

Development of Designer Molecules for Use in Future Superheavy Element Chemistry Experiments

Cody Folden

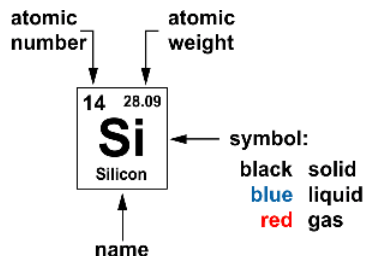
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Use of Homologs for Group 13 Chemistry

1 1.01 H Hydrogen																	2 4.003 He Helium						
3 6.94 Li Lithium	4 9.01 Be Beryllium																	5 10.81 B Boron	6 12.01 C Carbon	7 14.01 N Nitrogen	8 15.999 O Oxygen	9 18.998 F Fluorine	10 20.18 Ne Neon
11 22.99 Na Sodium	12 24.31 Mg Magnesium																	13 26.98 Al Aluminum	14 28.09 Si Silicon	15 30.97 P Phosphorus	16 32.06 S Sulfur	17 35.45 Cl Chlorine	18 39.95 Ar Argon
19 39.10 K Potassium	20 40.08 Ca Calcium	21 44.96 Sc Scandium	22 47.90 Ti Titanium	23 50.94 V Vanadium	24 51.996 Cr Chromium	25 54.94 Mn Manganese	26 55.85 Fe Iron	27 58.93 Co Cobalt	28 58.70 Ni Nickel	29 63.55 Cu Copper	30 65.37 Zn Zinc	31 69.72 Ga Gallium	32 72.59 Ge Germanium	33 74.92 As Arsenic	34 78.96 Se Selenium	35 79.90 Br Bromine	36 83.80 Kr Krypton						
37 85.47 Rb Rubidium	38 87.62 Sr Strontium	39 88.91 Y Yttrium	40 91.22 Zr Zirconium	41 92.91 Nb Niobium	42 95.94 Mo Molybdenum	43 (98) Tc Technetium	44 101.07 Ru Ruthenium	45 102.91 Rh Rhodium	46 106.40 Pd Palladium	47 107.87 Ag Silver	48 112.41 Cd Cadmium	49 114.82 In Indium	50 118.69 Sn Tin	51 121.75 Sb Antimony	52 127.60 Te Tellurium	53 126.90 I Iodine	54 131.30 Xe Xenon						
55 132.91 Cs Cesium	56 137.33 Ba Barium	57 138.91 La Lanthanum	72 178.49 Hf Hafnium	73 180.95 Ta Tantalum	74 183.85 W Tungsten	75 186.21 Re Rhenium	76 190.20 Os Osmium	77 192.22 Ir Iridium	78 195.09 Pt Platinum	79 196.97 Au Gold	80 200.59 Hg Mercury	81 204.37 Tl Thallium	82 207.19 Pb Lead	83 208.98 Bi Bismuth	84 (209) Po Polonium	85 (210) At Astatine	86 (222) Rn Radon						
87 (223) Fr Francium	88 226.03 Ra Radium	89 227.03 Ac Actinium	104 (261) Rf Rutherfordium	105 (262) Db Dubnium	106 (266) Sg Seaborgium	107 (262) Bh Bohrium	108 (265) Hs Hassium					112 (285) Cn Copernicium	113 (284) Nh Nihonium	114 (288) Fl Flerovium									
(119)	(120)	(121)					109 (266) Mt Meitnerium	110 (271) Ds Darmstadtium	111 (272) Rg Roentgenium					115 (288) Lv Livermorium	116 (292) Ts Tennessine	117 (293) Og Oganesson	(294)						



- alkali metals
- alkaline earth metals
- transitional metals
- other metals
- non metals
- noble gases

Lanthanides

58 140.12 Ce Cerium	59 140.91 Pr Praseodymium	60 144.24 Nd Neodymium	61 (145) Pm Promethium	62 150.40 Sm Samarium	63 151.96 Eu Europium	64 157.25 Gd Gadolinium	65 158.93 Tb Terbium	66 162.50 Dy Dysprosium	67 164.93 Ho Holmium	68 167.26 Er Erbium	69 168.93 Tm Thulium	70 173.04 Yb Ytterbium	71 174.97 Lu Lutetium
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Actinides

90 232.04 Th Thorium	91 231.04 Pa Protactinium	92 238.03 U Uranium	93 237.05 Np Neptunium	94 (244) Pu Plutonium	95 (243) Am Americium	96 (247) Cm Curium	97 (247) Bk Berkelium	98 (251) Cf Californium	99 (252) Es Einsteinium	100 (257) Fm Fermium	101 (260) Md Mendelevium	102 (259) No Nobelium	103 (262) Lr Lawrencium
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Superactinides (122-153)

