Spectroelectrochemistry as a Strategy for Improving Selectivity of Sensors for Security and Defense Applications

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ABSTRACT

Spectroelectrochemistry provides improved selectivity for sensors by electrochemically modulating the optical signal associated with the analyte. The sensor consists of an optically transparent electrode (OTE) coated with a film that preconcentrates the target analyte. The OTE functions as an optical waveguide for attenuated total reflectance (ATR) spectroscopy, which detects the analyte by absorption. Alternatively, the OTE can serve as the excitation light for fluorescence detection, which is generally more sensitive than absorption. The analyte partitions into the film, undergoes an electrochemical redox reaction at the OTE surface, and absorbs or emits light in its oxidized or reduced state. The change in the optical response associated with electrochemical oxidation or reduction at the OTE is used to quantify the analyte. Absorption sensors for metal ion complexes such as $[Fe(CN)_6]^{4-}$ and $[Ru(bpy)_3]^{2+}$ and fluorescence sensors for $[Ru(bpy)_3]^{2+}$ and the polycyclic aromatic hydrocarbon 1-hydroxypyrene have been developed. The sensor concept has been extended to binding assays for a protein using avidin–biotin and 17β-estradiol–anti-estradiol antibodies. The sensor has been demonstrated to measure metal complexes in complex samples such as nuclear waste and natural water. This sensor has qualities needed for security and defense applications that require a high level of selectivity and good detection limits for target analytes in complex samples. Quickly monitoring and designating intent of a nuclear program by measuring the Ru/Tc fission product ratio is such an application.

Keywords: spectroelectrochemical sensor, optically transparent electrode, polymer film

1. INTRODUCTION

The challenges to develop effective sensors with adequate selectivity and sensitivity to accurately detect and quantify specific components in a complex mixture are many. When analyzed in a chemical laboratory setting, a sample can be subjected to one or more procedures to provide selectivity and improve limit of detection for the target analyte(s). For example, a simple extraction of the analyte from an interfering matrix provides some selectivity and can improve sensitivity by preconcentrating into a smaller volume. Transforming the analyte in some other way such as by a chemical reaction that adds a fluorophore can dramatically improve sensitivity. Ideally a sensor is placed *in situ* and must be able to accurately respond to the analyte without any sample preparation. Therefore a strategy to provide adequate selectivity and sensitivity for the intended application is key to developing a successful sensor.[1,2] This is especially important for security and defense applications where erroneous measurements have significant implications.

Selectivity in Sensors

Optodes and electrodes are sensors where the primary mode of sensing has little selectivity. Analytes identified by wavelength of absorbance or emission (optical sensors) or oxidation/reduction potential (amperometric sensors) have many potential interferences. Adding a chemically selective film (membrane) increases selectivity by preventing interfering species from interacting with the electrode or surface of the optical sensor. [3-7]

Sensitivity in Sensors

Sensors that respond to analyte *in situ*, often do not have sufficient sensitivity when analyte concentration is very low. Anodic stripping voltammetry (ASV) is an electrochemical technique that provides extremely low detection limits ($\sim 10^{-11}$M)[4] by preconcentrating the analyte at the electrode surface prior to the stripping step. During the preconcentration step, the electrode is held for a period of time at a potential that reduces metal ions in solution to metals

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that accumulate at the electrode surface. This very high concentration of analyte is then measured by stripping it off the electrode by a rapid positive potential scan that oxidizes the deposited metal. The preconcentration step can improve sensitivity by a thousand-fold times or more. A chemically selective film can increase sensitivity of the sensor by preconcentrating the analyte at the surface of an electrode or optode. The film is allowed to contact the sample solution for a period of time during which analyte species partition into it. The resulting concentration of the analyte in the film is greater than in the solution.

Combining Techniques to Increase Sensitivity and Selectivity

Sensors employing one technique often do not provide sufficient selectivity or sensitivity in the presence of interferences. Combining sensing elements such as a film with optical and electrochemical responses increases selectivity, improves sensitivity, and reduces other common sensor problems such as stability and drift.[8,9] This is analogous to using combined analytical techniques such as gas chromatography/mass spectroscopy where the identification of compounds is based on both retention time and a mass spectrum.

We describe here a novel sensor that combines spectroscopy and electrochemistry in one device and achieves good sensitivity using preconcentration of analyte into a film.

2. SPECTROELECTROCHEMICAL SENSORS

Spectroelectrochemical Sensor Concept

Spectroelectrochemical sensors achieve three or four different modes of selectivity by combining spectroscopy, electrochemistry and partitioning into a film into a single device. The sensor (Figure 1) consists of an optically transparent electrode (OTE) coated with a thin, chemically selective film.

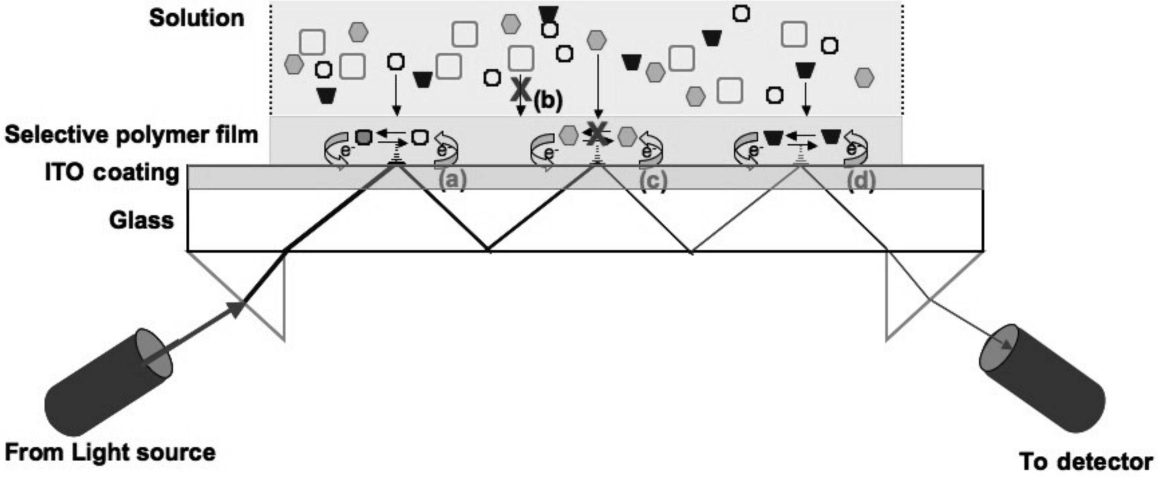

Figure 1. Spectroelectrochemical sensor concept: Attenuated total reflection occurs when light from evanescent waves, which penetrate the film at points a, c, and d, interacts with species contained in the polymer film. The sensor is selective for the species at point (a) which partitions into the film and can be electrochemically modulated between absorbing and nonabsorbing forms. Other species in solution are not detected because they do not do not partition into the film (b), do not have reversible electrochemistry, or (c) do not exhibit a change in spectral properties when electrochemically reduced or oxidized (modulated).

