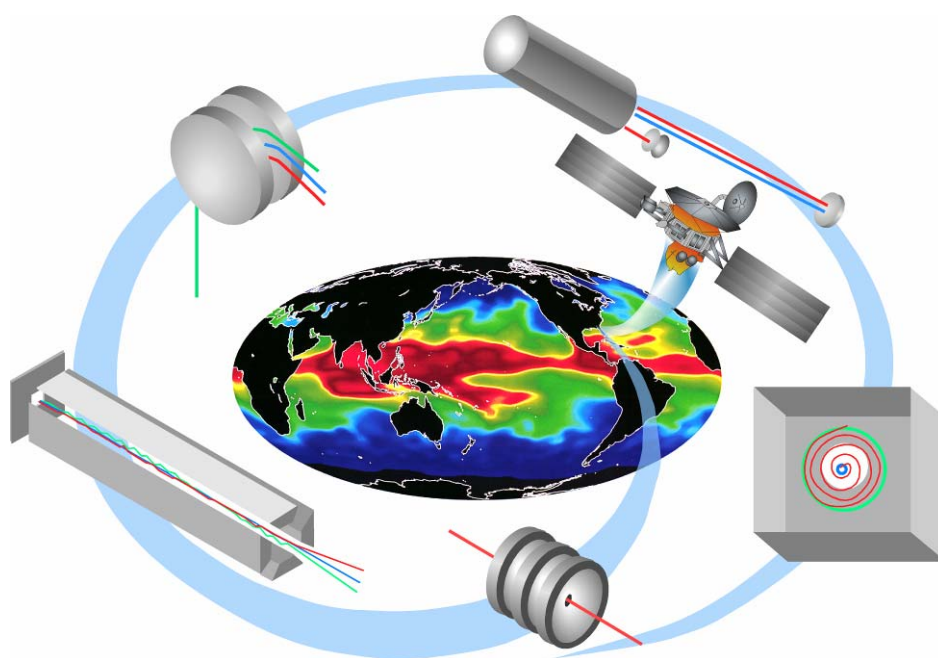


The 6th Workshop on Harsh-Environment Mass Spectrometry

Cocoa Beach, Florida

17 – 20 September 2007



Workshop at a Glance

Monday, 17 September

7:00 – 11:00 pm Welcome Reception (Tiki Lawn)

Tuesday, 18 September

7:30 am Continental Breakfast (Manatee Room)

8:30 am Welcoming Remarks

9:00 am – 12:00 pm Technical Session: Instrumentation – Novel MS Designs

12:00 – 1:30 pm Lunch (Dolphin Room)

1:30 – 3:00 pm Poster Session (Manatee Room)

3:00 – 4:30 pm Technical Session: Field Applications – Land & Space

4:30 pm Evening Free

Wednesday, 19 September

7:30 am Full Breakfast (Dolphin Room)

9:00 am – 12:15 pm Technical Session: Field Applications – Water

10:30 am Group Photo (Stairway)

12:15 – 2:30 pm Lunch on your own

2:30 – 4:30 pm Technical Session: Instrumentation – Interfaces

6:00 pm Catch Bus to Dinner (Meet in Lobby)

7:00 – 10:30 pm Dinner (Kennedy Space Center – Visitor Complex)

4:30 pm Evening Free

Thursday, 20 September

7:30 am Continental Breakfast (Manatee Room)

8:30 am – 11:30 pm Technical Session: Instrumentation – Miniaturization

WELCOME

On behalf of the Organizing Committee, we are pleased to welcome you to the 6th Workshop on Harsh-Environment Mass Spectrometry (HEMS), Cocoa Beach, FL, September 17-20, 2007.

In situ mass spectrometry (MS) in a wide variety of harsh environments - from outer space to Earth's oceans to battlefield scenarios – is rapidly becoming a reality. There are many common features to MS deployment in these vastly different conditions, including high reliability, small size, and low power requirements. The Harsh-Environment MS Workshop series was established to encourage interaction among those involved in the various aspects related to deployment of mass spectrometers in harsh environments.

Talks and posters for the Harsh-Environment MS Technical Sessions have been selected primarily for their focus on making mass spectrometer components and systems rugged and portable; interfacing mass spectrometers to the environment; autonomous sampling strategies; unattended operations; adaptive sampling; data processing and communications; enabling technologies; and miniaturization.

We have created a full program but each talk will include time for questions and brief discussion. Our goal is to engage the Workshop participants and stimulate thinking about both current developments and future needs in these rapidly developing areas.

This Proceedings folder has been designed as a working tool for easy note taking and post-workshop reference. Thank you for joining us, and we look forward to your participation.

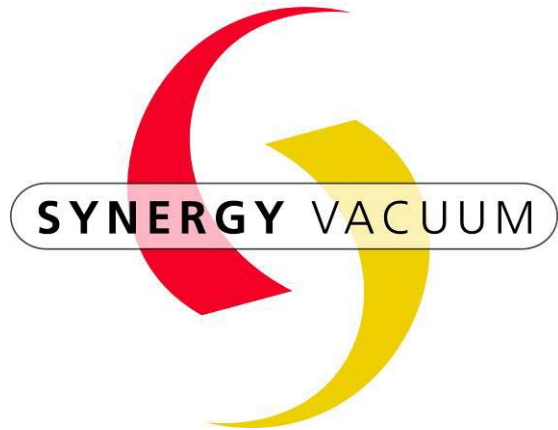
Hosted by ASRC Aerospace Corporation



A Special Thanks to our Sponsors



A Special Thanks to our Sponsors



A Brief History of the HEMS Workshop

The Harsh-environment Mass Spectrometry (HEMS) Workshop was created in 1999 as a means of encouraging interaction among people involved in deploying mass spectrometers outside of the typical laboratory setting. These environments are diverse, ranging from volcanoes and battlefields, to ocean depths, outer space and other rugged locales. Building mass spectrometers to withstand the rigors of such harsh and remote environments places a unique burden on engineering design and science objective planning, where operational requirements for power, size and durability must be met while achieving the goals of the scientific mission. We hope to foster and promote interaction between scientists and engineers through the informal setting of the HEMS Workshop and thus stimulate the development of HEMS technology and applications.

Our History

1st Workshop on Harsh-Environment Mass Spectrometers

February 21–23, 1999; St. Petersburg, Florida

Sponsored by the University of South Florida, Marine Science Department, Center for Ocean Technology

2nd Workshop on Harsh-Environment Mass Spectrometry

March 18–21, 2001, St. Petersburg, Florida

Presented by the University of South Florida, Marine Science Department, Center for Ocean Technology

The 3rd Harsh-Environment Mass Spectrometry Workshop & The 2nd NASA/JPL Miniature Vacuum Pumps Workshop

March 25–28, 2002, Pasadena, California

Presented by the Jet Propulsion Laboratory/NASA

The 4th Harsh-Environment Mass Spectrometry Workshop

October 7–10 2003, St. Petersburg Beach, Florida

Presented by the Center for Ocean Technology,
University of South Florida College of Marine Science

The 5th Harsh-Environment Mass Spectrometry Workshop

September 20–23 2005, Lido Beach, Sarasota, Florida

Presented by the Center for Ocean Technology,
University of South Florida College of Marine Science

The 6th Harsh-Environment Mass Spectrometry Workshop

September 17–20, 2007, Cocoa Beach, Florida

Presented by the ASRC Aerospace Corporation, Kennedy Space Center

Workshop Dinner

Debus Center – Kennedy Space Center – Visitor Complex

The traditional workshop dinner will be held at the Debus Center at Kennedy Space Center's Visitor Complex. While there we will be able to see several artifacts from NASA space programs as well as mingle in the Rocket Garden.



Travel back in time and history in the newly re-developed Rocket Garden. Here you can experience the very same Redstone, Atlas and Titan rockets that first put NASA Astronauts in space. Mercury, Gemini and Apollo capsules give an idea of the cramped quarters America's Astronaut pioneers endured. Dramatic new lighting brings these historic rockets back to life with an adventurous and patriotic scheme, highlighting each fuselage with brilliant white uplight, bathing the site with techno-blue accents and heating the engines with flickering red-orange light. This lighting restores these rockets to historic brilliance, and presents them in dramatic context that captures their "blast-off" glory.

For those interested in visiting the visitor's complex go to <http://www.kennedyspacecenter.com/visitKSC/index.asp>

Cocoa Beach / Cape Canaveral Restaurants:

Indian:

Punjab	321-799-4696	285 W. Cocoa Beach Cswy. (520)
--------	--------------	--------------------------------

Thai / Sushi:

Siam Orchid		1275 N. Atlantic Ave.
Thai Thai III	321-784-1561	8660 Astronaut Blvd.

