FINAL REPORT
U.S. Department of Energy

METAL ION ANALYSIS USING NEAR-INFRARED DYES AND THE "LABORATORY-ON-A-CHIP"

Principal Investigator: Dr. Greg E. Collins
Institution: Naval Research Laboratory
Collaborators: Dr. Qin Lu
Institution: GeoCenters, Inc.

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3. Executive Summary

The purpose of this project was to establish the groundwork for developing a portable, toxic metal ion sensor capable of sensitively and rapidly detecting trace levels of hazardous waste metal ions contaminating building materials evident at DOE waste sites. By enabling selective metal ion analysis in the field, timely decisions with regards to the proper choice of remediation tools to be applied in a given activity, accurate sorting of contaminated and noncontaminated materials, and the immediated determination of the success or failure of a given clean up effort can be assessed directly, in real time. Such a sensor would enable savings in time and money, while additionally minimizing exposure, benefiting health criteria.

The sensor being investigated here is based upon a small glass slide which has etched upon its surface, small microchannels, that enable capillary electrophoretic separations to be performed on a microscale. We have studied the synthetic coupling of fluorescent tags with macrocycles known to complex toxic metal ions, and the subsequent utilization of these molecules to enable the sensitive and selective separation of metal ions such as uranium on a microchip. We have demonstrated the rapid separation of seven different toxic metal ions, including cobalt, nickel and cadmium in under a minute utilizing the chromophore, PAR. Rhodamine-calix[6]arene was synthesized and shown on the microchip to be a highly selective chelating agent for uranium in the presence of various metal ion impurities. Arsenazo III was investigated both on chip and in the form of a remote fiber optic probe for the selective detection of uranium down to the low ppb range. By demonstrating the rapid and sensitive separation of uranium and various other metal ions on a capillary electrophoresis glass microchip, this project has made significant advancements towards the realization of a portable sensor for toxic metal ions contaminating DOE remediation sites across the country.

4. Research Objectives

The DOE currently has the daunting task of deactivating 7,000 contaminated buildings and decommissioning 900 contaminated buildings that remain from the United States' involvement in nuclear weapons development over the last 50 years.[1] In addition to decontaminating the metal and concrete building materials that comprise these building structures, this program will require the decontamination and disposal of more than 180,000 metric tons of scrap metal.[1] The DOE is also currently entrenched in a massive cleanup program of their nuclear weapons facilities in an effort to prevent serious environmental problems arising from the already widespread contamination of soils, sediments and groundwaters. Incredibly, more than 600 billion gallons of water and 50 million cubic meters of soil have been contaminated by more than 5700 known DOE groundwater plumes.[2] The primary concern is migration of these plumes and their potential threat to local and regional water sources. Sites of particular concern include the Snake River Aquifer in Idaho, contaminated groundwaters at the 100, 200 and 300 areas at Hanford, Washington, Oak Ridge/Savannah River groundwaters and contaminated sediments at the Nevada Test Site.[2] Numerous landfills also exist at DOE facilities which are estimated to contain over three million cubic meters of radioactive and hazardous buried water.[2] The challenges associated with these tasks are numerous, and have been outlined in various research needs statements associated with facility Decontamination and Decommissioning (D&D).

The Environmental Management team has highlighted the need for revolutionizing technologies capable of improving characterization, monitoring and certification of contaminated equipment and facilities with emphasis on real time characterization in the field. One of the specific science research challenges critical to the advancement of decontamination and decommissioning (D&D) is the application of new principles and innovations to support the development of sensors, detectors, or monitors for rapid, automated characterization and certification of levels of radionuclides, mercury, beryllium, and other toxic metals evident on the surface of scrap metal, equipment and facilities. The research discussed in this final report was directed specifically to address the basic research elements necessary to develop a portable, compact microchip capillary electrophoresis unit for rapid characterization and certification of ppb levels of toxic metal contaminants found or originating from scrap metal and building materials in real time within the field. The intent here is to reduce the cost and health risks imposed on workers by minimizing the time and labor associated with D&D measures, a goal which is achievable through the development of novel, portable, analytical instrumentation capable of real-time, sensitive and selective monitoring of metal-contaminated surfaces.

A critical problem facing the DOE in its remediation task is its inability to monitor the performance of the various remediation tools currently in hand or under development. In order to effectively prescribe appropriate and cost-effective remediation strategies, it is imperative that clean-up personnel understand both the pre-remediation conditions at a contaminated site, in addition to the influence a particular remediation approach has on that contaminant behavior. Ultimately, the DOE must validate and monitor the efficacy of any new remediation technologies developed within their Environmental Management Science Program. A problem specifically highlighted by end users attending the INEEL Science Integration Workshop in Idaho Falls, Idaho (October 20-22, 1998), for example, was in the timely characterization of radioactive and toxic metal ion contamination evident at their field sites.[3] Samples submitted for testing were both costly and untimely, taking as long as 3 months before results were returned and remediation could commence.