The sensors under development use glass with a thin layer of indium-tin-oxide (ITO) as the OTE. Light propagates through the OTE by total internal reflection and can interact with species contained in the selective film at each reflection point. The signal is the change in absorbance or fluorescence as the analyte is reversibly electrochemically modulated between oxidized and reduced states. To be detected, an analyte must 1) partition into the selective film, 2) undergo oxidation/reduction at the applied potential, and 3) absorb light of a specific wavelength in either the oxidized or reduced state. The sensor can be used to measure change in emission at a specific wavelength. Using fluorescence increases sensitivity and selectivity. The analyte would absorb at a specific excitation wavelength and the wavelength of emitted light would provide a fourth mode of selectivity for the sensor.

Demonstration of Spectroelectrochemical Sensor

The concept of the spectroelectrochemical sensor has been demonstrated using several different chemically selective films.[10-22] and two commonly used model analytes: ferrocyanide, $[Fe(CN)_6]^{4-}$, and ruthenium-tris(2,2'-bipyridyl), $[Ru(bpy)_3]^{2+}$, ions (Figure 2).[17,23] These analytes absorb at similar wavelengths, however they are oppositely charged and the redox potentials are far apart (Figure 3). Negatively charged films such as Nafion (Figure 4-a) preconcentrate cations such as $[Ru(bpy)_3]^{2+}$ and exclude negatively charged ions such as $Fe(CN)_6^{4-}$, whereas positively charged films such as QPVP (Figure 4-b) preconcentrate anions such as $Fe(CN)_6^{4-}$ and exclude cations such as $[Ru(bpy)_3]^{2+}$. Even if both analytes could partition into the same charged film, only one would be detected based on the range of potentials scanned.

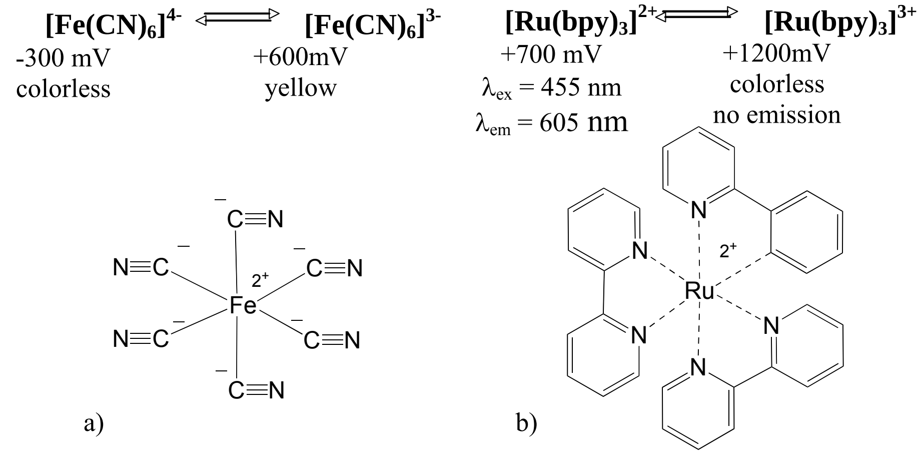

Figure 2. Model analytes a) ferrocyanide anion and b) ruthenium-tris(2,2'-bipyridyl) cation.

In one mode of operation, the sensor is placed in a flow cell, forming a three-electrode electrochemical cell. Analyte solution flows through the cell for the measurement. Optical fibers are used to direct light into the OTE and to collect the attenuated light after it has passed through the cell. Uptake of analyte into the preconcentrating film and absorbance modulation of ferrocyanide by the sensor are shown in Figure 4. The internally reflected light probes the analyte contained in the film as colorless ferrocyanide is oxidized to yellow ferricyanide, which absorbs at 420 nm. The concentration of ferrocyanide in the film increases as the ion partitions into the film. As a result, both the change in absorbance (ΔA) at 420 nm and the peak currents of the cyclic voltammogram (CV) increase.

Figure 5 shows a representative calibration curve for the detection of $Ru(bpy)_3^{2+}$ by fluorescence after partitioning into a Nafion film.

