

**ATTACHMENT A**

**FINAL PROGRESS REPORT**  
**Prepared for**  
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*Detection and Characterization of Chemicals  
Present in Tank Waste*

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## Executive Summary

A multifaceted, interdisciplinary research program has served to provide fundamental insights and practical technological advances toward the development of miniaturized, highly-sensitive, tunably-selective sensors for monitoring chemical constituents in complex vapor and liquid matrices.

Our aim is to support high-level waste management by improving methodologies and technologies for low cost, safe, and effective measurements of the chemical, physical, and radiological characteristics of DOE storage tanks as well as samples from surrounding areas.

The goal of our three-year project was 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 was to study and develop effective methods of immobilizing chemical selective phases for improved microsensor performance. Specifically, the focus has been on magnifying, controlling, and augmenting the chemi-mechanical responses of microcantilever (*MC*) sensors. Key advances have resulted from modifying the structures of these *MCs* with unique geometries and nanostructured surfaces that provide higher surface area for the binding of analyte and analyte-recognizing receptors. These novel surfaces also created new mechanisms of surface stress that have dramatically magnified the responses of *MCs*. Methods of uniformly coating the surfaces of smooth and nanostructured surfaces have been explored and advanced. These methods include vapor deposition, spin coating, and direct chemical

reaction to form self assembled monolayers. The methods of modifying MC surfaces are being expanded to include matrix assisted pulsed laser evaporation to facilitate controlled deposition of a wider array of selective phases. The chemically selective phases include bifunctional chelating polymers, siloxane-based GC polymers, and cavitand macrocycle receptors such as calixarenes and cyclodextrins (CDs). Using the basic structure of native CDs as a template, new CDs have been synthesized to increase the range of cavitand receptors available for selective binding of DOE significant analytes. The coating methods and range of coating types have provided analyte specificity for better control of *MC* response. The analytical capabilities of these chemical modified MCs have been augmented through the integration of strategies to simultaneously obtain infrared spectra of analytes adsorbed onto the *MC* surface using photothermal bending of the cantilevers as a novel readout method. Photo-induced stress has also been generated on these structures and it has been shown that the presence of adsorbed analyte influences this stress.

Our interdisciplinary research efforts have allowed us to better understand the behavior of micromechanical systems and their use as effective chemical microsensors. The continuous monitoring of both physical and chemical characteristics of hazardous chemicals is still one of the big challenges in DOE's long-term environmental management of waste tanks. It has been recognized that attempts to attain even a partial solution of this task, using conventional analytical means, will involve exponentially increasing costs. A more realistic approach to long-term management of DOE waste tanks is to develop a new generation of environmental sensors that would take advantage of recent advances in the

areas of nanotechnology, materials science, and MEMS. In addition, leak detection methods are needed that can detect tank waste leakage.

In addition to dramatically improved analytical performance the advantages of the MEMS-based sensors we have already developed will include capability of remote or unattended operation, simultaneous acquisition of multiple chemicals as well as physical characteristics. Therefore, comprehensive analysis of high-level hazardous wastes will become possible at moderate costs and with minimal risks involved.

Our accomplishment thus far indicate that chemical microsensors based on MEMS, which can be used to address needs in HLW tanks, are feasible. A natural extension of the previous efforts is the concept of hybrid sensors. Complex architectures of hybrid sensors arranged into arrays will extend this concept to analysis of a broader variety of chemical species that are otherwise very difficult to discriminate. In particular, combination of chemi-mechanical, electrochemical and Raman modes of transduction in a single MEMS device will facilitate distinguishing between nitrite/nitrite anions, ferro/ferri- cyanides, and strontium/cesium/mercury/lead cations. The proposed work outlined in the renewal proposal strives to achieve just that while we attempt to understand the fundamental mechanisms that provide enhanced analytical functionality of the nanostructured interfaces. In particular, our recent studies have demonstrated dramatic enhancement in chemi-mechanical transduction at the nanostructured interfaces which can be coupled as a common platform further utilizing Surface Enhanced Raman Spectroscopy.

## **Research Objectives**

The overall goal of this three-year project has been to develop and demonstrate novel multi-parameter micro-electro-mechanical system (MEMS) sensors based on Si and SiN<sub>x</sub> microcantilever (*MC*) structures that are robust and can be used to simultaneously detect the presence of target chemicals (analytes) in a mixture, radiation emitted from radioactive materials, and the heat generated by the absorption of photons of specific wavelength by the target analytes.

Specific goals developed at the inception of the project were to:

Understand the basic mechanism of adsorption-, photo-, and thermal-induced stresses in semiconductor surfaces.

