

7th Workshop on Harsh-Environment Mass Spectrometry

Santa Barbara, California
21 – 24 September 2009

Welcome

On behalf of the Organizing Committee, welcome to the 7th Workshop on Harsh-Environment Mass Spectrometry (HEMS), located here in beautiful Santa Barbara, California.

Deploying mass spectrometers outside of the typical laboratory setting means placing complex equipment in diverse environments. These range from volcanoes, battlefields, hazardous urban sites, and ocean depths, to outer space and other rugged locales. Building mass spectrometers to withstand the rigors of such harsh and remote environments poses unique technological challenges to engineering design and science objective planning. Stringent operational requirements for power, size and durability must all be met while achieving the goals of the scientific mission. By applying sound engineering principles, HEMS participants have reported design innovations in systems successfully deployed to the ocean depths, remote hazardous waste sites and even the planet Mars.

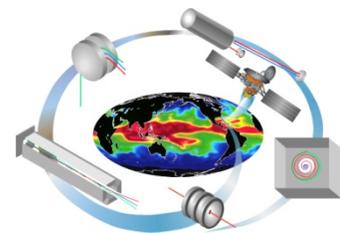
This 7th Workshop brings together academics, industry professionals, and government and business leaders to interact and discuss recent progress in fielding mass spectrometers to rugged environments. The workshop includes both oral presentations and a poster session, and will provide opportunity to interact with mass spectrometry vendors.

We have created a full program, and 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 Program has been designed as a working tool for easy note taking and post-workshop reference. Thank you for joining us; we look forward to your participation.

Sincerely,

Ben D. Gardner
President, HEMSS
Chairman, 7th HEMS Workshop Organizing Committee



7th HEMS Workshop

Organizing Committee

Ben D. Gardner, *Chairman*
R. Timothy Short, *Treasurer*
Strawn Toler, *Web/Materials*
C. Richard Arkin, *Abstracts*
Gottfried Kibelka, *Advertising*
Guido Verbeck, *Student Scholarships*
Steve Taylor, *Publications*
Lynell J. De Wind, *Registration/Program*

Harsh-Environment Mass

Spectrometry Society Board

Ben D. Gardner, *President*
R. Timothy Short, *Treasurer*
Strawn Toler, *Secretary*
Directors without Portfolio
Gottfried Kibelka
C. Richard Arkin
James Wylde

Our Sponsors

Sponsors since 2003



Sponsors since 2005



Sponsors since 2007



New Sponsors



Our History

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.

Past Workshops

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*

The 7th Harsh-Environment Mass Spectrometry Workshop

September 21–24, 2009, Santa Barbara, California

Presented by the *Hamilton Sunstrand Corporation*

Tuesday, September 22

Time	Topic	Speaker	Page #
7:00	Breakfast		
8:40	Welcoming Remarks	Ben Gardner	
9:00	The ULISSES Project: Utilization In-Situ Airborne MS based Instrumentation for the Study of Gaseous Emissions at Active Volcanoes	J. Andres Diaz	8
9:30	Discontinuous Atmospheric Pressure Interface for Miniature Mass Spectrometers	Liang Gao	9
10:00	Mid-morning Break		
10:30	Hot Cell MIMS: Direct analysis of semi-VOCs liberated from practically any type of solid sample	Frants R. Lauritsen	10
11:00	Magnet portable mass spectrometer with membrane inlet system	Stanislav Vlasov	11
11:30	A Compact, Stand-Alone, Integrated MS/Vacuum Package	Philip S. Berger	12
12:00	Workshop Lunch		
1:30	Poster Session	<i>see abstracts</i>	32-46
3:00	Switched Ferroelectric Plasma Ionizer (SwiFerr): A Robust Ion Source for Mass Spectrometry in Harsh Environments	Evan L. Neidholdt	13
3:30	Improving the Measurement Accuracy of Water Partial Pressure Using the Major Constituent Analyzer	Ben D. Gardner	14
4:00	E2M – The Enhanced Environmental Mass Spectrometer: Case Studies using the Mobile MS	Franziska Lange	15
Free Evening			

Wednesday, September 23

Time	Topic	Speaker	Page #
7:00	Breakfast		
8:30	Mars Phoenix Lander Thermal and Evolved Gas Analyzer	John H. Hoffman	16
9:00	Progress in Two-plate Ion Trap Mass Analyzers	Daniel Austin	17
9:30	Chip-Scale Quadrupole Mass Filters for a Micro-Gas Analyzer	Kerry Cheung	18
10:00	Group Photo/Mid-morning Break		
10:30	GUARDION™-7 Hand-Portable Gas Chromatograph-Toroid Ion Trap Mass Spectrometer (GC-TMS): Recent Enhancements and New Applications	Doug Later	19
11:00	High-Performance, Militarized Mass Spectrometer System	Jack Syage	20
11:30	Autonomous Light-weight Integrated Direct Sampling Mass Spectrometer for TIC and CWA Detection	Mitch Wells	21
12:00	Free for Lunch (<i>not provided</i>)		
1:30	Modeling the Orion Air Monitor	David E. Burchfield	22
2:00	Mars Organic Molecule Analyzer (MOMA): Instrument Concepts and Results	Luann Becker	23
2:30	Mid-afternoon Break		
3:00	Miniature QMF and LIT using LBMT for HEMS Applications	Stephen Taylor	24
3:30	Fabrication and Testing of Micro-cylindrical Ion Trap Arrays for Miniaturized Mass Spectrometer Development	R. Timothy Short	25
4:00	Achievable Resolution and Efficiency of Tandem Mass Spectrometry for Sub-mm Ion Traps	Guido F. Verbeck	26
6:30	Workshop Dinner @ Ty Warner Sea Center, Stearns Wharf		7

Thursday, September 24

Time	Topic	Speaker	Page #
7:00	Breakfast		
8:30	Status of the Rotating Electric Field Ion Mass Spectrograph (REFIMS) and Its Use in the Space Environment	James H. Clemmons	27
9:00	A Transportable Double-Focusing Mass Spectrometer	Gottfried Kibelka	28
9:30	Mobile GC/MS and Sampling Tools for Continuous Air Monitoring	Garth Patterson	29
10:00	Mid-morning Break		
10:30	Redesign of the Construction and Increase in the Performance of the Peripheral Devices of a Micro Mass Spectrometer	Régulo Miguel Ramírez Wong	30
11:00	Influence of Fast Temperature Program Rate and Fast Linear Velocity on GC-MS Analysis of Chemical Warfare Agent Degradation Products	Philip Smith	31
11:30	Program Survey and Close		
Workshop Ends			

Workshop Dinner: Ty Warner Sea Center

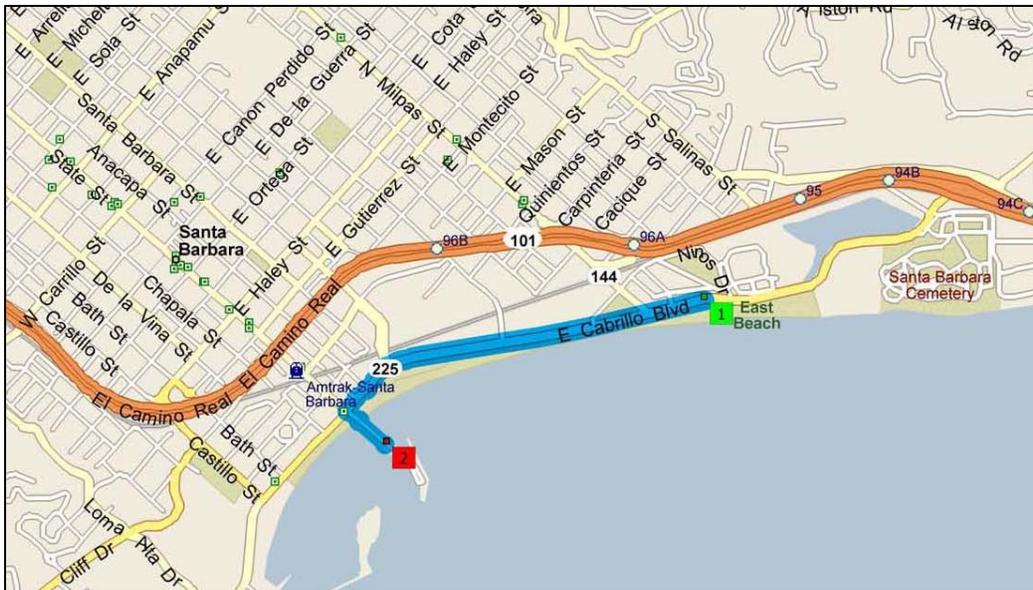


Located on Stearns Wharf at the end of State Street, the Ty Warner Sea Center is owned and operated by the *Santa Barbara Museum of Natural History* and offers numerous marine exhibits and aquaria and a window of the Santa Barbara Channel.