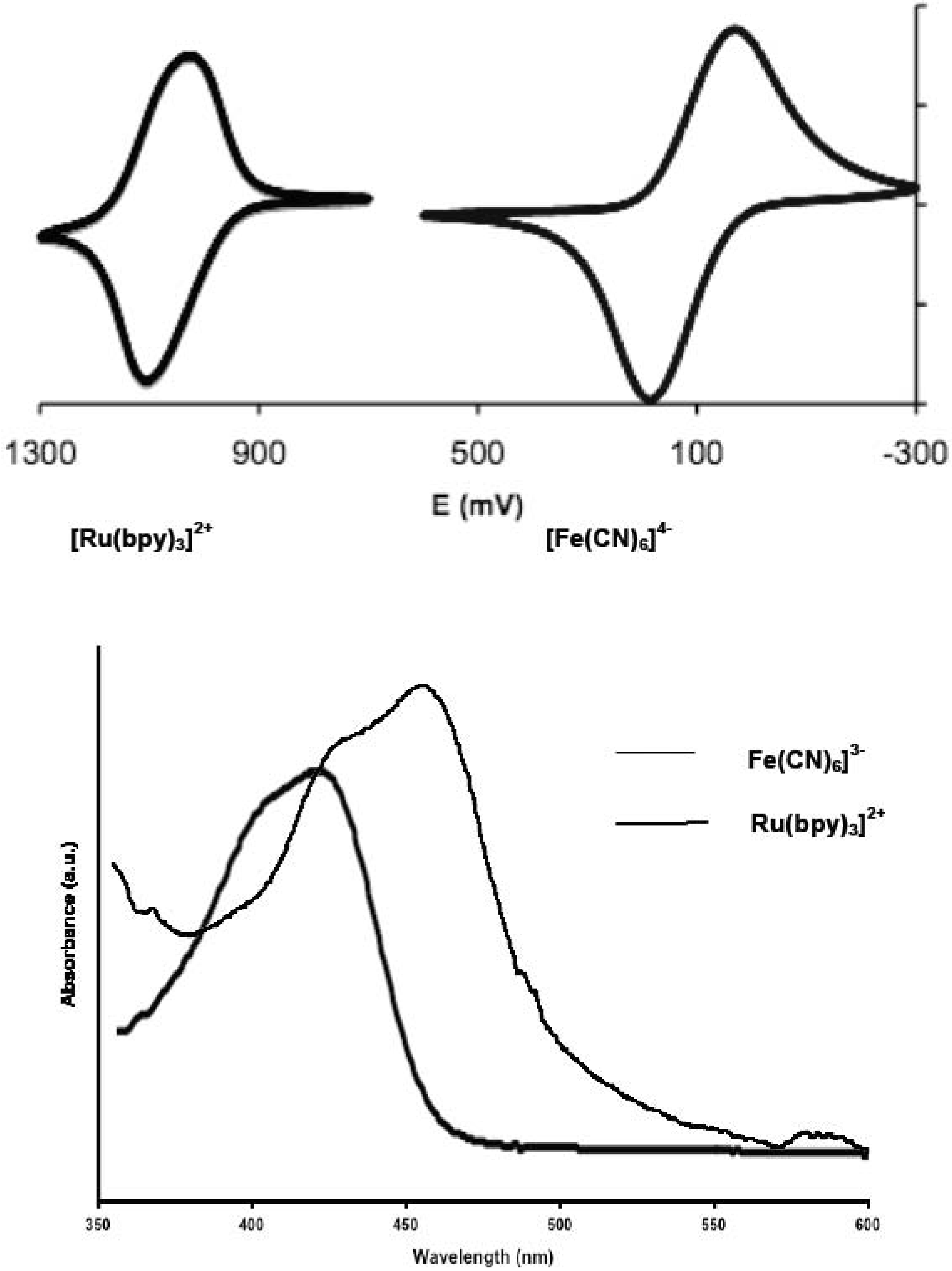

Figure 3. Cyclic voltammograms and absorption spectra (normalized) for the model analytes $[Ru(bipy)_3]^{2+}$ and $[Fe(CN)_6]^{3-}$.

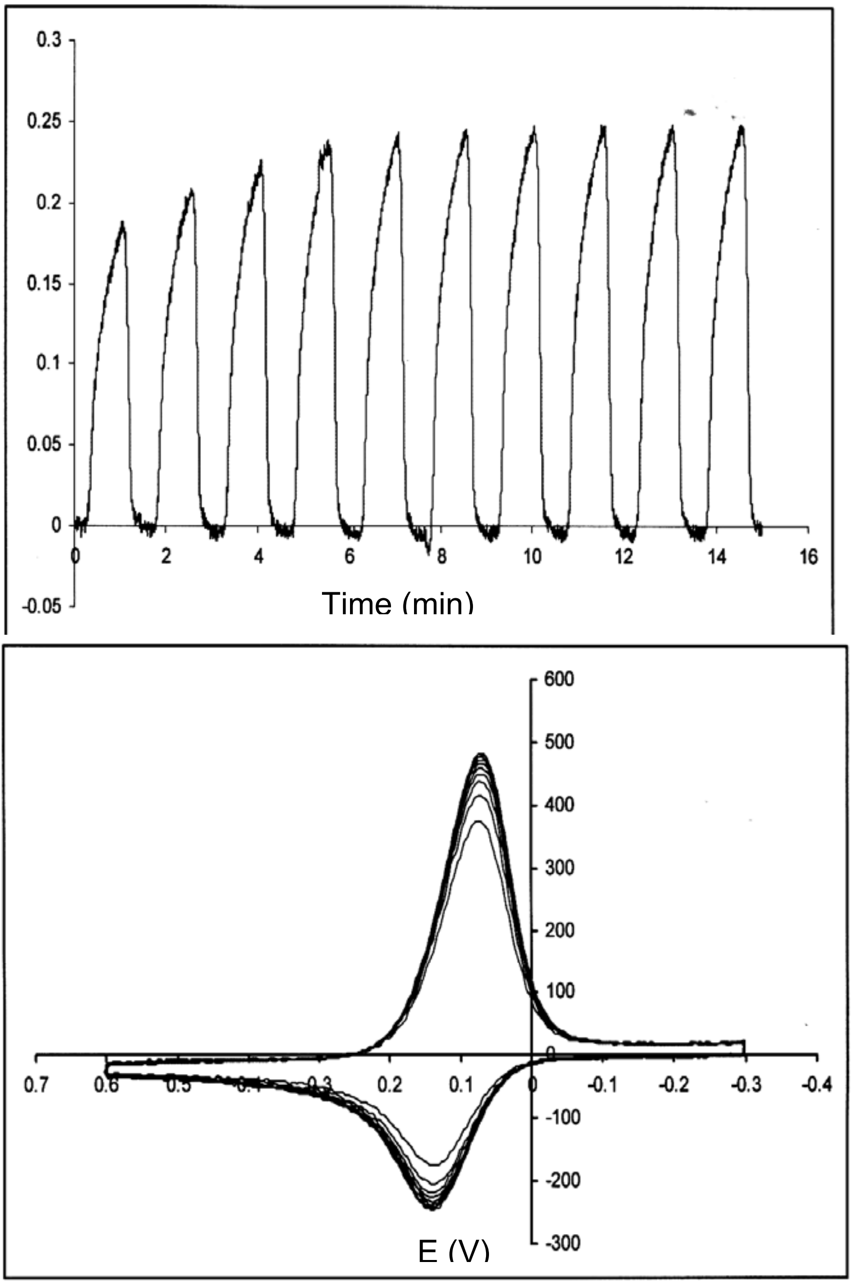

Figure 4. a) Cyclic voltammograms and b) optical modulation of absorbance versus time in minutes showing uptake of 0.1 mM ferrocyanide into 300 nm cross-linked QPVP film. The film was soaked overnight in supporting electrolyte (0.1 M KNO_3) before placing in the spectroelectrochemical cell. Potential was scanned from -300 mV to 600 mV (vs. Ag/AgCl) at 20 mV/s.

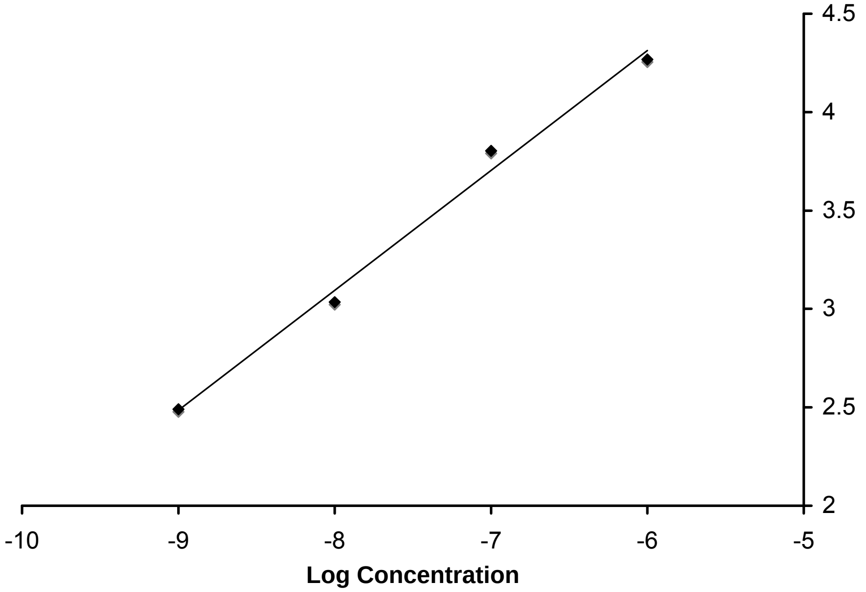

Figure 5. Calibration curve for $[Ru(bipy)_3]^{2+}$. Log-log plot of emission at 598 nm after 10 min. uptake for $1x10^{-9}$ M, $1x10^{-8}$ M, $1x10^{-7}$ M, and $1x10^{-6}$ M in 24 nm Nafion film.