Japanese:

Tokyo Japanese Steakhouse	321-799-0058	5840 N. Atlantic Ave
---------------------------	--------------	----------------------

French/Continental:

The Mango Tree	321-799-0513	118 N. Atlantic Ave.
----------------	--------------	----------------------

Chinese:

Yen Yen	321-783-9512	2 N. Atlantic Ave.
---------	--------------	--------------------

Cuban:

Roberto's	321-784-18668	26 N. Orlando Ave
-----------	---------------	-------------------

BBQ:

Slow & Low	321-783-6199	306 N. Orlando Ave.
------------	--------------	---------------------

Waterfront Dining:

Cocoa Beach Pier	321-783-7549	401 Meade Ave.
Coconuts	321-784-1422	2 Minutemen Cswy.
Lobster Shanty	321-783-0312	2200 S. Orlando Ave.
Grills Seafood /Tiki Bar	321-868-2226	Port Canaveral
Fishlips Bar & Grill	321-784-4533	Port Canaveral

Cocoa Beach / Cape Canaveral Bars:

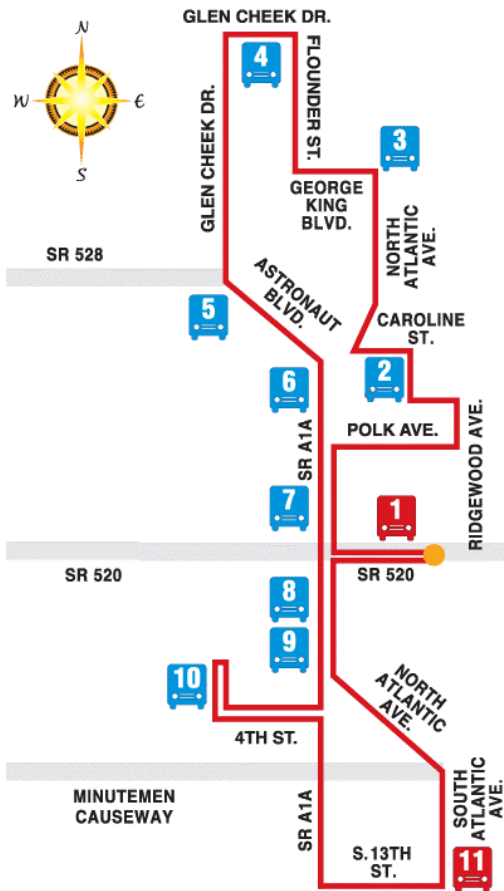
Jonathan's Pub (local dive / fresh squeezed drinks)	321-783-9368	140 N. Brevard Ave
---	--------------	--------------------

Coconuts (on the beach)	321-784-1422	2 Minutemen Cswy
----------------------------	--------------	------------------

Beach Shack Blues Bar (on the beach)	321-783-2250	1 Minutemen Cswy *Directly across from Coconuts
---	--------------	--

Paddy Cassidy's (Irish Pub / free wi-fi)	321-783-0810	2011 N. Atlantic Ave.
---	--------------	-----------------------

**** Port Canaveral is home to several bar/grills and is an after hours hot spot ****



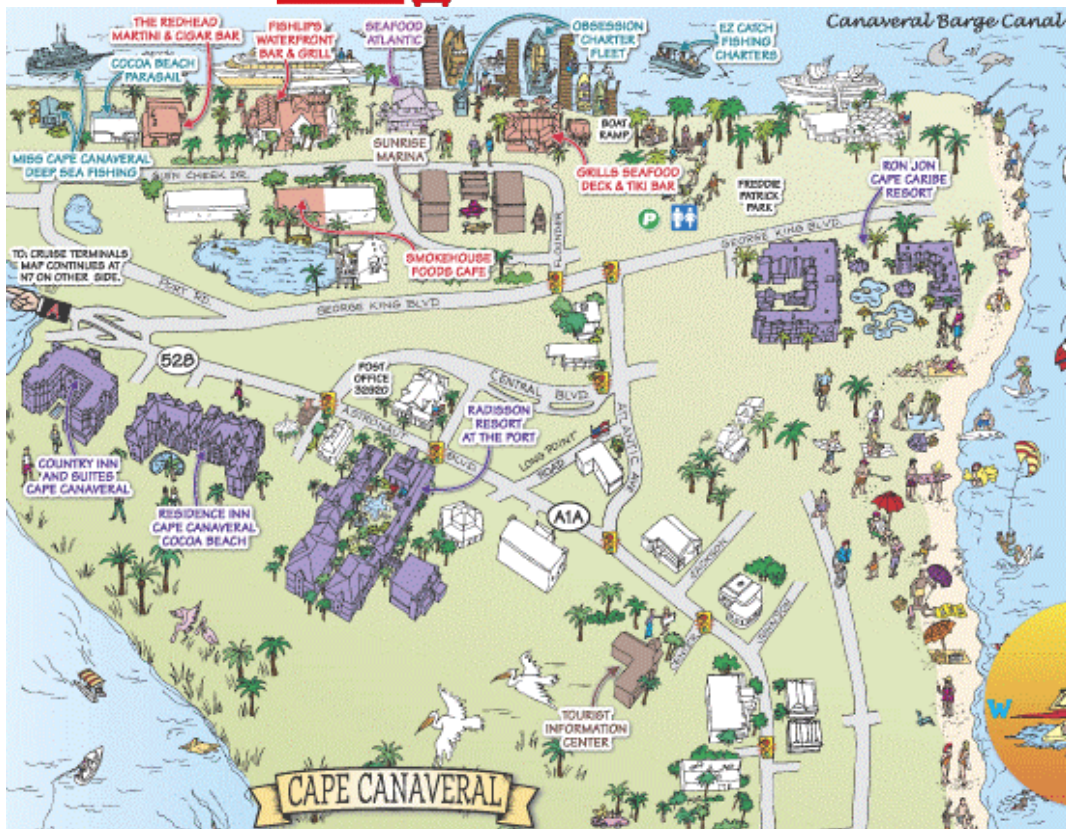
Beach Trolley

Beach trolleys are buses designed to look like trolleys. The service runs from Port Canaveral to 13th Street in Cocoa Beach. A ride on the trolley costs just \$1.25 with a special rate of .60 for seniors, veterans, disabled and students. There is no charge for children under five or for transfers to fixed route bus service. Bikes and surfboards are welcome.

Trolleys run from ~ 6:00 am to ~ 11:00 pm.

For bus information cal 321-633-1878

For detailed schedule information go to:
<http://routefinder.ridescat.com>



Tuesday 18 September

- 7:30 **Continental Breakfast, Manatee Ball Room**
- 8:30 Welcoming Remarks
- 9:00 **Technical Session I: Instrumentation – Novel MS Designs**
- 9:00 "Novel Ion Traps using Planar Resistive Electrodes: Implications for Miniaturized Mass Analyzers"
Daniel Austin, Brigham Young University
- 9:30 “The Gated Electrostatic Mass Spectrometer”
Fred A. Herrero, NASA Goddard Space Flight Center
- 10:00 **Mid-morning Break**
- 10:30 "MEMS Assembled Ion Optical Devices: Current Technology and a Look at Advantages and Disadvantages”
Guido F. Verbeck IV, University of North Texas
- 11:00 “A Single Chip Mass Spectrometer in MEMS Technology”
Jan-Peter Hauschild, Hamburg University of Technology
* Student Travel Award Recipient
- 11:30 “A Microfabricated Cylindrical Ion Trap Array for Batch Production of Small Chemical Sensors”
Friso van Amerom, University of South Florida and SRI International
- 12:00 **Workshop Lunch, Dolphin Room**
- 1:30 **Poster Session, Manatee Ball Room**
- 3:00 **Technical Session II: Field Applications – Land & Space**
- 3:00 “Development of Miniature Mass Spectrometry for In-Situ Characterization of the Environment”
Frants R. Lauritsen, University of Copenhagen
- 3:30 “The Development of a Vector Neutral Spectrometer for Space Environment Measurements”
Erik Syrstad, Space Dynamics Laboratory
- 4:00 “Mass Spectrometer-based Instrument for Volcanic Gas Monitoring”
Gary M. McMurtry, SOEST, University of Hawaii
- 4:30 **Evening Free**

Wednesday 19 September

- 7:30 **Full Breakfast, Dolphin Room**
- 9:00 **Technical Session III: Field Applications – Water**
- 9:00 “Field Testing of the Nereus Network”
Harry Hemond, MIT
- 9:30 “Short-term Oxidation-Reduction Processes within a Hypoxic Estuary, Using
an In Situ Mass Spectrometer”
Itziar Tueros, AZTI-Tecnalia, Marine Research Division
- 10:00 **Group Photo (Stairway)**
- 10:15 **Mid-morning Break**
- 10:45 “Underwater Mass Spectrometry: Developments and Calibration”
Ryan J. Bell, SRI International
- 11:15 “Application of the In-Spectr 200 Membrane Introduction Mass Spectrometer
for Measurements of Methane in Lake Constance (Germany) and the Western
Baltic Sea”
Michael Schlueter, Alfred-Wegener-Institute for Polar and Marine Research
- 11:45 “Mass Spectrometer for Mars Phoenix Lander”
John H. Hoffman, University of Texas at Dallas
- 12:15 **Lunch on your own**

Wednesday 19 September

2:30 Technical Session IV: Instrumentation – Interfaces

2:30 “Thermal Desorption Inletting for Portable Mass Spectrometer”
Stuart Cairns, DSTL

3:00 “Implementation of DART and DESI Ionization of a Fieldable Mass
Spectrometer”
Mitch Wells, ICx Griffin Analytical

3:30 “Characterization of a Multi-Port Inlet on a Rugged Mass Spectrometer”
Garth Patterson, ICx Griffin Analytical

4:00 “Mini 11 Handheld Mass Spectrometer with Glow Discharge Ion Source and
Atmospheric Pressure Interface”
Liang Gao, Purdue University Department of Chemistry

4:30 **Free Time**

6:00 pm Workshop Dinner Activities

6:00 pm Meet to Catch Bus for Workshop Dinner (Holiday Inn Lobby)

7:00 pm Dinner (Debus Center at Kennedy Space Center Visitor Complex)

10:00 pm First Bus Leaves from Dinner (Debus Center)

10:30 pm Last Bus Leaves from Dinner (Debus Center)

Thursday 20 September

- 7:30 **Continental Breakfast, Manatee Ball Room**
- 8:30 **Technical Session V: Instrumentation – Miniaturization**
- 8:30 Evaluation of Commercial Mass Spectrometers for NASA Applications
J. Andres Diaz, University of Costa Rica
- 9:00 “Quadrupole Miniaturization: Measured Performance for Different Size
Quadrupoles”
Randall Pedder, Ardara Technologies L.P
- 9:30 “Miniature High Vacuum Pumps for Analytical Instruments”
Robert Kline-Schoder, Creare, Inc.
- 10:00 **Mid-morning Break**
- 10:30 “Hand-Portable GC-TMS Instrument for Measurement of Chemical Agents
and Hazardous Compounds in Harsh Environments”
Douglas W. Later, Torion Technologies
- 11:00 “Development of a Palm Portable Mass Spectrometer”
Mo Yang, SamYang Chemical Co.
- 11:30 **Workshop Ends**

Presentation

&

Poster

Abstracts

Novel Ion Traps using Planar Resistive Electrodes: Implications for Miniaturized Mass Analyzers

Daniel Austin¹, Ying Peng¹, Miao Wang¹, Milton Lee¹, Aaron Hawkins¹, Samuel Tolley²,

¹Brigham Young University, C-310 BNSN, Provo, Utah

²Torion Technology, Inc.

