Project Summary

Project I.D. Number: 65340

Project Title: Detection and Characterization of Chemicals Present in Tank Waste

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Research Objective: The principal goal of this three-year project is to develop and demonstrate novel multi-parameter micro-electro-mechanical system (MEMS) sensors that are robust and can be used to simultaneously detect the presence of target chemicals in a mixture, radiation emitted from radioactive materials, and the heat generated by the absorption of photons of specific wavelength by the target chemicals. A major emphasis of this program is to study and develop effective methods of modifying MEMS surfaces with nano-scale structural features and chemical selective phases to improve sensor performance.

Research Progress: Research results after ~ 16 months of this 36 month project are described below.

Studies of Photo- and Adsorption-Induced Stress in Microstructures and Photothermal Spectroscopy

Micromechanical structures respond to chemical stimuli by undergoing changes in their bending and resonance frequency even when a small number of molecules adsorb on their surface. In our present studies, we extended this concept by studying changes in both the adsorption-induced stress and photo-induced stress as chemicals adsorb on the surfaces of *MCs*. By combining measurements of photo-induced and adsorption-induced stress in MEMS devices caused by target molecules with microcalorimetric spectroscopy both the presence and identity of target molecules can be determined. In addition, radioactive chemicals may also be identified by measuring the temperature changes of micromechanical sensors as they absorb emitted radiation.

(i) Studies of Adsorption-Induced Stress in MEMS. We investigated the effect of absorption of trace amounts of target molecules, 2-mercaptoethanol and diisopropyl methylphosphonate (DIMP), on micromechanical structures. Although gold coated surfaces adsorb DIMP effectively, the selectivity can be substantially improved by first coating the surface with self-assembled monolayers. The chemical selectivity of the layer is based on the interaction of Cu^{+2} bound to the MEMS surface by a carboxylate-terminated n-alkanethiol monolayer. Microcantilever MEMS devices with such surface coatings were exposed DIMP molecules by flowing a mixture of N_2 and DIMP vapor in a chamber containing the microcantilever. The modified MEMS respond proportionally and reversibly to the presence of DIMP molecules in a way that is distinguishable from any response to common organic solvents such as ethanol, methanol, or acetone.

(ii) Studies of Photo-Induced Stress in MEMS. In our studies, we used Au-coated Si microstructures to investigate the effect of molecular adsorption of DIMP and trinitrotoluene on the photo-induced bending of *MCs.* We measured the photo-induced stress before and after exposure to target molecules using a diode laser capable of delivering 10 mW and found that the photo-induced bending of microstructures depends on the amount of target analyte adsorbed on the surface of the MEMS device.

(iii) Studies of Photothermal Spectra Using MEMS devices. In the present studies we used our microcalorimetric spectroscopy technique and obtained photothermal IR spectra for trace quantities of target

chemicals (e.g., 2-mercaptoethanol, toluene, anthracene).

Investigations of Chemically Selective Coatings to Enhance Sensor Performance

Several approaches are being pursued to influence sensor selectivity and sensitivity: *(i)* metal chelating resins are immobilized onto solid scintillator fibers,[1] *(ii)* polysiloxane (GC-type) phases are spin-coated onto microstructures,[2] (*iii)* mercapto-modified receptor phases (e.g., derivatized cyclodextrins, CDs) are chemical bonded to Au-coated microstructures. The underpinning aim of this effort is to selectively increase sensor response factors for environmentally significant analytes.

(i) Resins. Dual mechanism bifunctional polymer resin, that exhibits a high specificity for Cs in alkaline solutions, has been immobilized onto solid scintillation fibers. By optimizing conditions it has been possible to produce stable, field-ready fibers that retain resin and fiber functions. Based on a scintillation mode of operation for ^{137}Cs â-emission, these fibers were found to respond linearly over a range of 1.4 to 1120nCi, (3.4×10^{-10} to 2.7×10^{-7} M ^{137}Cs), with an LOD of ~0.025 ppb ^{137}Cs.

(ii) Polysiloxane phases. SP 2340 and OV 25 were spin coated onto Si microstructures at thickness ranging from 50 to 500 nm. The responses to vapor phase chemicals follow selectivity trends that are consistent with conventional methods of classifying these GC stationary phases. Film and microstructure thickness were shown to dramatically effect response sensitivity.

(iii) Cyclodextrins. CDs that are fully mercaptanated at the primary hydroxyl positions have been synthesized and characterized by NMR spectrometry. Procedures for bonding these receptors to various Au-coated surfaces are being explored. Surface plasmon resonance and actual *MC* measurements for these modified surfaces are being performed. Molecular mechanics modeling techniques are used to predict receptor-analyte binding characteristics and to guide the synthesis of new CDs. Results of employing this rational method of imparting selectivity to sensing using MEMS are preliminary at this stage.

Surface Modification to Enhance Sensor Performance

Preliminary studies have been conducted to modify the surfaces of microstructures to enhance response in a general sense and to increase the surface area for the immobilization of chemical selective phases. We have successfully spin-coated silicate, meso-porous, sol gels onto microstructure surfaces and begun to evaluate their response characteristic in native and chemically functionalized forms. In addition, single and multilayer Au nano-scale beads have been chemically attached to silica and smooth Au surfaces. We expect that these architectures will produce greater surface areas for the binding of receptor phases and produce greater lateral stress on microstructures (increase response sensitivity) upon inclusion of chemicals into the receptor cavities.

Planned Activities: Advances in surface modification will be combined with CD-based receptor phases to produce *MC* sensors with high sensitivity and selectivity. Photo-induced responses and photothermal spectra for target chemicals interacting with microstructures modified with nano-features and receptor phases will obtained. The analytical figures of merit of this approach will be determined for a broadened set of target chemicals and synthetically generated receptor phases. We will continue to use molecular modeling techniques to aid in the rational design of chemically modified sensors. Eventually we will develop MEMS arrays with different receptor phases on the sensing elements. The interaction of MEMS devices with nuclear radiation (alpha and beta particles) will be studied to determine how the geometry and material properties of the microstructure affect such interactions.

Information Access:

1. J. Headrick, M. Sepaniak, S. Alexandratos, and P. Datkos, "Chelating Scintillation Fibers for Measurements of ^{137}Cs," *Anal. Chem.*, in press.

2. T. Betts, C. Tipple, M. Sepaniak, and P. Datskos, " Selectivity of Chemical Sensors Based on Micro-Cantilevers Coated with Polymeric Films," *Anal. Chim. Acta*, submitted for publication.