Lawrence Livermore National Laboratory

Studies of Flerovium Homologs with Macrocyclic Extractants

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UNLV
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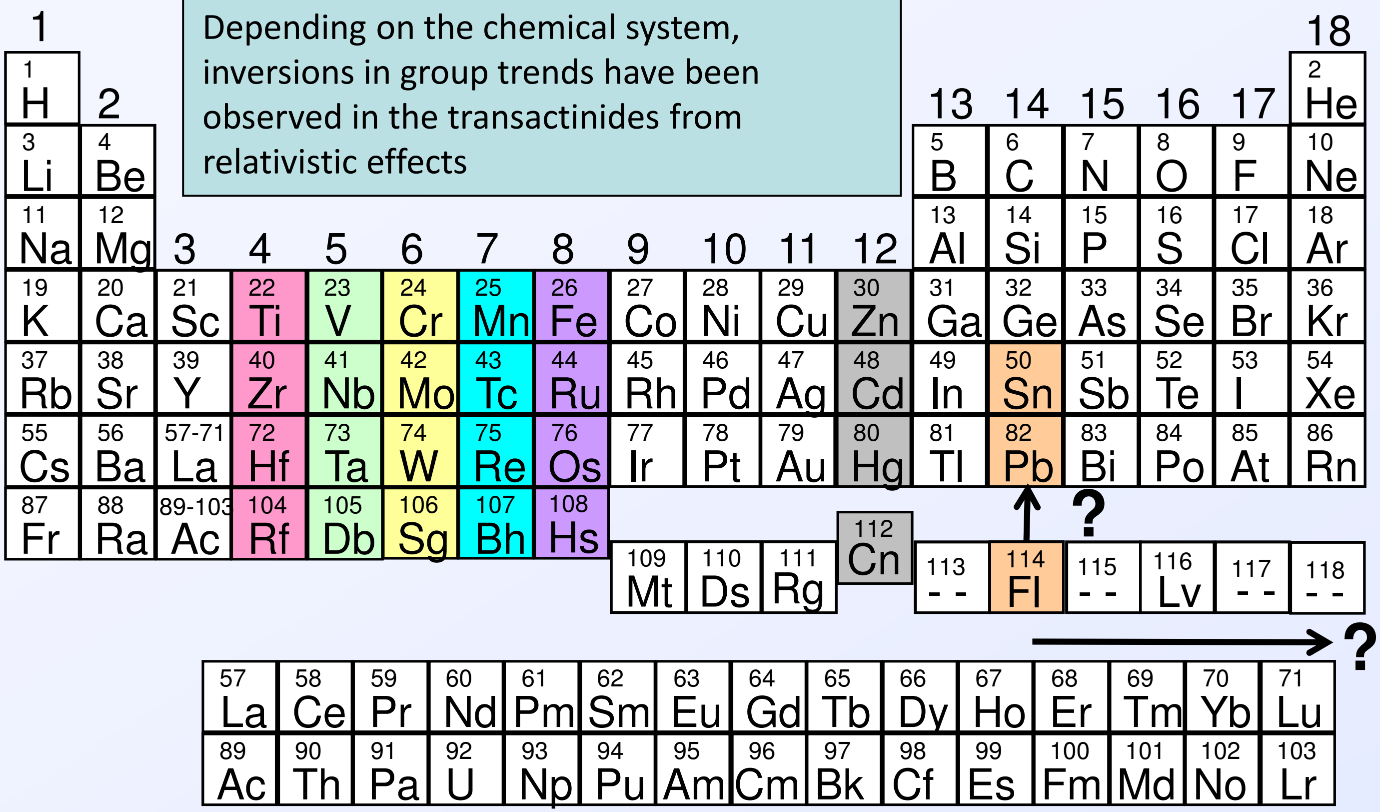
Chemical properties of the heaviest elements are determined through systematic studies of chemical groups

Some chemical experiments have been performed on Groups 4-8, 12 –

Depending on the chemical system, inversions in group trends have been observed in the transactinides from relativistic effects



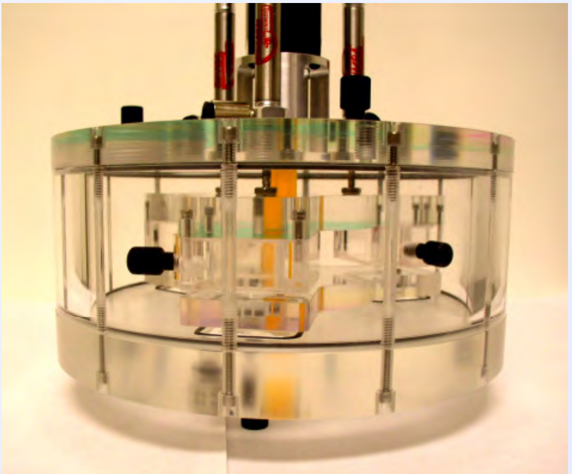
- Predictions of Fl chemistry indicate it could be a metal or inert gas
- Two gas-phase experiments (GSI and PSI/FLNR) show contradictory results

Aqueous phase chemistry of Fl would provide insight into where it truly fits in the Periodic Table

Automated radiochemistry is being developed for heavy elements and other applications

Accelerator target chamber

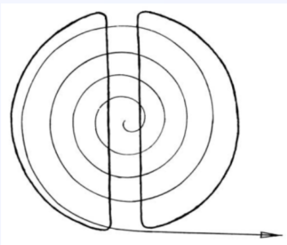
Accelerator - Chemistry Interface



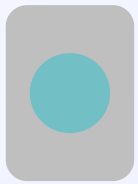
Automated chemistry system

Isotope Production and Integration of Automated Systems

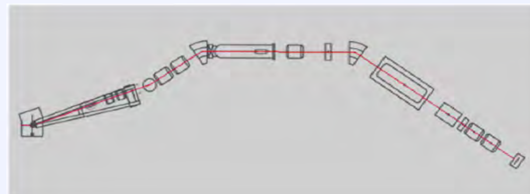
- Goal: Integrate chemical automation methods with isotope production, separation and transport at Texas A&M University Cyclotron



