

**FINAL REPORT**  
U.S. Department of Energy

**“FIELD PORTABLE MICROCHIP ANALYZER FOR AIRBORNE AND  
SURFACE TOXIC METAL CONTAMINATION”**

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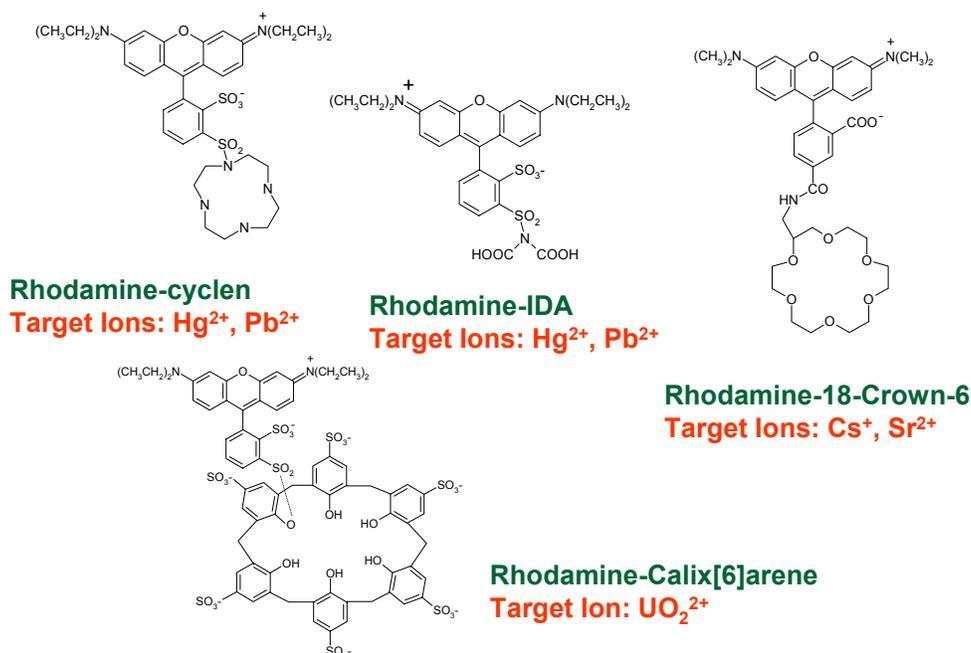
**PROJECT TITLE:** Field Portable Microchip Analyzer for Airborne and Surface Toxic Metal Contamination

**RESEARCH OBJECTIVE:** The primary research objective of this effort was 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 included  $\text{UO}_2^{2+}$ ,  $\text{Be}^{2+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cs}^+$ , and  $\text{Sr}^{2+}$ . Inexpensive, compact light sources were utilized as excitation sources, and detection was achieved using compact, inexpensive, photodiode array detectors. Particular emphasis was placed on developing viable, new extraction methods for metal ion sampling from both the air via a microimpinger which was 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 were exploited in this research, indirect and direct detection. Special emphasis was placed on maintaining the ultimate portability of the final microchip device through the careful selection of metallochromic dyes and fluorophores which were amenable with small, inexpensive light sources (e.g., LED's) and photodetectors.

**RESEARCH PROGRESS AND IMPLICATIONS:** This report summarizes work from 9/17/1998 through 9/16/2004, covering all six years of a six year project beginning 9/15/1998.

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 1). 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.

