

Project 90138

This report summarizes the NMSU activity over the first year of the project (i.e., the 11/03-8/04 period). This research effort aims at developing a portable analytical system for fast, sensitive, and inexpensive, on-site monitoring of toxic transition metals and radionuclides in contaminated DOE Sites. In accordance to our original objectives our studies have focused on various fundamental and practical aspects of microchip devices for monitoring metal contaminants. As described in this section, we have made a substantial progress, and introduced effective routes for improving the reliability of devices for field screening of toxic metals. This 11-mos activity has already resulted in 2 research papers (published or in press in major journals), and several invited presentations in major meetings. (Several more publications are expected in the late part of 2004.) The electrochemical sensors being investigated rely on the highly sensitive adsorptive stripping voltammetry (AdSV) technique to detect metal ions of interest to the DOE, particularly uranium and chromium. Traditionally, AdSV measurements of U and Cr require the use of mercury electrodes which are not suitable for field deployment. Our initial goal was thus to replace these toxic mercury electrodes with "environmentally-friendly" sensor materials. We have focused on bismuth-film electrodes, that were shown earlier by our laboratory to be extremely useful alternatives to common mercury electrodes for stripping voltammetric measurements of heavy metals. Bismuth is an environmentally-friendly element, with very low toxicity, and a widespread pharmaceutical use. Our NMSU team demonstrated recently the utility of bismuth electrodes for stripping detection of electrolytically deposited lead and cadmium. In the present effort we developed a sensitive adsorptive stripping voltammetric protocol at a bismuth coated glassy-carbon electrode for trace measurements of chromium (VI) in the presence of diethylenetriamine pentaacetic acid (DTPA). The new protocol is based on accumulation of the Cr-DTPA complex at a preplated bismuth film electrode held at negative 0.80V, followed a negatively-going square-wave voltammetric waveform. Factors influencing the stripping Cr response, including the film preparation, solution pH, DTPA and nitrate concentrations, deposition potential and deposition time, were systematically evaluated and optimized. The resulting performance compared well with that observed for analogous measurements at mercury film electrodes. Well defined Cr(VI) peaks were obtained for nanomolar levels of Cr in connection to short preconcentration times. A detection limit of 0.3 nM Cr(VI) was obtained using a 2 min accumulation. The sensitivity is coupled to good reproducibility and selectivity. A relative standard deviation of 5.1% was observed for 25 repetitive measurements of 20 nM Cr. Applicability to selective measurements in real (river water) environmental samples was demonstrated. The following metals were tested at the 25 nM level and found not to affect the response for 5 nM chromium(VI): Pb(II), Cd(II), Zn(II), Cu(II), Fe(III), Ni(II), and Co(II). A large (20-fold) excess of hydrated Cr(III) did not affect the response of 5 nM Cr(VI). This is consistent with previous studies which have shown the effective discrimination against hydrated Cr(III) species. In addition to the use of glassy-carbon substrates, we demonstrated the utility of disposable thick-film (screen-printed) electrodes for supporting the bismuth film. These bismuth-coated strip electrodes offered a similar chromium detection as that observed at the coated glassy-carbon electrodes. The attractive behavior of the new "mercury-free" chromium sensor holds great promise for on-site environmental and industrial monitoring of chromium (VI). We are currently examining the utility of bismuth film electrodes for sensitive adsorptive measurements of trace uranium. Efficient microchip assays of real-world environmental samples will require the incorporation of a continuous sampling capability (from the external environment) or rapid sampling of multiple discrete samples. We developed a rapid and reproducible sample introduction route into CE microchip devices based on a sharp sample-inlet tip placed alternately in the sample and buffer vials (2). Alternate placement of the inlet tip in vials containing the sample and buffer solutions permits a volume-defined electrokinetic sample introduction. Such fast and simple sample introduction leads to highly reproducible signals with no observable carry over between different analyte concentrations. Factors influencing the analytical performance of the new microchip interface were characterized and optimized. The attractive performance of the system was demonstrated in flow-injection and CE measurements. Employing an 8-cm long separation channel and a separation voltage of 4000 V offers high-throughput flow-injection assays of 100 samples/hr with a relative standard deviation of 3.7% (n=100). Such ability to continuously introduce real samples into micrometer channels would make "Lab-on-a-chip" devices compatible with real-life environmental applications. We also developed a simple, user-friendly and effective method for fabricating high-quality polymeric microchips based on an atmospheric pressure molding. The new fabrication route offers a substantial simplification of the entire

fabrication process, through a judicious coupling of light-initiated polymerization of methylmethacrylate (MMA) monomer solutions under ambient conditions with common photolithography and wet chemical etching techniques. This approach differs significantly from earlier fabrication schemes of plastic devices in that it does not require elevated pressures and temperatures (and related cooling) or a complicated replication equipment. Variables of the fabrication process were assessed and optimized. High-quality devices with well-defined channel and injection-cross structures, and highly smoothed surfaces were thus obtained. While the new approach was demonstrated in connection to PMMA microchips, it could be applied to other materials that undergo light-initiated polymerization. The new fabrication approach brings significant simplification of the process of fabricating microfluidic devices and should lead to a widespread low-cost production of microchips.