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

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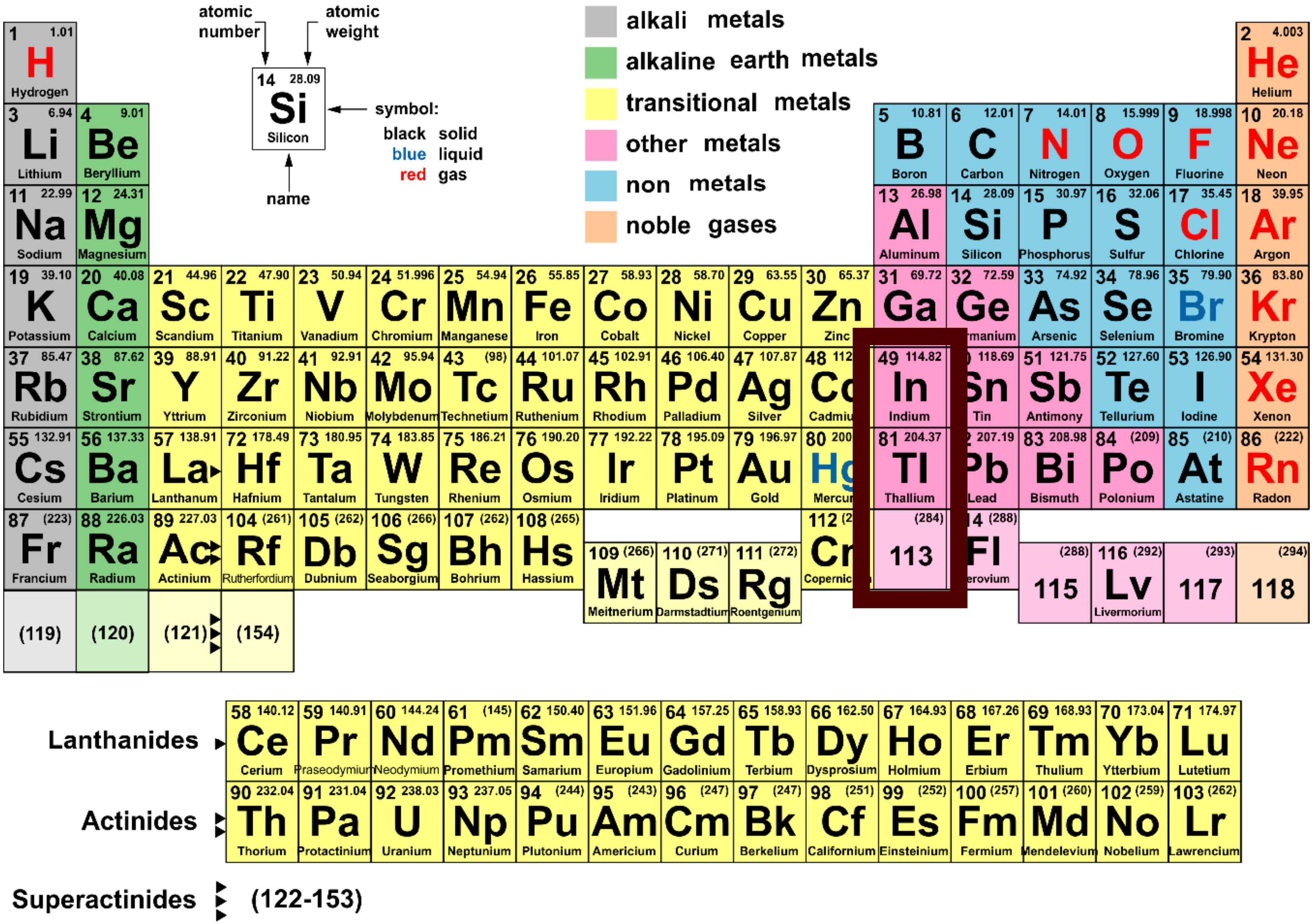
August 26, 2016

Use of Homologs for Group 13 Chemistry



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/H_2 atmosphere with $\Delta H_{ads}(113) = -158.6$ 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 $-\Delta H_{ads}$ can be given by such a thermochromatography study. In