In radiofrequency ion traps, electric fields are produced by applying time-varying potentials between machined metal electrodes. The electrode shape constitutes a boundary condition and defines the field shape. We have developed a new approach to making ion traps in which the electrodes consist of two ceramic discs, the facing surfaces of which are lithographically imprinted with sets of concentric metal rings and overlaid with a resistive material. A radial potential function can be applied to the resistive material such that the field between the plates is quadrupolar, and ions are trapped between the plates. The electric field is independent of geometry, and can be optimized electronically, or even changed while ions are trapped or between segments of a scan. Preliminary data demonstrate ion formation, trapping, and mass analysis.

This design has some advantages that make it an attractive choice for miniaturization. Obstacles to miniaturization of ion traps include fabrication tolerances, surface smoothness, alignment, limited access for ionization or ion injection, limited stopping distance for trapping externally-injected ions, small trapping volume, and device capacitance—especially for arrayed devices. This trap solves the mechanical issues by utilizing microlithography. Alignment is simplified because there are only two pieces. The open structure of the trap facilitates ion injection. The trap can take on a toroidal trapping geometry, in which case the trapping volume and sensitivity are increased, or it can produce a traditional Paul-trap field, providing higher mass resolution. Miniaturization is frequently associated with increased pressure in a mass analyzer, the idea being that as the trap dimensions decrease, the mean free path of ions can decrease, hence higher pressure and smaller pumps. With this planar electrode arrangement, the amplitude of ion motion can be decreased simply by moving the plates closer together (which does not increase capacitance nor change the field shape) and increasing the trapping frequency, rather than producing a smaller trap.

The Gated Electrostatic Mass Spectrometer

Fred A. Herrero

NASA Goddard Space Flight Center, Code 553, Greenbelt, MD

This talk describes the path taken by the author in going from electrostatic energy analyzers to a new type of time-of-flight mass spectrometer offering several advantages. We discuss the parallel plate electrostatic analyzer (PPA), used perhaps since the beginning of ion/electron optics, mostly as an auxiliary device in charged particle spectrometers. Its focusing properties for 90° and 60° total deflections made it desirable for some limited applications and in a more recent application a 90° PPA was modified to provide focusing of magnetosphere electrons over a field of view of $30^\circ \times 30^\circ$. The main disadvantage of the conventional PPA and other conventional energy analyzers is the large voltage required between the analyzer plates to select the energy of transmitted particles. This becomes a serious issue in space plasma physics investigations because the energies of interest for ions and electrons typically reach or exceed 40 keV. Limiting the deflection angle to small values offers space plasma investigators an energy analyzer that reaches 50 keV with 2 kilovolts instead of the 7 kilovolts required for the best conventional analyzer solution. This small deflection energy analyzer (SDEA) provides the low voltage advantage without reduction in field of view, energy resolution, and sensitivity. One useful property of SDEA is the simple geometrical shape that enables distribution of multiple SDEAs in two-dimensional arrays to increase sensitivity while keeping energy resolution constant. Low-energy experiments could also benefit from the SDEA approach to the PPA - very small voltages (usually less than 5 volts) are required for low energy (< 30 eV) operation in wind and temperature spectrometers for ionosphere-thermosphere investigations. At that point in the development of SDEA there was no motivation to use it in a mass spectrometer. But Lunar exploration changed that with a special challenge: Ions sputtered by solar wind ions from the surface of the Moon may be used to obtain the distribution of minerals on the Lunar surface. However, expected sputtered ion fluxes are so low that a mass spectrometer with an aperture of about 10 cm^2 is required. Furthermore, in order to make the spectrometer compatible with likely spacecraft, that aperture must fit on a $2 \times 2 \text{ ft}^2$ ($60 \times 60 \text{ cm}^2$) footprint. This provided the motivation for the Gated Electrostatic Mass Spectrometer (GEMS) that will be described in full detail in this paper, showing some of the laboratory data obtained thus far. We will see how GEMS arrays may be used to provide relatively high sensitivity with high mass resolutions.

**MEMS Assembled Ion Optical Devices: Current Technology and
a Look at Advantages and Disadvantages**

Guido F. Verbeck, IV

University of North Texas, PO Box 305070, Denton, TX

Miniature analytical devices have recently become a growing area to produce handheld, field-portable instrumentation. Because of the difficulty to micromachine optical components and features with small aberrations, it is necessary to incorporate new doped silicon micro-electro-mechanical system (MEMS) methods. This technique allows for precise manufacturing of small electrical and mechanical device assemblies.

I will introduce some of the devices currently being developed in my lab as well as an introduction to this new and growing field. My group have created and tested ten new MEMS based ion optical assemblies. This list includes the Bradbury-Nielsen Gate, cylindrical ion trap, time-lag focusing TOF, reflectron optics, einzel lens, electron beam collimator, periodic focusing, and ion mobility. Data will be presented showing the resolution, attenuation, and performance of each of these devices. With the ability to utilize multiple substrates such as Pyrex, sapphire, and aluminum nitride, we can make ion lenses that can withstand an applied potential $>2\text{kV}$ before breakdown.

I will also discuss some of the advantages and disadvantages of this technology. The smaller the devices, the more “space-charge” effects and aberrations play dominate roles. I will introduce these concepts, and look at ways of overcoming these potential problems.

A Single Chip Mass Spectrometer in MEMS Technology

Jan-Peter Hauschild, Eric Wapelhorst, Jörg Müller

Institute of Microsystems Technology, Hamburg University of Technology, Germany

The concept and its experimental proof of a planar integrated micro mass spectrometer (PIMMS) fabricated as single chip is presented. All essential components like the ion source, the ion optics, the mass separator, the energy filter, and the detector are integrated on a chip with a small size ($5 \times 10 \text{ mm}^2$). This size allows an operation of the PIMMS at a pressure of 1 Pa (7.5 mTorr), which can be generated by a one stage pumping system or a micro pump [1]. The concept and layout of this PIMMS is optimized for cost efficient mass fabrication using only standard MEMS processes.

The function principle is based on electron impact ionization and a synchronous ion shield (SIS) separator. The PIMMS generates ions by electron impact ionization: A microwave plasma electron source [2] provides the necessary electron beam (1 A/cm^2) for ionizing the sample gas. This electron beam impinges the sample gas in the ionization chamber. The generated ions are extracted from the ionization chamber, focused by the ion optics, and accelerated to a defined kinetic energy, i.e. their velocity is mass dependent. The SIS mass separator consists of several electrodes forming an ion channel. Within this channel a traveling electrical field is generated by two 180° phase shifted square wave (SW) signals applied to every second electrode. Only ions traveling synchronous with the electrical field pass the separator, the others are filtered out. By varying the frequency of the SW signals a mass interval can be scanned, where a frequency interval of 10 to 35 MHz corresponds to a mass range of 100 to 10 amu, respectively. Between mass separator and detector an energy filter, arranged as 90° electrostatic sector, reduces the negative impact of the distributed start energy of the ions.

The MEMS based fabrication offers the possibility of mass production, e.g. on a 4-inch wafer about 100 PIMMS are processed at the same time. All critical structures are fabricated by a single anisotropic deep silicon etching [3] step, eliminating the need for adjustment between the units of the PIMMS. Each side of these $300 \text{ }\mu\text{m}$ thick silicon structures is bonded to a glass substrate with metal structures for contacting the silicon electrodes.

Several gas compositions of carbon dioxide, nitrogen, argon, neon, and air have been identified using the PIMMS. With initial measurements of mass spectra the function principle of the PIMMS was proven, and it is already possible to separate argon (40 amu) from carbon dioxide (44 amu).

The entire system is very cost-efficient due to its small size and its mass producibility based on one simple photo mask for all critical structures. The vacuum and power requirements for the PIMMS are relaxed compared to those of state of the art mass spectrometers. The PIMMS is predestinated for mobile measurements, portable applications as well as specialized applications in harsh environments.

[1] M. Doms, J. Müller, "A Micromachined Vapor Jet Pump", *Sensors and Actuators A*, **2005**, 119, 462.

[2] J.-P. Hauschild, E. Wapelhorst, J. Müller "A Fully Integrated Plasma Electron Source for Micro Mass Spectrometers", *μTAS*, Boston, Massachusetts, USA, 2005

[3] Ayon, R. Braff, C.C. Lin, H.H. Sawin, M.A. Schmidt, "Characterization of a Time Multiplexed Inductively Coupled Plasma Etcher," *J Electrochemical Soc.*, **1999**, 146, 339.