Evaluate the use of moderately chemically selective coatings to enhance the response characteristics of *MC*-MEMS sensors for target analytes.

Study the use of photothermal infrared spectra obtained using *MC* systems as a means to derive analyte specificity in sensing applications.

Investigate the feasibility of combining gravimetric (adsorption)-based and micro-calorimetry-based methods to determine the composition of waste samples.

Develop radiochemical *MC*-MEMS detectors.

During the course of the project additional derived goals were to:

Compare and improve methods of applying analyte-selective coatings onto *MC* surfaces.

Structurally modify *MC* including surface meso- and nano-structuring to enhance response characteristics and develop new modes of analyte-induced surface stress.

Synthesize, model, and evaluate new cavitand receptor phases for *MC* sensing that provide higher degrees of analyte specificity

## **Methods and Results**

### **Studies of Photo- and Adsorption-Induced Surface Stress 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 surfaces. In our initial 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*.<sup>[1-3]</sup> 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 may be determined. In principle, radioactive chemicals may also be identified by measuring the responses of *MC*-MEMS sensors as they interact with emitted radiation.

(i) *Studies of Adsorption-Induced Stress in MC-MEMS.* We investigated the effect of absorption of trace amounts of target molecules, 2-mercaptoethanol and diisopropyl methylphosphonate (DIMP), on micromechanical structures.[1,2] Gas phase detection limits for 2-mercaptoethanol were less than 100 ppb (see Figure 6 in Reference 1). Although gold coated surfaces adsorb DIMP effectively, the selectivity can be substantially improved by first coating the surface with certain self-assembled monolayers (SAMs). The chemical selectivity of the layer is based on the interaction of  $\text{Cu}^{+2}$  bound to the MEMS surface by a carboxylate-terminated *n*-alkanethiol SAM. Details of the *MC* surface modification can be found in Reference 2. Microcantilever MEMS devices with such surface coatings were exposed to DIMP molecules by flowing a mixture of  $\text{N}_2$  and DIMP vapor in a chamber containing the *MC*. 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. Figure 5 in Reference 2 shows a signal to noise ratio of more than 10 for exposure to 63 ppb DIMP.

(ii) *Studies of Photo-Induced Stress in MEMS.* Native cantilevers can be stressed via the absorption of radiation and this can influence the adsorption of molecules on the cantilever surface.[2,3] In this manner, the photophysical process induces an element of selectivity. In addition, adsorbed molecules can influence photo-induced stress. For example, 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 at 790 nm and found that the photo-induced bending of microstructures depends on the amount of target analyte adsorbed on the surface of the MEMS device. [2] For an estimated adsorbed mass of DIMP of less than one  $\text{ng}/\text{cm}^2$  a reduction in the photo-induced response of nearly 50% was observed (see Figure 9 in Reference 2).

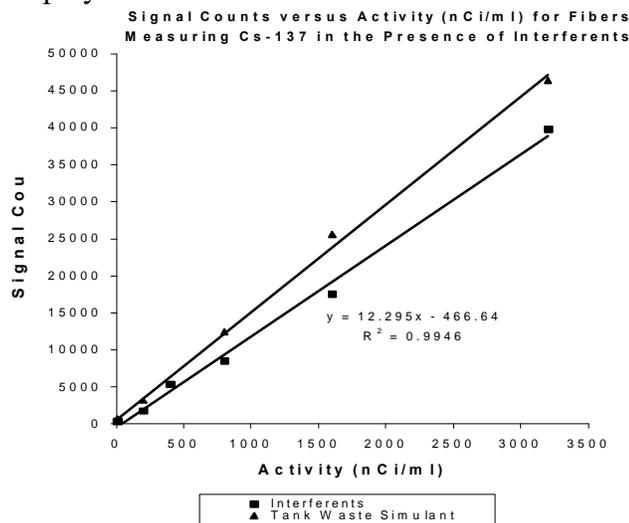
(iii) *Studies of Photothermal Spectra Using MEMS devices.* We used the microcalorimetric spectroscopy technique developed in our laboratory to generate photothermal IR spectra for trace quantities of target chemicals (e.g., DIMP, 2-mercaptoethanol, toluene, TNT). In one study, distinctive photothermal spectra were obtained in the 2.5 to 14.5  $\mu\text{m}$  spectral region for TNT and toluene adsorbates on *MC*-based MEMS that exhibited characteristic vibrational structure.[2] Although the signal to noise ratios for DIMP and TNT vibrational bands shown in Figures 10 and 12, respectively, in Reference 2 are quite low, the presence of vibrational structure is clearly evident. As expected, the band intensities seem to show greater correlation with spectra obtained by conventional means for the shorter wavelength (higher energy) bands.

