

2006 ERSD Annual Report
DOE-BER Environmental Remediation Sciences Project #90076

**Spectroelectrochemical Sensor for Pertechnetate Applicable to Hanford and Other
DOE Sites**

PI: William R. Heineman
Co-PIs: CJ Seliskar, SA Bryan, AS Del Negro, TL Hubler
Pacific Northwest National Laboratory, Richland, WA

Research Objectives:

The general aim of our work funded by DOE is 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 sensor is based on a unique combination of electrochemistry, spectroscopy and selective partitioning into a film that collectively provide an extraordinary level of selectivity for the target analyte. Our goal is a reversible sensor in which the fluorescent Tc-complex formed in the film is re-oxidized to TcO_4^- and free ligand. TcO_4^- in the film would then re-equilibrate with the sample. The sensor would therefore satisfy requirements for both applications described above. Making significant progress towards this goal has required us to discover new chemistry and spectroscopy for technetium itself. Indeed, we needed to find the first technetium complexes which fluoresced in solution at room temperature – we have made that breakthrough discovery this last year. **We are now in the unique position of being able to reach our goal of a reversible sensor for Tc.**

Research Progress and Implications:

Task 1: Refinement of the chemically-selective film for pertechnetate

In our search for new and better luminescent Tc complexes that can be made from TcO_4^- we have examined anew $[\text{Tc}(\text{dmpe})_3]^+$ (dmpe = 1,2-bis(dimethylphosphino)ethane) which we have previously studied as related to nuclear medicine procedures. Our results of years ago showed that non-aqueous $[\text{Tc}(\text{dmpe})_3]^+$ is part of a redox couple with well-defined, reversible electrochemistry that is accompanied by distinct absorbance changes in the visible wavelength region. We have now studied the spectroscopic properties of $[\text{Tc}(\text{dmpe})_3]^+$ in aqueous solution and have shown that it fluoresces at room temperature and that the fluorescence can be electromodulated. Spectroelectrochemical modulation is accomplished by either scanning or stepping the potential from -300 mV, at which no fluorescence is observed, to $+400$ mV at which excitation light is absorbed and fluorescence of $[\text{Tc}(\text{dmpe})_3]^{2+}$ is observed. $[\text{Tc}(\text{dmpe})_3]^{2+}$ is now the second type of luminescent Tc complex we have discovered and we have prepared a second manuscript which details some of our important results.

The Tc(I) complex is prepared in high yield by reduction of the Tc(VII) pertechnetate anion in a single step reaction with DMPE, where the diphosphine is both the reducing agent as well as the complexing ligand. The colorless Tc(I) complex is then isolated by metathesis with LiOTf for spectroelectrochemical studies in aqueous solvent. The purple $[\text{Tc}(\text{DMPE})_3]^{2+}$ can then be prepared by oxidation of the Tc(I) by HOTf and H_2O_2 in acetonitrile. The capacity of the Tc(VII) to be reduced in a single-step reaction

to the Tc(I) core suggests that a similar electrolytic reaction, where an applied potential reduces the Tc(VII) in the presence of ligand, will also produce the Tc(I/II) complex. Studies to establish and optimize the electrolytic preparation of the Tc(II) chromophore are ongoing in the Radiochemical Processing Laboratory at Hanford 300 Area .

We recently recognized the potential of the so-called *Dais* polymer material for sensing purposes. DAIS, more properly, SSEBS (sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene), is a sulfonated tri-block co-polymer of styrene, ethylene, and butylene. It is a polyelectrolyte in that styrene is partially sulfonated. As such, it has negatively charged groups, $-\text{SO}_3^-$, that form the basis for selective cation exchange and transport. DAIS-Analytical Corp. was the first to commercially prepare this material; it is now available from Aldrich in several different forms. Since this material has unique and promising properties, we have continued our evaluation of it for use in cationic Tc complex detection.