A Microfabricated Cylindrical Ion Trap Array for Batch Production of Small Chemical Sensors

F.H.W. van Amerom

University of South Florida & SRI St Petersburg, 140 7th Av S, St Petersburg, FL

A. Chaudhary / University of South Florida & SRI St Petersburg

R.T. Short / SRI St Petersburg

Portable miniature mass spectrometers are in demand for continuous monitoring of field sites for hazardous chemicals. Toward this goal, microelectromechanical systems (MEMS) fabrication techniques allow for batch production of very small structures in silicon (Si) with a precision necessary for miniaturized mass spectrometer components. In this abstract, we report on our improved fabrication method for a 5×5 μ -cylindrical ion trap (μ -CIT) array in a 1×1 cm² Si die, with r_o of 360 μ m and ratio z_o/r_o of 0.97. Preliminary mass spectral results are also presented.

Our initial approach to use two symmetrical half-CIT array structures in Si, bonded back-to-back, was modified to remove excess bulk Si in order to achieve lower capacitance, while maintaining conductive endplate surfaces to avoid surface charging. Several iterations of the fabrication process were carried out to optimize critical design parameters, such as thickness of the insulating SiO₂ layer, thickness of the Si₃N₄ endplate layer and ring electrode verticality. The fabricated μ -CIT array was then tested in an ion trap mass spectrometer experimental test setup.

Ionization of analytes was performed using a rasterable electron gun to individually address each μ -CIT in the array. This allowed investigations of mass spectral shifts among the traps and relative changes in intensities of the ejected ions. Mass spectra of trichloroethylene and perfluorotributylamine were obtained from the μ -CIT array using the mass instability scan, with trapping voltage (V_{rf}) frequencies in the range of 5.5 to 6.5 MHz and amplitudes of 10 to 80 V for trapping and ejection of ions. Resulting (FWHM) peak widths were on the order of 4-5 Th. These initial results indicate the feasibility of using MEMS fabrication techniques for the production of miniature CIT mass spectrometers in Si. Future strategies will include further optimization of mass resolution and characterization of operation of all μ -CITs together as an array.

Development of Miniature Mass Spectrometry for In-situ Characterization of the Environment

Frants R. Lauritsen

University of Copenhagen, Universitetsparken 5, Copenhagen, Denmark

This talk will present recent progress at Copenhagen University with the development of handheld, battery operated membrane inlet mass spectrometry for in-situ characterization of the environment. In particular a novel inlet system for fast screening of land sites for poly aromatic hydrocarbon (PAH) contamination in the soil will be presented together with the first in-situ applications. The complete analytical system has a total weight below 10 kg and analyses soil samples for their PAH content without any pretreatment with a turnover of 5-10 minutes per sample. Further, the first experiences with a recently acquired Mini-10 miniature mass spectrometer and its use as a mass selective detector to a miniature field transportable gas chromatograph (GC) will be presented. The field portable and battery operated micro GC (Varian CP4800) come with a thermal conductivity detector and will be interfaced to the Mini-10 via either a membrane inlet or a direct gas inlet system.

Quantification of a chemical plume using a moving sensor with a membrane covered interface is particular difficult, since the exposure time of the membrane covered sensor to the plume is unknown. If a steady state diffusion of sample molecules through the membrane is not achieved within the exposure time neither peak height nor peak area can be used alone for quantification. The talk will briefly address this matter and explain how a simple algorithm using both peak height and peak width as input can solve the problem.

The Development of a Vector Neutral Particle Spectrometer for Space environment Measurements

Erik Syrstad¹, James Dyer¹, Michael Watson¹, Charles Swenson²

¹Space Dynamics Laboratory, 1695 North Research Park Way, North Logan, Utah

²Utah State University

Satellite performance and lifetime is strongly dependent on the orbital environment. Models of the neutral atmosphere, derived from experimental mass spectrometric data, show drastically fluctuating number densities, especially in response to solar activity. These variations can affect several aspects of satellite and sensor performance, most notably spacecraft drag. Therefore, it is desirable to measure neutral particles in situ, to better understand the instantaneous effects of thermospheric variations. This requires the ability to accurately measure reactive species and to reject the thermal background signal due to local outgassing, while minimizing demands placed on valuable spacecraft resources. We are developing a compact Vector Neutral Particle Spectrometer (VNPS) with a variety of novel features intended to address the unique aspects of space environment measurements. The radially symmetric sensor has a very large toroidal field-of-view (2.83π sr), to avoid imposing spacecraft orientation requirements. Neutrals with incoming elevation angles from -45 to $+45^\circ$, and throughout the entire range of azimuth angles (0 to 360°), are analyzed and detected simultaneously without the use of moving parts or scanning potentials. A collisionless, open ionizer utilizes a well-defined electron beam to facilitate the detection of reactive species with minimal perturbation of the incoming velocity vector. A laboratory prototype ionizer has been demonstrated to efficiently transmit an intense (several milliamp) electron beam of 1 mm diameter over a 2 mm gap. Mesh-based ion optics components include a retarding potential analyzer, acceleration grid, and hemispherical deflection grid. Ions follow unique trajectories according to their precursor neutral entrance angles, and are detected by an imaging microchannel plate / cross delay-line anode operated in pulse counting mode. Ion trajectory simulations (SIMION 3D 7.0) indicate that incoming neutral angles can be determined with 1° accuracy. In addition to this ‘imaging mode’, the instrument may be operated in ‘MS mode’, in which acceleration and deflection potentials are tuned to produce a modulated ion beam suitable for time-of-flight analysis. Laboratory testing of the ion optics subassemblies is underway, with initial data showing excellent agreement with theoretical predictions.

Mass Spectrometer-based Instrument for Volcanic Gas Monitoring

Gary M. McMurtry¹, David R. Hilton², Tobias Fischer³, A. Jeffrey Sutton⁴, Tamar Elias⁴

¹SOEST, University of Hawaii

²Scripps Inst. Oceanography, Univ. California, San Diego

³Dept. of Earth and Planetary Sciences, Univ. New Mexico

⁴Hawaiian Volcanoes Observatory, USGS

One very harsh environment for terrestrial applications of mass spectrometry is active volcanoes, where continuous gas monitoring has both practical, hazards mitigation and basic research goals in observing and understanding the systematics of volcanic and hydrothermal systems. We developed and field tested an instrument that is capable of acquiring multiple-species gas chemistry data at active, low-to-moderate temperature fumaroles. The current prototype consists of a quadrupole mass spectrometer, a series of pumps, valves and control/data logging electronics housed in a corrosion-resistant container. We tested the instrument at the summit of Kilauea volcano in March, 2006, collecting time-series data from a 96°C fumarole (Sulphur Banks) at 15 minute intervals for nearly 3 days. Two temperature probes were utilized, a thermocouple placed in the gas stream and a thermistor which recorded ambient air temperatures inside the instrument housing. The fumarole gas composition, as indicated by sharp drops in the instrument response for N₂, O₂, Ar, and water vapor, and increases in CO₂ and SO₂ was reached at about 6.5 hours elapsed time.

The two most obvious gas/temperature trends in this brief time-series are: (1) sharp discontinuities caused by two of the standard “Giggenbach” bottle sampling interludes (despite some care given not to vent the gas line to atmosphere); and (2) two distinct types of thermal events. The two sampling interruptions caused decreases in temperature, and caused the responses of CO₂, N₂, O₂, Ar and water vapor and the ratio of CO₂/He to rise sharply. This appears consistent with contamination by cooler ambient air enriched in CO₂ relative to normal air (solfatara air). The two types of thermal events are similar in that both generally show enrichments of SO₂ and He, and decreases in CO₂/He, whereas the last, much hotter event displays increases in CO₂, N₂, O₂, Ar, and water vapor, in contrast to decreases in these gases during the two former events. The last thermal event correlates with a brief dry period on 17 March, after a previous week of almost continuous rainfall. An interesting increase in the HD/H₂ ratio suggests either HD-enriched H₂ gas or water vapor was introduced during the last thermal event, which is consistent with a fumarole influenced by evaporated, boiling water and atmospheric gases at depth.

During our tests we discovered several problematic issues that need to be overcome if the instrument is to be deployed for extended periods of time (months to years) in harsh and remote locations of active volcanoes. One of the main obstacles is the large amount of water vapor in fumaroles and the need for keeping that water out of the mass spectrometer. We have successfully achieved this using a series of traps and a condenser that still allow the other species to enter the instrument. Related problems are loss of some of the reactive gases within the instrument and/or traps and the precipitation of elemental sulfur in the pre-mass spec inlet system. Another issue that we are currently addressing is the relatively high power consumption of the instrument and condenser.

Field Testing of the Nereus Network

Harry Hemond

MIT, 48-425, Mass. Inst. Of Technology, Cambridge, MA

Measuring chemical and physical properties of natural water bodies with sufficient spatiotemporal resolution is a difficult problem when studying or monitoring processes that are transient, or produce steep spatial gradients or plumes. To address this problem, the Nereus underwater mass spectrometer has been deployed aboard an autonomous underwater vehicle (AUV). In addition to providing much-increased spatiotemporal coverage, the mass spectrometer/AUV combination obviates the need for sample preservation and is able to identify and quantify a wide variety of dissolved volatile chemicals. The analytical capabilities of a mass spectrometer, combined with those of a standard water quality multiprobe, provide measurement of a wide and useful range of parameters including pH, temperature, salinity, turbidity, and Pt electrode potential as well as multiple dissolved gas species such as methane, oxygen, nitrogen, and carbon dioxide.

The Nereus mass spectrometer/AUV is part of a hybrid data network that uses both radio (for overwater) and acoustic (for underwater) communication for the collection of chemical and physical data in real time. The network also includes fixed sensors located on buoys, providing continuous time records of such baseline parameters as thermal structure of the water column. In addition to providing real time data from instruments and sensors, the network provides AUV tracking information, and potentially can control the AUV and its instruments, whether surfaced or underwater, as part of an adaptive sampling system. To be accessible to a wide variety of potential users, the network is based on open-source software and low-cost off-the-shelf components.

