

Underwater Mass Spectrometry for *in situ* monitoring of Polar and Non-Polar Molecules.

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Introduction

Underwater Mass Spectrometry (UMS) is in a relatively early stage of evolution. This is particularly true of one of the most technically challenging components of UMS instruments, the mass introduction system. The mass introduction systems developed for UMS at the Center for Ocean Technology are currently configured with dimethyl polysiloxane (PDMS) membranes. Though the configuration of these membranes is simple and they provide very low detection limits, they are limited by their selective permeation of gases and non-polar, volatile organic compounds. Improvements in our UMS analyte introduction systems are currently being pursued through use of sorbent trapping procedures similar to those used for in-tube Solid Phase Microextraction (SPME). Extraction via SPME occurs as sample (seawater) is continuously pumped through nickel tubing that is lined internally with PDMS or trifluoropropylmethyl polysiloxane (TFP). Extracted compounds can then be thermally desorbed into the UMS vacuum chamber through a short gas chromatograph (GC) column. Varying the type of sorbent lining on the inner surface of the Ni tubing allows for the detection of large and small organic molecules of polar and non-polar nature.

Experimental

A Saturn 2000 Ion trap GC/MS has been modified for preliminary testing of the mass introduction system design. Two VICI Cheminert valves, shown on the left of figure 1, control the flow of various fluids through the sorbent trap, seen in the center of the photo. A peristaltic pump is used to pull the sample through the sorbent traps and a rotameter is used to monitor the flow of carrier gas. The sorbent trap shown in this figure was generously donated by the VICI Gig Harbor Group. The Saturn ion trap sits in the background.

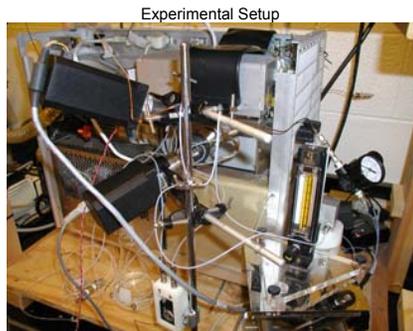


Figure 1. The bench top Saturn 2000 Ion Trap GC/MS shown here is being used for preliminary tests on the new introduction system. An identical ion trap has been packaged for underwater mass spectrometry using a membrane inlet.

The sorbent trap shown in figure 1 consists of Ni tubing lined internally with a hydrophobic monolayer of methyl groups, which, in turn is coated with several microns of TFP. Ni tubing was chosen for its inertness, durability, and thermal and electrical conductivity. Thermal desorption of extracted compounds was effected using a Thermocoax Ni heating wire and an Omega programmable temperature controller (not shown). A relatively large tubing inside diameter was chosen to preclude clogging under high particulate loading. Each of these components are controlled remotely through a Labview interface (figure 2).

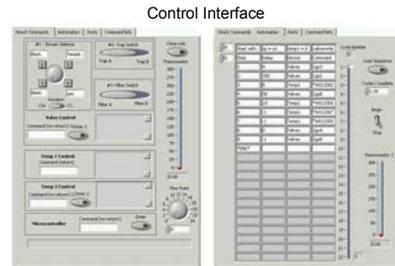


Figure 2. A screenshot of the Labview interface. The interface is designed to allow for direct and automated remote control of three valves, two temperature controllers and a microcontroller board. The microcontroller board also operates a variety mass spectrometer components.

A schematic of the system is shown in figure 3. There are several aspects to the design that allow for flexibility and functionality in diverse applications. Several available inlet ports on the stream selector valve permit the use of standards, blanks and additional reagents. An eight port two-way valve permits the use of a selection of sorbent traps, two at a time. The schematic also depicts use of a deactivated capillary as a transferline into the vacuum chamber; however, the most recent version replaces the deactivated capillary with a short GC column. Finally, an additional capillary restricts the flow of the carrier gas into the sorbent trap, whereupon a vacuum at ca. 200 Torr can be sustained within the sorbent trap. This vacuum is beneficial for several reasons: 1) low pressure promotes complete desorption of analytes, 2) at low pressure the sorbent trap can be effectively flushed with minimal carrier gas, and 3) at low pressure a high speed chromatograph is produced at optimum efficiency¹. A flushing gas is used to remove seawater from the sorbent trap prior to thermal desorption and transmission of analytes through the GC capillary.

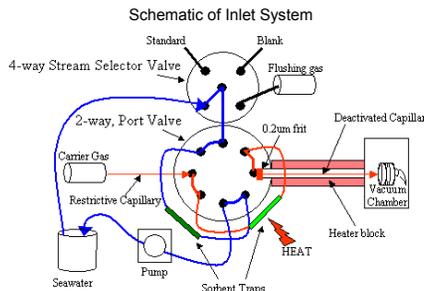


Figure 3. The inlet system is similar to that of in-tube SPME processes, analytes are adsorbed on the internal surface of the coated Ni tubing.

Results

Caffeine can be used as a chemical tracer of anthropogenic contaminants in the marine environment². As a non-toxic, stable, and polar molecule, caffeine is a useful analyte for assessing our system's ability to detect large polar compounds. The spectrum shown in figure 4 demonstrates the potential of our introduction system for detecting polar molecules. The spectrum can be compared to that obtained from the National Institute of Standards and Technology (NIST) database for caffeine (figure 5).

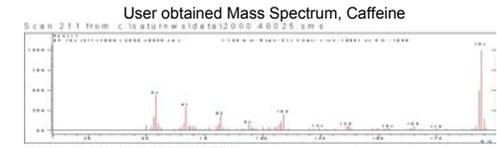


Figure 4. Caffeine spectrum obtained using the setup seen in figure 1. The sample, 100 ppm caffeine in deionized water, was extracted for 3min at a flow rate ca. 4mL/min. Complete thermal desorption took place in less than 3 minutes for temperatures between 100 °C – 200°C.

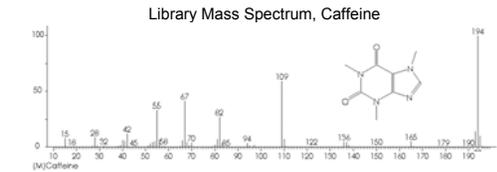


Figure 5. Caffeine spectrum obtained from the NIST database.

Future Work

Work in the coming months will involve trials over a range of concentrations, temperatures, pressures, and salinities. Inlet system parameters such as flow rate, extraction time, adsorption/desorption temperatures, coating thickness, and coating type will be optimized. Subsequent to optimization, the inlet system will be incorporated into an existing underwater mass spectrometer.

Developments in future will include the use of solvent desorption integrated with liquid chromatography and a nanospray interface.

Conclusions

Recent field investigations utilizing underwater mass spectrometer systems have demonstrated the versatility and sensitivity of underwater mass spectrometry. An improved analyte introduction system will allow UMS applications to expand beyond dissolved gases and non-polar molecules, and will allow for the pre-concentration of many suites of compounds that are as yet undetectable *in situ*.

References

- [1] "Theoretical and Practical Aspects of Short Open Tubular Columns at Subambient Pressures in Gas Chromatography/Mass Spectrometry", M. E. Hail, R. A. Yost, Analytical Chemistry. 1989, 61, p 2402.
- [2] "Caffeine in Boston Harbor seawater", R. Siegener, R. F. Chen, Marine Pollution Bulletin. 2002, 44(5), p 383-387.

Acknowledgements

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