Detection and Characterization of Chemicals in Tank Waste Using MEMS

Project I.D. Number: 65340

P. G. Datskos [865-574-6205, panospg@ornl.gov], S. Rajic, and L. R. Senesac, Oak Ridge National Laboratory, and M. J. Sepaniak, University of Tennessee

Problems/Needs

- Chemicals present in high level radioactive waste: organic chemicals, oxidizers, nitrate and nitrite salts (flammability, explosivity, and corrosion).
- Information is needed on physical parameters, and chemical and radioactive composition of waste for effective and safe tank remediation.
- New and improved physical and chemical characterization, and monitoring of waste present in storage tanks is needed. Can be achieved by developing methods and analytical systems, and that can provide *in situ* both chemical characterization and physical identification.

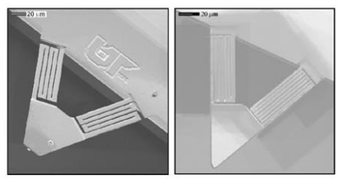
Goals

- Principal goal is to develop and demonstrate novel multi-parameter micro-electro-mechanical system (MEMS) sensors.
- Sensors will be robust and can simultaneously detect the presence of target chemicals in a mixture and the heat generated by the absorption of photons of specific wavelength by the target chemicals.
- Major emphasis is the study and development of effective methods of modifying MEMS surfaces with nanoscale structural features and chemical selective phases to improve sensor performance.

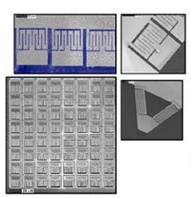
Approach

- Develop novel miniature sensors for chemical characterization and measurement of physical parameters based on a combination of gravimetric and photothermal detection.
- MEMS based sensors are especially well suited for detection of organic and inorganic species such as those found in waste tanks. For example, the presence and identity of nitrates, sulfates and phosphates can be determined using microcalorimetric spectroscopy.
- Using the ultrasensitive MEMS quantum or thermal detector arrays, the energy of a single particle or x-ray photon can be detected. Coupling gravimetric and microcalorimetric detection will allow the determination of physical parameters and chemical characterization.

Micromechanical Quantum or Thermal Detectors

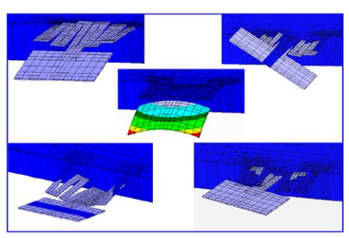


1999 R&D 100 Award Winning Micromechanical Photon Detectors

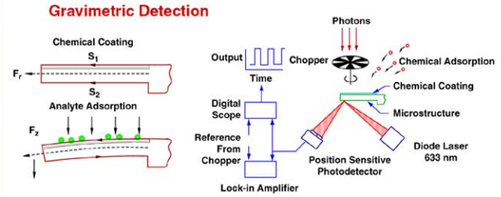


- ORNL fabricated small arrays of microstructures using rapid prototyping methods (made from InSb, GaAs, and Si/PT).
- Such devices can be used as micromechanical (photon or thermal) detectors for infrared radiation.
- These devices have been produced using new microfabrication approaches.

Modeling of Micromechanical Device Response



Gravimetric Detection



Adsorption-Induced Micromechanical Chemical Detection

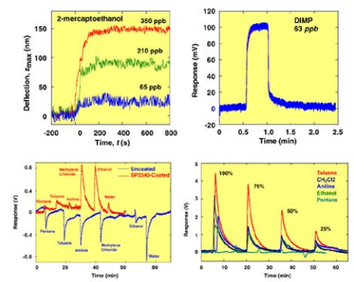
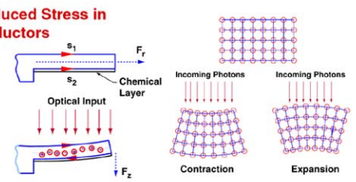


Photo-Induced Stress in Semiconductors



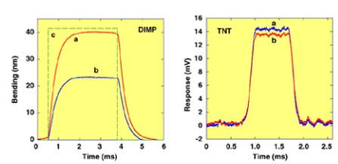
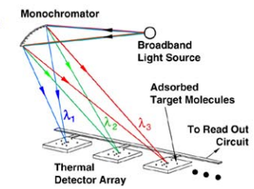


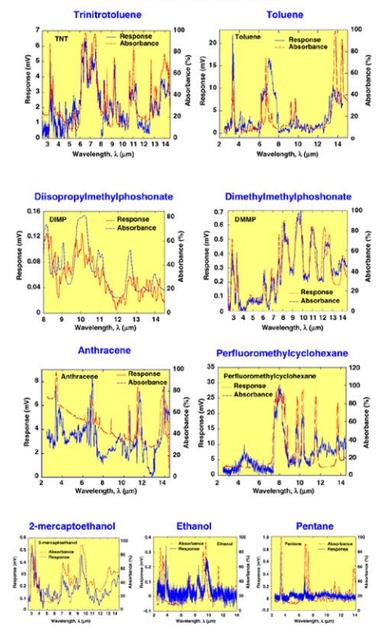
Photo-Induced Deflection of Gold-Coated Si Cantilever Exposed to Analyte

