

## Report for 2005NJ87B: Lab-on-a-chip device for monitoring trace level arsenic

### Publications

- Articles in Refereed Scientific Journals:
  - Wang, Xiaoyan, Somenath Mitra. 2006, Enhancing micro-scale membrane extraction by implementing a barrier film, *Journal of Chromatography A* (Article in Press)
  - Wang, Xiaoyan, Dawen Kou, Somenath Mitra, 2005, Continuous, on-line monitoring of haloacetic acids via membrane extraction, *Journal of Chromatography A*, 1089, 39-44
  - Wang, Xiaoyan, Chutarat Saridara, Somenath Mitra, 2005, Microfluidic supported liquid membrane extraction, *Analytica Chimica Acta*, 543, 92-98
  - Wang, Xiaoyan, Somenath Mitra, Development of a total analytical system by interfacing membrane extraction, pervaporation and high-performance liquid chromatography, *Journal of Chromatography A*, 1068, 237-242
- Conference Proceedings:
  - Wang, Xiaoyan, Somenath Mitra, 2005, Microfluidic supported liquid membrane extraction, "Annual Meeting of the American Chemical Society", San Diego, CA
  - Mitra, Somenath, Preconcentration Techniques in Chromatography, 2004, "Lecture at the symposium honoring Harold McNair, Eastern Analytical Symposium" Somerset, NJ

### Report Follows

### Problem and Research Objectives

Manufacturing (e.g. semiconductors and ceramics), agriculture, veterinary medicine and food preservation are some areas in which arsenic (both organic and inorganic) are used. All these lead to the release of the metal into the environment and consequently human contact. Exposure to inorganic arsenic may result in stomach and intestine irritation, skin lesions, nerve injury and increased risk of cancer (skin, bladder, kidney and lung). A recent review by Hung et. al (1) summarizes analytical methods for As monitoring. It reports atomic spectroscopy (e.g. graphite furnace atomic absorption, hydride generation-atomic fluorescence and inductively coupled plasma mass spectroscopy), neutron activation analysis and electrochemical techniques as the most commonly used methods for As monitoring.

Even though these techniques offer low detection limits (below 10ppb), they are expensive, time consuming and do not lend themselves to field or on-line monitoring. The currently available portable field sensors are not necessarily accurate and do not have high accuracy and precision (1). This coupled with the acknowledgement that arsenic's permanence in the environment necessitates long-term routine analysis (2) points to the urgent need for portable devices that allow for fast and reliable measurements. The majority of field instruments depend upon what is known as the Gutzeit method (3) in which a reducing agent is used to produce arsenic trihydride (which is a toxic gas). The lowest detection limits reported by these field instruments is around  $2\text{mgL}^{-1}$  or 2ppm (1).

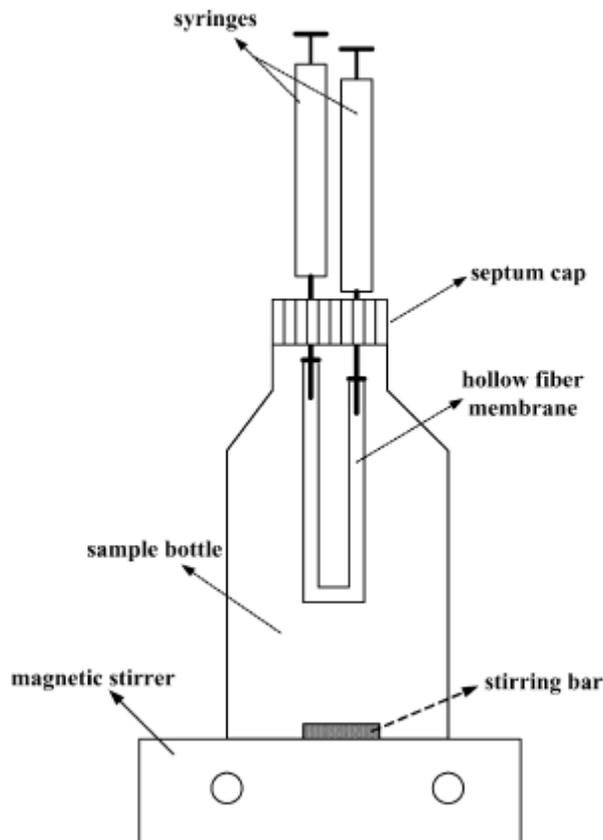
The study aims at the development of a low cost, lab-on-a-chip field instrument that is capable of determining the total inorganic arsenic concentration in water samples in a rapid, continuous, reproducible and accurate manner. The approach also precludes the tedious hydride generation methods used in conventional methodologies. By using a chelating agent and Supported Liquid Membrane Extraction (SLME) on a micro-scale platform, we propose to extract and concentrate As from aqueous samples, thus allowing for faster analysis and lower detection limits. The problem with trace analysis however lies in being able to effectively separate the analyte from complex matrices and achieving low detection limits. If the extraction process is lengthy or if the agitation of the sample (to enhance mass transfer) is forceful, then there may be significant loss of the extractant and consequently the analyte. It is therefore necessary to design the hollow fiber extraction in a manner that minimizes analyte loss and therefore results in good reproducibility and high enrichment.

