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Portable Analyzer Based on Microfluidics/Nanoengineered Electrochemical Sensors for In-situ Characterization of Mixed Wastes

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Research Objective

Required characterizations of the DOE's transuranic (TRU) and mixed wastes (MW) before disposing and treatment of the wastes are currently costly and have lengthy turnaround. Research toward developing faster and more sensitive characterization and analysis tools to reduce costs and accelerate throughputs is therefore desirable. This project is aimed at the development of electrochemical sensors, specific to toxic transition metals, uranium, and technetium, that can be integrated into the portable sensor systems. This system development will include fabrication and performance evaluation of electrodes as well as understanding of electrochemically active sites on the electrodes specifically designed for toxic metals, uranium and technetium detection. Subsequently, these advanced measurement units will be incorporated into a microfluidic prototype specifically designed and fabricated for field-deployable characterizations of such species. The electrochemical sensors being investigated are based on a new class of nanoengineered sorbents, Self-Assembled Monolayer on Mesoporous Supports (SAMMS). SAMMS are highly efficient sorbents due to their interfacial chemistry that can be fine-tuned to selectively sequester a specific target species. Adsorptive stripping voltammetry (AdSV) will be performed on two classes of electrodes: the SAMMS modified carbon paste electrodes, and the SAMMS thin film immobilized on microelectrode arrays. Interfacial chemistry and electrochemistry of metal species on the surfaces of SAMMS-based electrodes will be studied. This fundamental knowledge is required for predicting how the sensors will perform in the real wastes which consist of many interferences/ligands and a spectrum of pH levels. The best electrode for each specific waste constituent will be integrated onto the portable microfluidic platform. Efforts will also be focused on testing the portable microfluidics/electrochemical sensor systems with the selected waste samples at the Hanford site. The outcome of this project will lead to the development of a portable analytical system for *in-situ* characterization of MW and TRU wastes. The technology will greatly reduce costs and accelerate throughputs for characterizations of MW and TRU wastes.

Research Progress and Implications

This report summarizes results obtained during year three of the three year ERSP project. During the year 1 and 2 of the project, we have developed metal ion sensors based on carbon paste electrodes modified with different types of self-assembled monolayers on mesoporous silica (SAMMS) including acetamide phosphonic acid, glycynyl-urea, and thiol. The sensors were evaluated in batch experiments in order to determine the optimal

operating conditions. In the third year (FY06), we integrated SAMMS based sensors into 2 different platforms for two types of applications by using lead as the model toxic metal ion and Eu(III) as the surrogate of Ac (III) radionuclides. The first platform is based on screen-printed electrodes modified with SAMMS. We demonstrated the sensitive (detection limit 1.0 ppb) and selective detection of toxic metal ions and Eu (III) using SAMMS modified screen-printed sensors with a hand-held detector. This sensor platform allows the on-site quick testing of mixed wastes. The second platform is based on an automatic sequential injection system. SAMMS-modified electrodes were fabricated into a micro flow cell first and then integrated with a portable sequential system. High sensitivity and selectivity for detection of toxic metal ions with this automatic analytical system has been demonstrated. This automatic analytical system allows the on-site and on-line monitoring of the mixed waste. In addition to SAMMS, we also investigate the electrochemical sensors based on another new class of functional materials, carbon nanotubes. Demonstrated the highly sensitive detection of toxic metal ions using carbon nanotube based nanoelectrode arrays.