V. Pershina *et al.*, Chem. Phys. Lett. **480**, 157 (2009).

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

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

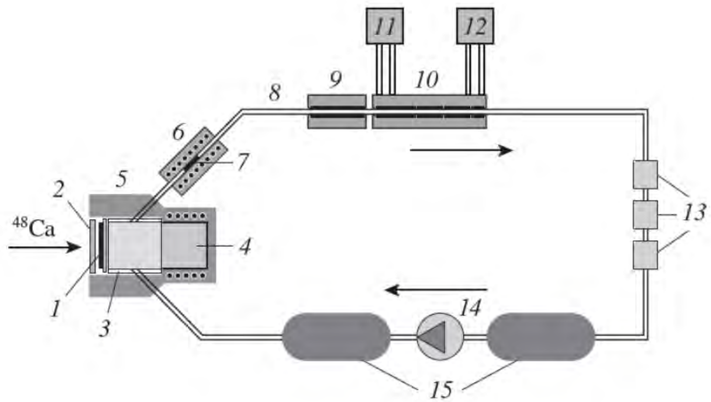


Figure 1 Schematic diagram of the experimental setup for studying the chemical properties of element 113: (*1*) ^{243}Am (1.5 mg cm^{-2}) + ^{nat}Nd (15 μg cm^{-2}) target on the backing of Ti (2 μm); (*2*) vacuum window (4 μm Ti foil); (*3*) cylindrical quartz insertion; (*4*) beam-stop with water cooling; (*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 °C and cold end at −50 °C; (*11*) water thermostat; (*12*) cryothermostat; (*13*) gas purification system; (*14*) pump; and (*15*) buffer volumes.

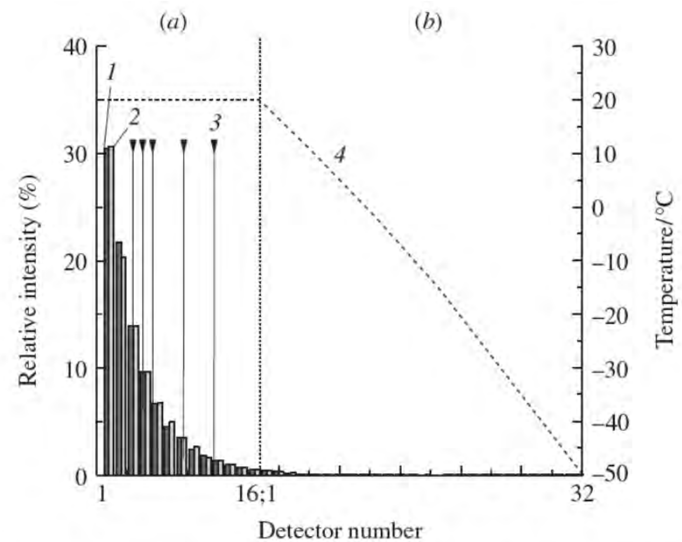
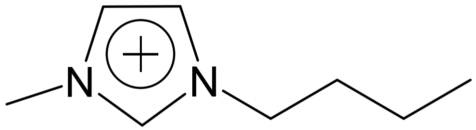


Figure 3 Distribution of (*1*) ^{185}Hg and (*2*) ^{211}At in the detector modules together with (*3*) the position of the observed decay chains attributed to ^{284}113; dashed line (*4*) represents the temperature gradient from +20 to −50 °C at (*a*) isothermal and (*b*) cryomodules of the detector.

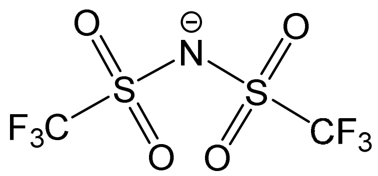
S. N. Dmitriev *et al.*, Mendeleev Comm. **24**, 253 (2014).

