FINAL SCIENTIFIC REPORT

DOE NUMBER: DE-FG02-05ER63976

Recipient: Arizona State University

Project Title: Portable Analyzer Based on Microfluidic/Nanoengineered Electrochemical Sensors for in Situ Characterization of Mixed Wastes

PI: Professor Joseph Wang

SUMMARY:

This project aimed on the development of compact microchip sensing devices for on-site monitoring of pollutants in contaminated DOE sites. As described in this report, we have made a substantial progress, and introduced effective routes for improving the on-site detection of toxic metals and for interfacing microfluidic (Lab-on-Chip) sensing devices with the real world. This activity has been very productive and has already been described in 12 research papers (published in major international journals). The resulting microchip sensor technology should allow testing for toxic metals and other major pollutants to be performed more rapidly, inexpensively, and reliably in a field setting. These new analytical capabilities resulted from the generous DOE support will facilitate the characterization and remediation of mixed waste contaminated sites.

ACCOMPLISHMENTS:

This project resulted in several major accomplishments that will facilitate the characterization of contaminated nuclear energy sites. In accordance to our original objectives our studies have focused on various fundamental and practical aspects of sensing and microchip devices for monitoring metal contaminants. We have made a substantial progress, and introduced effective routes for improving the on-site detection of toxic metals and for interfacing microchip sensors with the real world. In particular, we introduced highly sensitive electrochemical stripping protocols for ultrasensitive detection of uranium, beryllium or chromium, replaced the toxic mercury electrodes with environmentally-friendly 'green' bismuth sensors, and developed a simple sample introduction for microfluidic analytical devices. This activity has already resulted in 12

research papers (published in leading international journals). The resulting microfluidics/electrochemical sensor system would allow testing for toxic metals to be performed more rapidly, inexpensively, and reliably in a field setting. The attractive behavior of the new “mercury-free” metal sensors is particularly promising for on-site characterization of contaminated DOE sites.

PROJECT ACTIVITIES:

During this project, we made a substantial progress, and introduced effective routes for improving the on-site detection of toxic metals (relevant to the DOE) and for designing microfluidic (Lab-on-Chip) devices with an on-line continuous monitoring capability.

Sensors for Trace Metals.

The electrochemical sensors being developed rely on the highly sensitive adsorptive stripping voltammetry (AdSV) technique to detect metal ions of interest to the DOE, particularly uranium, beryllium and chromium.

Traditionally, AdSV measurements of U and Cr require the use of mercury electrodes which are not suitable attractive for field deployment. Our initial goal was thus to replace these toxic mercury electrodes with ‘environmentally-friendly’ sensor materials. In particular, we demonstrated that bismuth-film electrodes offer high-quality measurements of heavy metals that compare favorably with that of mercury electrodes. Bismuth is a ‘green’ element, with very low toxicity, and widespread pharmaceutical use. Our finding indicate that bismuth-coated electrodes offer an attractive analytical performance, analogous to that of their mercury counterparts.

Figure 1: Effect of the bismuth plating time (A), pH (B) and cupferron concentration (C) upon the stripping voltammetric response of 50 $\mu g/L$ uranium.

A major effort of our activity has been devoted to the development of a ‘mercury-free’ uranium sensor based on the bismuth film electrode. Bismuth-coated carbon-fiber electrodes have thus been successfully applied for adsorptive-stripping voltammetric measurements of trace uranium in the presence of the cupferron complexing agent. The new protocol is based on the accumulation of the uranium-cupferron complex at a preplated bismuth film electrode held at -0.30 V (vs. Ag/AgCl), followed by a negatively-sweeping square-wave voltammetric waveform. Factors influencing the stripping performance, including the film preparation, solution pH, cupferron concentration, adsorption potential and time have been optimized (Figure 1). The resulting performance compares well with that observed for analogous measurements

Figure 2: Stripping voltammograms for increasing uranium concentrations from 0 to 350 µg/L (A, a-g); the corresponding calibration plot (B); Background-subtracted stripping-voltammetric response.

at mercury film electrodes.

The response is linear up to 50 µg/L, with a detection limit of 0.3 µg/L (Figure 2). Good reproducibility was indicated from a series of 15 repetitive measurements of 50 µg/L uranium that resulted in reproducible uranium peaks, with a relative standard deviation of 3.8%.

Potential interferences are examined. Applicability to sea water samples is

demonstrated. The attractive behavior of the new “mercury-free” uranium sensor holds great promise for on-site environmental and industrial monitoring of uranium.

Trace detection of chromium(VI) is also of major concern in contaminated DOE sites. Traditionally, this requires an adsorptive stripping detection of the Cr-DTPA complex at a mercury drop electrode. In this effort we developed a bismuth-coated

electrode for adsorptive-stripping measurements of trace chromium(VI). The new protocol is based on accumulation of the Cr-DTPA complex at a preplated bismuth film electrode held at -0.80V , followed a negatively-going square-wave voltammetric waveform. Factors influencing the stripping Cr response, including the film preparation, solution pH, DTPA and nitrate concentrations, deposition potential and deposition time, were systematically evaluated and optimized. The resulting performance compared well with that observed for analogous measurements at mercury film electrodes. Well defined Cr(VI) peaks were obtained for nanomolar levels of Cr in connection to short preconcentration times. A detection limit of 0.3 nM Cr(VI) was obtained using a 2 min accumulation. The sensitivity is coupled to good reproducibility and selectivity. A relative standard deviation of 5.1% was observed for 25 repetitive measurements of 20 nM Cr. Applicability to selective measurements in real (river water) environmental samples was demonstrated. The following metals were tested at the 25 nM level and found not to affect the response for 5 nM chromium(VI): Pb(II), Cd(II), Zn(II), Cu(II), Fe(III), Ni(II), and Co(II). A large (20-fold) excess of hydrated Cr(III) did not affect the response of 5 nM Cr(VI). This is consistent with previous studies which have shown the effective discrimination against hydrated Cr(III) species. In addition to the use of glassy-carbon substrates, we demonstrated the utility of disposable thick-film (screen-printed) electrodes for supporting the bismuth film. These bismuth-coated strip electrodes offered a similar chromium detection as that observed at the coated glassy-carbon electrodes.