Pershina *et al.* Comments on Element 113 Adsorption on Au

Even though it is predicted to be chemically more inert than Tl, element 113 should rather well adsorb on the gold surface in the He/H₂ atmosphere with $\Delta H_{\text{ads}}(113) = -158.6$ kJ/mol which requires very high T_{ads} . Since the gold plated silicon detectors in the gas-phase chromatography experiments cannot be heated above 35 °C, element 113 will adsorb right at the beginning of the chromatography column with a negative temperature gradient, being indistinguishable in this way from Tl. Thus, only a low limit of $-\Delta H_{\text{ads}}$ can be given by such a thermochromatography study. In

Dubna Element 113 Chemistry Experiment by Dmitriev *et al.*

- Dmitriev *et al.* reported a broad distribution of 113 on room-temperature Au surfaces with $-\Delta H_{\text{ads}} > 60$ kJ/mol.

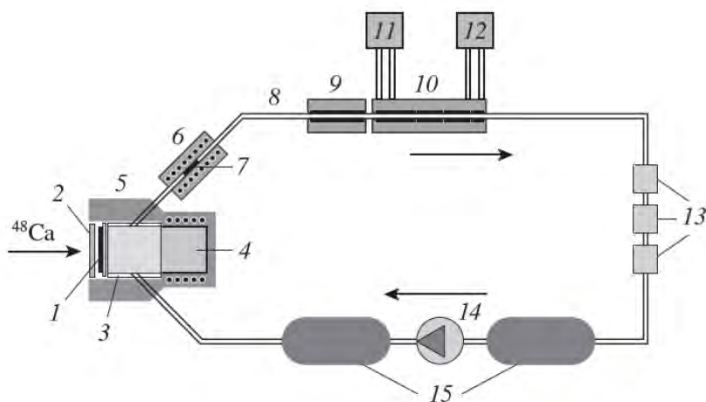


Figure 1 Schematic diagram of the experimental setup for studying the chemical properties of element 113: (1) ^{243}Am (1.5 mg cm^{-2}) + $^{\text{nat}}\text{Nd}$ ($15 \text{ } \mu\text{g cm}^{-2}$) target on the backing of Ti ($2 \text{ } \mu\text{m}$); (2) vacuum window ($4 \text{ } \mu\text{m}$ Ti foil); (3) cylindrical quartz insertion; (4) beam-stop with water cooling; (5) target chamber; (6) oven; (7) quartz filter; (8) transport capillary; (9) isothermal detector of 16 pairs of Au(Si) detectors at ambient temperature; (10) cryodetector of 32 pairs of Au(Si) detectors; warm end at $+20^\circ\text{C}$ and cold end at -50°C ; (11) water thermostat; (12) cryothermostat; (13) gas purification system; (14) pump; and (15) buffer volumes.

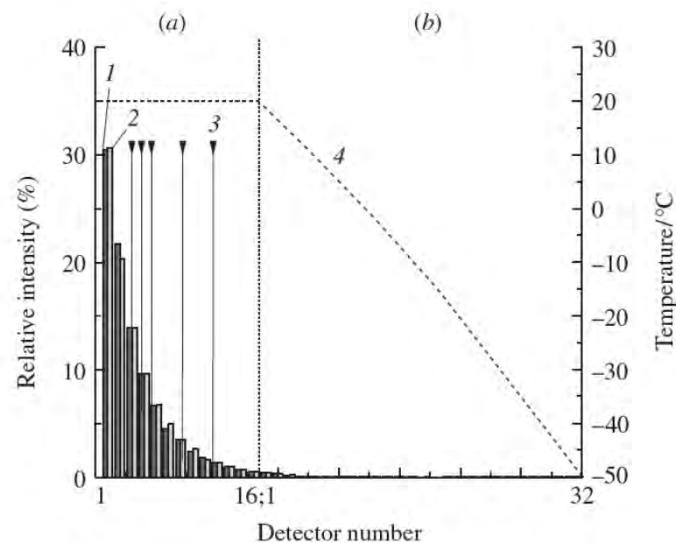


Figure 3 Distribution of (1) ^{185}Hg and (2) ^{211}At in the detector modules together with (3) the position of the observed decay chains attributed to $^{284}\text{113}$; dashed line (4) represents the temperature gradient from $+20$ to -50°C at (a) isothermal and (b) cryomodules of the detector.

