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*Principal Investigator:* William R. Heineman PH: 513-556-9210  
Department of Chemistry FAX: 513-556-9239  
University of Cincinnati  
P.O. Box 210172  
Cincinnati, OH 45221-0172  
email: [william.heineman@uc.edu](mailto:william.heineman@uc.edu)

*Co-Investigators:* Carl J. Seliskar PH: 513-556-9213  
Department of Chemistry FAX: 513-556-9239  
University of Cincinnati  
P.O. Box 210172  
Cincinnati, OH 45221-0172  
email: [carl.seliskar@uc.edu](mailto:carl.seliskar@uc.edu)

Samuel A. Bryan; PH: 509-372-3861  
Pacific Northwest National Laboratory  
Radiochemical Processing Laboratory  
P.O. Box 999, MS P7-25  
Richland, WA 99352  
email: [sam.bryan@pnl.gov](mailto:sam.bryan@pnl.gov)

Timothy L. Hubler; PH: 509-373-0249  
Pacific Northwest National Laboratory  
Environmental Molecular Sciences Laboratory  
P.O. Box 999, MS K8-93  
Richland, WA 99352  
Email: [tim.hubler@pnl.gov](mailto:tim.hubler@pnl.gov)

*Doctoral Students at University of Cincinnati:*

Susan Ross, Ph.D. 2000  
Mila Maizels, Ph. D. 2000  
Michael Stegemiller, 3<sup>rd</sup> year  
Jennifer DiVirgilio-Thomas, 3<sup>rd</sup> year  
Imants Zudans, 2<sup>nd</sup> year  
Tanya Rarog, 2<sup>nd</sup> year  
Sean Conklin, 1<sup>st</sup> year

*Masters Students at University of Cincinnati:*

Mark Wanamaker, M.S. 2000  
Debra Verhoff, 1<sup>st</sup> year

*Undergraduate Students at PNNL under the ERULF (Energy Research Undergraduate Laboratory Fellowship) Program:*

Krista Hammack  
Adam Still  
Jana Mounts

## 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 ( $\text{TcO}_4^-$ ).

### RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work during the period 9/15/99 to 9/14/00, which is the 1<sup>st</sup> year of this project. Our effort focused on specific tasks 1, 2, and 3 of the proposed research. All of the experiments thus far have used  $\text{ReO}_4^-$  and  $\text{MnO}_4^-$  as nonradioactive surrogates for  $\text{TcO}_4^-$ .

#### 1) *Choice of materials and fabrication of the chemically selective layer that initially traps $\text{TcO}_4^-$ .*

- The electrochemistry of  $\text{ReO}_4^-$  reduction has been examined by cyclic voltammetry. Reduction of  $\text{ReO}_4^-$  on bare ITO (indium tin oxide), which is the optically transparent electrode (OTE) to be used for the sensor, was verified. However, cyclic voltammograms show that the reduction of  $\text{ReO}_4^-$  is complicated by being so negative as to overlap with a large reduction wave due to hydrogen evolution. This overlap is not expected to be a problem with  $\text{TcO}_4^-$ , which is more easily reduced than  $\text{ReO}_4^-$  by about 300 mV. However, it makes the use of  $\text{ReO}_4^-$  as a surrogate for  $\text{TcO}_4^-$  more difficult. Investigation of other electrode materials such as Pt, Au, carbon, and Hg-film deposited on Au showed little or no improvement in the cyclic voltammetry to be gained by using other electrode materials. Because of this overlap problem, electrochemical reduction of  $\text{MnO}_4^-$ , which is easily reduced, was also used as a secondary nonradioactive surrogate for  $\text{TcO}_4^-$ . Cyclic voltammograms for  $\text{MnO}_4^-$  were well-defined, making this a good system for some aspects of sensor development.
- Three polymers have been evaluated as candidates for the preconcentrating film, all immobilized in a porous glass film on ITO by the sol gel process: PDMDAAC (polydimethylidiammonium chloride), PVTAC (polyvinylbenzyltrimethylammonium chloride), and QPVP (quarternary polyvinylpyridine). All showed good uptake of  $\text{ReO}_4^-$  and  $\text{MnO}_4^-$ .