1.1 Screen-Printed Electrodes Modified with Functionalized Mesoporous Silica for Voltammetric Analysis of Toxic Metal Ions

For the first platform, reusable screen-printed sensors based on SAMMS modification have been developed because of their advantages of ease-of-use, simplicity and low costs. Mercury-free sensors for lead (Pb^{2+}) assay based on chemical modification of screen-printed carbon electrodes (SPCEs) with acetamide phosphonic acid self-assembled monolayer on mesoporous silica (Ac-Phos SAMMS) have been developed. The analysis of Pb using SPCEs-based adsorptive stripping voltammetry (AdSV) includes two steps. Pb^{2+} ions are firstly adsorbed on electrode surface in a Pb^{2+} solution during a preconcentration step, followed by a measurement step using one drop of acidic solution (50 μL) as a medium for stripping voltammetry. The preconcentration of Pb^{2+} at SAMMS-based sensors utilizes the binding affinity of the acetamide phosphonic acid and Pb^{2+} , which can be accomplished at open circuit potential without electrolyte and solution degassing. Due to the strong covalent bonding of the functional groups on mesoporous silica, the SAMMS-based sensors with a built-in three electrode system can be reused for tens of measurements with minimal degradation, enabling the establishment of the calibration curve and lowering the costs. Linear calibration curve was found in the range of 0 to at least 100 ppb Pb^{2+} after 5 min of preconcentration. The detection limit was calculated from $3S/N$ to be 0.91 ppb of Pb^{2+} . Reproducibility (%RSD) was found to be 5% for a single sensor (six measurements) and 10% for five sensors. The reproducibility can be improved through the precision of manufacturing of the sensors, in which SAMMS modification can be done in situ, increasing the user-friendliness of the sensors. Cadmium, lead, and copper can also be detected simultaneously at the SAMMS modified screen-printed sensors.

1.2. Screen-Printed Electrodes Modified with Functionalized Mesoporous Silica for Voltammetric Analysis of Europium

Europium (Eu^{3+}) is often present in nuclear wastes and used as Am(III) mimic. It also has a very similar in size to U(IV), Np(IV), and Pu(IV). Having considered its significance, we have recently developed sensors for Eu using a highly efficient solid sorbent, the self-

assembled salicylamide on mesoporous silica (Sal-SAMMS) for Eu preconcentration. Disposable sensors for the assay of toxic metal ions are gaining popularity because of their ease-of-use, simplicity and, low costs. Most screen-printed electrodes for trace metal ion analysis have been based on mercury film, or mercury oxide particles. Disposal of electrodes containing mercury leads to occupational and environmental health concerns. Therefore, we developed mercury-free screen-printed electrodes for europium by *in situ* modification of the carbon electrodes with Sal-SAMMS as shown in Figure 1. A manuscript summarized our findings is in press (*Analyst*, **2006**, DOI: 10.1039/b609211j)