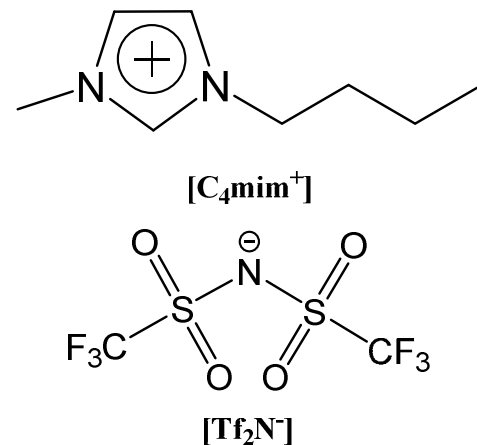
“Designer Molecules” Under Study at Texas A&M

- Ionic Liquids

- E. E. Tereshatov *et al.*, *Solvent Extr. Ion Exc.* **33**(6), 607 (2015).

doi:[10.1080/07366299.2015.1080529](https://doi.org/10.1080/07366299.2015.1080529)

- E. E. Tereshatov *et al.*, *J. Phys. Chem. B* **9**, 2311 (2015). doi:[10.1021/acs.jpccb.5b08924](https://doi.org/10.1021/acs.jpccb.5b08924)

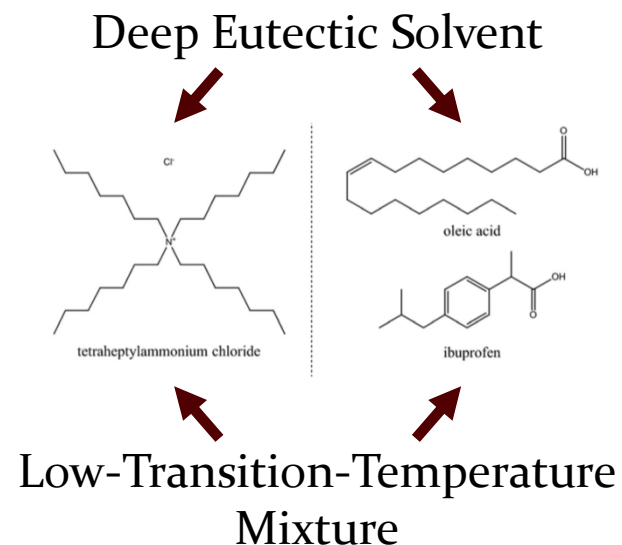


- Deep Eutectic Solvents

- E. E. Tereshatov *et al.*, *Green Chem.* **18**, 4616 (2016). doi:[10.1039/C5GC03080C](https://doi.org/10.1039/C5GC03080C)

- Low-Transition-Temperature Mixtures

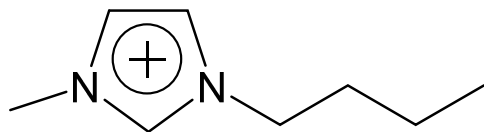
- E. E. Tereshatov *et al.*, *Green Chem.* **18**, 4616 (2016). doi:[10.1039/C5GC03080C](https://doi.org/10.1039/C5GC03080C)



Separation of In and Tl Using Ionic Liquids

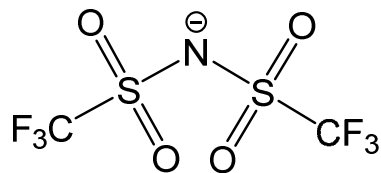


Evgeny Tereshatov



[C₄mim⁺]

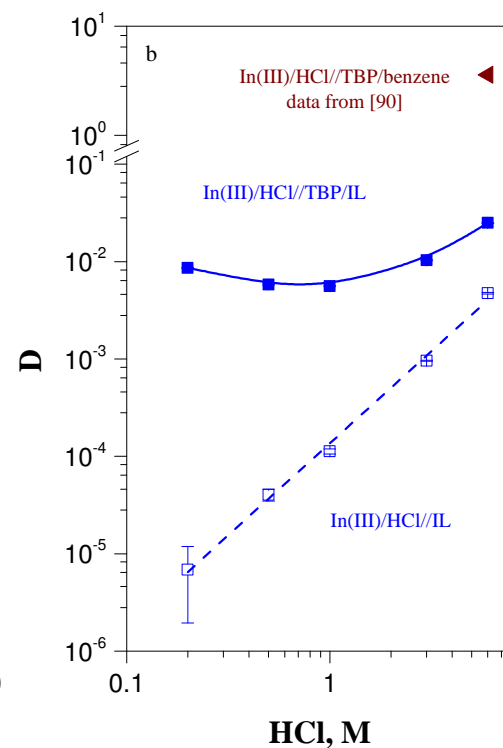
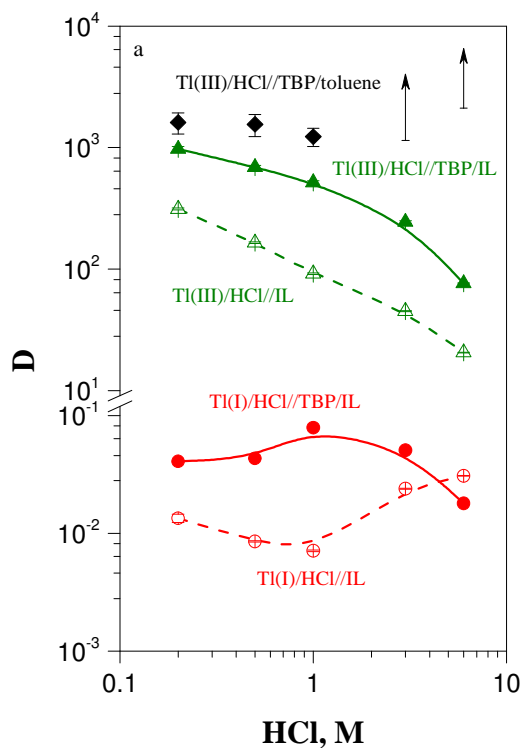
1-butyl-3-methylimidazolium