Calorimetric Spectroscopy Concept

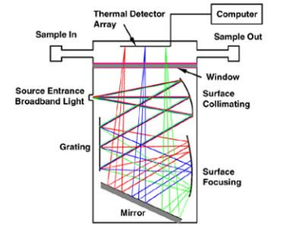
- Target molecules adsorbed on thermal detector surfaces
- Detector surfaces illuminated with discrete wavelengths
- Photons absorbed and excite target molecules on selected detector elements
- Preferential detector element heating produces unique photothermal spectrum



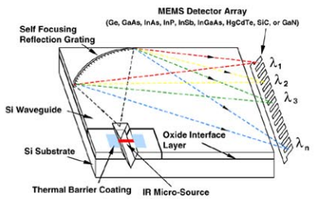
Photothermal Signature



1998 R&D 100 Winning CalSpec



Coin-Sized CalSpec



Summary

- Study the use of chemically-specific coatings and photo-induced stress to enhance the sensitivity of micromechanical thermal detectors for chemicals found in waste tanks.
- Use of photothermal spectra to derive the specificity for model organic and inorganic chemicals.
- Use of a combination of microcalorimetry and microcalorimetric spectroscopy to determine the chemical and radioactive composition of the waste.
- At the end of the project, the proposed detection methods could be adapted into an on-line process analysis tool that can be used in waste remediation efforts.

Future Directions

- Modifying semiconductor MEMS surfaces with nanoscale structural features and chemical selective phases to enhance sensor performance and produce micromechanical sensors with high sensitivity and selectivity.
- Photo-induced responses and photothermal spectra for target chemicals interacting with microstructures modified with nano-structure and receptor phases will obtained.
- Interaction of semiconductor MEMS devices with nuclear radiation (alpha, beta and gamma particles) will be investigated to determine how the geometry and material properties of the microstructure affect such interactions.

Information Access

- P.G. Datskos, "Chemical Detection Based on Adsorption-Induced and Photo-Induced Stresses in MEMS Devices," *Detection and Remediation Technologies for Mines and Minelike Targets IV*, SPIE, **3710**, 344 (1999).
- P.G. Datskos, and I. Sauers, "Detection of 2-mercaptoethanol Using Microcantilevers," *Sensors and Actuators* ***B*** **61**, 75 (2000).
- J. Headrick, M. Sepaniak, S. Alexandratos, and P. Datskos, "Chelating Scintillation Fibers for Measurements of ^{137}Cs," *Anal. Chem.*, in press.
- 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.

ORNL 2000-1148C EFG

IMPARTING CHEMICAL SELECTIVITY TO MICRO-ELECTRO-MECHANICAL-SYSTEMS BASED ON MICROCANTILEVERS

Michael Sepaniak, Thomas Betts, Chris Tipple, Bryan Fagan, Nickolay Lavrik, and Panos Datskos

Department of Chemistry
University of Tennessee
Knoxville, TN 37996-1600

Engineering Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

Objectives of Work

- *Explore methods of immobilizing various chemically selective coatings on MEMS, microcantilever (MC) surfaces.*

- *Study the response characteristics of chemically modified MCs to various analytes of interest.*

- *Physically modify MC surfaces with nano- or micro-structure to increase the available chemical coating for analyte binding and enhance response by magnifying analyte-induced MC bending.*

- *Rationally design macrocycle receptors as chemical phases that provide desirable molecular recognition characteristics using molecular mechanics modeling and synthetic methods.*

- *Conduct detailed evaluation of the analytical figures of merit for chemically modified MC sensors for measuring DOE significant analytes.*

- *Work toward the development of sensor arrays and the implementation of photon absorption modes of analyte measurement.*

Modification of Microcantilever Surfaces for Improved Selective Response

Reagents Phases Under Investigation *(selectivity & improved response)*

- polysiloxane GC phases ✓
- sol gels ✓
- cyclodextrins ✓
- DMBP polymers
- calixarenes

Nano-Structuring Approaches *(general improvement in response)*

- meso-porous sol gels ✓
- Au nano-beads ✓
- silica nano-beads
- amorphous Au (dissolution of Au-Ag alloys)

✓ - reported herein

- see J. Headrick, M. Sepaniak, S. Alexandratos, P. Datkos, "Chelating Scintillation Fibers for Measusrements of ^{137}Cs," *Analytical Chemistry*, in press, Spring 2000 (copies available).

Microcantilever Apparatus

MEMS-Based on microcantilevers, *MC* (see SiNx, ion milled *MC* in Figure 1) can be used for sensing. Analyte induced differential stress Δs can result in deflection (Z) where *n* and *E* are, respectively, the Poisson's ratio and Young's modulus for the substrate, *t* is thickness of the MC and *l* is effective length.

$$Z_{max} = \frac{3l^2 (1 - n)}{Et^2} Ds$$

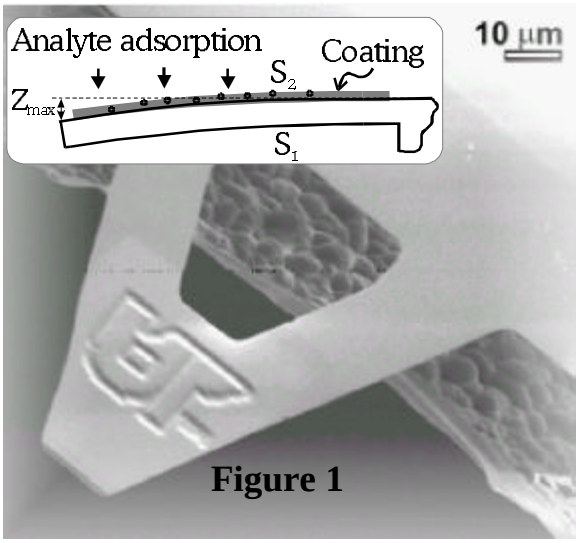


Figure 1

MC deflection (Z_{max}) can be accomplished by using an apparatus as in Figure 2.