“Designer Molecules” Under Study at Texas A&M

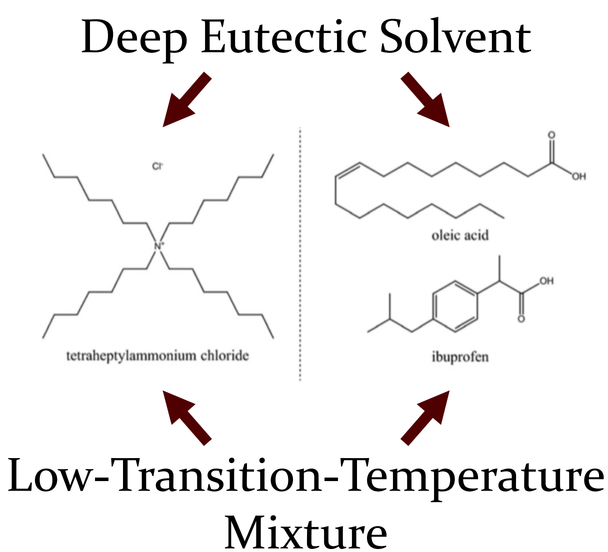
- Ionic Liquids
  - E. E. Tereshatov *et al.*, Solvent Extr. Ion Exc. **33**(6), 607 (2015). doi:10.1080/07366299.2015.1080529
  - E. E. Tereshatov *et al.*, J. Phys. Chem. B **9**, 2311 (2015). doi:10.1021/acs.jpcb.5b08924
- Deep Eutectic Solvents
  - E. E. Tereshatov *et al.*, Green Chem. **18**, 4616 (2016). doi:10.1039/C5GC03080C
- Low-Transition-Temperature Mixtures
  - E. E. Tereshatov *et al.*, Green Chem. **18**, 4616 (2016). doi:10.1039/C5GC03080C



[C_4mim^+]

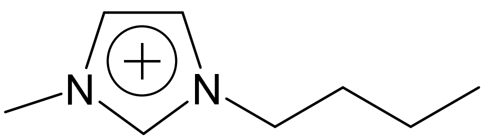


[Tf_2N^-]



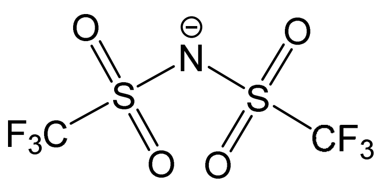
Separation of In and Tl Using Ionic Liquids

Evgeny Tereshatov



[C_4mim^+]

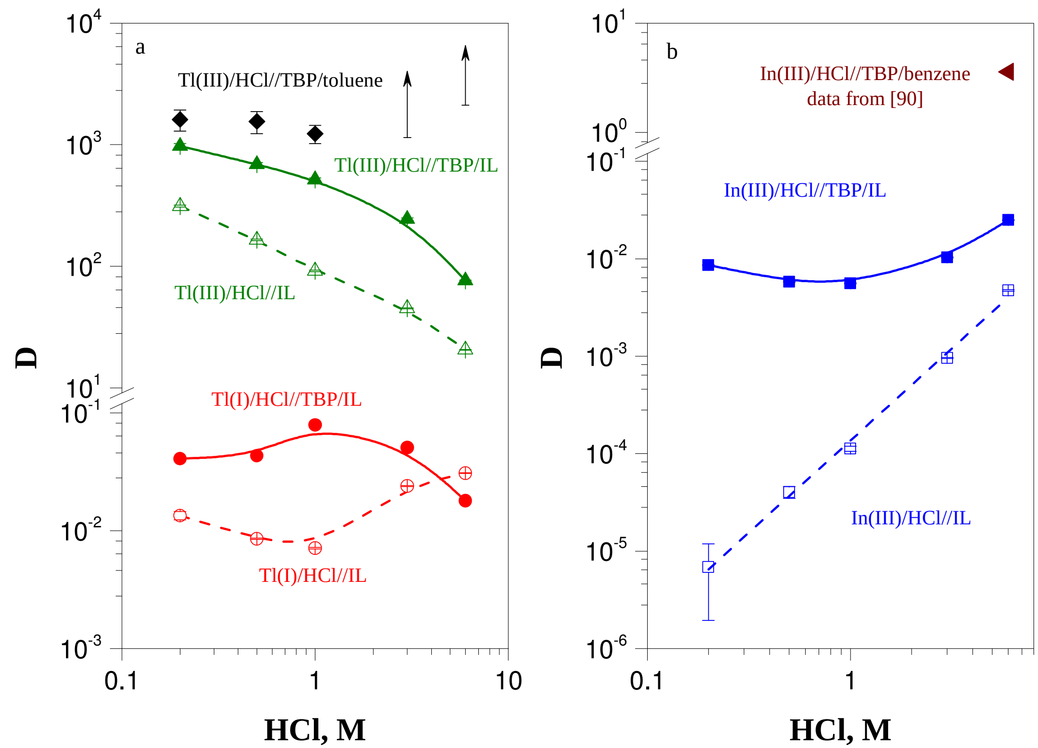
1-butyl-3-methylimidazolium



[Tf_2N^-]

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.