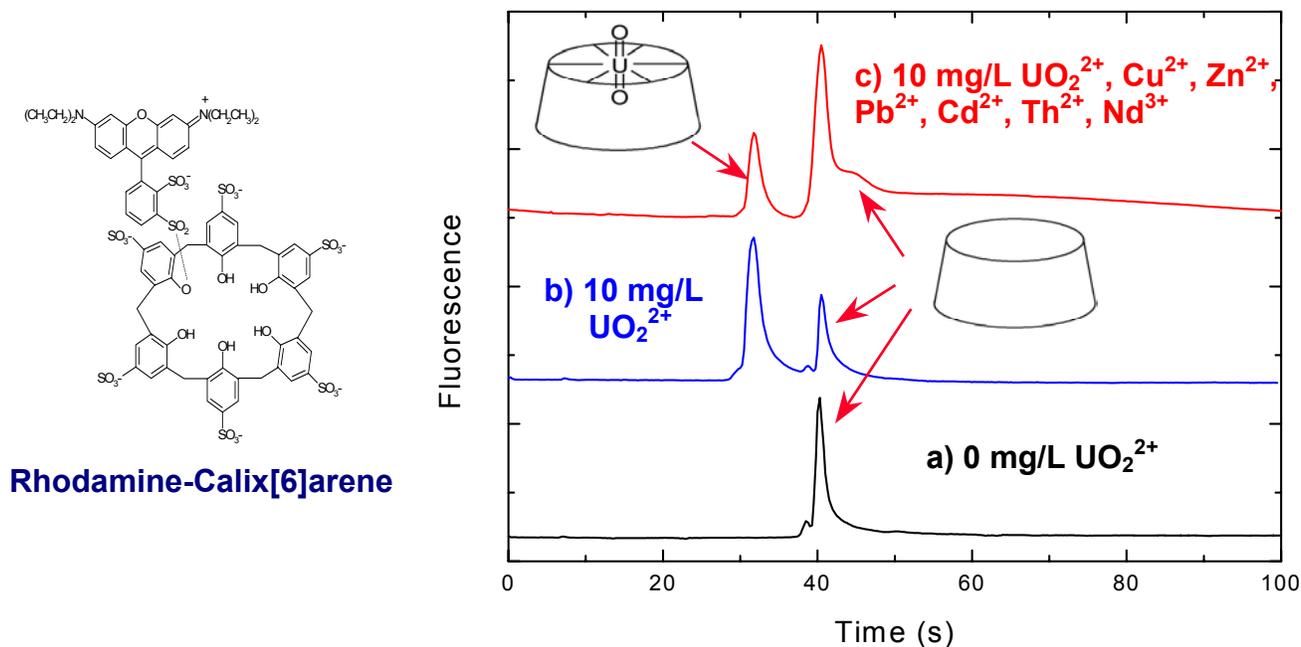
The application of these new fluorophore tagged metal complexation agents to the microchip identified problems for several of these new fluorophores due to kinetic instability of the metal-ligand complex following application of the high potential, separation field. Despite intentionally utilizing ligands 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 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 metal ion complexation. Following complexation of the uranyl ion, the calixarene likely adopts a pseudoplanar penta- or



**Figure 1:** Metal complexation ligands successfully tagged with fluorophores.

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 2). Furthermore, the addition of various transition, alkali and rare earth metal ions did 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*, as well as on an independent, science news website, [www.sciencebase.com](http://www.sciencebase.com).

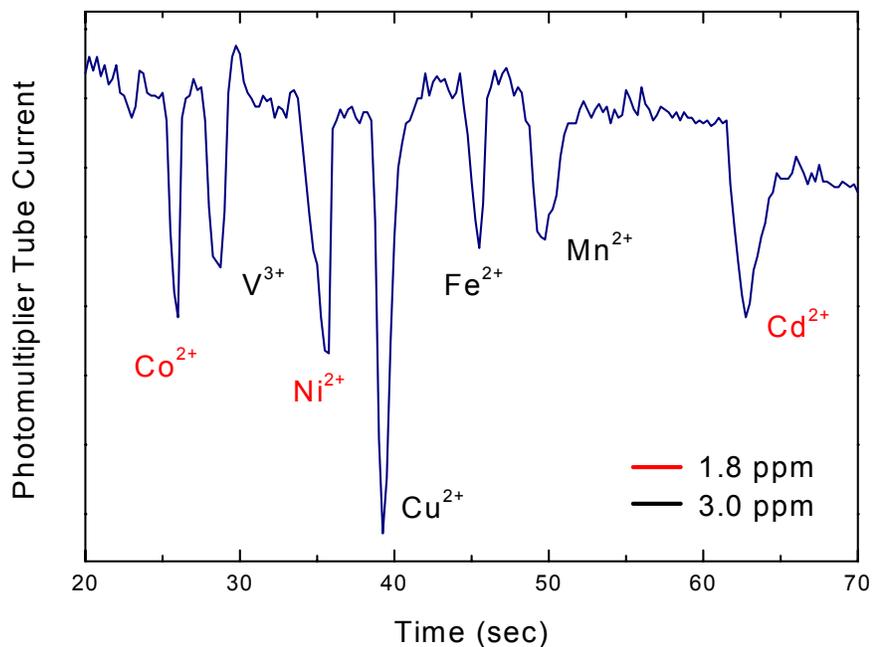
Problems encountered with kinetic instability for many of the synthesized ligands, however, led to the investigation of metallochromic absorbing dyes possessing high molar absorptivities and large bathochromic shifts in their maximal absorbing wavelengths following metal complexation. Providing the spectral shift was large enough, the dye could 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, ensuring metal complexation and preventing problems associated with kinetic instability. Two commercially available metallochromic dyes, PAR and Arsenazo III, were successfully applied to the microchip for the rapid separation of complex mixtures of metal ions in less than a minute. Each of these approaches will be discussed, next.



