Po and Hg adsorption on Au surfaces functionalized with self-assembled monolayers

A.M. Bukowski,[1,2] A.S. Kirkland,[1,2] P. Bartl,[3] J. John,[3] A. Yakushev,[4,5] V. Zach,[6] and C.M. Folden III[1,2]
[1]*Cyclotron Institute, Texas A&M University, College Station, Texas 77843 USA*
[2]*Department of Chemistry, Texas A&M University, College Station, Texas 77843 USA*
[3]*Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, 115 19 Prague, Czech Republic*
[4]*SHE Chemistry Department, GSI Helmholtzzentrum fur Schwerionenforschung, Darmstadt, 64291, Germany*
[5]*SHE Chemistry Section, Helmholtz Institute Mainz, Mainz, 55099, Germany*
[6]*Nuclear Physics Institute, Czech Academy of Sciences, 250 68 Řež, Czech Republic*

Experiments studying the chemical properties of superheavy elements (SHEs) typically use "one-atom-at-a-time" techniques, such as gas-phase chromatography, which can measure the adsorption enthalpy of SHEs on various surfaces. A recent study of the SHE Nh (Z=113) found that it sorbed too strongly onto a Au surface, preventing the measurement of its adsorption enthalpy [1,2]. To address this challenge in these one-atom-at-a-time set-ups, our group proposes a method to change the interactions of heavy elements with Au surfaces, namely by the addition of self-assembled monolayers (SAMs). The functionalization of Au surfaces with SAMs aims to tune the adsorption of products on the surface of Au, providing additional information on the adsorption enthalpy of heavy elements. SAMs selectivity has been previously tested in online gas-phase experiments for Ir (Z=77), Er (Z=68), and At (Z=85) with both 1-(11-mercaptoundecyl)imidazole and 12-mercaptododecanoic acid (MDDA) SAMs [3,4]. The current work describes recent experiments performed in the SHEs homologs laboratory [5] at the U120M accelerator in Řež (Czech Republic), demonstrating that Po and Hg adsorption changed between a bare Au surface and a SAM-functionalized Au surface in an isothermal gas chromatography column [see the SAMs shown in Fig 1].

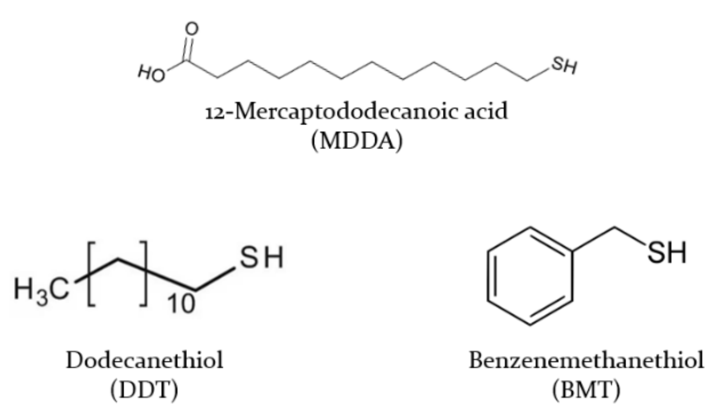

Fig. 1. SAMs molecules used in heavy element adsorption studies.

In November 2024, a first set of experiments was completed comparing Po adsorption on bare Au and MDDA-functionalized chips. Po activity, produced by the $^{208}Pb(^{3}He, 6\text{-}7n)^{205,204}Po$ reaction, was passed through an array of non-functionalized chips, and separately through an array of chips functionalized with MDDA. Gamma ray spectra showed that both the Au and functionalized surfaces adsorbed ^{204}Po ($t_{1/2}$ = 3.52 h) and 205Po ($t_{1/2}$ = 1.74 h). The Po data had a steeper slope and therefore adsorbed more strongly onto the functionalized surface than the Au surface [see Fig. 2].

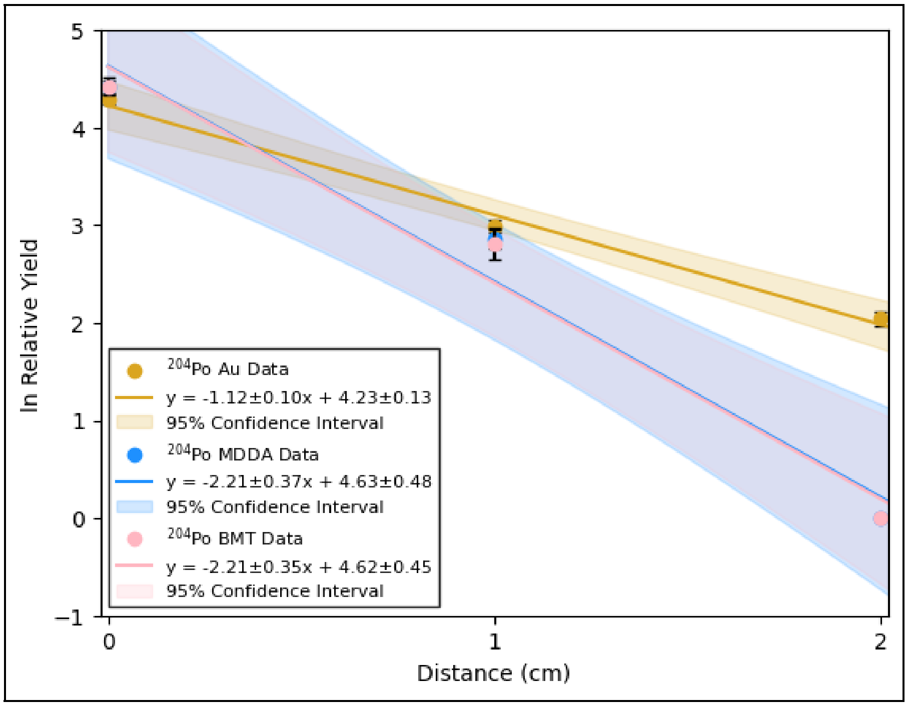

Fig. 2. Relative Po adsorption on Au-coated, 12-mercaptododecanoic acid (MDDA)-functionalized, and benzenemethanethiol (BMT)-functionalized glass chips.