Because the $[\text{Tc}(\text{dmpe})_3]^{+/2+}/\text{SSEBS}$ film system has great promise for sensing TcO_4^- we have begun measurements of the distribution coefficients of both cationic species in the SSEBS material. SSEBS can be obtained with several different degrees of sulfonation (ion exchange capacity) and this suggests that one might tune the sensing film to one or both of these cations. Our most recent experiments with aqueous $[\text{Tc}(\text{dmpe})_3]^+$ have shown a K_d value with SSEBS of 4.4×10^3 mL/g and this value increases with lower concentrations of the complex. We are now extending these measurements to the $[\text{Tc}(\text{dmpe})_3]^{2+}$ complex.

Importantly, aqueous $[\text{Tc}(\text{dmpe})_3]^+$ is efficiently sorbed into the SSEBS polymer material on the surface of the spectroelectrochemical sensor. The rapid uptake by a SSEBS polymer-coated spectroelectrochemical sensor has been measured and electromodulation demonstrated. We are currently defining the optimal conditions for this system and, in October, 2006, will measure the limits of detection with the sensor containing the SSEBS sensing film.

The fluorescence response to electrochemically cycling $[\text{Tc}(\text{dmpe})_3]^+$, which is loaded into a SSEBS film on the sensor, between Tc(I) and Tc(II) is easily done by stepping the potential between -300 mV (Tc(I), nonfluorescent) and 700 mV (Tc(II), fluorescent). The degree of electromodulation is nearly complete after a short period of time as indicated by the strong change in fluorescence signal on reduction to the Tc(I) complex. It is clear that the fluorescence is turned on and off as the trapped complex is cycled between its two oxidation states. Modulation of the fluorescence signal is the critical procedure in the spectroelectrochemical sensor concept, which relies on measurement of this change in fluorescence, ΔF , to measure concentration and to distinguish the target species from others that might be in the sample.

Task 2: Continued development of sensor prototype and associated portable instrumentation

We continue to use a fully functional portable instrument with the spectroelectrochemical sensor. The instrument is composed of the sensor, a small imaging spectrograph fitted with a Peltier-cooled CCD camera, two small diode lasers (404 nm, 532 nm) as the excitation sources, and a potentiostat. The instrument now has a very versatile configuration and can be used not only with the spectroelectrochemical sensor but also remotely with standard absorbance and luminescence cells which allows

us to work on a variety of hot samples in the Radiochemical Processing Laboratory. We have again used this instrument extensively at PNNL in July and August 2006 for its detection capabilities and adaptability to a laboratory radioactive environment. There we measured films with sorbed fluorescent Tc analogues as well as aqueous solutions of these same compounds. The instrument currently resides in the Radiochemical Processing Laboratory at Hanford 300 Area where it is the principal spectroscopic tool for investigating the spectroscopy of technetium compounds. One of us (Co-PI CJS) spent all of July and the first week of August 2006 working with the PNNL Co-PIs and the instrument and will travel there again in October for an additional 10 days for new experiments on Tc compounds.

Task 3: Demonstration of sensor performance on TcO_4^- standards and samples from the vadose zone and subsurface water at Hanford Site

We have evaluated new pertechnetate preconcentration materials at PNNL (see Task 1). The laboratory samples examined to this point are higher in concentration than the native vadose zone samples. Once the detection limit is defined, we will test the vadose zone samples provided by Jeff Serne at PNNL. In addition, we are currently establishing the detection limits for the $[Tc(dmpe)_3]^+$ cation using the SSEBS electromodulated film technique discussed in Task 1 above.

Recent groundwater monitoring activities adjacent to the T tank farm of the Hanford Site have unexpectedly shown extremely high concentrations of ^{99}Tc in new monitoring well 299-W11-25 (exceeding 181,000 pCi/L). There are also trends of increasing ^{99}Tc at a number of downgradient detection monitoring wells (299-W11-40, 299-W11-39, and 299-W42). The associated ^{99}Tc plume is migrating toward and encroaching on the Columbia River. Subsequent to this discovery the high level of concern expressed by the State of Washington has suddenly raised the importance of a reliable sensor for Tc in the pertechnetate form. Our recent breakthroughs on this difficult project should enable us to provide such a sensor.