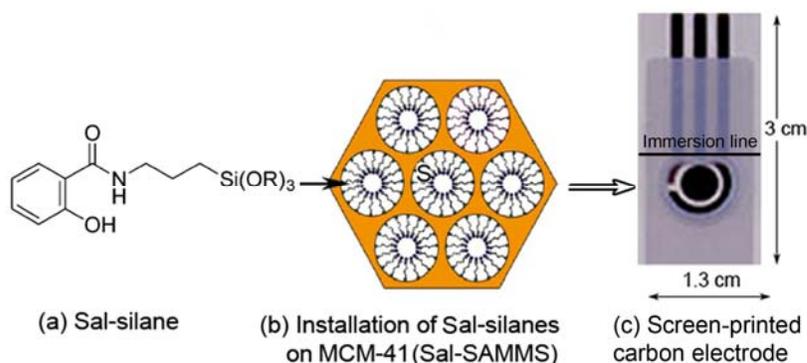


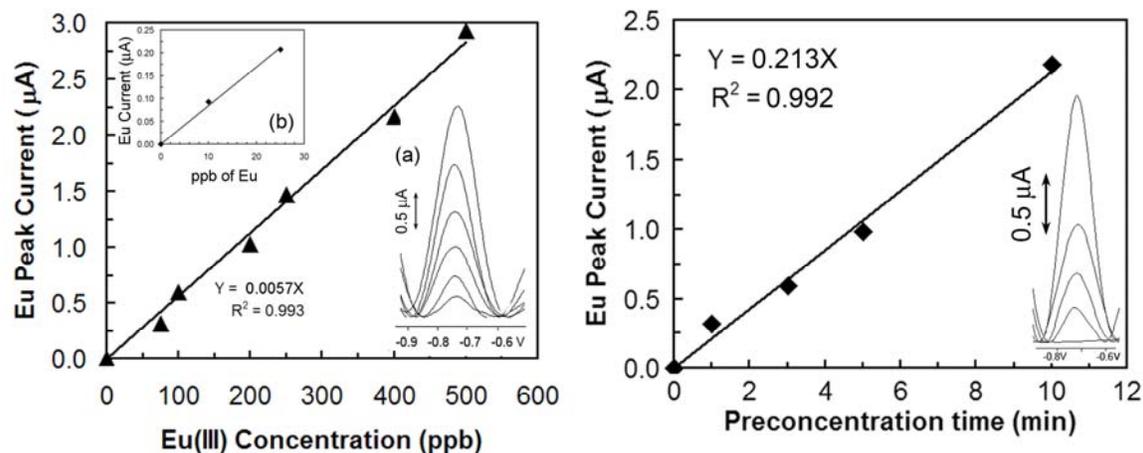
Figure 1. Hand-held electrochemical analyzer with Sal-SAMMS modified screen-printed carbon sensor

From batch sorption experiments, Sal-SAMMS sorbent had the distribution coefficients (K_d) for Eu of 0, 129, 17,000 and 48,000 mL/g at pH 1, 2.5, 4.5 and 6.5, respectively. K_d is a mass-weighted partition coefficient between the liquid supernatant phase and SAMMS solid phase; sorbents having K_d above 10^4 mL/g are considered outstanding. Without SAMMS, the graphite-ink modified sensors could not detect below 500 ppb of Eu after 5 min preconcentration (not shown).

Factors affecting preconcentration step (pH of samples, preconcentration time and Eu concentration in the samples) and detection step (type, concentration, and pH of the electrolyte solution, the potential and duration of the cathodic electrolysis, and the detection potential) were optimized. Optimal Eu detection was obtained after 3 - 5 min

preconcentration in Eu samples (pH 2 - 6), electrolysis at -0.9V for 60s in a new medium (0.1 - 0.2 M NH_4Cl , pH 3.5), followed by a square-wave voltammetric detection of Eu in the same electrolyte.

Figure 2(a) shows a linear voltammetric response of Eu measured after a 5-minute preconcentration period in 0.05 M acetate solutions containing Eu^{3+} ranging from 75-500 ppb (higher concentrations were not studied since they are often not applicable in real waste), while Figure 3(b) shows the effect of preconcentration time on the voltammetric response of 100 ppb Eu^{3+} solution.



Figures 2. (a) Linear voltammetric responses of Eu^{3+} after 5 min preconcentration and 10 min in inset, and (b) linear voltammetric responses of 100 ppb Eu^{3+} as a function of preconcentration time.

The large working linear calibration curves in Figures 2(a-b) were attributed to the large number of the functional groups of the Sal-SAMMS on the electrode surface. The preconcentration of Eu at Sal-SAMMS was not interfered by 0.05 M sodium acetate buffer. Sal-SAMMS was designed to have high affinity for Eu^{2+} even large excess of alkaline and alkaline earth metals; for example, in solutions having 10,000-fold by mole in excess of NaNO_3 , K_d for Eu was still in the order of 10^4 mL/g, suggesting that the sensors may be used effectively in complex matrices (e.g., real world samples). Other lanthanides and actinides are less likely to interfere with Eu sorption on Sal-SAMMS at this Eu concentration range because the large capacity of SAMMS will minimize the competitive binding.

The experimental detection limits for Eu^{3+} were 75 ppb after 5 min preconcentration and improved to 10 ppb after 10 min preconcentration. Longer preconcentration time would improve the lower detection limits. The Sal-SAMMS screen-printed sensors had good reproducibility (in term of percent relative standard deviation (%R.S.D.)) for the Eu^{3+} detections both at a single and various electrode surfaces. For a single electrode surface the %R.S.D for five measurements of 100 ppb Pb^{2+} (5 min preconcentration) was 10%. For five electrodes (all having 10 wt. % of Sal-SAMMS), the %R.S.D was 10%. The

reproducibility can be improved with increased precision of *in situ* SAMMS modification in the manufacturing process.

