Fundamental Studies of Monolayer-Protected Nanoparticles by Gas Chromatography

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Project Summary:

Monolayer-protected nanoparticles (MPNs) are gaining considerable interest in the nanotechnology field, especially for chemical sensor development. The selectivity achieved for chemical sensing with gold MPNs is dominated by the chemical structure and functionality selected for the organic surface layer, which is a thiol-linked chemical functionality bound on the surface of each gold nanoparticle. There is considerable interest to study MPN materials in more detail to understand their sorptive properties. Knowledge of the sorptive properties of MPNs would provide valuable insight into the thermodynamics of vapor sorption by MPNs and therefore their possible applications. In this work, gas chromatography (GC) serves as a versatile platform for the characterization of gold MPNs. GC retention time data can be related to thermodynamic properties of the MPNs, while the band broadening observed in the GC data can be readily related to the mass transfer characteristics of the MPNs. It is planned that a wide range of chemical sensing layers (monolayers) on the MPNs will be explored. Ideally, each of the MPN materials will provide a different GC retention factor for the wide array of analyte vapors that will be studied. The variations in chemical selectivity, as observed through GC retention data, should engender the MPN materials useful for a broad range of either sensor array or GC stationary phase applications.

To date the work done on this project has progressed at a steady pace with excellent results. The synthesis and characterization of three monolayer protected gold nanoparticle stationary phase has been completed. The methodology for production of a MPN-based stationary phase for GC capillary columns has been established (Figure 1). Based upon the efficiencies and reduced plate height studies as a function of linear flow velocity, we concluded that a dodecanethiol MPN stationary phase operated at nearly the optimum possible performance level and was then compared to a commercially available stationary phase (Figure 2). Using the same experimental parameters we concluded that the dodecanethiol MPN stationary phase at its optimum is operating essentially the same as the commercial AT-1 stationary phase. The robustness of the MPN phase has also been studied with consistent performance observed over several months. Using the same methodology the production of multiple columns has been achieved with acceptable levels of reproducibility. This is promising for successful future studies and applications of the MPN phase. Studies using smaller capillaries, high-speed injection, and application of the dodecanethiol MPN within a GC x GC format are currently underway. This is a very successful application of nanoparticle technology with actual instrumental devices and the establishment of an efficient thin film stationary phase now allows for the thermodynamic studies of the dodecanethiol MPN nanoparticle material. However, continued development of MPN stationary phases, whether they be ones previously used or ones newly developed, is needed in order to insure accurate and successful characterization of the sorptive properties of the nanoparticles as well as to continue the implementation of the nanoparticles in cutting edge analytical instrumentation.

Publications, Presentations and Proposals:

1. "Open Tubular Gas Chromatography using Monolayer Protected Gold Nanoparticles as the Stationary Phase." G. M. Gross, D. A. Nelson, J. W. Grate, R. E. Synovec, 26th International Symposium on Capillary Chromatography and Electrophoresis in May 2003, Las Vegas NV**.**

2. G.M. Gross, D.A. Nelson, J.W. Grate, R.E. Synovec, *"Monolayer Protected Gold Nanoparticles as a Chromatographic Stationary Phase for Open Tubular Gas Chromatography"* submitted *Anal. Chem.* March 2003.

Figures:

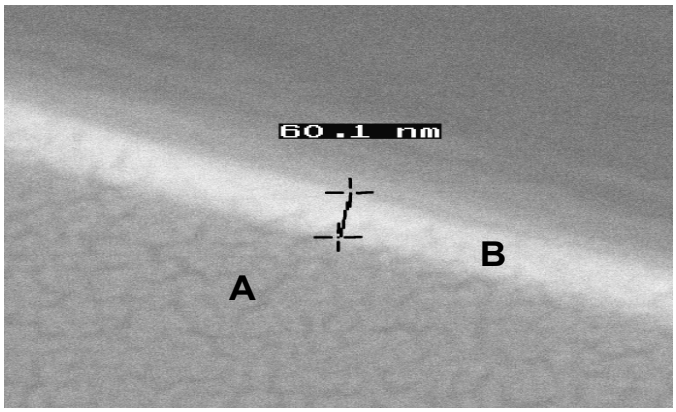

Figure 1. Scanning electron microscope image of the MPN stationary phase within the GC capillary column. Area 'A' is the silica capillary. Area 'B' is the gold-based MPN stationary phase, essentially 60.1 nm thick. This image was obtained using an end-on cross sectional view of a representative section of the GC column.