#### *Conclusions:*

- ITO is not an ideal OTE for the sensor when tested with  $\text{ReO}_4^-$ , but other materials are no better. Key experiments should be repeated with  $\text{TcO}_4^-$ , which is expected to perform better at ITO.
- All three polymers (PDMDAAC, PVTAC, and QPVP) immobilized in porous glass are satisfactory as films for preconcentrating  $\text{ReO}_4^-$  and  $\text{MnO}_4^-$  on the ITO. These polymers should also be satisfactory with  $\text{TcO}_4^-$ , but this should be verified by repeating key experiments with  $\text{TcO}_4^-$ .

#### 2) *Choice of ligand that binds reduced Tc species within the chemically selective layer.*

- A variety of ligands for binding the reduced Tc species to form a coordination compound within the sensing layer have been evaluated for the requisite electrochemical and spectral properties: O-donor ligands (methylene diphosphonate, hydroxyethylidene diphosphonate, gluconate, tartrate, and citrate) and S-donor ligand (dimercaptosuccinic acid). In all cases, clean formation of a complex with good electrochemical and optical properties was not accomplished by electrochemical reduction of  $\text{ReO}_4^-$  in the presence of the ligand. Success was achieved by chemical reduction using  $\text{Sn}^{2+}$  and  $\text{NaBH}_4$  by which a complex was formed with the ligand gluconate. The problem is in part due to the difficulty in reducing  $\text{ReO}_4^-$  electrochemically at ITO. This may not be a problem with  $\text{TcO}_4^-$ , which is more easily reduced.
- The concept of “bait and switch” upon which the proposed sensor is based has also been investigated with  $\text{Cu}^{2+}$  as the model system.  $\text{Cu}^{2+}$  provides a more straightforward system with which to develop some aspects of the sensor. With this system, we have succeeded in showing that  $\text{Cu}^{2+}$  can be attracted into a polymer film on ITO and electrochemically reduced to  $\text{Cu}^{1+}$ . The electrogenerated  $\text{Cu}^{1+}$  then reacts with a coimmobilized ligand to form a colored complex that the sensor detects by spectroelectrochemical modulation.
- In anticipation of doing work with  $^{99}\text{TcO}_4^-$ , two members of the UC group have taken and passed the training course for Radiation Worker II at PNNL/Hanford. This will allow UC to be directly involved in  $^{99}\text{TcO}_4^-$  experiments in February.

*Conclusions:*

- Key experiments performed on  $\text{ReO}_4^-$  should be repeated with  $\text{TcO}_4^-$  at PNNL to verify that complications in forming the required complex in the sensing film are due to the difference in the electrochemistry of  $\text{ReO}_4^-$  and  $\text{TcO}_4^-$ .
- Of the ligands tested thus far, gluconate formed a complex with Re that provides the requisite properties for sensing  $\text{ReO}_4^-$ . Other ligands should be evaluated as outlined in the research proposal.

3) *Synthetic Strategy for Co-immobilization of the Binding Ligand Set*

- A basic synthetic strategy has been adopted for covalent binding of the selective ligands into the polymer matrix. For PDMDAAC polymer systems, this strategy consists of preparation of diallylamides that can undergo cyclopolymerization with the DMDAAC monomer to become an integral part of the PDMDAAC polymer (the ligand set is covalently bound to the rest of the polymer). Diallylamides are generally prepared from carboxylic acids with diallylamine via DCC (dicyclohexylcarbodiimide) coupling or via direct reaction of the amine with an acid chloride derivative. For example, tris-(DMSA)Re(VI) was reacted with diallylamine using DCC to give the hexaamide (each carboxylic acid group of the DMSA ligands is amidated). The per-amidated Re complex was then copolymerized with DMDAAC to give a polymer with a templated ligand set for Re. This co-polymer was immobilized on quartz crystal microbalance slides (with Pt electrodes) using a silica sol gel. Electrochemical studies of the films thus created showed a reversible oxidation wave in the region from 0 to 1.2 V (SCE). An associated reversible mass gain/loss was also observed concurrently with the cyclic voltammogram. This indicates a redox cycle between Re(VI) and Re(VII) (presumably as  $\text{ReO}_4^-$ ), with uptake of water from the surrounding solution as a reason for the increase in mass of the film. One consequence of this interpretation is that  $\text{ReO}_4^-$  is not exiting the ion-exchange film.
- Other ligands have been examined including catechols and phenanthrolines. These materials can also be derivatized with diallylamine and co-polymerized with PDMDAAC.