[Tf₂N⁻]

bis(trifluoromethanesulfonyl)imide

- Separation factors of $>10^7$ were obtained for In(III) and Tl(III).



E. E. Tereshatov *et al.*,
Solvent Extr. Ion Exc. **33**(6), 607 (2015).

Extraction of In Using Deep Eutectic Solvents

- In(III) was extracted by the N_{7777} -Cl-based DESs.
- In contrast, Tl(III) was extracted by the ILs.

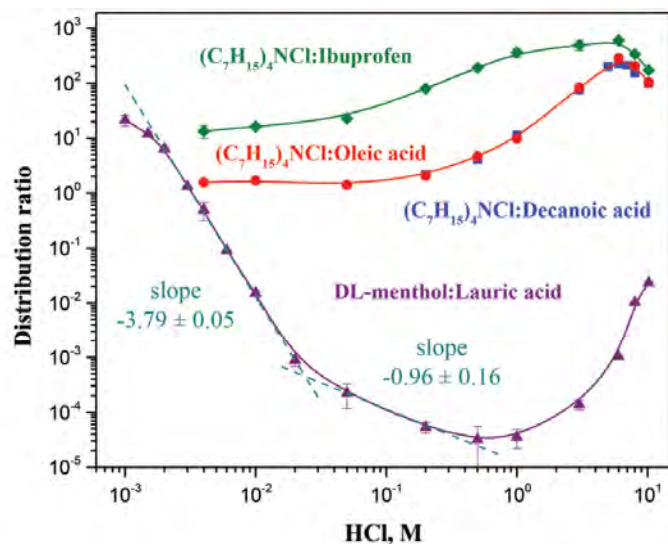


Fig. 3 Effect of aqueous hydrochloric acid concentration on the extraction efficiency of In into quaternary ammonium- and menthol-based hydrophobic mixtures. The solid lines are drawn to guide the eye.

