Project Title: Metal Ion Analysis Using Near-Infrared Dyes and the "Laboratory-on-a-Chip"
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RESEARCH OBJECTIVE: The primary research objective of this effort is to develop a portable, capillary electrophoresis 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 work summarizes the present status after 4 years of a 6 year project beginning October 1, 1998.

In order to expand the capabilities of the microchip sensing platform beyond the previously demonstrated UO$_2^{2+}$ detection to include various other toxic metal ions of interest to DoE, a number of different promising fluorescent and colorimetric chelating agents were investigated for their application to the microchip.

Chrom azurol is a colorimetric dye known to exhibit excellent selectivity for complexing beryllium, resulting in an easily monitored wavelength shift from yellow to blue in color. The metal complexation chemistry for beryllium detection was optimized, paying particularly close attention to the pH, buffer and surfactant components in order to optimize the sensitivity and bring it into the parts-per-trillion regime using spectrophotometric methods. Unfortunately, chrom azurol was found to be poorly suited for application to the microchip. Significant difficulties were encountered in enabling the electroosmotic or electrophoretic transport of chrom azurol down the narrow microchannels of the microchip, apparently due to chemical adsorption of the dye to the glass walls. Despite efforts to modify the pH, ionic strength and type of surfactant utilized in the buffer medium, and despite making polymeric modifications to the microchannel walls in order to aid in the prevention of chemical adsorption, the problem persisted. The sensitivity and selectivity of the chrom azurol system for beryllium were so impressive, however, that we are currently investigating the application of this dye system to a fiber optic flow injection device for application as a field portable, beryllium monitor.

In the previous year, we demonstrated the rapid microchip separation of seven different metal ions, Co, V, Ni, Cu, Fe, Mn and Cd, utilizing the colorimetric metal chelating agent PAR and a green LED light source for absorbance detection of the separated metal chelates. Our current research efforts have been focused on expanding the number of metal ions quantitated simultaneously, through the application of parallel microchip separation channels compactly organized onto a single glass platform. In an effort to complement the metal ions already demonstrated separable using PAR, we examined the applicability of the metallochromic ligand 5-
Br-PAPS to the capillary electrophoresis microchip. This ligand has also proven to be very successful, expanding the number of metal ions separable in less than a minute to include: Cd, Pb, Cu, Co, Ni, and Hg.

While the LED based detection protocol utilized for the detection of metal ions is very inexpensive and amenable to miniaturization, the limitation is in its limits of detections, which vary from 50 ppb to 500 ppb, depending upon the toxic metal ion being quantitated. In order to realize dramatic improvements in these detection limits, in addition to making the microchip platform amenable to building material solid surface sampling, we have begun investigating the application of solid phase extraction techniques for generating concentrated liquid samples that can be subsequently analyzed by our microchip technique. As a first step, we have explored the liquid extraction of metal ions contaminating a small plexiglass substrate using 0.1 M nitric acid. Following neutralization of this extracted sample, the sample is buffered to pH 4.9 and the metal complexing agent, 5-Br-PAPS, is added. The liquid extractant is passed through a miniature, packed solid phase extraction column wherein the metal chelates are strongly adsorbed. The metal chelates are eluted in methanol, with concentration enhancements as high as 1000 times. This research has required adaptation and demonstration of the microchip’s separation capabilities in nonaqueous solvents, as opposed to the traditionally utilized aqueous buffer solutions, in order to take advantage of the concentration enhancements realized by solid phase extraction. We have successfully separated a mixture of three metal ions, Pb, Co and Ni, on the microchip following extraction from a small piece of plexiglass, obtaining detection limits from 2-15 ng/cm².

PLANNED ACTIVITIES:

Construction of a miniature, transportable high voltage box capable of six high voltage outputs, detection monitoring and light source regulation is currently being constructed in an effort to develop a truly portable, metal ion sensing microchip platform. As part of this effort, we are also designing a new, more user friendly microchip support stage which will facilitate the introduction and removal of microchips and the application of high voltages to the individual reservoirs. We will continue to examine solid phase extraction techniques and their coupling to the microchip, expanding the technique to include various surfaces of interest to DoE remediation efforts, including glass, plexiglass, soil, metal, and concrete. Other parallel microchip detection techniques will be studied, including indirect detection of metal ions such as Cs and Sr utilizing a quartz capillary and a fiber optic coupled deuterium light source. Finally, we will examine the application of a PCB antibody which is labeled with fluorescein for the sensitive detection and separation of various PCB’s on the microchip.

INFORMATION ACCESS

- “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).