We describe recent field results of the system at our test site in Upper Mystic Lake near Boston, MA, particularly as they relate to key practical issues such as i) creating electrical and mechanical interfaces between the mass spectrometer and an AUV, ii) providing autonomous, but remotely modifiable, operation of the mass spectrometer, iii) providing adequate localization of the AUV when submerged, and iv) obtaining real-time acoustic transmission of mass spectrometric data during submerged missions in an acoustically challenging environment. In addition to providing greatly expanded chemical data sets, we suggest that streams of spatiotemporally-diverse, real-time chemical data such as in-situ mass spectrometry can provide will also facilitate advances in research methods heretofore not traditionally applicable to studies of natural water geochemistry, such as real-time adaptive sampling and data fusion methodologies.

Short-term Oxidation-Reduction Processes within a Hypoxic Estuary, using an In Situ Mass Spectrometer

Itziar Tueros, Victoriano Valencia, Angel Borja

AZTI-Tecnalia, Marine Research Division, Portualdea, Pasaia Spain

The Oiartzun river estuary (Basque Coast, Northern Spain) holds the second commercial harbor of the region. The special morphology of the estuary (like a small fjord) is strongly modified for navigation purposes. The corresponding catchment and river flow are very small, whereas the estuarine volume is relatively high. The estuary is mesotidal, with high residence times of the water masses, especially for some inner locations. The water clean-up has experienced important improvements in recent years; however, high organic matter loads (mainly from domestic wastes) are still discharged into the inner locations. This produces strong and relatively fast oxygen consumption, enhanced by organic matter rich, heavily reduced sediments. This leading frequently to hypoxia events (measured), denitrification (observed, measured) and sulphate reduction (empirical sulphide smell). The aims of this contribution are:

- To determine if the concentrations of the molecular species (non ionic forms in the dissociation or hydrolysis equilibria), associated to the abovementioned processes, are high enough to be detected
- To determine these patterns in quantitative or qualitative ways

The study was undertaken by means of an In-Spectr 200-200 Underwater Mass Spectrometer (UMS), manufactured by Applied Microsystems, based in the model developed in the University of South Florida. The UMS was used to analyze surface and bottom samples, along a tidal cycle, together with CTD sampling (temperature, salinity, dissolved oxygen, pH, light transmission, and chlorophyll) and Niskin bottles (to analyze ammonium, nitrite, nitrate, phosphate, silicate, sulphide, TOC...).

Hence, this contribution couples classical marine monitoring data (CTD continuous profiles), with discrete depth water samples (Niskin bottles), and continuous in-situ UMS measurements. The results are used for calibration/quantification of UMS data and a monitoring improvement, with better spatial and temporal resolution.

Underwater Mass Spectrometry: Developments and Calibration

Ryan J. Bell¹, Strawn K. Toler¹, Peter G. Wenner², R. Timothy Short¹, Robert H. Byrne²

¹ SRI International, 140 7th Ave S, COT 100, St Petersburg, Florida, 33701

² University of South Florida, 140 7th Ave S, St Petersburg, Florida, 33701

An underwater mass spectrometer that employs a 200-amu linear quadrupole mass filter and a high-pressure membrane inlet system has been developed for in-situ chemical analysis of marine and freshwater systems. Analyte permeation through a silicone membrane allows introduction of dissolved gases and volatile organic compounds into the analyzer's vacuum chamber for analysis. The membrane is supported against ambient hydrostatic pressure by a sintered rod. Presently, the depth rating of the mass spectrometer is limited to 1200 m by the instrument's external aluminum pressure housing.

Prior to deployments, for analysis of dissolved gases (e.g. methane, nitrogen, oxygen, argon and carbon dioxide) the mass spectrometer is calibrated using water samples equilibrated with gas standards. Since it is inconvenient to control hydrostatic pressure within an underwater instrument, measurement of gas concentrations are influenced by compression of the silicone membrane at depth. Gas concentrations must be obtained through calibrations with respect to pressure.

The underwater mass spectrometer has been deployed in a number of locations for a variety of applications. Recent deployments include depth profiling of dissolved gas concentrations in the Gulf of Mexico, surface contouring of gas concentrations related to primary productivity in Hillsborough River (Tampa, FL) and multi-day monitoring of the sediment-water interface to estimate real-time biogenic gas production within the sediment. Details about deployments and underwater mass spectrometer calibration methodologies will be presented.

Application of the In-Spectr 200 Membrane Introduction Mass Spectrometer for Measurements of Methane in Lake Constance (Germany) and the Western Baltic Sea.

Michael Schlüter, Torben Gentz

Alfred-Wegener-Institute for Polar and Marine Research

Organic rich sediments in the marine environment or lakes are considerably enriched in methane as well as other trace gases. These gassy sediments are sources for methane which emanates into the water column by ebullition or diffusion through the sediment-water interface. Unfortunately, standard techniques as water sampling by Rosette Samplers and measurement by gas chromatography (GC) often fail to detect gas plumes released from pockmarks, mud volcanoes or gas hydrate fields.

To bypass the disadvantages of discrete water sampling and time consuming GC analysis an online measuring system, based on the In-Spectr 200 Membrane Introduction Mass Spectrometer was applied for studies of methane concentrations in Lake Constance and the Western Baltic Sea. The system was used in situ in water depths of ~50m as well as onboard ship. In the later case a submersible pump, which can be operated down to 180m water depth was applied for continuous water sampling. To further improve the detection limit on methane a cold trap was applied. The data derived online by the In-Spectr 200 were verified by gas chromatography.

In March and August 2007 the CH₄ concentrations in surface and bottom waters of Lake Constance were measured along several transects crossing pockmarks and gassy sediments. Measurements by the In-Spectr 200 allowed the mapping of the CH₄ concentration in the bottom water around pockmarks located in 80m and 13m water depth. Concentrations of up to 1100nM were measured at pockmark sites, whereas concentrations close to the detection limit (~20nM) were observed in the surroundings. Even in surface waters above the pockmarks CH₄ concentrations of 600nM were observed. The data were compared to results obtained by Rosette Samplers and water samples collected by scuba divers.

Mass Spectrometer for Mars Phoenix Lander

John H. Hoffman, Roy C. Chaney

University of Texas at Dallas, 800 W. Campbell Rd., Richardson, TX

The Phoenix Mars Scout Mission is the first of the PI directed low cost missions to Mars. It was selected by NASA for the August 2007 launch opportunity. This mission is a lander that will advance the NASA theme for studying the planets, called “Follow the Water”. The landing site for Phoenix will be near 70 degrees north, in the region that the Mars Odyssey orbiter neutron spectrometer has observed a large excess of hydrogen. Interpretation of that data suggests a large quantity of water ice exists just below the surface, possibly in the range of 10 to 20 cm down. One of the lander instruments is an arm with a scoop that can dig a trench up to a meter deep in the surface of Mars to look for water ice and water bearing minerals. Selected samples from the trench are brought to the Thermal Evolved Gas Analyzer (TEGA) that consists of, a), a set of 8 small ovens that can heat the samples, first to melt any ice contained in them, then heat the residue to 1000 degrees C to decompose the minerals, and, b), a small mass spectrometer that analyzes the effluents from the ovens to determine the presence of water and identify evolved gases, possibly hydrocarbons, as well as define the mineralogical composition of soil samples. Isotopic ratios of the principal elements in the samples will be determined and compared to the isotopic ratios of the atmospheric gases, also measured by the mass spectrometer. A gas enrichment cell is included that takes samples of the atmosphere, removes the active gases, carbon dioxide and nitrogen, thereby enriching the abundances of the noble gases by 1 ½ orders of magnitude in order to improve the accuracy of their isotopic ratio measurements. Humidity of the atmosphere will also be measured. The oven section of the TEGA instrument was developed by the Lunar and Planetary Laboratory of the University of Arizona. The mass spectrometer, developed by the University of Texas at Dallas, is a magnetic sector instrument having 4 mass channels that cover the range from 1 to 140 Da. Four electron energies ranging from 90 to 23 eV are available to vary the cracking patterns of complex molecules. Ions are detected by ceramic electron multipliers that feed pulses to a preamp-counter that has a dynamic range of 6 decades. Two electron emission current levels extend the dynamic range to 7 decades. Data storage is in the central electronics module for periodic transmittal to earth via Mars orbiting spacecraft relay. Operation of the MS is controlled via daily commands from earth. Modes include full sweeps of the mass range and hop modes wherein 7 closely spaced (in delta M) count accumulations are taken running over the top of a selected peak. A curve fit routine determines the peak amplitude. This mode is used for isotopic ratio determination by hopping between 2 or 3 mass peaks multiple times. Calibrations have been done with Mars analogs and simulated atmosphere gas mixtures.

Thermal Desorption Inletting for Portable Mass Spectrometers

Stuart Cairns,

DSTL, Fort Halstead, Kent, TN14 7BP, UK

A number of different sample collection and analysis techniques are available for field analysis using commercial portable mass spectrometers. There is however no widely available technique for the simple collection and analysis of contamination on surfaces using wipes. This type of technique is widely available for ion mobility spectrometry type equipments, and is often used for wiping/swabbing of baggage in airports. This sample collection technique offers quick, cheap and simple sampling of contamination on surfaces that are hard to collect by other techniques. Thermal desorption (TD) is the most common method for the analysis of surface wipes. The difficulties of attaching an efficient TD device to a portable mass spectrometer with size and power limitations will be discussed. This will also be linked with the need for separation of sample after TD and prior to mass spectral analysis. The preliminary results from the coupling of a thermal desorption inlet to a commercial portable ion trap mass spectrometer will be shown and discussed. A comparison of TD desorption of wipes followed by sample separation, with new soft ionisation surface sampling techniques such as desorption electrospray ionisation (DESI) and direct analysis in real time (DART) will be made.