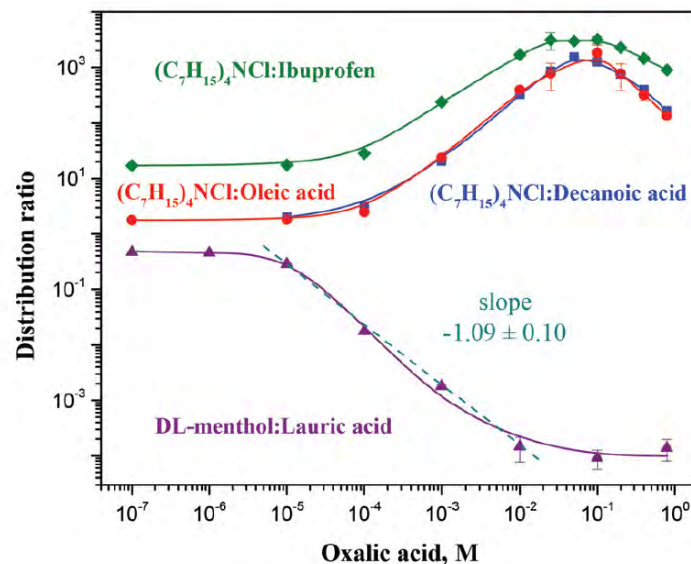


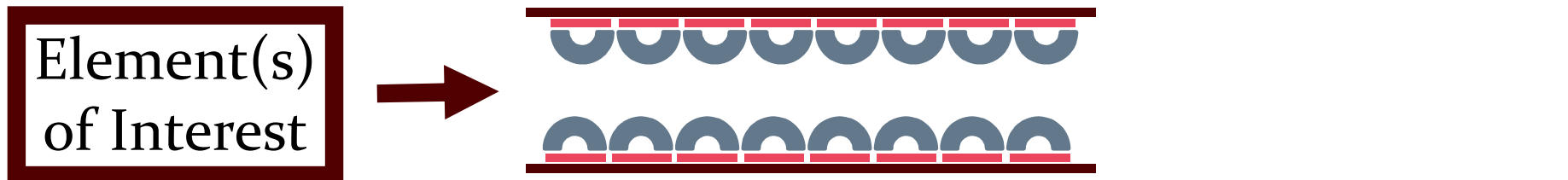
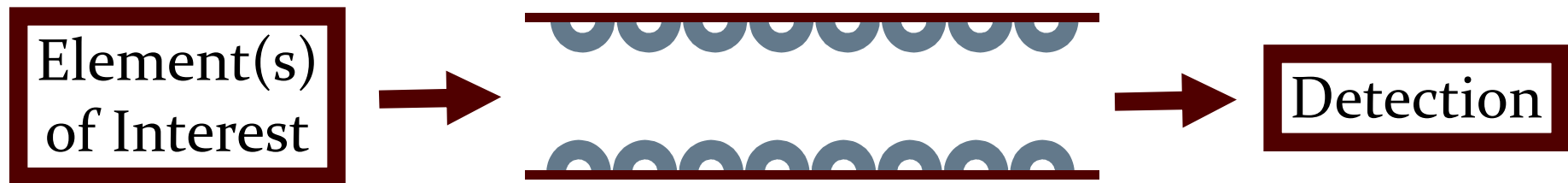
Fig. 4 Effect of oxalic acid concentration on the extraction of In into quaternary ammonium- and menthol-based hydrophobic mixtures in the presence of 4×10^{-3} M HCl. The solid lines are drawn to guide the eye.

Table 2 Results of In back-extraction from ammonium-based mixtures in HCl and oxalic acid media

Mixture	Forward extraction		Back-extraction	
	Acid	D_{In}	Acid	D_{In}
$(C_7H_{15})_4NCl$ -oleic acid	6 M HCl	280	0.2 M HCl	3
	0.01 M oxalic acid	390	0.1 M DTPA	3.67×10^{-2}
$(C_7H_{15})_4NCl$ -ibuprofen	6 M HCl	600	0.1 M DTPA	3.69×10^{-1}
	0.01 M oxalic acid	1700	0.1 M DTPA	4.71×10^{-2}

How can liquid-phase chemistry be applied to gas-phase experiments?

- There is a secret weapon. The company that sells the ionic liquids (ILs) can polymerize them and attach them to surfaces. This can potentially be used to make a column with a much stronger enthalpy of adsorption.



Thermochromatography Column with IL-Coated Detectors

What We Propose

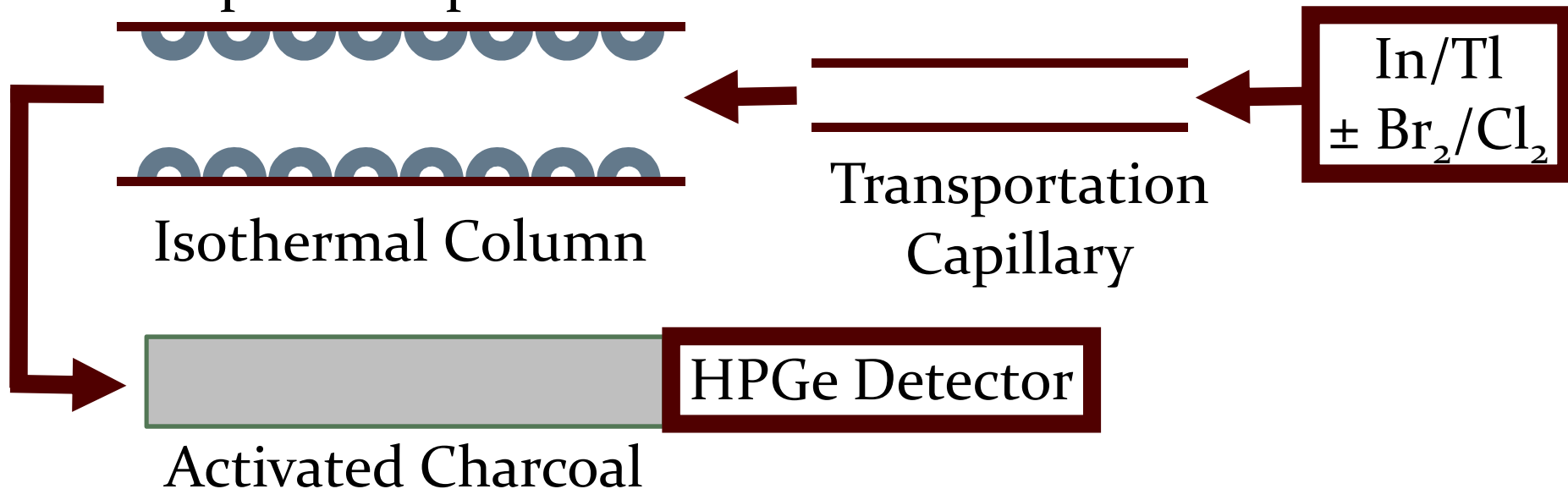
- We cannot do a superheavy experiment alone.
- We (Texas A&M) would like to join the element 113 collaboration.
- We will conduct a proof-of-principle homolog (In/Tl) experiment at Texas A&M using IL-coated chromatography columns in 2017.
- If successful, we propose to do an element 113 experiment using this technique at GSI.