Ty Warner Sea Center
211 Stearns Wharf
Santa Barbara, California, 93101

Telephone: 805-962-2526
<http://www.sbnature.org/>

Directions from Hotel Mar Monte (1) to Ty Warner Sea Center (2)



Santa Barbara, California

Sun-drenched, relaxed and nestled seductively between Los Angeles and San Francisco. Sample the world-class hotels and resorts and delectable restaurants that tempt even the well-seasoned traveler. From State Street and the Santa Ynez Mountains to the Channel Islands and the wine country, Santa Barbara is one of America's best-kept secrets.

Websites for places to eat, things to do and places to shop:

- <http://www.santabarbaraca.com/>
- <http://www.santabarbara.com/>
- <http://www.sbchamber.org/>

The ULISSES Project: Utilization In-Situ Airborne MS based Instrumentation for the Study of Gaseous Emissions at Active Volcanoes

J. Andres Diaz¹, Yetty Madrigal¹, Edgar Rojas¹, Gabriela Duarte¹, Daniel Castillo¹, Sergio Achi¹, Karolina Mesen¹, C Richard Arkin², Eric Gore³, Timothy P. Griffin³

¹*Gas Sensing Lab. CICANUM, Physics School. Universidad de Costa Rica, San José, Costa Rica*

²*ASRC Aerospace Corp., Kennedy Space Center. FL. USA*

³*National Aeronautics and Space Administration, NE-F2, Kennedy Space Center. FL, USA*

As part of the on-going research collaboration between the Gas Sensing Lab at the University of Costa Rica and the Hazard and Gas Detection Lab at Kennedy Space Center, on the use of both ground and airborne mass spectrometer systems applied to volcanoes, a new initiative for the study and visualization of gaseous volcanic emission using in-situ mass spectrometer instrumentation is described.

The data provided by the ULISES project is a key step towards a better comprehension of the geophysical phenomena surrounding eruptive activity. In-situ gas data consisting of helium, carbon dioxide, sulfur dioxide, and other gas species, is acquired with a small mass spectrometer system. Mass spectrometry and global position system (GPS) data is plotted over ground imagery, topography, and remote sensing data. This combination of gas and imaging data allows 3-dimensional visualization of the volcanic plume and the mapping of gas concentration at several volcanic structures. The combined set of data can demonstrate a better tool to assess hazardous conditions by visualizing and modeling possible scenarios of volcanic activity. In addition, its further correlation with remote sensing data can be used for inter-comparisons with same time data taken by other aircraft and space borne instruments.

With different transportation platforms, a portable mass spectrometer system, smaller than the previous AVEMS system flown on NASA WB-57 aircraft, using a compact turbo-pump, two miniature diaphragm pumps, a small mass spectrometer and autonomous control electronics is used for *in-situ* measurement at different volcanic locations in Costa Rica. The first airborne demonstrations this year also points in the direction of using unmanned aerial vehicles (UAVs) as future airborne platform and its unique opportunity to serve in calibration/validation of satellite remote sensing data.

Discontinuous Atmospheric Pressure Interface for Miniature Mass Spectrometers

Liang Gao¹, Zheng Ouyang², R. Graham Cooks¹

¹*Department of Chemistry, Purdue University*

²*Weldon school of Biomedical Engineering, Purdue University*

Discontinuous atmospheric pressure interface (DAPI) was developed to couple atmospheric pressure ionization (API) sources to miniature mass spectrometers. Through DAPI, gases carrying ions of interest are pulsed into the ion trap at a high flow rate rather than continuously at a low flow rate, so that API sources can be used with minimally capable pumping systems. A pumping speed as low as 0.35 L/s enables the operation of an ion trap mass spectrometer fitted with a DAPI interface. Various operation methods have been developed to improve analytical capabilities of miniature mass spectrometers. A multiple pulse ion introduction method is developed to accumulate ions before mass analysis, which improves LOD further. In conjunction with the method, a broad-band waveform is used to allow the entire ion trapping capacity to be used for ions of interest. In another experiment, axial CID can be realized by applying a potential to the DAPI capillary. More complete fragmentation spectra were obtained, although parent ion isolation cannot be performed.

Hot Cell MIMS: Direct analysis of semi-VOCs liberated from practically any type of solid sample

Frants R. Lauritsen

Department of Pharmaceutics and Analytical Chemistry, Copenhagen University

Recently we introduced the hot cell MIMS idea, where solid samples as well as liquid micro extracts can be analyzed without any pretreatment for their potential liberation or content of semi-volatile organic compounds (semi-VOCs). This talk will present the fundamental ideas that makes fast analysis of semi-VOCs possible using "standard" and field portable membrane inlet mass spectrometry. Examples of the analysis of chemicals liberated from soil, plastic and plant materials will be presented.

A possible application of a portable hot cell MIMS system is real-time identification of drugs found near intoxicated persons or at crime scenes. A match of the hot cell MIMS electron ionization mass spectrum and a database spectrum rapidly identifies the chemical. We will demonstrate the direct analysis of pills containing anti depressive drugs (Citalopram, Venlafaxine, Sertralin and Paroxetine) commonly used in suicidal attempts in Scandinavia.

Magnet portable mass spectrometer with membrane inlet system

Stanislav Vlasov, Dmitrii Lebedev, Iskander Amanbaev, Viktor Kogan
Saint-Petersburg State Polytechnical University

Presentation is devoted to calculation, development and testing of a portable magnetic sector mass spectrometer with membrane inlet. Mass analyser of the instrument, includes electrostatic cylindrical capacitor and permanent magnet system with small sector angle and supplies double-focusing of an ion beam. Special electron impact ion source and two Einzel lenses provide z-compression of the beam at the entrance of the linear segmented detector array. The ion-optic scheme of the detector allows carrying out simultaneous and independent scanning of the separate sub ranges of the whole mass range at the dynamic range of $\sim 10^7$. Mass spectrometer equipped with a membrane inlet system for VOC's and SVOC's detection. The construction details and testing results are discussed.

A Compact, Stand-Alone, Integrated MS/Vacuum Package

Philip S. Berger, Blake Leonard
Ceramitron, LLC

Reducing the size, weight and power consumption of a mass spectrometer has been the object of significant ongoing research for over 30 years, driven especially by NASA's need to place highly sensitive chemical detectors in very remote and harsh environments. As the latest instruments have continued to shrink, the key remaining "Achilles Heel" limiting the deployment of these smaller, ruggedized MS units is the vacuum system. Ceramitron, LLC has recently tackled this problem with a novel design that eliminates the mechanical pumps and vacuum chamber and substitutes a self-contained package featuring chemical sorption pumps integrated into the vacuum enclosure. The result is a rugged, general purpose chemical/gas sensor that reduces weight and power consumption by nearly two orders of magnitude over conventional MS offerings.

In even the smallest MS devices, the empty volume inside the vacuum chamber occupies most of the space, and stainless steel enclosures contribute to the bulk of the weight. Ceramitron's tiny double-focusing magnetic-sector MS measures only $50 \times 620 \times 10$ mm, weighs <150g and consumes <10W. The device enclosure doubles as the vacuum chamber with an internal volume of <5ccm. A small ion pump (IP) and a non-evaporable getter (NEG), both residing inside in an attached enclosure, maintain an operating pressure between $10E-6$ and $10E-4$ Torr. Gas "pulsed" into the analyzer provides low duty cycle sampling of the target compounds.

Ceramitron's double-focusing MS sensor, constructed entirely from fiberglass (ultimately, from alumina) is hermetically sealed and is intended to be delivered commercially as a service-free consumable, easily replaced in the field by minimally-trained operators. A service life of 2-12 months is expected, depending on the application, with a sensor replacement cost of ~\$400.

Low duty cycle applications include monitoring of landfills, GHG depth profiling using weather balloons, military standoff detectors, down-hole gas measurements, and terrestrial and extra-terrestrial research applications on unmanned platforms.

Switched Ferroelectric Plasma Ionizer (SwiFerr): A Robust Ion Source for Mass Spectrometry in Harsh Environments

Evan L. Neidholdt, J.L. Beauchamp
California Institute of Technology

We describe a novel ion source, the switched ferroelectric plasma ionizer (SwiFerr), for ambient analysis of trace substances for use in autonomous and portable instrumentation. The device takes advantage of the high electric field resulting from polarization switching in ferroelectric barium titanate (BaTiO_3). The source comprises a [001] oriented barium titanate plate with a metallic rear electrode and a metallic grid front electrode. When a high voltage AC waveform is applied to the rear electrode with the front grid electrode remaining at ground potential, the resulting electric field on the face of the crystal promotes electron emission and results in plasma formation between the sample face and the grounded grid at ambient pressure. Interaction with this plasma and the resulting reagent ions effects ionization of trace neutrals in the device. The source consumes less than one watt of power under normal operation, and ionizes molecules with acidic and basic functional groups easily. SwiFerr has proven quite versatile for ambient analysis of both vapor phase and solid phase samples, including solvents, amines, organic acids, and pharmaceuticals. Ionization of vapor phase samples of the amines triethylamine, tripropylamine, tributylamine and pyridine results in observation of the singly protonated species in the positive ion mass spectrum with good sensitivity in the low ppm range. Aerodynamic sampling of powdered samples was used to record mass spectra of the pharmaceuticals loperamide and ibuprofen. The source, which requires no reagent gases or solvents, lends itself easily to miniaturization and incorporation in field portable devices used for the rapid detection and characterization of trace substances and hazardous materials in a range of different environments.