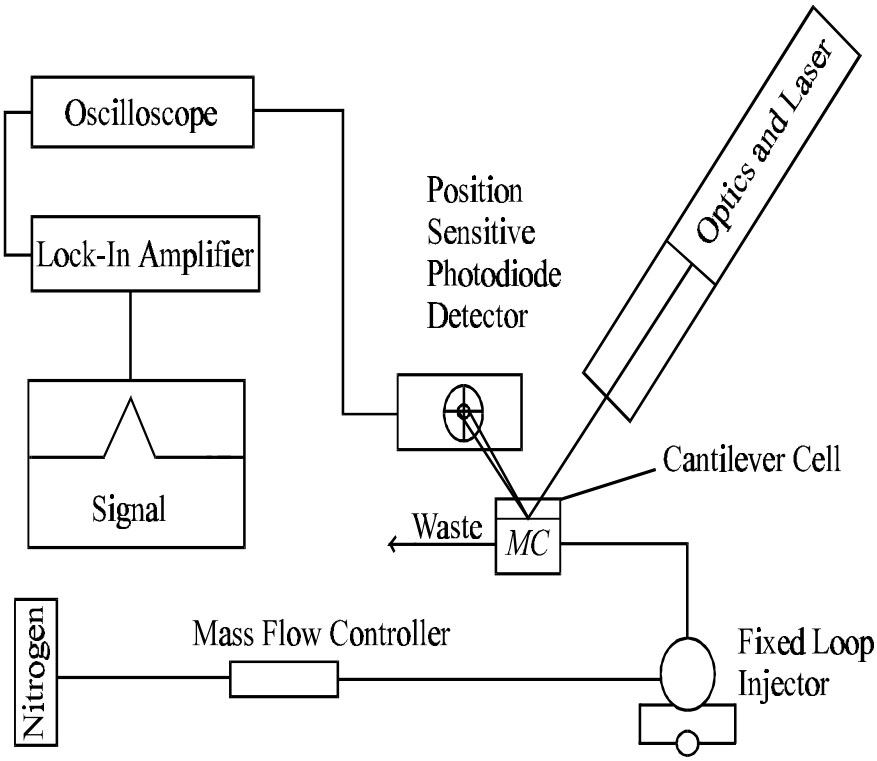


Figure 2

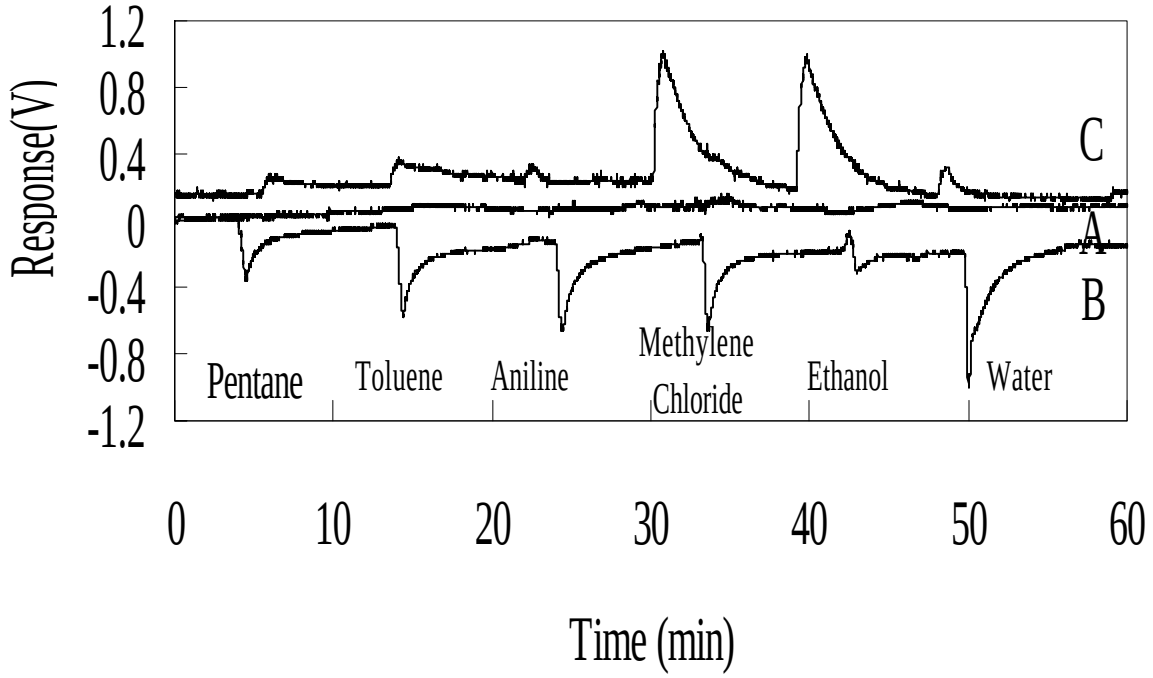
Photograph of SP2340-Coated Cantilever

Details

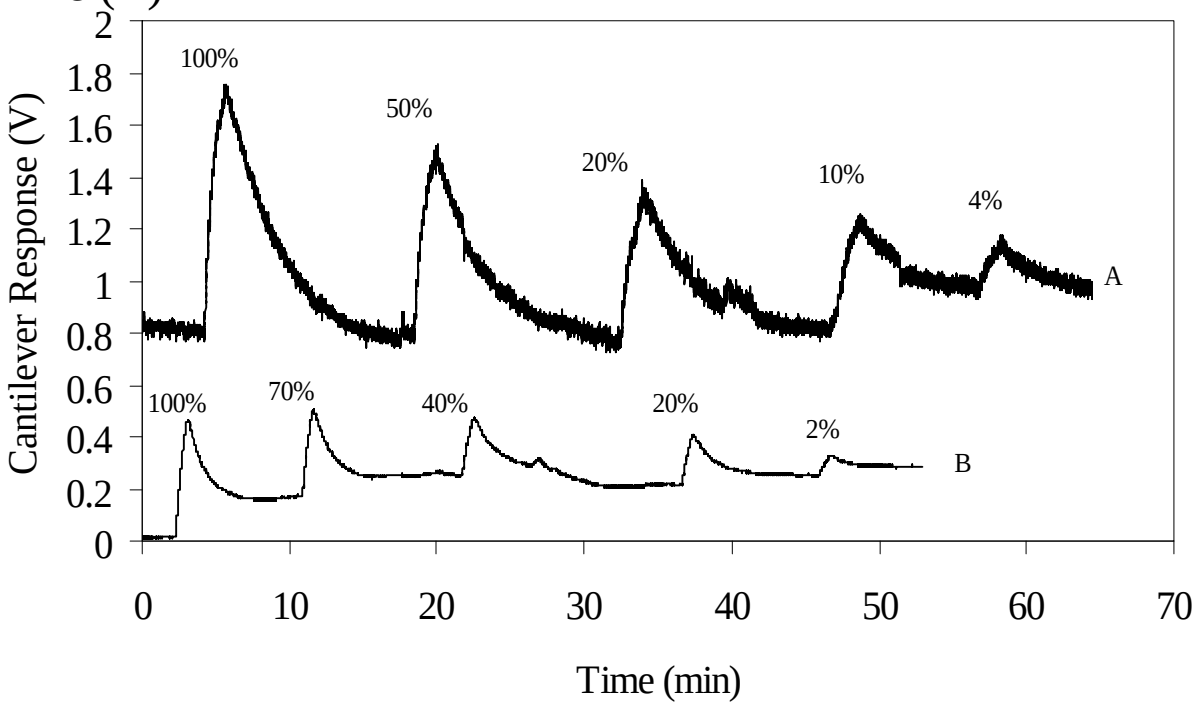
Phase is dissolved in acetone (0.03 – 3.0 w/w%) and spin coated on silicon cantilevers at thickness of ~50-50 nm. The excess phase is removed from backside of cantilever using FIB (the process is in progress in the photo). FIB is also used to reduce the thickness of the silicon from 600 nm as supplied by manufacturer.

Cantilever Responses

Headspace Injections of Chemicals for Blank (A), FIB (B) and SP-2340 Spin Coated (C) Cantilevers



Quantitative Responses to Headspace Dilutions of Ethanol (A) and Aniline (B)



Response Characteristics of MC Normalized to Vapor Pressure

Analyte	Response Factors (maximum signal/vapor pressure) Volts /Atm		
	Uncoated (Trace B)	SP 2340 Coated (Trace C)	*D*
Pentane	-0.54	0.15	0.69
Toluene	-15	4.6	20
Aniline	-690	120	810
$MeCl_2$	-1.0	1.8	2.8
Ethanol	-1.6	11	13
Water	-26	5.5	31

- Blank phase response is similar to adsoption strengths on silica gel.
- The stress caused by absorption of analytes by SP 2340 phase overcomes that by the blank.