Surfaces contaminated with radionuclides such as strontium and uranium, as well as toxic heavy metals, such as lead and mercury, pose a particularly difficult characterization problem for remote, real-time monitors. Because of the complex matrix of metal ions evident, the portable, sensor system utilized to characterize these substrates must possess a high degree of selectivity, in addition to sensitivity. While a hand held Geiger counter is a very sensitive monitor of a radionuclide's presence, the absence of any selectivity and its inability to monitor non-radioactive elements of environmental concern (e.g., Pb and Hg), make this monitor useful primarily as an internal means for clean-up personnel to verify the successful remediation of radioactive elements from a given field site. Other radiation monitors, such as gamma ray spectrometers, possess the necessary sensitivity and selectivity, but lack the portability, cost effectiveness and simplicity of operation to be implemented in the field. The intent of this final report is to demonstrate that the "laboratory-on-a-chip" technology has matured to the point that its application to DOE on-site remediation projects of surface contamination can be expected to result in future savings with respect to both time and money, while simultaneously minimizing the health risks of clean-up crews who depend upon immediate assessments of radionuclide and heavy metal concentrations in the field.

The miniaturization of chemical analysis instruments using micromachining techniques is receiving increased attention as the concept of performing liquid chromatography on a chip has become a reality (see Figure 1).[4] Because micromachined pumps are still not practical, the primary boon to this field has been the incorporation of capillary electrophoresis technology onto a microchip.[5] By the simple application of potentials to micro-channels etched within a glass substrate, the valveless control of fluid flow becomes possible (electroosmosis), enabling picoliter injections of sample with pre- or post-column derivatization and mixing.[6] Separations

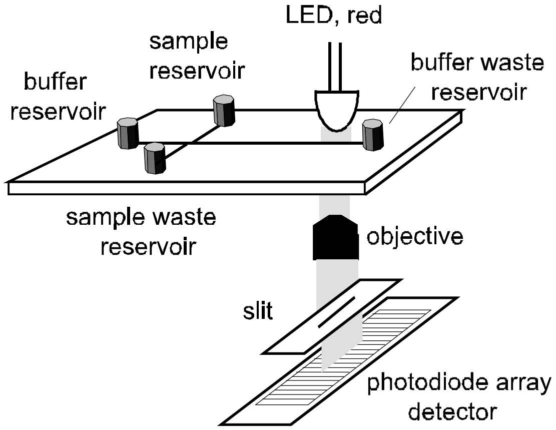


Figure 1: Diagram of a glass slide with lithographically etched lines for performing capillary electrophoresis. Also shown are the light source and photodetector for monitoring the separation.

are attained down the length of the column via 1) electrophoresis- the differential migration of ions within an applied field according to size and charge; and 2) electrochromatography-the differential retention of analytes with a stationary phase coated on the side of the column.[7]

There are many advantages to the laboratory-on-a-chip: rapid analysis times, small and portable in design, possibility for one-time use disposable columns, small sample sizes, and affordability. Commercial capillary electrophoresis (CE) instruments have already demonstrated excellent selectivity and sensitivity for monitoring complex metal ion mixtures, indicating that the potential exists for achieving comparable results on a microchip.[8] During the course of this project, we have demonstrated the viability of the capillary electrophoresis microchip for performing rapid, sensitive and selective quantitation of complex metal mixtures.[9,10,11,12] Our ultimate goal is to develop a truly portable, capillary electrophoresis microchip that will allow selective radionuclide and heavy metals analysis in the field following a metals extraction step from 1) a piece of steel, concrete, or other building structure, 2) collected soil or groundwater sample, or 3) an air sample. This sort of field portable, metals analysis instrument benefits from the generation of little to no waste. Injection sizes for the microchip are in the picoliter range, and flow rates are in the picoliter/s range, which means that decisions on the contaminated nature of a particular sample can be made quickly, in real time, and without the generation of large quantities of new waste.

As was mentioned previously, the "laboratory-on-a-chip" benefits from its simplicity in design (see Figure 1). The laboratory-on-a-chip consists of a pattern of lines or channels etched into a small, glass plate (typical width - 50 μm; depth - 20 μm), with a coverplate thermally bonded to the surface to define the liquid pathways. A set of liquid reservoirs are utilized to supply the mobile phase and sample to be injected, and there are two waste reservoirs for collecting any excess sample not injected and the mobile phase waste at the conclusion of the separation. A picoliter sample plug can be injected onto the column by simply flipping voltage switches in the following two-step procedure. First, a potential is applied such that liquid flows between the sample reservoir and sample waste reservoir, but does not flow between the buffer reservoir and buffer waste reservoir. In this way, a plug of analyte fills the void in the cross between the two lines. Second, the potentials are flipped so that flow is maintained between the buffer and buffer waste reservoirs, while preventing any flow between the sample and sample waste reservoirs. Electroosmotic or electrophoretic forces then enable the chromatographic separation of the injection plug to commence down the separation column. Using this simple approach, it becomes simply a matter of etching a slightly different pattern onto the glass slide and utilizing various potentials to the reservoirs in order to do pre- and/or post-column derivatization. These advances enable the metal complexation, separation, and post-separation reagent additions for metal ion analysis to potentially all be performed on chip. The separation is typically monitored via fluorescence or absorbance by positioning a microscope objective to collect and focus the emitted light onto a photodetector as the separated species travel down the capillary column.