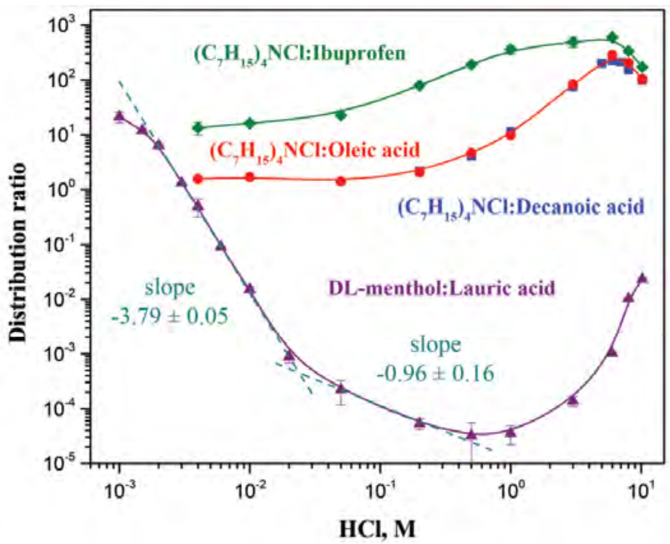


Fig. 3 Effect of aqueous hydrochloric acid concentration on the extraction efficiency of In into quaternary ammonium- and menthol-based hydrophobic mixtures. The solid lines are drawn to guide the eye.

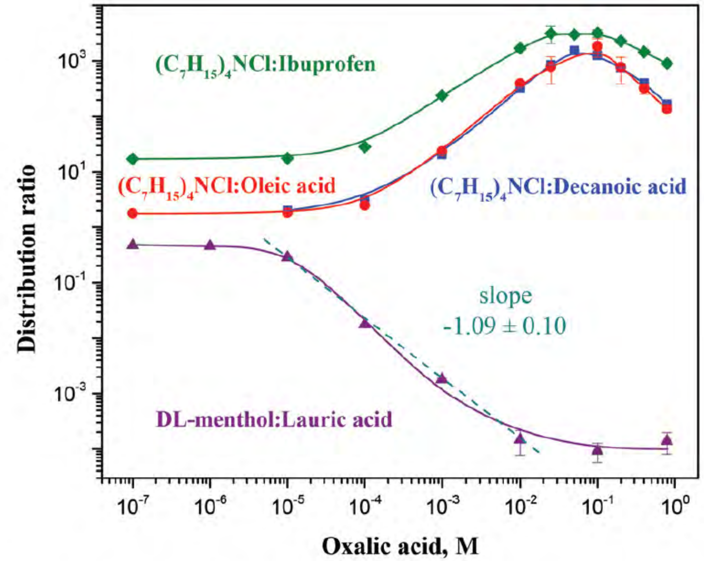


Fig. 4 Effect of oxalic acid concentration on the extraction of In into quaternary ammonium- and menthol-based hydrophobic mixtures in the presence of 4×10^{-3} M HCl. The solid lines are drawn to guide the eye.

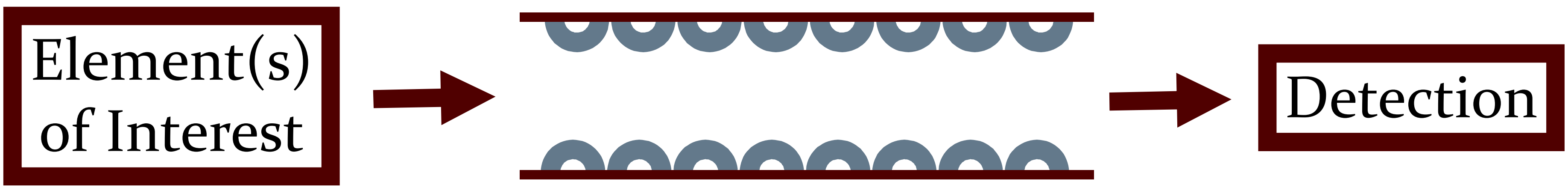
Table 2 Results of In back-extraction from ammonium-based mixtures in HCl and oxalic acid media