**Figure 2:** 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  $\text{MgCl}_2$  (pH = 8.3), a) 0 mg/L  $\text{UO}_2^{2+}$ ; b) 10 mg/L  $\text{UO}_2^{2+}$ ; c) 10 mg/L  $\text{UO}_2^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Th}^{2+}$ , and  $\text{Nd}^{3+}$ .

Micellar electrokinetic chromatography (MEKC) was 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. The detection of seven, transition metal PAR metal chelates (Figure 3) 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,  $\text{Co}^{2+}$ ,  $\text{V}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Cd}^{2+}$  was achieved in under 65 seconds, with the resolution of each metal ion in excess of 1.60 (Figure 3). Detection limits obtained included 400 ppb for  $\text{Ni}^{2+}$  and 470 ppb for  $\text{Co}^{2+}$ .

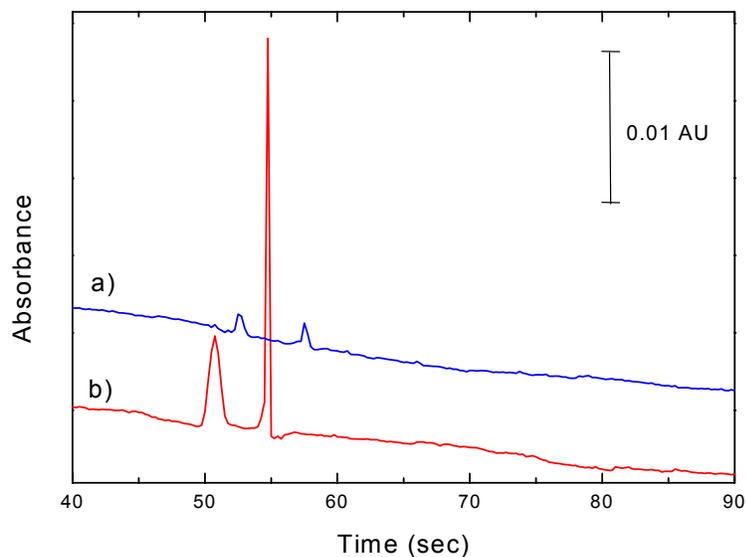
Arsenazo III, a metallochromic ligand colorimetrically sensitive to the metal complexation of lanthanide and actinide metal ions, was applied to a capillary electrophoresis microchip for the detection of uranium (VI) and various lanthanide metal ions (Figure 4). In order to enhance colorimetric sensitivity, the glass microchip contained 100  $\mu\text{m}$  deep by 200  $\mu\text{m}$  wide microchannels (instead of the commonly employed 20  $\mu\text{m}$  deep by 50  $\mu\text{m}$  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 was 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



