

Project Title: Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone
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Progress Report

RESEARCH OBJECTIVE

The general aim of this project is to continue the design and implementation of a new sensor technology that offers the unprecedented levels of specificity needed for analysis of the complex chemical mixtures found at DOE sites nationwide. The new sensor concept combines the elements of electrochemistry, spectroscopy and selective partitioning into a single device that provides three levels of selectivity. The specific goal of this project is the development of a sensor for technetium (Tc) that is applicable to characterizing and monitoring the Vadose Zone and associated subsurface water at the Hanford site. The first goal is a sensor that determines technetium in the chemical form pertechnetate (TcO_4^-).

RESEARCH PROGRESS AND IMPLICATIONS

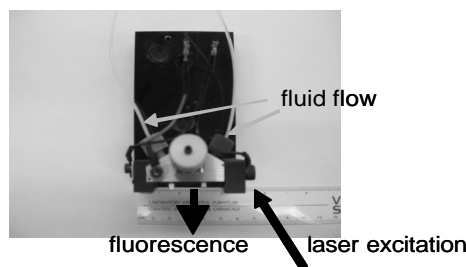
This report summarizes work during 6/16/02 - 6/15/03 of a four-year project that began on 9/15/99. During this period our efforts have focused on four areas that are discussed in the following sections.

- Demonstration of fluorescence spectroelectrochemical detection
- Demonstration of fluorescence of Tc-complexes
- Demonstration of electrochemical modulation of fluorescence of Tc-complex
- Development and characterization of selective films

1. Demonstration of fluorescence spectroelectrochemical detection

The excellent detection limits of fluorescence spectroscopy are well known, and fluorescence is often the method of choice when achieving a low detection limit is important^{1,2}. Consequently, we are developing a fluorescence-based spectroelectrochemical sensor, which will enable us to extend the applicability of the sensor to significantly lower limits of detection. We have reported the electrochemistry and absorption spectroscopy of model analyte $\text{Ru}(\text{bpy})_3^{2+}$ in the Nafion- SiO_2 and other coated sensors³⁻⁸. We have now done “proof of principle” measurements of the fluorescence of $\text{Ru}(\text{bpy})_3^{2+}$ entrapped in a chemically selective film (Nafion) on an ITO-glass MIR optic. To excite the fluorescence we used the evanescent wave mode of excitation. Using the HeCd laser line at 441.6 nm, the fluorescence⁹⁻¹⁴ of $\text{Ru}(\text{bpy})_3^{2+}$ can be easily excited and measured by collecting fluorescence from a single fluorescent spot on the top side of the MIR optic. For fluorescence data acquisition, the end of a fiber optic was butted up against a single spot and the fluorescence collected was dispersed by a monochromator and detected with a phototube with photon counting. When a potential was applied to the ITO, the fluorescence decreased as $\text{Ru}(\text{bpy})_3^{3+}$ was formed. This decrease, and the recovery of $\text{Ru}(\text{bpy})_3^{2+}$ with reversing the potential, was associated with concentration and potential. With such measurements, we initially demonstrated that the limit of detection based on fluorescence changes of just one fluorescing $\text{Ru}(\text{bpy})_3^{2+}$ spot was at least $\approx 10^{-10}$ M and that is four orders of magnitude lower than we have reported with absorbance mode and the same sensor. We have now also built our first small volume fluorescence spectroelectrochemical sensor and this is shown in **Figure 1**. The fluid volume of the sensor is about **4 microliters** and the cell can operate either under flow or non-flow conditions. Coupling of the fluorescence excitation source to the MIR is by efficient

Fig. 1. A top view of the new small volume (4 μL) fluorescence spectroelectrochemical sensor is shown. The size is shown by a centimeter-scale ruler at the base. Excitation and emission are denoted by arrows. Electrical connections are made at either side and fluid flow tubes can be seen for the sensor.