The feasibility of performing capillary electrophoresis of metal ions on a quartz microchip was first demonstrated by Ramsey et al.[13] Their studies were based on the fluorescent, metal complexation ligand, 8-hydroxyquinoline-5-sulfonic acid (HQS), a fluorophore whose excitation wavelength is in the UV, and, therefore, is dependent upon the use of an argon ion laser (351.1-363.8 nm, 10 mW) for the excitation source. Their work demonstrated the superb sensitivity and separation capabilities inherent with the laboratory-on-a-chip. They reported excellent mass detection limits of 85, 61, and 134 amol, and concentration detection limits of 46, 57, and 30 ppb for Zn, Cd, and Al, respectively. Research generated from this effort became the second demonstration of the capabilities of the capillary electrophoresis microchip for performing complex metal ion separations.

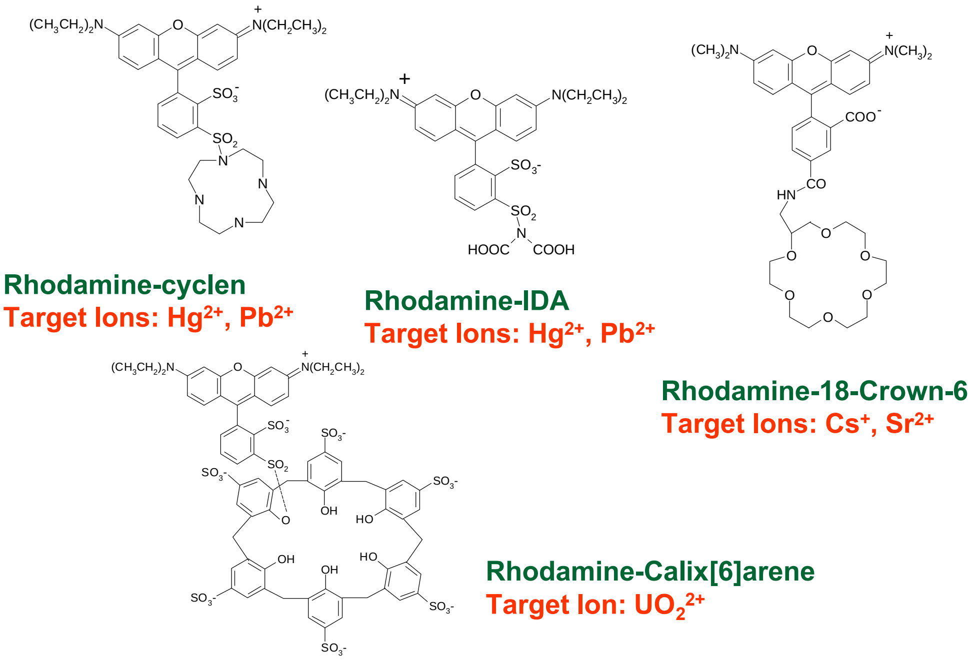
The research objectives for this program are summarized as follows: 1) to synthesize a new class of red fluorescing tagged macrocycles that will take advantage of the inherent metal complexation properties of the macrocycle, while fluorescing in a region of the spectrum with very little background fluorescence; the linear and macrocyclic chelating agents chosen for near infrared tagging include ethylenediaminetetraacetic acid, cyclen, *tetra*-aceticacid-cyclam, and calix[6]arene; these choices capitalize on the extensive knowledge base already established with respect to the performance of selective and efficient binding ligands for radionuclides and heavy metal ions contaminating DOE remediation sites; 2) to characterize the fluorescence and complexation behavior of this new class of complexation agents; and, 3) to implement these new materials into the design of a portable monitor for radionuclide and heavy metal analytes that utilizes the "laboratory-on-a-chip" technology for performing capillary electrophoresis on a microchip. Inexpensive, compact light sources will be utilized as excitation sources, and detection will be achieved using compact, inexpensive, photodiode array or miniature photomultiplier tube detectors.

5. Methods and Results

This final report summarizes our activity over the first three years of this project, from September 15, 1998 to September 15, 2001.

Initial efforts focussed on tailoring commercially available metal complexation agents (e.g., EDTA, cyclen, calix[6]arene) with visible and near infrared fluorophores in order to synthesize a new class of complexation agents. Four different metal complexation ligands were synthesized: cyclen, calix[6]arene, iminodiacetic acid (IDA) and 18-crown-6 were each covalently linked to the fluorophore, rhodamine B (see Figure 2). Each of these molecules were purified and fully characterized by electrospray mass spectrometry. Three different covalent linkage schemes have been investigated: succinimidyl ester, isothiocyanate, and sulfonyl chloride. Rhodamine sulfonyl chloride demonstrated the greatest success with respect to its reactivity and final product stability. Difficulties were encountered in obtaining the desired product for reactions involving EDTA, presumably due to the reactivity of the carboxylic acid functional groups. The application of protective groups may be a means of overcoming this obstacle.

The application of these new fluorophore tagged metal complexation agents to the microchip identified problems for several of these new fluorophores due to kinetic instability of the metal-ligand complex following application of the high potential, separation field. Despite intentionally utilizing ligands bearing high thermodynamic stability constants for the metal ions of interest, kinetic instability of the metal complexes during their electrophoretic separation down the microchannel caused dissociation of the complexes and poor separation efficiencies as



Rhodamine-cyclen
Target Ions: Hg^{2+}, Pb^{2+}

Rhodamine-IDA
Target Ions: Hg^{2+}, Pb^{2+}

Rhodamine-18-Crown-6
Target Ions: Cs^{+}, Sr^{2+}

Rhodamine-Calix[6]arene
Target Ion: UO_2^{2+}

Figure 2: Metal complexation ligands synthetically tagged with fluorophores in this program.