### Methodology

The first part of the project therefore consisted of the improvement of the hollow fiber membrane extraction process. This was done by coating the membrane with a barrier film. This film was made by soaking the membrane in an organic solvent for a few seconds before extraction. Dihexyl ether, n-undecane, 1-octanol and n-decane were investigated as the barrier solvents. The membrane was held in place by two 50  $\mu\text{l}$  syringes (Hamilton, Reno, NV, USA), one of which was used to inject the acceptor into the lumen and the other for withdrawal of the extract. The PAHs anthracene, naphthalene, fluorene, phenanthrene, pyrene and acenaphthene were used as the analytes. The coated

membrane, filled with acceptor, was placed in a solution of the analytes and stirred (Cimarec 3, Barnstead/Thermolyne, Dubuque, Iowa, USA) for a given time period. At the end of this time, the extract was withdrawn and analyzed using HPLC-UV.

The diagram below illustrates the set-up.



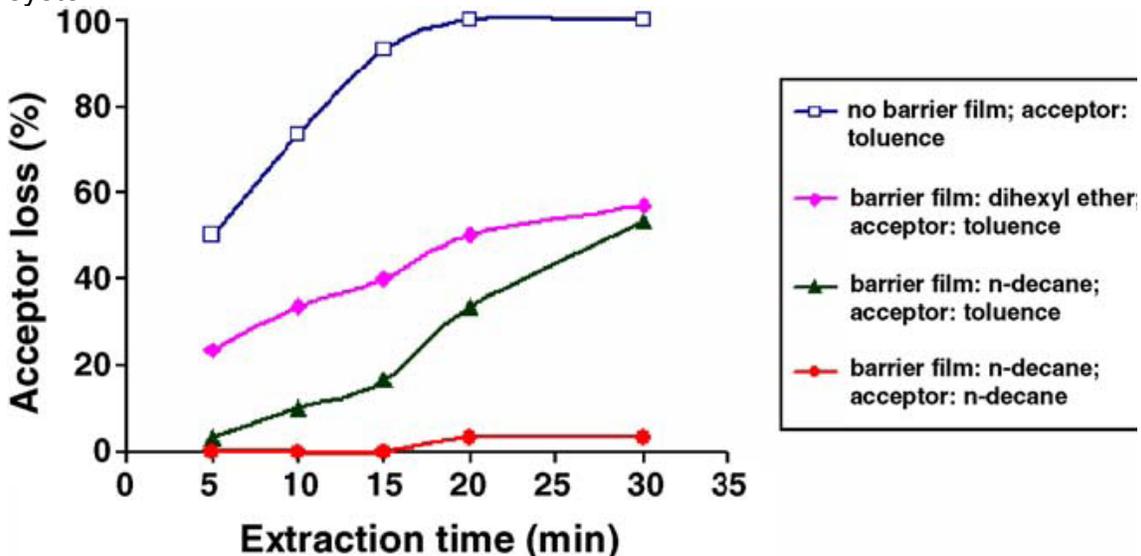
**Figure 1** Schematic diagram of the hollow fiber microextraction assembly.