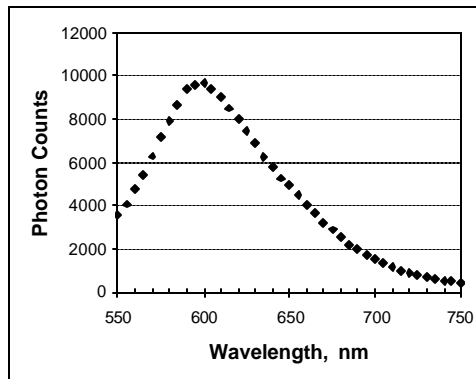


prism coupling as in our previous cell designs. At this point the transparent electrode size is essentially determined by the size of the prism used to couple light into the MIR optic and it is clear, in principle, that we could greatly reduce the electrode size if we can use another more compact means of laser light coupling to the MIR optic. Fluorescence detection is currently achieved by butting a single fiber optic against the back side of the MIR optic and gathering the fluorescence of only one fluorescent spot.

This sensor design has allowed us to get a better estimate of the limits of detection that we can expect from such a measurement. We have found that we can relatively easily detect picomolar $\text{Ru}(\text{bpy})_3^{2+}$ as **Figure 2** demonstrates.

The next steps in improving the design of this sensor include trying other types of gathering optics (e.g., linearly arrayed fiber bundle, Powell lens with fiber optic bundle, etc.). We also **Fig**

2.. The fluorescence spectrum of 1×10^{-12} M $\text{Ru}(\text{bpy})_3^{2+}$ at equilibrium with a Nafion film on the ITO OTE in the small volume fluorescence cell. Fluorescence excitation: 441.6 nm (HeCd laser). Spectrum measured with Acton 0.3 m monochromator and photon counting detector.



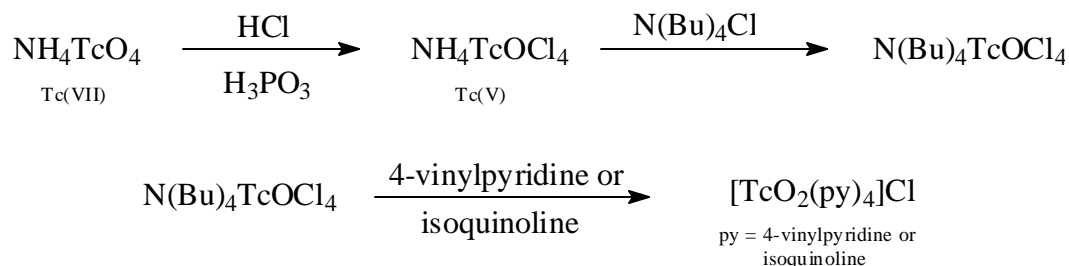
know from our results with this type of design that we can reduce the chemically-selective film thickness considerably and still achieve very low limits of detection. Thus, we will examine the extent to which we can reduce the thickness (also decreasing the response time) and still achieve acceptable limits of detection.

It is now absolutely clear that the fluorescence spectroelectrochemical sensor can reach limits of detection of at least 10^{-12} M given even a low-to-moderate quantum yield fluorescent material. As a result we find this result very exciting since the limit of detection for an analogous Tc-based fluorescent species would need to be about 10^{-10} M.

The conclusions of our most recent work on the fluorescence spectroelectrochemical method are as follows: 1) The new small volume sensor allows limits of detection for a model fluorescent analyte of at least 1×10^{-12} M; 2) The cell liquid volume has been dramatically reduced and now is only about 4 μL ; 3) From photon counting statistics it is clear that the limit of detection for the current version of the sensor could be as low as 10^{-13} M; 4) Improvements in the collection and excitation optics of the cell could yield even lower detection limits.

2. Demonstration of fluorescence of Tc-complexes

New Tc (V) complexes were prepared using the synthetic methods of Cotton et al.¹⁵ and Clarke et al.^{16,17}. Starting with 300 mg of NH_4TcO_4 , the precursor to the new pyridyl ligand complexes that are fluorescent was prepared by reducing the pertechnetate to the $\text{N}(\text{Bu})_4[\text{Tc}(\text{O})\text{Cl}_4]$ complex using H_3PO_3 as the reductant in the presence of HCl . The product was then divided and the exchange reaction with 4-vinylpyridine or isoquinoline gave the desired Tc(V) complexes, as shown below.