Chemically Selective Films

Charged polymers have been used to form the thin chemically selective films on the surface of the OTE. Ideally, the films will preconcentrate the analyte as well as exclude at least some potentially interfering species in the sample. The selective film is critical to development of a sensor that is selective for and has sufficient sensitivity to the target analyte. The films must be transparent and not interfere with either the electrochemical reaction or the optical properties of the analyte. Complete regeneration by removal of the analyte from the film after each measurement is desirable so that the sensor can be used for multiple measurements. Additionally, films must be stable, remaining intact on the OTE surface after repeated measurements.

Films that have been used in the sensor include QPVP (quaternized poly(4-vinyl pyridine)),[24,25] PDMDAAC (poly(dimethyl diallylammonium chloride)), PVTAC (poly(vinyl tetraammonium chloride),[26] Nafion, [23] partially sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene, (SSEBS),[27] and sol-gel composites of QPVP, PDMDAAC, PVTAC and Nafion with SiO_2. Choice of material for the film determines the selectivity of the film for the analyte relative to other components of the solution.[5,28-35]

Equilibration time and magnitude of the response are dependent upon the thickness of the film as well as the choice of material. Film thicknesses used in the sensor have ranged from 6 nm to about 1000 nm when dry. Thinner films reach equilibrium faster than thicker films, however the maximum absorbance or fluorescence is greater in thicker films (Figure 6). Uptakes of $[Ru(bipy)_3]^{2+}$ into Nafion films reached maximum fluorescence approximately 200 s after the solution contacted 12 nm films as compared to 24 nm films which required over 700 s to reach maximum emission (λ_{ex} = 442 nm; λ_{em} = 605 nm). The maximum emission for the 24 nm films was 30,000 versus 10,000 for the 12 nm films. Nafion films are easily and completely regenerated and can be reused for several measurements without delaminating or decreasing response.

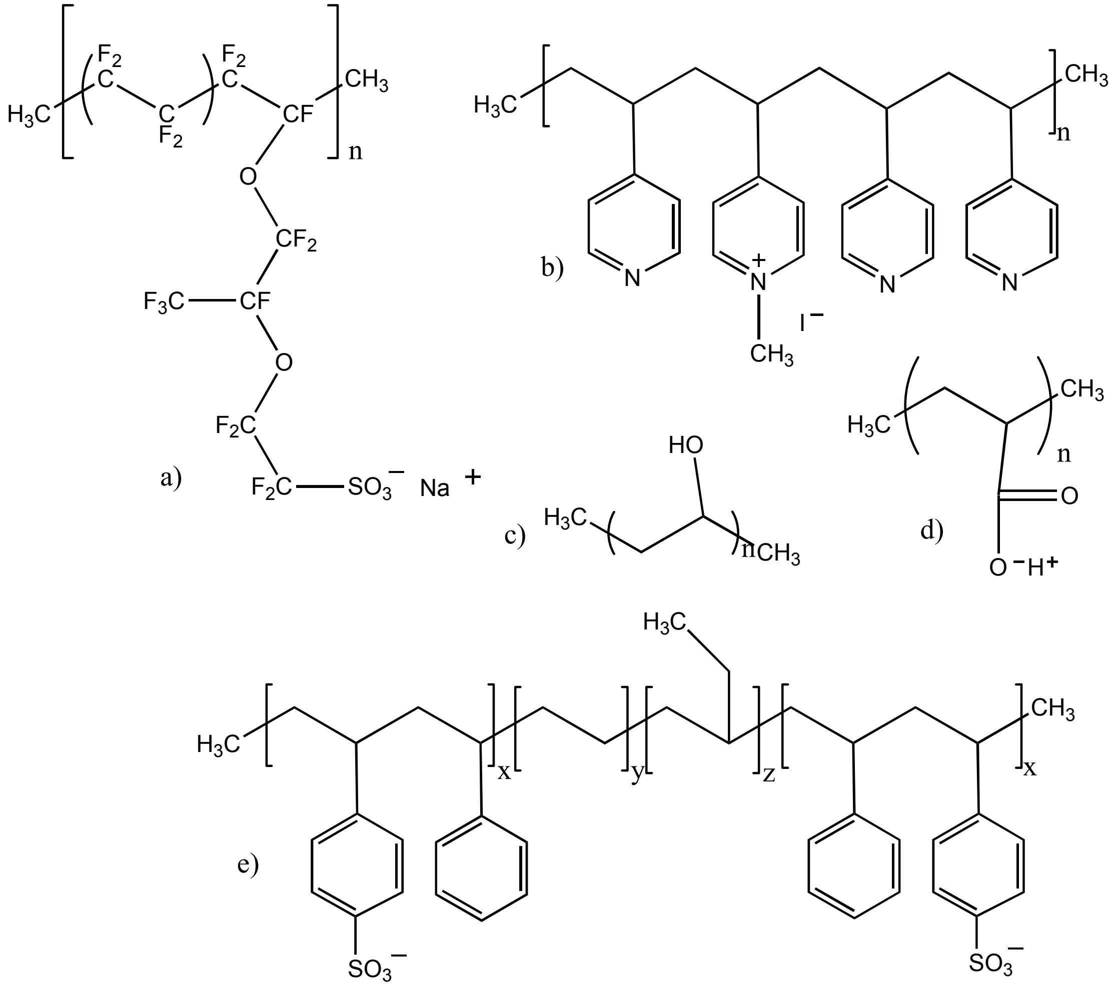

Figure 6. Structures of a) Nafion, b) QPVP, c) PVA, d) PAA matrix and e) SSEBS, some of the charged polymers that have been used to form the permselective films for the sensor.

