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

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Detection and Characterization of Chemicals
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Detection and Characterization of Chemicals Present in Tank Waste

The 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 molecules.The goal of this program is to study and develop effective methods of immobilizing chemical selective phases for improved microsensor performance

1. Investigations of Photo-Induced and Adsorption-Induced Stress in Micromechanical Structures and Photothermal Spectroscopy

Microcantilevers 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 target chemicals adsorb on the surface of microcantilevers. For example, microcantilevers that have adsorbed molecules will undergo photo-induced bending that depends on the number of absorbed molecules on the surface. However, microcantilevers that have undergone photo-induced bending will adsorb molecules on their surfaces in a distinctly different way. Coating the surface of a microstructure with a different material can provide chemical specificity for the target chemicals. Therefore 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 can also be identified by measuring the temperature changes of micromechanical sensors as the 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 composite self-assembled monolayer coating transiently adsorbs molecules of DIMP vapor, which causes the microcantilever to bend. We found that our derivitized 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. During the exposure time, we observed no measurable change in the resonance frequency of the MEMS.

(ii) Studies of Photo-Induced Stress in MEMS

In our studies we used gold-coated Si microcantilevers to investigate the effect of molecular adsorption of DIMP and trinitrotoluene on the photo-induced bending of microcantilevers. We measured the photo-induced stress both before and after exposure to target molecules using a diode laser capable of delivering 10 mW and found that the photo-induced bending of microcantilevers depends on the amount of target analyte adsorbed on the surface of the MEMS device.

(ii) Studies of Photothermal Spectra Using MEMS devices

In the present studies we used our microcalorimetric spectroscopy technique and obtained photothermal spectra for trace quantities of target chemicals. More specifically we photothermal spectra over the wavelength region 2.5 to 14.5 •m of 2-mercaptoethanol, diisopropyl methylphosphonate, and toluene anthracene.

2. Investigations of Chemically Selective Coatings to Enhance Sensor Performance

Three general approaches are taken; *(i)* Organo-silane phases are vapor deposited (polysilane GC types) or chemical bonded (trichloroalkylsilane ALC@ types) onto treated silicon substrates, *(ii)* chelating resins are immobilized onto solid scintillator fibers, and *(iii)* thiolated-alkyl phases are covalently attached to gold substrates as self assembled monolayers. The underpinning goal is to selectively increase sensor response factors for environmentally significant analytes. Approaches *(i)* and *(iii)* are directed toward the sensing of semi volatile organics while approach *(ii)* is directed toward radioactive metals.

Approach (i) Results and Plans: Phenyl/methyl and cyanopropyl gum phases commonly employed in GC were deposited onto silicon substrates by vapor-deposition methods; trichlorophenylsilane and octadecyltrichlorosilane phases commonly employed in LC were deposited by solution-bonding reactions. Successful deposition of uniform films onto silicon chips were confirmed by scanning electron microscopy; it was found that cleaning silicon wafers with piranha solution (3:1 18M H_2SO_4/30% H_2O_2) until wetting contact angles <5E were achieved is necessary to obtain a uniform film thickness. The relative affinity and selectivity of these phases for volatile organic compounds is currently being determined by exposing the modified substrates to analyte solutions followed by quantitative analysis by GC/MS. Thus far, silane-modified substrates exhibit only modest selectivity and affinity relative to blank substrates, but also highlight the importance of film thickness. *Future studies* will focus on applying these deposition techniques, including spin coating, directly to preparing MEMS and evaluating the response characteristics of the sensors.

Approach (ii) Results and Plans: Dual mechanism bifunctional polymer (DMBP) has been shown to bind Cs (I) in alkaline solutions in other EMSP-sponsored research. The resin is composed of phenol-formaldehyde chains grafted onto a diphosphonate-based resin. Comprehensive studies of resin selectivity have not been performed. In this work, resin has been immobilized onto solid scintillation fibers. By optimizing conditions it has been possible to produce stable, field-ready fibers that retain both resin and fiber function. Based on a scintillation mode of operation for ^{137}Cs b-emission, calibration curves were generated using a relatively short 100 second count times and very basic photon counting instrumentation. Using 350 mL sample solutions, these were found to be linear over a range of 1.4 to 1120nCi, ($3.4\text{x}10^{-10}$ to $2.7\text{ x}10^{-7}$ M ^{137}Cs), with a LOD of 0.69 nCi (~25 parts per trillion ^{137}Cs). *Future studies* will involve detailed characterization of the chemical selectivity of this approach. In addition, the capabilities of using a MEMS mode of b-emission detection will be evaluated, as well as the use of sol-gel based coatings.

Approach (iii) Results and Plans: Thiolated-alkyl phases including propanethiol, 1-dodecanethiol, p-thiocresol, 1-thioldodecanoic acid (TDA) have been investigated for their ability to form self-assembled monolayers (SAM=s) on gold surfaces. Preliminary studies have been performed using the QCM technique. Based on the QCM data, it is evident that SAM=s are being formed on gold surfaces after short exposure to the thiol compounds. FT-IR has been attempted on the SAM=s but to date no results have been obtained. The TDA has been applied directly to gold coated MEMS and sensitive response to the pesticide diisopropyl methylphosphonate has been accomplished. *Future studies* will include the expansion of the TDA work, the synthesis of thiolated cyclodextrins and their evaluation as highly selective MEMS phases, and the incorporation of cyclodextrins or other macrocycles into polymeric matrices to be spin coated onto MEMS sensing surfaces.

During the first year efforts we developed a novel method to detect the presence of target chemicals that is based on the adsorption-induced and photo-induced stress in micromechanical structures. We also we employed our microcalorimetric spectroscopy technique to obtain photothermal spectra of target chemicals.