The UV-Vis absorption and fluorescence spectra of $[\text{TcO}_2(\text{isoquinoline})_4]\text{Cl}$ and $[\text{TcO}_2(4\text{-vinylpyridine})_4]\text{Cl}$ complexes in acetonitrile are displayed in **Figure 3**. The absorption spectrum for each has a low energy absorption band at approximately 480 nm. The fluorescence spectra were recorded using a 488 nm excitation from an Ar^+ laser source. The emission maximum for

the isoquinoline complex is approximately 580 nm while the 4-vinylpyridine complex shows emission maxima at approximately 540 and 570 nm.

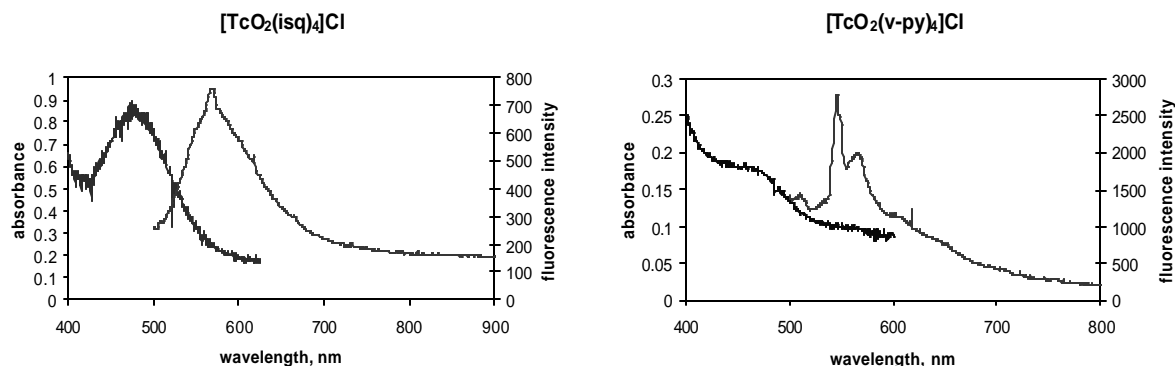


Fig. 3. Absorbance and emission spectra for $[\text{TcO}_2(\text{isoquinoline})_4]\text{Cl}$ and $[\text{TcO}_2(4\text{-vinylpyridine})_4]\text{Cl}$.

(We use the term *fluorescence* in this proposal to describe these emissions. For preciseness, we note for the record that the “fluorescences” of the ruthenium, rhenium and technetium complexes are more correctly called phosphorescences, i.e., emissions from nominally triplet spin states¹⁸. Nonetheless, it is common in the literature to call these emissions fluorescences.)

3. Demonstration of trapping of reduced Tc and electrochemical modulation of fluorescence of Tc-complex

The electrochemistry of TcO_4^- was demonstrated in the presence of isoquinoline. A cyclic voltammogram of an acetonitrile solution containing 1.6×10^{-2} M Bu_4NTcO_4 and 1.7 M isoquinoline is shown in **Figure 4**. The cyclic voltammogram was recorded at ITO using 0.1M Bu_4NCl as the supporting electrolyte. There is not a well defined reduction wave, but there is no TcO_2 deposition at the electrode as observed in the absence of the isoquinoline ligand. Under the electrochemical conditions applied, the Tc(V) -isoquinoline complex is formed directly from TcO_4^- without further reduction to TcO_2 . Evidence of the electro-generated Tc(V) -isoquinoline complex is also shown in **Figure 4**. The fluorescence spectra (taken as function of time) show the growth and disappearance of the Tc(V) fluorescent complex as it undergoes electromodulation. The electrochemically generated fluorescence spectrum of the Tc -isoquinoline complex matches that obtained from the chemically synthesized and characterized compound discussed in the previous section.

The coupled electromodulation of the fluorescence spectra of the electroactive Tc complex, demonstrates the feasibility of a fluorescence-based spectroelectrochemical sensor for TcO_4^- .