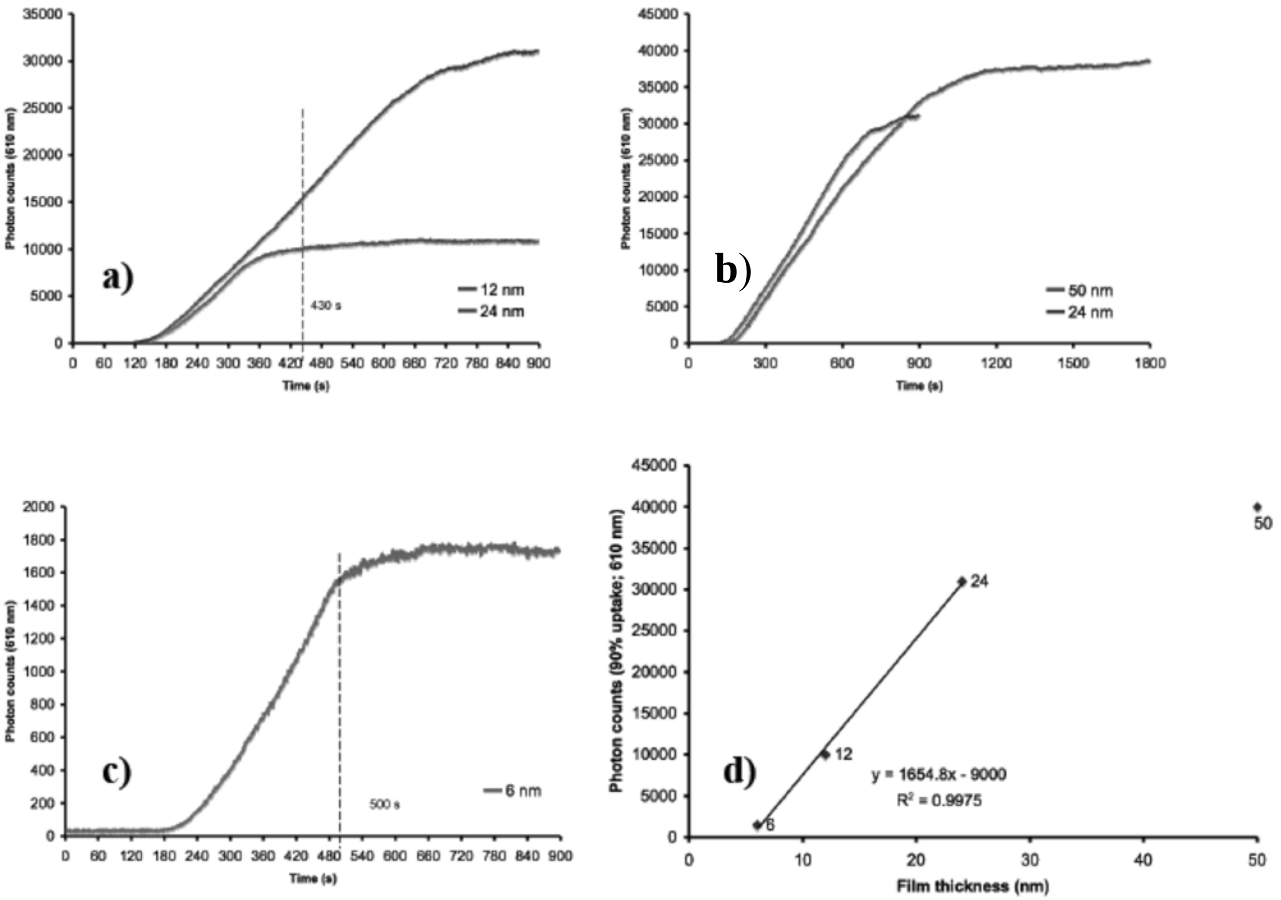

Figure 7. Effect of film thickness. Uptake of 1x10^{-6} M $[Ru(bipy)_3]^+$ in 0.1 M KNO_3 supporting electrolyte solution into a) 12 nm and 24 nm Nafion films, b) 24 nm and 50 nm Nafion films, and c) 6 nm Nafion films. Emission at 605 nm was monitored continuously for 900 s. A comparison of maximum emission of the four films is shown in d).

Instrumentation

Typical instrumentation that we have used with the spectroelectrochemical sensor is shown schematically in Figure 8. A Delrin® flow cell with a volume of approximately 0.5 mL was used for the spectroelectrochemical measurements.[36] [15,17,23,27,37] The flow rate of solution through the flow cell was controlled with a syringe pump. Electrochemical potentials were measured versus a Ag/AgCl (3M NaCl) reference microelectrode (Cypress Systems) positioned at the center back of the cell. The auxiliary electrode was platinum foil placed at the back of the cell surrounding the inlet for the reference electrode. The working electrodes were 10 mm x 40 mm ITO coated on glass (20 Ω/sq., 150 nm ITO layer on 1737F glass) (Thin Film Devices, Anaheim, California) with a chemically selective thin film coated onto the ITO layer. An Epsilon potentiostat was used for electrochemical modulation of the thin layer cell. The cell was fastened to an x-y stage in an angle plate. Light from a Xenon arc lamp (ILC Technology, model 302 UV) was focused into a monochromator (Bausch & Lomb 0.25 m). Light exiting the monochromator was directed through a multimode fiber then coupled into and out of the ITO glass by means of two Schott SF6 coupling prisms (Karl Lambrecht). Contact between the prisms and ITO glass was maintained by use of a standard index fluid (Cargill, refractive index 1.57). The optical fibers were also fastened to the angle plate to maintain fixed angles to the sensor. After multiple internal reflections, the exiting light was focused into a second optical fiber for absorption measurments. Attenuated light from the thin layer cell was directed to a monochromator with photon counting PMT (Acton, SpectraPro 300i 0.3 m focal length; NCL controller with Spectrasense software). For fluorescence detection the second optical fiber was used to collect light emitted from the first reflection point of the excitation beam.