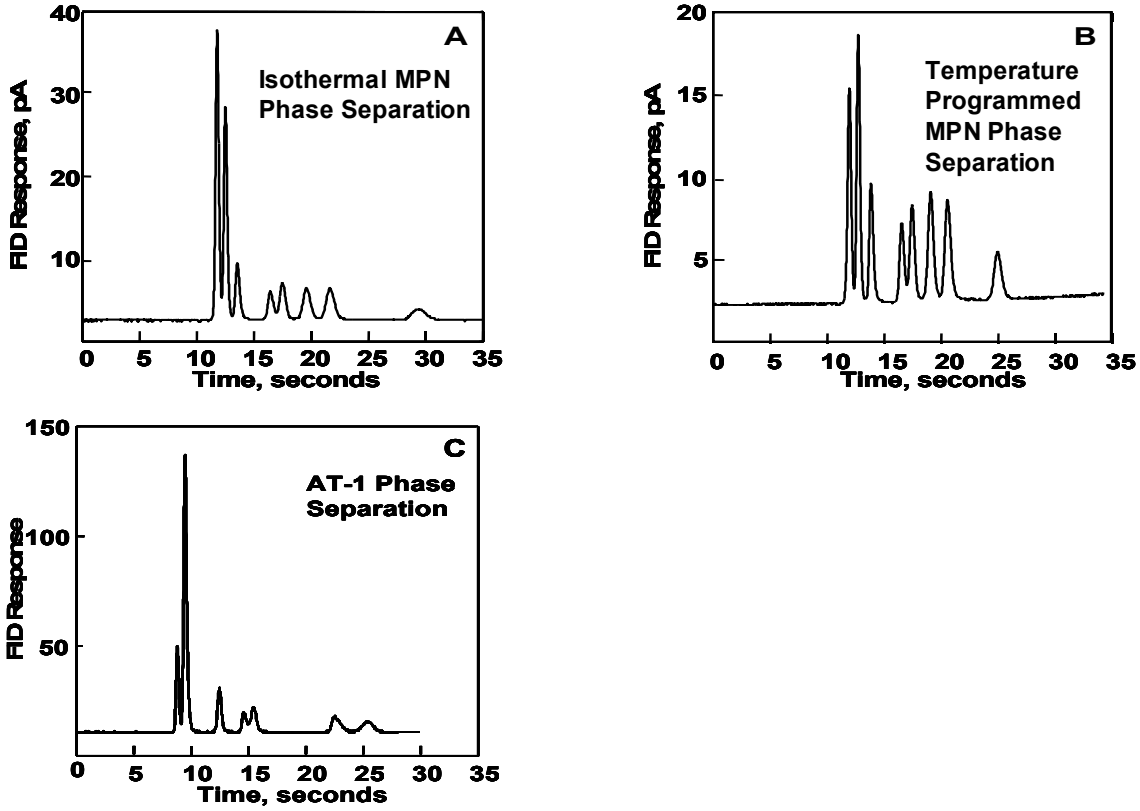

Figure 2. Eight-component mixture separated with both isothermal and temperature programmed methods using the dodecanethiol MPN stationary phase. The boiling point range was 78-174 ^{o}C with the following elution order: ethanol, benzene, 1-butanol, 3-heptanone, chlorobenzene, 3-octanone, anisole, and decane. (A) Isothermal separation at 50 ^{o}C. (B) Temperature programmed separation from 40 – 80 ^{o}C at 70 ^{o}C per minute. All other parameters were the same as those in Figure 2. (C) Isothermal separation at 50 oC on the AT-1 commercial stationary phase. Elution order: ethanol, benzene, 1-butanol, chlorobenzene, 3-heptanone, anisole, 3-octanone, decane. Note how the MPN stationary phase separation (A), while differing in selectivity and resolution, is comparable to the commercial column as seen by the peak widths and shapes.