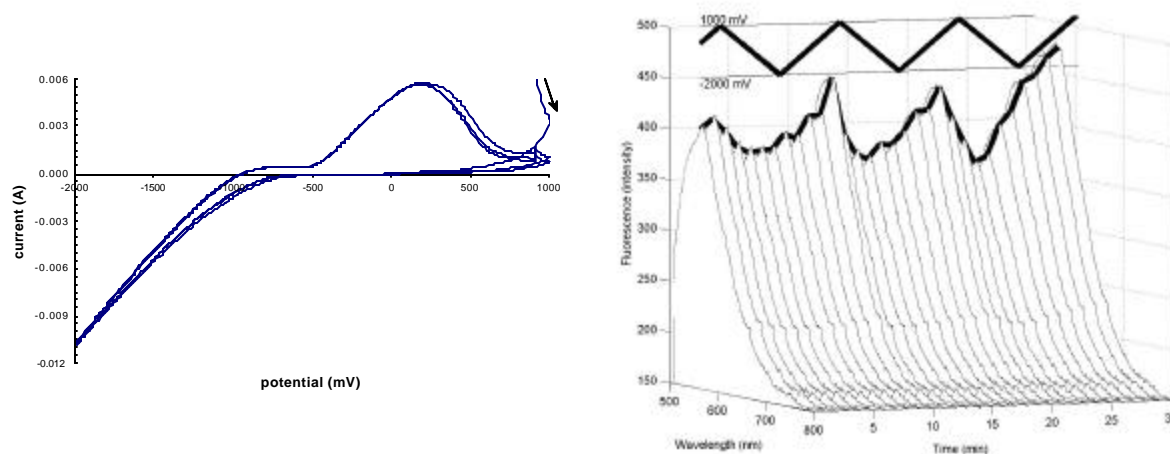


Fig. 4. (left) Cyclic voltammogram of TcO_4^- at ITO in the presence of isoquinoline (50mV/s scan rate). (right) The fluorescence spectra of the Tc-isoquinoline complex during electrochemical-modulation as a function of time; the time-phased potential modulation between 1000 and -2000 mV is displayed above the fluorescence spectra (10mV/s scan rate; excitation using 488 nm Ar^+ laser source). The CV and fluorescence spectra shown are of three consecutive scans.

4. Film Characterization

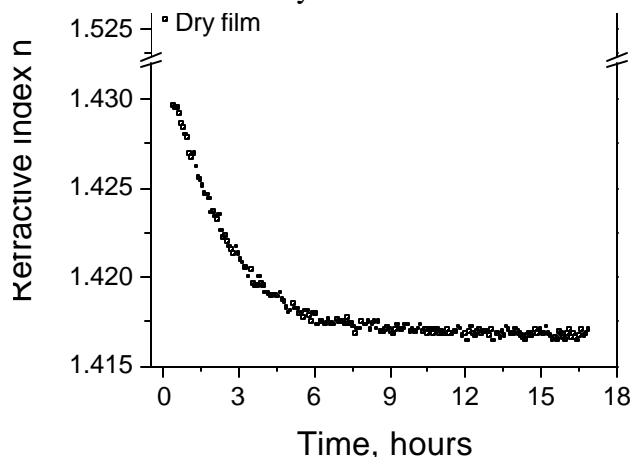
A new liquid flow cell design for *in situ* ellipsometric measurements on transparent multilayer samples using variable angle spectroscopic ellipsometry has been developed and used to study the films for the spectroelectrochemical sensor. In this cell, films made on transparent substrates are in direct contact with liquid solution. Ellipsometry measurements are made through the transparent substrate, that is, from the back-side relative to the incident light so that films are in continuous contact with the liquid. This cell is not limited to just one angle of incidence of light allowing the films to be characterized at several angles before, during, and after liquid contact. The spectral range of measurements is limited only by absorption of light in the underlying transparent substrate and not by the liquid solution that the film is in contact with. As a demonstration, we have measured and analyzed the dynamics of an indium tin oxide film on glass undergoing acid etching. Data from this *in situ* experiment were successfully modeled and the ITO layer thickness decreased uniformly during the etching process with an average etch rate of 0.23 nm/min.

A chemically selective film is a crucial component of a chemical sensor. *In situ* dynamic studies of three distinctly different chemically selective films have been made with the new cell. Spectroscopic ellipsometry was used to determine film thickness and refractive index changes in time as these films were exposed to aqueous electrolyte solution.

