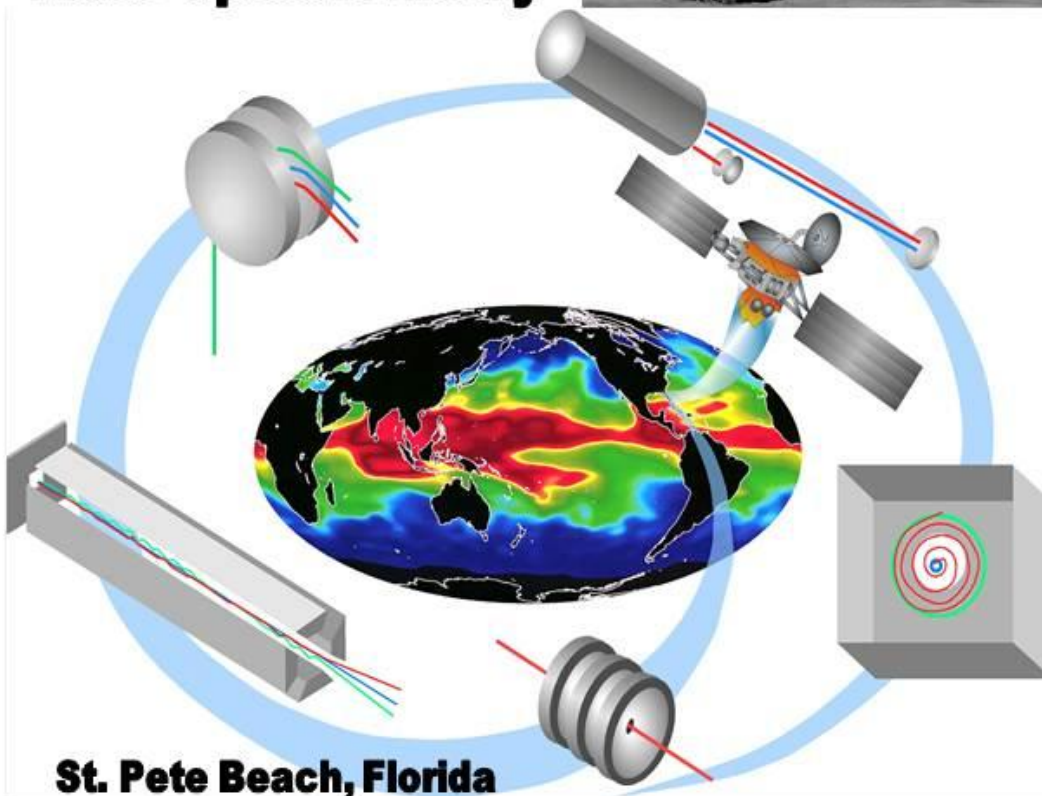
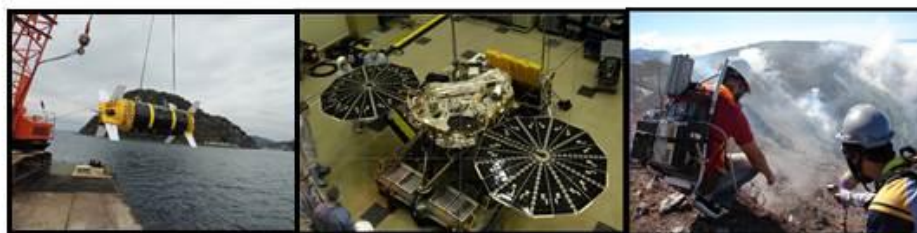


The 9th Workshop on Harsh-Environment Mass Spectrometry



**St. Pete Beach, Florida
September 15-18, 2013**



WELCOME

On behalf of the Organizing Committee and HEMS Board, welcome to the 9th Workshop on Harsh Environment Mass Spectrometry (HEMS).

During this anniversary of the events on 9/11, in the wake of the Gulf Oil Spill, and recent space exploration we are reminded of the eminent need to ruggedize and portabilize one of the most versatile and sensitive chemical sensors of our day. We are all fortunate to be part of this active community, and I appreciate all the contributions of this group to take these instruments well beyond the boundary of the lab. To places such as: battlefields, space, active volcanoes, below our seas, and often hazardous environments. This community has also led the way to novel front-end development, peripherals, and ruggedization techniques.

The 9th Workshop is a culmination of academics, government leaders, and industrial professionals brought together by a common interest to forward progress for field mass spectrometry and ruggedization. Dissemination of individual group progress will be carried out in oral and poster formats. The well needed sponsorship and vendors will offer an opportunity to interact directly with the companies and groups with market products.

The program will include time for discussion between presentations, as well as a social platform to meet and discuss projects and future directions for deployable mass spectrometry. Thank you for supporting HEMS and I look forward to the current presented research, and the discussions for future directions.

Sincerely,

Guido F. Verbeck
President HEMS
Chairman, 9th HEMS Workshop Organizing Committee

STUDENT TRAVEL AWARD WINNERS:

Kenion Blakeman, University of North Carolina Chapel Hill, Chapel Hill, NC
Christopher Pulliam, Purdue University, West Lafayette, IN
Zach Russell, Duke University, Durham, NC

9th HEMS Workshop

Organizing Committee

Guido Verbeck, *Chairman*
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Strawn Toler, *Web/Materials*
Gottfried Kibelka, *Student Scholarships*
Steve Taylor, *Publications*
Barbara Walton, *Program*
Lynell De Wind, *Program*

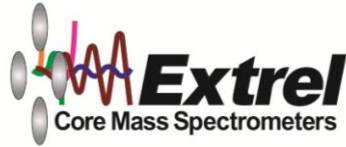
Harsh-Environment Mass Spectrometry Society Board

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Richard Arkin
Gottfried Kibelka
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Thank You to Our Sponsors



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.

Previous 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, 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 Sundstrand Corporation

The 8th Harsh-Environment Mass Spectrometry Workshop

September 19-21, 2011; St. Pete Beach, Florida

Presented by the University of North Texas

The 9th Harsh-Environment Mass Spectrometry Workshop

September 15-18, 2013; St. Pete Beach, Florida

Presented by the University of North Texas

For programs, proceedings, and participants please visit:

<http://www.hems-workshop.org/Archive.html>

Sunday, September 15

Time	Topic	Speaker	Page #
7:00 pm	Registration		
	Meet & Greet (Light Refreshments will be available 7-9pm)		
	(See Page 13 for Floor Plans of Don CeSar)		

Monday, September 16

Time	Topic	Speaker	Page #
7:00	Breakfast		
8:40	Welcoming Remarks	G. Verbeck	
9:00	Exploring Subglacial Environments from the Microbe's Perspective	J. Mikucki	14
			
9:30	Designing for Harsh Environments	C.R. Arkin	15
10:00	Mid-Morning Break		
10:30	Mass Spectrometry Fundamentals: A Hands-on University Lab Course	P. Berger	16
11:00	Stochastic Regression Modeling of Noisy Spectra	A. Kearsley	17
11:30	A Coded Aperture Magnetic Sector Mass Spectrometer	Z. Russell Student Award Winner	18
12:00	Lunch on your own		
1:30	Looking for Alternatives to High Resolution Mass Spectrometry	W. Spencer	19
2:00	A Field Deployable Ion Trap Mass Spectrometer with Atmospheric Pressure Interface	A. Lee	20
2:30	Development of a Loeb-Eiber Mass Filter for Portable Mass Spectrometry	G. Jackson	21
3:00	New TMP Bearing Suspension System and Advantages of the "Floating Suspension" to Portable MS Systems	D. Vincett	22
4:00	Poster Session	See Abstracts	40-55
	(Light Refreshments will be available during poster session)		
Evening Free			