Improving the Measurement Accuracy of Water Partial Pressure Using the Major Constituent Analyzer

Ben D. Gardner, Phillip M. Erwin, Wai Tak Lee, Amber M. Tissandier, Souzan M. Thoresen
Hamilton Sundstrand Space Systems International

The Major Constituent Analyzer (MCA) on board the International Space Station (ISS) is a mass spectrometer-based system designed to monitor the major constituents of the ISS internal atmosphere. Of these, nitrogen, oxygen, methane, carbon dioxide, and hydrogen are being monitored as originally designed. Obtaining accurate water vapor measurements, however, has been problematic. The primary issue for water vapor measurement is the adsorption of water onto the interior surfaces of the ISS sampling lines, MCA internal sample transport lines, and the MCA analyzer itself. Whenever the partial pressure of water in the sample stream changes, a new equilibrium between the adsorbed and gas phases must be reached before a measurement will reflect the actual partial pressure. Thus, while changes in the partial pressures of the other major constituents are detected in real-time, accurate measurement of the water partial pressure is delayed. Unfortunately, the time required to reach equilibrium is longer than current MCA operating parameters allow, so the measured values are not accurate.

This issue was apparent early on in the MCA program, when the temporal characteristics of humid air being transported from sample points in the ISS modules through various lengths of tubing was unknown. The decision was made at that time to descope water from the measurement process until a future date when the problem could be properly addressed. Recently, the MCA program has been authorized to revisit the issue as a sustaining engineering task and implement the findings as part of a series of upgrade and improvement tasks through NASA change request CR10773A.

This paper describes the basis for identifying the primary contributors to the water desorption time constant within the MCA, and an improved method for accurately determining the water vapor partial pressure. The method includes a revised procedure for calibrating the MCA water channel as well as a strategy, based on the modeling, for accurately estimating ISS humidity levels within the sampling times allocated for each module. The improved method is scheduled for implementation into the MCA firmware in the fall of 2009.

E2M – The Enhanced Environmental Mass Spectrometer: Case Studies using the Mobile MS

Franziska Lange, Rainer Lippe, Thomas Ludwig
Bruker Daltonics

E2M is a compact robust quadrupole mass filter with a membrane inlet. It has been designed for mobile application. It affords reliable identification of organic compounds in solid, liquid or gaseous samples. The instruments air/surface probe provides fast results in monitoring modes. Combined with a gas chromatograph over the complete E2M system delivers a versatile field deployable GC/MS capability. Non-complicated controls and data acquisition enhance the instruments ease of operation. Data evaluation is fully automated. User configuration enables several spectra libraries to be selected for substance identification.

The ruggedized instrument can be installed on a vehicle and run from the vehicles power supply. Typical applications are environmental protection, mobile on-site analysis, event monitoring, first responders or homeland defence.

Applications range from direct surface sampling allowing rapid identification, for a multitude of drugs using the air/surface probe or identification of drugs in complex mixtures using the GC oven. Compared to quick tests the latter method is not limited to substance specific reactions. Thus the constitution of different drug compositions (thinned down compounds, impurities etc.) can be clarified. Other applications include on-site analysis of volatile organic compounds in soil and air, carried out at a ground polluted site caused by industrial processes. E2M with mounted GC oven in thermodesorption mode was used to analyse air from a dump trapped on TENAX®-tubes. Different volatile substances were detected and identified using the NIST library. At another former industrial site soil samples from drill cores were analyzed using direct application of the air/surface probe. Several chlorinated solvents could be detected.

Mars Phoenix Lander Thermal and Evolved Gas Analyzer

John H. Hoffman

Physics Department, University of Texas at Dallas

The Phoenix mission to Mars consisted of a spacecraft that landed in the far northern region of the planet on May 25, 2008 with the goals, among others, of verifying the presence of water on Mars and determining the mineralogy of the surface materials. It incorporated a robotic arm capable of digging trenches in the surface and depositing samples in two of the onboard instruments, the Wet Chemistry Laboratory and the Thermal Evolved Gas Analyzer (TEGA). The latter consisted of a set of 8 very small ovens that heated samples up to 1000° C and a mass spectrometer, the Evolved Gas Analyzer (EGA), to analyze gases evolved during the heating process. The EGA consisted of a magnetic sector-field mass analyzer having a mass range of 1 to 140 Da, an electron bombardment ion source, a gas handling manifold, associated electronics and a vacuum maintenance pump. At a depth of about 5 cm below the surface a very hard material was exposed. Analysis of the material confirmed the presence of water ice mixed with the soil. In addition, magnesium perchlorate was found in the soil at an abundance of nearly 1%, which was totally unexpected. However, no hydrocarbons were found. Details of these results will be presented.

Progress in Two-plate Ion Trap Mass Analyzers

D. Austin, Z. Zhang, A. Hawkins, Y. Peng, B. Wang, B. Hansen

Brigham Young University

We report on a new method for building ion trap mass analyzers. The electric fields for trapping and analysis are made between two lithographically patterned plates. Potentials are established on each plate in such a way as to produce the appropriate potential distribution between the plates. This design has been used to produce three ion traps: a quadrupolar (Paul) trap, a toroidal trap, and a combination-in-space of the quadrupolar and toroidal traps. In each design, the potential distributions are established using sets of concentric ring electrodes patterned on each plate. Each ring is set to a different RF amplitude using a capacitive voltage divider. The electric field shape, including higher-order multipoles, can be modified by changing the RF amplitudes on one or more of the rings. As a result, this approach has great flexibility in terms of the type and shape of electric field that can be produced. The quadrupole trap is operated using 700 V RF at 1.1 MHz, and uses axial modulation for ion ejection. This trap has so far demonstrated good mass resolution (typically 500-700), mass range (50-400), and tandem capabilities. The two-plate approach can be used to make rugged, miniaturized mass analyzers for handheld and portable applications.

Chip-Scale Quadrupole Mass Filters for a Micro-Gas Analyzer

Kerry Cheung, L. F. Velasquez-Garcia, A. I. Akinwande
Massachusetts Institute of Technology

Microelectromechanical systems (MEMS) technology holds the promise of making devices smaller, faster, better, and cheaper. The Micro-Gas Analyzer (MGA) project at MIT attempts to leverage MEMS capabilities to create a low-cost, high-performance, portable mass spectrometer. Batch-fabrication of various components for the MGA such as ionizers and electrometers have been demonstrated to date, but the mass filter component still has room for exploration.

Chip-scale quadrupole mass filters achieved entirely through wafer-scale processing have been designed, fabricated, and characterized. The device integrates the quadrupole electrodes, ion optics, and housing into a single monolithic block, eliminating the electrode-to-housing misalignments inherent in other quadrupoles that results in degraded performance. To achieve this integration, unconventional square electrode geometry was utilized. Since the quadrupole potential is a boundary value problem, the electric fields around the central axis of the device has minimal distortion arising from the non-ideal electrodes. This concept formed the basis of the micro-square electrode quadrupole mass filter (MuSE-QMF).

The MuSE-QMF demonstrated mass filtering with a maximum mass range of 650 amu and a minimum peak-width of 0.5 amu at mass 40, corresponding to a resolution of 80. These results are equal to or better than other reported MEMS-based quadrupoles. More importantly, the design concept can be extended to much more complex architectures that were previously unachievable. Batch-fabricated quadrupoles in arrays, in tandem, or with integrated pre-filters can have significant impact on the future of portable mass spectrometry. Additionally, experimental characterization of the MuSE-QMF makes a case for operation in the second stability region as a means for achieving good performance with non-ideal electrodes. Results also suggest some novel behavior for the square geometry, motivating new studies on quadrupole ion dynamics.

GUARDION™-7 Hand-Portable Gas Chromatograph-Toroid Ion Trap Mass Spectrometer (GC-TMS): Recent Enhancements and New Applications

Doug Later¹, Christopher R. Bowerbank¹, Joseph L. Oliphant¹, Tiffany C. Wirth¹, Edgar D. Lee¹, Charles S. Sadowski²

¹*Torion Technologies, Inc.,*

²*Smiths Detection*

The demand for miniaturized mass spectrometers that are highly selective, sensitive and can make rapid measurements in harsh environments is increasing for a variety of applications. At the 2007 HEMS conference, Torion reported on the development of the world's smallest hand-portable GC-TMS. The instrument features a low thermal mass capillary gas chromatograph (GC) with rapid temperature programming and a miniature toroidal ion trap mass spectrometer (TMS) with a mass range from 45 to 500 Daltons. The configuration of the miniature toroidal ion trap mass spectrometer (TMS) allows more ions to be stored for a given trap radius. The 2 mm r^o of this analyzer also allows operation at significantly lower RF voltages than laboratory-scale instruments. The GC-TMS system is totally self-contained with dimensions of 18.5 x 14 x 7 in, weighs less than 28 pounds, is battery operated, and hand-portable. Samples are injected using a novel SPME fiber syringe. The GC-TMS analysis cycle time is 4-5 min, including GC cool down time and data processing. This hand-portable GC-TMS is ideally suited for rapid measurements of chemical agents, explosives, and hazardous substances in harsh environments encountered in field testing.

