Mass Spectrometry of Separated Gold and Silver Nanocrystal Compounds

T. Gregory Schaaff and Phillip F. Britt

Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6365

Interesting and potentially useful electronic, magnetic and chemical properties depend upon cluster size and distribution of size more than any other feature. However, all too often, studies are based on heterogeneous systems, in which interesting and potentially useful (quantum or chemical) size-effects are convoluted due to statistical distributions. One hurdle to overcome in nanometer-scale materials is heterogeneity of sample, both for the fundamental understanding of chemical and physical properties and for their ultimate use. Aerosol- and laser desorption-based ionization, combined with modern mass spectrometric methods can be used to analyze and evaluate nanostructured materials. We have utilized UV-Vis absorption spectroscopy and laser desorption ionization mass spectrometry (LDI-MS) to monitor the separation of gold-thiolate (Au:SR) and silver-thiolate (Ag:SR) cluster compounds by their respective metallic core size by both fractional crystallization (FC) and gel permeation chromatography (GPC).

The GPC was performed with a Waters HPLC using a column bank consisting of Styragel HR1, HR3 and HR5E columns. The GPC columns were calibrated using a mixture of polyethylene standards. The longest retention time (i.e. for the monomer) was 34.52 min (denoted by the arrow in Figure 1. LDI-MS was used to determine the components of a mixture of Au:SR compounds having core-masses of 14 kDa, 22 kDa and 36 kDa by measuring the abundance of high-mass fragment ions generated by irradiation of neat films at 327 nm. LDI-MS was then used to monitor the FC separation of the components by cluster core-size. The chromatograms for a set of 28 kDa (core-mass) Au:SR cluster compounds in THF are shown in Figure 1, where R=dodecane (C12), hexane (C6) and butane (C4). As the chain length decreases, a large poorly resolved peak appears at longer retention times. The appearance of this peak was not concentration dependent and likely indicates an increased interaction of the cluster compounds with the polystyrene packing material at shorter thiolate chain lengths. Typical interactions with polystyrene column packing material involve dipole (or induced dipole) interactions between the polarizable polystyrene spheres and polar molecules.

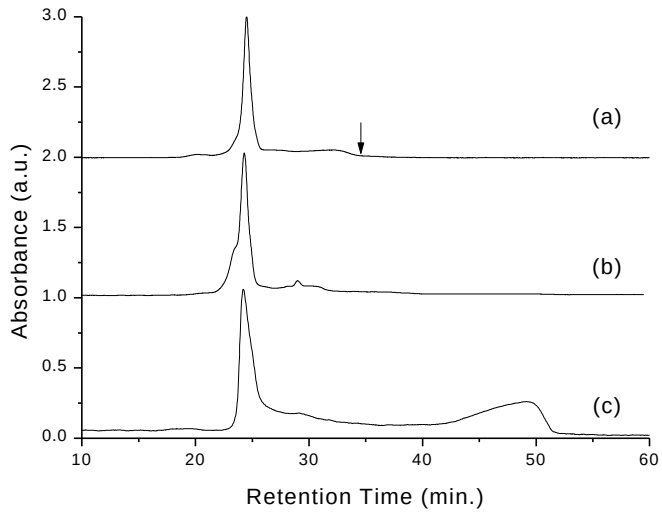

Figure 1: Chromatograms for Au:SR cluster compounds with R=C12(a), C6(b) and C4(c) monitored at 525 nm.

A common phenomenon observed for metallic clusters is termed electron ‘spill-out’ in which the electron density of the cluster can extend well beyond the metallic core. As such, the whole cluster assembly can be considered as consisting of a highly polarizable sphere surrounded by a dense dielectric, which inhibits interactions of the cluster core with the column. The cluster compounds may then interact with the column when the r’/r ratio is below a given amount (where r’ = metallic core radius and r = total radius (core+thiolate)). The whole cluster assembly can then be envisioned as a large polarizable sphere when the chain length hydrocarbons can no longer shield any induced-dipole (van der Waals) interactions with the column.

To test this hypothesis, we first separated two distinct compounds by fractional crystallization with metallic core masses of 28 kDa and 66 kDa. After separation and analysis by LDI-MS and UV-Vis absorption spectroscopy, these two compounds were mixed and injected into the HPLC. Figure 2a shows the chromatogram (at 525 nm) for the ‘spiked’ 28 kDa/66 kDa core mass Au:SC6 cluster

compounds. The 28 kDa Au:SC6 cluster compounds elute at the same R.T. (see chromatogram Figure 2a) as observed in studies involving FC separated 28 kDa cluster compounds (Figure 1b). However, the larger 66 kDa Au:SC6 cluster compounds elute at retention times after that measured for the monomer standard, indicating interactions with the column similar to that of the 28 kDa Au:SC4 cluster compounds. The optical absorption corresponding to each peak taken on line with a photodiode array detector was identical to the optical absorption of the initial 28 and 66 kDa cluster compounds before mixing and the collected fractions retained the same optical features. The LDI-MS of the collected fractions were similar to that of the initial compounds (before mixing).

