DtBuC18C6- H_3O^+ complex with charge balanced by an additional H_3O^+ , leading to the ligand dependency value being less than 2.

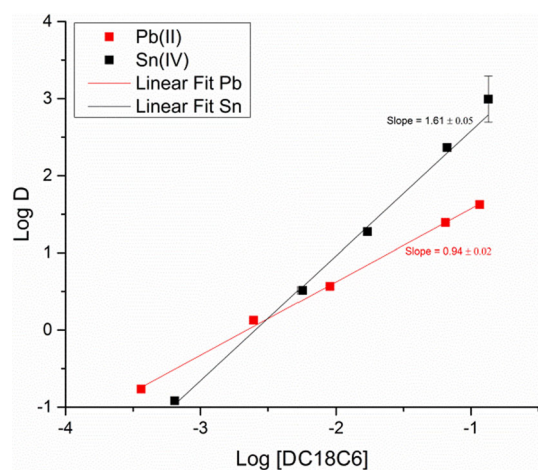


Fig. 5 Distribution ratios for the extracted $^{212}\text{Pb(II)}$ and $^{113}\text{Sn(IV)}$ as a function of DtBuC18C6 concentration in dichloromethane. The solid lines indicate the results of a linear regression fit to the Pb and Sn data, with slopes indicated

Conclusions

The extraction behavior of Pb(II) and Sn(IV) from HCl media was studied using Eichrom Pb resin, which contains the 4',4''(5'')-di-tert-butylidicyclohexano-18-crown-6 extractant. In agreement with previously reported data, the batch results show Pb(II) extracts at low HCl concentrations, from 0.04 to 2 M. It was also observed that Sn(IV) extracts above 1 M HCl. The extracted Pb species is most likely the Pb^{2+} ion in the crown ether cavity, with the charge balanced by a Cl^- counterion. Due to the formation of SnCl_6^{2-} , Sn most likely extracts as an ion-association complex between the negatively charged Sn chloro-complex and positively charged hydronium crown ether complexes.

The results also showed that the reaction kinetics were relatively slow on the scale of minutes to hours to achieve full equilibrium. However, the k' for both Pb(II) and Sn(IV) was >50 within a few seconds, indicating that the separation can be performed on the second timescale, even though complete equilibrium is not reached.

The column studies established separation schemes to isolate pure Pb(II) or Sn(IV) fractions from the Pb resin through the modification of the HCl concentration. The increased number of theoretical plates in the column system compared to that of the batch system allows for much faster flow rates, such as the 2 mL/min used in this work, while retaining full extraction of both analytes. Thus, the column experiments confirmed the results from batch studies and provide evidence that the Pb resin is suitable for the selective extraction of both Pb(II) and Sn(IV). If an appropriate apparatus was developed and the extraction behavior of FI was studied using this same crown ether comparing to the behavior of Pb(II) and Sn(IV), the results

would indicate whether FI behaves more like Pb(II) or Sn(IV).

Speciation studies examined the species that was extracted by DtBuC18C6. The slope from linear regressions of the K_d of Sn(IV) and Pb(II) as a function of the concentration of DtBuC18C6 was found to be 1.61 ± 0.05 and 0.94 ± 0.02 , respectively. This confirms the notion that Pb(II) extracts directly into the crown ether cavity, and gives strength to the notion that one (with H_3O^+ counterion) or two positively charged DtBuC18C6- H_3O^+ complexes extract one SnCl_6^{2-} species.

Before an on-line FI experiment can be performed, further experiments are necessary to determine the maximum rate at which the extraction can be carried out while maintaining the same level of separation. Future work is also needed to develop a continuous automated chemistry apparatus capable of running columns and preparing samples on the time scales required for a FI experiment. Assuming an automated system was capable of performing the chemical separations and sample preparation on the desired time scales, the chemical system presented in this work would be capable of determining whether FI in the aqueous phase is more Sn(IV) or Pb(II) like. An on-line experiment would first need to be performed and optimized with the short-lived Pb and Sn homologs produced in the same manner FI would be, so direct comparisons between FI and the homologs could be made. If FI was seen in an on-line experiment optimized for Sn elution (high HCl concentrations) one would expect FI to be forming more negatively charged complexes and be extracting based on ion exchange. Similarly, a system optimized for Pb elution (low HCl concentration) would indicate, if seen, that FI extracts into the crown ether cavity most likely as a cation.

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