- Selectivity for Blank is fairly similar to that for the highly polar SP 2340 phase (the exception is water which is known to strongly adsorb on silica gel).

Effect of Thickness on Response (S/N)

SP 2350 Film

	50	150	400 nm
Ethanol	145	85	35
Aniline	110	40	20

Silicon Cantilever

	460	360	300	260 nm
Ethanol	5	31	85	67
Aniline	-	10	40	24

Response Characteristic Correlate with GC Phase Classification Schemes

	SP 2340	OV 25
	" polycyano "	" polymethylphenyl "

Relative McReynolds Constants for Some Classification Compounds

Butanol (y')	103	87
2-pentanone (z')	90	89
Pyridine (s')	108	120

Note: Values listed above are % of the average constants for the phase.

Signal-to-Noise Ratios for Some Test Analytes

Ethanol	56	24
$MeCl_2$	53	48
Aniline	8	20

Results

The McReynolds constants indicate that SP 2340 will respond better to alcohols than OV 25, whereas the OV 25 is expected to respond better to the base aniline. The $MeCl_2$ (hydrogen bond acceptor with dipole moment) is expected to exhibit similar responses. These trends are generally observed in the listed S/Ns. Thus, GC phase classification schemes may assist in selecting phases for the elements in a sensor array that respond differentially to the chemicals of interest.