Since the last HEMS conference several enhancements have been implemented that improve the performance of this miniaturized GC-TMS. For example, a constant mass flow of helium from the GC column improves the mass spectral reproducibility of the TMS. This is because charge exchange between the ionized helium from the GC carrier gas and the separated compounds entering the toroidal ion trap is the primary ionization mechanism. A constant pressure in the TMS results in a more constant collision rate between the helium background gas and ions in the trap, which keeps mass resolution consistent over the analytical run. Constant mass flow during the GC temperature program is now possible with electronic pressure control (EPC) of the helium carrier gas. Better chromatographic performance in terms of chromatographic and mass resolution, as well as improved chromatographic peak shape at higher GC temperatures, has been achieved with EPC.

From the TMS side, a better understanding of the toroidal ion trap technology has resulted in other performance improvements. A major advantage of the toroid over a standard Paul ion trap is that ion storage capacity, before space charge effects become critical, is greatly increased because the ions are stored in a toroidal geometry as opposed to a spherical geometry. Modeling experiments of the TMS system using SIMION and comparison with as-built data have now been completed. Information gleaned from these experiments has led to not only a better understanding of the fundamental operational mechanism of the toroidal ion trap, but also improvements in the traps surface finish, GC interface positioning, and optimization of the mechanical aspects of the entrance lenses and exit slits. Such improvements have extended the operational time between maintenance cycles and improved the instruments mass resolution.

High-Performance, Militarized Mass Spectrometer System

Jack Syage¹

Jointly developed by: Syagen Technology, Inc.¹ and Northrop Grumman Corporation

In this work we address the need for high-performance, real-time chemical analysis for military vehicle use. The system that we describe is fully ruggedized to withstand the rigors of reconnaissance vehicles in which detection is done while the vehicle is moving along rough terrain. The militarized MS system is based on a previous design and consists of a quadrupole ion trap, time-of-flight (QitTof) system with a dual photoionization/electron ionization (PI/EI) source. A key feature of the QitTof analyzer is the capability to do MS screening at 60 Hz followed by MS/MS confirmation at 30 or 60 Hz. This enables the detection of a large targeted compound list including chemical warfare agents (CWAs) and toxic industrial compounds (TICs) although the detectable range of compounds extends beyond these categories. The MS system is able to detect vapor and liquid samples using an automated sampling system.

The PI/QitTof MS technology has been tested on over 12 CWAs including VX, GA, GB, GD, GF, HD, HN-1, HN-3, BZ, DL, CR, and CX as well as about 40 precursors, decomposition products, and simulants. MS and MS/MS spectra were recorded and real-time detection limits are at the pg level for direct sampling (without GC) of injected or thermally desorbed samples. A trial of 13 TICs demonstrated below Army reconnaissance requirement detection levels for all TICs. The MS system is fully automated including autotuning, auto-mass calibration, and has an algorithm to automatically set the alarm levels for all targeted compounds.

Acknowledgements: Northrop Team: Danielle Dickinson, et. al; Syagen Team: Karl Hanold, et.al.

Autonomous Light-weight Integrated Direct Sampling Mass Spectrometer for TIC and CWA Detection

Mitch Wells, Garth Patterson, Dennis Barket, Jr., Miriam Fico, Brent Rardin

ICx Technologies, Inc.

Mass spectrometry (MS) is a preferred method of analysis due to fast response time, high sensitivity, selectivity in detection, and the high levels of molecular information generated. These advantages are directly applicable to ensuring public safety, such as air monitoring for toxic industrial compounds (TICs) and chemical warfare agents (CWAs). Griffin Analytical Technologies has developed a direct sampling MS which brings the power of MS to field analyses through the use of innovative sample-introduction techniques, ruggedized vacuum systems, and a miniaturized mass analyzer.

The MS system combines a cylindrical ion trap (CIT) mass analyzer with a fast sampling preconcentration inlet and direct leak capillary inlet. Gas-phase samples are drawn through one of two sorbent pre-concentration tubes where organic analytes selectively adsorb to the sorbent material. These tubes are then exposed to the MS vacuum chamber for analyte desorption under heat. Continuous coverage is achieved by simultaneously sampling and desorbing between multiple tubes. Samples not amenable to sorbent sampling, such as light inorganic gases, are admitted through a direct capillary leak. Analyte ionization is internal to the CIT via electron ionization (EI). Electrons are generated from a rugged glow discharge (GD) EI source, significantly reducing the maintenance requirements of the instrument.

Data will be presented to illustrate typical instrument response times for both the direct leak inlet (typically seconds) and individual sorbent tube channels (typically <1 minute). Instrument calibration for several TICs and CWA simulants indicate limits of detection for average sampling times using the solid sorbent inlet are in the low ppb range, below the concentrations deemed immediately dangerous to humans for those compounds. Direct leak limits of detection are usually higher, but are still adequate to provide valuable information on immediate danger levels for most analytes.

The MS data generated with this instrument illustrate the ability of the MS to collect data with unit mass resolution using air as a bath gas in the CIT rather than helium. A list of the chemicals targets is created with their respective spectra. During the analysis of an air sample, the mass spectral data are compared with this list of library spectra for the compounds of interest in order to generate an alarm if selected compounds are detected. The system has been thoroughly challenged during in-house chemical testing with individual and mixtures of TICs and interferences. Testbed deployment of the system to a variety of real-world sites, including airports, train stations, and subway stations has also been completed.

Modeling the Orion Air Monitor

David E. Burchfield, Ph.D., Wai-Tak Lee, Ph.D., Andrew N. Pargellis, Ph.D.
Hamilton Sundstrand

This paper presents the development of a dynamic system model that describes the performance of a sensor-class mass spectrometer used in air monitoring applications. The instrument, currently the basis for the International Space Station's Major Constituent Analyzer and the Orion Crew Exploration Vehicle Air Monitor, is a single-focusing magnetic sector, focal plane mass spectrometer, capable of monitoring species from hydrogen (H_2 , m/z 2) through carbon dioxide (CO_2 , m/z 44), simultaneously, using dedicated Faraday collectors. This class of instrument is similar to the dual sector analyzers that are currently used to monitor air for contaminants on nuclear submarines, and the double-focusing analyzer previously flown to Mars as part of the Viking Lander program, but is here optimized for NASA crew safety applications. Specific applications of the dynamic model to optimizing instrument resolution, system response time to water vapor, and automating the tuning of the analyzer are discussed for the Orion sensor and related dynamic environment implementations.

Mars Organic Molecule Analyzer (MOMA): Instrument Concepts and Results

L. Becker¹, T. Cornish², M. Antione², R. Cotter³, T. Evans-Nugyen³, V. Doroshenko⁴, Goesmann⁵, F. Raulin⁶, F. Goesmann⁷, Harald Steininger⁸, P. Ehrenfreund⁸

¹ *Johns Hopkins University, Physics and Astronomy Department, USA*

² *Johns Hopkins Applied Physics Laboratory, USA*

³ *Johns Hopkins School of Medicine USA*

⁴ *Science and Engineering Services Inc., USA*

⁵ *Max-Planck-Institute for Solar System Research Katlenburg-Lindau, Germany,*

⁶ *Laboratoire Interuniversitaire des Systèmes Atmosphériques, LISA-UMR, Université Paris, France*

⁷ *Max Planck Institute of Planetary Science, Katlenburg-Lindau*

⁸ *Leiden Institute of Chemistry, Leiden, The Netherlands*

The Mars Organic Molecule Analyzer (MOMA) is a powerful multi-source mass spectrometer-based instrument suite for investigation of potential life on Mars. MOMA has been selected as a core element of the Pasteur payload on the ESA ExoMars mission that will launch in 2016. The MOMA instrument is the next generation design for *in situ* life detection instrumentation. The MOMA suite includes a gas chromatograph (GC) and a 266 nm Nd:Yag laser allowing for several methods of volatilizing and ionizing chemical compounds from intact samples over a broad mass range with little or no sample manipulation. Both the LD and GC share an ion-trap mass spectrometer for the detection of volatile (amino acids) and more 'labile' or heavier (small peptides) up to 2000 atomic mass units (amu). The Ion Trap Mass Spectrometer (ITMS) provides enhanced mass resolution over a broad dynamic range and detailed structural information (MS/MS) on specific (single mass) organic molecules and compounds in a given sample substrate. In this paper, we present our current MOMA-LDMS prototype design and some preliminary results on organic compounds of interest including several Martian 'analogue' samples.