Beryllium is another important toxic metal of great relevance to the DOE. We developed an effective adsorptive-stripping voltammetric protocol for trace measurements of beryllium at a preplated mercury film electrode (MFE), based on the adsorptive accumulation of the arsenazo-I/Be complex. The arsenazo-I complexing agent dye has been shown earlier useful for absorption spectrophotometric measurements of trace beryllium. However, there are no early reports on the voltammetric detection of arsenazo-I or related electrochemical measurements of its metal complexes. We demonstrated that the adsorptive accumulation of Be-arsenazo-I complex onto the MFE results in a highly sensitive and reproducible AdSV protocol for measuring trace levels of beryllium. Optimal conditions were found to be a 0.05 M ammonium buffer ($\text{pH } 9.7$) containing $5\text{ }\mu\text{M}$ arsenazo I, an accumulation potential of 0.0 V (vs. Ag/AgCl) and a

square-wave voltammetric scan. The new procedure obviates the need for renewable mercury drop electrodes used in early stripping protocols for beryllium. A linear response is observed over the 10 - 60 $\mu\text{g l}^{-1}$ concentration range (90 sec accumulation; **Figure 3**), along with a detection limit of 0.25 $\mu\text{g l}^{-1}$ beryllium (10 min accumulation).

Microfluidic Chips with an On-line Continuous Monitoring Capability.

Efficient microchip assays of real-world environmental samples will require the incorporation of a continuous sampling capability (from the external environment) or rapid sampling of multiple discrete samples. We developed a rapid and reproducible sample introduction route into capillary-electrophoresis (CE) microchip devices based on a sharp sample-inlet tip placed alternately in the sample and buffer vials (**Figure 4**). Alternate placement of the inlet tip in vials containing the sample and buffer solutions permits a volume-defined electrokinetic sample introduction. Such fast and simple sample introduction leads to highly reproducible signals with no observable carry over between different analyte concentrations. Factors influencing the analytical performance of the new microchip interface were characterized and optimized. The attractive performance of the system was demonstrated in flow-injection and CE measurements. Employing an 8-cm long separation channel and a separation voltage of 4000 V offers high-throughput flow-injection assays of 100 samples/hr with a relative standard

deviation of 3.7% (n=100). Such ability to continuously introduce real samples into micrometer channels would make “Lab-on-a-chip” devices compatible with real-life environmental applications.

Figure 4. Structure of the microfluidic chip system with on-line continuous monitoring capability. The separation channel (a) is joined by a sharp sample inlet tip (b), a side sharp running-buffer inlet tip (c) and a detector compartment (d).

PRODUCTS

Publications:

1. “Adsorptive Stripping Voltammetric Measurements of trace Uranium at Bismuth Film Electrodes”, L. Lin, J. Wang, Y. Lin and W. Sadik, Anal. Chim. Acta 535(2005)9.
2. “Catalytic Adsorptive Stripping Determination of Trace Chromium (VI) at Bismuth Film Electrodes”, L. Lin, N. Lawrence, S. Thongngamdee , J. Wang and Y. Lin, Talanta, 65(2005)144.

3. "Continuous Monitoring with Microfabricated Capillary Electrophoresis Chip Devices", J. Wang, W. Siangproh, S. Thongngamdee and O. Chailapakul, *Analyst*, 130(2005)1390.
4. "Electrochemical Sensors for Environmental Monitoring: Design, Development and Applications", Deepa G. Patil, G. Hanrahan, and J. Wang, *J. Environ. Monit.*, 6(2004)657.
5. "Continuous Monitoring with Microfabricated Capillary Electrophoresis Chip Devices", J. Wang, W. Siangproh, S. Thongngamdee and O. Chailapakul, *Analyst*, 130(2005)1390.
6. "Adsorptive Stripping Voltammetric Measurements of Trace Beryllium", J. Wang, S. Thongngamdee and D. Lu, *Anal. Chim. Acta*, 564(2006)248.
7. "Adsorptive Stripping Voltammetric Measurements of Trace Molybdenum at the Bismuth Film Electrode", J. Wang, S. Thongngamdee and D. Lu, *Electroanalysis*, in press.
8. "Stripping analysis at Bismuth Electrodes: A Review", J. Wang, *Electroanalysis*, 17(2005)1341.
9. "Catalytic Adsorptive Stripping Voltammetric Measurements of Trace Vanadium at Bismuth Film Electrodes", J. Wang, D. Lai, S. Thongngamdee, Y. Lin and W. Sadik, submitted.
10. "Separation and Detection of Nitrophenols at Capillary electrophoresis Microchips with Amperometric Detection, J. Wang, J. Fischer, J. Barek, *Electroanalysis*, 18(2006)195.
11. G. Chen, Y. Lin and J. Wang, "Monitoring environmental pollutants by microchip capillary electrophoresis with electrochemical detection", *Talanta*, 68(2006)497.
12. "Electrochemical and Optical Bioassays of Nerve Agents based on OPH-Mediated Growth of CuFeCN Nanoparticles", A. Sanchez, T. Vazquez, J. Wang, A. Mulchandani and W. Chen, *Electrochem. Communications*, 7(2005)1371.