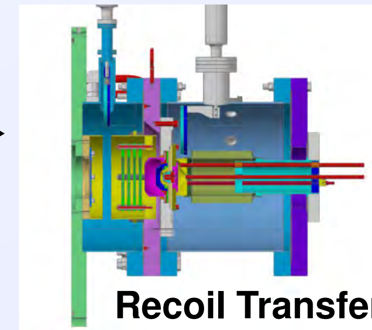
Cyclotron (Texas A&M University)



Target



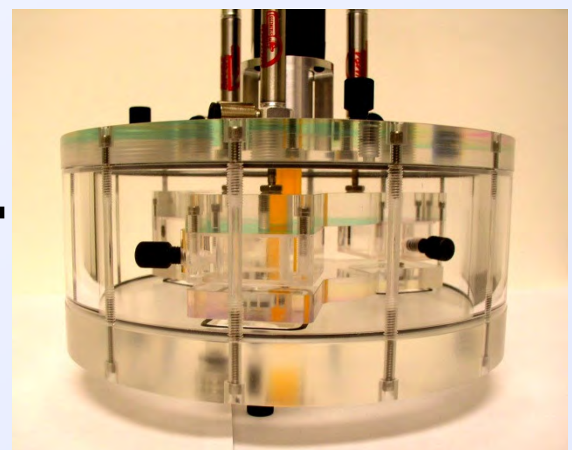
MARS Physical Pre-Separator



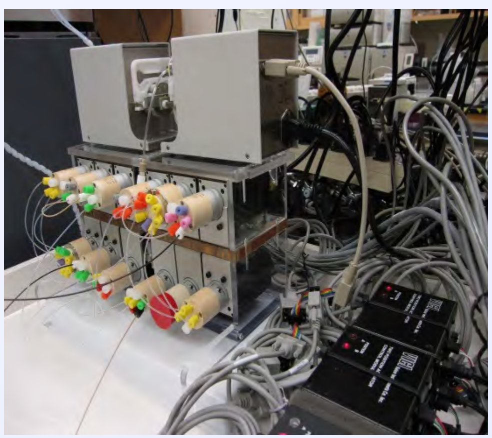
Recoil Transfer Chamber (RTC)

CYCLOTRON INSTITUTE
TEXAS A&M UNIVERSITY

- Gas-liquid interface and automated radiochemistry developed for use at CAMS
- Leverage existing capability and adapt to atom-at-a-time chemistry
- Meets requirements for rapid chemistry

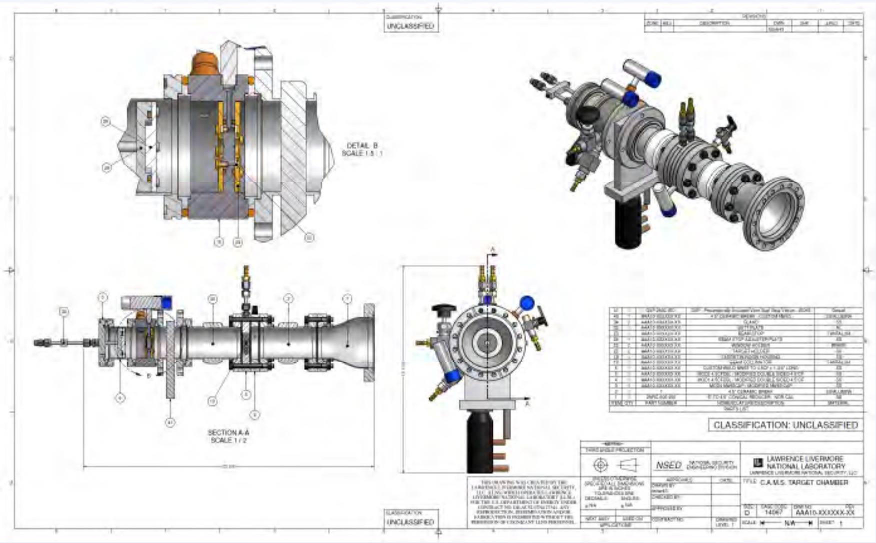


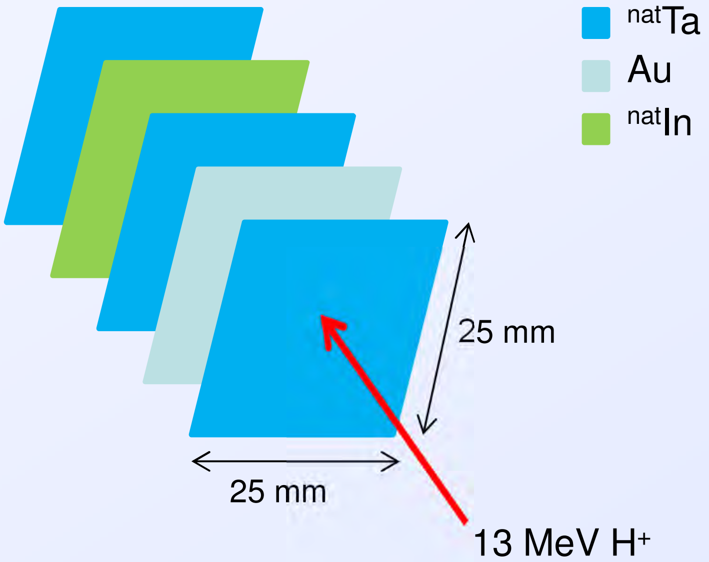
Gas-Liquid Interface for Transferring Transactinides to Automated Radiochemistry (GLITTAR)

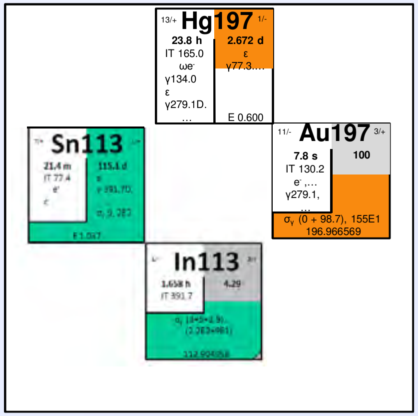


Super Heavy Element Liquid Automation (SHELA)