Sol-Gel *Process*

Hydrolysis

$$\equiv Si-OR + H_2O \rightleftharpoons \equiv Si-OH + ROH$$

Condensation

$$\equiv Si-OR + HO-Si\equiv \rightleftharpoons \equiv Si-O-Si\equiv + ROH$$

$$\equiv Si-OH + HO-Si\equiv \rightleftharpoons \equiv Si-O-Si\equiv + H_2O$$

Modification of MCs with Sol-Gels To -

- Provide silica gel-based adsorptive sites.
- Increase effective surface area for binding via porous nano-structure.
- Provide silanol sites for covalent attachment of chemically selective reagents.

Sol-Gel Cantilever Preparation

Cantilever Cleaning

Piranha solution (3:1, H_2SO_4:H_2O_2) for $\geq$ 3 hours.

Sol-Gel Preparation

1. 125 µl H_2O
2. 15 µl 0.01 M HCl
3. 250 µl MeOH
4. 300 µl TMOS

Spin Coating Procedure

6 hours into the sol-gel process, 50µl of sol is deposited onto the spinning cantilever holder. The holder is initially spinning at 1500 rpm for 10 seconds, followed by a spin rate of 6000 rpm for 2 minutes to evaporate all remaining solvent. Sol-gel thickness was in the range of 50 – 100 nm.

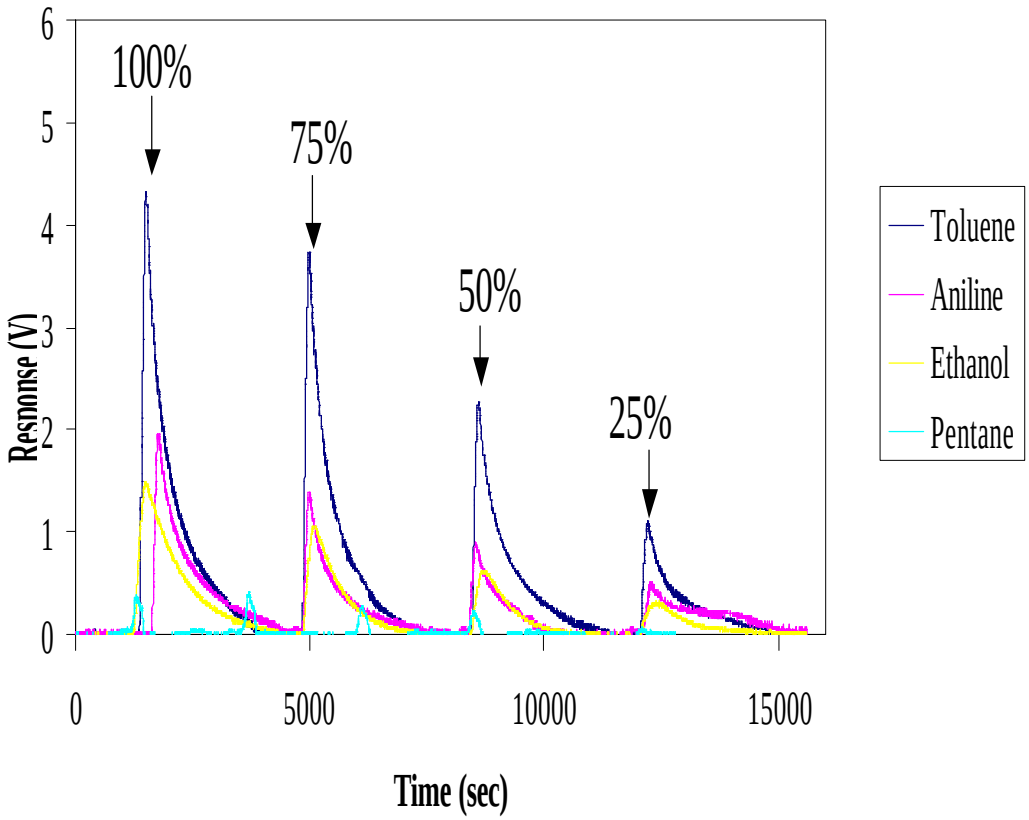
Curing

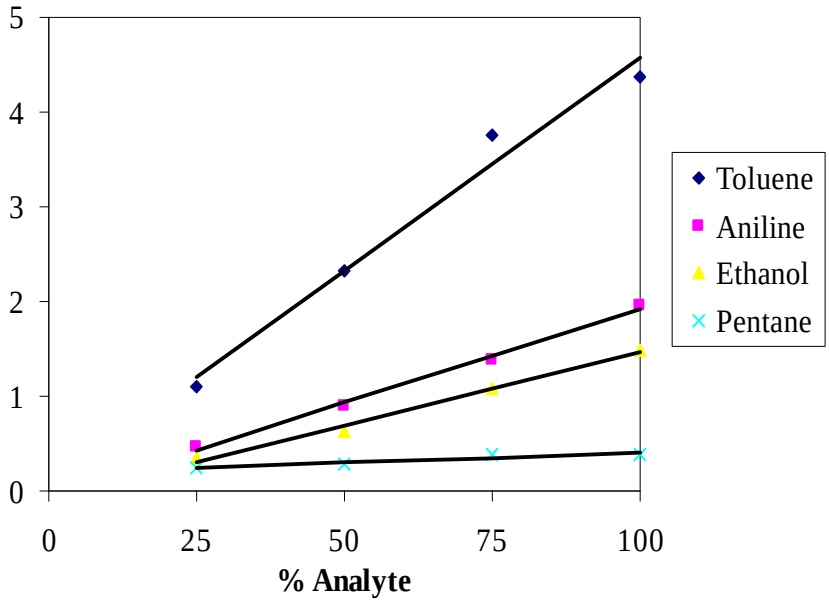
Cantilevers placed in oven at 100 ^{o}C for 12 hours