## Investigations of Chemically Selective Coatings to Enhance Sensor Performance

The selectivity and response characteristics described above for measurements DIMP are based on selective complexation with surface bound metal. Several other approaches and phases have been investigated as a means to influence sensor selectivity and sensitivity: (i) metal chelating resins are immobilized onto solid scintillator fibers,[4] (ii) polysiloxane (GC-type) phases are spin-coated onto microstructures,[5] and (iii) cavitand receptor phases.[2,6,7] Among the cavitands employed are thick coatings of vapor deposited calixarenes, thick coatings of cyclodextrins (CDs) chemically modified to increase volatility and permit vapor deposition, and SAMs of thiolated CDs. 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 as  $\sim 3\text{-}5\ \mu\text{m}$  particles onto solid scintillation fibers using thin coatings of adhesive. By optimizing conditions it has been possible to produce stable, field-ready fibers that retain resin and fiber functions for liquid phase measurements. The resin is a phenol-formaldehyde grafted polystyrene polymer that functions well in strongly basic solutions. Based on a scintillation mode of operation for  $^{137}\text{Cs}$  -emission, these fibers were found to respond linearly over a range of 1.4 to 1120nCi, ( $3.4 \times 10^{-10}$  to  $2.7 \times 10^{-7}$  M  $^{137}\text{Cs}$ ), with an LOD of  $\sim 0.025$  ppb  $^{137}\text{Cs}$ . Theoretical treatments of expected sensitivity for  $\beta$ -emission launched into the fiber core were developed and agreed reasonably well with observed experimental signals. Cesium ion measurements were also performed in tank waste stimulant. A calibration plot (Reference 4, Figure 6) appears below. Advanced deposition techniques such as matrix assisted pulsed laser evaporation (MAPLE) are being investigated at this time and should provide a means to deposit these classes of polymer resins onto *MC* surfaces.

**Figure 1:**



(ii) *Polysiloxane phases*. SP 2340 and OV 25 were spin coated onto Si microstructures at thickness ranging from 50 to 500 nm. Film and microstructure thickness were shown to dramatically effect response sensitivity to various organic vapors (see Figures 4-6 in

Reference 5). These polymeric coatings actually caused a reversal in the direction of analyte vapor induced bending (Reference 5, Figure 3). The table below from Reference 5 shows the response characteristics of the SP 2340 *MC* for vapor phase analytes. By coating the different elements in a sensor array with different phases the analytical capability of the sensor is enhanced. It is desirable to have the phases respond differently to the analytes of interest. An advantage of our GC phase approach is that the responses of these *MC* sensors could be rationalized based on selectivity trends that are consistent with conventional methods of classifying GC stationary phases.

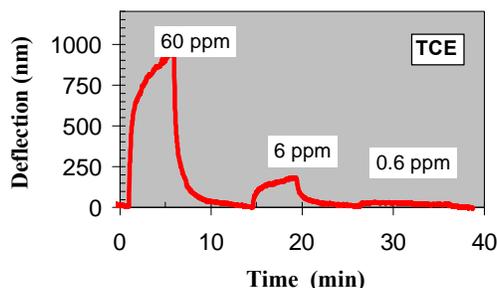
**Table 1.** Response characteristics of *MC* normalized to vapor pressure.

Analyte	Normalized Response Factor (maximum signal/vapor pressure, volts/atm))		<i>D</i>	Selectivity Factor (Response relative to Pentane)	
	Uncoated	SP2340 Coated		Uncoated	SP2340 Coated
Pentane	-0.54	0.15	0.69	1	1
Toluene	-15	4.6	20	27	31
Aniline	-690	120	810	1300	820
CH <sub>2</sub> Cl <sub>2</sub>	-1.0	1.8	2.8	1.8	12
Ethanol	-1.6	11	13	3.0	75
Water	-26	5.5	31	48	37

(iii) *Cyclodextrins & Calixarenes.* Macrocycle cavitand receptors composed of  $\alpha$ - and  $\beta$ -CDs that are fully thiolated at the primary hydroxyl positions have been synthesized and characterized by NMR spectrometry. Procedures for bonding these receptors to various Au-coated surfaces to create SAMs have been investigated. Surface plasmon resonance and actual *MC* measurements for these modified surfaces have been performed and revealed approximately monolayer coverage. [7] Molecular recognition of analytes by these receptors can be quite selective and are based on the size, shape, and chemical properties (H-bonding, dipole interactions, dispersive interactions) of both the CD and the analyte. Molecular mechanics and dynamics modeling techniques are used to predict receptor-analyte binding characteristics and to guide the synthesis of new CDs. Microcantilevers with SAMs of CDs have been characterized extensively for gas phase measurements [2,6,7] and are currently under investigation for liquid phase measurements (see next section).