Tuesday, September 17

Time	Topic	Speaker	Page #
7:00	Breakfast		
8:15	Announcements		
8:30	A "Mobility Filter" that Widely Protects a Mass Spectrometer from Neutral Molecule Contaminations	H. Wollnik	23
9:00	High Pressure Nitrogen and Air Mass Spectrometry with Microscale Ion Traps	K. Blakeman Student Award Winner	24
9:30	Field Optimization of Ion Trap Performance	G. Brucker	25
10:00	Group/Photo & Mid-Morning Break		
10:30	Trapping and Analysis of Externally Generated Ions in a Miniature Cylindrical Ion Trap	C. Cavanaugh	26
11:00	Design of Small-sized Static Mass Spectrometer for Determination of Biomarkers in Expired Air	A. Antonov	27
11:30	Development of Outside the Lab Mass Spectrometers for Rapid Trace Detection	L. Rorrer	28
12:00	Lunch on your own		
1:30	Portable Mass Spectrometry for Post-Detonation Nuclear Forensics	T. Evans-Nguyen	29
2:00	Development of Unmanned Aerial Vehicle Mass Spectrometer (UAV-MS) Systems for Calibration and Validation of Satellite Remote Sensing Data using In-Situ Volcanic Plume Analysis	J. Diaz	30
2:30	Mid-Afternoon Break		
3:00	Development of a Membrane Inlet Mass Spectrometry-Based Strategy for Environmental Monitoring	W. Hoffmann	31
3:30	Comparative Household Chemical Analysis Using Ambient Ionization Coupled to Miniature Mass Spectrometry	C. Pulliam Student Award Winner	32
4:00	Paper Spray Ionization Under Harsh Environment and Gas Phase Ion Molecule Reaction Under Titan Simulate Environment	A. Li	33
4:30	Turbopump Preselection of Analytes Based on Molecular Weight	W. Whitten	34
6:30	Workshop Dinner at The Don CeSar		

Wednesday, September 18

Time	Topic	Speaker	Page #
7:00	Breakfast		
8:15	Announcements		
8:30	The Role of Non-evaporable Getter Pump Technology in Portable Mass Spectrometry	B. Garcia	35
9:00	Recent Results from Curiosity's SAM Instrument at Gale Crater and Looking Ahead to MAVEN	S. Getty	36
9:30	In situ Membrane Introduction Mass Spectrometry for Subsea Characterization of Light Hydrocarbons	T. Short	37
10:00	Mid-Morning Break		
10:30	Integration and Ruggedization of a Commercially Available Gas Chromatograph and Mass Spectrometer (GCMS) for the Resource Prospector Mission (RPM)	K. Loftin	38
11:00	A Miniature LIMS System for Accurate Isotope Composition Measurements in situ Planetary Surfaces	A. Riedo	39
11:30	Program Survey and Closing		

The Don CeSar Beach Resort:



Opened in 1928 by Thomas Rowe, the "Pink Lady" or Don Ce-Sar, quickly became a hot spot for the rich and famous during the Jazz Age. Patrons included, Clarence Darrow, F. Scott Fitzgerald, Lou Gehrig, Franklin D. Roosevelt, and Al Capone. The New York Yankees called this place home during spring training for three years during the Great Depression. In December 1942, the hotel was reopened as a military hospital, and in 1945 it was converted again into a Veterans Administration Regional Office. Almost 30 years later, the hotel was bought by a Holiday Inn franchise owner and reopened in 1973 as The Don CeSar. It was named to the National Register of Historic Places in 1975, and has been the film site for movies (Once Upon a Time in America and Thunder in Paradise), music videos (Tom Petty and the Heartbreakers), and provided material for comedian Ron White as he talk about his stay at the Don CeSar in Blue Collar Comedy Tour: One for the Road.

St. Pete Beach, Florida

Restaurants:

- Snapper's Sea Grill
- Verducci Trattoria Pizzeria
- MadFish
- Sandbar Bills
- Vida de Cafe



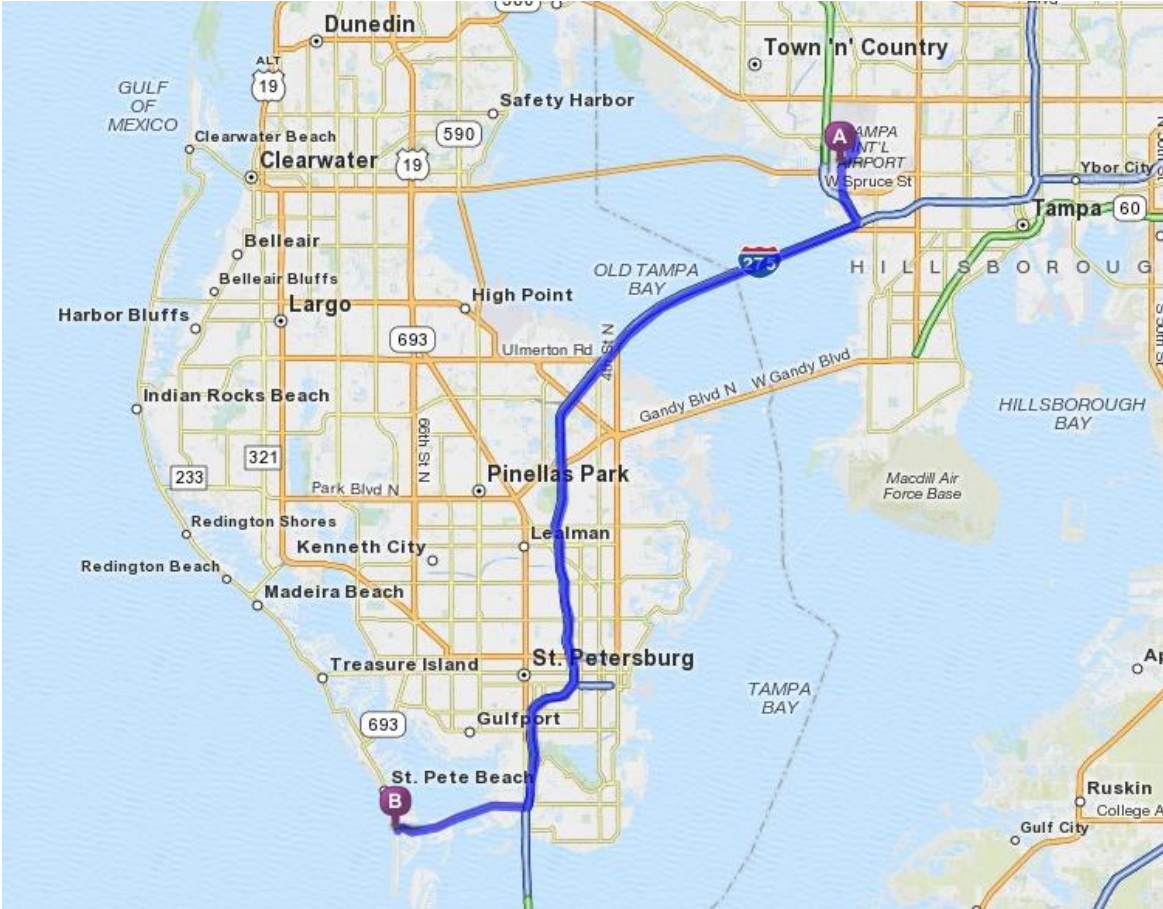
Directions and Map

From:
Tampa International Airport (TPA)
4100 George J Bean Outbound Pkwy
Tampa, FL 33607

To:
Don CeSar Beach Resort
3400 Gulf Blvd.
St. Pete Beach, FL 33706



****Please be advised, there is a \$.50 toll between the airport and the Don CeSar****



Exploring Subglacial Environments from the Microbe's Perspective

Jill Mikucki, W. Berry Lyons, Slawek Tulaczyk and the WISSARD Science Team

Department of Microbiology, University of Tennessee, Knoxville, TN

Subglacial environments are one of the most difficult portions of the cryosphere to access and only recently, in collaboration with large-scale drilling projects, are ecologists beginning to explore the subglacial biome. Understanding the persistence of life in extended isolation and the evolution and stability of subglacial habitats requires an integrated, interdisciplinary approach. The intense logistics involved in Antarctic subglacial research drilling underlines the need for ruggedized instrumentation that is capable of real-time, *in situ* biogeochemical measurements to maximize our understanding of these systems, despite our limited access. Here we describe the status of Antarctic subglacial exploration with a focus on Blood Falls, a hypersaline, subglacial brine that releases at the surface of Taylor Glacier in the McMurdo Dry Valleys. Geomicrobiological analyses at Blood Falls revealed a unique community of marine microorganisms that persist independent of photosynthetically derived carbon inputs by catalytically cycling sulfur to facilitate Fe(III) reduction and organic matter oxidation. These data suggest that the sulfur cycle is important in driving subglacial ecosystem function; *in situ* measurements of oxygen, iron and sulfur species *in situ* would improve our model of subglacial microbial processes. We will also discuss highlights of the recent investigation of Subglacial Lake Whillans. As we move forward with the exploration of subglacial systems, including Lake Vostok and Lake Whillans, existing models, such as the we describe here, will provide important insight into ecosystem structure and function, allow for the development of relevant tools for geomicrobiological examination of other subglacial environments on Earth and prepare us for the exploration of icy extraterrestrial targets.