Aqua Regia Treatment

Cantilevers soaked in HCl:HNO3, 3:1 to remove gold layer and sol-gel on backside

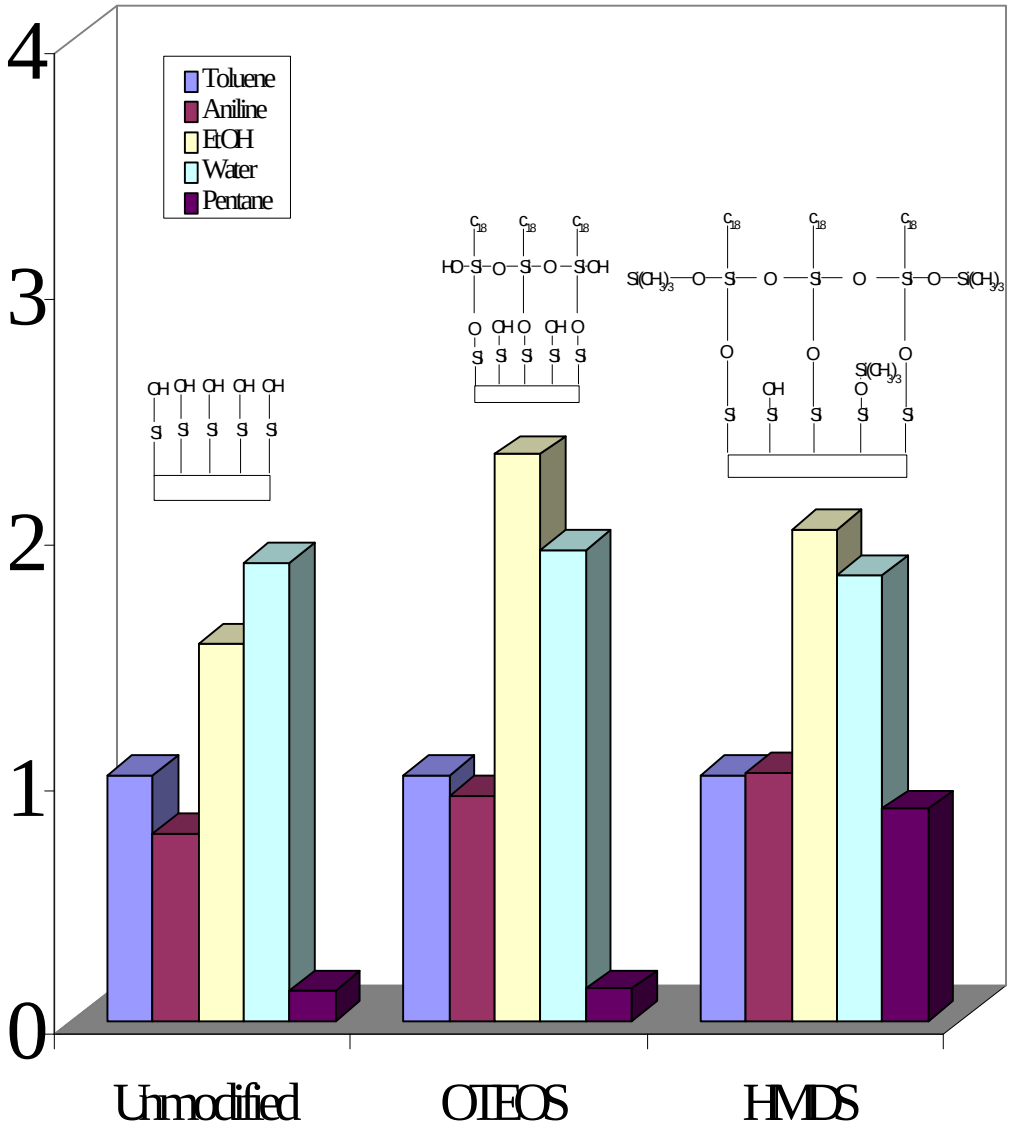
Response of Unmodified Sol-Gel Cantilever to Selected Analytes





- Toluene
  $R^2 = 0.9775$
- Aniline
  $R^2 = 0.9968$
- Ethanol
  $R^2 = 0.9927$
- Pentane
  $R^2 = 0.8857$

Response of Modified Sol-Gel Cantilever to Selected Analytes



Cyclodextrins as Macrocycle Receptor Phases in MC sensing

- Available in native (alpha, beta, and gamma) and many derivatized forms (an excellent reaction platform)
- Apolar cavity for hydrophobic interactions with analytes (shaped somewhat like a tea cup with truncated bottom)
- Polar interactions with secondary hydroxyl (or other functional groups
- Size, shape, and chiral recognition possible
- Can be functionalized at primary hydroxyl sites for immobilization on cantilever surface

Molecular Mechanics Modeling Approach

A grid search method of conducting molecular mechanics modeling is used to systematically probe the interaction space between the solute and the CD with appropriate degrees of freedom and resolution. A program was written for Sybyl 6.5 to incrementally translate and rotate the solute molecule into the cyclodextrin. (Figure 1). The interaction energy can then be used to create a 3-D energy contour plot (Figure 2).