Planned Activities:

A New Collaboration: PNNL-UWY-UC

To broaden our expertise and efforts in discovering new luminescent complexes of technetium, we have formed a new collaboration which consists of the Co-PIs from PNNL/EMSL (Andrew Del Negro, Samuel A. Bryan) and UC (Professors Carl J. Seliskar and William R. Heineman) and a new collaborator from the University of Wyoming (Prof. B. Patrick Sullivan). It is important to note that before we began working to find luminescent technetium complexes no such complexes had been reported in the literature. It was, in part, through this new collaboration that we have made groundbreaking progress in identifying new luminescent complexes of technetium. This collaboration has already produced one *Journal of the American Chemical Society* Communication and another is about to be submitted for review. These two Communications summarize some of our very recent progress.

Information Access:

Presentations at Scientific Meetings

Characterization of trans-dioxotechnetium(V) and technetium(II)phosphine excited states and spectroelectrochemical detection of pertechnetate. SA Bryan*, AS Del Negro, Z Wang, TL Hubler, WR Heineman, CJ Seliskar, and BP Sullivan. 2006. Presented at the

61st Northwest Regional Meeting of the American Chemical Society, Reno, NV, June 25-28th, 2006.

Characterization of trans-dioxotechnetium(V) and technetium(II)phosphine excited states and spectroelectrochemical detection of pertechnetate. SA Bryan* A; Del Negro, Andy; Wang, Zheming; Hubler, Timothy L; Heineman, William R; Seliskar, C Presented at the Actinide Separations Conference, Richland, WA, May 22-25th, 2006.

Luminescent trans-Dioxotechnetium (V) Excited States and Spectroelectrochemical Detection of Pertechnetate. Andrew S. Del Negro*, Zheming Wang, Timothy L. Hubler, and Samuel A. Bryan, Northwest Regional Meeting of the American Chemical Society, Fairbanks, AK June 17, 2005.

Poly(4-vinylpyridine-co-styrene) Selective Films that Preconcentrate Anions for Spectroelectrochemical Detection, L. K. Morris*, W. R. Heineman, C. J. Seliskar, 230th ACS National Meeting, Washington, DC, Aug. 28-Sept. 1, 2005. (Poster session)

Sensors Based on Spectroelectrochemistry: Detection of Metal Ions in the Symposium on Electrochemical Science for Sensing and Energy Conversion, W. R. Heineman*, C. J. Seliskar, 2005 Center for Integrated Molecular Systems (CIMS), Pohang University of Science & Technology, Pohang, Korea, Sept. 22-23, 2005. (Invited paper)

Sensors based on Spectroelectrochemistry: A Strategy for Improved Selectivity in the Symposium on Analytical Electrochemistry, W. R. Heineman*, C. J. Seliskar, 56th Annual Meeting of the International Society of Electrochemistry, Busan, Korea, Sept. 25-30, 2005. (Invited paper)

Sensors Based on Spectroelectrochemistry: Strategies for Improved Selectivity in the Symposium on New Trends in Spectroelectrochemical Methods for Chemical Analysis, W. R. Heineman*, C. J. Seliskar, T. Battaglia, N. Pantelic, C. Wansapura, L. Morris, S. Andria, T. Sakova, A. Doepke, T. Clinton, Pittcon 2006, Orlando, FL, March 12-17, 2006

Sensors Based on Spectroelectrochemistry: Detection of Metal Ions, W. R. Heineman*, C. J. Seliskar, Matrafured 05, International Conference on Electrochemical Sensors, Matrafured, Hungary, Nov. 13-18, 2005. (Invited lecture).

Sensors Based on Spectroelectrochemistry: Strategies for Improved Selectivity in the Symposium on New Trends in Spectroelectrochemical Methods for Chemical Analysis, W. R. Heineman*, C. J. Seliskar, T. Battaglia, N. Pantelic, C. Wansapura, L. Morris, S. Andria, T. Sakova, A. Doepke, T. Clinton, Pittcon 2006, Orlando, FL, March 12-17, 2006. (Invited lecture).

Sensors Based on Spectroelectrochemistry: A Strategy for Improved Selectivity, W. R. Heineman*, Spring 2006 Ernest B. Yeager Symposium of the Cleveland Section ECS, Cleveland, OH, June 16, 2006. (Invited lecture).