*Conclusions:*

- The synthetic strategy for covalent attachment of the Re-DMSA ligand set in PDMDAAC has been achieved, thus providing a preorganized cavity for uptake and reduction of  $\text{TcO}_4^-$ .
- The Re-templated polymer films have shown reversible electrochemical oxidation/reduction, but show an increase in mass as Re is oxidized to Re(VII) (presumably as  $\text{ReO}_4^-$ ). In order to regenerate the film for sensing  $\text{TcO}_4^-$ , it may be necessary to explore other polymers for the films that contain varying amounts of neutral co-polymers to reduce the ionic charge of the overall polymer.

#### PLANNED ACTIVITIES

- Key experiments will be repeated with  $\text{TcO}_4^-$  to verify the uptake observed for  $\text{MnO}_4^-$  in the three polymer films: PDMDAAC, PVTAC, and QPVP.
- Key experiments will be repeated with  $\text{TcO}_4^-$  to determine if the complex observed with gluconate ligand by chemical reduction of  $\text{ReO}_4^-$  can be obtained by electrochemical reduction of  $\text{TcO}_4^-$ .
- These experiments with  $\text{TcO}_4^-$  are planned to be performed at PNNL during February.
- Other ligands that might provide better electrochemical and optical characteristics will be examined including  $\text{N}_2\text{S}_2$  donor ligands.

#### INFORMATION ACCESS

##### *Presentations:*

1. Spectroelectrochemical Sensor for Ferrocyanide and Technetium, W.R. Heineman\*, C.J. Seliskar, S.A. Bryan, T.L. Hubler, Environmental Management Science Program (EMSP) National Workshop, Atlanta, April 24-27-2000.
2. Strategies for New Chemical Sensors, W.R. Heineman, Sensor Technology for the New Millennium Symposium, University of Pittsburgh, April 29, 2000.
3.  $\text{Cu}^{2+}$  Bait and Switch Sensor, T. Rarog\*, C. J. Seliskar, W. R. Heineman, 32<sup>nd</sup> ACS Central Regional Meeting (CMACS), Covington, KY, May 16-19, 2000.
4. Evaluation of Silica Composites Containing Quarternized Poly(4-vinylpyridine) as an Anion Exchanger of Per technetate,  $\text{TcO}_4^-$  Ions for Use in Chemical Sensors, S. Conklin\*, W. R. Heineman, C. J. Seliskar, 32<sup>nd</sup> ACS Central Regional Meeting (CMACS), Covington, KY, May 16-19, 2000.
5. Optical Study of Thin Sol-Gel Films on ITO for Spectroelectrochemical Sensor, I. Zudans\*, C. J. Seliskar, W. R. Heineman, 32<sup>nd</sup> ACS Central Regional Meeting (CMACS), Covington, KY, May 16-19, 2000.
6. Strategies for New Chemical Sensors, W. R. Heineman, 3<sup>rd</sup> Mediterranean Basin Conference on Analytical Chemistry (MBCAC III), Antalya, Turkey, June 4-9, 2000.
7. Combining Electrochemistry and Spectroscopy into a Single Sensor, W. R. Heineman\*, M. Maizels, M. Stegemiller, J. DiVirgilio-Thomas, S. Ross, M. Wanamaker, M. Clager, A. Slaterbeck, Y. Shi, L. Gao, T. H. Ridgway, C. J. Seliskar, 8<sup>th</sup> Int'l Conference on ElectroAnalysis (ESEAC/SEAC 2000), Bonn, Germany, June 11-15, 2000.
8. Chemical Sensors for Monitoring during Stewardship, W.R. Heineman, Post Closure Stewardship Technology Needs Meeting, University of Cincinnati, September 19-20, 2000.
9. Selective Ion-Exchange Films for Technetium Sensors, S.A. Bryan, T.L. Hubler, W.R. Heineman, C.J. Seliskar, K.L. Hammack, A.N. Still, and J.L. Mounts, 220th ACS National Meeting, Washington, DC. August 2000.