

Project Title: Metal Ion Analysis Using Near-Infrared Dyes and the "Laboratory-on-a-Chip"

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Number of graduate students/post-doctorates: 1

RESEARCH OBJECTIVE: The primary research objective of this effort is to develop a portable, capillary electrophoresis (CE) microchip capable of sensitively and rapidly monitoring hazardous waste metal ions critical to the successful deactivation and decommissioning (D&D) of contaminated equipment and structures at various DOE sites. Hazardous waste metal ions to be adapted for sensing on the microchip include UO_2^{2+} , Be^{2+} , Cr^{6+} , Hg^{2+} , Pb^{2+} , Co^{2+} , Ni^{2+} , Cs^+ , and Sr^{2+} . Particular emphasis will be placed on developing viable, new extraction methods for metal ion sampling from both the air via a microimpinger which is integrated onto the microchip itself, and from contaminated surfaces, both techniques being amenable to on-line introduction onto the microchip. Two different detection methods for monitoring the electrophoretic separations taking place down the microchannel will be exploited in this research, indirect and direct detection. Special emphasis will be placed on maintaining the ultimate portability of the final microchip device through the careful selection of metallochromic dyes and fluorophores which are amenable to use of small, inexpensive light sources (e.g., LED's) and photodetectors.

RESEARCH PROGRESS AND IMPLICATIONS: This report summarizes work from 6/17/03 through 6/22/04, covering the sixth year of a six year project beginning October 1, 1998.

Airborne sampling and subsequent analysis of toxic metals (e.g., beryllium, mercury) is an important area for miniaturization onto the microchip platform in order to deal with the entire range of remediation hazards encountered at DoE waste sites. We are investigating methods for dramatically miniaturizing liquid impinger air sampling down to the microliter volume scale in order to better accommodate the small injection volume requirements of the microchip, as well as minimize solvent consumption and waste generation. We have successfully microfabricated microimpinger based devices in both PDMS and glass substrates, according to the design shown in Figure 1. The advantage of glass as a substrate material is that we can obtain improved separation resolution over capillary electrophoresis based separations performed in PDMS. The microimpinger consists of a system of microchannels leading from the gas sample inlet into a 20-50 microliter reservoir that contains the trapping reagent for the analyte of interest. We have found that the optimal number of inlet microchannels is between three and five. Fewer than three microchannels results in lower impinger efficiency, and above five microchannels, the bubbles

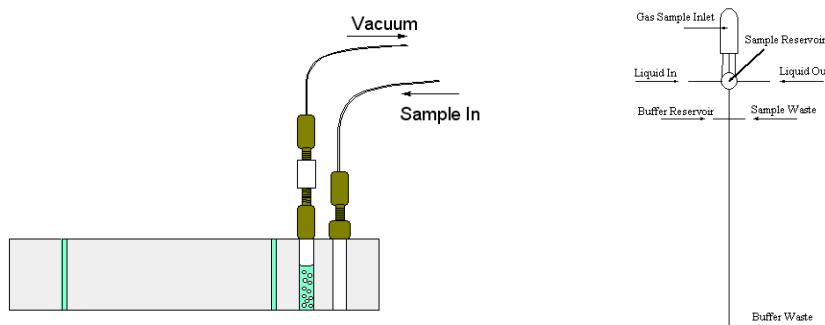


Figure 1: Microimpinger design for air sampling (left- side view; right- top view).

tend to coalesce into a single bubble with much lower surface area and, hence, lower extraction efficiency.

Contamination of actinides on concrete is an important but challenging analytical sampling problem for any analytical technique, including the CE microchip. Concrete contains a large background concentration of calcium, that will typically overwhelm most metal complexation dyes used to perform extractions. We have found excellent success, however, in the utilization of Arsenazo III for uranium extraction from concrete, as well as steel and Plexiglas, typical materials encountered at D&D remediation sites. Arsenazo III was previously demonstrated within this program to give very sensitive separations for uranium in the presence of numerous lanthanide impurities. The current optimized extraction procedure consists of rinsing the surface with pH 2 buffered malonic acid in order to extract all available uranium. Arsenazo III and EDTA are then added to the extract to selectively complex the uranyl ion, and this organic complex is passed through a C_{18} microcolumn to concentrate the organic metal complex. Elution is achieved using methanol, with the sample being analyzed either on the microchip or by UV/Vis, taking advantage of a unique spectroscopic peak at 654 nm. Interferents examined included iron, cerium, magnesium, aluminum and thorium, all of which presented no problems for this Arsenazo III extraction scheme. In the extraction of uranium from concrete, a wash efficiency of 94% was obtained, while the extraction efficiency for removing the Arsenazo III metal complex off the C_{18} column was 93%. The dynamic range for uranium detection on concrete surfaces using Arsenazo III ranged from 0.187 – 1.50 mg/cm².

