

Project ID: **54639**

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

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RESEARCH OBJECTIVE (From the original proposal)

The goal of this program is to develop, optimize and deploy a silicon-based micromachined stripping analyzer for field monitoring trace levels of chromium and uranium. Such system will integrate the sample-handling steps and necessary chemical reactions (using a flow-injection operation) with the actual adsorptive stripping measurement on a small planar chip. Besides the drastic reduction in the size of the analytical system, such miniaturization should lead to increased speed, minimal reagent consumption and disposal, higher sensitivity and improved precision, and would thus revolutionize the way by which toxic metals are being monitored.

RESEARCH PROGRESS AND IMPLICATIONS

Two avenues have been explored over the past 2.5 years for achieving the overall goal of field monitoring of Cr and U, as well as of other toxic metals. These include a micromachined hand-held flow stripping analyzer and a remotely deployed submersible stripping probes. Both routes should allow testing of trace metals more rapidly and easily in a field setting.

Remotely deployable submersible sensors, capable of monitoring metal contaminants both in time and location are advantageous for environmental monitoring. Over the past year we expanded the scope of our remote monitoring capability by integrating a sample processing capability. Such coupling of the sample handling with the actual stripping detection on a cable platform represents a powerful and innovative approach for in-situ environmental analysis.

Our initial flow probe was designed for delivering internally the ligand and catalyst (DTPA-NO₃⁻) essential for adsorptive-catalytic measurements of trace Cr (1). Such renewable-reagent sensor thus relies on delivery the reagent solution, its complexation reaction with the Cr ion collected in a semi-permeable microdialysis sampling tube, and transport of the complex to the downstream detector. The resulting in-situ sensor has a detection limit of 0.1 ppb Cr, as well as good precision and stability (e.g, RSD of 6% at 25 ppb), with no carry-over (memory) effects (e.g., [Fig. 1](#)). A stable response was observed for both Cr (VI) and Cr (III) species.

Performing on-cable various sample manipulations was shown to offer additional advantages. For example, a 'built-in' acidification capability was employed for monitoring the total metal concentration (2). Such on-cable acidification of the collected samples offered an in-situ release (decomplexation) of metals bound to various ligands. This was documented for samples rich with NTA and EDTA. The released metals were detected by stripping potentiometry. The design of the flow probe is shown in [Figure 2](#). The versatility of this submersible 'microlaboratory' was demonstrated also for circumventing in-situ common problems associated with stripping analysis (3). In particular a judicious choice of the internal solution was shown useful for addressing the formation of intermetallic compounds or overlapping signals. These were accomplished through an internal delivery of a third element or a masking agent, respectively.

Additional efforts in the direction of remote electrochemical sensors have led to the developments of useful probes for in-situ monitoring of trace mercury (4) and nitroaromatic explosives, such as TNT (5), in connection to potentiometric stripping and square-wave voltammetric detection, respectively.

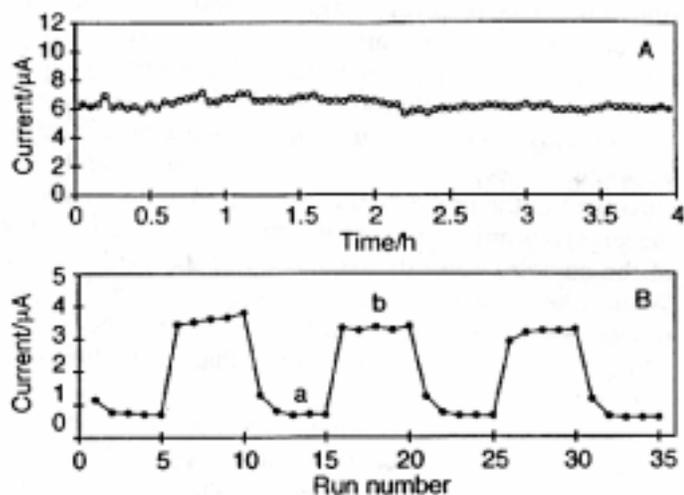


Figure 1. Performance of the in-situ probe for monitoring trace Cr: (A) Stability and (B) carry-over experiments. (A) Repetitive measurements of 25 ppb Cr(VI); response to alternate exposures to low (5ppb) and high (25ppb) Cr(VI) levels. Preconcentration time, 30 sec. (From ref. 1.)