a result. Such was not the case for the newly synthesized ligand, rhodamine-calix[6]arene, however. This fluorescent metal chelate demonstrated excellent selectivity and sensitivity for the uranyl ion in the presence of a complex mixture of metal ions. Uncomplexed calixarenes reside in a barrel-shaped geometry which is well suited for uranyl ion metal complexation. Following complexation of the uranyl ion, the calixarene 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 (< 45 sec) of the free ligand from the uranyl-complexed ligand (Figure 3).[9] 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. Success observed in microchip separations of uranyl ions from a complex mixture of metal ions was highlighted as a short news item in *Chemical & Engineering News*,[14] as well as on an independent, science news website, www.sciencebase.com.[15]

Problems encountered with kinetic instability for many of the synthesized ligands, however, lead to the investigation of metallochromic absorbing dyes possessing high molar absorptivities and large bathochromic shifts in their maximal absorbing wavelengths following metal complexation. Providing this spectral shift is large enough, the dye may be added directly to the BGE of the separation buffer without perturbing the sensitivity of the detector for monitoring the absorbance of the metal-ligand complex. With dye present throughout the separation microchannel, the equilibrium is shifted to ensure metal complexation, preventing

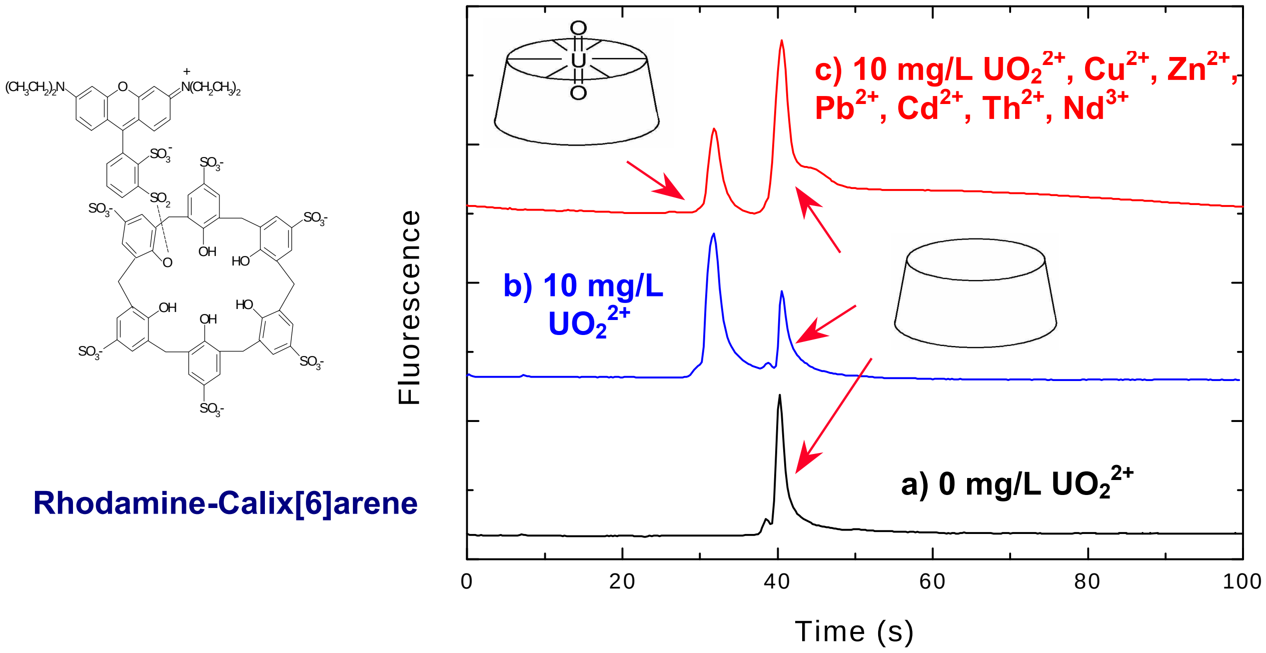


Figure 3: Microchip separations obtained using 10^{-4} M rhodamine-calix[6]arene in a buffer solution containing 10 mM sodium borate, 50 mM boric acid and 2 mM $MgCl_2$ (pH = 8.3), a) 0 mg/L UO_2^{2+}; b) 10 mg/L UO_2^{2+}; c) 10 mg/L UO_2^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Th^{2+}, and Nd^{3+}.

problems associated with kinetic instability. Two commercially available metallochromic dyes, PAR and Arsenazo III, have been successfully applied to the microchip for the rapid separation of complex mixtures of metal ions in less than a minute.[10] Each of these techniques will be discussed below.

Micellar electrokinetic chromatography (MEKC) has been utilized in the electrophoretic separation of seven transition metal ions, colorimetrically complexed by 4-(2-pyridylazo)resorcinol (PAR) on a glass capillary electrophoresis (CE) microchip.[11] The detection of seven, transition metal PAR metal chelates (Figure 4) was demonstrated on a microchip using a green light emitting diode (LED, 540 nm) and a miniature photomultiplier tube (15 V power requirement). The optimally determined background electrolyte contained 10 mM ammonium phosphate buffer (pH 7.5), 1 mM PAR to prevent kinetic lability problems, and 75 mM SDS for enhanced resolution. The separation of seven transition metal ions, Co^{2+}, V^{3+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+} and Cd^{2+} was achieved in under 65 seconds, with the resolution of each metal ion in excess of 1.60 (Figure 4). Detection limits obtained included 400 ppb for Ni^{2+} and 470 ppb for Co^{2+}.