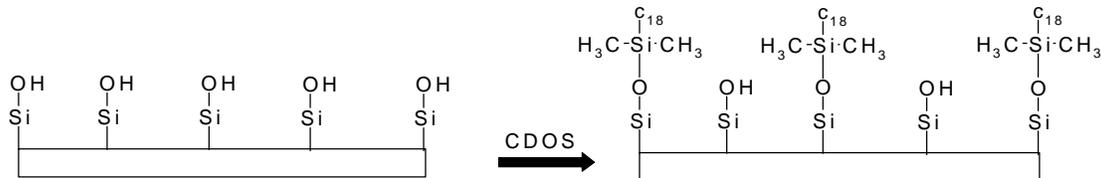
In an alternate approach, the hydroxyl groups of common CD have been alkylated to create structures that can be vapor deposited in rather thick layers on *MC* surfaces. Experiments with these phases are in the early stages. The calixarenes represent another class of macrocycle that has been studied for cantilever measurements.[2] Although distinctive selectivity patterns are not very likely with thick layers of calixarenes (or CDs), many of these macrocycle structures are easily processed by vapor deposition. Figure 2 below shows the response of a *MC* modified with a 50 nm thick layer of butylcalix[4]arene to tetrachloroethylene (TCE) vapors at different concentrations.

**Figure 2:**



### Surface Modification to Enhance Sensor Performance

Various 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 *MC* surfaces.[8] The sol solutions were prepared by combining tetramethoysilane, with a water, methanol, and hydrochloric acid solution. After approximately 6 hours of crosslinking the sol was spin coated onto silicon *MC* in films that were optimally 50 nm thick. These meso-porous films can be readily functionalized with organosilanes to alter response characteristics. For example, the chemical modification shown below produced a sol with hydrophobic alkane character that showed increased sol-*MC* response to n-pentane vapors (see Figure 4 in Reference 8).

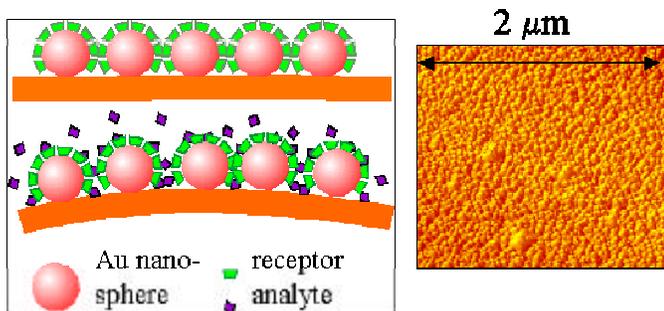


Two technological approaches were used to create a nanostructured Au *MC* surfaces.[6,7] The first approach involved assembling monodisperse Au beads (typically 20 nm diameter) onto a 4-aminobenzenethiol modified *MC* Au surface. The second approach produced a granular Au surface and involved vapor deposition of a Au:Ag alloy followed by dissolution of the Ag using 0.2 w/v% H<sub>2</sub>AuCl<sub>4</sub> solution. The latter dealloyed surface approach produced granular layers up to 75 nm thick and with surface roughness RMS values (AFM data) that range from 8 nm for the 20 nm gold beads to 45 nm for 75 nm dealloyed surface. In both cases, SAMs of receptors (e.g., thiolated  $\alpha$ - and  $\beta$ -CDs) were formed on the nanostructured surfaces (a cartoon depiction and AFM appear in Figure 3).

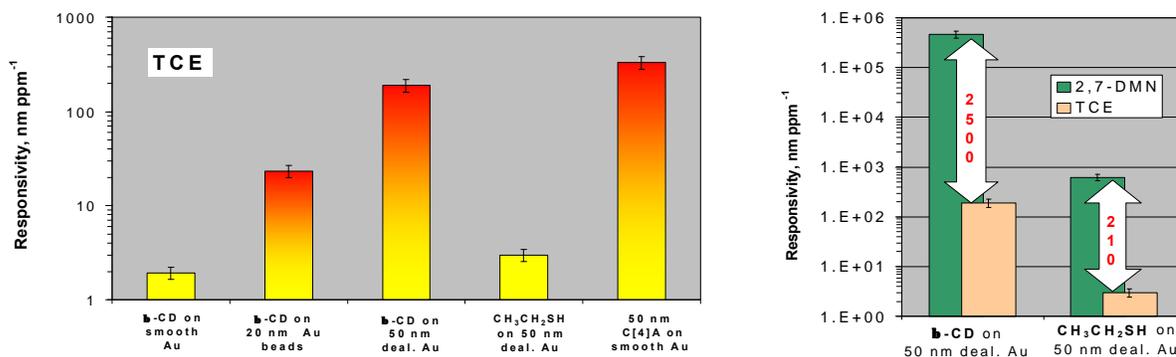
Receptor phases as monolayers offer the advantages of quick equilibration and also serve to preserve the binding site of the receptor (unlike thick coatings). Unfortunately, the range