2. Automated Portable Analyzer based on Sequential Injection and Nanostructured Electrochemical Sensors

For the second platform, a fully automated portable analyzer for toxic metal ion detection based on a combination of a nanostructured electrochemical sensor and a sequential flow injection system has been developed (Figure 3). The sensor was fabricated from a carbon paste electrode modified with acetamide phosphonic acid self-assembled monolayer on mesoporous silica (Ac-Phos SAMMS) which was embedded in a very small wall-jet (flow-onto) electrochemical cell. The electrode was solid-state and mercury-free. Samples and reagents were injected into the system and flowed through the electrochemical cell by a programmatic sequential flow technique which required minimal volume of samples (less than 0.5 mL) and reagents and allowed the automation of the analyzer operation. The portable analyzer was evaluated for lead (Pb) detection due to the excellent binding affinity between Pb and the functional groups of Ac-Phos SAMMS as well as the great concern for Pb toxicity. Linear calibration curve was obtained in a low concentration range (1–25 ppb of Pb(II)). The reproducibility was excellent; the percent relative standard deviation was 2.5 for seven consecutive measurements of 10 ppb of Pb(II) solution. Excess concentrations of Ca, Ni, Co, Zn, and Mn ions in the solutions did not interfere with detection of Pb, due to the specificity and the large number of the functional groups on the electrode surface. The electrode was reliable for at least 90 measurements over 5 days. This work is an important milestone in the development of the next-generation metal ion analyzers that are portable, fully automated, and remotely controllable.

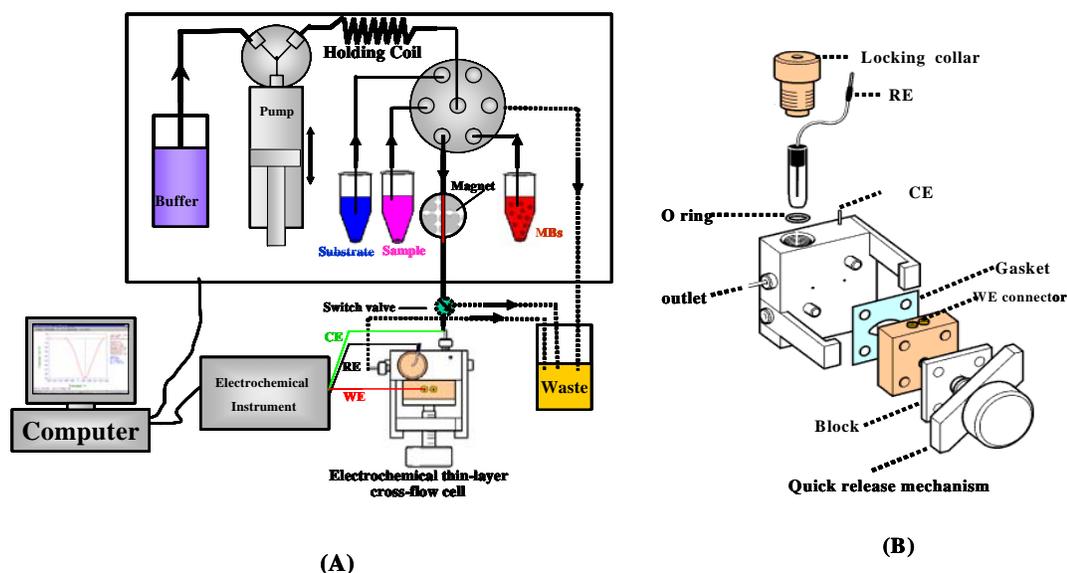


Figure 3. Portable Sequential Injection System with Electrochemical Flow Cell

3. Detection of Toxic Metals in Real Samples

Electrochemical sensors are often suffered from inorganic electrolyte, organic molecules and proteins in real samples. Therefore we tested the sensors modified with thiol-SAMMS, as a representative, in real samples including Hanford groundwater, and river water to assess the effectiveness and robustness of the sensors.