Implementation of DART and DESI Ionization on a Fieldable Mass Spectrometer

Mitch Wells

ICx Griffin Analytical, 3000 Kent Ave., West Lafayette, Indiana 47906

Direct Analysis in Real Time (DART) and Desorption Electrospray Ionization (DESI) have been shown to have promise for detection of a wide variety of materials, including explosives and chemical warfare agents (CWAs), on “real-world” surfaces. In the work reported here, these two sources were coupled to a small, mobile, rugged tandem mass spectrometer having an atmospheric pressure ionization (API) inlet, to investigate the opportunity for using these methods for security and defense-related applications in the field.

A Griffin 400 mobile MS was modified to include an API inlet to allow testing with electrospray ionization (ESI), DART, and DESI. Commercial DART (IonSense, Inc.) and DESI (Prosolia, Inc.) sources were obtained from the manufacturers and mounted on the MS with minimal modifications. Explosive residues, including TNT and RDX, and CWA simulants, including dimethyl methylphosphonate and methyl salicylate, were detected by spotting solutions of the materials onto a variety of surfaces and allowing the solvent to dry. The residues were then subjected to DESI or DART ionization processes before mass analysis via MS and MS/MS.

A three-stage differential pumping system was designed to provide API capability for the Griffin 400 mobile MS. The system utilized small drag and hybrid turbodrag pumps, backed by diaphragm pumps, to evacuate the three vacuum stages to pressures of 700 mTorr, 10 mTorr, and 5×10^{-5} Torr respectively. This configuration allowed the full MS system to be packaged within the Griffin 400 chassis, measuring approximately 50 cm x 50 cm x 50 cm, with no external pumping required. For the preliminary studies reported here, the commercial versions of DART and DESI sources were mounted on the front of the instrument with mounting structures that allowed optimization of the source/inlet relative positions, angles, etc. Data were collected to determine the detection and identification capability for both sources using MS and MS/MS detection. The effects of relevant source variables, including ionization polarity, gas flow rate, temperature, and sample position relative to the ion source and ion sampling inlet, were studied to explore the applicability of both sources to use in field scenarios, where ease of use and minimization of consumables is desirable.

Characterization of a Multi-Port Inlet on a Rugged Mass Spectrometer

Garth Patterson

ICx Griffin Analytical, 3000 Kent Ave., West Lafayette, Indiana

Laboratory analyses often afford the scientist a vast array of analytical techniques and capabilities. Field operators rarely have this luxury; as they are often forced to employ highly specific analyses or rely on more portable, non-selective techniques. These restrictions result in limited information or less definitive data, viz. high false alarm rates. Mass spectrometry could potentially alleviate these issues, as it is extremely valuable in the laboratory setting but can be limited in the field for a variety of reasons including limited sample introduction techniques, complexity, cost, and durability.

The Griffin 450 GCMS addresses these limitations of mass spectrometry as it offers a wide range of sample introduction techniques in a rugged and transportable package. For rapid separation, the system utilizes a low thermal mass gas chromatograph. A cylindrical ion trap mass analyzer provides multi-dimensional mass analysis; and intuitive software allows the user to obtain high quality analyses without significant user input.

The reach of the instrument is extended by using a detachable, lightweight sample collection device, the Griffin X-Sorber, to collect samples remotely for transfer back to the Griffin 450. The X-Sorber includes two solid sorbent tubes for sample collection. During collection additional information is logged, including GPS location, identification of the user, sample tube identification number, volume of sample, and time of sampling. The sampling flow rate is controlled and sample collection can be automatically started and stopped at predefined times. When the X-Sorber is returned to the instrument, all of the information is transferred and logged with the collected data. Two sorbent tubes are included in the sampler and can be sampled independently or together allowing for multiple collection areas or the collection of archivable samples, respectively.

Representative data including EPA methods 8260 and 8270, pesticide analysis, toxic industrial chemicals, explosives, and chemical warfare agent simulants will be presented. A detailed technical description of the hardware and software will also be provided.

Mini 11 Handheld Mass Spectrometer with Glow Discharge Ion Source and Atmospheric Pressure Interface

Liang Gao¹, Andy Sugiarto¹, Jason Harper¹, Jason S Duncan¹, Ray S. Milks¹, Bob Kline-Schoder², R. Graham Cooks¹, Zheng Ouyang³

¹ Department of Chemistry, Purdue University

² Creare Inc., Hanover

³ Weldon School of Biomedical Engineering, Purdue University

The wide applicability of mass spectrometry makes it an extremely valuable method for chemical analysis. However, the size, weight and power consumption of the mass spectrometers limit the in-field applications of the mass spectrometry. A handheld tandem mass spectrometer, Mini 11 mass spectrometer, has been recently developed to provide a solution for this problem. This instrument employs a rectilinear ion trap mass analyzer and weighs 10 lbs, has a size of 10" L x 6" W x 5" H and a power consumption of 35W. A digital control board with wireless communication capability was developed to execute pre-programmed scan functions, collect spectra and transfer data to the remote computer. The vacuum system consists of a KNF UN84.3 diaphragm pump with 5L/min pumping speed and a micro hybrid turbomolecular pump with 5L/s pumping speed. A glow discharge electron impact (GDEI) ion source was used to ionize the sample molecules introduced through a membrane, a GC capillary inlet or directly via a low flow direct leak to atmosphere. The GDEI source was shown to have advantages of low power consumption and long lifetime under high pressure operation. The effects of the discharge voltage and pressure on the discharge current were investigated. The intrinsic relationship between the discharge current and the pressure at a given discharge voltage could be used to indicate the vacuum status of the instrument. Spectra of various volatile organic compounds were recorded with the GDEI source. A mass range over m/z 800 and resolution of 2 amu was achieved.

Evaluation of Commercial Mass Spectrometers for NASA Applications

Jorge Andres Diaz¹, Stacey R. Gillespie², C Richard Arkin²

¹ NTCR S.A. (NASA Contractor) and Universidad de Costa Rica, San Jose, Costa Rica.

² ASRC Aerospace, Hazard & Gas Detection Lab (ASRC-14), Kennedy Space Center, FL

An evaluation of commercially available small mass analyzers and mass spectrometer systems was performed during the summer of 2007 as a first step to identify MS candidates for various NASA harsh environment and extreme condition applications. The project is similar to a previous effort focused on identifying and testing miniature mass spectrometer systems which was presented at the 3rd HEMS Workshop. The 2007 MS Evaluation Project took place at the Hazard & Gas Detection Lab from Kennedy Space Center, in which vendors with products that met a minimum list of requirement including size, weight, mass range, gas species detection, detection limit, accuracy, resolving power, power consumption and software interface were invited to be part of the evaluation. The commercial MS instruments that accepted the invitation were evaluated under similar vacuum condition and same gas delivery system parameters. Gas concentration varying from ppm levels to 100%, flow rates from 250-1000 sccm depending on the test and constant inlet pressure were provided at each one of the 4 test stations set-up for the evaluation. A common set of operations and tests in both nitrogen and helium backgrounds was performed to determine detection limit, accuracy, drift, dynamic range, response time, recovery time and clear out time for each unit. Ten MS products were evaluated including products from Extorr, Inficon, Hiden Analytical, Pfeiffer, MKS, SRS and VTI. Preliminary results are presented for each unit and compared to the target application specifications.

Quadrupole Miniaturization: Measured Performance for Different Size Quadrupoles

Randall E. Pedder¹, David Kilgour²

¹ Ardara Technologies L.P.

² Dstl Fort Halstead, UK, Explosives Detection Equipment Team, Detection Department

There are a number of research groups and companies currently focused on miniaturizing quadrupole mass filters to enhance their portability, by reducing their size, weight and power requirements. It is generally acknowledged that there will be a reduction in performance anticipated with the reduction in quadrupole size. In this work, we fabricated seven quadrupoles with different rod diameters (1, 2, 4, 6, 9, 12, and 20 mm rod diameters), and measured their absolute sensitivities to measure the actual relationship. We maintained constant conditions of argon partial pressures, using the same ionizer and detector for all seven quadrupoles, and experimentally determined the relationship between rod diameter and absolute sensitivity at various mass resolutions. We also determined the relationship between measured absolute sensitivity as a function of RF frequency, by operating four different rod diameter quadrupoles at five different RF frequencies. This presentation will also include a discussion of other practical aspects of quadrupole miniaturization, with specific focus on Paschen Curve implications, which ultimately limit the maximum usable voltage with regards to operating pressure.

Miniature High Vacuum Pumps for Analytical Instruments

Robert Kline-Schoder, Paul Sorensen

Creare Inc., 16 Great Hollow Road, Hanover, NH 03755

NASA, other government agencies, and commercial industry have acute needs for miniaturized high vacuum systems. Recent advances in sensor technology at NASA and commercial laboratories have led to the development of highly miniaturized mass spectrometers, and miniaturized versions of other analytical instruments are under development. However, the vacuum systems required to support these sensors remain large, heavy, and power hungry. In particular, high vacuum systems of adequate performance continue to be too large for systems such as time-of-flight, quadrupole, and ion trap mass spectrometers that are intended to be man-portable or to be deployed on UAVs, balloons, or interplanetary probes. The terrestrial, man portable applications impacted by this problem include military and homeland defense systems for detecting hazardous materials as well as portable leak detectors for commercial use.

For 10 years, Creare has been developing the technologies required to design and build miniature high vacuum pumps. During this time, we have designed and built two small high vacuum pumps that have the following pumping characteristics: a compression ratio for air that is greater than 10^8 ; a pumping speed of about 5 L/sec; and 10 W power consumption for an exhaust pressure of 10 Torr. The smallest of these pumps has a mass of 130 g, a diameter of 1.3 in., and an overall length of 2.3 in (i.e. the size of a d-cell battery). The slightly larger pump has a mass of 500 g, a diameter of 2.0 in., and an overall length of 4.6 in (i.e. the size of a soda can). The larger version is being space qualified for use on a NASA Mars mission scheduled for launch in 2009.