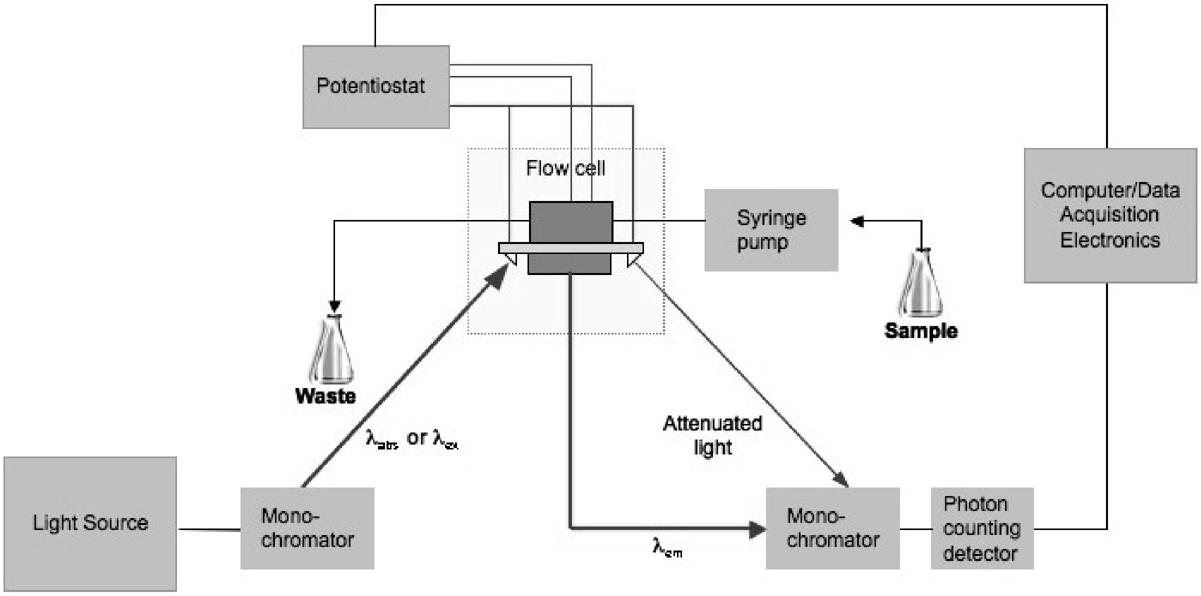

Figure 8. Instrumentation for the spectroelectrochemical sensor. The sensor is placed in a flow cell, forming a 3-electrode electrochemical cell. A platinum auxiliary electrode is permanently attached to the back of the flow cell and a micro-reference electrode (Ag/AgCl) is placed in the cell after filling with analyte solution. Alignment of the optical fibers to the sensor is achieved by placing the flow cell and optical fiber holders in an angle plate.

Applications

Stored Radioactive Waste and Surrounding Ground Water

Sensors are needed for characterizing nuclear waste stored in subsurface tanks. At the Hanford Washington site, plutonium was produced during the 1940s and continued during the Cold War, generating billions of gallons of liquid and solid radioactive waste .[28,38-41] The waste, containing many fission product radionuclides, hazardous chemicals, and high concentrations of metal salts of nitrates, nitrites, hydroxides, phosphates, sulfates, and carbonates, has been stored in approximately 170 underground storage tanks at the site since the 1940s. The chemical environment within the tanks is extremely harsh, including high ionic strength, high pH, high radioactivity and associated dose, and in some cases high temperature. Sensors developed for the purpose of characterizing tank waste must have exceptional selectivity and ruggedness because of the multitude of components and harsh conditions. The capability of the spectroelectrochemical sensor to perform under these harsh conditions was successfully demonstrated with a sensor that determined the ferrocyanide concentration from a sample of Hanford tank waste.[24] The ferrocyanide in this waste was in the form of the $Cs_2[NiFe(CN)_6]$ cage complex, added to the tanks as a means to trap and precipitate the $^{137}Cs^+$ ion, and remove it from the waste liquid phase.

Sensors are also needed for monitoring subsurface water at the Hanford site. Liquid waste, containing ^{99}Tc and other hazardous materials, discharged to the ground in trenches or from leaking storage tanks has contaminated the ground beneath the facility with at least some of the contamination reaching the water table. Monitoring the discharge and leakage plumes and preventing further groundwater contamination from them has particular importance at the Hanford site, which is located on the Columbia River, the fourth largest river in North America. ^{99}Tc has an extremely long half-life and has the potential to migrate through soil to the Columbia River as soluble pertechnetate (TcO_4^-), its most common ionic form under groundwater chemistry conditions. At present, monitoring the plumes heading toward the

Columbia River is done by laboratory-based analysis of samples obtained on a regular basis from groundwater and soil testing wells. A real-time sensor for Tc in the chemical form of pertechnetate, TcO_4^-, is needed to reduce sample monitoring delays. Since TcO_4^- does not have the required electrochemical and optical properties for its immediate detection, we are therefore developing a sensor based on the formation of a fluorescent technetium complex after it partitions into a selective film. Working initially with Re, the non-radioactive analogue to ^{99}Tc, we have developed an absorbance based sensor for $[Re(dmpe)_3]^+$ which is partitioned within a selective polymer film and spectroelectrochemically detected [42]. Re and Tc compounds generally have nearly identical chemical properties,[43-48] making Re an acceptable non-radioactive analogue for ^{99}Tc, which has no non-radioactive isotopes. We subsequently demonstrated the ability to directly sense Tc using the spectroelectrochemical sensor technique for the $[Tc(dmpe)_3]^+$ complex[49]. After partitioning into the sensor film, $[Tc(dmpe)_3]^+$ can be reversibly oxidized to $[Tc(dmpe)_3]^{2+}$, followed by fluorescence based detection at the nanomolar level in aqueous solution.

Recently we showed that an absorbance based spectroelectrochemical sensor was successful in detecting $[Ru(bpy)_3]^{2+}$ within natural well water, river water and in treated tap water samples without the addition of supporting electrolyte[50]. Variations in water hardness and conductivity among these samples had little effect on the calibration curves and detection limits. Thus, the sensor can be used directly on water samples of these types. .

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are environmental contaminants that are produced by the incomplete combustion of carbon containing compounds. Long term exposure to PAHs may cause cancer and damage to lungs, liver, skin and kidneys.[51,52] PAH contamination generally results from mixtures of PAHs rather than from a single compound and most PAH mixtures contain pyrene as a major constituent.[51] Pyrene metabolizes to 1-hydroxypyrene (1-PyOH) and 1-hydroxypyrene glucurinide (1-py-Oglu), both of which can be detected in urine to assess human exposure to environmental PAHs.

A spectroelectrochemical sensor for the indirect detection of 1-PyOH has been demonstrated.[53] 1-PyOH was oxidized under acidic conditions to diquinonepyrene. Diquinonepyrene has reversible electrochemistry and fluoresces at 425 nm in its reduced form, dihydroxypyrene. The ITO electrode was modified by coating with a 20 nm Nafion film. 1–PyOH was preconcentrated by the film and oxidized to dihydroxypyrene. Dihydroxypyrene, which emits at 425 nm was reversibly reduced to diquinonepyrene by scanning the potential between 500 and -200 mV. The change in fluorescence at 425 nm was used to create a calibration curve for 1-PyOH. The linear range for the indirect detection of 1-PyOH was $5x10^{-9}$ M to $1x10^{-6}$ M.

A spectroelectrochemical sensor was also developed to quantify both 1-PyOH and 1-PyOglu without separation.[54] Approximately 80% of pyrene metabolites excreted in urine are 1-PyOglu. A common approach to assess human PAH exposure is to first convert all metabolite to 1-PyOH. 1-PyOH is then analyzed by HPLC by fluorescence detection with detection limits in the 1 nM range. Using the excellent sensitivity and selectivity achieved by the spectroelectrochemical sensor, 1-PyOH and 1-PyOglu can both be detected in a single 30 min analysis. The detection limits were $1x10^{-8}$ M and $9x10^{-11}$ M for 1-PyOH and 1-PyOglu, respectively.