Carrier-Free Isotope Production at LLNL Center for Accelerator Mass Spectrometry (CAMS)



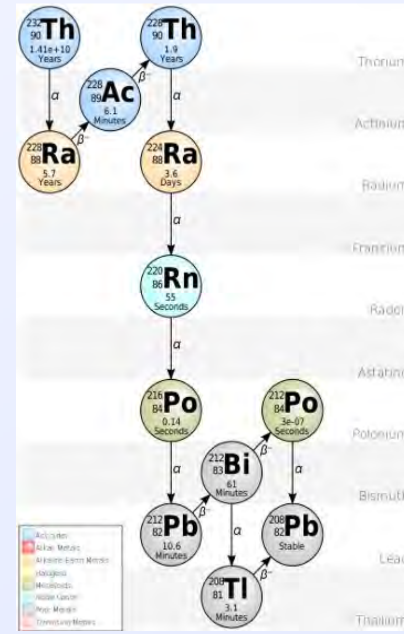




^{212}Pb Generator

- ^{232}U solution with all daughters in secular equilibrium.
- Added to AG 50w x 8 cation exchange column in 1 M HCl.
- Retains all radionuclides above ^{212}Pb in decay chain.

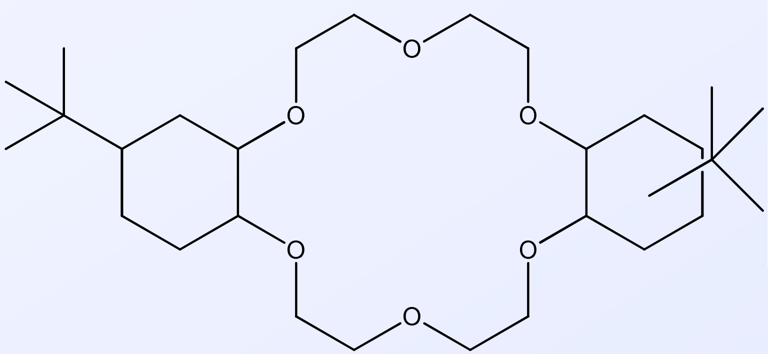
AG 50w x 8 generator



Elution	Solution
^{212}Pb	2.0 M HCl
^{212}Bi	0.5 M HCl

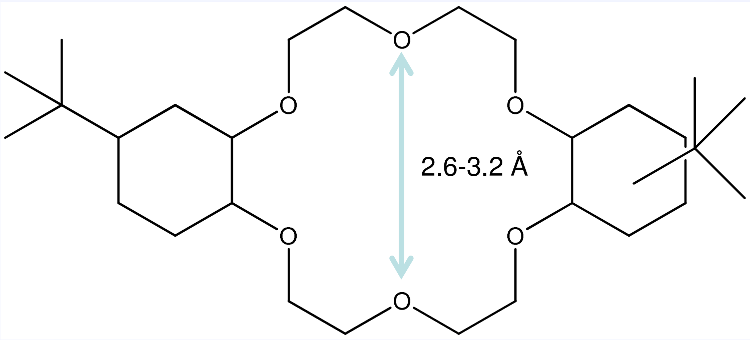
Macrocyclic Extractants

- Crown complexes unusually stable
  - Binding of cations by electrostatic ion-dipole interaction between cations and the negatively charged ring (oxygen, sulfur, etc.) donor atoms.
- Macrocyclic ligands are known to extract Pb based on cavity size, ionic radius, and complexation
  - Suitable starting place

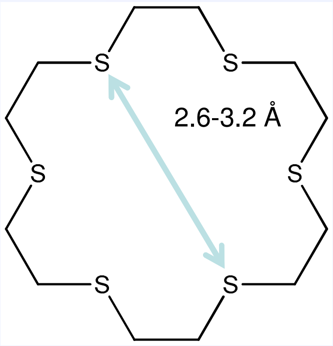


Element	Oxidation State	Coordination Number	Ionic Radius (Å)
Sn	II	VI	0.93
	IV	VI	0.690
Pb	II	VI	1.19
Sb	III	IV / VI	0.76
	V	VI	0.60
Bi	III	VI	1.03

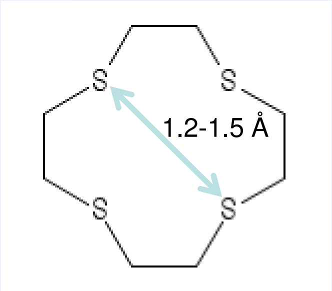
Eichrom's Pb Resin, Hexathia-18-Crown-6, and Tetrathia-12-Crown-4



Eichrom's Pb Resin extractant:
di-t-butylcyclohexano-18-crown-6



Hexathia-18-crown-6



Tetrathia-12-crown-4

- 0.75M di-t-butylcyclohexano-18-crown-6
- Isodecanol solvent
- Available as free resin
- Available as 2mL pre-packed cartridges

- Sulfur analog of 18-crown-6 and 12-crown-4.
- Thia-crown ethers should extract softer metals, such as Pb/Hg.
- Little known extraction studies.
- Synthesized in-house (HT18C6)

Batch Study Results

- All results are presented as k', the number free column volumes to reach peak maximum for a given elution.