These three films have demonstrated the usefulness of dynamic spectroscopic ellipsometry in deciphering a range of film behaviors from film robustness to film failure. Ellipsometry experiments were performed using a liquid flow cell and the films positioned on the back-side of glass substrates. The three films studied were Nafion- SiO_2 , PDMDAAC- SiO_2 and PVTAC-PVA. The first two of these represent rigid silica (SiO_2) networks in which an ion exchange polymer is immobilized. The third film consists of an all polymer based composite with an ion exchange

polymer entrapped by cross-linking the host polymer PVA. Each of these three films exhibited different dynamic behavior on soaking in aqueous electrolyte solution. The Nafion-SiO₂ film remained essentially unchanged over time and represents a robust useful sensor film. The PDMDAAC-SiO₂ film underwent large changes and ultimately catastrophically failed when exposed to solution for a long period of time. The PVA-PVTAC film swelled by approximately a factor of 1.5 when exposed to solution but remained intact, fully functional and bound to the substrate surface over time. A sample of the results for this thin film system is shown below.

Fig. 5. Refractive index n_f of PVA-PVTAC film on SF11 glass substrate during the course of soaking in 0.1 M KNO₃. The value for the dry film is shown above the break in vertical axis. Refractive index is given at the wavelength of 700 nm.



Knowledge of sensor film properties is important in understanding how chemical sensor works or fail and in the modeling of chemical sensor response. In the case of film failure, determination of the underlying reasons can often be deduced from dynamic measurements of ellipsometry parameters.

5. Conclusions

The spectroelectrochemical sensor has been demonstrated on a variety of chemical systems including a real sample from Hanford. The following conclusions are pertinent to the proposed research.

- Fluorescence offers a means of dramatically increasing the sensitivity of the sensor and we have demonstrated a limit of detection ($< 10^{-12}$ M) that is 100 times lower than that needed for pertechnetate.
- Tc-complexes made do fluoresce and these complexes can be electrochemically modulated leading to fluorescence modulation, which is the second step in operation of a spectroelectrochemical sensor for TcO₄⁻.
- Dynamic ellipsometry can be used to better understand the behavior of films for the spectroelectrochemical sensor.

8. List of Collaborations

- *May to December 2002* – David Monk performs second extended research visit to PNNL.
- *February 2003* – William Heineman, Carl Seliskar, Sam Bryan, and Tim Hubler meet at PNNL to discuss research progress and future aims and prepare renewal grant proposal.

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PLANNED ACTIVITIES

During the next year we plan to continue development of the chemically-selective film for TcO₄⁻. This will include the following specific aims.

1. Developing a chemically selective film that preconcentrates TcO₄⁻ into the sensing region.
2. Developing ligands that bind Tc forming fluorescent complexes that can be electrogenerated by reducing TcO₄⁻ within the chemically selective film.
3. Demonstrating that these complexes can be electrogenerated and that their fluorescence signal can be electromodulated.
4. Co-immobilizing the ligands with the preconcentrating polymer.
5. Demonstrating the sensor concept.

We shall also continue development of the sensor prototype and associated portable instrumentation.

INFORMATION ACCESS

Publications:

- Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device: An Overview, W. R. Heineman, C. J. Seliskar, J. N. Richardson, *Australian J. Chemistry*, 56, 93-102, 2003.
- Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 11. Design and Evaluation of a Small Portable Sensor for the Determination of Ferrocyanide in Hanford Waste Samples, M. L. Stegemiller, W. R. Heineman, C. J. Seliskar, T. H. Ridgway, S. A. Bryan, T. Hubler, R. L. Sell, *Environ. Sci. & Technol.*, 37, 123-130, 2003.
- In Situ Measurements of Sensor Film Dynamics by Spectroscopic Ellipsometry. Demonstration of Back-side Measurements and the Etching of Indium Tin Oxide, I. Zudans, C. J. Seliskar, W. R. Heineman, *Thin Solid Films*, 426, 238-245, 2003.