of stress change that may occur with analyte binding on SAM-MCs is very small and, depending on the interface, can be near the level of the intrinsic bending noise of the *MC*. For example typical interfacial energy for hydrated organic surfaces in contact with water are only about 10 nN/m, about twice the bending noise. This severely limits sensitivity and dynamic range. Addressing this fundamental limitation became an important element in our work. To this end, the nanostructured surfaces are expected to offer a few important advantages over traditional smooth *MC* surfaces: (i) increase surface area for receptor or analyte binding, (ii) greater analyte induced stress due to short range steric and other forces in surface crevices, and (iii) less slippage when thick receptor phase coatings are used. Indeed, the response characteristics of these specially prepare *MCs* were enhanced by as much as two orders of magnitude as seen in the Figure 4. Nanostructuring in this manner produced some changes in observed selectivity for a given type of receptor. Also, SAMs of the  $\beta$ -CD cavitand receptor showed a far great range of selectivity that a SAM of a simple short chain alkane (see Figure 4). Nanostructured *MCs* were also shown to produce large deflections from bioaffinity interactions of proteins occurring on their surfaces.[7]

**Figure 3:**



**Figure 4:**



## **Productivity**

The goals outlined earlier in this appendix have largely been accomplished. The mechanisms by which adsorption, photophysical, photothermal processes cause stress in *MC* surfaces are better understood. Methods of applying a wide variety of chemically selectivity coating have been developed specifically for miniaturized *MC* surfaces and the response characteristic of the cantilevers were shown to be altered dramatically and predictably through incorporation of these phases on the surfaces. Photothermal IR spectra have been obtained for gas phase measurements. By addressing sensitivity and liquid matrix issues the spectroscopic approach promises to provide an essential element of specificity for integrated sensors.

It was discovered early in these studies that fundamental limitations exist regarding the degree to which adsorption of analytes on smooth surfaces cause stress and this significantly limits chemi-mechanical response. To circumvent this limitation a concerted effort was made to devise and test ways to nanostructure cantilever surfaces, thereby creating new mechanisms of analyte-induced stress. Substantial improvement in chemi-mechanical response resulted from this work. The original proposed studies focused on moderately selective polymeric coatings as a means to alter response. These experiments were successful and so our goals were expanded to explore more selective phases. New macrocycle cavitands were synthesized and methods to use these as selective phases on nanostructured surfaces successfully conducted. These phases were used mostly for gas phase measurements of organic chemicals. Liquid phase measurements using these nanostructured, cavitand modified *MCs* are in progress. Some progress was made at utilizing chelating resins for selective sequestering of radioactive metals (Cs <sup>137</sup>). This work was performed using a solid scintillation optical fiber approach because methods of immobilizing resin materials onto cantilevers proved to be lacking. The matrix assisted pulsed laser evaporation technique is currently under investigation to address this issue for future *MC* work.

We have attempted to use cantilevers for radiochemical measurements. Unfortunately, this approach did not prove fruitful for the measurement of  $\beta$ -emitters. The configurations of conventional cantilevers were not suited to capturing the energy of these particles and coupling this energy into *MC* response. Because considerable progress was made in other areas of the proposed studies efforts regarding this goals were reduced.

## Personnel Supported

In addition to the PI (Dr. Datskos) and Co-PI (Dr. Sepaniak) the following personnel have received at least partial support with EMSP funds:

Tim Gibson, UT Chemistry	Ph.D. 1999
Bryan Fagan, UT Chemistry	M.S. 2000
Jeremy Headrick, UT Chemistry	Ph.D. Candidate
Chris Tipple, UT Chemistry	Ph.D. Candidate
Larry Scenesac, UT Physics	Ph.D. 2000
Dr. Nickolay Lavrik, UT Chemistry	Post Doctoral Associate
Dr. Thomas Betts, Kutztown University, PA	Visiting faculty member
Dr. Slo Rajic, ORNL	Staff Scientist

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