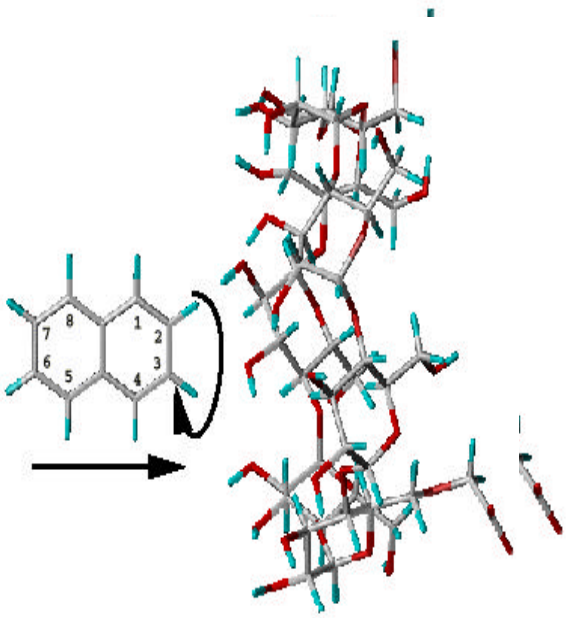


Figure 1 **Figure 2**

Key Objectives:

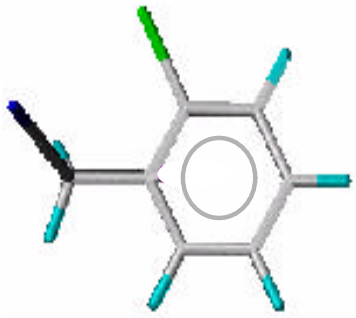
- Correctly find the best conformations of the complex.
- Correctly determine the energies of these conformations.
- Determining the most appropriate way to use this data to determine a representative average interaction energy <*e*>.

$$\langle e \rangle = \frac{S\, g_i\, e_i \exp-(e_i/kT)}{S\, g_i \exp-(e_i/kT)}$$

MicroCantilever Sensors-Modeling

- Mercapto-CDs can be immobilized on gold coated *MCs* to impart tunable selectivity.

- Preliminary MM modeling experiments are being performed to pick suitable CDs for selective *MC* detection of various toxins such as the tear agents shown below. Strategies used to synthesize Mercapto-CDs will be modified based on the MM modeling results.



Bromobenzylcyanide (BBCN)

O-Chlorobenzylmalonitrile (CBMN)

Interaction Energy (kcal/mol)

Solute	**HM-α-CD**	**HDMM-α-CD**	**HM-β-CD**
BBCN:	**-18.79**	**-15.32**	**-17.77**
CBMN:	**-20.09**	**-15.42**	**-18.84**

- As expected the hexakis-2,3-dimethyl-6-mercapto-α-CD, HDMM-α-CD, with the secondary hydroxyl groups of hexakis-6-mercapto-α-CD, HM-α- CD, replaced by methyl groups exhibits less favorable interaction energies in general because of weaker electrostatic interactions.

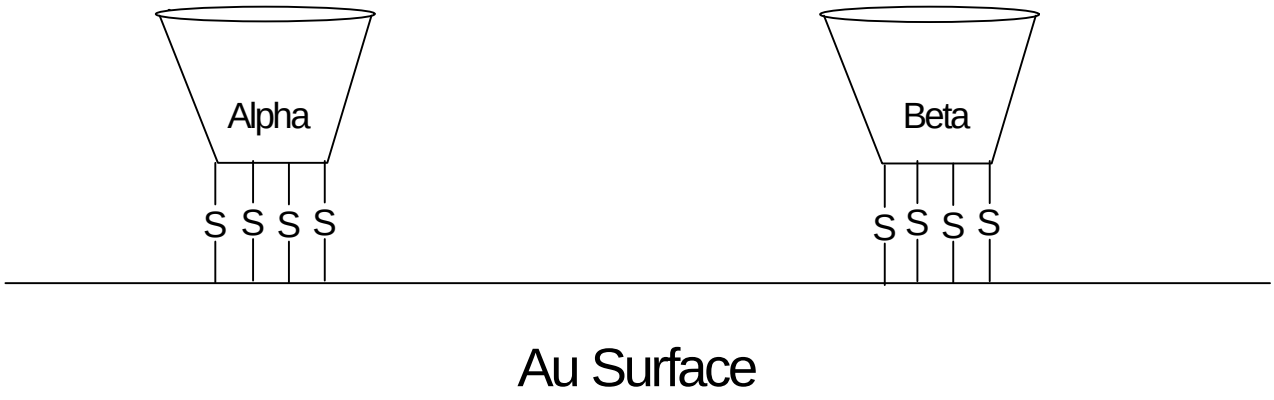
- The CBMN appears to have stronger interactions due to its more electronegative halogen and an additional cyano group.