Arsenazo III, a metallochromic ligand colorimetrically sensitive to the metal complexation of lanthanide and actinide metal ions, was applied to a capillary electrophoresis microchip for the detection of uranium (VI) and various lanthanide metal ions (Figure 5).[12] In

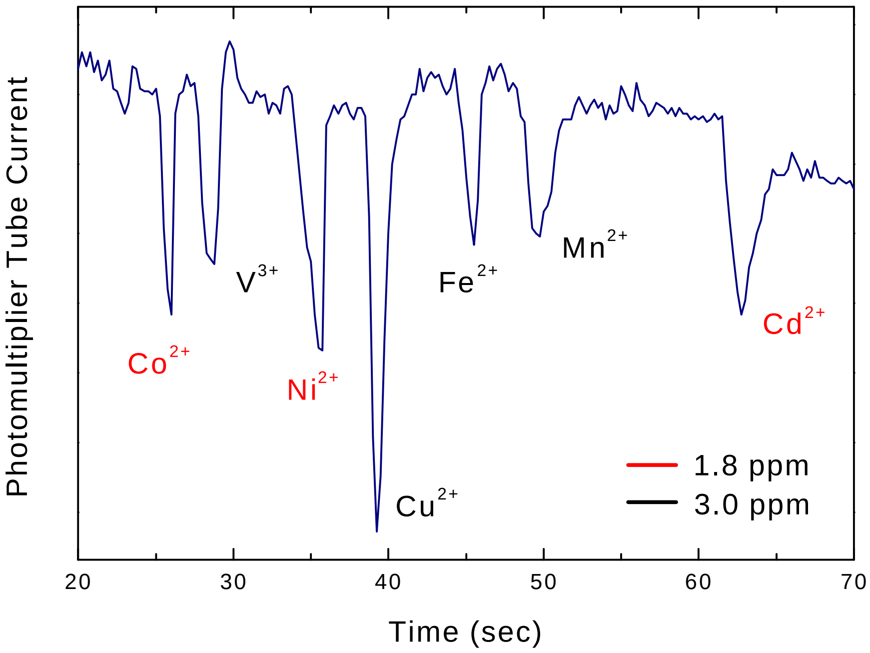


Figure 4: Microchip separation of seven different transition metal ions by MEKC.

order to enhance colorimetric sensitivity, the glass microchip contained 100 ìm deep by 200 ìm wide microchannels (instead of the commonly employed 20 ìm deep by 50 ìm wide microchannels) etched in a simple cross pattern with an 80 mm separation channel length and an 8 mm injection channel length. Detection of the Arsenazo III metal complexes is achieved using a red light emitting diode (LED) light source and a photodiode array detector. Carbowax 20M was incorporated into the background electrolyte in order to eliminate the electroosmotic flow and prevent dye adsorption on the microchannel walls. Separation of uranium from four lanthanide metal ions was demonstrated in under two minutes. The addition of DTPA to the background electrolyte eliminated any interference from lanthanide, transition and alkaline earth metal ions. Direct load injection of a pre-complexed metal ion mixture onto the microchannel gave a detection limit of 23 ppb uranium (VI) in the presence of seven lanthanide impurities (1.5 ppm each) in under 55 seconds. This detection limit is near the EPA’s established drinking water standard for uranium at 20 ppb, indicating the excellent sensitivity achievable on these microchip devices when utilizing a highly stable (low noise) LED and a large molar absorptivity dye.

In the search for new metallochromic dyes applicable to the microchip for the detection of uranium and other toxic metal ions, we typically begin our assessment with studies of these dye systems on a commercial, capillary electrophoresis unit. A capillary electrophoresis (CE) method utilizing 4-(2-thiazolylazo)-resorcinol (TAR) was developed for the separation of uranium, cobalt, cadmium, nickel, titanium and copper metal ions (Figure 6).[16] TAR was chosen as the visible absorbing chelating ligand because of its ability to form stable complexes with a wide variety of metals. Optimum separation of the six metal chelates was achieved in a 15 mM $Na_2B_4O_7$-NaH_2PO_4, pH 8.3 buffer containing 0.1mM TAR. Method validation included