In order to make a complete laboratory-on-a-chip platform for performing the spectrophotometric dye concentration and subsequent elution in tandem with the capillary electrophoretic separation of metal ions, we have focused our efforts over the past year on the incorporation of solid phase extraction columns directly onto the microchip itself. This has been accomplished by investigating a number of different approaches. The first approach examined and the one we've seen the greatest level of success to date, is in the preparation of a microcolumn bed that supports C_{18} coated silica beads that are held in place by a photoinitiated polymethacrylate porous hydrogel (see left side of Figure 2). Concentration enhancements as high as 300 times have been observed, with detection limits for the test case dye, Rhodamine B, being in the picomolar range. Similar success has been observed in the preparation of porous sol gel compositions directly into the microchannel, taking advantage of the covalent linkage of this porous glass with the walls of the microchip (see right side of Figure 2). TMOS has been used as the primary sol gel precursor, with the degree of hydrophobicity being increased through the introduction of trimethoxysilanes containing a single alkyl chain from C_3 - C_{18} . As seen in the right side of Figure 2, this material has great promise for excellent extraction efficiency due to its incredibly high surface area and capability for porosity control during preparation. Finally, C_{18} coated paramagnetic beads were investigated as an extraction material due to their potential for being held in place within the microchannel by an external magnet, and, subsequently removed electroosmotically following the removal of the magnet. Unfortunately, the beads supplied were not spherical in nature, leading to difficulties in attaining high packing densities, and the applied

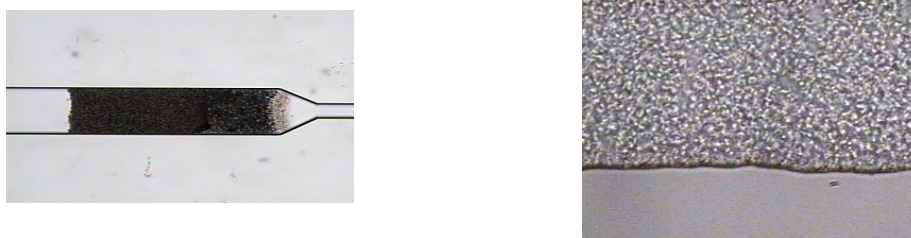


Figure 2: Solid phase extraction on a microchip (left side- C_{18} silica beads; right side- sol gel).

magnetic strength was insufficient for accurately supporting the beads in place under the types of back pressures being generated.

PLANNED ACTIVITIES:

Our future activities include synchronizing the extraction methods on a microchip directly with the injection and separation of these preconcentrated samples. We will also examine the implementation of several previously optimized microchip CE approaches for metal ions (e.g., PAR, Br-PAPS, Arsenazo III), and place these in parallel on a single microchip in order to further extend the range of analytes monitored on a single microchip, in addition to ensuring some redundancy in the sensor response for verifying the presence of particular toxic metal ions and preventing any problems associated with false alarms.

INFORMATION ACCESS

- “Sensitive Detection of Beryllium Using a Fiber Optic Waveguide Cell,” G. Deng, G.E. Collins and L. Wei, **Talanta**, 60, 9 (2003).
- “Nonaqueous Microchip Separation of Metal Ions Extracted from a Solid Support using Br-PAPS,” G.E. Collins and G. Deng, *J. Chrom. A*, 989, 311 (2003).
- “Remote Fiber Optic Flow Cell for the Detection of Uranium (VI) in Groundwater,” G.E. Collins, Q. Lu, S. Abubeker and E. Vajs, *Applied Spectroscopy*, 56, 464 (2002).
- “Radionuclide and metal ion detection on a capillary electrophoresis microchip using LED absorbance detection,” G.E. Collins and , *Sensors and Actuators, B*, 76, 244 (2001).
- “Microfabricated capillary electrophoresis sensor for uranium (VI),” G.E. Collins and Q. Lu, *Anal. Chim. Acta*, 436, 181 (2001).
- “Microchip separations of transition metal ions via LED absorbance detection of their PAR complexes,” Q. Lu and G.E. Collins, *Analyst*, 126, 429 (2001).
- “Separation of uranium (VI) and transition metal ions with 4-(2-thiazolylazo)resorcinol by capillary electrophoresis,” L. Evans III and G.E. Collins, *J. Chrom. A*, 911, 127 (2001).
- “The selective detection of uranium (VI) on a microchip using a derivatized 4-sulfonic calix[6]arene,” Q. Lu, J.H. Callahan and G.E. Collins, *Chem. Comm.*, 19, 1913 (2000).
- “Microchip used for uranium detection,” *C&E News*, October 16, 2000, p. 23.