'Lakeside' Landing at Subglacial Lake Whillans



WISSARD Drill Camp

Design for Harsh Environments

C. Richard Arkin, Damion Lucas

Engineering Service Contract, Kennedy Space Center, FL

Often in the MS instrumentation community it is common to develop new systems as proof-of-concepts or rapid prototypes in order to demonstrate a new advance in technology. An unnecessarily large fraction of such new systems fail during the technology transfer process due to factors unrelated to the new technology. Yet end-users unfamiliar with the technology tend to view the technology itself as a failure. This talk will review some basic design concepts to consider at the onset of prototype development that can mitigate risks of reduced performance, or failure, in the field. Topics include reviews of design best practices for electrical, mechanical, fluid, and material system aspects. Additional topics will focus on human factors issues such as- ease of operation (especially by non-experts), ease of maintenance, and damage mitigation.

Mass Spectrometry Fundamentals: A Hands-on University Lab Course

Philip S. Berger

Ceramitron, LLC, St. Louis, MO

Mass spectrometers arguable comprise the consummate mix of physics, chemistry, engineering, and materials. Unfortunately, the "black box" approach to MS taught in most university programs fails to connect students with the inner workings of these amazing machines, portending an alarming decline in future innovations to drive this technology. Our proposed MS Fundamentals course address this concern by teaching students to design, build, and test their own miniature MS instruments in a single-semester laboratory class.

Using Simion to model and simulate new designs, the geometry is then implemented in printed circuit boards to form the physical instrument. Students, working in teams of 2-3, can thus simulate classical and novel MS instruments, translate the electrical boundary conditions using PCBs, and construct 3-D models by simply stacking boards together to form ion course, analyzer and detector volumes, and even gas-tight enclosures that replace traditional vacuum chambers. Ceramitron has fabricated scores of working MS units using this construction method. By eliminating virtually all of the discrete elements in favor of photolithographic metallization, we have drive the cost of MS prototyping down by nearly two orders of magnitude. Average unit cost: ~\$60.

Four teams of three students each can design, fabricate, and test four different MS designs in a single class. Aggregating their designs into a single artwork allows an outside PCB fab shop to run them as a single batch, then dice the difference models, for a significant savings in setup charges. Optimally, each team would receive four identical copies of its design to test and evaluate. Total cost: < \$2000

A number of universities are considering adopting this powerful teaching tool which could significantly drive development of compact, innovative MS devices suitable for remote and harsh operating environments.

Stochastic Regression Modeling of Noisy Spectra

Anthony J. Kearsley¹, Yutheeka Gadhyan², William E. Wallace¹

¹*National Institute of Standards and Technology, Gaithersburg, MD*

²*University of Houston, Houston, TX*

Deploying mass spectrometers in harsh environments often means compromising signal to noise ratio for the benefit of small size, ruggedness, low energy consumption and other technical considerations. Poor signal to noise presents the operator with the difficult proposition of having to determine the existence, position, and intensity of any and all peaks in the mass spectrum. Here we present a method to model mass spectra using stochastic differential equations (SDE) where both the drift (signal) and diffusion (noise) coefficients depend on time. The benefit of the SDE model is that it seeks to decompose the spectrum into signal plus noise. SDE modeling could yield enhanced peak picking information, a method to eliminate (or filter) peaks that have the same characteristic of approximated noise, and a simulation tool to generate large amounts of meaningful spectra in very little time.

A Coded Aperture Magnetic Sector Mass Spectrometer

Zachary E. Russell, Evan Chen, Jason Amsden, Scott Wolter, Charles Parker, Jeff Glass, and David Brady

Duke University, Electrical & Computer Engineering, Durham, NC

STUDENT AWARD WINNER

The ultimate goal of this project is to develop a coded aperture microfabricated mass spectrometer (CAMMS) [1]. This instrument concept is based on integrating aperture coding [2], used primarily in optical spectroscopy, with a carbon nanotube-based field emission source, charged particle optics on a microfabricated MEMS (MicroElectroMechanical Systems) platform and a permanent magnet magnetic sector. MEMS technology has been shown to be an excellent platform for the development of miniaturized charged particle devices [3]. However, decreased throughput and small sample sizes in microfabricated instruments are expected to lead to diminished performance. To minimize this degradation in performance we are investigating the principles of multi-aperture coding [1]. Use of coded apertures can eliminate the historical trade-off between resolution and signal intensity in a mass spectrometer. Our current focus is proof of concept work on the application of coded apertures to ion optics in a testbed with a traditional thermal electron ionization ion source. The charged particle simulation program SIMION is utilized to inform system design as well as to establish appropriate working conditions for electrostatic lens systems. This presentation will include: (i) the microfabricated system concept, (ii) the coded aperture-testbed design and optimization, and (iii) results from Hadamard coded apertures that have been shown to provide a 15x increase in throughput as compared to single slits without sacrificing mass resolution.

[1] C.B. Parker, D.J. Brady, J.T. Glass, and M.E. Gehm, Coded mass spectroscopy, US Patent 7,399,957 (2008).

[2] Brady, D.J. and A. Optical Society of, Optical imaging and spectroscopy, 2009, Hoboken, N.J.; [Washington, D.C.]: Wiley ; Optical Society of America

[3] S. Natarajan, C. B. Parker, J. R. Piascik, K. H. Gilchrist, Brian R. Stoner, and Jeffrey T. Glass, "Analysis of 3-panel and 4-panel microscale ionization sources," J. Appl. Phys., Vol. 107, 124508, June (2010).

Looking for Alternatives to High Resolution Mass Spectrometry

William A. Spencer

Savannah River National Laboratory, Aiken, SC

The Savannah River National Laboratory is looking for alternatives to large high resolution mass spectrometers for measurement of trace ppm and ppb level impurities in bulk gases as well as support for helium and deuterium analysis. Alternative systems based on simple NDIR detectors and micro gas chromatography with helium plasma detectors are currently under investigation. The laboratory has investigated using smaller quadrupole mass spectrometers with high frequency drivers to achieve resolutions suitable for 4He and D_2 resolution. Additional techniques using multi-pass Raman probes and FTIR spectrometers are being tested. The presentation will cover some of the trades between the instrumentation, the compounds detected, and the detection ranges that can be achieved. The goal of the research is to achieve a compact boxed sized analyzer with superior detection capability equivalent to that achieved with a large multi-sector high resolution gas mass spectrometer.

A Field Deployable Ion Trap Mass Spectrometer with Atmospheric Pressure Interface

Arnold Lee, Alexander Misharin, Victor Laiko, Konstantin Novoselov, Vladimir Doroshenko

MassTech, Inc., Columbia, MD

A miniature quadrupole ion trap mass spectrometer with atmospheric pressure interface will be reported. The instrument does not use any external pumps or gas tanks, is capable of battery operation, and its weight (34 kg), size (30x43x50 cm), and power consumed (150-250 W) make it ideal for numerous field applications. It has wide m/z 30-2500 mass range, better than unit mass resolution, and tandem mass spectrometry capabilities. The ways to reduce the size, weight, and power consumption will be discussed. Operation of the instrument with different ionization sources, including atmospheric pressure (AP) chemical ionization, electrospray (ESI), secondary ESI (sESI), direct analysis in-real-time (DART), and AP matrix-assisted laser desorption/ionization (AP-MALDI), will be reported. AP-MALDI analysis of low femtomole amounts of peptides reveals that sensitivity of the instrument is on par with current commercially available desktop quadrupole ion trap mass spectrometers. Other reported applications will include toxic industrial chemical and pesticide analysis, explosive trace detection, and microbial identification.

Development of a Loeb-Eiber Mass Filter for Portable Mass Spectrometry

Glen P. Jackson, Feng Jin, William D. Hoffmann

West Virginia University, Morgantown, WV

A novel Loeb-Eiber mass filter is being developed in our group that will allow operation at pressures above 1 Torr, thereby eliminating the need for a turbo or ion-pump and the associated space and power requirements. Another advantage of the Loeb-Eiber design is that only a low amplitude (<10 Vpp) radio frequency (rf) voltage is needed, which eliminates large matching networks or amplifiers. The Loeb-Eiber mass spectrometer therefore has great potential for portable, miniature instruments. We have built and tested several geometries of filters that enable one-pass filtering on flight paths less than 75 μm . The current generation Loeb-Eiber mass filter is produced using a silicon-on-insulator fabrication technique for microelectrical mechanical systems (SOI-MEMS) to precisely fabricate micro-positioned electrodes. Ions from a glow discharge ion source were filtered using amplitude modulation waveforms at 5-10 KHz at a fixed operating frequency between 50-80 MHz, depending on the secondary transformers used. We will present the latest experimental and simulation results from our findings.