	Forward extraction		Back-extraction	
Mixture	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}

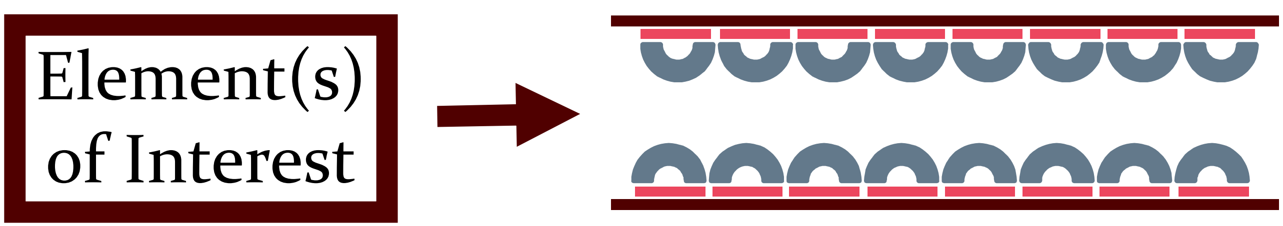
EET *et al.*, Green Chem. **18**, 4616 (2016).

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.



Isothermal Column



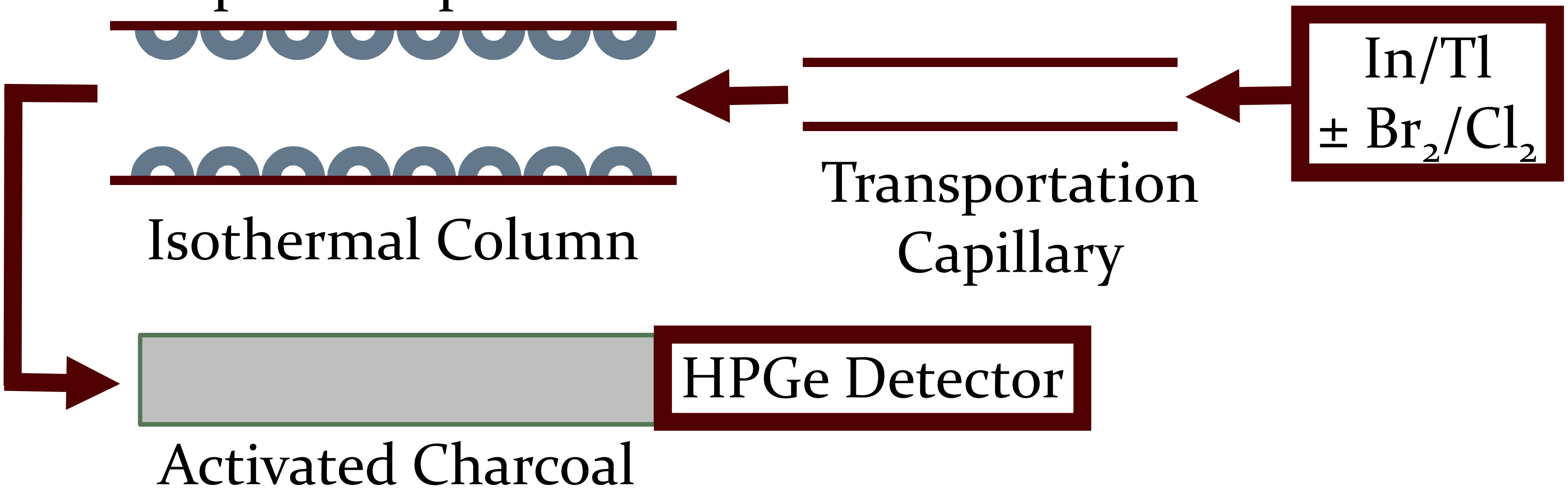
Thermochromatography Column with IL-Coated Detectors

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.

