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

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SPECIFIC DOE PROBLEMS BEING ADDRESSED: The DoE has been tasked to deactivate and/or decommission numerous buildings and release sites across the United States. The enormity of this task is phenomenal when we consider the quantity of metal and concrete within these buildings, all of which may or may not be contaminated with various radionuclides and heavy metals, and all of which must be decontaminated/decommissioned, analytically characterized, and disposed of in a safe manner. Unfortunately, current characterization techniques for radionuclides and/or heavy metals typically require lengthy analysis times at external laboratories, causing costly delays from a health and fiscal standpoint.

The goal of this project is to develop a real-time, field portable monitor for radionuclides and heavy metals which will assist in the segregation of contaminated and non-contaminated scrap metal and concrete materials via the identification of the type and extent of radionuclide and heavy metal contamination apparent on building materials. The expected affordability of this technology will permit sensors to be employed in the field at a multitude of remediation sites, and the more rapid characterization times in the field will help reduce life cycle costs, mortgages, and health risks, while enabling big savings for the DoE.

RESEARCH OBJECTIVE: The primary objective of this project is to develop a sensitive and selective, portable sensor for radionuclides and heavy metals that utilizes a "laboratory-on-a-chip" platform for enabling low-cost, timely characterization of DoE remediation sites. This will be accomplished by synthesizing a new class of metal complexation ligands that are covalently linked to red fluorescing dyes, and utilizing these dyes for the selective quantitation of target metal pollutants through their selective separation down the microchannel of a "laboratory-on-a-chip." Inexpensive, compact light sources will be utilized as excitation sources, and detection will be achieved using compact, inexpensive, photodiode array detectors.

RESEARCH PROGRESS AND IMPLICATIONS: This work summarizes the present status as of June 20, 2001 for a 3 year project beginning October 1, 1998.

Synthesis and characterization: Four different metal complexation ligands, cyclen, calix[6]arene, iminodiacetic acid (IDA) and 18-crown-6 have been successfully linked covalently to the fluorophore, rhodamine. Each of these molecules have been purified by column chromatography, and fully characterized by electrospray mass spectrometry. Three different covalent linkage schemes have been investigated: succinimidyl ester, isothiocyanate, and sulfonyl chloride. Rhodamine sulfonyl chloride has demonstrated the most success with respect to its reactivity and final product stability.

Laboratory-on-a-Chip: Two separate microchip analysis platforms have been designed and fully interfaced to a computer for data collection, one for performing absorbance-based detection and the other for fluorescence. The absorbance-based detector utilizes a red LED light source and a photodiode array detector, while the fluorescence based system utilizes a green Nd:YAG laser and a miniature photomultiplier tube. Two metal complexation ligands, in particular, have demonstrated excellent promise with respect to the selective, microchip detection of uranium, and these will be discussed here.

With regards to fluorescence detection, rhodamine-calix[6]arene, a new, fluorophore tagged macrocycle synthesized in this program, has demonstrated excellent selectivity and sensitivity for the uranyl ion in the presence of a complex mixture of metal ions. Calixarenes form a barrel-shaped geometry which is well suited for uranyl ion metal complexation. The uranyl ion likely adopts a pseudoplanar penta- or hexa-coordinate structure that helps explain its enormous selectivity factors for uranium over other metal ions ($> 10^{12}$). It is for this reason that calix[6]arene has been coined the term, "super-uranophile." Our investigations on the microchip have established rapid separations (< 50 sec) of the free ligand from the uranyl-complexed ligand. Furthermore, the addition of various transition, alkali and rare earth metal ions does not result in the formation of any additional separation peaks, thereby, verifying the high selectivity of this ligand for uranium.

Simple absorbance based detection methods are also being pursued based upon the commercially available metal complexation dye, Arsenazo III. This dye is particularly well-suited for adaptation to the laboratory-on-a-chip in this project due to its capability for lanthanide/actinide metal complexation, and the overlap of these metal complex absorbance peaks with the output of a red LED excitation source. Arsenazo III has the additional advantage of not complexing the vast majority of transition and alkali/alkaline earth metal ions which predominate at any remediation site. With citric acid in the separation buffer, we have demonstrated the selective separation of a mixture of uranium from three other lanthanides, Sm, Gd, and Ce in under two minutes. If EDTA is additionally added to the separation buffer, Arsenazo III will only complex colorimetrically to uranium, making its identification on a microchip very simple and highly selective.

Remote Probe: Optimization and initial characterization of a remote probe for extremely low levels (1.4 $\mu\text{g/l}$) of uranium (VI) in groundwater has been accomplished. The monitor takes advantage of a small length of Nafion cation exchange membrane tubing, which permits diffusion of the uranyl ion into an internally renewable reagent solution of Arsenazo III. The sensitive, colorimetric metal complexation of uranium (VI) by Arsenazo III is measured by recording the absorbance change in a fiber optic SMA Z-cell which is coupled to a red light emitting diode. The entire system is packaged on a 2" x 11" breadboard and attached to a 100 foot power and data transmission cord.

PLANNED ACTIVITIES: For the absorbance based laboratory-on-a-chip approach, continued research is necessary to assess real world extraction situations, as well as to investigate the possibility of simultaneously separating and detecting other actinides of interest, e.g., plutonium, via the laboratory-on-a-chip. Prototype should be finished by September 2001. With regards to the remote probe, we are currently examining an actual groundwater sample from the IT Corporation in Las Vegas, Nevada to assess the feasibility of this monitor.

INFORMATION ACCESS

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