Microcantilever Sensors for In-Situ Subsurface Characterization
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Research Objectives

Real-time, in-situ analysis is critical for decision makers in environmental monitoring, but current techniques for monitoring and characterizing radionuclides rely primarily on liquid scintillation counting, ICP-MS, and spectrofluorimetry, which require sample handling and labor intensive lengthy analytical procedures. Other problems that accompany direct sampling include adherence to strict holding times and record maintenance for QA/QC procedures. Remote, automated sensing with direct connection to automated data management is preferred. Therefore, a wide spread need exits at DOE sites for miniature, integrated, low-power consuming, in-situ sensors that are capable of simultaneous multiple analyte detection, and that can be packaged to include wireless monitoring. Currently available technologies impose severe limitations on simultaneous, real-time detection of multiple analytes due to excessive power consumption and a lack of integration with wireless technology. Here we propose integration of a microcantilever sensor array platform with wireless telemetry. Though the microcantilever platform has been demonstrated for in-situ detection of individual analytes, a microcantilever array capable of simultaneous detection of multiple analytes, its integration with wireless telemetry, and field deployment has not yet been demonstrated. Specifically, we will address key chemicals in two general groups: RCRA heavy metals (lead, chromium (VI), mercury, zinc, beryllium, arsenic, cadmium, and copper) and transuranic elements (uranium, neptunium, and plutonium). Although these two general groups and the members of each group are chemically different, having no general molecular recognition characteristics in common, they have one characteristic in common in that many are electrochemically active. Many of the heavy metals exist in groundwater or in mixed wastes as oxidized ionic species (Pb(II), Cr(VI), Hg(II), Cd(II), and Cu(II)) that can be electroplated on gold, platinum, or nickel surfaces. The overall goal of this proposed research is to develop novel, field deployable miniature sensors with extremely high sensitivity, and exceptional selectivity. These sensors, with integrated wireless communication, once deployed will be able to provide real-time concentration and speciation of multiple contaminants and their variation with time. Four tasks have been devised to accomplish these goals; 1) Development of piezoresistive cantilever arrays, 2) Development of a miniature readout syste, 3) Development of chemical selectivity, and 4) Application of microcantilever sensors for contaminant detection and monitoring.

Research progress and implications

We have successfully demonstrated detection of a number of DOE specific metal ions with high sensitivity and selectivity. In most of the cases we have used chemically specific coatings based on self-assembled monolayers. For example, we have detected extremely small concentrations (sub ppb) of Cr in groundwater (from Hanford site) with exceptional selectivity. It is interesting to note that the extreme selectivity was maintained even in the ground water in the presence of other interferents. Our sensitivity was much better than the spectrophotometric method used in routine analysis.

We have developed a general method in which chemical selectivity has been achieved by coating one side of the microcantilevers with a selective film such as a self-assembled monolayer (SAM) of an alkanethiol reagent having a head group suitable for molecular recognition. The transduction part of the microcantilever sensor is based on binding the molecular recognition agent to one surface of the cantilever so that the adsorption-induced stress change can be detected via bending of the microcantilever. Selective coatings have been developed for sensing Cr (VI), Cs^+, Hg^{2+}, CH_3Hg^+ (monomethylmercury), Ca^{2+}, Cu^{2+}, HF, and H^+, and work is in progress to develop coatings that are selective for TcO_4^- (or ReO_4^-), and Sr^{2+}.

During these experiments we realized that electrochemically active metal ions could be detected by using a cantilever as a working electrode. In this case, electrodeposition of electro-active metal ions on cantilever surface results in cantilever bending. We have successfully detected Cu, Cr, Hg and Pb using electrochemical cantilevers. The electrochemically-induced cantilever bending is more sensitive than simply measuring current and this method may be useful in studying the details of adsorption at an electrode surface, which precedes electron transfer.

