ANNUAL PROGRESS REPORT

PROJECT TITLE: DEVELOPMENT OF AN IN-SITU MICROSENSOR FOR THE MEASUREMENT OF CHROMIUM AND URANIUM IN GROUNDWATER IN DOE SITES

DOE AWARD NUMBER: DE-FG07-96ER62306

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ORGANIZATION: New Mexico State University

PERIOD COVERED: Sep. 15, 1996 - Sept. 14, 1997

PROJECT DESCRIPTION (from original proposal):

The goal of this project is to develop, optimize and deploy a silicon-based micromachined stripping analyzer for field monitoring of trace levels of chromium and uranium. Such system will integrate sample-handling steps and necessary chemical reactions (using a flow-injection operation) with the already proven adsorptive stripping operation 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 revolutionize the way by which toxic metals are being monitored.

PROGRESS TO DATE:

Our work during the first year has focused on three directions: a. design and fabrication of the micromachined flow system for stripping measurements of chromium and uranium; b. design and evaluation of a remote sensor for in-situ monitoring of chromium and uranium; and c. developing and characterizing new electrodes for adsorptive stripping measurements of chromium and uranium.

a. Micromachined Flow System.

Upon receiving the Award, we immediately proceeded with the sub-contract to Battelle PNL for their microfabrication of the miniaturized

stripping metal analyzer. The PI went to PNL (Richland, WA) for a two-day visit. During that visit, the PI toured PNL facilities and had a thorough discussion with the PNL team on the project objectives and system characteristics. NMSU and PNL thus jointly developed the concept of the proposed micromachined analyzer, and subsequently in late 1996 completed the design of the proposed microsystem.

We jointly agreed that a stacked component approach will be used for creating the miniaturized metal analyzer. Such approach will be based on stacking vertically multiple module layers (20x20mm), including the micropump, reaction channel, mixing channel, reservoirs, and detector, with holes to allow the fluid flow (Figure 1). We gave particular attention to the design of the detector module, with its flow channel, iridium microelectrodes array, along with the silver reference and platinum counter electrodes (Figure 2).

Subsequently, PNL has created and ordered the masks needed for fabricating the stacked flow system, and in early 1997 stated the actual fabrication effort. During the spring and summer PNL sent to NMSU two deliveries, consisting of most of the system modules (with the exception of the pump. Figure 3 displays a microscopic image of the microfabricated array of the iridium microelectrodes. The NMSU team evaluated these modules microscopically and tested the detector module experimentally under different practical (sensing) scenarios. Unfortunately, the detector module suffered from several problems (lift off, poor adhesion/sealing) associated with the fabrication process, that did not allow us extensive electrochemical testing. We have thus made several telephone conference to address these problems and improve the production quality, We except a new delivery of an improved detector module in mid. October 1997.

b. Remote Sensor for in-situ Monitoring of Chromium and Uranium.

To meet the goal of continuous environmental monitoring of chromium and uranium, we have successfully explored a novel strategy for remote in-situ sensing of these metals. For this purpose, we designed and fabricated a new renewable-reagent flow probe, integrating microdialysis sampling of the target metal with the adsorptive stripping detection of their complexes (Figure 4). Such innovative probe relies on the delivery of the corresponding ligand solution through a microdialysis sampling tube and transport of the resulting complex to the downstream detector. We have characterized, optimized and successfully tested the new probe in

connection with the uranium-propyl gallate system. The optimized protocol allows sensitive measurements of trace (10^{-8}M) uranium at 20 min intervals, and offers a highly stable response (with a relative standard deviation of 1.7%, $n=20$). Tests with untreated river water and groundwater samples were also successful. The microdialysis sampling has been shown useful to minimize surfactant interference (see enclosed publication). A second-generation probe was designed during the summer and is currently being tested towards the monitoring of trace chromium. These developments will provide the DOE with deployable in-situ metal sensors, suitable for early detection of sudden contamination, that minimize errors, labor, cost and delays, associated with conventional laboratory analysis.

c. New Sensing Electrodes for Trace Chromium and Uranium

The development of in-situ electrochemical sensors for trace chromium and uranium requires special attention to the indicator working electrode. Traditionally, adsorptive stripping laboratory measurements of chromium and uranium have relied on the use of stationary mercury drop electrodes (that are not suitable for field deployment). We demonstrated during the fall of 1996 that iridium-based mercury microelectrodes offer an excellent alternative to mercury drop electrodes, and successfully address the various steps and manipulations anticipated under field deployment. The same electrode was used over a period of over five weeks, performing hundreds of measurements with a relative standard deviation lower than 10%, and offering detection limits of around 0.5 ppb ($\mu\text{g/l}$) chromium and uranium. Such highly stable and favorable response of the iridium based electrodes (see enclosed reprint for details) makes them very attractive for the proposed in-situ monitoring; such electrodes were thus selected for the design of the micromachined system.

Conclusions. Over the first year we have made a significant progress towards the goal of designing field-deployable electrochemical sensors for trace chromium and uranium in environmental matrices. Despite technical difficulties in the microfabrication effort, other aspects of the project have proceeded so successfully, offering great promise for the task of in-situ monitoring of these important metals.

Publications Resulted from the 1st year Effort:

1. "Adsorptive Stripping Measurements of Cr and U at Iridium-based Mercury Electrodes", J. Wang, J. Wang, B. Tian and M. Jiang, Anal. Chem. 69(1997)1657.
2. "Renewable-Reagent Electrochemical Sensor for Monitoring Trace metal Contaminants", J. Wang, J. Lu, D. Luo, J. Wang, B. Tian and K. Olsen, Anal. Chem. 69(1997)2640.
3. "Remote Electrochemical Sensor for Monitoring Inorganic and Organic Pollutants", J. Wang, Trends Anal. Chem. 16(2)(1997)84.

(b) Stacked Architecture

Figure 1 : Planar (a) and (b) Stacked uTAS Equivalents.

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= exposed,
rest covered
by Si₃N₄

Fig. 2

Fig. 3