Development of Spectroelectrochemical Sensor for Detection of 1-Hydroxypyrene, T. Pinyayev*, W. R. Heineman, C. J. Seliskar, 232nd ACS National Meeting, San Francisco, CA, Sept. 10-14, 2006.

Publications

Investigations of the Optical Properties of Thin, Highly Absorbing Films under attenuated Total Reflection Conditions. Leaky Waveguide Mode Distortions, A. Piruska, I. Zudans, W. R. Heineman, C. J. Seliskar, *Talanta* **65**, 1110-1119 (2005).

Spectroelectrochemical Sensor for Technetium: Preconcentration and Quantification of Pertechnetate in Polymer-Modified Electrodes, 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, *ACS Volume based on the symposium Subsurface Contamination Remediation: Accomplishments of the Environmental Management Science Program*, E. Berkey and T. Zachary Eds., ACS Symposium Series 904, American Chemical Society, Washington, DC, pp 306-321 (2005).

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 14. Enhancing Sensitivity of a Metal Complex Ion by Ligand Exchange, T. Shtoyko, J. N. Richardson, C. J. Seliskar, W. R. Heineman, *Electrochimica Acta*, *50*, 3191-3199 (2005).

Dynamic In Situ Spectroscopic Ellipsometry of the Reaction of Aqueous Iron(II) with 2,2'-Bipyridine in a Thin Nafion Film, N. Pantelic, C. M. Wansapura, W. R. Heineman and C. J. Seliskar, *J. Phys. Chem. B* *109*, 13971-13979 (2005).

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 18. Preparation and characterization of cross-linked quaternized poly(4-vinylpyridinium) films. S. D. Conklin, C. J. Seliskar, W. R. Heineman, *Electroanalysis* *17*, 1433-1440 (2005)

Making and Using a Sensor for Cu⁺²: An Introduction to Polymers and Chemical Sensing, J. R. Paddock, A. T. Maghasi, C. J. Seliskar, W. R. Heineman, *J. Chem. Ed.* *82*, 1370-1371 (2005).

Luminescence from the trans-Dioxotechnetium(V) Chromophore, A. S. DelNegro, Z. Wang, C. J. Seliskar, W. R. Heineman, B. P. Sullivan, S. E. Hightower, T. L. Hubler and S. A. Bryan, *J. Amer. Chem. Soc.* **43**, 14978-14979 (2005).

Studies of the Dynamics of Thin Ion Exchange Films by Spectroscopic Ellipsometry and Attenuated Total Reflectance Spectroscopy, Nebojsa Pantelic, Aigars Piruska and Carl J. Seliskar, accepted for the publication in "Recent Developments in Advanced Materials and Processes", book of selected papers presented at the Seventh YUCOMAT 2005. *Materials Science Forum Edition*, 431-438 (2006).

The Fluorescence Spectroelectrochemistry of Aqueous $[\text{Tc}(\text{dmpe})_3]^{+2+}$
(dmpe = 1,2-bis(dimethylphosphino)ethane), Andrew S. Del Negro, Samuel A. Bryan,
Nebojsa Pantelic, Laura Morris, William R. Heineman, and Carl J. Seliskar; manuscript
in preparation.

Highly Oxidizing Excited States of Re and Tc Complexes, Andrew S. Del Negro, Carl J.
Seliskar, William R. Heineman, Sean E. Hightower, Samuel A. Bryan, and B. Patrick
Sullivan, *J. Amer. Chem Soc.*, manuscript submitted.

Personnel

University of Cincinnati

William R. Heineman (Co-PI)

Carl J. Seliskar (Co-PI)

Necati Kaval (Research Associate, PhD)

Laura Morris (PhD graduate student)

Sara Andria (PhD graduate student)

Nebojsa Pantelic (PhD graduate student)

Aigars Piruska (PhD graduate student)

PNNL-RPL/EMSL

Samuel A. Brian (Co-PI)

Andrew S. Del Negro (postdoctoral, now Co-PI)

Tim L. Hubler (Co-PI)