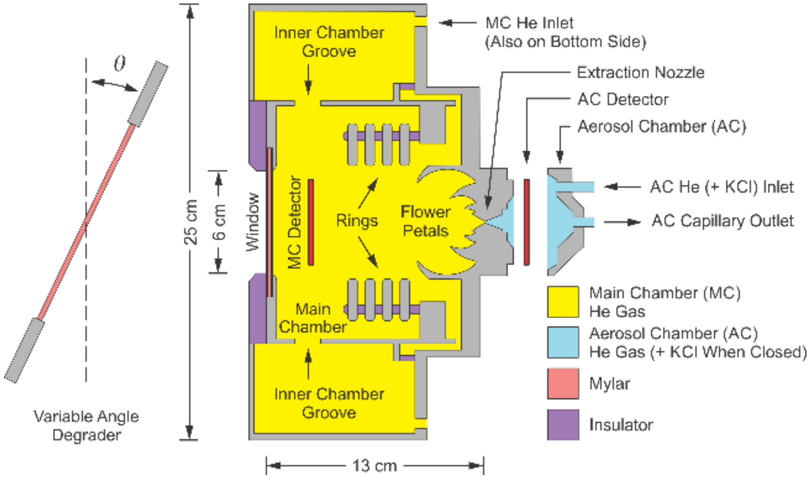
Texas A&M Proposed Homolog Experiment

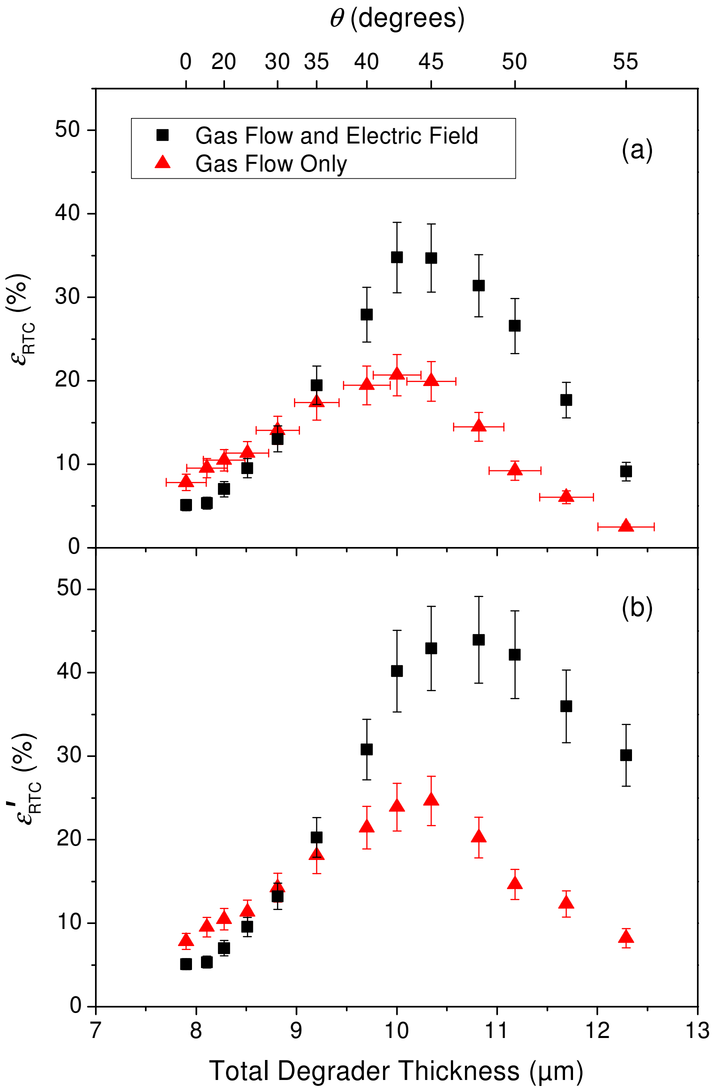
- Possible Nuclear Reactions:
  - $^{63}Cu(^{48}Ca, 6n)^{105}In$ (EC + β^+, $t_{1/2}$ = 5.07 min, 131, 260 keV γ)
  - $^{93}Nb(^{16}O, 6n)^{103}In$ (EC + β^+, $t_{1/2}$ = 65 s, 188 keV γ)
  - $^{150}Sm(^{48}Ca, p5n)^{192}Tl$ (EC + β^+, $t_{1/2}$ = 9.6 min, 999 keV γ)
  - $^{181}Ta(^{16}O, 6n)^{191m}Tl$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