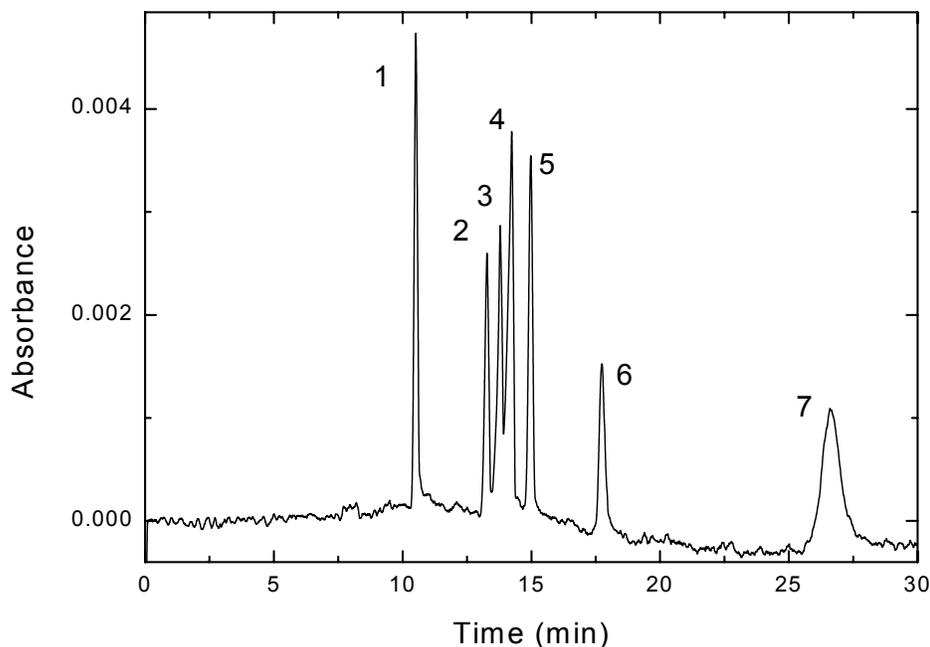
**Figure 3:** Microchip separation of seven different transition metal ions by MEKC.

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 5). 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  $\text{Na}_2\text{B}_4\text{O}_7\text{-NaH}_2\text{PO}_4$ , pH 8.3 buffer containing 0.1mM TAR. Method validation included 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.

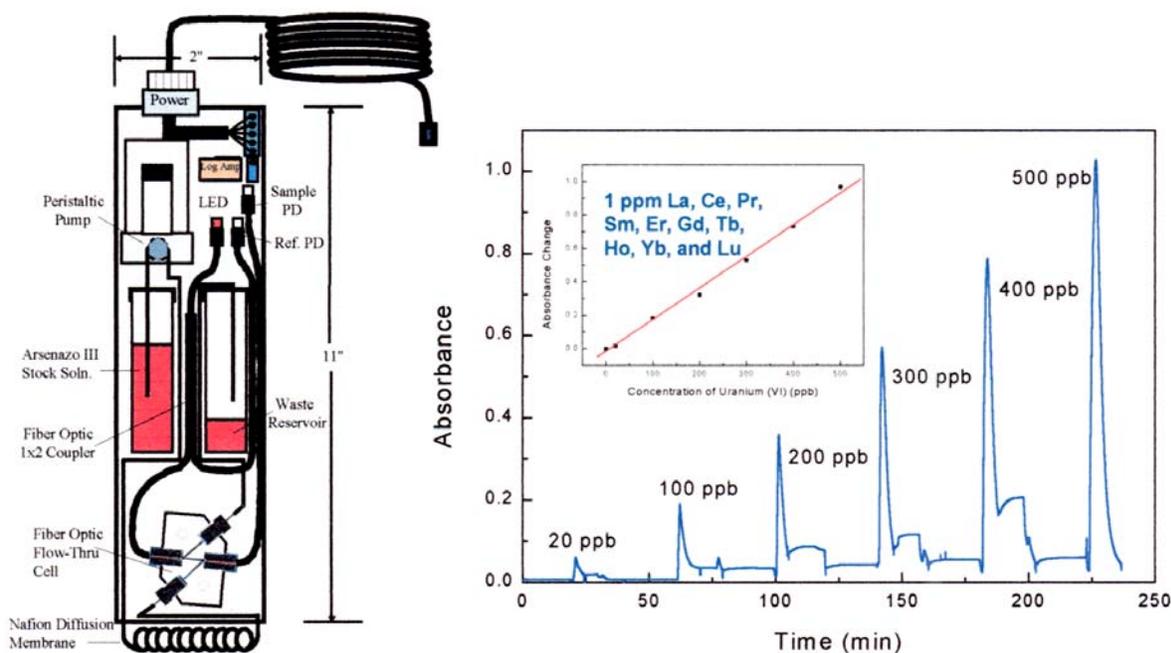


**Figure 4:** Microchip separation of the 1:1 and 1:2 metal to ligand  $\text{UO}_2^{2+}$ -Arsenazo III complexes (4.6 ppm), in the presence of 1.5 ppm  $\text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Pr}^{3+}$ , and  $\text{Ce}^{3+}$  with 1 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 5:** Separation of TAR complexes in 15 mM  $\text{NaH}_2\text{PO}_4$ - $\text{Na}_2\text{B}_4\text{O}_7$ , pH 8.3,  $1 \times 10^{-4}$  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).