Security and Defense Application

The ability to quickly monitor and designate intent of a nuclear program is of concern to the international community. In this regard, the measurement of the fission products can be used as a sentinel for plutonium production. The production of the fission products technetium and ruthenium in power or research reactor fuel increases with increasing neutron irradiation. However, the production of the two elements proceeds at different rates according to the integrated flux. The molar ratio of the yields of Ru and Tc are shown in Figure 9 as functions of irradiation for a low enriched uranium (LEU) light water-moderated power reactor fuel[55] and for the graphite-moderated N Reactor fuel[56]. It is seen that the yields are distinctly different for the two reactors and for changes in irradiation. The N Reactor fuels have Ru/Tc ratios greater than 2, while the high burn-up fuels, such as employed in power reactors, the Ru/Tc molar ratio would be expected to be much greater than 2 (approaching 3 or higher).

One potential method to covertly obtain plutonium is through the placement of fertile natural uranium materials in the vicinity of a power reactor core through a blanket (surrounding the core) or in additional fuel pins or assemblies within the core. This method of obtaining plutonium is called “diversion of neutrons”. The fission products arising from the irradiation of the fertile natural uranium blanket or fuel pin materials would have ratios differing from those of the declared fuel, with the consequence that the Ru/Tc fission product ratio would be significantly reduced. Hence, the determination of an anomalous Ru/Tc ratio within fuel associated with the undeclared blanket materials would indicate the presence of additional "blanket" fuel. The ratio of ruthenium to technetium within the fuel processing stream can then be an indicator of the intended use of the reactor fuel. For fuel experiencing low burn-up as in the case for "diversion of neutrons" scenario for ^{239}Pu breeding, the Ru/Tc molar ratio would be measured at ≤ 2, as indicated in Figure 9.

Current methods for fission product analysis involves ICP methods requiring large fixed equipment, and extensive laboratory preparations, which would preclude impromptu field analysis. Using the spectroelectrochemical sensors demonstrated within our laboratory, with the selectivity and sensitivity for both ruthenium and technetium, a hand held device for in-field analysis is possible.

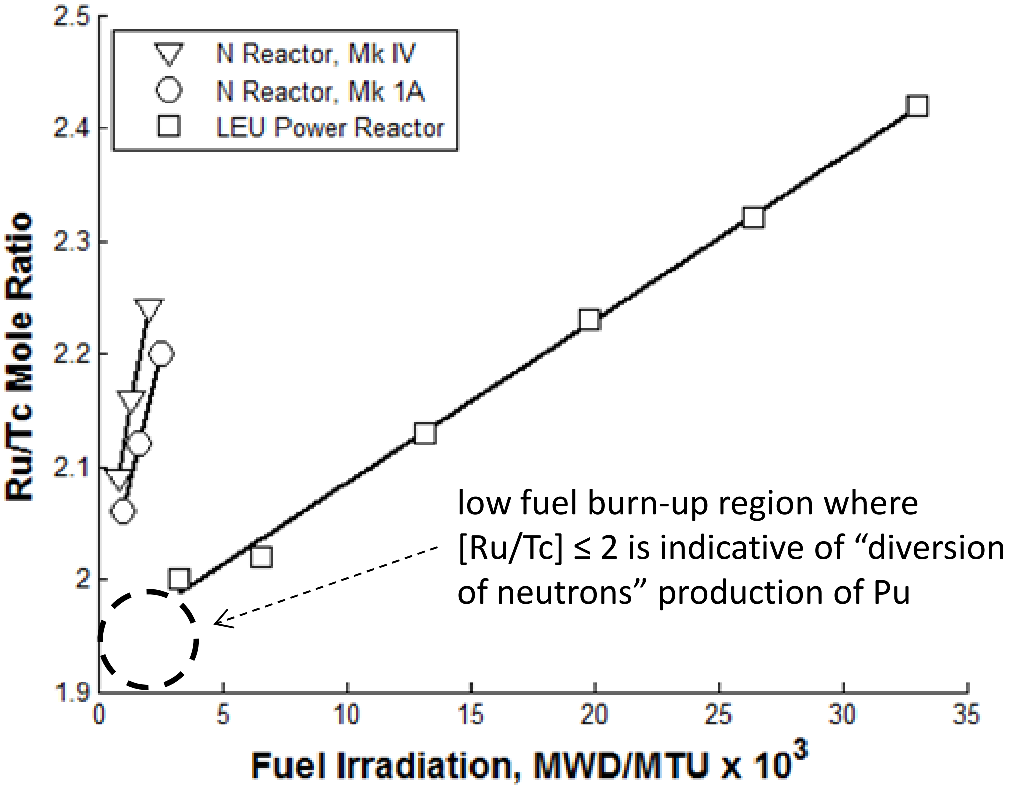

Figure 9. Ru/Tc fission product ratio as a function of irradiation exposure in N reactor (Mk IV and Mk 1A) and low enriched uranium (LEU) fuels.

3. CONCLUSIONS

Sensing based on spectroelectrochemistry provides additional selectivity that is often needed for complex samples. Finding the appropriate film enables low limits of detection to be achieved by strong partitioning into the film for detection. Sensors have been developed for metal ions and organic compounds. Applications have been demonstrated for sensing in radioactive waste and natural water. The sensor has the potential to determine the ratio of ruthenium to technetium within the fuel processing stream, which can be an indicator of the intended use of the reactor fuel.