Using the MiniTech program by Minitex Machinery Corporation, the extraction module (3.5 cm x 4.8 cm) was made by machining channels with a 3-axis (x,y,z) TechDesign Labvolt Milling Machine. 18cm of a polypropylene hollow fiber membrane with an internal diameter of 0.6mm and an average pore size of 0.2 microns (Accurel Q 3/2, Membrana GmbH, Wuppertal, Germany) was then placed in the channels and using syringe pumps, the sample solutions and extractants were pumped through the device for 10 to 30 minutes. Since this is the development stage the optimal flow rate, extraction time and extractant concentrations have not yet been determined. The extract was then collected and concentrations determined using absorption spectroscopy.

### Principal Findings and Significance

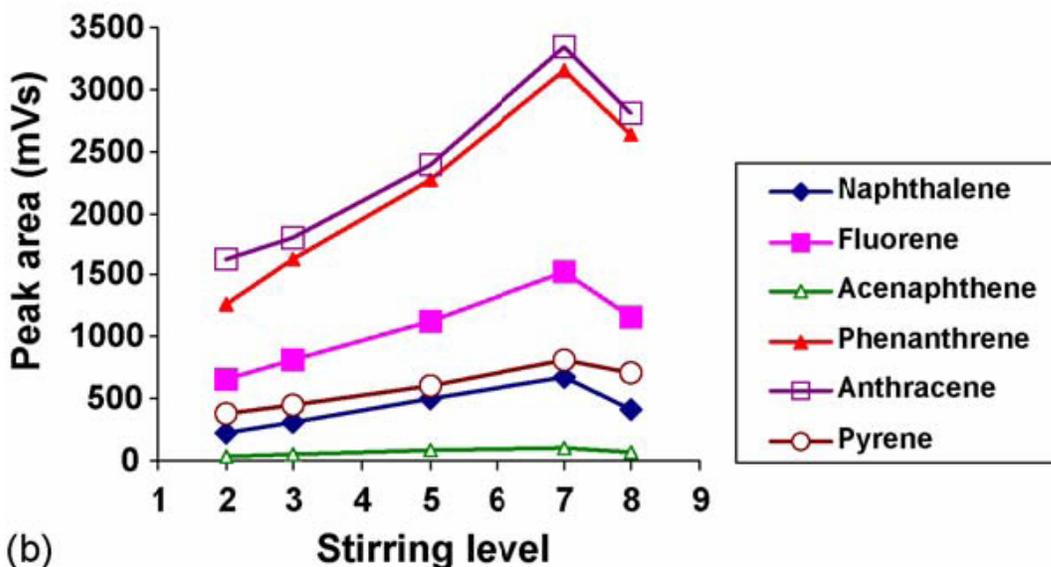
When n-decane was used as the acceptor as well as the barrier film, acceptor loss was minimal and hence enrichment was greatest. This is illustrated in the graph below. For a 20 minute extraction without the barrier film, all the

acceptor was lost compared to the small loss with the n-decane/n-decane system.



**Figure 2** shows acceptor loss as a function of time

Once a suitable acceptor/barrier film combination was chosen, stirring level was investigated to determine its effect on analyte enrichment. Stirring level was varied between 2 and 8 arbitrary units. It was discovered that up to level 7, enrichment was enhanced and so level 7 was chosen as the optimal stirring speed. This is illustrated in the graph below



**Figure 3** illustrates the effect of stirring speed on peak area

The barrier film allowed for stabilization of the acceptor and so longer extraction times could be used which translates into greater enrichment. It also allowed for greater reproducibility and lower detection limits.

**Table 1** shows effect of barrier film on acceptor loss and enrichment factor.

Barrier film	Water solubility (20 °C)	Boiling point (°C)	Enrichment factor						Acceptor loss (%)
			Naphthalene	Fluorene	Acenaphthene	Phenanthrene	Anthracene	Pyrene	
Without barrier film	0.515 g/L <sup>a</sup>	110.6 <sup>b</sup>	nd <sup>c</sup>	67.5	nd	68.0	54.6	76.6	73.3
Dihexyl ether	Insoluble	226.6	nd	164.1	nd	150.3	129.3	175.4	33.3
1-Octanol	Insoluble	194.5	nd	117.9	nd	117.9	77.3	117.6	26.7
<i>n</i> -Undecane	Insoluble	196.0	248.7	120.6	95.6	121.2	87.2	125.9	10
<i>n</i> -Decane	0.009 ppm	174.0	485.6	146.2	185.7	144.0	94.6	158.2	10

<sup>a</sup> Toluene's water solubility.