Miniature QMF and LIT using LBMT for HEMS Applications

Stephen Taylor¹, Boris Brkic¹, Neil France¹, Adam T. Clare¹, Chris J. Sutcliffe¹, Paul R. Chalker¹, Liang Gao², Scott A. Smith², R. Graham Cooks²

¹*University of Liverpool*

²*Purdue University*

We present the design, construction and test results of a quadrupole mass filter (QMF) and linear ion trap (LIT), both fabricated using Digital Light Processing (DLP), which is a low-cost 3D Layer Based Manufacturing Technique (LBMT). LBMT's are a class of rapid manufacturing technologies, which allow digital manufacture at the microscale without the need for expensive tooling. Instead of removing material via a reductive process, there is a repetitive addition of material in a layer wise manner. An advantage of DLP is that smooth, lightweight, electrode structures of any geometry may be quickly realized at low cost. Both the QMF and the LIT were fabricated with hyperbolic profiles. The QMF was incorporated into a portable residual gas analyzer and was used to obtain hydrogen and helium spectra in the 1-6 Da mass range with a resolution of 70. The LIT was incorporated into a portable mass spectrometer system and experimental mass spectra were obtained for methamphetamine ($m/z=150$), cocaine ($m/z =182,304$) and rhodamine B ($m/z = 443$) with a resolution of 246. For rhodamine B, tandem MS capability was also demonstrated. The mass range (and resolution at large m/z) of the LIT was demonstrated by spectra obtained from ultramark 1621 ($m/z < 1900$). The spectra obtained for the DLP trap occur at a considerably lower RF voltage than a rectilinear ion trap of similar size, which is a consequence of the hyperbolic electrode geometry in the DLP case. Low voltage operation is especially important with regard to harsh environment applications requiring low power consumption for extended periods of operation.

Fabrication and Testing of Micro-cylindrical Ion Trap Arrays for Miniaturized Mass Spectrometer Development

R. Timothy Short, Friso H.W. van Amerom, Ashish Chaudhary
SRI International

The ultimate goal of SRI International (SRI) mass spectrometer miniaturization efforts is to develop a method for very cost-effective fabrication of highly sensitive miniaturized mass spectrometers. Microelectromechanical systems (MEMS) fabrication technologies appear to offer the best opportunity for achieving this goal. Researchers at SRI have investigated the possibility of extreme miniaturization of cylindrical ion trap mass spectrometers (CIT MSs) by using MEMS fabrication methods, and have validated the MEMS approach for fabricating arrays of very small CITs (radii ≈ 0.35 mm) in silicon. Arrays of CITs operating in unison offer the possibility to recover the sensitivity losses encountered by miniaturizing individual CITs.

The approach in CIT array design has been to fabricate two identical arrays of half-CIT structures (each trap with a half-thickness ring electrode and an aperture endplate) which were then bonded back-to-back to form a full CIT array chip. Design and fabrication iterations optimized operation and performance. Experimental data from CIT arrays demonstrated the ability to increase mass spectral sensitivity by integrating signals from individual CITs in the array. Further optimization of the CIT geometry and fabrication process produced mass spectra with better than unit mass resolution.

Computer simulations to guide fabrication processes avoid excessive manufacturing iterations by predicting optimum CIT geometries, primarily with respect to the axial-to-radial dimension ratio (z_0/r_0) and aperture size. These simulations predict optimum operating pressures for the micro-CITs that are several orders of magnitude higher than those for conventional size commercial ion trap mass spectrometers. Therefore, high vacuum pumps may not be required for mass spectrometer systems based on this technology. To realize truly handheld mass spectrometer technology, further miniaturization and integration of ion sources, detectors, and vacuum systems will be necessary.

Achievable Resolution and Efficiency of Tandem Mass Spectrometry for Sub-mm Ion Traps

Guido F. Verbeck¹, David Rafferty²

¹*University of North Texas*

²*1st Detect Corp.*

Currently, as mass spectrometer approach hand-portability, separation front-ends are typically left off, due to the high gas loads placed on the device. With stand alone mass spectrometry, small mechanical and chemical pumps can be employed to reduce size, power need, and ruggedize. This leads to customizable front-end sample inlet systems, designed for selectivity within a controlled chemical environment-coupled directly to the mass analyzer. Tandem mass spectrometry becomes a necessity to greatly reduce false positives, and aid in correct determination of the constituents. Both theoretical and experimental data on the efficiency of MS/MS on sub-mm ion traps will be presented. The work will focus on the isolation resolution, intensity of fragment ions, and peak resolution.

Status of the Rotating Electric Field Ion Mass Spectrograph (REFIMS) and Its Use in the Space Environment

James H. Clemmons

The Aerospace Corporation

The Rotating Electric Field Mass Spectrograph (REFIMS) is presented and discussed. Its principle of operation is discussed and advantages and disadvantages of its use are presented. Its development path is traced, with particular attention placed on variants of the instrument. The improvements made possible by the advent of modern design tools, such as the SIMION computer code, are shown. A flexible prototyping system currently used in the development laboratory is shown and discussed, and results from the system are presented. A design developed for a sounding rocket flight in the Earth's ionosphere is described, and results from calibration runs are presented. Thoughts for future directions conclude the presentation.

A Transportable Double-Focusing Mass Spectrometer

Gottfried Kibelka, Omar Hadjar, Scott Shill, Scott Kassan, Chad Cameron

OI Analytical

Spatially dispersive, non-scanning mass spectrometers (MS) provide full mass spectra continuously, thus enabling rapid analytical techniques. Miniaturizing a sector-field MS and joining it with a detector array that combines high spatial resolution and fast linear response results in a transportable instrument offering speed and precision. The presented instrument is based on a double-focusing sector-field MS of Mattauch-Herzog geometry. A modified charge coupled device (CCD), sensitive to charged particles (ion-CCD), is mounted in the focal plane to detect the ions. The ion-CCD allows the simultaneous collection of all dispersed ions, recording a complete mass spectrum at a rate of up to 350 mass spectra per second. The 2126 discrete detector elements (pixels) distributed over 5.1 cm as well as the integrated readout circuitry of the detector are well suited for the detection of ion beam currents in the low "Femto-Amps". The pitch of the ion-CCD allows for sub-amu resolution (6-250 amu). The resolution in both mass and time makes the MS a good fit for fast GC applications of volatile organic compounds and gases.

Mobile GC/MS and Sampling Tools for Continuous Air Monitoring

Mitch Wells, Garth Patterson, Dennis Barket, Jr., Cynthia Liu
ICx Technologies, Inc.

ICx Technologies develops and manufactures fieldable analytical instrumentation based on mass spectrometry (MS) technology. The small cylindrical ion trap (CIT) mass analyzer is housed in a smaller vacuum manifold and can be used at higher pressure, requiring less stringent vacuum pumping than traditional laboratory mass spectrometers. This small MS is interfaced with a low-thermal-mass (LTM) GC having a wide variety of sample inlets that can accept samples from vapor, liquid, and solid phases. This very versatile GC-MS system provides onboard air sampling, as well as a handheld vapor sampler that can be operated in harsh environments while in protective posture (e.g. MOP gear), and then directly interfaced with the GC-MS for analysis. This talk will present our most recent results on using the GC-MS onboard air sampler and the handheld air sampler for monitoring low concentration VOCs in ambient air in a variety of environments.

Internal lab and office air from multiple locations were monitored and characteristic signatures for isolated chemicals were obtained. The internal air analysis showed a wide variety of chemicals, such as hexane, cyclohexane, D5 (decamethylcyclopentasiloxane), and limonene. Over the course of 24 hours, these chemicals provided a chemical map of the staff's activity. The relative concentration of D5, a common ingredient in personal care products, began to rise at approximately 6:00 am and ebbed at around 6:30 pm. Additionally, limonene and hexane/cyclohexane signatures were present due to a staff member eating an orange prior to entering the lab and another staff member sonicating instrument parts in hexane, respectively. External air analysis was accomplished by plumbing a line from the instrument to a window and showed a completely different chemical signature demonstrating the presence of naphthalene, methyl naphthalene, and acenaphthalene. One week prior to this analysis, the parking lot was resurfaced and this activity is likely responsible for the chemicals detected by the GC-MS. Naphthalene provided the strongest signature however, the relative concentration fluctuated based on temperature and cloud cover. High exposure to sunlight proved to be the most important condition to releasing the chemicals from the parking lot surface.

The handheld air sampler was used for longer-term monitoring of air to detect trace levels of VOCs such as toluene. A calibration curve for toluene showed a detection limit of ~10 parts-per-trillion (ppt) with a linear dynamic range of at least three orders of magnitude for 40 minutes sampling time (20 L of air sampled). Air sampling in various locations inside and outside office buildings in a local business park, including in a brand new laboratory; interestingly, this new lab showed a toluene background concentration of over 100 times any of the other locations, presumably due to the offgassing of the new building materials.