Texas A&M Proposed Homolog Experiment

- Possible Nuclear Reactions:

- $^{63}\text{Cu}(^{48}\text{Ca}, 6n)^{105}\text{In}$ (EC + β^+ , $t_{1/2} = 5.07$ min, 131, 260 keV γ)
- $^{93}\text{Nb}(^{16}\text{O}, 6n)^{103}\text{In}$ (EC + β^+ , $t_{1/2} = 65$ s, 188 keV γ)
- $^{150}\text{Sm}(^{48}\text{Ca}, p5n)^{192}\text{Tl}$ (EC + β^+ , $t_{1/2} = 9.6$ min, 999 keV γ)
- $^{181}\text{Ta}(^{16}\text{O}, 6n)^{191\text{m}}\text{Tl}$ (EC + β^+ , $t_{1/2} = 5.22$ min, 70.8 keV x-ray)

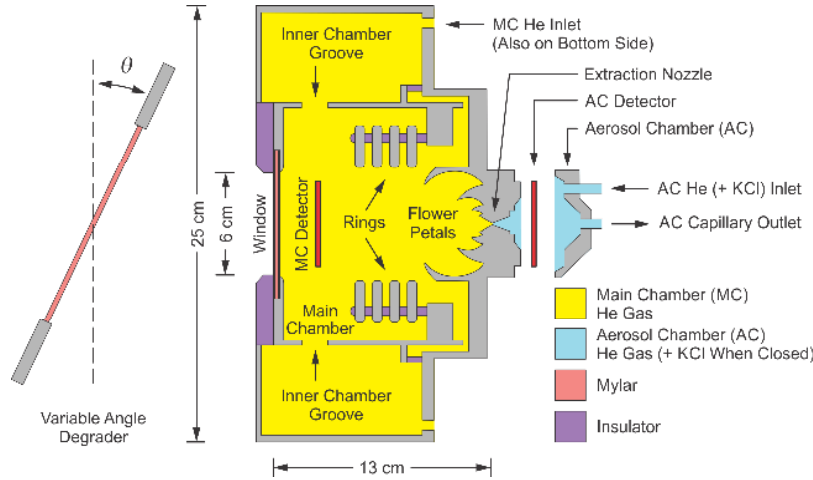
- Proposed Experiment:



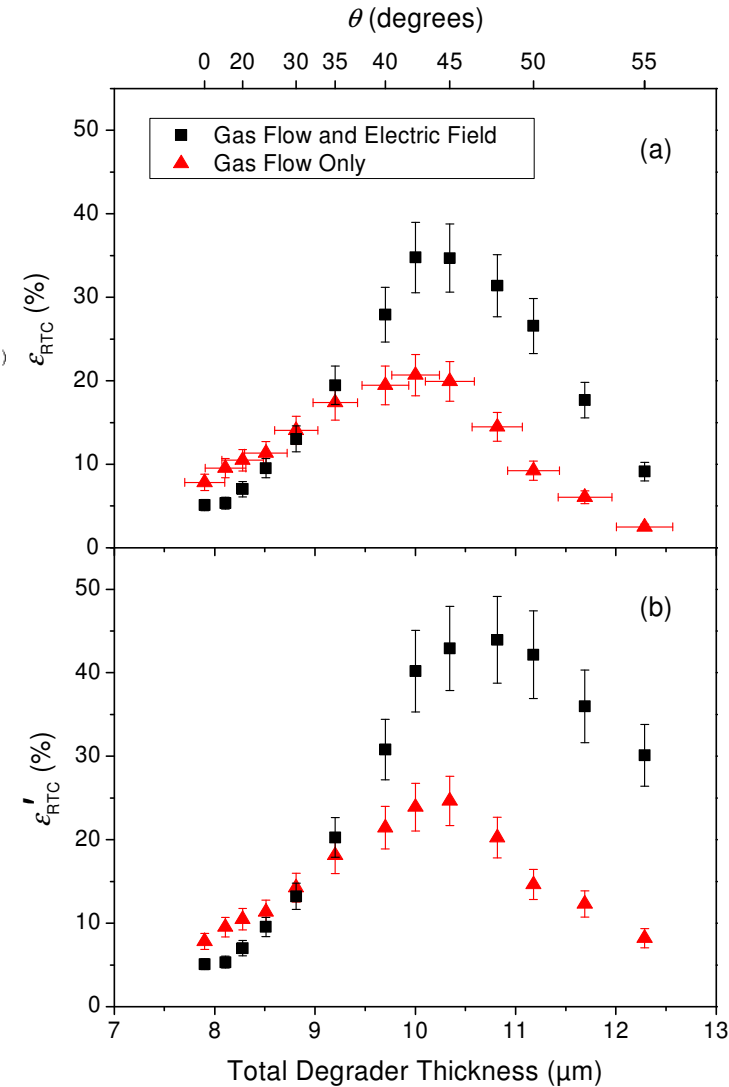
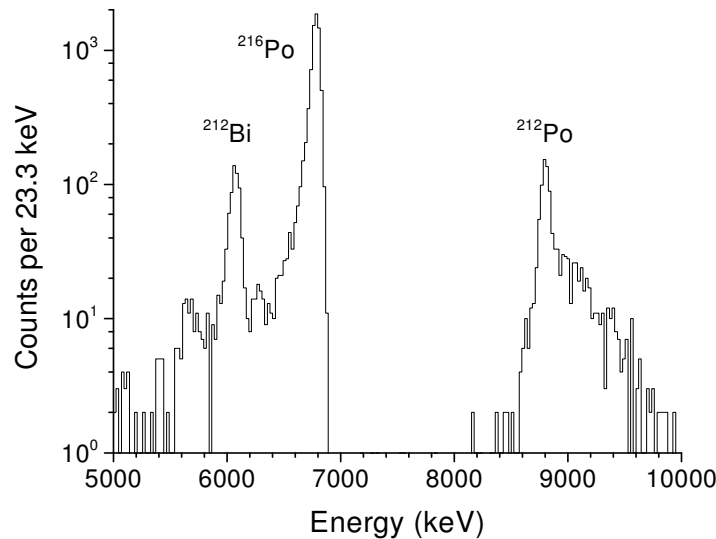
Texas A&M Recoil Transfer Chamber