- k' can be determined from D_w and a resin multiplication factor:

$$k' = (D_w)\left(\frac{d_{extr}}{0.4}\right)\left(\frac{v_s}{v_m}\right)$$

$$D_w = \left(\frac{A_o - A_s}{A_s}\right)\left(\frac{mL}{g}\right)$$

Resin	Correction Factor (F)
Pb	0.55

$$F = \left(\frac{d_{extr}}{0.4}\right)\left(\frac{v_s}{v_m}\right)$$

Batch Study

10-20 mg resin

1 mL 0.001-Conc. HCl

Mix to wet resin

20 µL ^{212}Pb, ^{197}Hg, or ^{113}Sn spike, 2 M HCl

Equilibrate for 3 hours

Count by HPGe during equilibration

Remove Resin

Count by HPGe

Batch Results

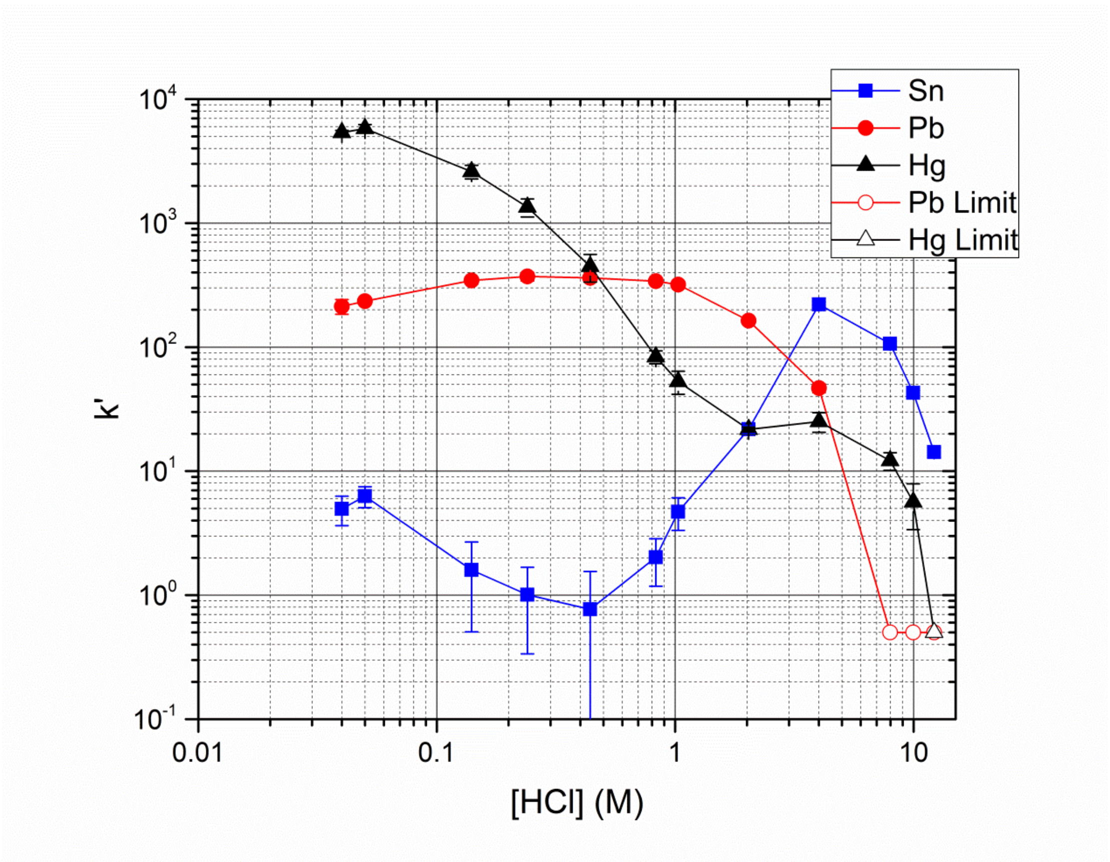


Figure. The batch uptake (k') of $^{212}Pb^{2+}$, $^{113}Sn^{4+}$ and $^{197}Hg^{2+}$ as a function of hydrochloric acid media on Pb resin (50-100 μm) with a 3 hour equilibration time.

Kinetics Study

10-20 mg resin

1 mL 4 (Sn), 1 (Pb), or 0.4 (Hg) M HCl

Mix to wet resin

100 µL ^{212}Pb, ^{197}Hg, or ^{113}Sn spike

Equilibrate for 30s-24hr hours

Remove Resin (~10s)

Count by HPGe

Kinetics Results

(A)