Redesign of the Construction and Increase in the Performance of the Peripheral Devices of a Micro Mass Spectrometer

Régulo Miguel Ramírez Wong, Maria Reinhardt, Jörg Müller, Henning Wehrs, Gregory Quiring
Technische Universität Hamburg-Harburg

The Planar Integrated Micro Mass Spectrometer (PIMMS) presented by Hauschild et. al. (HEMS 2007) has been partly redesigned and its peripheral devices further improved in performance and size. The microplasma used for ionization has been optimized such that the electron extraction current increases by one order of magnitude from $\sim 2.5 \mu\text{A}$ to $\sim 37 \mu\text{A}$. Impedance matching and waveguide length reduction has allowed an RF power reduction down to $\sim 200\text{mW}$. By using the printed circuit board (PCB) for the PIMMS module as a vacuum-tight flange (Vacuum-PCB) for the vacuum vessel, the evacuated volume has been reduced to 0.5L. The backside of the Vacuum-PCB is used to make electrical, sample and plasma gas connections to the PIMMS. Gases are fed into the PIMMS through capillaries and valves which are spatially separated from the electronics. The two-channel signal generator previously used for the synchronous-ion-shield (SIS) separator has been replaced by a new four-channel one with a signal rise time $< 1\text{ns}$ for a 1pF load. The rectangular signals can be swept in the range DC-70MHz with a resolution smaller than 0.1Hz. The strategic placement of the generator on the vacuum-PCB allows the rectangular signals to arrive virtually undistorted at the finger electrodes of the SIS separator. The ion current measurement takes place in the immediate vicinity of the detector in the PIMMS, making it insensitive to vibrations and improving its time response ($\tau = 3\text{ms}$). This high input impedance circuit is located on the PIMMS module and converts the ion current (pA range) into a proportional voltage which is then measured at the backside of the vacuum-PCB. The combination of these improvements has led to an increase in the performance of the PIMMS, making it able to measure concentrations $< 1\%$. The total volume of vacuum vessel and pumping unit is 4.5L and weights 5kg.

Influence of Fast Temperature Program Rate and Fast Linear Velocity on GC-MS Analysis of Chemical Warfare Agent Degradation Products

N. Martin; A. Shufutinsky; G. Delong; P. Smith

Uniformed Services University

The chemical warfare agent O-ethyl S-2-diisopropylaminoethyl methyl phosphonothiolate (VX) and numerous VX degradation products containing the diisopropylaminoethyl functional group are known to produce poorly-diagnostic mass spectra by gas chromatography-mass spectrometry (GC-MS) when typical 70 eV electron ionization (EI) is used with a quadrupole mass filter detector. To address this issue three detection methods were evaluated; lab based chemical ionization (CI) GC-MS, field portable ion trap GC-MS and vehicle based EI GC-MS. Chemical ionization reliably produced $M+H^+$ ions useful in the laboratory to definitively identify these analytes, but this method is less amenable for field deployment. Degraded VX was analyzed using a field-portable GC-MS system employing a cylindrical ion trap mass spectrometric detector, and ion/molecule reactions leading to formation of protonated species ($M+H^+$) were noted for all analytes studied. However, as the injected mass of analyte was increased the effects on resulting mass spectra observed included mass axis shifts due to space charge effects and pronounced signal for the dimer ($2M+H^+$) of the degradation product diethyl methanephosphonate. Additional samples were analyzed using a vehicle based GC-MS system equipped with a low thermal mass resistively heated GC column capable of completing rapid analyses. While the quadrupole mass filter used with this instrument and 70 eV EI predictably produced mass spectra for VX-related compounds with no discernible ion/molecule interactions, the lack of diagnostic mass spectra was problematic. This can be compensated through the use of GC retention index (RI) data.

Development of an APPIS-IMS Instrument for space applications

Luther W. Beegle¹, Brett Beckett², Ernest Ryu³, Hugh I. Kim¹, Isik Kanik¹

¹*Jet Propulsion Laboratory*

²*New Mexico State University*

³*California Institute of Technology*

Ion mobility spectroscopy (IMS) is an effective technique for detecting organic compounds in a sample. In order to detect a sample using an IMS, the molecule must undergo ionization. However, current ionization processes pose a significant challenge in utilizing IMS for an outer-space mission. An outer-space instrument must be low mass, small volume, and power efficient. Current lab based ionization methods fail to adhere to these criteria. To solve this problem JPL has been researching a new Ambient Pressure Pyroelectric Ion Source (APPIS) system. APPIS is a compact, low-power ion source that utilizes the characteristics of a pyroelectric crystal. When a sharp temperature gradient is applied to the crystal, electrical discharge occurs at the surface of the crystal. This discharge ionizes compounds on and near the surface of the crystal. Our aim is to utilize this effect for IMS by controlling the temperature gradient of the crystal with a Peltier module system. A Peltier module utilizes the thermoelectric-Seebeck effect to create a temperature difference between the front and back surfaces of the module. When two of these modules are used, the crystal can be heated and cooled causing constant ionization. This method meets the criteria listed previously. The APPIS system integrated with an IMS is suitable to obtain reliable and accurate data in harsh environments.

Real Time Monitoring of Pilot-Scale Biomass Gasification Using a Molecular Beam Mass Spectrometer

Daniel Carpenter¹, Whitney Jablonski²

¹*National Renewable Energy Lab (NREL)*

²*University of North Texas*

Thermochemical conversion (i.e. gasification) of biomass to produce renewable transportation fuels is a leading technology option for reducing U.S. dependence on foreign oil while relieving pressure on global food resources. The National Renewable Energy Laboratory (NREL), working with DOE's Biomass Program, has developed conceptual process designs and seeks to enable cost-competitive production of advanced lignocellulosic biofuels. Gasification of biomass produces a CO- and H₂-rich syngas; it also results in the co-formation of volatile, high-molecular-weight "tar" compounds that must be removed before downstream syngas processing. Tars can be catalytically converted into usable H₂ and CO, but quantitative measurement of these compounds is essential to assess the effectiveness of this approach. A transportable molecular beam mass spectrometer (MBMS), designed to be operated remotely, is being used at NREL to provide real-time, continuous monitoring of high-temperature, steam-laden process gas. It is equipped with several integrated system controls that allow it to interface with a variety of chemical process streams. It is able to sample gases and vapors directly from their reactive environment at elevated temperatures and at ambient pressure by using a three-stage, differentially-pumped vacuum system. Samples are extracted through an orifice and undergo free-jet expansion, causing rapid cooling and an abrupt transition to molecular flow sufficient to quench reactions and prevent condensation. The analyte is thus preserved in its original state, allowing light gases to be sampled simultaneously with heavier, condensable or reactive species without loss of sample. Components of the molecular beam are then analyzed with a commercial quadrupole mass spectrometer. Results are presented here from a parametric gasification study that evaluated several feedstocks and process parameters. A multivariate statistical study of the mass spectral data was undertaken to identify aspects of the system's global chemistry that can be used to minimize tar formation for the different feedstocks.

Deployable Remote Miniature Cylindrical Ion Trap Spectrometer (ReMiCIT)

James D. Fox, Guido F. Verbeck

University of North Texas

We present here the initial platform for a launchable, deployable remote mass analyzer. The mass-spec is designed to be deployable, remotely operated, rugged and cost effective. It has the capability for direct sampling and alternative front-ends. This makes it an excellent candidate for the detection of trace amounts of a chemical that might be hazardous to field personnel and fire fighters. The ReMiCIT can send data to a remote site to be analyzed immediately and in real time, and is robust enough to withstand field damage as the system is encased in a rugged chamber. Deployability is credited to its overall size, 6.25 inches in diameter, comparable to the size of a standard softball. The theory of operation and current milestones are presented. The aim of the project is to create some over reaching goals to aid in the development of future needs.

Online membrane inlet mass spectrometry (Inspectr200-200) for quantification of the methane concentration field around Pockmarks

T. Gentz, M. Schluter

Alfred-Wegener-Institute for Polar and Marine Research, Bremerhaven, Germany

Worldwide, the release of methane from sediments of lakes, coastal regions as well as ocean margins is observed. The gas release is often associated with specific features like pockmarks (morphological depressions at the seafloor), mud volcanoes, cold seeps as well as occurrence of gas hydrates. For such sites gas plumes were observed by underwater camera systems as well as acoustic techniques.

Compared to such semi-quantitative information, rather little-known is the concentration field of CH₄ as well as other gases around e.g. pockmarks. This is mainly to the laborious sampling schemes (e.g. by Rosette Water Sampler) and rather time consuming CH₄ analysis by gas chromatography.

We investigated the CH₄ concentration field around pockmarks in Lake Constance by application of membrane inlet mass spectrometry (Inspectr200-200) combined with a submersible pump system. By this means very steep horizontal and vertical gradients of methane concentrations were observed in bottom as well as surface waters. Compilation of the continuous gas analyses allowed a 3D visualisation of the CH₄ concentration field above pockmarks and computation of methane inventories for the water column.

