Overview of DR R’s Research Interests

- Environmental analysis of heavy metals in sediments, fish, and other matrices

- Development of methodologies for the determination of methyl mercury in fish and other matrices

- Evaluation of new micro-columns as sample adsorbents and GC columns in lab-on-a-chip designs
Heavy Metals in Sediments and Fish
Several instruments are used for elemental determinations:

- **Graphite furnace atomic absorption spectrometry**
- **Inductively coupled plasma spectroscopy**
- **Automated mercury analyzer** – based on atomic absorption from reduction of mercury via SnCl$_2$ (sub-ppb limits of detection)
The Bioaccumulation of Methylmercury

Biomagnification of Methylmercury in the Ecosystem

Methylmercury Bioaccumulation in Organisms
Gas Chromatography-Atomic Fluorescence Spectroscopy (GC-AFS)
Current research is focused on simply extracting methylmercury as the chloride salt (MeHgCl) and using EtHgCl as an internal standard. Both of these can be separated using GC.

MeHg-R + HCl → MeHgCl

An extraction procedure is being developed for removal of MeHg from tissue by using saturated salt solutions and sonication methods.
SPME – Solid Phase MicroExtraction

- Methodology for coating fibers with new adsorbent (Tenax) for high temperature applications (>300 C) being developed.
- Currently limited by 3 um coating on the fiber. Needs to be 10-50 um to compete with commercially available fibers.
SPME – Solid Phase MicroExtraction

10 ppb PAH Mix in Water

- 100 um PDMS
- 3 um Tenax

Relative intensity

Time (min)

7  8  9  10  11  12  13  14  15

10 ppb PAH Mix in Water
Micro-GC columns and Preconcentrators
Micro-GC and Preconcentrators

- Significant interest in the development of low power micro-instrumentation
- Major obstacles in micro-GC include low sample capacity (for separations) and low breakthrough volumes (for preconcentration of analytes)
- One possible solution is to use columns consisting of nanofabricated columns throughout the primary column channel

This width is comparable to the diameter of a human hair!!!

- Two NSF collaborations with Virginia Tech for which we are responsible for evaluating:
  - Column performance relative to conventional capillary columns for separations using different stationary phases, column coating techniques, and column architectures.
  - Performance of preconcentration adsorbers with respect to breakthrough volumes (sample capacity) using various stationary phases and column geometries.
MEMS (microelectromechanical systems) Column Evaluation

VOC vapor mix

1) Dichloromethane
2) Chloroform
3) Carbon tetrachloride
4) Dibromomethane
5) Toluene
6) Tetrachloroethylene
7) Chlorobenzene
8) p-xylene
9) 1,1,2,2-tetrachloroethane
10) Bromobenzene
Micro-preconcentrators for micro-GC applications
What provides the best medium for maximum adsorption?

~1 cm
Microconcentrator Performance

Toluene Retention

Isopropanol Retention

SNP  Tenax  T&S 1  T&S 2

SNP  Tenax  T&S 1  T&S 2
New column coating technology

In the sol-gel coating method, the surface treatment, deactivation, column coating, and immobilization occur simultaneously, not in individual steps.

Advantages:
Single step process greatly simplifies procedure
Polymer physically bonds to the column walls at active hydroxide sites

Process already available:
<table>
<thead>
<tr>
<th>Materials</th>
<th>Function</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(dimethylsiloxane) (PDMS)</td>
<td>stationary phase polymer</td>
<td><img src="image1.png" alt="PDMS structure" /></td>
</tr>
<tr>
<td>methyltrimethoxysilane (MTMS)</td>
<td>precursor</td>
<td><img src="image2.png" alt="MTMS structure" /></td>
</tr>
<tr>
<td>poly(methylhydrosiloxane) (PMHS)</td>
<td>deactivation reagent</td>
<td><img src="image3.png" alt="PMHS structure" /></td>
</tr>
<tr>
<td>trifluoroacetic acid, 95% (TFA)</td>
<td>catalyst</td>
<td>CF₃COOH</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>solvent</td>
<td>CH₂Cl₂</td>
</tr>
</tbody>
</table>
Separation of Aromatics

Test mix: benzene, toluene, chlorobenzene, xylene in pentane (1 ppthousand by volume)
Temperature: 30°C - 15°C/min - 80°C; Pressure: 5 psi
<table>
<thead>
<tr>
<th>Stationary Phase</th>
<th>Sol-Gel Time (min)</th>
<th>Optimum Pressure (psi)</th>
<th>Theoretical Plates (per meter)</th>
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</thead>
<tbody>
<tr>
<td>DB-5 (standard)</td>
<td>---</td>
<td>7.5</td>
<td>7080</td>
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<tr>
<td>PDMS sol-gel</td>
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<td>5</td>
<td>5840</td>
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<tr>
<td>Ucon sol-gel</td>
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<td>PDMDPS sol-gel</td>
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<td>MEMS-SNP</td>
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