Our experimentation with the metallochromic dye, Arsenazo III, also led to the development of a remote fiber optic diffusion probe (2" dia. x 10" length) designed for selectively detecting uranium in groundwater (Figure 6). 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.



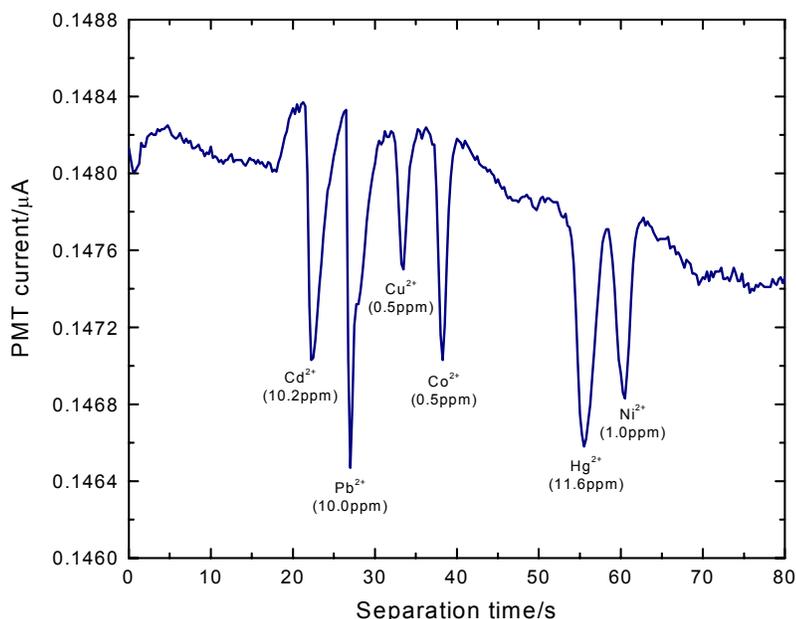
**Figure 6:** Diagram of the remote fiber optic diffusion probe for monitoring uranium in groundwater, and a sample response to sequentially increasing concentrations of uranium (VI) in wellwater.

In order to expand the capabilities of the microchip sensing platform 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 this dye system has been applied to a fiber optic flow injection device for application as a field portable, beryllium monitor, as will be discussed later in relation to the solid phase extraction effort for sampling.

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 (see Figure 7). 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 achievable sensitivities, which will 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 investigated the application of solid phase extraction techniques for generating concentrated liquid samples that could be subsequently analyzed by our microchip technique. As a first step, we 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 was buffered to pH 4.9 and the metal complexing agent, 5-Br-PAPS, added. The liquid extractant was passed through a miniature, packed solid phase extraction column wherein the metal chelates were strongly adsorbed. The metal chelates were eluted in methanol, with concentration enhancements as high as 1000 times. This research 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 being realized by the solid phase extraction. We 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/cm<sup>2</sup>.

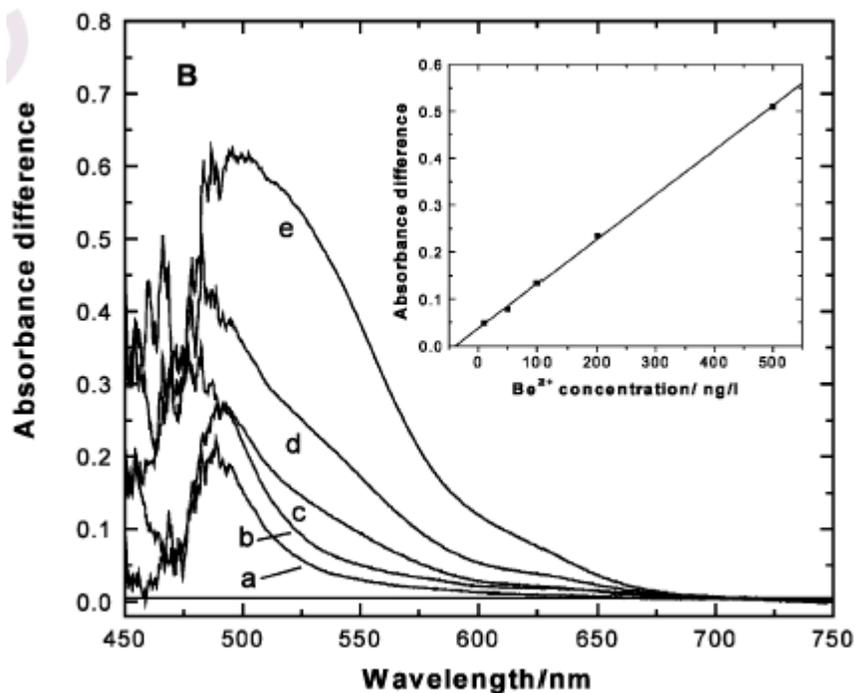
A critical element to the success of any analytical sensor technique applied to the EMSP D&D effort, will be specifically in this area of developing new methods for sampling metal



