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

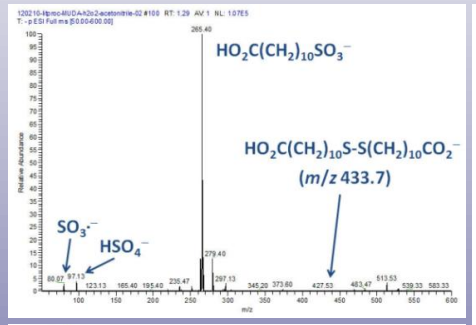
Brian W. Gregory, Department of Chemistry & Biochemistry, Samford University, Birmingham, AL 35229-2236

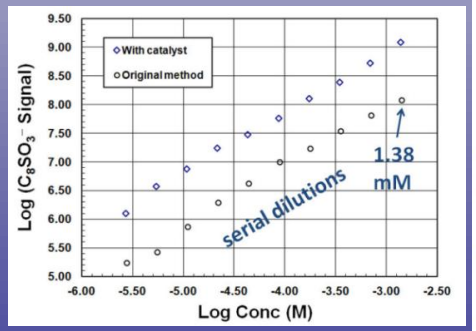
Our research has focused on examining the requirements necessary for using electrospray ionization ion trap mass spectrometry (ESI-IT-MS) as a *quantitative* tool for mixed alkanethiol self-assembled monolayers (SAMs). Our analyses have focused on negative-ion MS of the most stable oxidation product (alkylsulfonates, RSO_3^-) produced by reaction with H_2O_2.[1] 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.

During the third year of this grant, we have further optimized our solution methodology to eliminate the formation of disulfide byproducts formed during H_2O_2 oxidation, as well as tested and reconfigured our switching valve system in order to improve the sample-to-sample reproducibility provided by our thin-layer flow cell (TLFC).

We have now been able to show that:

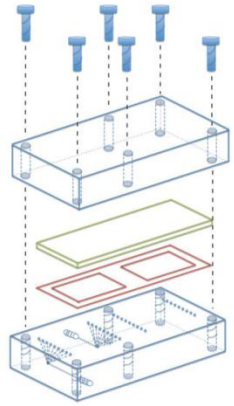
- With the use of the catalyst methyltrioxorhenium(VII), disulfide formation has been practically eliminated in our H_2O_2 oxidation procedure. MS intensities for RSO_3^- have increased 10-fold as a result!
- After switching to the use of right-angle valves, the reproducibility in flushing the TLFC compartments has improved significantly, with the best precisions ≤ 1-2%RSD.
- A decrease in MS signal and loss in precision occur at long times following preparation of the filling solution. This may be due to slow changes in the state of association between RSO_3^- species, which may affect ionization efficiencies. Potential sources of this variation and methods to eliminate them are currently being investigated.





[1]R. Roberts, J.A. Driver, D.M. Brown, S.H. Amin, and B.W. Gregory, *Anal. Chem.* 2011, *83*, 9605-9613.

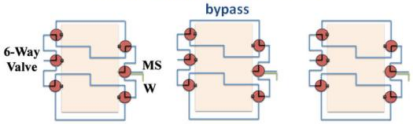
Thin-Layer Flow Cell



- Two-compartment design
- Silicone gasket (red)
  → 0.013 cm thick
- Au/glass slide (green)
  → Au/SAM facing downward
- Laminar solution flow thru compartments
- Each compartment contains:
  → Volume = 37-38 µL
  → Exposed area ≅ 2.9 cm²

New Right Angle Valve Configuration

Methodology for Compartment A



FILL (Fill A with RSO_3^-/H_2O_2 solution)

RINSE (Isolate A and rinse bypass with solvent)

FLUSH (Reconnect A and flush with solvent to MS)

Note: Each Compartment has its own bypass!

Data Using New Valve Configuration

MS Signal for $C_8SO_3^-$ and $C_5SO_3^-$ (IS)