Characterization of a Carbon Nanotube Field Emission Electron Gun for the VAPoR Miniaturized Pyrolysis-Time-of-Flight Mass Spectrometer

Stephanie Getty, Mary Li, Nicholas Costern, Larry Hess, William Brinckerhoff, Paul Mahaffy, Daniel Glavin, VAPoR Team

NASA Goddard Space Flight Center

Low power, robust technologies are appealing for in situ planetary science throughout the Solar System. We are developing the VAPoR (Volatile Analysis by Pyrolysis of Regolith) instrument towards studying soil composition, volatiles, and trapped noble gases in the polar regions of the Moon. VAPoR will ingest a soil sample and conduct analysis by pyrolysis and time-of-flight mass spectrometry (TOF-MS). We will describe miniaturization efforts within this development, including a carbon nanotube (CNT) field emission electron gun that is under consideration for use as the electron impact ionization source for the ToF-MS. The cathode consists of a patterned array of CNT towers grown by catalyst-assisted thermal chemical vapor deposition. Ultra-clean MEMS fabrication and integration techniques were employed toward three goals: low extraction voltage (<100 eV) during operation to be resonant with gas ionization energies, maximized current transmission through the grid, and mitigation of current fluctuations due to adsorbate-assisted tunneling. We have characterized the performance of the CNT cathode and integrated electron gun through rigorous modeling, current-voltage measurements, and emission lifetesting at variable partial pressures of nitrogen gas to investigate the effects of mechanical sputtering. Implications for *in situ* mass spectrometry in planetary science will be discussed.

High-throughput detection of improvised explosive devices (IEDs) by walkthrough portal with wire linear ion-trap mass spectrometric technology

Yuichiro Hashimoto, Hisashi Nagano, Yasutaka Suzuki, Hideki Hasegawa, Minoru Sakairi, Masuyuki Sugiyama, Yasuaki Takada

Hitachi, Ltd., Central Research Laboratory

The threat of improvised explosive devices (IEDs) has become a serious problem in many countries. The throughput of commercial explosives trace detectors, lower than 500 persons per hour, is not high enough for investigations at ticket gates of train stations in Japan where 2000 persons per hour pass through. To obtain this high throughput, both high selectivity and high sensitivity are required for trace detectors. We previously reported a wire linear ion-trap (wire LIT) mass spectrometric technology. The wire LIT enabled selective MS/MS detection and more sensitive detection than a conventional quadrupole ion trap. As the next step toward high-speed screening of passengers, we have been developing and testing a novel high-throughput vapor-sampling portal combined with the wire LIT. We will present the detection results for explosive trace such as triacetoneperoxide (TATP). We already confirmed that detection of TATP was accomplished within 3 seconds with the new sampling portal.

This work was supported by Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government.

Review of In-Situ Mass Spectrometers Applied to Volcanic Activity Monitoring

Yetty Madrigal¹⁺, Edgar Rojas¹⁺, J. Andres Diaz¹, C Richard Arkin²

¹*Gas Sensing Lab. CICANUM, Physics School. Universidad de Costa Rica, San José, Costa Rica*

²*ASRC Aerospace Corp., Kennedy Space Center. FL. USA*

⁺*Undergraduate Physics Student*

The continuous measurement of SO₂ emissions and other gases such as He, CO₂, H₂S, are an important complementary tool in the prediction of volcanic eruptions. Detection of real time changes in molecular gas concentration levels and flux are important indicators of new magma rising from the magmatic chamber that can lead to a catastrophic eruption.

In-situ mass spectrometry applied to volcanic environments offer an opportunity to obtain measurements of precursor gases in an active volcano. This analytical technique, enabled through miniaturization, automation and rugged components together with remote control, allows real time, long term evaluation of gas activity at volcanoes.

There have been several research initiatives and multiple projects that have brought MS to volcanoes for the purposes described above. The scope of this poster is to present a review of the research conducted to date on the use of mass spectrometer instruments for monitoring in-situ volcanic gas emissions.

The review includes only those projects using “in situ” mass spectrometry, not taking into account projects which involve the analysis of gas samples at the lab. It is intended to explore the different target gases, operating conditions of each of the prototypes and systems used, providing a data base of instruments, system components, and lesson learned.

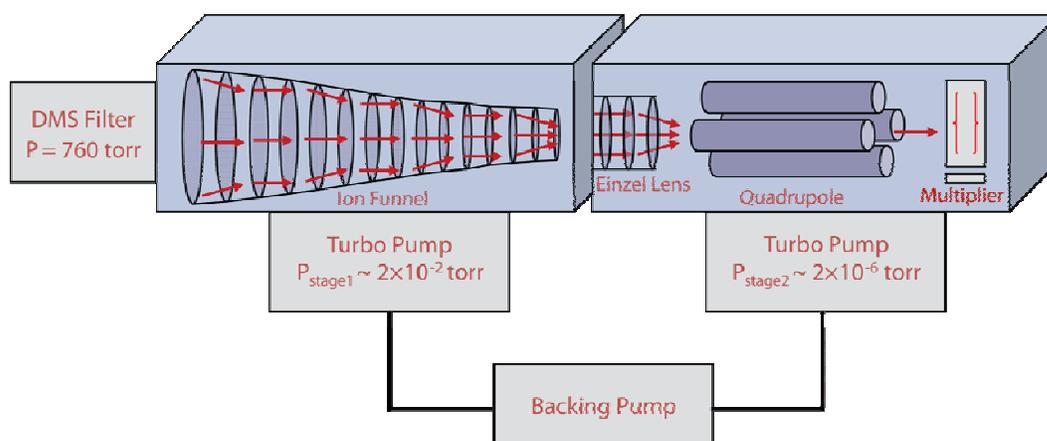
Differential Mobility Spectrometry/ Mass Spectrometry

Manuel Manard, Rusty Trainham

USDOE Special Technologies Laboratory (Operated by National Security Technologies, LLC)

Progress toward the development of a field-portable, prototype differential mobility spectrometry / mass spectrometer (DMS/MS) is described. The current design uses a DMS unit as a chemical filter, separating ions at ambient pressures via the non-linear dependence of an ion's mobility on the RF electric field strength. Here, ions are subjected to an asymmetric alternating RF electric field. The mobility of an ion in high electric fields ($E > 10,000 \text{ V/cm}^2$) is not independent of the electric field strength; thus, alternating between high and low fields changes the ion mobility. This gives rise to unstable trajectories for some ionic species, causing them to collide with the walls of the analyzer region. A DC compensation voltage is superimposed on the RF field, serving to stabilize the trajectories of ions of interest and allowing them to successfully traverse the DMS portion of the instrument for injection into the inlet of a MS.

The MS portion of the system uses two stages of differential pumping in order to step the pressure down from ambient (760 torr) to a region suitable for mass spectrometry to be performed ($\sim 10^{-5} - 10^{-6}$ torr). Ions are transported through stage one ($\sim 5 \times 10^{-2}$ torr) through the use of an electrodynamic ion funnel. An ion funnel is a stack of closely spaced ring electrodes with decreasing internal diameters. A combination of RF and DC potentials are used to focus the ion beam at these intermediate vacuum pressures. Ions exit the ion funnel through a small orifice and enter the high vacuum portion of the instrument. This chamber houses electrostatic focusing lenses, a commercially available quadrupole mass analyzer, and an electron multiplier detector. The focusing lenses will direct the ion beam into the quadrupole for mass selection. The quadrupole and electron multiplier are capable of mass selecting and detecting compounds with less than ppm concentrations and have a linear dynamic range of over six orders of magnitude.



Schematic representation of the DMS/MS system
Ion trajectories are symbolized by the arrows

Anharmonic Resonant Trap Mass Spectrometry (ART MS)

Jeffrey G. Rathbone, Gerardo A. Brucker, Ken Van Antwerp
Granville-Phillips Product Center, Brooks Automation, Inc.

This poster describes a novel mass spectrometer, under development at the Granville-Phillips® Product Center of Brooks Automation, Inc., based on mass separation technology recently discovered by A. Ermakov and B. J. Hinch at Rutgers University. The new mass spectrometer uses purely electrostatic fields to store ionized gases within a cylindrical ion trap. Ions are generated directly inside the trap by electron impact of gas molecules. An anharmonic trapping potential well confines the ion trajectories of all ion masses, and of a wide range of initial energies, to stable oscillatory motions along the axis of the trap. Mass selective ejection is achieved through a novel autoresonant energy pumping process. The new mass spectrometer has unlimited mass range, is capable of achieving high sensitivity at high and ultrahigh vacuum levels, has demonstrated very fast scan rates, is very compact, and requires extremely low power to operate as it uses only static bias potentials and a very small RF signal levels (in the 100mV range). The sensor currently under development is approximately 15 cm in length, with a 2.5 cm ion-trap component capable of scanning a mass range of 1-300amu with a mass resolving power of >130x. The entire structure that includes the ionizer, mass analyzer and detector was integrated into a pre-existing Stabil-Ion® gauge total pressure ionization sensor envelope. The improved sensor provides fast sampling speeds of approximately 70ms for 1-100amu scans and mW RF ion-trap drive requirements that allow for a remote gauge cable connection to the controller electronics. The simple structure and intelligent electronics were developed to allow for self-calibration of partial pressure measurements and automated recalibration of the electron multiplier detector. A novel dual-filament ionization source design was incorporated into the ion trap to allow fast and easy field replacement of filaments. Small size, low power consumption and reliable operation make ART MS technology an ideal candidate for in situ mass spectrometry in a wide variety of remote sampling applications.