New TMP Bearing Suspension System and Advantages of the "Floating Suspension" to Portable MS Systems

Dave Vincett

Agilent Technologies

A "Mobility Filter" that Widely Protects a Mass Spectrometer from Neutral Molecule Contaminations

H.Wollnik, G.A.Eiceman, A.S.Tarassov, S.Davila, and C.Yuan

Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM

Presented is a small "mobility filter" that allows analyte ions to enter an evacuated mass spectrometer embedded in an ion-source buffer gas, while this gas is moved to an exhaust together with undesired neutral molecules. The purpose of this "contamination remover" is to bar these neutral molecules and in particular all nonvolatile molecules - like for instance phosphates - from entering the mass spectrometer where they could form detrimental deposits. In particular this device protects inlet capillaries or apertures where such deposits could clog these narrow passages.

This "mobility filter" is also capable to eliminate the in many cases abundantly available cluster or solvent ions of low masses and high mobilities and so allow precise mass analyses of larger analyte molecules. In some special cases also saturation effects can be avoided or at least reduced since space-charge effects caused by low mass ions can be avoided.

High Pressure Nitrogen and Air Mass Spectrometry with Microscale Ion Traps

Kenion Blakeman, Craig Cavanaugh, J. Michael Ramsey

University of North Carolina, Chapel Hill, NC

STUDENT AWARD WINNER

There are numerous field measurement problems that would benefit from handheld mass spectrometry including safety and security applications where rapid detection of hazardous chemicals is required. Miniature cylindrical ion traps (CITs) allow high-pressure operation, significantly reducing pumping technology requirements and thus enable mass spectrometry platforms with small size, weight, and power (SWaP). Our initial work in high pressure ion trap mass spectrometry was limited to helium buffer gas. Nitrogen and air have larger collision cross sections, which results in lower mass resolution. However, they are ideal buffer gasses for handheld mass spectrometry since they are easily obtained from the atmosphere.

A differentially pumped vacuum system was used to allow ionization and mass analysis at pressures up to 2 Torr, while maintaining electron multiplier pressure below 30 mTorr. A glow discharge source was used for internal electron ionization. CITs with radii of 500 μm , 350 μm , and 225 μm were used for mass analysis. Headspace samples of volatile organic species were used as analytes.

A CIT with $r_0 = 500 \mu\text{m}$ was used to characterize the effects of nitrogen and air buffer gas pressure on mass-to-charge resolution for p-xylene from 0.5 to 1.7 Torr at constant RF drive frequency. We observe a linear decrease in resolution with increasing buffer gas pressure. Because RF voltage requirements increase with RF frequency, CITs with critical dimensions below 500 μm were used to investigate the effects of RF drive frequency on resolution at 1 Torr air from 6 to 20 MHz. Mass spectral resolution decreased linearly with RF drive frequency, counteracting peak broadening from high buffer gas pressure.

This work demonstrates that high pressure microscale CIT operation in nitrogen and air addresses pumping challenges associated with miniaturizing mass spectrometers. The resulting reduction in SWaP represents a significant advance in the pursuit of handheld mass spectrometers.

Field Optimization of Ion Trap Performance

Gerardo Brucker

Brooks Automation, Longmont, CO

A new generation of residual gas analyzers based on autoresonant ion trap mass spectrometry (ARTMS) technology has recently become commercially available and is rapidly gaining market acceptance for both laboratory and field applications. Our latest investigations into this novel ion trap technology have focused on a detailed understanding of the role of ion generation and storage on the mass spectrometer's performance. (1) The rate of ion formation, (2) the initial energetics of the ions stored inside the trap, (3) the shape of the electrostatic trapping potential and (3) the characteristics of the radiofrequency signal sweep used to eject the ions all have significant impact on the overall performance of an ART MS instrument. Variability in ion formation rates and energetics due to mechanical assembly tolerances, can lead to detectable unit-to-unit variations in ion trap performance which can be easily corrected through adjustment of (1) the electron beam focusing and (2) the shape of the electrostatic trapping potential. This presentation describes a straight forward methodology that has been developed in our research laboratory to systematically optimize ion trap performance and also an automated tuning procedure (Auto-Tune) that is built into the control software and can be used to restore trap performance each time an ART MS sensor is fitted with a new filament assembly or modified in any way for field applications

Trapping and Analysis of Externally Generated Ions in a Miniature Cylindrical Ion Trap

Craig Cavanaugh, Kenion Blakeman, Mac Gilliland, J Michael Ramsey

University of North Carolina, Chapel Hill, NC

A handheld mass spectrometer would offer unprecedented in-field chemical analysis capability. To achieve this goal, the size, weight, and power (SWaP) of the mass spectrometer must be minimized. By operating the entire mass spectrometer at high buffer gas pressures (> 500 mTorr), turbomolecular pumps are no longer required, greatly reducing SWaP. High pressure mass spectrometry has been demonstrated in our lab using cylindrical ion traps (CITs) with $r_0 = 500 \mu\text{m}$ and internal electron impact ionization (EI).

Particular attention needs to be paid to the in-trap path length and mean free path when trapping externally generated ions in a miniature CIT. Due to scaling, the in-trap path length is reduced compared with a traditional scale CIT ($r_0 = 1 \text{ cm}$). At 1 mTorr buffer gas pressures, typically used for conventional scale ion traps, miniature CITs are unable to trap externally generated ions. However, the reduced mean free path at high pressures aids in trapping by reducing ion kinetic energies in shorter distances, resulting in successful trapping in miniature CITs.

We have demonstrated trapping of externally generated ions in miniature CIT's using custom electron and glow discharge ion sources. Mass spectra have been recorded in helium, nitrogen, and air buffer gases across a broad range of pressures and ion kinetic energies and compared with internal EI signals. The low pressure threshold for external ion injection has been found for mesitylene in helium and nitrogen buffer to be 270 and 20 mTorr, respectively. Externally generated ions were trapped at pressures exceeding 1 Torr buffer gas with signal-to-noise improving with increasing pressure while internal EI signals decreased with increasing pressure.

This work suggests the feasibility of coupling high pressure mass spectrometry with ambient ionization techniques such as ESI and APCI, greatly expanding the scope of chemical detection accessible to a handheld mass spectrometer.

Design of Small-sized Static Mass Spectrometer for Determination of Biomarkers in Expired Air

Andrei Antonov¹, V.T. Kogan¹, D.S. Lebedev¹, Yu.V. Chichagov¹, A.V. Kozelnok², Yu. V. Tuboltsev¹, and S.A. Vlasov¹

¹*Ioffe Physical-Technical Institute of the Russian Academy of Sciences, Saint-Petersburg, Russia*

²*Alamazov Federal Heart, Blood, and Endocrinology Centre, Saint-Petersburg, Russia*

Design of multifunctional small-sized static mass spectrometer for early diagnosis of diseases through the determination of marker compound concentration in expired air and its condensate is presented. Instrument is aimed for identification both volatile and nonvolatile compounds. Gases and volatile compounds in expired air are monitored in on-line mode. Membrane and capillary inlet systems provide high sensitivity of analysis. Determination of nonvolatile compounds in condensate of expired air performs in signal accumulation mode. Electromembrane ion source coupled with ion transport system to mass analyzer is designed for studying of condensate composition. Results of preliminary tests are presented.

Development of Outside the Lab Mass Spectrometers for Rapid Trace Detection

Leonard Rorrer, Mitch Wells, Phil Tackett, Mike Stump, Dennis Barket, Jr.

FLIR Mass Spectrometry, West Lafayette, IN

FLIR Mass Spectrometry (Griffin Analytical) has developed a range of MS systems for use outside of traditional laboratory environments - for example in mobile labs, at entry checkpoints, in cargo facilities, on ships, at hazmat sites, or at crime scenes. The Griffin 460 is a portable GC-MS system designed for use with the range of sampling accessories to provide a powerful analytical tool for a wide range of samples that just cannot be taken back to a lab. When results are needed more quickly than provided by a GC time scale, direct-sampling mass spectrometry is required. Direct-sampling mass spectrometers have been designed by FLIR MS to use either a harvest-and-release thermal desorption inlet for trace detection of surface samples, or a membrane inlet for rapid detection of air contamination. In addition, FLIR MS has designed an ambient ionization mass spectrometer which features either a simplified geometry DESI/ESI ionization source for rapid detection directly from surfaces or a remote sampling wand with APCI for detection of explosives from surfaces which cannot be presented to the instrument itself.

