

*Project Title:* Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone  
*DOE Report Number:* N.A.  
*Grant Number:* FG07-99ER62311  
*Project ID Number:* 70010  
*Publication Date:* June 15, 2001

*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:*

Jennifer DiVirgilio-Thomas, Ph. D. 2001  
Michael Stegemiller, 4<sup>th</sup> year  
Imants Zudans, 3<sup>rd</sup> year  
Tanya Rarog, 3<sup>rd</sup> year  
Sean Conklin, 2<sup>nd</sup> year  
David Monk, 2<sup>nd</sup> year  
Jennifer Hodges-Thomas, 2<sup>nd</sup> year  
Jean Wherley, 1<sup>st</sup> year

*Masters Students at University of Cincinnati:*

Mark Wanamaker, M.S. 2000  
Debra Verhoff, 2<sup>nd</sup> year

*Undergraduate Students at University of Cincinnati enrolled in summer NSF REU (Research Experiences for Undergraduates) program:*

Michael Drake

Ted Riestenberg

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

Krista Hammack

Adam Still

Jana Mounts

Matthew Thornton

Colin Carver

*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 9/15/00 - 6/15/01 of a three-year project that began on 9/15/99. During this period effort was focused on Specific Tasks 1 and 2 of the proposed research. Until recently, all of our experiments used  $\text{ReO}_4^-$  and  $\text{MnO}_4^-$  as nonradioactive surrogates for  $\text{TcO}_4^-$ . Several months ago, two students spent one week at PNNL performing key experiments with  $\text{TcO}_4^-$ . These experiments confirmed that we have developed films that preconcentrate  $\text{TcO}_4^-$  at the sensor and that the preconcentrated  $\text{TcO}_4^-$  undergoes electrochemical reduction. Thus, we have succeeded in the first step in developing a sensor for  $\text{TcO}_4^-$ .

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

The optically transparent electrode (OTE) on which the spectroelectrochemical sensor is based is indium tin oxide (ITO) deposited on glass. As described in our previous report, we investigated the electrochemistry of  $\text{ReO}_4^-$  and  $\text{MnO}_4^-$  as nonradioactive surrogates for  $\text{TcO}_4^-$  on this material by cyclic voltammetry. The electrochemistry of  $\text{TcO}_4^-$  reduction has now been examined on bare ITO by cyclic voltammetry. Reduction of  $\text{TcO}_4^-$  commences at ca. -0.7 V vs. Ag/AgCl. The reduction wave blends with reduction of solvent and a clear peak is not observed. Other waves in the voltammogram suggest that a film is forming on the ITO surface that lowers the overpotential for solvent reduction.

As reported earlier, three polymers have been evaluated as candidates for the preconcentrating film that is coated on the ITO transparent electrode: PDMDAAC (polydimethyldiallylammonium chloride), PVTAC (polyvinylbenzyltrimethylammonium chloride), and QPVP (quarternary polyvinylpyridine). PDMDAAC, QPVP, and PVTAC have been immobilized in a porous silica film on ITO by the sol gel process. PVTAC has also been prepared as a polymer blend trapped in a network of PVA (polyvinyl alcohol) that is covalently bonded to the ITO. These films have all undergone the following development: measurement of film thickness by ellipsometry,

observation of film quality by scanning electron microscopy, and optimization of procedures for preparation of reproducible films. All films have demonstrated good uptake of anions such as ferrocyanide and the surrogates  $\text{ReO}_4^-$  and  $\text{MnO}_4^-$ .

Three of these four films have now been examined with  $\text{TcO}_4^-$ : QPVP in porous silica, PDMDAAC in porous silica, and PVTAC-PVA. These films show uptake of  $\text{TcO}_4^-$  and improvement of the electrochemical properties of  $\text{TcO}_4^-$  as studied by cyclic voltammetry. Immersion of an ITO electrode coated with a film in a solution of  $\text{TcO}_4^-$  shows the development of a reduction wave for  $\text{TcO}_4^-$  that has partitioned into the film. Compared to a bare ITO, this reduction shows three differences. First the reduction wave occurs as a well-defined wave with a distinct peak potential that is clearly separated from the solvent reduction wave. Second, the reduction wave has an oxidation wave counterpart. This behavior is suggestive of a change in the basic mechanism of reduction caused by the presence of the film. Third, the current is significantly enhanced compared to a bare electrode, indicating uptake of  $\text{TcO}_4^-$  by the polymer composite films. Composite films exhibited uptake increasing in the order  $\text{QPVP} > \text{PDMDAAC} > \text{PVTAC} > \text{PVTAC-PVA}$ .

The acquisition of an ellipsometer and an ESEM have enabled us to pursue more fundamental studies of the above films. The ellipsometer has been used to accurately measure film thickness and optical constants such as refractive index, which are important parameters in sensor performance. The ESEM has given us the ability to non-destructively examine sensor surfaces before and after use.

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

As described in the previous report, 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 by performing experiments with the surrogates  $\text{ReO}_4^-$  and  $\text{MnO}_4^-$ . Two ligands have now been evaluated with  $\text{TcO}_4^-$ : an N-donor ligand ethylenediamine (en) and an S-donor ligand meso-dimercaptosuccinic acid (DMSA). Cyclic voltammetry was performed on mixtures of ligand and  $\text{TcO}_4^-$  in an attempt to form a complex with an electrochemically formed lower oxidation state of Tc. In neither case was a complex formed that exhibited the desired reversible electrochemistry.

Another strategy that was tested involves ligand exchange between a preformed Re complex with ethylenediamine ( $\text{Re(en)}_2\text{O}_2$ ) and an electrochemically formed lower oxidation state of Tc. Preliminary results are consistent with the electrogenerated Tc having displaced Re to form a Tc complex with the ligand.