The challenges of designing and building miniature turbomolecular/molecular drag pumps include: design of pump geometry in regions where little data exist, the need for precision machining of components, and the electromagnetic and mechanical design of very high speed, efficient, miniature electric motors. Data will be presented that show the performance, over a wide temperature range, of a brassboard prototype of the pump NASA currently plans to deploy on the Mars Science Laboratory mission.

Hand-Portable GC-TMS Instrument for Measurement of Chemical Agents and Hazardous Compounds in Harsh Environments

Douglas W. Later¹, Samuel E. Tolley¹, Jesse A. Contreras², Jacolin A. Murray², H. Dennis Tolley², Stephen A. Lammert¹, Edgar D. Lee¹ and Milton L. Lee²

¹ Torion Technologies, Provo, UT 84602

² Brigham Young University, Provo, UT 84602

There is an increasing demand for hand-portable and small footprint analytical instrumentation that can be used for dedicated target compound monitoring and detection in harsh environments, such as field measurement applications. In this presentation, we describe a completely hand-portable self-contained GC-TMS system comprised of a low thermal mass toroidal gas chromatograph (GC) and a miniature toroidal ion trap mass spectrometer (TMS). The capillary GC system contains a 5-m X 100-um i.d. capillary column coated with 5% phenylmethylpolysiloxane stationary phase. Sample introduction is achieved by a novel solid phase micro-extraction (SPME) syringe device customized for single-handed operation and recording of injection custody information. The SPME injection port is a custom designed low thermal mass device that enables rapid heating. Mass analysis is performed using a miniature toroidal ion trap that allows the use of lower RF voltages and higher pressures, reducing power consumption and vacuum requirements while still maintaining dynamic range and good detection sensitivity and selectivity. Included in the instrument are the batteries, carrier gas supply, and microprocessor control. This GC-TMS, is easy to use, and requires minimum training for operators to become proficient in its use.

The complete GC-MS system is mounted in a 18-1/2" x 14-1/16" x 6-15/16" (47 cm x 35.7 cm x 17.6 cm) water tight, crushproof, dust proof protective case, and weighs less than 10.1 Kg (23.6 lbs) including batteries (~330 W-hr) and on-board helium tank. The average power consumption of 5.2 W-hr per sample, which allows for greater than 50 runs before the batteries need changed. The portable helium gas supply can be used for greater than 150 consecutive samples. A 6" LCD screen allows for monitoring the total-ion chromatogram as well as mass spectra of eluting compounds.

The high heating efficiency of the injector and column arrangement makes it ideal for fast heating and cooling cycles while minimizing power consumption. A complete sample analysis, including data analysis and cool down, is much less than 5 min. At the end of each analysis, mass spectra are compared against an on-board library for analyte identification. Library files that match the GC-TMS fingerprint of an analyte are listed and displayed along with a corresponding threat index, and match confidence level. Linear mass calibration of the system was obtained over a mass range of 50 to >500 m/z with unit-mass resolution. Detection of target chemicals will be demonstrated for several chemical agents including GA, GB, GD, GF, HD, and VX, as well as TICs and TIMs.

This project was funded by the Department of Defense, Defense Threat Reduction Agency (DTRA-01-03-C-0047) and Dugway Proving Ground (W911S6-06-C-0011).

Development of a Palm Portable Mass Spectrometer

Mo Yang, Tae-Young Kim, Han-Gyu Kim, Hyun-Cheol Hwang, Seok-Kyung Yi, Mo Yang

Analytical Instrumentation Research Institute, Sam Yang Chemical Co., Seoul, Korea

A palm portable mass spectrometer (PPMS) has been developed with a weight of 1.44 kg (3 lb) and a size of 1547 cm³ (8.2 x 7.7 x 24.5 cm) that can be operated with a battery with an average power consumption of 5 W. A miniaturized ion trap consists of four parallel disks with a center hole has been used as a mass separator. A small ion getter pump served for maintaining high vacuum inside the chamber and the sample gas was introduced in pulse mode. A micro computer has been developed for controlling various power supplies, RF generation, mass spectrum measurement, data processing, and self diagnosis, etc. The detection sensitivity of the organic gases diluted in the air has been demonstrated up to 6 ppm for TIC and 50 ppm for CWA.

Further development of the PPMS for application in real-time CWA detection /identification, environmental air pollution monitoring, and material analyses in space exploration, on the Mars, Mercury, Moon, and comets, will be discussed in detail.

* This research has been fully supported by the Korea Dual Use Technology Center.

POSTER ABSTRACT

Real Time Monitoring of Processes in Permeable Sediments by Underwater Mass Spectrometry

Strawn Toler, Bell, RJ¹, Savidge W², Jahnke, R², Short, RT¹

¹ SRI International, St. Petersburg, FL

² Skidaway Institute of Oceanography, Savannah, GA

As part of a larger collaborative project to study benthic boundary layer processes, part of our work has recently focused on understanding processes in permeable sediments on the continental shelf off the coast of Georgia by measuring biogenic gas production with an in situ mass spectrometer. The overall project, headed by the Skidaway Institute of Oceanography, is an instrumentation observatory designed to span a wide range of spatial and temporal scales in order to achieve an understanding of benthic exchange processes in a permeable sand environment. The underwater membrane inlet mass spectrometer will be deployed during seasonal instrument deployment and recovery cruises to measure real time dissolved gas concentrations (O₂, CO₂, CH₄, N₂ and Ar) in the porewaters at various depths in the sediment.

During a recent cruise on the R/V Savannah an underwater mass spectrometer was deployed on the seafloor for 43 hours. It was connected by a 200m tether to the Naval R2 tower in the South Atlantic Bight at a depth of approximately 30 m and communication was established via Ethernet radio between the tower and the ship. Sampling occurred from within a benthic chamber which will be described. Data from this cruise will be discussed, as well as future plans for sample interfaces to further probe the sediment.

Magnetic Sector Mass Spectrometers for Use in Harsh Environment

William Niu, Ben Gardner

Hamilton Sundstrand Corporation, 2771 N. Garey Ave, Pomona, CA

One of the most important practical factors in operating mass spectrometers in a harsh environment is long-term stability, which is greatly effected by environmental parameters such as temperature, pressure, shock and vibration. Each of these has a potential adverse impact on mass spectrometer analytical performance, and thus each must be considered in mass spectrometer design and engineering. Of the various mass spectrometer technologies, the magnetic sector instrument has been deployed for many harsh environment applications due to its simplicity, stability and suitability to rugged environments.

Hamilton Sundstrand has developed magnetic sector mass spectrometers in a broad spectrum of applications ranging from deep sea to space. The mass spectrometer in nuclear submarines continuously monitors the cabin atmosphere and only requires maintenance action every two to three years to replace filaments and pump components. Magnetic sector instruments have been critical equipment to a number of space missions including Skylab, Space Shuttle, Viking Mars Lander and International Space Station, where opportunity for service or repair are limited or non-existent. Currently, we are developing a sensor-class, small magnetic mass spectrometer for the Crew Exploration Vehicle. All these applications require continuous operation with high accuracy and stability. This paper will examine the attributes and design considerations of the magnetic sector mass spectrometer for deployment in submarine and space applications.

Laser Ablation Ion Funnel (LAIF) for *In-Situ* Mass Spectrometry on Mars

Robert Hodyss¹, Keqi Tang², Richard D. Smith², and Paul V. Johnson¹

¹ Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA

² Pacific Northwest National Laboratory

NASA has invested a great deal of resources in the development of various instruments for in situ analysis of extraterrestrial bodies. As a result, there currently exists a wealth of instrumentation suitable for detailed in situ analytical investigation. One common characteristic among the majority of these instruments is that they require extensive sample handling in order to extract and ionize atoms and/or molecules, before interrogation by the instrument in question can take place. A promising means of reducing the complexity of the sample handling required by instruments such as those discussed above is to employ laser ablation ionization. Laser ablation is a very attractive technique for in situ ionization of rock and soil samples since a laser is able to sample the surface of a rock or soil with minimal manipulation of the sample and no sample preparation. We are developing a front-end instrument that will exploit the advantages of laser ablation ionization while avoiding the pitfalls discussed above. This instrument, namely the laser ablation-ion funnel (LAIF), ionizes rock and soil samples in the ambient Martian environment with no sample preparation. The LAIF then efficiently captures transports and injects the product ions into a mass spectrometer for in situ analysis. We have demonstrated the operation of the LAIF in a simulated Martian atmosphere of 5 Torr CO₂, and will present mass spectra of several different mineral samples obtained with the LAIF interfaced to a commercial ion trap mass spectrometer (LCQ Deca XP). We also present preliminary results examining the influence of laser power on the ionization process.

A Design and Simulation Tool for Miniature Mass Spectrometers

Steve Taylor, Thomas J Hogan, Neil France, John R Gibson

University of Liverpool, Department of Electrical Engineering and Electronics

The ongoing trend towards miniaturization in mass spectrometry has resulted in the realization of miniature and microengineered forms of all of the main MS instruments (e.g. QMS, Ion Trap, magnetic sector) some of which are now commercially available. One of the driving forces behind the trend towards miniaturization is the application of MS techniques in harsh or hitherto inaccessible environments. We present here a mass spectrometer computer simulation tool that accurately simulates the mass spectra experimentally obtained from a miniature QMS operated under a wide range of conditions.