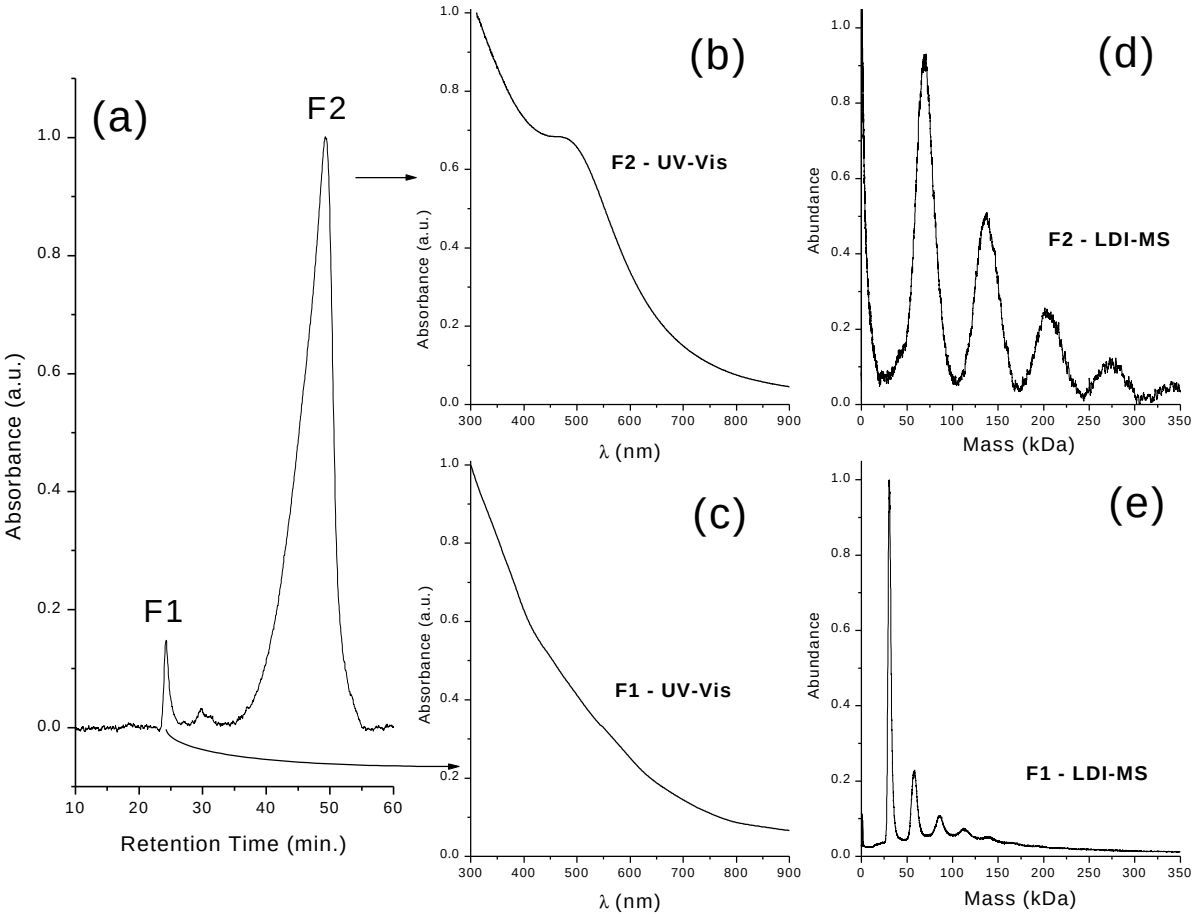

Figure 2: Chromatogram of 'spiked' Au:SC6 cluster compound sample. Fractions were collected from 15 separate chromatographic separations. The ultraviolet-visible absorption spectra for the separated compounds are shown in (b) and (c) , and the LDI mass spectra are shown in ((d) and (e). Both the UV-Vis absorption spectra and LDI-MS match those of the initial compounds (i.e. before mixing and separating by HPLC).

From these and other studies, standard polystyrene GPC does not seem to have the resolving power to completely separate individual components in a narrow size range. However, if the polarizability of the Au and Ag cluster cores can be utilized through shorter-chain thiolate ligands, interactions with suitable columns may yield better chromatographic *size-separation* for metallic nanocrystal cluster compounds.

[1]Schaaff, T.G. et al. *J. Phys. Chem. B* **2001**, *105*, 8785-8796.
[2]Kresin, V. *Phys. Rev. B* **1988**, *38*, 3741-3746.

This work was funded by Division of Chemical Sciences, Geosciences and Biosciences - Office of Basic Energy Sciences US Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.