We have observed that the cantilever bending is extremely sensitive to electrochemical current in the solution. Based upon this observation we have developed a technique where the cantilever serves as a reference/counter electrode for electrochemical reactions occurring on another working electrode. This method has the potential for high sensitivity, robustness, and simplicity, and it will be of great advantage for using electrochemical methods of detection in nanofluidic devices in which very small electrodes will be utilized. The current from these electrodes is very small and careful shielding and stable amplifiers are required to measure these small currents. Measurement of cantilever bending does not require as sophisticated instrumentation as does current measurement.

The electrified cantilever has many advantages. The dimensions of the electrochemically active area of the metal-coated microcantilevers that will be employed in the proposed work are such that these can be classified as ultramicroelectrodes (the nomenclature is somewhat inappropriate, but derives

from the convention practice of referring to submillimeter dimension electrodes as microelectrodes). Several points are important: (1) the dimension of the microcantilever electrode is comparable to the diffusion distance that is established on the time scale of the potential variations ($x = (Dt)^{1/2}$); the diffusion distance for 10 msec is roughly 1 micron. Furthermore, the thickness of the double layer and the dimensions of the electrode are comparable. Convective transport to the surface will be small compared to the diffusional flux at times longer than 10 to 100 msec. (2) The current and the double layer capacitance scale as the area of the electrode while the resistance scales as the separation distance between the polarizing electrodes. For very small electrodes (having small current and small capacitance), the placement of the counter electrode with respect to the electrode under investigation becomes less important. The RC time constant limitation on how fast potential variations can be applied to an electrode is such that processes that are comparable to adatom rearrangement on a surface can be examined. Furthermore relatively resistive media can be used for electrochemical polarization. Pure water (or water with very low electrolyte concentration such as groundwater) and organic solvents have been used for electrochemical measurements with ultramicroelectrodes.

Development of a multi-modal cantilever array sensor system capable of detecting many analytes simultaneously will have significant impact on DOE's remediation needs.   The DOE Office of Science "Environmental Remediation Science Program Strategic Plan" quotes "inherent complexity of the subsurface and our limited ability to observe processes and interactions as they occur in these systems have proven to be major obstacles to predictive simulation of contaminant behavior at the field level". The challenge of limited ability to monitor processes could be addressed by developing a distributed, unattended sensor network with unprecedented sensitivity and selectivity. These sensors will help in developing a fundamental scientific understanding of subsurface contamination and processes and will require the development of cost effective monitoring techniques and in-situ and remote monitoring methods that allow real-time detection and quantification of contaminant flow in fractures. Continuously monitored detection methods are a viable alternative to well-based sampling methods, such as groundwater monitoring.

Our vision is that microcantilever-based sensors, in combination with wireless telemetry, can be a cost effective means of remotely monitoring a variety of DOE needs. We envision an integrated sensor system packaged into a cylinder 2 inch in diameter and 2 inches long that includes battery package and wireless telemetry. This package can be lowered into wells for long-term, unattended monitoring of multiple analytes at desired intervals. For initial trials, the lowering wire can be used for getting the signal to the surface and to an independent wireless unit. This is necessary to avoid radio frequency reflection problems encountered in the wells. However, the wireless can be integrated into the system for certain other applications.

Planned activities

Deployment of inexpensive, miniature, real-time sensors capable of multi-analyte detection with speciation will play a crucial role in characterization, monitoring, and long-term stewardship of subsurface systems. Planned activities include development of a sensor system capable of detecting multiple chemicals simultaneously. The integrated sensor system will be based on a piezoresistive cantilever array. The array will be micromachined out of a silicon wafer with 40 independent cantilevers in a microfluidic well. Each of the cantilevers in the array will have a metal coating (gold) for independent electrochemical control. Measurement of the cantilever the bending will be accomplished with an imbedded piezoresistive element. The active element will be completely encapsulated in silicon nitride for electrical insulation. The silicon nitride layers on each side of the active element will have different thicknesses such that the neutral plane of bending will be inside the silicon nitride encapsulating layer.