**Figure 7:** Microchip separation of six metal ions using 5-Br-PAPS.

contaminated surfaces. We investigated 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 applied was 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 found we could 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 found it was beneficial to add a secondary metal complexation agent, such as DTPA or EDTA, in order to preferentially complex and prevent interferences from troublesome ions that are ever present in the environment. Following extraction of the ions, the reagents were passed through a microcolumn solid phase extraction (SPE) apparatus, which enabled the organically chelated metal ions to be quantitatively adsorbed and subsequently eluted in a suitable organic solvent. By implementing microcolumn SPE, the adsorbed metal ion chelates could be eluted in very small eluent volumes (< 5 microliters), a feature resulting in major concentration enhancements that were 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 also pursued methods for performing nonaqueous based capillary electrophoresis on a microchip, an approach which enabled direct coupling of the CE microchip separation of metal ions to the SPE process.

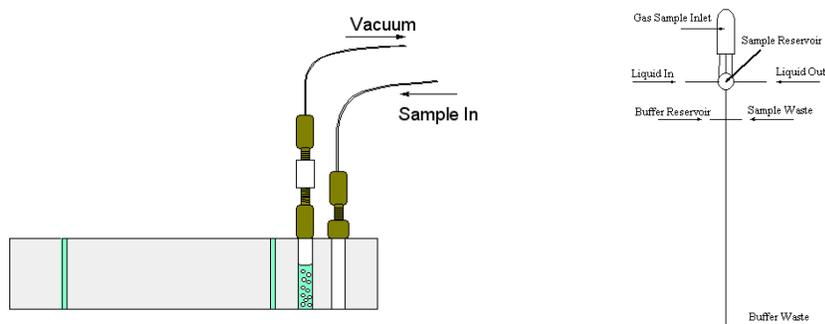
In conjunction with developing new methods for extracting beryllium off of surfaces, concentrated Chromazurol S beryllium metal chelates were examined and very sensitively monitored using a hand held fiber optic spectrophotometer. By using a long pathlength liquid



**Figure 8:** Absorption spectra and calibration curve obtained for Be<sup>+</sup> detection using fiber optic spectrometer with a 50 cm fiber optic liquid waveguide capillary cell: a) 10, b) 50, c) 100, d) 200, e) 500 ng/L beryllium.

waveguide capillary cell (50 cm), beryllium levels were detected down to 30 ng/l in solution or 0.5 ng/cm<sup>2</sup> from a contaminated Plexiglas surface (see Figure 8). 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 were another area of active research. Considering the types of clean-up operations taking place at the superfund sites, there continues to be a true need to implement improved air sampling techniques and on-line detection of these contaminants to improve safety during these operations. We investigated methods for dramatically miniaturizing liquid impinger air sampling down to the microliter volume scale. In this way, we project that it should be possible to directly couple these devices to a capillary electrophoresis microchip in much the same way as a micro-SPE system, dramatically minimizing the generation of waste from a traditional impinger system, for example. We successfully microfabricated microimpinger based devices in both PDMS and glass substrates, according to the design shown in Figure 9. The advantage of glass as a substrate material is the improved separation resolution over capillary electrophoresis based separations performed in PDMS. The microimpinger consisted of a system of microchannels leading from the gas sample inlet into a 20-50 microliter reservoir that contained the trapping reagent for the analyte of interest. We found that the optimal number of inlet microchannels was