We have designed and fabricated different configurations of the micromachined metal analyzer (e.g., Figure 3). Such hand-held flow systems integrate the sample processing step with the stripping detector. We used an arrangement of functional modules (inch²), stacked on top of each other, to form the miniaturized flow system. These include the sample and ligand reservoirs, micropumps, mixer, reaction coil, flow detector, and electronic control. This represents the smallest metal analyzer ever reported. Such dramatic scaling down has been very challenging (from the microfabrication angle) and led to various challenges or obstacles (e.g., solution leaks, pump stability, peeling off of electrode layers), and hence to delays in our planned Fall 99 delivery. We are working closely with our new subcontractor (Case Western Reserve University) for addressing these challenges, and have requested a 1-year no-cost extension for completing the planned evaluation of the microanalyzer and demonstration of its attractive analytical/field performance.

PLANNED ACTIVITIES

During the 99 summer, and in FY2000, we expect to expand the on-cable sample-manipulations capability, by integrating more challenging processes, in a so called 'Lab-on-Cable'. Such submersible 'microlaboratory' will perform all the necessary sample pretreatment steps, should have a major impact upon the monitoring of priority pollutants. We have recently completed the design of this device, and planning to characterize, optimize, and test it thoroughly during the coming 15 months.

We are also planning to receive from our subcontract the final design of the micromachined flow metal analyzer early this summer, and expect to assess and optimize its performance during the Fall 99 period, and extensively test and demonstrate its unique capabilities in lab and field settings during the FY 2000 season.

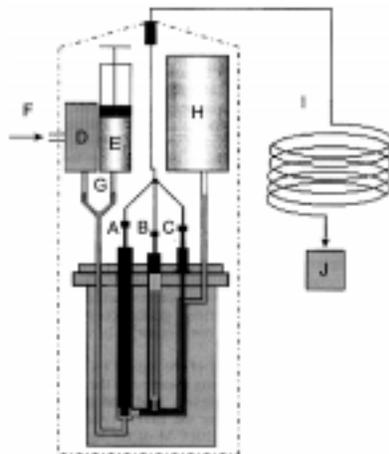


Figure 2. Schematic of the acid-delivered remote total-metal sensor. (From ref. 2.)

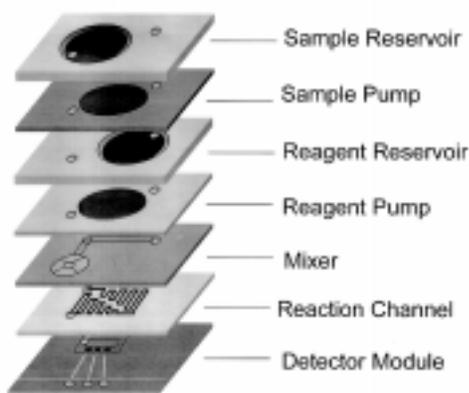


Figure 3. View of the stacked micromachined flow analyzer for adsorptive stripping monitoring of metal contaminants. (From ref. 6.)

List of Publications (3rd year Funding Period):

1. "Flow Probe for *in-situ* Electrochemical Monitoring of Trace Chromium", J. Wang, J. Lu, B. Tian, D. MacDonald, and K. Olsen, *Analyst*, 124(1999)349.
2. "Electrochemical Flow Sensor for *in-situ* Monitoring of Total Metal Concentrations", J. Wang, B. Tian, J. Lu, *Anal. Communications*, 35(1998)241.
3. "In-situ Flow Probe for Improving the Performance of Electrochemical Stripping Analysis", J. Wang, J. Lu, and M. Augelli, *Fres. J. Anal. Chem.*, 364(1999)28.
4. "Remote Electrochemical Sensor for Monitoring Trace Mercury", J. Wang, B. Tian, J. Lu, and D. MacDonald, *Electroanalysis* 10(1998)399.

5. "Remote Sensor for Monitoring TNT in Natural Waters", J. Wang, R. Bhada, J. Lu, and D. MacDonald, *Anal. Chim. Acta*, 361(1998)85.

6. "Stripping Analysis into the 21st century: Faster, Smaller, Simpler, and Better", J. Wang, B. Tian, J. Lu, C. Yarnitsky, K. Olsen, and W. Bennet, *Anal. Chim. Acta*, 385(1999)429.