Marisa Alfonso



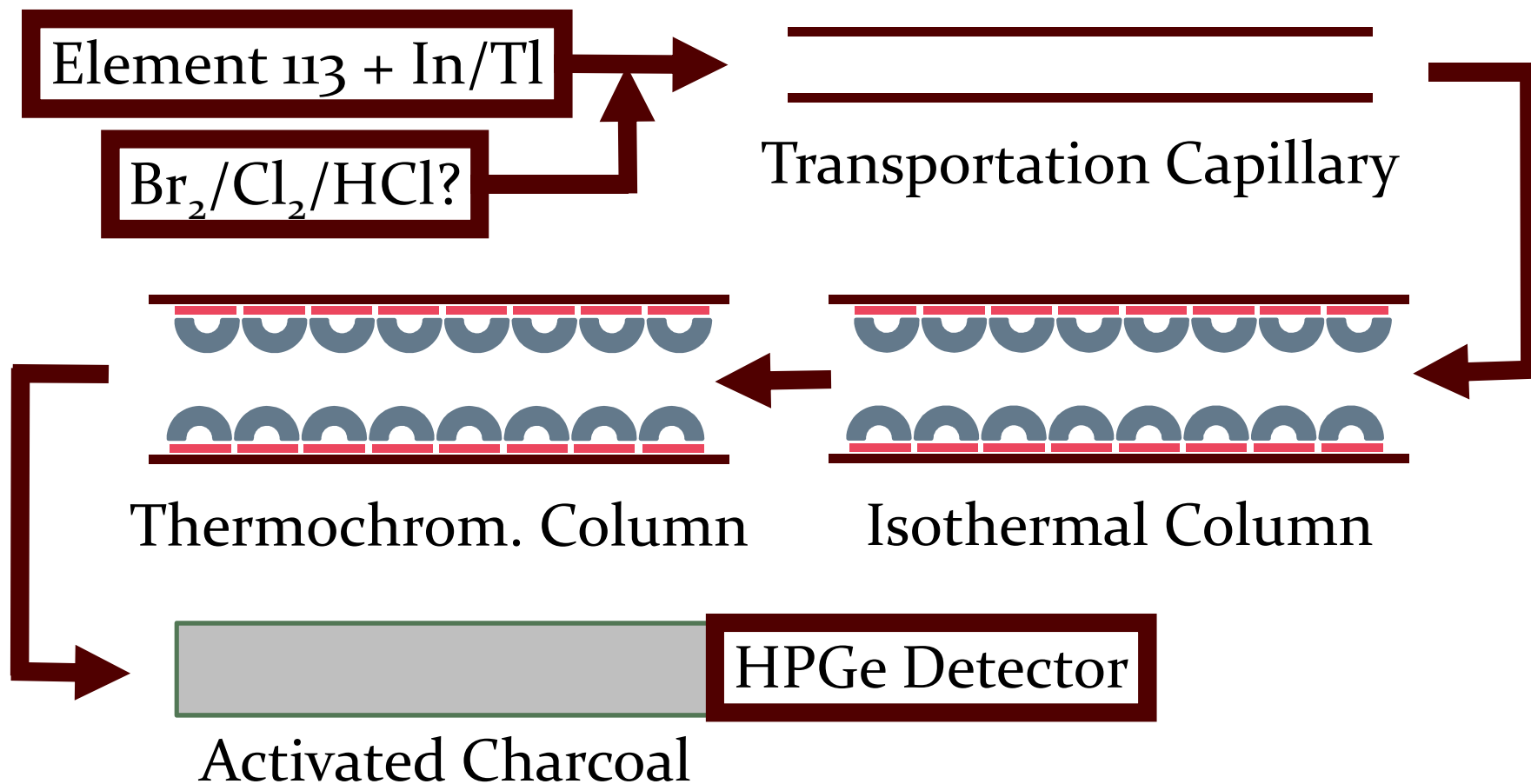
^{228}Th Source
 $t_{1/2}(^{216}\text{Po}) = 145 \pm 2 \text{ ms}$