Portable Mass Spectrometry for Post-Detonation Nuclear Forensics

Theresa Evans-Nguyen¹, Kenyon Evans-Nguyen², Hilary Brown², Jennifer Speer², Friso van Amerom³, Di Wang⁴, Jing Wang⁵, Tianpeng Wu⁵, Adrian Avila⁵, Francy Sinatra¹, Spiros Manolakos¹, Erik¹

¹*Draper Laboratory, Tampa, FL*

²*University of Tampa, Tampa, FL*

³*Mini-Mass Consulting*

⁴*Johns Hopkins University-School of Medicine*

⁵*University of South Florida*

Radiological Dispersal Devices (RDDs, aka dirty bombs) are composed of two components, a conventional explosive such as TNT, RDX, or black powder and a radionuclide such as Cesium-137, Strontium-90, or Cobalt-60. The application of post-detonation debris analysis of RDDs was studied for analysis by three parts of an ideal portable mass spectrometer. First, ambient ionization methods including LDI, DESI, and DART were applied to the study of surfaces sampled with both inorganic and organic species for simultaneous analysis. Rapid sample filtration using Differential Mobility Spectrometry was studied both in simulation and experimentally to demonstrate filtration of isobaric species as well as atomic ions. Finally, an ion trap mass spectrometer using digital frequency scanning methods was investigated for the potential low power, high resolution metrics necessary for isotopic analysis. Results presented suggest feasibility of a specialized mass spectrometer designed for rapid analysis of elemental and organic constituents in a fieldable package by thoughtful consideration of these operational metrics.

Development of Unmanned Aerial Vehicle Spectrometer (UAV-MS) Systems for Calibration and Validation of Satellite Remote Sensing Data using In-Situ Volcanic Plume analysis

Jorge Andres Diaz¹, David Pieri², Kenneth Wright³, Paul Sorensen⁴, Robert Kline⁴, Brandon Smith⁴, Richard Arkin⁵, Ernesto Corrales¹, Alfredo Alan¹, Oscar Alegria¹ and Yetty Madrigal¹

¹*GasLab, CICANUM. Universidad de Costa Rica. San Jose, Costa Rica*

²*Jet Propulsion Laboratory, California Institute of Technology. Pasadena, CA*

³*Inficon Inc. East Syracuse, NY*

⁴*CREARE Inc. Hanover, NH*

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The advancements of small unmanned aerial vehicles (UAV), along with the development of a variety of sensor packages, have enabled in situ and proximal remote sensing measurements of volcanic plumes. Using Costa Rican volcanoes as a Natural Laboratory, the University of Costa Rica as host institution, in collaboration with NASA and JPL, is continuing with an initiative to develop field-deployable unmanned airborne MS systems to perform volcanic gas & ash plume research and in-situ volcanic monitoring and gas composition analysis in conjunction with orbital assets and state-of-the-art models of plume transport and composition.

Several small and miniature mass spectrometer based systems (named *ULISSES*) have been integrated for different UAV platforms and lab tested. The different ULISSES MS versions are then combined with temperature, pressure, relative humidity, electrochemical cell SO₂, and GPS sensors payload that have been already UAV deployed into the active plume of Turrialba volcano in Costa Rica, generating 3D plots of SO₂ concentration near the volcano while simultaneously, remote sensing data is collected from the ASTER and OMI space borne instruments and compared with the in-situ data. The first UAV Mission deployment performed in March of 2013 demonstrated a path to study and visualize gaseous volcanic emissions using mass spectrometer and gas sensor based instrumentation in harsh environment conditions to correlate in situ ground/airborne data with remote sensing satellite data for calibration and validation purposes

The latest ULISSES MS version involves the use of miniature turbo pump from Creare Inc, similar to the ones used by the Mars Science Lab (MSL) of the Curiosity Rover; and the Transceptor XPR3 Miniature Quadruple MS (1.8cm rods, $r_o < 0.38\text{mm}$) from Inficon, capable to operate in the mtorr vacuum range.

The deployment of such technologies improves on our current capabilities to detect, analyze, monitor, model, and predict hazards presented to aircraft by volcanogenic ash clouds from active and impending volcanic eruptions.

Development of a Membrane Inlet Mass Spectrometry-Based Strategy for Environmental Monitoring

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Across the country increased energy demand has led to an upsurge of urban exploration for energy sources, particularly natural gas and oil. Along with this increase in exploration comes an increased need to accurately monitor effluent streams in real time to develop leak mitigation strategies along with sufficient regulatory statutes. With the continual growth of urban and suburban oil and gas exploration, BTEX components have continued to be at the forefront of monitoring technologies. Our goal is to develop a mass spectrometric based monitoring process incorporating a polydimethylsiloxane membrane inlet to act as a broad-spectrum analyzer to help understand the risks of environmental contamination by BTEX components. To accomplish this, we have incorporated a custom-built membrane inlet system on a commercial mass spectrometer and made the system suitable for portable operation. The goal of this work was: 1) to determine if membrane inlet mass spectrometry is amenable to analytes of environmental importance, 2) to evaluate the response time of various membrane inlet geometries, 3) based on the most efficient membrane inlet geometry, determine the limits of detection for both a Faraday type detector and an electron multiplier, and 4) to apply that membrane inlet to some real-world samples to get an understanding of the response factors. Initial testing on acetonitrile showed that the membrane inlet was a good candidate for monitoring at environmentally important levels, and subsequent evaluation revealed limits of detection that were two orders of magnitude lower than the OSHA PEL for a Faraday cup detector and three orders of magnitude lower for the electron multiplier.

Comparative Household Chemical Analysis Using Ambient Ionization Coupled to Miniature Mass Spectrometry

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STUDENT AWARD WINNER

Household chemical products are manufactured for the purpose of dispersal over our homes and gardens. We polish furniture, clean glass, remove carpet stains, and kill insects with these complex chemical mixtures and give little thought to how they may enter our bodies simply by breathing or touching the treated surfaces. In this study low-temperature plasma (LTP), desorption electrospray ionization (DESI), and paper spray/leaf spray ionization – all ambient ionization methods used on the native samples in situ - are used with tandem mass spectrometry on a miniature mass spectrometer to analyze various surfaces. The characteristics of bulk solutions of various household chemicals ranging from candles to dehumidifiers to herbicides have been determined. The high vapor pressure of typical analytes makes LTP ionization highly amenable to their detection when coupled to a miniature mass spectrometer. The portability and robustness of the miniature mass spectrometer (Mini 10.5) and the LTP ionization method facilitates chemical analysis outside of the laboratory. (DESI coupled with the mini MS is more difficult to perform in a portable fashion due to the relative large amounts of solvents and the miniature vacuum pump.) Figures of merit of the ambient methods of the ambient ionization techniques will be presented as well the common ingredients detected in the household chemicals and lawn chemicals. The compounds present are confirmed by MSn experiments done using the miniature mass spectrometer. Application of direct leaf spray to treated lawns is a highlight of this work.

Paper Spray Ionization Under Harsh Environment and Gas Phase Ion Molecule Reaction Under Titan Simulate Environment

Anyin Li¹, Fred Jjunju¹, Eric Boone², Michael Wleklinski¹, Kerri A. Pratt², R. Graham Cooks¹

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Simulated Harsh Environment Ambient Ionization : *in-situ* soft ionization using the lake liquids on Titan would reveal the chemical evolution of precipitated Titan haze aerosol and the organic identity of Titan soil. Using porous substrates, solvents of no polarity or extreme high viscosity were found to be amenable with electrospray type soft ionization. Analytes being ionized include: 1) polar, insoluble analyte deposited on the paper triangle; 2) functionalized soluble analytes dissolved in the non-polar solvents or deposited on the paper triangle; 3) non-functionalized hydrocarbons dissolved in the non-polar solvents or deposited on the paper triangle. In a parallel experiment, this type of experiment was successfully carried out at a temperature of -20 °C to simulate direct analysis of snow sample in field missions. **Simulated Atmospheric Ion Chemistry**: The presence of polycyclic aromatic hydrocarbons (PAHs) in Titan's atmosphere has been suggested by laboratory simulations and observations. PAHs are also believed to be among the most abundant and widespread organic compounds in the universe. Using collisional activation reactive PAH ions were generated by dissociation of precursor ions. The reaction took place in an ion trap filled with nitrogen (5 mBar, simulating the pressure of Titan's main haze layer) and the product ions were subsequently mass-analyzed downstream using an Orbitrap mass analyzer. A number of aryl cations were found to react by addition of molecular nitrogen. The reactivities were elucidated by high resolution mass spectrometry. And the fixed nitrogen were found to react with other reagent to form other functionalities.