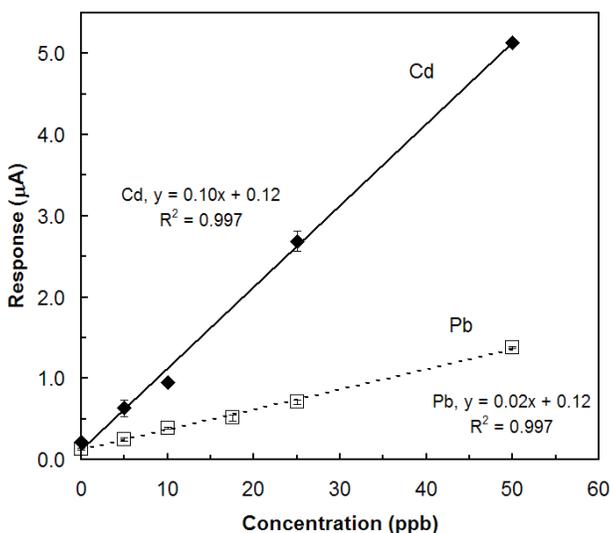


Figure 4. Linear voltammetric responses of Cd and Pb in Hanford groundwater after 3 minute preconcentration, Y-error bars represent the measurement errors.

Figure 4 shows that when used in complex Hanford groundwater, the SH-SAMMS sensors can detect both Pb and Cd without significant sample pretreatment besides filtering the groundwater through a regular filter paper, and adjusting pH of the filtrate to 6.5. Attributed to the high selectivity and affinity of SH-SAMMS to the metal ions (e.g., $K_d = 1.2 \times 10^6$ mL/g in groundwater and 5.6×10^5 mL/g), other ionic species in the groundwater did not negatively affect the preconcentration, and hence the detection of Pb and Cd. Linear range was obtained in the useful linear range of 0 to at least 50 ppb of Pb and Cd. The lower detection limits in ground water is 2 ppb of Pb and the reproducibility was 4.8 for 5 measurements of 25 ppb Pb in the groundwater. In river water, Pb responses were comparable to those in groundwater; the linear slopes were 0.029 uA/ppb Pb for river water and 0.025 uA/ppb Pb in groundwater and intercepts were 0.20 uA for river water and 0.12 uA for groundwater, suggesting that the sensors can be used in both waters without significant matrix effects.

Once we are successfully develop sensors for actinides, lanthanides, and anions like chromate and arsenate, the sensors will be integrated into the portable analyzer that has been previously reported. Remotely control function will be added into the existing automation feature of the analyzer. The portable analyzer will be used to analyze Hanford

wastes. The results will be verified by the-state-of-the-art inductively coupled plasma-mass spectrometry (ICP-MS).

Planned Activities

We plan to integrate our nanoengineered sensors with a lab-on-cable (Pacific Northwest National Laboratory/Arizona State University [PNNL/ASU]) system for *in situ* and in-well identification and quantification of uranium and toxic heavy metals (Cr and Hg) in subsurface soil sediments and natural waters. The development of the nanoengineered sensors/in-well monitoring technology will assist field scientists and engineers involved in the remediation effort of the contaminated sites to (1) accurately identify types, amounts, and source locations of contaminants entering the vadose zone and groundwater, (2) directly determine the speciation of the contaminants within soil sediment matrix and groundwater and their lateral and depth distribution, (3) validate the model assumptions for subsurface contaminant transport, and (4) track the performance of the remediation activities and optimize remediation processes.

Plan activities in FY 07 include: 1) Fabrication and characterization of electrochemical sensors based on SAMMS thin-films and carbon nanotube nanoelectrode arrays; 2) Evaluate the carbon nanotubes nanoelectrode arrays and SAMMS-based electrodes for the detection of U (VI) and Cr(VI).

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