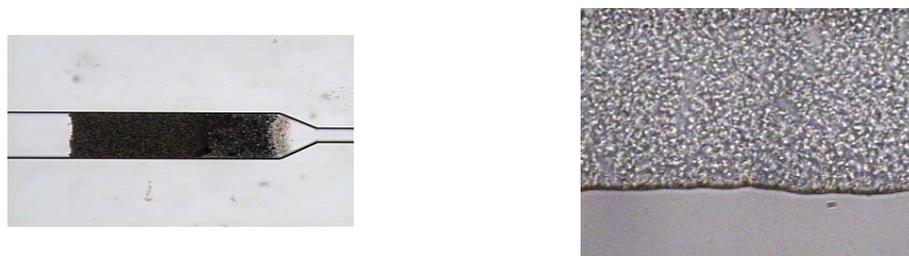
**Figure 9:** Microimpinger design for air sampling (left- side view; right- top view).

between three and five. Fewer than three microchannels resulted in lower impinger efficiency, and above five microchannels, the bubbles tended 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 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 microchip separations for uranium in the presence of numerous lanthanide impurities. The optimized extraction procedure consisted of rinsing the surface with pH 2 buffered malonic acid in order to extract all available uranium. Arsenazo III and EDTA were then added to the extract to selectively complex the uranyl ion, and this organic complex was passed through a  $C_{18}$  microcolumn to concentrate the organic metal complex. Elution was 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/cm<sup>2</sup>.

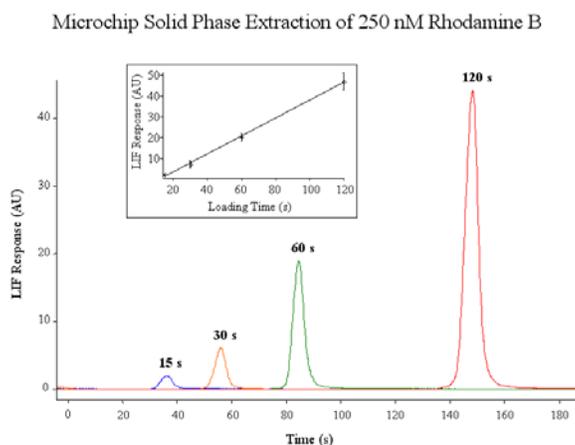
In order to make a complete laboratory-on-a-chip platform for performing the spectrophotometric dye concentration and subsequent elution in tandem with the capillary electrophoretic separation of metal ions, we examined the incorporation of solid phase extraction columns directly onto the microchip itself. This was accomplished by investigating a number of different approaches. The first approach examined and the one we've seen the greatest level of success, 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 10). Concentration enhancements as high as 300 times have been observed on the microchip, with detection limits for the test case dye, Rhodamine B, being in the femtomolar 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 10). 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<sub>3</sub>-C<sub>18</sub>. As seen in the right side of Figure 10, 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<sub>18</sub> 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 magnetic strength was insufficient for accurately supporting the beads in place under the types of back pressures being generated.



**Figure 10:** Solid phase extraction on a microchip (left side- C<sub>18</sub> silica beads; right side- sol gel).

Shown in Figure 11 is an example of an on-chip micro solid phase extraction experiment for the extraction of Rhodamine B, a fluorescent dye, from water. These results were obtained from the C<sub>18</sub> coated silica beads, although similar results have been observed for the sol-gel packed microchannels. As the extraction time increases, we observe a linear increase in the fluorescence intensity of the eluted peak. Note also the significant peak intensities achieved for nM levels of dye, a result arising from the superb extraction efficiencies evident with these micro packed beds.



**Figure 11:** Linear increase in LIF response observed for Rhodamine B extraction with increasing extraction time.

**INFORMATION ACCESS:**

- “Extraction, Preconcentration and Colorimetric Detection of Uranium on Building Materials,” P.A. Greene, C.L. Copper, D. Berv, J.D. Ramsey and G.E. Collins. **Talanta**, submitted September 2004.
- “Compact, High Voltage Power Supply for the Lab on a Chip,” G.E. Collins, P. Wu, Q. Lu, J.D. Ramsey, R.H. Bromund, **Lab on a Chip**, 4, 408 (2004).
- “Sensitive Detection of Beryllium Using a Fiber Optic Waveguide Cell,” G. Deng, G.E. Collins and L. Wei, **Talanta**, 60, 9 (2003).
- “Analysis of Inorganic and Organic Ions Using Capillary Electrophoresis Microchips,” H.D. Willauer and G.E. Collins, **Electrophoresis**, 24, 2193 (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.