In Press

- Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 15. Development of Portable Spectroelectrochemical Instrumentation, D. J. Monk, T. H. Ridgway, C. J. Seliskar, W. R. Heineman, *Electroanalysis*.
- Spectroelectrochemical Sensing: Miniaturized Sensors, S. E. Ross, Y. Shi, C. J. Seliskar, W. R. Heineman, *Electrochimica Acta*.
- Development and Application of Novel Thin-film Spectroelectrochemical Sensors Possessing Three Modes of Selectivity, W. R. Heineman, C. J. Seliskar, J. N. Richardson, *Russian J. Electrochem.*

Submitted

- Spectroelectrochemical Sensing Based on Attenuated Total Internal Reflectance Stripping Voltammetry. 1. Determination of Lead and Cadmium, T. Shtoyko, A. T. Maghasi, J. N. Richardson, C. J. Seliskar, W. R. Heineman, *Anal. Chem.*

Presentations:

Talks at Conferences (*presenter)

- Sensors Based on Spectroelectrochemistry, W. R. Heineman*, T. Rarog, S. D. Conklin, J. R. Paddock, I. Zudans, D. J. Monk, T.H. Ridgway, C. J. Seliskar, Interact 2002, Sydney, Australia, July 21-25, 2002. (Plenary lecture)
- The Spectroelectrochemical Sensor with a Chelating Agent for Cu(EN)₂²⁺, T. Rarog*, W. R. Heineman, C. J. Seliskar, 224th ACS National Meeting, Boston, MA, Aug. 18-22, 2002. (Poster session)
- Spectroelectrochemical Sensor for Pertechnetate in the Vadose Zone in the symposium on Additional Aspects of Nuclear Chemistry and Technology, D. J. Monk*, T. H. Ridgway, W. R. Heineman, C. J. Seliskar, S. A. Bryan, T. L. Hubler, 224th ACS National Meeting, Boston, MA, Aug. 18-22, 2002.
- Spectroelectrochemical Sensing: Miniaturized Sensors, W. R. Heineman*, M. L. Stegemiller, S. E. Ross, T. H. Ridgway, C. J. Seliskar, 53rd Meeting of the International Society of Electrochemistry, Dusseldorf, Germany, Sept. 15-20, 2002. (Main lecture)
- Development of Spectroelectrochemical Sensors for Monitoring Mercury and Lead in the symposium on Environmental Analysis Using Sensors and Electrodes, A. T. Maghasi*, C. J. Seliskar, W. R. Heineman, Pittcon 2003, Orlando, FL, March 9-14, 2003.
- Ligands and Their Polymerizeable Analogs as Analog Tools for Spectroelectrochemical Sensing in the symposium on Sensors - Biological, D. J. Monk*, T. H. Ridgway, W. R. Heineman, C. J. Seliskar, Pittcon 2003, Orlando, FL, March 9-14, 2003.
- Modeling of Spectroelectrochemical Sensor, A. Piruska*, C. J. Seliskar, W. R. Heineman, Pittcon 2003, Orlando, FL, March 9-14, 2003. (Poster session)

- Development of Spectroelectrochemical Binding Assay Using Labeled Ligand with an Electroactive Probe, H. Kuramitz*, A. Piruska, Y. Umezawa, H. B. Halsall, C. J. Seliskar, W. R. Heineman, Pittcon 2003, Orlando, FL, March 9-14, 2003. (Poster session)
- Spectroelectrochemical Sensor for the Determination of Concentration of Aqueous Iron, C. M. Wansapura*, W. R. Heineman, C. J. Seliskar, Pittcon 2003, Orlando, FL, March 9-14, 2003. (Poster session)
- Spectroelectrochemical Sensor for Technetium: Preconcentration and Quantification of Technetium in Polymer-modified Electrodes in the symposium on Environmental Management Science Program Symposium Environmental Sensing and Monitoring: Effects of Radiation Exposure on Humans and Biota, D. J. Monk, M. L. Stegemiller, S. Conklin, J. R. Paddock, W. R. Heineman*, C. J. Seliskar, T. H. Ridgway, S. A. Bryan, T. L. Hubler, 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003.
- An Attenuated Total Reflectance Sensor for Copper: An Experiment for Analytical or Physical Chemistry, T. Shotoyko*, I. Zudans, J. N. Richardson, C. J. Seliskar, W. R. Heineman, 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003. (Poster session)
- Characterization of Cross-linked Polymer Films for Incorporation into Spectroelectrochemical Sensors, L. E. Faulkner*, S. Conklin, W. R. Heineman, 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003. (Poster session)