Instrument behavior is described by determining the individual trajectories of large numbers of ions (108) as they are injected from the ion source into the mass spectrometer. From the computer simulated mass spectra instrument resolution and sensitivity may be calculated and overall instrument performance determined for a user selected mass (analyte) range. The simulation tool also allows the user to see the effect of instrument design changes and importantly the effect of manufacturing tolerances on the resulting mass spectra.. In the case of the QMS the effects of the ratio of circular electrode radius r to electric field radius r_0 on the performance characteristics have been investigated for Mathieu stability zone 1 ($a \approx 0.237$, $q \approx 0.706$) and zone 3 ($a \approx 3.16$, $q \approx 3.23$) operation. We demonstrate that the performance sensitivity to r/r_0 ratio is different for zone 3 than those previously reported for zone 1. The magnitude and variation of the 'tail' in the mass spectral peak shapes apparent for zone 1 is much decreased for zone 3 and does not influence instrument resolution. Variation in ion trajectories and associated power spatial frequency spectra when operated in zone 1 and zone 3 with varying r/r_0 geometrical ratios are also presented. We demonstrate that these provide an alternative method for determining an ideal value for r/r_0 in QMS instruments. The effect of instrument size and operating conditions (voltages and frequencies) may also be readily simulated using the program and by this means the choice of an MS instrument for a given application may be determined.

Our simulation methodology is generic and our approach is therefore applicable to other types of MS instruments (e.g. magnetic sector and GC-MS) and we also present preliminary results simulating these systems.

POSTER ABSTRACT

Designing a Compact ExB Spectrometer Using SolidEdge™ STL files with Simion™ and 3-D Plastic Prototype Printer

William A. Spencer¹, Jerome J. Geathers², Laura L. Tovo¹,

¹ Washington Savannah River Company

² SCUREF

A prototype compact electrostatic and magnetic sector mass spectrometer was constructed based on the Diaz and Gentry crossed field concepts using Simion™ ion modeling and Solid Edge™ CAD 3D software. Assembly of the parts was facilitated by using a 3-D printer driven from the CAD software. The ion source was a miniature design taken from a Mass Sensor R8 spectrometer. Based on Simion models that used STL files that were created from the CAD rendering of the ion source, the ion source was mounted on a polycarbonate part that was designed using SolidEdge™ and then printed using a 3-D plastic prototype printer. The plastic part oriented the ion source against square neodymium boride magnets and detector assembly. Different field strengths and sizes of magnets were tested. Magnets up to 50 mm square and 12 mm thick were used. Instead of an exit slit and conventional detector, a Burle ion imaging detector system provided a fluorescent image of the ion emissions. This innovative detector allowed multiple ion focal points to be detected simultaneously and optimum orientation of the detector versus physical boundary limitations could be made. Movies of the ions during scanning were obtained. The following presentation will discuss the design concepts, the potential for low cost mass spectrometry, and some of the performance parameters involving the prototype plastic parts. The system was designed for atmospheric gas monitoring and other applications requiring measurement of low masses.

WSRC-STI-2007-00375

Compact Ambient Pressure Pyroelectric Ion Source for Harsh Environment Mass Spectrometry

Evan Neidholdt, J.L. Beauchamp

California Institute of Technology, Pasadena, CA

We present the construction and implementation of a compact, low power ambient pressure pyroelectric ionization source (APPIS) for harsh environment mass spectrometry. In the present implementation, APPIS comprises a z-cut lithium niobate or lithium tantalate crystal with an attached resistive heater mounted with the -z face exposed in front of the atmospheric pressure inlet of an ion trap mass spectrometer. The source will work with any instrument possessing an atmospheric pressure inlet. This source is simple and robust and might prove useful in applications where unattended operations in harsh environments, long service lifetimes, and durability are desirable characteristics. Positive and negative ion formation alternately result from thermally cycling the crystal over a narrow temperature range, typically less than 30 K from ambient. Both cations and anions can be produced from a single face of the crystal, but not detected at the same time. At a fixed temperature, the net charge of the crystal face due to polarization is compensated by charged species of the opposite sign that accumulate at the interface. A decrease in temperature leads to an increase in polarization and a net surplus of negative compensating charges on the -z face. Anions are detected at this time. As the crystal is heated, the decrease in polarization results in a net surplus of positive charge on the -z face. Cations are detected at this time. Ionization of 2-(butylamino) ethanethiol or diethyl phosphoramidate, simulants for the CBW agents VX and Tabun, respectively, results in the detection of singly protonated monomers or dimers of each in the positive ion mass spectrum. Ionization of 1,1,1,3,3,3-hexafluoroisopropanol or benzoic acid results in observation of the singly deprotonated species and their clusters in the negative ion mass spectrum. Processes in which ion formation occurs directly on the highly charged crystal surface may contribute to the observed signal, as well as observed electrical discharges on the crystal surface. Video observation of the crystal z faces during temperature cycling reveals localized electrical discharges on the face of the crystal. An inductive pickup was used to investigate a correlation between discharging and ion production. A significant fluence of ions is observed during periods of electrical quiescence, suggesting the possibility of protonation and deprotonation occurring due to reactions of molecular species at the crystal face, with release of ions to the gas phase.

POSTER ABSTRACT

Detection of Explosives using a Portable SPME/GC-Cylindrical Ion Trap Mass Spec

Amber L. Russell¹, Anthony J. Bednar², Denise K MacMillan³, Charolett A. Hayes¹, Beth Porter¹, Nate D. Nulherin⁴, Louise Parker⁴

¹SpecPro, 3909 Halls Ferry Rd., Vicksburg, MS

²Engineer Research and Development Center, 3909 Halls Ferry Rd, Vicksburg, MS

³Environmental Protection Agency, 109 TW Alexander Drive, RTP, NC

⁴Cold Regions Research and Engineering Laboratory, 72 Lyme Rd, Hanover, NH

Long term monitoring at Department of Defense sites is required to demonstrate successful remediation and regulatory compliance. The monitoring programs are expensive with the majority of the costs related to sampling, shipping, and analysis. Field analytical technologies can reduce monitoring costs compared to fixed laboratories, however the field instruments must produce data that is acceptable for regulatory purposes. The goal of this work is to test a field analytical method for munitions constituents found in ground water at a formerly used Department of Defense site.

A Griffin Analytical Technologies Minotaur 300 cylindrical ion trap (CIT) was used to develop an analytical method for the detection of munitions constituents. The munitions constituents of interest were TNB, RDX, 1,3-DNB, TNT and 2,4-DNT, all known contaminants of the field site. Concentrations of the munitions constituents in the ground water of the site ranged from ~40 ppb to 16 ppm. The CIT was equipped with a Restek RTX-TNT heated gas chromatography capillary column, which allowed for confident identification of the target analytes and separation from interferences. Solid phase micro-extraction (SPME) fibers were chosen to eliminate chemical waste generated in the field and reduce sample volumes.

The method developed on the Minotaur 300 was transferred to the field ruggedized Griffin Analytical Technologies Minotaur 400 mass spectrometer for the field work. Standard low flow sampling was used to collect water from monitoring wells at the site, which was then extracted with SPME fibers and analyzed immediately on the Minotaur 400. Additionally 500 mL samples were transported to our fixed laboratory for analysis by the traditional EPA method for explosives, SW-846 Method 8330. The SPME results taken in the field and run immediately show better detection of the low level constituents, compared to SPME fibers collected in the field and run later in the lab. The GC-MS results taken on the Minotaur 400 will be compared with the results from the traditional EPA method for explosives. With the Minotaur 400 we were able to detect RDX from the solid phase extraction (SPE) by GC-MS, however, we were never able to detect HMX, also a known contaminant of the site.

The results of this work demonstrate successful field analytical technologies for the detection of munitions constituents in ground water. We are currently investigating other techniques for improved detection of RDX and HMX.

A Novel Resistive Glass Atmospheric Pressure Ion Mobility Spectrometer

Mark Kwasnik¹, Joe Caramore¹, Katrin Fuhrer², Marc Gonin², Katherine Barbeau³,
Facundo M. Fernandez¹

¹ School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA

² TOFWERK AG, Thun, Switzerland.

³ Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA

Ion mobility spectrometry (IMS) is a rapid gas phase separation technique which discriminates between compounds based on their mass-to-charge ratio and molecular cross-section. Atmospheric pressure IMS does not require a vacuum system or any other high power consumption components and is, therefore, well-suited as an ion introduction interface for portable mass spectrometry (MS). Combining IMS and MS effectively adds a 2nd dimension of analysis and a capability for real time, high-throughput separation of complex environmental samples. In this work, we present the first results produced by an atmospheric pressure IMS based on resistive glass drift tube technology. The use of resistive glass tubes ensures a highly-homogeneous electrical field in the drift region and simplifies the design, construction, and connections of the spectrometer. The use of resistive glass tubes also allows for modifications in the length of the drift region in order to customize the instrument for specific applications requiring higher resolving power or having a size constraint. The final goal of the work presented here is to develop a modular and fieldable instrument capable of producing molecular-level information about environmentally-relevant compounds by combining the advantages of increased sensitivity and matrix tolerance of nano-electrospray, the speed of IMS analysis, and the power of MS to identify unknowns.

Environmental analysis often entails identification and quantitation of trace analytes. In order to improve sensitivity of the IMS for trace analysis, we demonstrate the application of an ion-gating multiplexing scheme which encodes the ion beam by applying an arbitrary gating waveform to the Bradbury-Nielson ion gate. The multiplexing scheme increases the duty cycle of the IMS from <0.5% up to 50%, improving the signal-to-noise ratio of the spectral data collected. Data on the performance of this new IMS drift cell while operating in standalone mode with Faraday plate detection along with preliminary data when operated in IMS-MS mode while coupled to a time-of-flight mass spectrometer will be presented.