

CONF-960753--2

JUL 23 1996

OSTI

LIQUID CHROMATOGRAPHIC ANALYSIS AND CHARACTERIZATION OF INORGANIC NANOCLUSTERS

J.P. Wilcoxon and S.A. Craft, Organization 1152
Sandia National Labs, Albuquerque, NM 87185, USA

Abstract--We describe the application of the techniques of high pressure liquid chromatography (HPLC) to analyze and characterize various types of inorganic nanoclusters. Both metal and semiconductor nanoclusters were grown in inverse micelles and we demonstrate how the nanoclusters can be separated from the surfactants and other byproducts of the reaction by using a variety of HPLC columns. We also discuss passivation of the cluster surface to prevent aggregation. The HPLC columns separate the clusters based upon a combination of size exclusion and chemical affinity mechanisms and the optical properties of the purified clusters are determined on-line using a variety of detectors. These include a photodiode array for collecting absorbance spectra, a fluorescence detector to monitor luminescence, and a conductivity detector to monitor surface charge on the nanoclusters. We illustrate the analysis of nanoclusters using HPLC by showing data from semiconductor Si, MoS₂ nanoclusters and Au nanoclusters. An extremely novel luminescence was observed from very small metal nanoclusters.

INTRODUCTION

High pressure liquid chromatography (HPLC) is a widely used technique for the analysis and purification of organic molecules including polymers and drugs but has been only sparingly employed in the analysis of inorganic materials.(1,2)

EXPERIMENTAL

We synthesize nanoclusters using inverse micelles, which consist of small surfactant aggregates called micelles in inert oils.(3,4) This allows us to avoid the use of water and to exclude molecular O₂ during the reaction. Thus, very aggressive reductions may be effected, allowing a wide range of metallic and semiconductor nanoclusters to be formed.

However, as in all chemical synthesis, byproducts and unwanted chemicals are produced which must be separated from the desired nanoclusters. Though other extraction procedures may be employed to purify nanoclusters, we find that using HPLC separation yields improved characterization of the inherent chemical, optical, and electronic properties of nanoclusters, especially surface structure.

We find that two generic types of columns are most useful for HPLC analysis of nanoclusters in oils, bonded phase columns and polymeric gel columns. Our HPLC system has a variety of detectors which may be used to analyze the eluting chemical/nanoclusters. These include a photodiode array (PDA) for absorbance, a refractive index detector (RI), a photoluminescence(PL) detector, and a conductivity detector. Total absorbance and

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

photoluminescence may be obtained on-line as a function of elution time. This allows the absorbance and luminescence characteristics of purified nanoclusters to be determined. We also have a completely air-free microvalve-based fraction collection system which allows automated collection of large amounts of purified nanoclusters for further analysis by HRTEM, electron diffraction and scattering (including dynamic light scattering, DLS) methods.

Figure 1 shows an analysis of silicon nanoclusters synthesized by room temperature metal hydride reduction in a nonionic surfactant system. The elution peak corresponding to the Si clusters (identified as nanocrystalline Si with $D \sim 2.4$ nm by HRTEM and AA analysis) is separated from the other chemicals by the bonded phase column. The excess stabilizer is also removed, providing HPLC-grade nanoclusters in air-free, optically clear acetonitrile (the mobile phase used). Total absorbance and photoluminescence from the pure nanoclusters was also collected on-line (not shown). These small nanoclusters showed photoluminescence in the visible blue region and had structured absorbance.

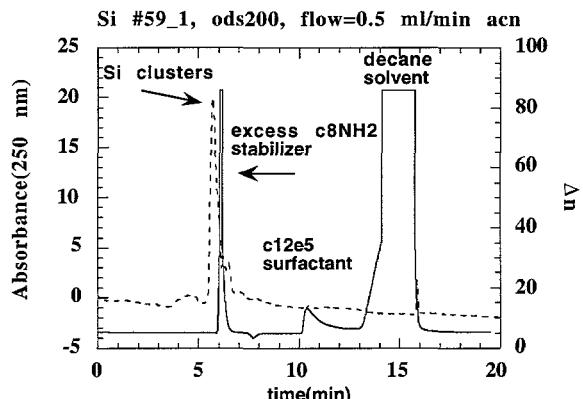


Figure 1. Coplot of absorbance (dotted line) at 250 nm and refractive index increment Δn (solid line) vs. elution time for Si nanoclusters synthesized in an oil continuous (decane) nonionic (c12e5) surfactant system and stabilized using octyl amine, c8NH₂.

Not all cluster synthesis results in only one size of nanocluster (as above) and HPLC is also useful to identify and remove other nanocluster "impurities" from a solution. These different nanoclusters may differ only in surface chemistry, shape, or mean size (molecular weight). HPLC is sensitive to all these effects depending on the type of column selected. For example, a pure size exclusion SEC column, (i.e. no specific chemical adsorption) allows the smallest clusters or chemicals to spend more time in the pores of the column and thus take much more time to elute than the bigger nanoclusters/chemicals.

Figure 2 shows the absorbance and fluorescence signal from a Si nanocluster sample which had two sizes of nanocluster. The fluorescence signal shows that only the small Si nanoclusters, which are in a vast numerical majority, have appreciable room temperature visible photoluminescence.

We find that each type of nanocluster material has particular column requirements to ensure successful HPLC analysis. The biggest distinction occurs between metals which are very hydrophobic and often have no detectable surface charge, and semiconductor metal sulfides, selenides and oxides, which are often charged and more hydrophilic. To avoid excess "sticking"

to the column we usually select very hydrophobic columns (e.g. a C18 terminated silica bonded phase column) to use with these types of nanoclusters.