Turbopump Preselection of Analytes Based on Molecular Weight

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We have been exploring the exploitation of the mass dependence of turbopump efficiency for preconcentration of analyte species for chemical analysis. The eventual goal is to develop a concentrator front end for a portable mass spectrometer that will increase the sensitivity for species of particular interest to potential sponsors. These analytes include CW agents, explosives, toxic industrial chemicals, noble gases, and some biological molecules. It is well known that turbomolecular pumps are in general less effective for light species such as H₂ and He than for the more massive atmospheric constituents. A theoretical analysis of turbopump behavior shows that the compression ratio depends on the ratio of blade velocity to the thermal velocity of the atoms or molecules being pumped. The velocity ratio is proportional to the square root of the mass, thus heavier species are pumped more effectively. In this talk, we will show how a turbopump can be used to discard heavy matrix species from a mixture of gases and will discuss methods of performing the inverse process.

The Role of Non-evaporable Getter Pump Technology in Portable Mass Spectrometry

Bob Garcia

SAES Getters USA, Inc., Colorado Springs, CO

The presentation will include details regarding the reduced size, weight, low energy consumption and overall pumping performance of this technology. The advantages of faster, cleaner, low energy consumption and vibration-free pumping in a small transportable mass spectrometry system will be discussed. How to incorporate this technology while providing continuous pumping, weight reduction, less or no magnetic interference or need of a pump power supply will be covered.

Recent Results from Curiosity's SAM Instrument at Gale Crater and Looking Ahead to MAVEN

Stephanie A. Getty, Paul R. Mahaffy, and the SAM and MAVEN Teams

NASA/GSFC

The Sample Analysis at Mars (SAM) Instrument Suite is presently operating on board the Mars Science Laboratory Curiosity rover. SAM is a mass spectrometer with tunable laser spectrometer equipped with high temperature pyrolysis for evolved gas analysis and gas chromatography. SAM is capable of highly sensitive atmospheric and solid sample investigations emphasizing atmospheric constituents, key isotopic abundances, and the search for Martian organics. At the core of SAM is a highly sensitive quadrupole mass spectrometer with unit mass resolution over the mass range of 2-535 Da. Direct atmospheric measurements are done by direct inlet into the electron ionization source, or through an enrichment front-end employing cooled adsorbents. A sample manipulation system accepts regolith or drilled rock powders delivered by Curiosity's arm. The sample is accepted into one of 72 sample cups that can be heated by pyrolysis capable of reaching 1100°C. In evolved gas analysis mode, delivering volatiles directly to the QMS, the pyrolysis experiment provides characteristic decomposition temperatures for major and minor mineral phases and the release of volatiles entrained in the rock and regolith. Six chromatography analytical columns are present, each with a dedicated thermal conductivity detector. GCMS analyses can provide highly detailed information about the organic content of delivered samples. The TLS can accept atmospheric samples or pyrolysis-evolved gases for precise abundance measurements and isotope ratios for key carbon-containing gases, such as CO₂ and CH₄. Since landing at Gale Crater on August 6, 2012, SAM has conducted a series of atmospheric and solid sample analyses, providing new understanding about the composition of the Martian atmosphere, surface, and near-subsurface. The development of SAM at Goddard Space Flight Center will be discussed, and recent results from the surface investigations at Mars will be presented. An overview of the Neutral Gas and Ion Mass Spectrometer for MAVEN will also be given.

In situ Membrane Introduction Mass Spectrometry for Subsea Characterization of Light Hydrocarbons

R. T. Short, S. K. Toler, R. J. Bell, A. M. Cardenas-Valencia, J. Dholakia, S. Untiedt

SRI International, St. Petersburg, FL

The oil and gas industry, and organizations that environmentally monitor deep ocean and coastal regions, have a need to detect and characterize light hydrocarbons in these regions. Hydrocarbons can enter the water column through natural seepage from the sea floor, or through unintended leaks and spills from drilling operations and transportation of oil and gas to shore. The ability to perform this analysis in situ greatly enhances achievable spatial and temporal densities. In addition, real-time in-water chemical measurements allow for rapid decision-making, provide adaptive sampling strategies, and offer the possibility of tracking chemical gradients to trace leaking chemicals to their source. SRI International's in situ membrane introduction mass spectrometry (MIMS) instruments can quantitatively detect light hydrocarbons in water at trace levels, while simultaneously monitoring the concentrations of all light, stable dissolved gases to a depth of 2000 meters.

We will discuss the design and operational parameters of our new in situ MIMS instrument, which is deployable on smaller platforms, such as the Bluefin BF-12 autonomous underwater vehicle (AUV). We will also present results from recent deployments of our MIMS systems to characterize hydrocarbon seeps in the Gulf of Mexico, the Santa Barbara Channel, and Tampa Bay.

Integration and Ruggedization of a Commercially Available Gas Chromatograph and Mass Spectrometer (GCMS) for the Resource Prospector Mission (RPM)

Kathleen Brooks Loftin¹, Timothy Griffin¹, Janine Captain¹, Richard Kidd², Ken Wright³, and Gottfried Kielbka⁴

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³ *Inficon, Inc.*

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The Resource Prospector is a mission to prospect for lunar volatiles (primarily water) at one of the two lunar poles, as well as demonstrate In-Situ Resource Utilization (ISRU) on the Moon. The Resource Prospector consists of a lander, a rover, and a rover-borne scientific payload. The Regolith and Environment Science and Oxygen & Lunar Volatile Extraction (RESOLVE) payload, will be able to (1) locate near subsurface volatiles, (2) excavate and analyze samples of the volatile-bearing regolith, and (3) demonstrate the form, extractability and usefulness of the materials. The gas chromatograph mass spectrometer (GCMS) is the primary instrument in the RESOLVE instrumentation suite responsible for identification and quantification of the volatiles evolved from the lunar regolith. Specifically, this instrument must have: a low mass, a low power consumption, be able to perform fast analyses of samples ranging from less than one to greater than ninety nine percent water by mass, be autonomously controlled by the payload's software and avionics platform, and be able to operate in the harsh lunar environment. The RPM's short mission duration is the primary driver of the requirement for a very fast analysis time currently base lined at less than 2 minutes per sample. This presentation will discuss the requirements levied upon the GCMS design, lessons learned from a preliminary field demonstration deployment, the current design, and the path forward.

A Miniature LIMS System for Accurate Isotope Composition Measurement *in-situ* Planetary Surfaces

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The development of space instrumentation capable of sensitive measurements of elements and their isotopes in solar system objects is of considerable interest to current space research. Accurate measurements of isotope variations in planetary materials provide an insight into a number of geochemical processes and constraint the time of planetary material formation (crystallisation ages). Isotopes are also robust tracers of presolar events and stellar processes producing elements. Both, a detailed understanding of the chronology of the early solar system and dating of planetary materials require precise and accurate measurements of isotope composition in various planetary materials. However, accurate *in situ* measurements of isotope abundance in solar system objects are extremely challenging and until now, they were not attempted in space research. We present the results of the performance investigations conducted by a miniature laser ablation reflectron time-of-flight mass spectrometer designed by our group for *in situ* space research. The studies indicate that the instrument can be used for sensitive and accurate measurements of the elemental and isotopic composition of extraterrestrial material. Both, a ns-laser (266 nm, 5 ns, 20 Hz) and a fs-laser (775 nm, 190 fs, 1 kHz) were used for laser ablation and ionisation to investigate analytical figure of merits (dynamic range, detection sensitivity and accuracy of measurements, etc.). The studies are performed with high spatial resolution by focussing a pulsed laser radiation to the spot size of about \varnothing 20 μ m and 40 μ m, respectively on the sample surface. Measurements are conducted with high dynamic range of at least 108 and mass resolution ($m/\Delta m$) of up to 800 – 900 (measured at 56Fe). High detection sensitivity is achieved on both metallic and non-metallic elements (tens of ppb). A measurement procedure for accurate and precise isotope analysis will be discussed in detail. The procedure will allow LIMS to measure the isotope composition of elements (e.g. Pb) with a measurement accuracy and precision down to the sub per mill level.

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Portable Membrane Inlet Mass Spectrometer for Illegal Human Migration Detection

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Border security and defence worldwide faces tremendous challenges due to threats from terrorism and/or national/transnational criminal organizations. More specifically during the last few decades, a continuous increase of transportation of illicit substances and weapons as well as illegal human trafficking has been noticed and is of particular concern. Human body odor chemical fingerprints are parts of an innovative and demanding research field. They are of interest in homeland security and forensics applications as well as for medical applications to aid diagnosis and provide sources of medical information.