Chemical selectivity will be achieved by a combination of self-assembled monolayers (SAMs) and electrochemical control. We have developed a number of SAMs capable of providing very high selectivity to a limited number of analytes. The piezoresistive cantilevers will be designed in such a way that the SAMs could be immobilized on one side of a cantilever using electrochemical techniques. This is accomplished by coating the top surface of the cantilever with a 40 nm gold layer (Ti adhesion layer) for independent control of their electrical potential. It has been demonstrated that electrochemically depositing SAMs increases SAM quality while decreasing SAM formation time.

A number of cantilever elements will be used as a reference for common mode rejection. The electrochemical control will be used for immobilizing self-assembled monolayers as well as detection of electro-active species for chemical recognition. The sensor system will be incorporated with a wireless unit for data transmission.

Specific activities include; Development of piezoresistive cantilever arrays, Development of readout electronics, Development of selective layers (SAMs), Demonstration of contamination detection using an array format.

To demonstrate the applicability of microcantilever sensors for environmental detection and monitoring, sensors will be tested and validated for multi-analyte detection in both laboratory column flow-through systems and field groundwater monitoring wells at the DOE ERSP FRC site in Oak Ridge, Tennessee. Key performance parameters to be evaluated will include the sensitivity, selectivity, reproducibility, linearity and stability (or potential fouling) when subjected to subsurface environmental conditions. The testing and validation will progress in three phases, including initial batch equilibrium testing using site groundwater, tests in laboratory column flow-through systems and field groundwater detection at selected monitoring wells. Major contaminants of interest will include uranyl ions, pertechnetate, nickel, cobalt, and calcium, which are known to be present in the groundwater at the FRC site.

The controlled batch test will determine the sensitivity or detection limit of microcantilever sensors for a given anlytes or multi-analytes. These studies will

also determine the linearity of signal responses to analyte concentration changes and the selectivity or potential interferences from other metal ions or anions present in the groundwater. Initially simulated groundwater with known chemical compositions, pH and interference ions will be used, and it may be composed of varying concentrations of carbonate, chloride, nitrate, sulfate, and metal ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}/Fe^{3+}, Al^{3+}, etc. Calibrations and iterations will be made using an array of cantilevers with enhanced selectivity for one of the analytes of interest. An important consideration in this analysis is to find concentrations, which give a linear response to simplify calibrations. After these initial tests, actual groundwater samples will be obtained from the FRC site, both from the Area 1 (with a low pH and high ionic strength) and the Area 2 (with neutral pH and relatively low ionic strength) monitoring wells, and subjected to testing. If analytes of interest (e.g., Cr(VI)) are not present in the groundwater, they can also be spiked into the groundwater at varying concentrations for evaluating the signal response of microcantilever sensors under realistic groundwater conditions.

The above batch tests are performed under equilibrium conditions. Additional tests will be performed in column flow-through systems to simulate in situ, real-time monitoring scenarios. This experiment will also evaluate the potential kinetic effect, and it is important to find the maximum flow rate that can be use before pump pulsations adversely affect the cantilever response. This will be accomplished through the use of packed sediment columns (e.g., ~1 6-in glass column) using the FRC background or contaminated sediments. One of the scenarios is to monitoring the sorption, desorption or flushing of contaminants of interest in and out of the sediment column. As an example, contaminated FRC sediments from Areas 3 or 1 contain relatively high concentrations of uranium, technetium, nickel, calcium, aluminum, nitrate, sulfate, etc (we can devise sensors for the first four species), and they can be desorbed or leached out by flushing with acid or bicarbonate solutions at varying concentrations. Specific analytes of interest can also be added into the influent solution for testing. Experimentally, two multi-analyte microcantilever sensors can be attached to both the influent and effluent sides of the sediment column for real-time monitoring. In order to validate the analytical accuracy and stability of the sensors, the influent and effluent samples will also be taken at varying time intervals and analyzed independently by other techniques such as kinetic phosphorescence and inductively coupled plasma - mass spectrometry (ICP-MS).

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