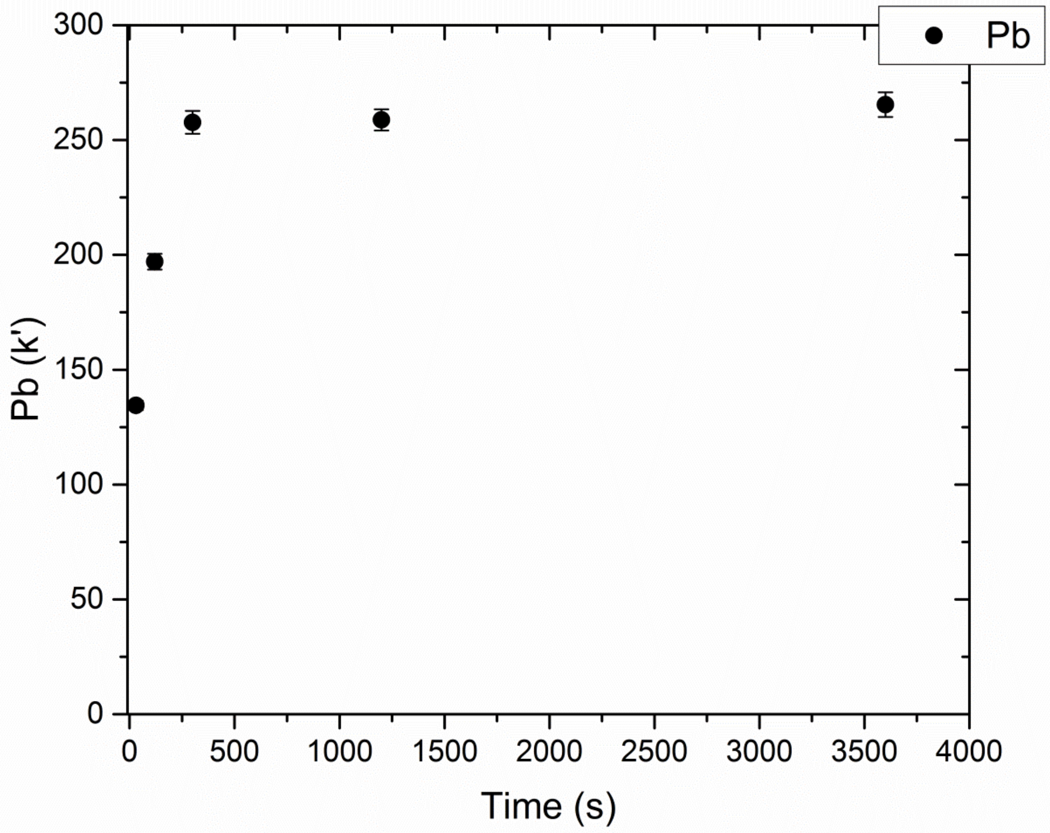


Figure. (A) Kinetics of ^{212}Pb in1 M HCl media and **(B)** ^{113}Sn in 4 M HCl media **(C)** ^{197}Hg in 0.4 M HCl media on Pb resin (50-100 µm) with a varying equilibration times.

Kinetics Results

(B)

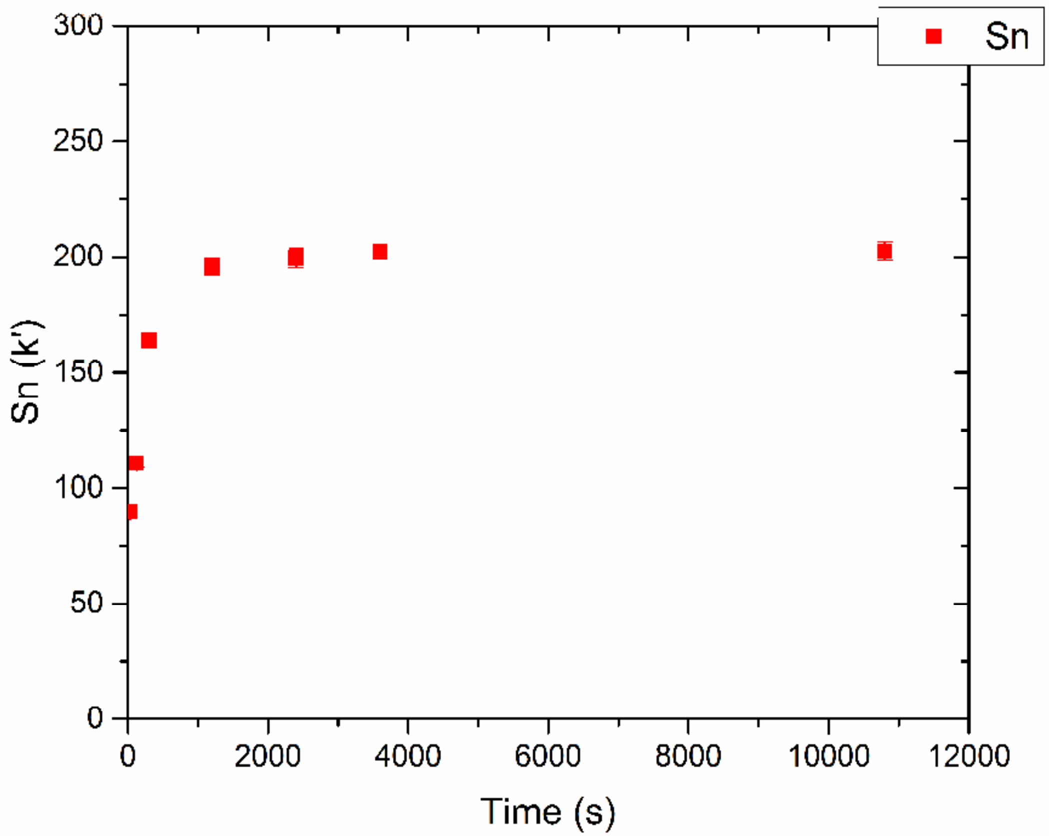


Figure. (A) Kinetics of ^{212}Pb in1 M HCl media and **(B)** ^{113}Sn in 4 M HCl media **(C)** ^{197}Hg in 0.4 M HCl media on Pb resin (50-100 μm) with a varying equilibration times.

Kinetics Results

(C)

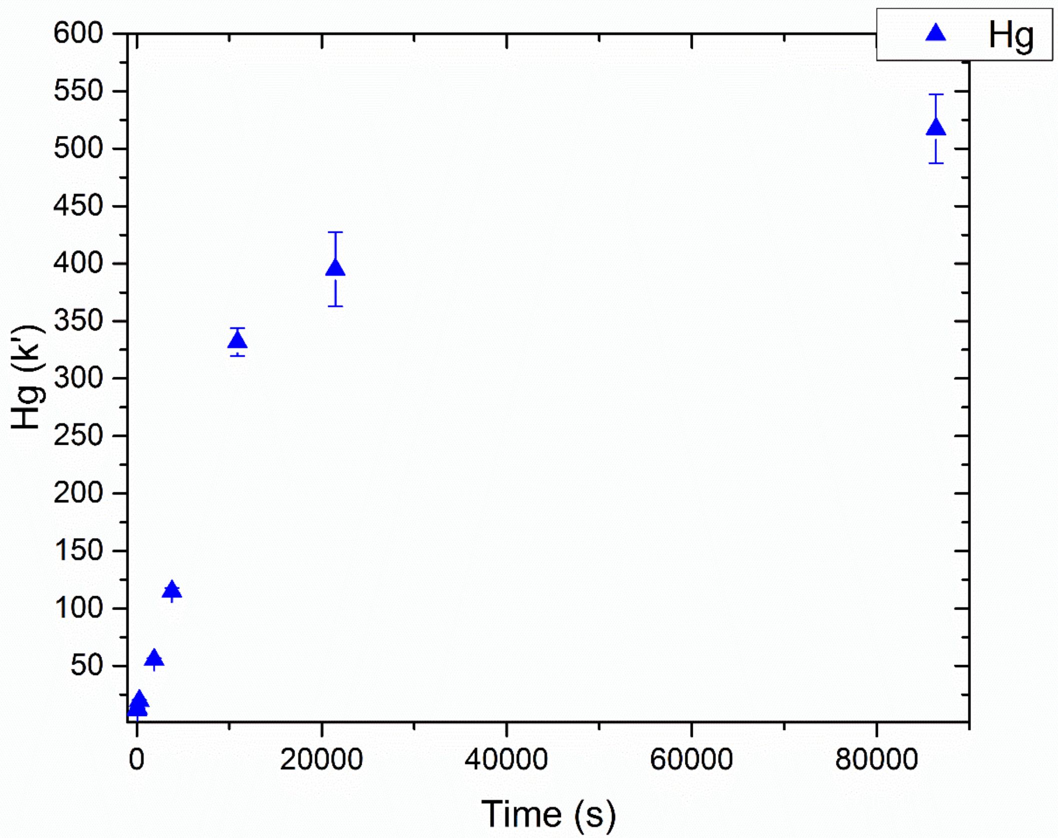
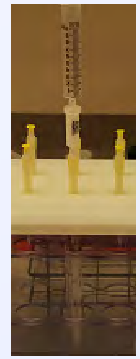