This study demonstrates the use of a portable membrane inlet mass spectrometer (MIMS) for the detection of Volatile Organic Compound (VOC) emissions from human body in a confined space. In our experiments the confined space used was a small size shipping container simulator. The tests ran under reproducible conditions for over a month and were done both for single man and three man-participants. Different types of membranes were tested to examine their selectivity. During the tests, VOCs with masses in the range 1-200amu from human breath, sweat, skin and body glands were emitted into the simulator ambient air and constantly monitored. The observed VOCs can be used as characteristic markers (alarms) of human presence. Components such as NH₃, CO₂, CO, water, acetone, isoprene, carboxylic acids and many hydrocarbons were detected and their relative abundances were recorded, resulting in characteristic chemical profiles for human presence.

Airports, ports and land borders are harsh and demanding environments facing a wide range of security issues. Onsite MIMS could potentially be used to provide accurate and fast detection of hidden personnel at border checkpoints and in shipping containers of cargo services.

Miniaturized Planar Electrode Linear Ion Trap (LIT) Mass Analyzer

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Our group has previously demonstrated several designs of radiofrequency ion traps in which electric fields are created between two ceramic plates with lithographically patterned electrodes. RF voltages applied to the electrodes through capacitor voltage dividers establish correctly shaped fields. Of the designs, the linear ion trap is the most promising for further miniaturization.

We have now demonstrated that the same plates used to create the LIT with 4.38 mm plate spacing ($y_0 = 2.19$ mm) can also work at 1.96 mm plate spacing ($y_0 = 0.98$ mm). Although the plates are identical, the capacitor values are different from the larger spacing in order to optimize the higher-order terms of the electric fields. Other parameters were explored, including the effect of the germanium layer deposited on top of the electrode pattern. We also optimized performance by varying the RF ramp, ionization time, cooling time, ac frequency and voltage.

For the next generation device we are trying to move away from capacitors entirely, as the uncertainty of the capacitance translates into uncertainty in the trapping fields, and also because the capacitors require too much RF power. The current design uses only the resistance of the germanium overlayer, combined with spacing and dimensions of electrodes, to create the proper field shape. Plate spacing on this new design is set at 690 microns, which results in a y_0 value of 245 microns (the characteristic trapping dimension in the ejection direction).

The electric field and higher-order nonlinear effects in the trapping field profile have been optimized using SIMION 8 for the newly designed planar LIT. Based on the modeled field we expect performance equal or better than that of the rectilinear trap or the previous versions of the planar LIT, even with the very small size. This small size device will have a high aspect ratio, so that a relatively large number of ions can be trapped and analyzed.

Miniature Vacuum Pumps for Portable Mass Spectrometry

Paul Sorensen¹, Robert Kline-Schoder¹, Brandon Smith¹, R. Graham Cooks², Zheng Ouyang², Chien-Hsun Chen²

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For a number of years, Creare has been developing high vacuum turbo molecular pumps for specialized space applications specifically for the low atmospheric pressure on Mars. Two Creare turbo pumps are currently operating on the SAM instrument on the Curiosity rover, and a smaller pump is being space qualified for the MOMA instrument on the ExoMars mission to be launched by ESA in 2018. These pumps are extremely compact and consume very little power while maintaining high pumping performance. To back the turbo pumps, Creare is developing a miniature scroll roughing pump resulting in complete pumping system for terrestrial applications and much smaller than current commercially available systems. In collaboration with Purdue university, Creare has recently tested this pumping system on a portable mass spectrometry systems. The poster will present a system description and performance data as well as comparisons of our pumping system with commercially available systems.

Vacuum Compatible Mass Spectrometer Electronics for the RESOLVE Mission

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The RESOLVE lunar prospecting mission requires gas chromatograph mass spectrometer (GCMS) instrumentation capable of operating in ambient lunar conditions. The driving requirement for the instrument electronics is being capable of operating at lunar ambient pressure, expected to be a vacuum environment. While technology for building vacuum capable electronics for space mass spectrometers already exists, RESOLVE is making use of commercial instrumentation for cost savings and because commercial electronics are congruent with the mission cost and risk profile. The selected instrument, available commercially from Xylem / OI Analytical, is being re-designed for RESOLVE and only select circuit assemblies will be used in the future substantially 'as-is' since they are application specific and the specific functionalities required to run the mass spectrometer are fully tested and meet measurement requirements. To use the commercial boards in a vacuum environment, a development and test program is underway at JPL to 'ruggedize' the boards. For the instrument integrated high voltage (IHV) board, we have designed a mounting and thermal management system which will manage heat flow in the printed wiring board assembly and stiffen the board so that it will survive both vacuum and expected vibration loads. Thermal vacuum testing is complete on the IHV subassembly and the board is verified functional from -10 C to +40 C in vacuum, with no degradation in instrument analytical performance. For the instrument digital (DIG) camera board, we have iterated on a design which was verified during a stratospheric balloon test campaign in September 2012. The DIG board is also verified in thermal vacuum testing within the same temperature range as the IHV board. Both boards will be included in an electronics box assembly to be tested in thermal vac at JPL, with plans to perform a vibration test on the assembly at a future date. After thermal vac, the box will be delivered to Kennedy Space Center (KSC) and integrated by KSC with the rest of the RESOLVE test hardware, to complete a demonstration of the RESOLVE GCMS subsystem in a relevant Lunar environment.

Mass Spectroscopy Based Instrument Development at the Jet Propulsion Laboratory

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Mass spectrometer (MS) based instruments provide unique capabilities for fundamental planetary science investigations whose major themes are: Noble Gas Studies (measuring atmospheric noble gas abundances & isotopic ratios); Atmosphere Surveys (studying the composition of atmospheric gases & aerosols); Organic Material Analyses (determining the organic composition/structure of surface materials); Geochronology (determining geologic ages of rocks by measuring isotope ratios); and Environmental Monitoring on manned space missions. Because of the broad range of future missions requiring MS-based instrumentation, JPL's Solar System Exploration Directorate has supported developing in-house Miniature Magnetic Sector (MMS) and Quadrupole Ion Trap (QIT) mass spectrometers. As a result of this support JPL is developing state-of-the-art MS instrumentation and supporting technologies that can be employed on future Discovery, New Frontiers, and Flagship missions such as a Venus probe or lander, Saturn, Uranus or Neptune probe, Titan lander, Mars Sample Return, Mars Geochronology Mission, and icy moon and small body landers.

JAXA's Technology Roadmap & Application of "Mass Spectrometry"

Hirokazu HOSHINO

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In-situ analyses including mass spectrometry at the lunar and planetary surface have not been considered as the space technology roadmap of JAXA so far. There have been several mass spectrometers on-board Japan's spacecrafts such as Nozomi Mars explorer, Kaguya lunar orbiter and Bepi-Colombo/MMO for Mercury mission, but they are especially for measuring space plasma and atmosphere environments where ionization is not essentially needed. When neutral solid materials on the Moon and planets need to be treated for mass spectrometry on site, an ionization system such as laser ablation should be considered and there are some possibilities for applying measurements such as K-Ar or other chronology. The aim of detecting amino acid from the aspect of astrobiology, analyzing the composition of the complex and measuring isotopic ratio for the classification of rocks or other purposes etc, is both the scientific and exploration purposes. In order to ensure quantitative measurements, detection systems such as multi-turn TOF-MS will be considered. Strategic and feasibility study for pursuing an installation of the equipment onboard will be discussed.

Membrane Interface Evaluations for Underwater Mass Spectrometers

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A component that has enabled the development of underwater mass spectrometry is a mechanically supported membrane interface probe. Our two research groups have used metallic porous frits that support polydimethyl siloxane (PDMS) membranes embedded in a heated membrane probe assembly, allowing the deployment of the underwater membrane introduction mass spectrometer (MIMS) instruments to ocean depths of 2000 meters. The fabrication of such frits has consisted of shaping larger Hastalloy C porous frits to the size required to support a PDMS capillary of 0.64 mm ID and 1.19 mm OD using a diamond-coated wheel and Dremel tool. This procedure is time-consuming and cumbersome, and the porosity of the final frits is likely not reproducible. To facilitate the fabrication of the membrane assembly, we report on the use of new porous metallic structures. Frits with diameters of approximately 3.0 mm (1/8") and known porosities (48.3 % and 32.5%) were produced by the Fraunhofer Institute in Dresden, Germany, using powder metallurgical processes. We used these frits to fabricate new membrane interface assemblies. Using a new custom-heated membrane probe with the new porous frits, we performed calibrations relating dissolved methane concentrations to mass spectrometer response (m/z 15) using linear least-squares fitting procedures. Both the limit of detection (methane concentration in the tens of nanomolars) and the sensitivity (on the order of 10^{-1} pico-amps/nanomole of methane) were found to be comparable with those obtained with the previously fabricated Hastalloy C frits. The calibration parameters for the new assembly were also found to be a function of the flow rate, temperature, and sample hydrostatic pressure.

