Determination of Surface Mole Fractions in Mixed Binary Alkanethiol Self-Assembled Monolayer Films on Gold by Electrospray Ionization Mass Spectrometry

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The focus of this research is to examine the feasibility of using electrospray ionization ion trap mass spectrometry (ESI-IT-MS) to quantitatively examine mixed n-alkanethiol self-assembled monolayers (SAMs). With detection limits in the pmol range, ESI-IT-MS has the sensitivity to be useful for investigations of SAMs (surface coverages ≅ 7-8 pmol/mm^2). Since alkanethiols tend to spontaneously oxidize in solution, our analyses have focused on negative-ion MS of the most stable oxidation product (alkylsulfonates, RSO_3^-) produced by reaction with H_2O_2. We expect these studies to significantly advance the use of ESI-IT-MS as a *quantitative* tool for SAMs, as our approach should be applicable to SAMs more complex than those investigated here.

Our focus during this second year of the grant has been to design, construct, and test a suitable flow valve system that will provide optimal solution flow and rinsing characteristics for our redesigned thin-layer flow cell (TLFC).

With our TLFC/flow valve system, we have now been able to show that:

- **As the syringe pump flow rate increases, the filling behavior of each compartment is characterized by shortened filling times and reduced widths for the leading edge of the solution front.**
- **With increasing flow rates, flushing the content of each compartment (after being filled with analyte solution) to the MS results in smaller integrated peaks areas, which is a consequence of analyte ionization suppression.**
- **The reproducibility associated with flushing the compartment contents at moderate flow rates (200 μL/min) yields integrated areas that differ by < 5%, indicating that a high degree of signal reproducibility can be obtained with our newly designed TLFC/flow valve system.**