<sup>b</sup> Toluene's boiling point.

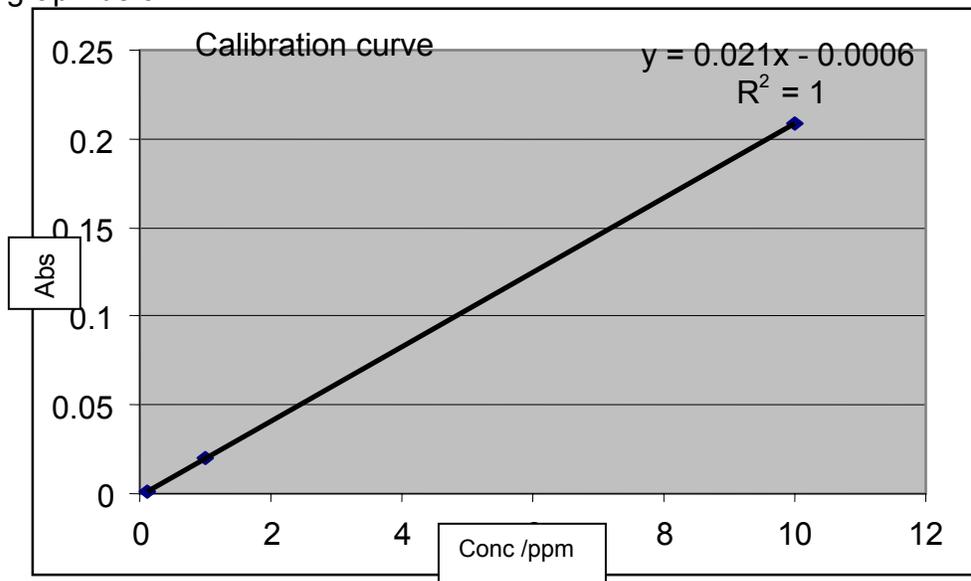
<sup>c</sup> Not detected.

Initial findings indicated that the microfluidic channels are capable of absorbing significant amounts of metals. To verify this, the membrane was removed from the channels and an aqueous sample containing known amounts of a metal was allowed to flow through the channels and the absorbance of the exiting solution measured. The initial concentration of the sample solution was 1ppm.

**Table 2** below illustrates absorption by the microfluidic device by comparing initial and final concentrations.

Initial Conc/ppm	Final concentration/ ppm	Sample Flow Rate /mlmin <sup>-1</sup>	Extractant Flow Rate /mlmin <sup>-1</sup>
1.00	0.22	0.41	0.08
1.00	0.46	0.20	0.05
1.00	0.70	0.43	0.05

The final concentrations were calculated using the calibration equation. See graph below:



The results also indicate that increasing the flow rate of the sample solution leads to an even greater absorption by the polycarbonate device. This could be explained by the fact that the surfaces come in contact with a larger amount of sample in a given time.

In light of these findings, it was decided that an acrylic material coated with silica would be investigated as an alternative. Jack Rundel under the direction of his advisor (Vincent Remcho) at Oregon State University is in the process of coating the microfluidic channels. The material is first cleaned by sonicating it in methanol. It is then blow dried with nitrogen and then a RF sputtering system is used to deposit a thin silica film with a thickness of about 500nm. Once this is in place, we will then focus on optimizing the method to extract, concentrate and detect arsenic. Sodium m-arsenite and sodium arsenate dibasic heptahydrate will be used to make standard As(III) and As(V) solutions. Dibutylphosphonate(DBP) and tributylphosphate(TBP) will be investigated as possibilities for the supported liquid membrane. To allow for valid comparisons with our detection module we will first use GFAAS to quantify the arsenic. When it is determined that significant extraction and enrichment is being achieved, the detection module will then be coupled to the extraction module to determine its effectiveness.

### References

1. Hung, D.Q., Nekrassova, O., Compton, R. G. *Talanta* 64(2004) 269-277
2. Melamed, D. Monitoring Arsenic in the Environment: A Review of the Science and Technologies for Field Measurements and Sensors. EPA 542/R-04/002
3. Kinniburgh, D.G., Kosmus, W. *Talanta* 58 (2002) 165–180