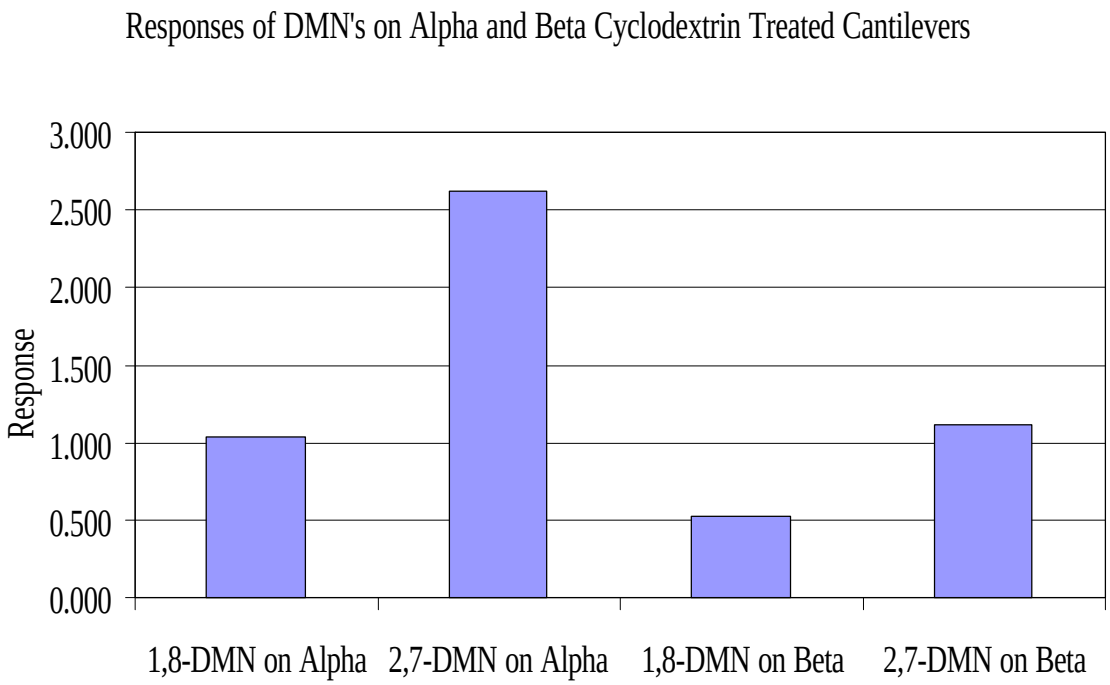
Synthesis of CDs for MC Applications

- Siloxane linkages to silica surfaces
- Thio linkages to gold surfaces

Hexakis-alfa- and heptakis-beta-6-mercapto-CDs have been synthesized

Molecular Recognition Using MCs With Cyclodextrin Receptors

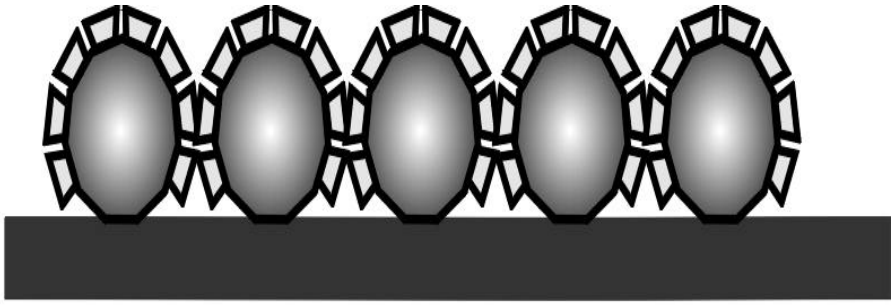




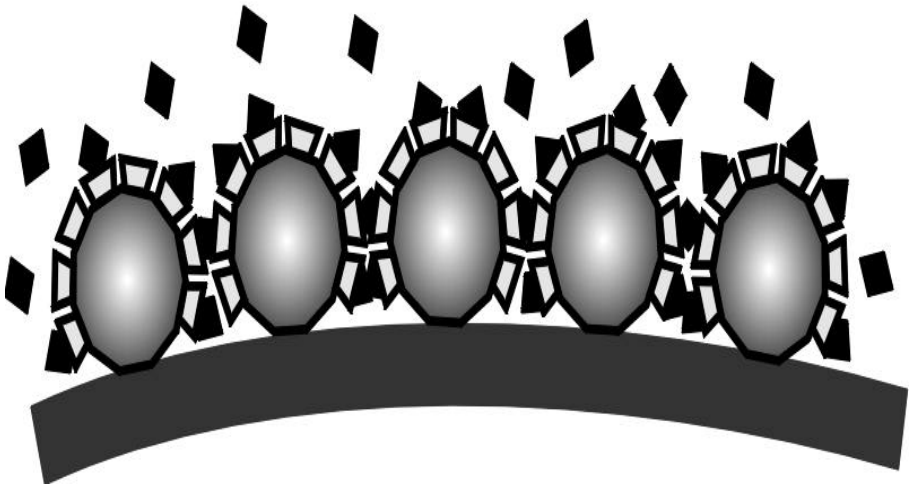
LOD with current non-optimized system is roughly 50 ppb for these DMN analytes

Nano-structuring (with beads) With Aim of Enhancing Analyte-Induced Bending

A.



B.



Depicted above in Figure A is a monolayer of cyclodextrins (⏢) on microbeads attached to *MC* surface. As the solute (◆) is introduced to the sensor in Figure B, stresses are translated to the *MC* surface causing bending which is measured as the signal. SPR results indicate feasibility of this approach.

Acknowledgements

Research was conducted at the University of Tennessee and Oak Ridge National Laboratory and supported by the U.S. Department of Energy, Environmental Management Science Program, Project I.D. Number 65340.