Figure 3 illustrates the advantage of on-line absorbance detection of purified nanoclusters for four different sized MoS₂ samples and illustrates the shift in the absorbance edge due to quantum confinement.(5) Impurities in the parent samples did not permit data to be obtained much below 250 nm in any of the samples and distorted the relative intensities of all the peaks below 300 nm. The purified samples show the distinct structured absorbance spectra often found in nanocrystalline, monodisperse semiconductor particles. The sizes were determined independently for each peak by either HRTEM or DLS.

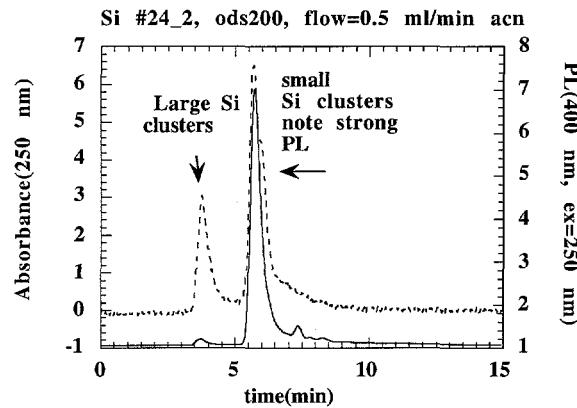


Figure 2. Coplot of absorbance (dotted line, monitored at 250 nm) and PL signals, (solid line, excitation at 250 nm) vs. elution time for Si nanoclusters with two different sized species separated by the porous column.

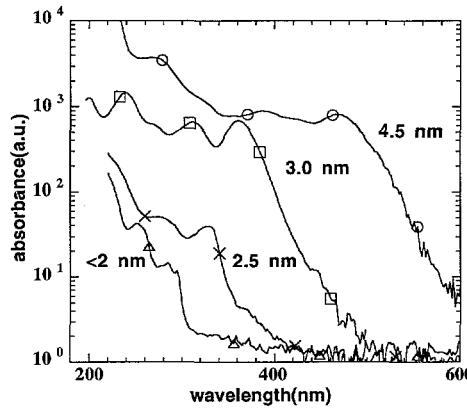


Figure 3. Plot of PDA total absorbance spectra for four different sized MoS₂ nanoclusters purified and analyzed using HPLC. Sizes were determined independently using TEM and/or DLS. Symbols identify each separate curve.

Unexpected observations are often obtained using HPLC analysis.(6) Figure 4 shows a commercially purchased sample of nanosize Au colloids in water (Polysciences, nominal

diameter=5 nm). These colloids were analyzed by HPLC using a SEC column. The mobile phase was water. In addition to the many chemical impurities found in the samples, we discovered two peaks which showed visible absorbance. Both peaks showed the well-known absorbance features characteristic of colloid gold (though the second elution peak had huge broadening of the plasmon). The first peak was identified with the D~5 nm colloids, and the second peak eluting at longer times (smaller colloids) was also identified as colloidal Au. It is interesting to observe the fluorescence signal (emission at 440 nm) found only for the smaller Au fraction. Though these clusters are in the numerical minority, they have considerable visible emission. This observation has been confirmed with many very small (i.e.<5 nm) Au and Ag clusters synthesized in both inverse micelles and in water.

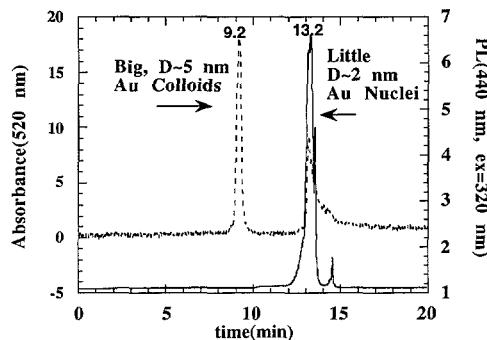


Figure 4. Coplot of absorbance (dotted line) and PL (solid line)signals vs. elution time for a commercial (Polysciences) sample of Au colloids (average diameter 5 nm) in water.

CONCLUSION

HPLC is a useful analysis and characterization method for a wide variety of nanoclusters. The principal problems encountered are the tendency for clusters to stick permanently to the column materials and the relation of the elution time to the hydrodynamic volume of the nanocluster and its surface characteristics. However, the sensitivity of HPLC to the latter is one of its advantages over other characterization methods.

ACKNOWLEDGMENTS

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contracts #DE-AC04-94AL85000 and #DE-AC02-76CH00016.

REFERENCES

1. C. H. Fischer, H. Weller, L. Katsikas, and A. Henglein, *Langmuir*, **5**, 429-432, (1989).
2. K. A. Littau, P.J. Szajowski, A.J. Muller, A.R. Kortan, and L.E. Brus, *J. Phys. Chem.*, **97**, 1224, (1993).
3. J.P. Wilcoxon, T. Martino, E. Klavetter, and A.P. Sylwester, in *Nanophase Materials*, ed. H. Hadjipanayis and R. Siegel, Elsevier Sci., 770-780, (1993).
4. J.P. Wilcoxon, DOE patent #5,147,841, issued Sep. 15, 1992.
5. J.P. Wilcoxon and G.A. Samara, *Phys. Rev. Rapid Comm.*, **51**, 7299, (1995).
6. J.P. Wilcoxon, J.E. Martin, F. Parsapour, and D. Kelley, *Science*, submitted.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.