Figure. (A) Kinetics of ^{212}Pb in1 M HCl media and **(B)** ^{113}Sn in 4 M HCl media **(C)** ^{197}Hg in 0.4 M HCl media on Pb resin (50-100 μm) with a varying equilibration times.

Column Study

1 mL 0.4 M HCl with 10 cps $^{212}Pb/^{113}Sn/^{197}Hg$

Front end count



2 mL pre-packed column, 2 mL/min flow (2 mmHg)

Table. Column elution fractions.

Fraction	[HCl]	Number of Fractions (1 mL each)
Load	0.4 +10 µL H_2O_2	1
Elute Sn	Load + 0.4	8
Elute Pb	8	9
Elute Hg	Conc.	11

Back end count

Note: ^{113}Sn fractions counted 24hrs later to allow for secular equilibrium of ^{113}In

Column Study Results

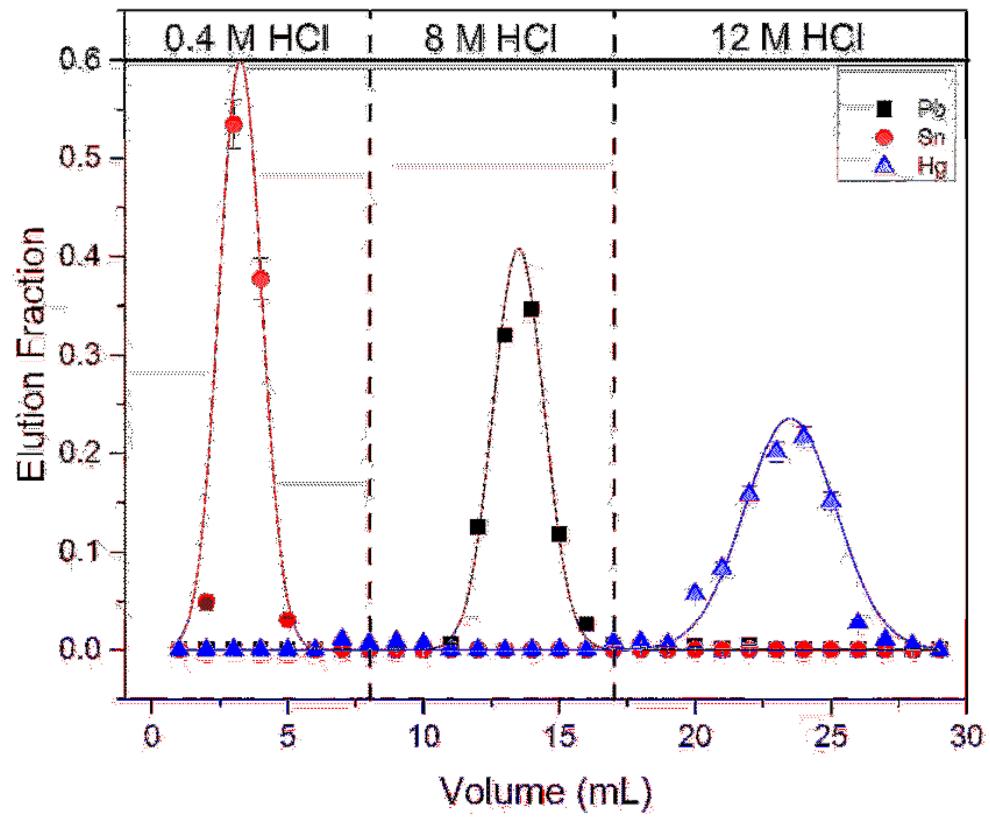
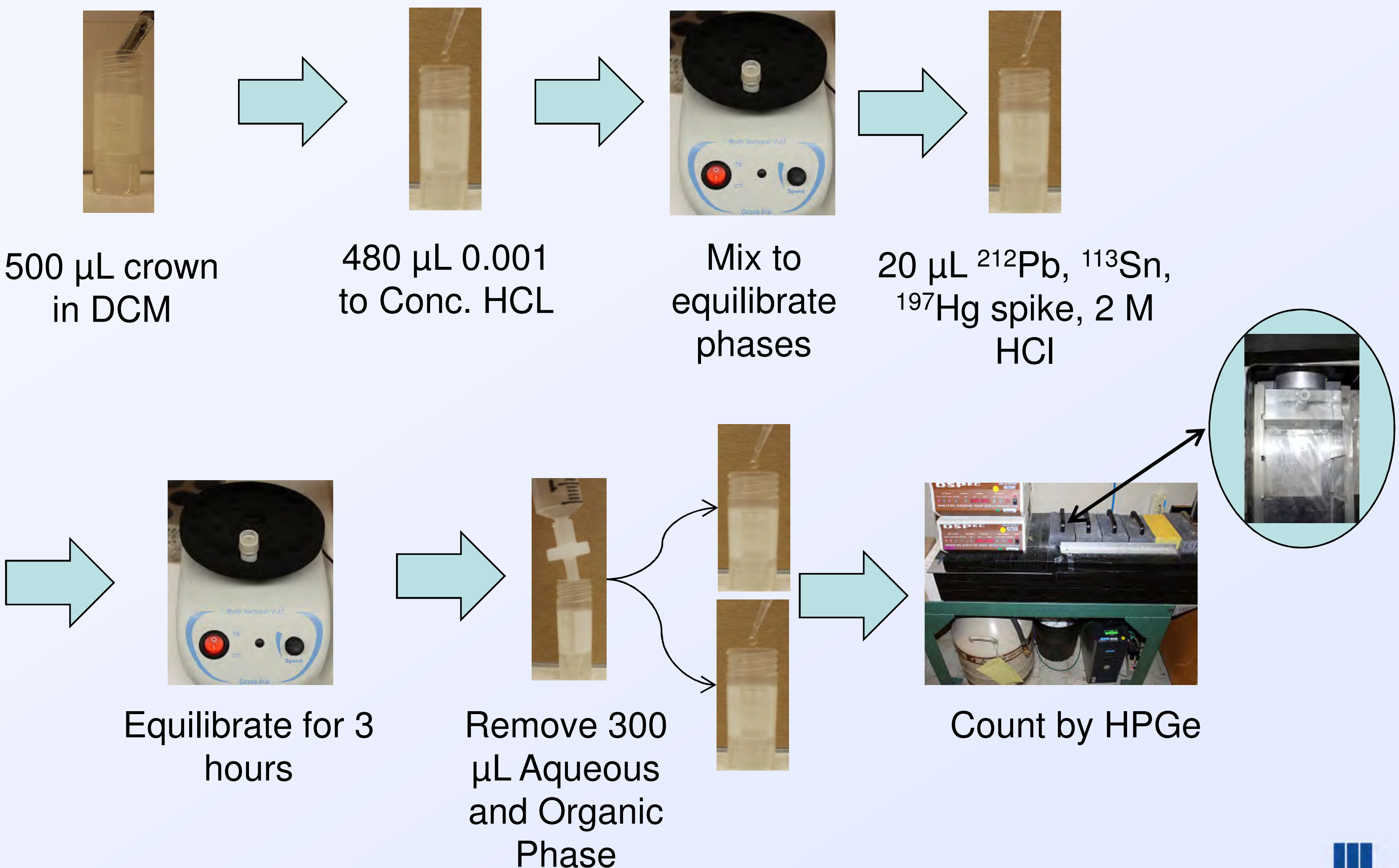


