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 report summarizes work from 6/20/02 through 6/16/03, covering the fifth year of a six year project beginning October 1, 1998.

A critical element to the success of any analytical sensor technique applied to the EMSP D&D effort, is the development of new methods for sampling metal contaminated surfaces. We have been investigating a number of different approaches for quantitatively extracting metals from various building material surfaces (glass, Plexiglas, steel, cement) for subsequent introduction to the microchip for analysis. The general approach being applied is to utilize a buffered solution of metal complexation dye, such as Br-PAPS, Chromazurol S or Arsenazo III, to efficiently extract the surface bound metal ions. Through proper choice of the ligand, we have found we can introduce an additional element of selectivity to the subsequent CE microchip separation, e.g., Br-PAPS for transition metal ions, Chromazurol S for beryllium, and Arsenazo III for actinides. In some cases we have found it is beneficial to add a secondary metal complexation agent, such as DTPA or EDTA, in order to preferentially complex and prevent interferences from troublesome ions ever present in the environment. Following extraction of the ions, the reagents are passed through a microcolumn solid phase extraction (SPE) apparatus, which enables the organic chelated metal ions to be quantitatively adsorbed and subsequently eluted in a suitable organic solvent. By implementing microcolumn SPE, the adsorbed metal ion chelates can be eluted in a very small volume of eluent (< 5 microliters), a feature which results in major concentration enhancements that are on the order of 1000 times the original concentration found in the aqueous wash solution used to extract the surface bound metals. As part of this effort, we have been actively pursuing methods for performing nonaqueous based capillary electrophoresis on a microchip, an approach which will enable direct coupling of the CE microchip separation of metal ions to the SPE process.

In conjunction with developing new methods for extracting beryllium off of surfaces, the concentrated Chromazurol S beryllium metal chelates were examined and very sensitively monitored using a hand held fiber optic spectrophotometer. By using a long pathlength liquid waveguide capillary cell (50 cm), beryllium levels could be detected down to 30 ng/l in solution or

0.5 ng/cm^2 from a contaminated Plexiglas surface. The addition of a cationic surfactant, cetylpyridinium chloride was critical to enhancing the sensitivity of this approach. Two spectrophotometrically shifted bands were observed upon complexation with beryllium, one that predominates at concentrations below 100 µg/l (510 nm), and a second band that dominates above 100 µg/l (610 nm).

Airborne sampling issues (e.g., beryllium, mercury) associated with DoE remediation activity was another area of active research in our laboratory over the last year. Considering the types of clean-up operations taking place at the superfund sites, there is a true need to impement improved air sampling techniques and on-line detection of these contaminants to improve safety during these operations. We are investigating methods for dramatically miniaturizing liquid impinger air sampling down to the microliter volume scale. In this way, we project that it will be possible to directly couple these devices to a capillary electrophoresis microchip in much the same way as a micro-SPE system, while minimizing the generation of waste from a traditional impinger system, for example. To accomplish this goal, we have successfully microfabricated a number of PDMS based microimpingers for performing air sampling. These devices are showing significant promise, and we are currently optimizing their performance based upon the dimension and number of air sampling microchannels built into these devices.

PLANNED ACTIVITIES:

Our future activities include continuing to optimize methods for sampling and extraction of contaminants of interest, from surfaces, liquids (i.e. groundwater) and air, and ultimately coupling these techniques directly to a completely microfabricated and fully automated miniaturized system. As part of the micro-SPE effort, we will pursue the introduction of C18-coated silica particles into microchannels which will be directly coupled to the separation cross of the CE microchip. We will initially test prototypes of these structures in PDMS, and then compare these results to glass microfabricated structures later. As part of this microfabrication effort, 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

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