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Development of an In-Situ Microsensor for the Measurements of Chromium and Uranium in Groundwater at DOE Sites

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Research Objective

The goal of this research is to develop novel electrochemical sensors for in-situ environmental monitoring of trace uranium and chromium. Such innovative remote/submersible and micromachined stripping-based devices will greatly enhance the detection of trace metals in a field setting, and should revolutionize the way such contaminants are being monitored.

Research Progress and Implications

This report summarizes our activity over the first 1.5 years of a 3-year project. This effort has led to the replacement of conventional stripping electrochemical protocols and systems with new innovative strategies for field monitoring of trace uranium and chromium, based on remotely deployable submersible sensors and micromachined hand-held total stripping analyzers. Eventually, these developments will allow to move the measurement of these metals to the field and to perform them more rapidly, reliably and inexpensively.

Improved Stripping Procedures for U and Cr

Traditionally, Cr and U have been measured separately using the adsorptive accumulation of their complexes with DTPA and propyl gallate (PG), respectively. To facilitate their on-site detection, we have developed new adsorptive stripping protocols that allow the simultaneous and rapid detection of Cr and U down to low ppb concentrations. One such new scheme involves the use of a mixed ligand (DTPA/PG) solution that allows simultaneous trace measurements in a single run (1). Numerous experimental parameters were optimized to assure that the attractive performance of the individual single-element protocols are not compromised. Simultaneous measurements in groundwater samples were documented. Alternately, we employed a single but more 'universal' ligand (cupferron) for the simultaneous monitoring of Cr and U (2). Under optimal conditions, competition of these metals for the ligand and coadsorption effects were minimized, and different concentrations of the mixture components can be tolerated.

Micromachined Stripping Analyzer

A major goal and focus of this project has been the development of a miniaturized stripping analytical system, produced by micromachining technology. Such new micromachined stripping analyzers - integrating all the sample manipulations steps (including complex formation) with the adsorptive stripping measurement - will require minimal amounts of sample and reagent and will result in faster and cheaper operations.

The newly designed microsystem uses an arrangement of functional modules, stacked on top of each other (to form a miniaturized flow system), including the sample and ligand/reagent reservoirs, two micro/piezo pumps, mixer, reaction coil, a silicon-based electrochemical detector and a micropotentiostat. The detector has a flow-through channel with an array of iridium microelectrodes, along with reference and counter electrodes, prepared by a photolithographic process. The size of the modules is 24x24 mm². The complete pocket-size microanalyzer has been assembled and delivered. Preliminary results are very encouraging, with both trace (ppb) Cr and U yielding well-defined signals. Yet, we still face various technical challenges, such as limited stability of the microfabricated reference

electrode or of the array of iridium microelectrodes, and an insufficient pumping capability. These limitations are currently being addressed, along with fundamental studies on the scaling-down effects.

Submersible Probe for In-Situ Detection of Trace Cr and U

Remotely-deployable submersible sensors, capable of monitoring Cr and U both in time and location, are advantageous in various situations. Such in-situ monitoring capability offers a rapid return of the chemical information and avoids errors associated with sample collection and storage. We have thus developed a new remotely deployable flow-probe, based on the coupling of the internal ligand delivery and microdialysis sampling for the in-situ detection of Cr and U (3). Such a renewable-reagent remote adsorptive stripping sensor relies on the continuous delivery of the ligand, its complexation reaction with the metal collected by the semi-permeable sampling tube, and transport of the complex to the downstream electrode compartment. Besides the in-situ detection, the microdialysis sampling offers minimization of surfactant effects and extended linear range (compared to conventional adsorptive stripping measurements) due to its filtration and dilution actions. In-situ sensing of metal speciation is also being investigated.

Conclusions

Our work over the first half of the project has resulted in novel and powerful protocols for in-situ electrochemical analysis of trace Cr and U. Such developments offer great promise for performing metal testing more rapidly, easily, and inexpensively in a field setting. These advances bring significant changes to the monitoring of Cr and U, and of toxic metals, in general.

References

1. J. Wang et al, Anal. Chim. Acta 354(1997)275.
2. J. Wang et al, Electroanalysis 9(1997)1247.
3. J. Wang et al, Anal. Chem. 69(1997)2640.

Planned Activities

Future work will aim at addressing problems encountered in the micromachining of the miniaturized stripping analyzer (Summer 1998), integration and miniaturization of the remote flow probe (Fall 1998), characterization and optimization of both in-situ detection schemes (Fall 1998 and Winter 1999), their extensive in-situ testing (Spring and Summer 1999) and final reporting (Fall 1999). Based on our accomplishments so far, we are very optimistic that these studies will lead to powerful tools for in-situ detection of Cr and U. Fabrication on the micromachined system will focus on improving the stability of the reference electrode and the adhesion of the insulator surrounding the iridium ones. Attention will be given also to the integration of a micropump, compatible with the entire microsystem. Efforts with the remote metal sensor will include integration of the electronic control circuits and the micropump with the sensing element in a single submersible unit. A new software will be developed to control the entire sequence of events of both operations, as well as their data processing. Both systems will undergo extensive evaluation and testing.

In the long run, we will combine the two schemes by developing a fully submersible remotely deployed miniaturized stripping analyzer (in a 'lab-on-a cable' configuration), and will combine this powerful metal detection capability with continuous monitoring of other priority pollutants.

Other Access To Information

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