In April 2025, Po was again produced and adsorbed onto functionalized SAMs made of dodecanethiol (DDT) and benzenemethanethiol (BMT) [see Fig 2]. This variation of SAM terminal groups allowed for a study of adsorption in the presence of varying electron density. In addition, Hg was produced by the $^{nat}Pt(^{3}He, 3\text{-}6n)^{196\text{-}191}Hg$ reactions and passed over Au-coated chips and MDDA-functionalized chips. ^{192}Hg ($t_{1/2}$ = 4.85 h) and ^{193}Hg ($t_{1/2}$ = 3.80 h) were produced in the greatest yields and were compared. Like Po, Hg also adsorbed more strongly onto the functionalized surface than the Au surface, showing a trend between elements and experiments [see Fig. 3].

These experiments expanded the data available on heavy elements adsorbed onto SAMs and will help determine how much the chemistry of heavy elements affects their adsorption onto organic surfaces. Hg is known to be more volatile than Po [6,7], therefore comparing their adsorption can help determine how important volatility is in adsorption studies. We have confirmed that functionalizing Au surfaces changes the interaction that heavy elements have, which can be applied to Au-coated silicon detector arrays. The data collected in these experiments is a first step in discovering how heavy elements react with organic thiol-based surfaces. Further experiments are planned for November 2025.

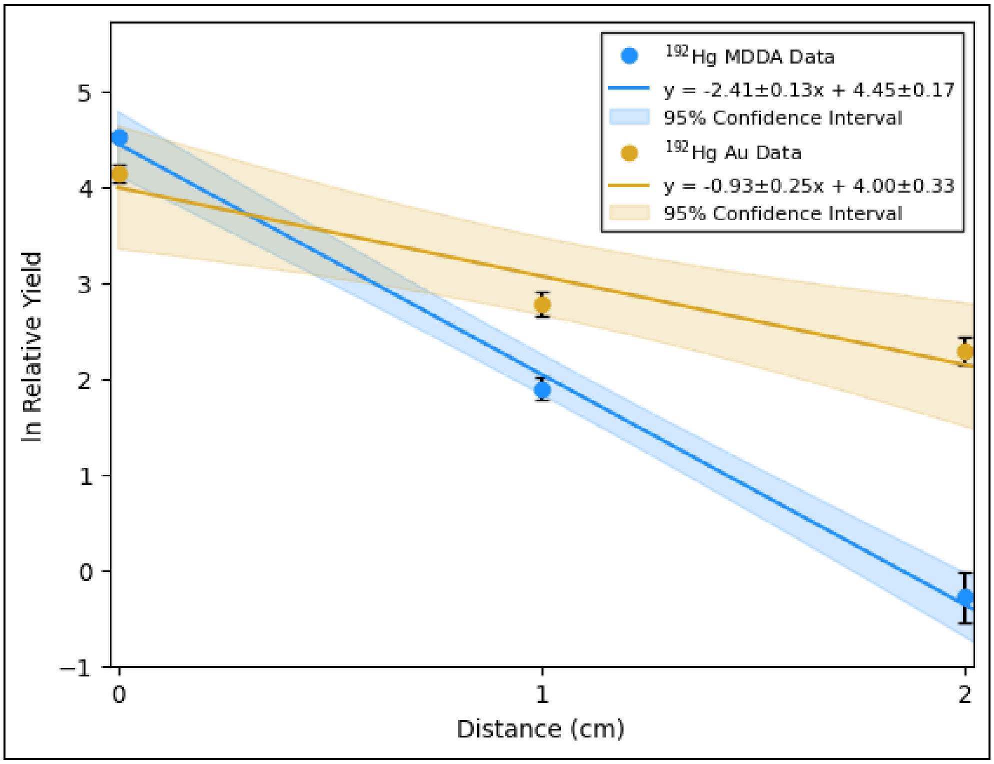

Fig. 3. Relative Hg adsorption on bare Au and 12-mercaptododecanoic acid (MDDA)-functionalized Au.

[1] A. Yakushev *et al.*, Front. Chem. **12**, 1 (2024). doi:10.3389/fchem.2024.1474820

[2] A. Yakushev *et al.*, Front. Chem. **9**, 1 (2021). doi:10.3389/fchem.2021.753738

[3] V. Zakusilova, Ph.D. Thesis, University of Strasbourg, 2022, available at https://www.theses.fr/2022STRAE020.

[4] V. Zakusilova, E.E. Tereshatov, M. Boltoeva, and C.M. Folden III, Appl. Surf. Sci **642**,158356 (2024); doi:10.1016/j.apsusc.2023.158356

[5] P. Bartl *et al.*, Nucl. Instrum. Methods Phys. Res. A1052, 168280 (2023); doi:10.1016/j.nima.2023.168280

[6] A. Yakushev *et al.*, Radiochim. Acta **93**, 1 (2009); doi:10.1524/ract.93.1.1.58298

[7] E. Maugeri *et al.*, Radiochim Acta **104**, 11 (2016). doi:10.1515/ract-2016-2573