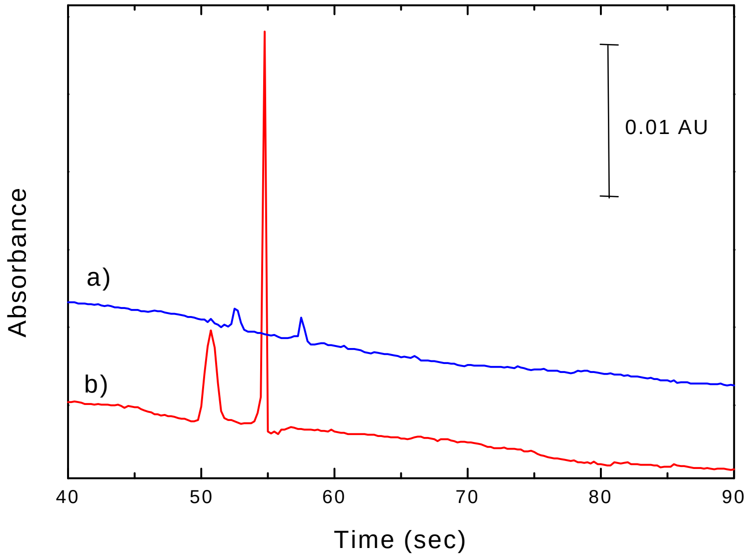


Figure 5: Microchip separation of the 1:1 and 1:2 metal to ligand UO_2^{2+}-Arsenazo III complexes (4.6 ppm), in the presence of 1.5 ppm Nd^{3+}, Eu^{3+}, Er^{3+}, Gd^{3+}, La^{3+}, Pr^{3+}, and Ce^{3+} with 1 mM DTPA added to the BGE and an electrostatic injection consisting of a) a 50 second floating load, and b) a five second direct load. BGE consisted of 15 mM citric acid, adjusted with Tris to pH 5, 0.1 mM Arsenazo III, 0.5% CW20M, 20% ethanol; separation voltage –8500 V/85 cm.

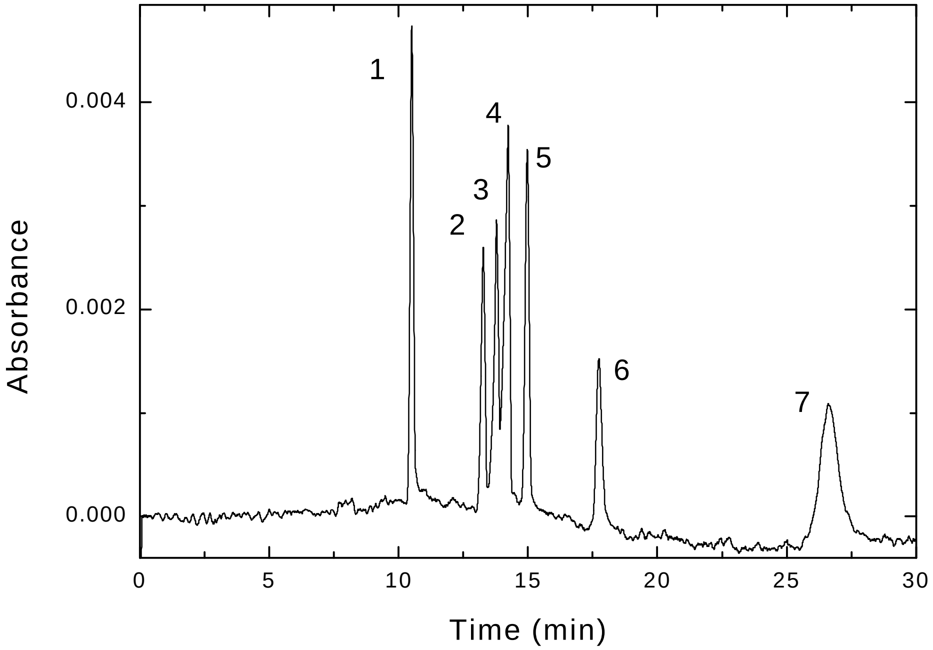


Figure 6: Separation of TAR complexes in 15 mM NaH_2PO_4-$Na_2B_4O_7$, pH 8.3, $1x10^{-4}$M TAR (optimum conditions). 1- cobalt (5 ppm), 2 - free TAR, 3 – copper (5 ppm), 4 – cadmium (5 ppm), 5 – nickel (2.5 ppm), 6 - titanium (15 ppm) and 7 – uranium (30 ppm).

injection and method precision studies, as well as detection limit and linear dynamic range determination. High ppb to low ppm (w/w ratio) detection limits were achieved with linear dynamic ranges between 0.1 ppm and 75 ppm.

Our experimentation with the metallochromic dye, Arsenazo III, also lead to the development of a remote fiber optic diffusion probe (2" dia. x 10 " length) designed for selectively detecting uranium in groundwater (Figure 7).[17] This probe is based on the colorimetric complexation of uranium by Arsenazo III, and takes advantage of a cationic diffusion membrane (Nafion) through which uranyl ions can diffuse, while confining the anionic dye, Arsenazo III. A miniature peristaltic pump transports the reagent from the diffusion membrane to an LED, fiber optic flow cell where the absorbance is monitored to indicate the presence or absence of uranium. The sensitivity for uranium, following a twenty minute soak time, is well below the EPA standard of 20 ppb for uranium in drinking water. The selectivity for uranium has been optimized through a combination of pH and the addition of masking agents to the sample reagent. A host of different metal ion impurities have been surveyed for false alarms, and the most difficult metal ion to mask out is calcium, due primarily to the large concentration of calcium found in many water sources. We have determined that 30 ppm or less calcium does not generate a false alarm, however. Wellwater samples collected from Maryland gave zero false alarms, while water samples higher in salinity, e.g. seawater, continue to cause some problems. Further research is required to generate a system which minimizes the amount of stock reagent solution necessary to continuously monitor uranyl in groundwater for extended periods of time, e.g., months to years.