M. C. Alfonso *et al.*, NIMA 798, 52 (2015).

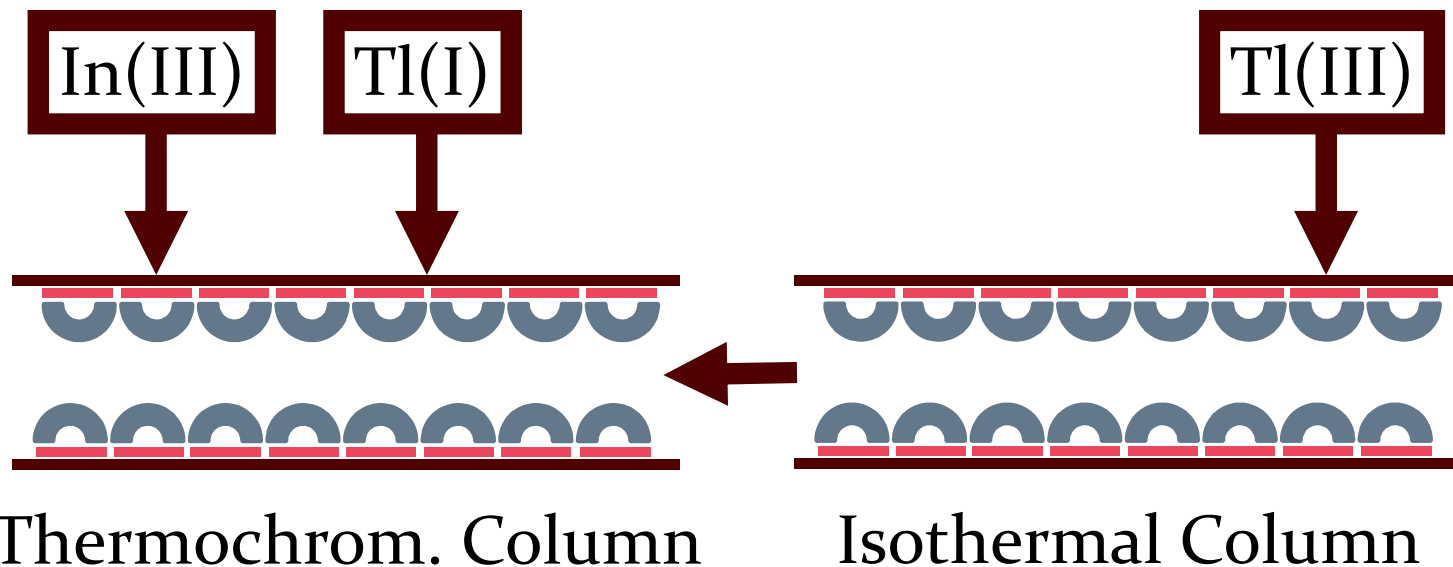
Proposed GSI Element 113 Chemistry Experiment

- The GSI experiment would be a full-blown scheme:



What do we hope to see?

- *If the gas-phase adsorption is similar to the liquid-phase, then there should be very different deposition profiles for In(III), Tl(I), and Tl(III):*



- This gives us a wide dynamic range. It could work regardless of whether element 113 is more like In or Tl, or has a 3+ state.

Summary

- We have studied the application of modern classes of “designer molecules” to the chemistry of the group 13 homologs In and Tl.
- The properties of these molecules are tunable and allow us to see substantial differences in the chemistry of In(III), Tl(I), and Tl(III).
- We propose to join the element 113 chemistry collaboration and perform homolog experiments at Texas A&M.
- We have proposed an element 113 experiment at GSI that leverages existing equipment and collaborative efforts, and provides a wide dynamic range.

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