New Structures and Measurements of a Planer Integrated Micro Mass Spectrometer (PIMMS) with Integrated Micro-Channel

Maria Reinhardt, Régulo Miguel Ramírez Wong, Jörg Müller, Henning Wehrs, Gregoriy Quiring
Technische Universität Hamburg-Harburg

New measurements with a planar integrated micro mass spectrometer (PIMMS), firstly described by Hauschild et. al. (HEMS 2007), are presented. The small (70mm²) PIMMS chip contains all essential components of a mass spectrometer. These are etched in a 300 μm thick silicon wafer and bonded to a glass substrate with metal structures. Some of these components haven been changed and improved. The system modifications include: optimization of the plasma chamber, implementation of a clamp for a micro-channel plate (MCP) and extension of the mass separator.

By inserting the MCP into the clamp, the measured current increases up to two orders of magnitude. The extension of the mass separator improves the resolution of the spectrum, which agrees with theoretical calculations. This, combined with the application of a new control device of the mass separator (synchronous ion shield - SIS) results in an increase of the total resolution from $R = 10,8$ (old structures) to $R = 32$ (new structures)(measured at Full Width Half Maximum). The measurements became faster and less sensitive to ambient noise by improving the periphery. It is now possible to measure a spectrum of 150 amu in 4.5 seconds. Measurements with air confirm the higher resolution and current. The air spectrums show low concentrated gases like argon at 0.9% and carbon dioxide at 0.04%.

Development and mathematical modeling of a Membrane Inlet Mass Spectrometer for environmental monitoring

Farnoush Salarzaei¹, Boris Brkic¹, Steve Taylor¹, Thomas Hogan¹, Ryan Bell², Tim Short²

¹*University of Liverpool, Department of Electrical Engineering & Electronics-Brownlow Hills;*

²*SRI International, Florida*

Online monitoring of analytes in marine environments is receiving increased attention for a range of applications, including the detection of dissolved gases and volatile organic compounds (VOC's) in water. Some of the analytes of interest are dissolved carbon dioxide, methane, benzene, toluene, tetrachloroethane, trichloroethylene, dimethylsulphide, chloroform and bromoform. In addition to being a main concern of environmental protection agencies, these compounds are also of interest to the oceanographic and atmospheric community. Produced water from active oil and gas fields contains many such dissolved VOC's. It is important to monitor these analytes to not only to mitigate their environmental impact but also to maximise the extraction of oil reserves.

A widely used monitoring method is membrane inlet mass spectrometry (MIMS) which is capable of detecting trace organics in aqueous solutions [1].

The technique is simple and sensitive, provides detection limits in the low ppb range, has no need for pre-concentration. Further, multi-component mixtures can be simultaneously analysed in a few minutes.

Our MIMS system consisted of a PDMS probe inlet, coupled to a portable quadrupole mass spectrometer (QMS) system. Two different QMSs were investigated to monitor analyte concentrations in the range from 10 ppb to 2000 ppm.

In this paper, we present a novel approach for the simulation of MIMS data obtained from monitoring crude oil constituents, such as benzene, toluene and xylene (BTX), both in the laboratory and in the field. By using QMS2-Hyperbolic and QMS-Ion simulation programs, which are multi-ion (>107) trajectory simulations [2], we were able to simulate the performance of the complete system including the MIMS probe and the QMS. The model is therefore capable of modelling full mass spectra across the mass range from 0-200 Da. To test the model, experimental results are compared with the theoretical predictions in each case.

[1] Bell, R.J., Short, R.T., van Amerom, F.H.W. & Byrne, R.H., 'Calibration of an In Situ Membrane Inlet Mass Spectrometer for Measurements of Dissolved Gases and Volatile Organics in Seawater Environ. Sci. Technol. 41, 8123-8128 (2007)

[2] T.J.Hogan and S.Taylor, 'Performance simulation of a quadrupole mass filter operating in the first and third stability zones' IEEE Trans. on Instrumentation and Measurement, 57 (3) pp.498-508 (2008)

Miniature Vacuum System for Portable Instruments

Paul Sorensen, Robert Kline-Schoder

Creare, Inc.

NASA, other government agencies, and commercial industry have acute needs for miniaturized high vacuum systems. Advances in sensor technology in academia, at NASA, and in commercial laboratories have led to the development of miniaturized and rugged mass spectrometers. 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 over 10 years, Creare has been developing the technologies required to design and build miniature high vacuum systems. Recently, we designed a vacuum system that consists of a custom turbomolecular/molecular drag pump and a low power diaphragm roughing pump. Our pumping system has the following pumping specifications: an ultimate pressure for air of approximately 10^{-7} torr; a pumping speed of about 5 L/sec; and an exhaust pressure of 1 atm; and the following physical characteristics: Mass of approximately 750 g, a diameter of approximately 2.0 in., and an overall length of approximately 6.6 in. Data will be presented that show the performance of a brassboard prototype.

Why High Resolution Mass Spectrometry is Sometimes a Desire – The Problem of Measuring Methane, Ammonia, and Water in a HDT Environment

William A. Spencer

Savannah River National Laboratory

Methane, ammonia, and water are common gases in industrial processes and their production values are often desired to track performance of a process. However these gases can be difficult to analyze in a mass spectrometer because the mass spectral patterns overlap and the ammonia and water molecules tend to undergo exchange with surfaces that are encountered or can be produced by the ionization filament. The problem becomes increasingly difficult when values below 1% are required because the isotopic blends of $^{12}\text{C}/^{13}\text{C}$, $^{14}\text{N}/^{15}\text{N}$, and $^{16}\text{O}/^{18}\text{O}$ come into play. The measurement becomes extremely challenging when one has to also consider the possibilities of mixtures with hydrogen, deuterium, and tritium isotopes. There are 144 different mass fragments between masses 12 and 28 for a common 70 eV electron impact spectrum. To help solve this problem, one approach used at SRNL is to simulate the mixtures based on NIST fragmentation patterns and the trinomial distribution pattern for the HDT blends. The simulation helps the analyst identify the important mass fragments that should appear for an expected blend as well as visualize the expected pattern from mass spectrometry. The difference between the expected pattern and the measured pattern can often be used to rapidly identify what is happening in a process. An enhanced simulation takes the fragment numbers and converts them to a predicted mass peak shape according to the resolution and characteristics of the mass spectrometer. This allows one to observe the effect of resolution on the fragmentation pattern and the measurement.

SRNL-MS-2009-00134

Underwater Mass Spectrometry: Developments and Deployments

Strawn Toler, R. Timothy Short, Ryan Bell

SRI International

The Chemical Sensors group at SRI St. Petersburg is developing and operating underwater mass spectrometers (UMS) for chemical monitoring and profiling of our oceans, coastal regions, harbors, and internal waterways. We have developed a method to calibrate underwater mass spectrometers to make quantitative measurements of dissolved gases and volatile organic compounds (VOCs) to depths of 2000 meters. Our UMS instrument operates moored, tethered, remotely, or autonomously, allowing users to customize deployments to suit a wide variety of situations. Recent field operations, which have varied widely, included (1) depth profiling of methane hydrate fields to determine the fate of methane released from hydrates, (2) pore water sampling to quantify dissolved gas concentrations as a function of depth in the sediment, and (3) chemical surveying with the UMS on a remotely operated vehicle to provide real-time measurements of dissolved gas and VOC concentrations.

We have designed and constructed a deep-water, positive-displacement syringe pumping system which provides significantly improved sample flow rate stability compared with that of constant force pumps, such as piston pumps. The syringe pump system also allows for the introduction of reagents into the sample flow stream to induce chemical reactions that convert non-volatile and/or polar compounds into volatile non-polar species, which are then detectable with a membrane introduction mass spectrometer MIMS system. We have also designed and constructed a programmable sediment probe that interfaces with the underwater MIMS system. The probe, which was integrated with the modular programmable syringe pumping system, can be extended into the sediment for pore water sampling, or retracted for direct sampling of the water column above the sediment. Water is drawn through a thin porous filter in the probe tip, and is then analyzed by the MIMS system.

Details about system developments and data from recent deployments will be presented.

Characterization of Mobile water mass-spectrometer for direct analysis metals in water samples

Stanislav Vlasov, Dmitrii Lebedev, Viktor Kogan, Anatolii Pavlov, Yurii Chichagov
A.F.Ioffe Physical Technical Institute, St.Petersburg, Russia

The results of testing of portable magnet mass spectrometer designed for direct determination of metals in water samples is considered. Sample introduction, compound extraction and measuring processes are carried out automatically in the instrument. The ion source construction was designed to supply high electron impact ionization efficiency for the molecules, which were desorbed from the inlet system extractor. Desorption temperature ($20^{\circ}\text{C}\div 1500^{\circ}\text{C}$) of the extractor surface is held according to the types of compounds measured. To supply reliability of the identification process and to increase the mass spectrometer sensitivity, the same mass spectrum sub ranges were scanned at different desorption temperatures. The results of testing of the instrument with Zn, Cu, Fe, Cd, As in a water sample are presented. The correlation between the pH variation of a sample and instrument sensitivity are discussed.