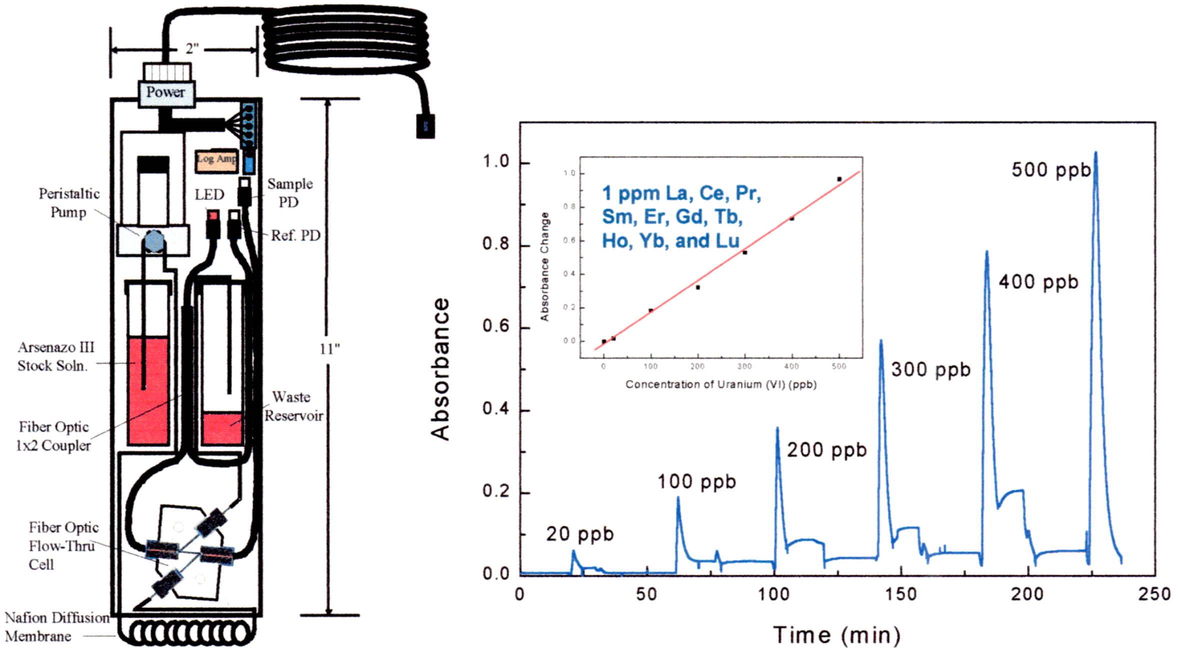


Figure 7: Diagram of the remote fiber optic diffusion probe for monitoring uranium in ground water, and a sample response to sequentially increasing concentrations of uranium (VI) in wellwater.

6. Relevance, Impact and Technology Transfer

By demonstrating the rapid and sensitive separation of uranium and various other metal ions on a capillary electrophoresis glass microchip, this project has made significant advancements towards the realization of a portable sensor for toxic metal ions contaminating DOE remediation sites across the country. Development of this type of sensor would enable metal analysis of D&D building materials in the field, permitting real-time sorting of contaminated vs. noncontaminated materials, evaluation of the efficacy of remediation tools, and decreased characterization times which will reduce costs and health risks to users. As will be discussed in the future work section, there are two areas of research which remain in order to successfully apply this system to DOE Environmental Management problems: 1) broadening the response of the microchip to be inclusive of numerous toxic metal ions of interest, and 2) examining the basic research issues surrounding the actual extraction of these metals from both the air and structural building surfaces (e.g. steel and concrete) and how these samples can effectively be applied to the microchip platform.

7. Project Productivity

This research project was very productive, both in meeting the primary research objectives originally defined, and in stimulating written and oral papers. Results stemming from this project were highlighted as an EMSP "Success Story" in a poster prepared by EMSP for presentation at the 2000 EMSP National Workshop held in Atlanta, Georgia.[18] This, combined with the national exposure afforded by the C&E New short news item,[14] are indications of the validity of the methods we're pursuing. Six publications in peer reviewed journals, four presentations at professional national meetings, and eight presentations at various workshops have stimulated much interest in the project.

8. Personnel Supported

Dr. Greg E. Collins-PI, Naval Research Laboratory

Dr. Qin Lu- Research Chemist, GeoCenters, Inc.

Dr. Lawrence Evans III- NRC Postdoc, Naval Research Laboratory

Ms. Sitra Abubeker- Undergraduate student, Clark Atlanta University

Ms Elizabeth Vajs- High School Senior, Thomas Jefferson HS Mentorship Program

9. Publications

1. "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**, in press.

2. "Microfabricated Capillary Electrophoresis Sensor for Uranium (VI)," G.E. Collins and Q. Lu, **Analytica Chimica Acta**, <u>436</u> 181 (2001).

3. "Microchip Separations of Transition Metal Ions via LED Absorbance Detection of their PAR Complexes," Q. Lu and G.E. Collins, **Analyst**, 126 429 (2001).

4. "Separation of Uranium(VI) and Transition Metal Ions with 4-(2-Thiazolylazo)-resorcinol by Capillary Electrophoresis," L. Evans III and G.E. Collins**, J. Chromatography A**, 911 127 (2001).

5. "Radionuclide and Metal Ion Detection on a Capillary Electrophoresis Microchip Using LED Absorbance Detection," G.E. Collins and Q. Lu, **Sensors and Actuators B**, 76 244 (2001).

6. "Microchip Used for Uranium Detection," **Chemical & Engineering News**, October 16, 2000, p. 23.

7. "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, **Chemical Communications**, 19 1913 (2000).