## *Conclusions:*

- ITO is an acceptable OTE for the sensor when tested with  $\text{TcO}_4^-$ .
- All three polymers (PDMDAAC, PVTAC, and QPVP) incorporated as composites are satisfactory for preconcentrating  $\text{TcO}_4^-$  on ITO. They also improve the electrochemical characteristics of  $\text{TcO}_4^-$ .
- The first step to building a successful sensor has been accomplished.
- Preliminary results suggest that an EN complex with Tc has been electrogenerated that might form the basis for the  $\text{TcO}_4^-$  sensor.

*Instrument laboratory.*

Through a large grant from the Ohio Board of Regents Hayes Fund, a consortium of three Ohio universities (OSU, M. Madou, PI; UC, C.J. Seliskar, UC-PI; and CWRU, C.C. Liu-CWRU-PI) devoted to MEMS and fabrication of chemical sensors resulted in purchase of new major equipment. The UC share of this grant allowed us to establish a chemical sensors instrumentation laboratory in our research area containing a Philips ESEM, a Woolham spectroscopic ellipsometer, a BiaCore SPR, a Metricon prism coupler, and several items of Buehler sawing, grinding and polishing equipment for sensor fabrication. This new facility is available to us free of charge to further reinforce our effort on our EMSP grant activities.

## PLANNED ACTIVITIES

Given the encouraging results that were obtained for  $\text{TcO}_4^-$  at PNNL, a graduate student from UC will spend the summer at PNNL doing more experiments with  $\text{TcO}_4^-$ .  $\text{TcO}_4^-$  uptake into the polymer films will be quantified. The strategy of ligand exchange between a preformed Re complex such as  $\text{ReEN}_2\text{O}_2$  and an electrochemically formed lower oxidation state of Tc will be further explored. Other ligands for complex formation with electrochemically reduced  $\text{TcO}_4^-$  will be evaluated.

We have observed that parameters such as film thickness and presoaking affect the rate of uptake of anions into the film. We are beginning a more systematic study of these parameters and their influence on sensor performance.

## INFORMATION ACCESS

### *Publications:*

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 6. Sensing with a Mediator, *Anal. Chem.*, 72(15), 3461-3467 (2000). J. M. DiVirgilio-Thomas, W. R. Heineman, C. J. Seliskar.

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 5. Simulation of Sensor Response for Different Excitation Potential Waveforms, *Anal. Chem.*, 72(22), 5567-5575 (2000). A. F. Slaterbeck, M. L. Stegemiller, C. J. Seliskar, T. H. Ridgway, W. R. Heineman.

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 9. Incorporation of Planar Waveguide Technology, *Anal. Chem.*, 72(22), 5549-5555 (2000). S. E. Ross, C. J. Seliskar, W. R. Heineman.

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 7. Sensing of  $\text{Fe}(\text{CN})_6^{4-}$ , *Electroanalysis*, 12(17), 1356-1362 (2000). M. Maizels, C. J. Seliskar, W. R. Heineman.

Novel Spectroelectrochemical Sensor for Ferrocyanide in Hanford Waste Simulant in *Nuclear Site Remediation: First Accomplishments of the Environmental Management Science Program*, ACS Symposium Series 778, 364-378, ACS, New Orleans, LA, 2001. (P. G. Eller and W. R. Heineman, Eds.). M. Maizels, M. Stegemiller, S. Ross, A. Slaterbeck, Y. Shi, T. H. Ridgway, W. R. Heineman, C. J. Seliskar, S. A. Bryan.

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 8. Selectivity at Poly(vinyl alcohol)-Polyelectrolyte Blend Modified Optically Transparent Electrodes, *Electroanalysis*, L. Gao, C. J. Seliskar, W. R. Heineman. In press.

*Presentations:*

Chemical Sensors for Monitoring During Stewardship, Post Closure Stewardship Technology Needs Meeting, W. R. Heineman, University of Cincinnati, September 19-20, 2000.

Computer Controlled Remote Spectroelectrochemical Sensor System, D. J. Monk\*, T. H. Ridgway, W. R. Heineman, C. J. Seliskar, M. Stegemiller, R. Q. Voorhees, Pittcon 2001, New Orleans, LA, March 4-9, 2001. (Poster session)

Spectroelectrochemical Sensor for Copper with Four Modes of Selectivity, T. Rarog\*, C. J. Seliskar, W. R. Heineman, Pittcon 2001, New Orleans, LA, March 4-9, 2001. (Poster session)

Evaluation of Silica Composites Containing Quaternized Poly(4-vinylpyridine) for Use in a Spectroelectrochemical Sensor for Technetium, S. D. Conklin\*, W. R. Heineman, C. J. Seliskar, Pittcon 2001, New Orleans, LA, March 4-9, 2001. (Poster session)

Selective Ion-Exchange Films for Technetium Sensors, S.A. Bryan, T.L. Hubler, W.R. Heineman, C.J. Seliskar, K. Hammack, A.N. Still, J. Mounts, 220th American Chemical Society National Meeting, Washington D.C., August 20-24, 2000.

Preparation of new polymer coatings for detection of pertechnetate ion. T.L. Hubler, S.A. Bryan, C.T. Carver, M.E. Thornton, 56th Northwest Regional Meeting of the American Chemical Society in Seattle WA, June 14-17, 2001.

Separating and sensing the pertechnetate ion: use of electroactive vinylferrocene-based polymers and smart materials for spectroelectrochemical detection of  $TcO_4^-$  T.L. Hubler, J.H. Sukamoto, S.A. Bryan, L. Liang, and G.M. Anderson, 56th Northwest Regional Meeting of the American Chemical Society in Seattle WA, June 14-17, 2001.