4. ACKNOWLEDGEMENT

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References

[1] Z. Jusys, H. Massong, and H. Baltruschat, *J. Electrochem. Soc.* **1999**, *146*.
[2] J. Wang, R. K. Bhada, J. Lu, and D. MacDonald, *Anal. Chim. Acta* **1998**, *361*.
[3] J. Janata, *Principles of Chemical Sesnors*, Springer, 2009.
[4] P. T. Kissinger and W. R. Heineman, *Laboratory Techniques in Electroanalytical Chemistry*, Dekker, 1984.
[5] P. Ugo and L. M. Moretto, *Electroanalysis* **1995**, *7*, 1105.
[6] H. F. Walton and R. D. Rocklin, *Ion Exchange in Analytical Chemistry*, CRC Press, 1990.
[7] W. Kaim and A. Klein, *Spectroelectrochemistry*, Royal Society of Chemistry, 2008.
[8] J. Fraden, *Handbook of Modern Sensors*, Springer, 2004.
[9] P. Grundler, *Chemical Sensors: An Introduction for Scientists and Engineers*, Springer-Verlag, 2007.
[10] S. E. Andria, N. Pantelic, W. R. Heineman, and C. J. Seliskar, *Anal. Chem.* **2009**, *81*, 6756.
[11] L. Gao and C. J. Seliskar, *Chem. Mater.* **1998**, *10*, 2481.
[12] L. Gao, C. J. Seliskar, and W. R. Heineman, *Anal. Chem.* **1999**, *71*, 4061.
[13] L. Gao, C. J. Seliskar, and W. R. Heineman, *Electroanalysis* **2001**, *13*, 613.
[14] Z. Hu, A. F. Slaterbeck, C. J. Seliskar, T. H. Ridgway, and W. R. Heineman, *Langmuir* **1999**, *15*, 767.
[15] Y. Shi, C. J. Seliskar, and W. R. Heineman, *Anal. Chem.* **1997**, *69*, 4819.
[16] Y. Shi, A. F. Slaterbeck, S. Aryal, C. J. Seliskar, W. R. Heineman, T. H. Ridgway, and J. H. Nevin, *SPIE* **1998**, *3258*, 56.
[17] Y. Shi, A. F. Slaterbeck, C. J. Seliskar, and W. R. Heineman, *Anal. Chem.* **1997**, *69*, 3679.
[18] A. F. Slaterbeck, M. L. Stegemiller, C. J. Seliskar, T. H. Ridgway, and W. R. Heineman, *Anal. Chem.* **2000**, *72*, 5567.
[19] M. L. Stegemiller, W. R. Heineman, C. J. Seliskar, T. H. Ridgway, S. A. Bryan, T. Hubler, and R. L. Sell, *Environ. Sci. Technol.* **2003**, *37*, 123.
[20] B. H. Swaile, E. A. Blubaugh, C. J. Seliskar, and W. R. Heineman, *Anal. Chem.* **1998**, *70*, 4326.
[21] S. E. Andria, J. N. Richardson, N. Kaval, I. Zudans, C. J. Seliskar, and W. R. Heineman, *Anal. Chem.* **2004**, *76*, 3139.
[22] S. Conklin, W. R. Heineman, and C. J. Seliskar, *Electroanalysis* **2007**, *19*, 523.
[23] N. Kaval, C. J. Seliskar, and W. R. Heineman, *Anal. Chem.* **2003**, *75*, 6334.
[24] S. D. Conklin, W. R. Heineman, and C. J. Seliskar, *Electroanalysis* **2005**, *17*, 1433.
[25] S. D. Conklin, W. R. Heineman, and C. J. Seliskar, *Electroanalysis* **2007**, *19*, 523.
[26] J. H. Thomas, J. M. Drake, J. R. Paddock, S. Conklin, J. Johnson, C. J. Seliskar, H. B. Halsal, and W. R. Heineman, *Electroanalysis* **2004**, *16*, 547.
[27] N. Pantelic, S. E. Andria, W. R. Heineman, and C. J. Seliskar, *Anal. Chem.* **2009**, *81*, 6756.
[28] P. V. Bonnesen, G. M. Brown, S. D. Alexandratos, L. B. Bavoux, D. J. Presley, V. Patel, R. Ober, and B. A. Moyer, *Environ. Sci. Technol.* **2000**, *34*, 3761.
[29] B. Brunetti and P. Ugo, *J. Electroanal. Chem.* **1999**, *460*, 38.
[30] O. Buriez, L. M. Moretto, and P. Ugo, *Electrochimica Acta* **2006**, *52*, 958.
[31] C. R. Martin and K. A. Dollard, *J. Electroanal. Chem.* **1983**, *159*, 127.
[32] C. R. Martin, I. Rubinstein, and A. J. Bard, *J. Am. Chem. Soc.* **1982**, *104*, 4817.
[33] G. Schiavon and G. Bontempelli, *J. Electroanal. Chem.* **1993**, *356*, 67.
[34] M. N. Szentirmay and C. R. Martin, *Anal. Chem.* **1984**, *56*, 1898.
[35] P. Ugo, V. Zangrando, L. M. Moretto, and B. Brunetti, *Biosens. Bioelectron.* **2002**, *17*, 479.
[36] S. E. Andria, C. J. Seliskar, and W. R. Heineman, *Anal. Chem.* **2010**, *82*, 1720.
[37] A. S. D. Negro, Z. Wang, C. J. Seliskar, W. R. Heineman, B. P. Sullivan, S. E. Hightower, T. L. Hubler, and S. A. Bryan, *J. Am. Chem. Soc.* **2005**, *2005*, 14976.
[38] B. Gu, G. M. Brown, P. V. Bonnesen, L. Liang, B. A. Moyer, R. Ober, and S. D. Alexandratos, *Environ. Sci. Technol.* **2000**, *34*, 1075.
[39] HEIS, 2003.
[40] E. H. Schulte and P. Scoppa, *The Science of the Total Environment* **1987**, *64*, 163.
[41] D. J. Monk, M. L. Stegemiler, S. Conklin, J. R. Paddock, W. R. Heineman, C. J. Seliskar, T. H. Ridgway, S. A. Bryan, and T. L. Hubler, in *Subsurface Contamination Remediation Accomplishments of the Environmental Management Science Program*Eds. E. Berkey and T. Zachry), American Chemical Society, **2005**.
[42] L. Morris, C. J. Seliskar, W. R. Heineman, A. Del Negro, and S. A. Bryan, *Electroanalysis* **2009**, *21*, 2091.

[43] J. R. Kirchhoff, M. R. Allen, B. V. Cheesman, K. Okamoto, W. R. Heineman, and E. Deutsch, *Inorg. Chim. Acta* **1997**, *262*, 195.
[44] J. R. Kirchhoff, W. R. Heineman, and E. Deutsch, *Inorg. Chem.* **1988**, *27*, 3608.
[45] A. A. Woolf, *Quarterly Review of the Chemical Society* **1961**, *15*, 372.
[46] Y. Deng, C. J. Seliskar, and W. R. Heineman, *Anal. Chem.* **1997**, *69*, 4045.
[47] A. Verbruggen, *EANM Congress 2005* **2005**, 68.
[48] E. Deutsch, K. Lisbon, J.-L. Vanderheyden, A. R. Ketring, and H. R. Maxon, *Int. J. Radiat. Appl. Instrum. Part B* **1986**, *13*, 465.
[49] S. Chatterjee, A. S. D. Negro, M. K. Edwards, S. A. Bryan, N. Kaval, N. Pantelic, L. K. Morris, W. R. Heineman, and C. J. Seliskar, *Anal. Chem.* **2011**, *83*, 1766.
[50] E. A. Abu, S. A. Bryan, C. J. Seliskar, and W. R. Heineman, *Electroanalysis* **2012**, *24*, 1517.
[51] F. J. Jonganeelen, R. B. Anzion, C. M. Leijdekkers, R. P. Box, and P. T. Henderson, *Int Arch Occup Environ Health* **1985**, *57*, 47.
[52] C. H. Walker, *Organic Pollutants: An Ecotoxicological Perspective*, CRC Press: Taylor and Francis Group, 2008.
[53] T. S. Pinyayev, C. J. Seliskar, and W. R. Heineman, *Anal. Chem.* **2010**, *82*, 9743.
[54] R. A. Wilson, C. J. Seliskar, G. Talaska, and W. R. Heineman, *Anal. Chem.* **2011**, *83*, 3725.
[55] M. J. Bell, *ORGEN-ORNL, ORNL-4628*, Oak Ridge National Laboratory, Oak Ridge, TN, 1973.
[56] D. C. Hedengren, *ORIGEN2, RHO-SD-CP-TI-077*, Rockwell Hanford Operations, Richland, WA, 1985.