Figure. Separation of Sn(IV), Pb(II) and Hg(II) with 2 mL pre-packed Pb resin (50-100 µm**)** on vacuum box with 2 mL/min flow rate.

Thiacrown Liquid-Liquid Studies



^{197}Hg Extraction by Hexathia-18-Crown-6

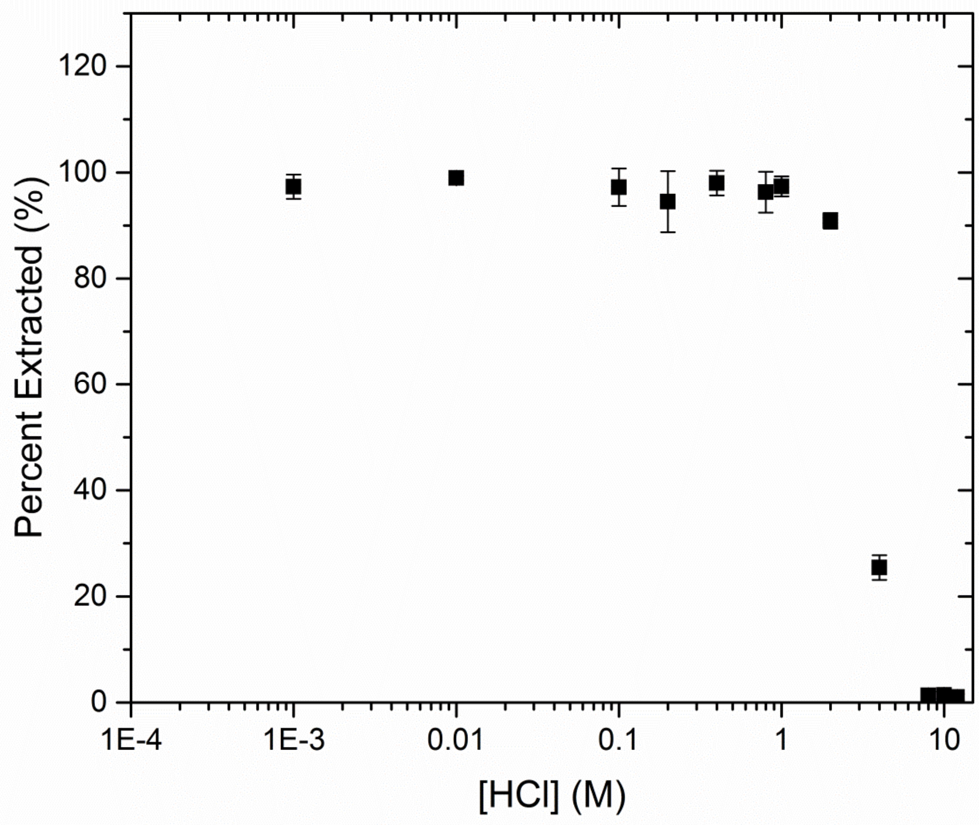
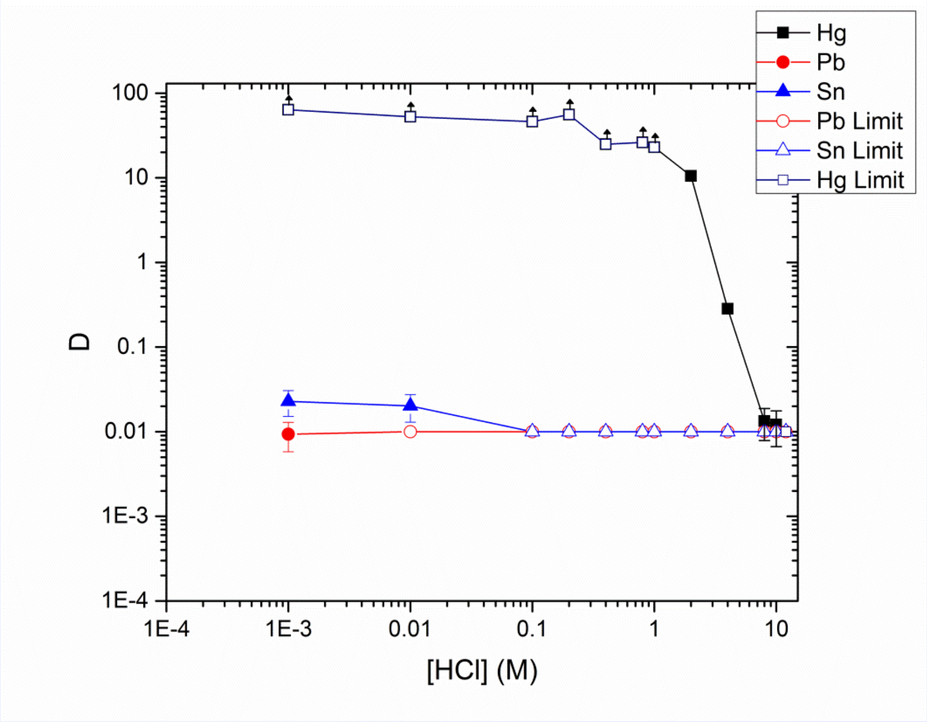