10. Interactions

This research project resulted in participation at the following meetings, workshops, conferences, seminars, etc:

1. "Fiber Optic Based Chemical Sensor for the Selective Detection of Uranium (VI)," G.E. Collins, **PACIFICHEM 2000**, Honolulu, Hawaii, 14-19 December 2000.

2. "Selective Detection of Uranium (VI) using a Capillary Electrophoresis Microchip," G.E. Collins and Q. Lu, **American Chemical Society 220th National Meeting**, Washington D.C., 20-24 August 2000.

3. "Sensitive and Selective Metal Ion Analysis Utilizing the 'Laboratory-on-a-Chip,'" G.E. Collins and Q. Lu, **8th International Meeting on Chemical Sensors**, Basel, Switzerland, 3-5 July 2000.

4. "Metal Ion Analysis Using Fluorophore-tagged Metal Complexation Ligands and the 'Laboratory-on-a-Chip,'" G.E. Collins, Q. Lu, **Fall 1999 National American Chemical Society Meeting**, New Orleans, LA, 22-26 August 1999.

5. "Capillary Electrophoresis Microchips for the Detection of Toxic Metal Ions and Explosives," G.E. Collins, **Branch Lunch Discussion**, NRL, April 24, 2001.

6. INVITED "Novel Microchip Sensors for Selective Metal Ion Detection," G.E. Collins, **NRL Sigma Xi Young Investigator Award Presentation**, NRL, August 8, 2000.

7. "Remote Detection of Uranium using a Diffusion Membrane Probe," S. Abubeker, Q. Lu and G.E. Collins, mentor- G.E. Collins, **National Science Foundation Summer Research Program Final Oral Report**, August 2000.

8. “Sensitive and Selective Heavy Metal and Radionuclide Analysis Using the Laboratory-on-a-Chip,” Q. Lu and G.E. Collins, **EMSP Sensors Initiative Workshop**, Idaho National Engineering and Environmental Laboratory, June 2000.

9. “Sensitive and Selective Heavy Metal and Radionuclide Analysis Using the Laboratory-on-a-Chip,” G.E. Collins, L. Evans and Q. Lu**, Environmental Management Science Program National Workshop**, Atlanta, Georgia, April 25-27, 2000.

10. “Molecular Switching Devices and Laboratory-on-a-Chip Studies of Molecular Dynamics and Recognition,” G.E. Collins, **NRL Branch Review**, September 28, 1999.

11. “The Development of ‘Laboratory-on-a-Chip’ for On-Site Heavy Metal and Radionuclide Analysis,” G.E. Collins, **Second Savannah River Site Workshop on Integration of End User’s Needs with Research Projects for Environmental Management Science Program (EMSP)**, November 17-18, 1998.

12. “Heavy Metal and Radionuclide Analysis using Near-Infrared Dyes and the Laboratory-on-a-Chip,” G.E. Collins, **INEEL Science Integration Workshop**, Idaho Falls, Idaho, October 20-22, 1998.

Towards the end of the project, Tim P. O’Rourke (INEEL) notified me that DOE Nevada was looking for a sensor for field testing which could monitor uranium levels in groundwater 2000 feet below the surface down 2” bore holes. Due to previous success we had observed with our remote fiber optic uranium probe, discussions were commenced concerning the possibility of field testing this sensor. As a first test, the decision was made to have DOE Nevada send a sample of their groundwater known to be free of any contamination from uranium, in order to ensure that any other background metal ions contained within the groundwater would not influence the measurement of uranium by the sensor probe. Unfortunately, the sample sent to us was not free of uranium, but contained 100 ppb uranium. We, therefore, reported a huge signal from the sensor, but it was unclear how much of the signal arose from our primary interferent, calcium, and how much from uranium. The chemistry utilized within the probe is intended to operate with zero false positives in groundwater containing calcium levels below 30 mg/l. According to documentation received from DOE Nevada, their groundwater samples contain up to 80 mg/l of calcium, a situation leading to false positives. As a result we are currently attempting to change the chemistry utilized within the sensor probe in order to deal with background levels of calcium as high as 90 mg/l.

11. Transitions: none

12. Patents: none

13. Future Work

The research accomplished to date has confirmed our original assertion, that the capillary electrophoresis microchip has the potential to enable field portable, metal ion sensing of hazardous waste metal ions, potentially meeting many of D&D’s instrumentation needs with respect to real time monitoring of toxic metal analytes in the field. Future work is necessary to extend the capabilities of the microchip beyond the presently demonstrated capabilities for monitoring low ppb levels of uranium (VI) to hazardous waste metal ions which include Be^{2+}, Hg^{2+}, Pb^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, Cs^{+}, and Sr^{2+}. In addition, it is critical that we examine the basic research issues surrounding the actual extraction of these metals from both the air and structural building surfaces (e.g. steel and concrete), in order to address the specific needs required by D&D operations in the field. Future research plans include: 1) development of new methods for universally detecting a wide array of metal ions simultaneously in a single run using **indirect detection** techniques; 2) examination of more selective **direct detection** techniques utilizing metallochromic dyes; 3) exploration of new **parallel, microchip designs** capable of simultaneously separating a complex mixture of metal ions in a parallel fashion; 4) implementation of new methods for achieving successful **extraction** and introduction of toxic metal analytes to the microchip.

14. Literature Cited

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15. Feedback: none

16. Appendices: none