Texas A&M Recoil Transfer Chamber

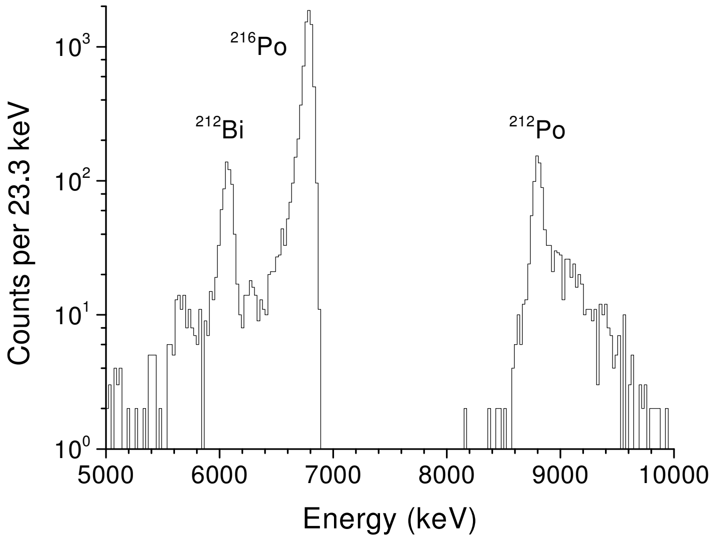
Marisa Alfonso





^{228}Th Source

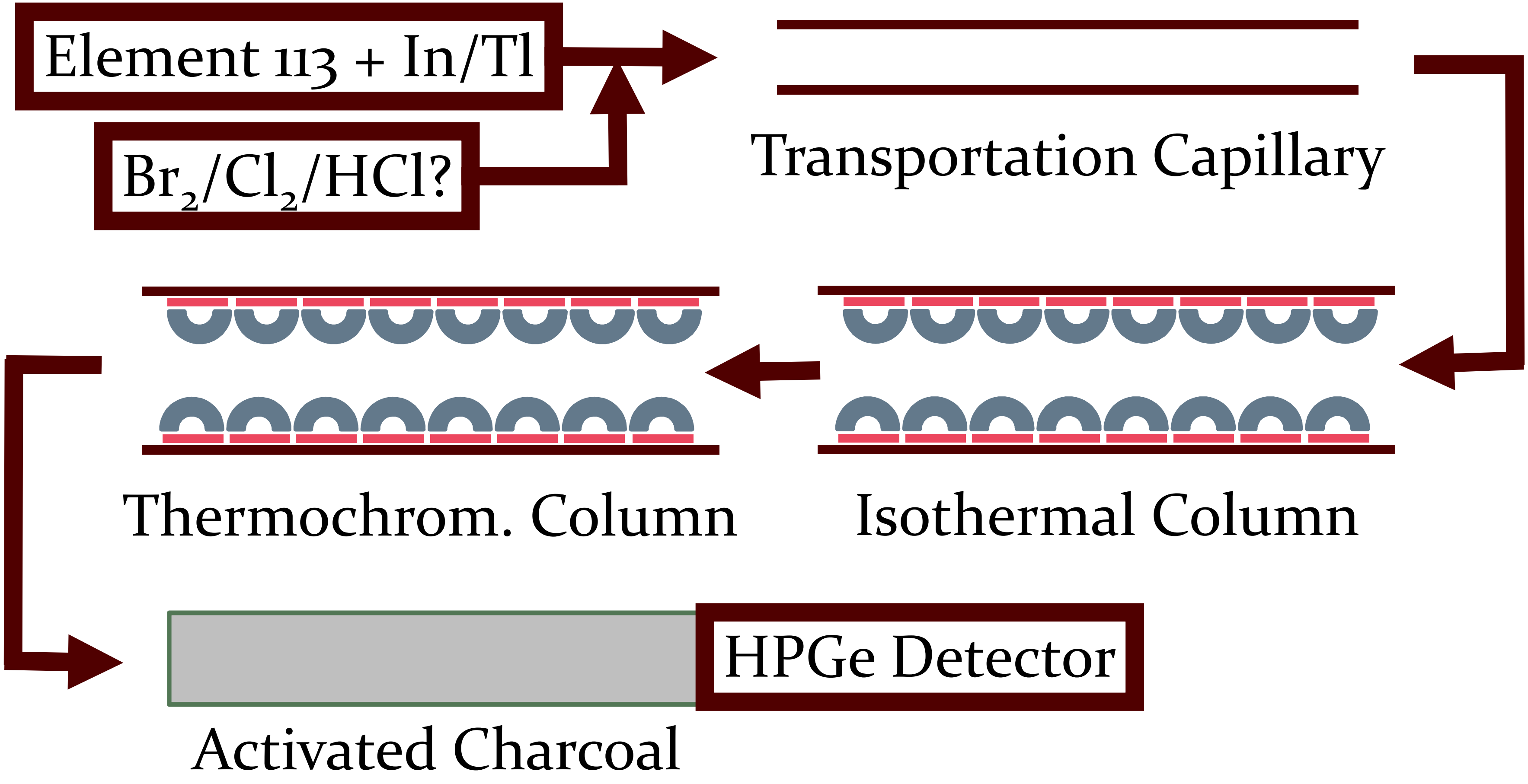
$t_{1/2}(^{216}\text{Po})$ = 145 ± 2 ms



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

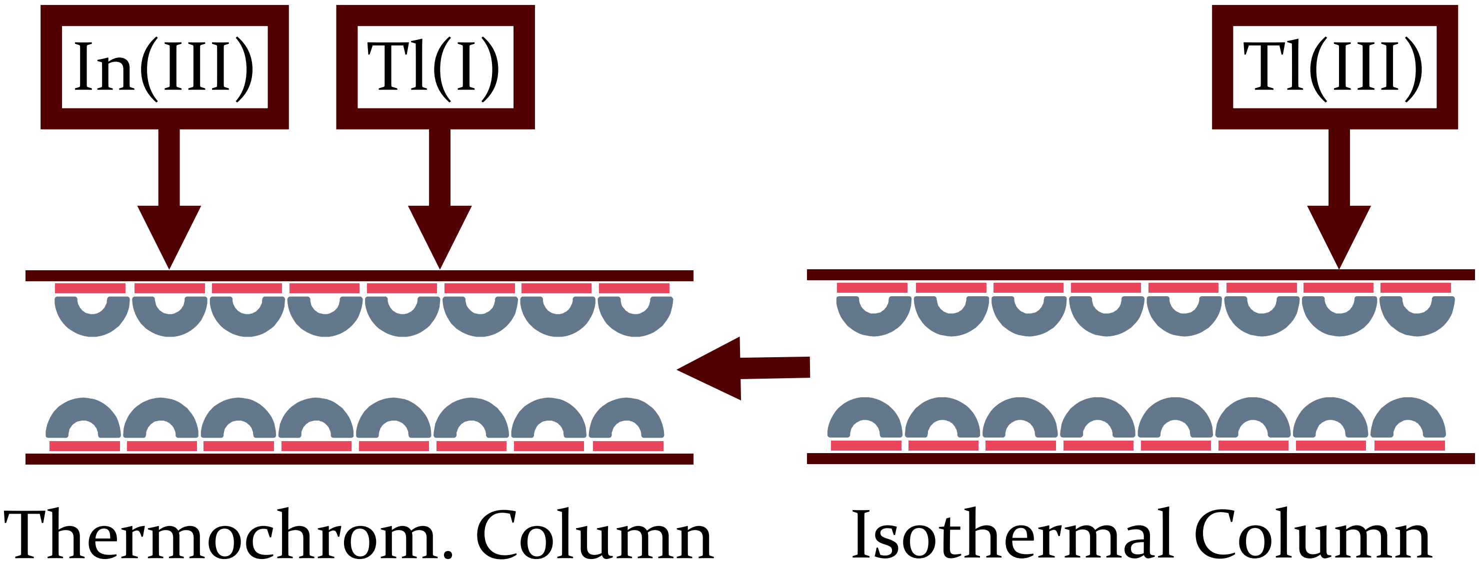
Proposed GSI Element 113 Chemistry Experiment

- 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(III), and Tl(I):



- 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.

Acknowledgements: Collaborators and Funding Agencies

- M. Yu. Boltoeva
- V. Mazan
- E. E. Tereshatov
- K. A. Tran
- M. F. Volia

- Cyclotron Institute staff