Figure. ^{197}Hg extraction by ~0.003 M hexathia-18-crown-6 in dichloromethane.

^{197}Hg, ^{212}Pb, and ^{113}Sn Extraction by Tetrathia-12-Crown-4 and Hexathia-18-Crown-6



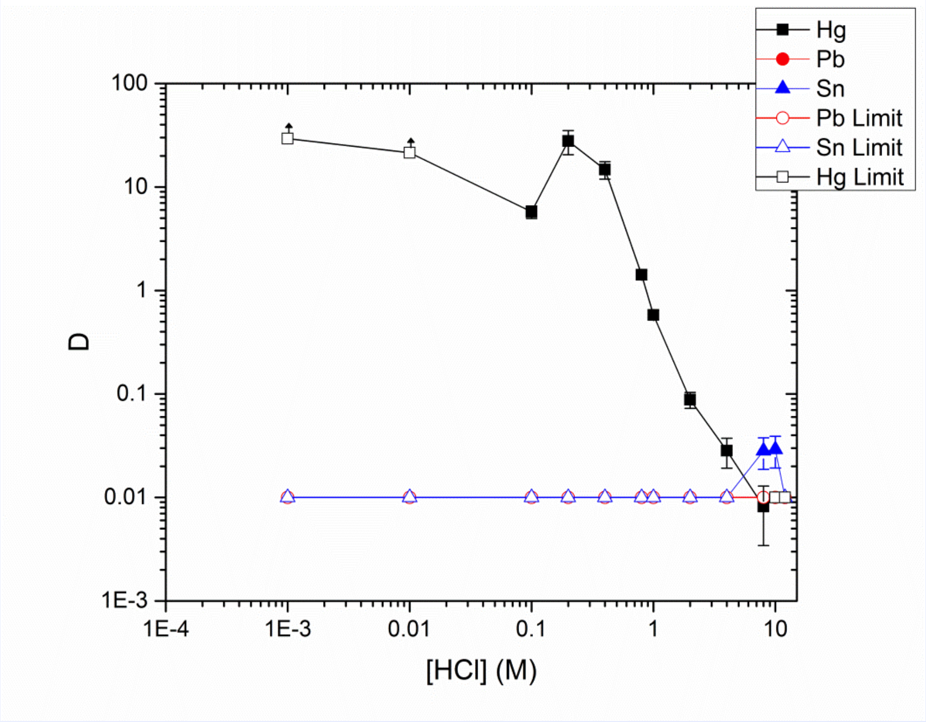


Figure. ^{197}Hg, ^{212}Pb, and ^{113}Sn extraction by ~0.0001 M hexathia-18-crown-6 (Left) and ~0.0001 M tetrathia-12-crown-4 (Right) in dichloromethane.

Conclusions Pb Resin

- Pb, Sn, and Hg can be fully separated with the Eichrom Pb resin.
  - Pb and Sn can be separated on the second time scale.
  - Hg has very slow sorption and desorption kinetics and therefore cannot be effectively separated from Pb/Sn without long wait times between elution.
    - Not effective for a transactinide chemical system, if Hg-like character is desired.

Conclusions Thiacrowns

- Hg kinetics on both TT12C4 and HT18C6 is much faster than the analogous crown ether.
- Extraction is presumably Hg coordinating with the sulfur ring atoms (not in the cavity).
- Pb/Sn show no extraction most-likely due to the fact that the un-substituted thiacrown ethers have charge density oriented perpendicular to the ring verses into the center of the cavity like normal crown ethers.
- Adding a substituent like potentially di-benzohexathia-18-crown-6, etc. can force the charge density to mimic that of a normal crown ether (toward the cavity) and thus should show far increased extraction of Pb as well as Hg.

Future Work

- Continue to investigate the thiacrown ethers.
- Synthesize thiacrowns with substituents that will force the charge density to mimic that of the traditional crown ether, to see if (as expected) it will extract Pb when this condition is met.
- Investigate the kinetics more completely, initial studies indicate the thiacrowns vastly increase the extraction kinetics for Hg and one would expect the same should occur for other soft-metals like Pb once the proper thiacrown for the extraction is found.
- Due to the low solubility of thiacrown ethers in most organic solvents, work on incorporating them into a resin of some form.

Acknowledgements

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