Micro-ion Trap Mass Spectrometer for (pre)-biotic Organic Compound Analysis on Comets

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Comets are believed to be a mixture of interstellar and nebular material, and volatiles in comets are attributed to interstellar chemistry. Similar species of carbonaceous compounds are observed in ices in interstellar molecular (ISM) clouds. Comets are likely to be pristine reservoirs of primitive material and carbonaceous compounds in our solar system. They could be major contributors to the delivery of prebiotic organic compounds, from which life emerged through impacts on early Earth.

Mass spectrometers (MSs) are powerful tools for chemical analysis; when miniaturized, they are optimal for space applications. The goal of this work is to surpass current miniaturization of space-flight mass spectrometers by using MEMS technology to create a prototype MS based on micro-cylindrical ion trap (μ -CIT) array technology, as the next step toward the exploration of distributions of chemicals of astrobiological relevance in space.

We are using a microfabrication approach based on earlier work, in which ~ 60 micro-traps formed a closely packed hexagonal array in a silicon (Si) chip. Simulations were performed in SIMION to determine the optimum geometries for ring-electrode-to-endplate-electrode spacing. Deep reactive ion etching (DRIE) was used to etch cylindrical holes in the ring and endplate electrodes, and to etch a gap to create a stand-off structure, resulting in more space between the ring and endplate electrodes to reduce device capacitance and potential electrical breakdown. COMSOL was used to model the integrated μ -CIT array chip to confirm strategies to minimize capacitance. To operate all traps simultaneously, an ultraviolet-LED (UV-LED), coupled with micro-channel plates (MCPs), will be used as a broad-beam electron source in a fully packaged micro mass spectrometer assembly of ~ 20 cm³. The shape of the μ -CIT array chip for this work was adjusted to fit a very small form-factor micro-ion trap MS assembly, with a miniature vacuum chamber (3 x 3 x 5 cm) to house the total MS assembly. The planned prototype MS assembly consists of a UV electron ionization source, a μ -CIT array chip, an MCP detector, and multi anodes to detect ions from each μ -CIT individually. Progress on the design, construction, and testing of the prototype MS will be presented.

Gas detection using a MEMS TOF Mass-Spectrometer: First Results

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A new generation of MEMS mass-spectrometers has been designed for gas analysis. These devices are fabricated using micro technology techniques: the fabrication process is mainly based on Deep Reactive Ion Etching (DRIE) of a silicon wafer, on a metallic layer deposition/patterning and on a silicon/glass wafer bonding technique. The chip is 1.5cm x 3cm. All the elements of a mass-spectrometer can be structured on the same die (ion source, electrostatic lenses, injection stage, analyzer). Two analyzer's configurations have been designed; one uses a simple drift zone and the other one uses a reflectron associated to a drift zone.

The ionizer uses the electron impact (EI) technique to ionize the injected gas sample. It produces ionic currents in the order of hundreds of pA up to several nA with maximum of 50 nA.

The linear TOF configuration - simple drift zone analyzer - has been tested using electron pulses of 50 ns to produce ions. Mono charged ions are accelerated in the focalization and have an energy of 70 to 200 eV, then they are injected in the drift zone which is 5 mm. A Photonis APD2 Minitof micro-channel-plates (MCP) detector is placed at the output. The detector's time dependant signal is recorded on a wideband oscilloscope synchronized by the electron pulse. The time-of-flight is between 0.5 to 4 μ s for the injected gases.

This study has demonstrated the feasibility of the MEMS TOF mass-spectrometer. Mass spectra have been obtained on simple gases such as Helium, Argon, Krypton, Xenon and Ethanol. This micro mass-spectrometer has a resolving power close to 1 over a mass range of 1 to 100 Da.

Further improvements consisting in using the reflectron - and connecting the MEMS mass-spectrometer to a chromatograph - are in progress.

Ambient Ionization Mass Spectrometry for Simultaneous Analysis of Organic and Inorganic Radiological Dispersion Device (RDD) Components

Hilary Brown, Jennifer Speer, and Kenyon Evans-Nguyen

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Radiological dispersion devices (RDDs) consist of inorganic (radionuclides) and organic (explosive) components. Field-portable ambient ionization techniques that are capable of conducting simultaneous molecular and elemental analysis of RDDs are desired for post-detonation forensic analysis. To this end, desorption electrospray ionization (DESI) and laser ionization (LI) sources were coupled to a linear ion trap mass spectrometer. Preliminary data using DESI-MS confirms that explosive compounds such as RDX can be detected as well as soluble metal salts like CsCl. Source collision induced dissociation (CID) was used to enhance the signal of the metal salts by breaking up adducts and to reduce chemical noise by fragmenting organic components. Laser ionization coupled with mass spectrometry (LI-MS) was capable of ionizing solid metals (e.g., Lead and Cobalt) and refractory materials (e.g., Strontium titanate). Because DESI, LI, and ion traps are all readily fieldable technologies, the fusion of these techniques is promising for building portable, “universal” mass spectrometers capable of simultaneous organic, inorganic, elemental, and isotopic analysis in the field.

Development of a Compact, Isobaric Chamber for High Pressure Mass Spectrometry of Ambient Organics

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Considerable effort has been directed towards development of compact mass spectrometry systems over the past decades. This work has resulted in many transportable instruments that retain most of the functionality and performance of their benchtop counterparts. Realization of a mass spectrometer with a handheld form factor has remained elusive, despite all of these efforts. Eliminating the turbomolecular pumps required by nearly all these instruments allows a significant reduction in system size, weight, and power (SWAP). High pressure mass spectrometry (HPMS) conducted at pressures > 1 torr will allow the use of small, rugged mechanical pumps and has been the focus of our lab for the past several years. We have previously developed and demonstrated HPMS with the use of microscale quadrupole ion traps.

Towards the development of a hand held mass spectrometer we have developed an extremely compact and light weight vacuum chamber to house the ion source, mass analyzer, and detector. These components are all contained in a chamber with dimensions less than 1" × 1" × 2" and pumped with a single mechanical pump. Ambient air is introduced at low flow rates and used as sample introduction and for the ion trap buffer gas. Direct current glow discharge is used as a low power electron source for in-trap electron impact ionization. The formed ions are then mass analyzed in sub-millimeter ion traps and detected using a Faraday cup and charge sensitive amplifier detector. Mass spectra will be shown of several organic analytes sampled from ambient atmosphere, and the instrument performance metrics will be compared at varying buffer gas pressures up to 1 torr.

Microfabricated Ion Sources for Portable Mass Spectrometers

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This project involves the development of MEMS-based cathodes [1-3] for use in miniature mass spectrometers. The cathodes employ a carbon nanotube (CNT)-based field-emission source which consumes at least an order of magnitude less power than conventional thermionic sources. The CNT emitter arrays are used as impact ionization sources and have demonstrated electron currents in excess of 150 μA . Field emission sources also tend to be more robust than their conventional counterparts and the arrays of CNTs enable a “self-healing” effect whereby neighbouring CNTs replace those damaged during operation. Incorporating the CNT field emitters into a MEMS-based electron source brings about certain advantages in size, power, and cost without significant loss in sensitivity. Current lifetime data shows continuous performance in excess of 130 hrs. Current development efforts are focused on improving the lifetime of the CNT-based field emission cathodes, as well as optimization for continuous and rapid on/off applications. Improving adhesion properties between the CNTs and the MEMS platform through the use of multi-layer metal catalysts are being explored to improve device lifetime. We are also investigating geometrical designs that integrate electron and ion optics onto the MEMS platform to minimize energy and angular dispersion while also enhancing current density and cathode lifetime. The charged particle simulation program SIMION is employed to demonstrate and optimize new system designs as well as to establish appropriate working conditions for the different cathode designs.

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Development of a Dual Ion Source Hyperbolic Linear Ion Trap Mass Spectrometer for *In Situ* Detection of Organic Molecules on Mars

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The Mars Organic Molecule Analyzer (MOMA) is a joint venture between NASA and the European Space Agency to develop a lightweight, low power, dual source (GC and LDI) mass spectrometer based investigation of organics on Mars. MOMA's unique capabilities make it a key analytical instrument on the ExoMars rover, set to launch in 2018. The main ExoMars goal is to search for molecular "signs of life" in the martian environment. Details, along with comparisons to the Sample Analysis at Mars (SAM) mass spectrometer on NASA's Curiosity rover, will be presented. The MOMA mass spectrometer consists of a custom hyperbolic linear ion trap mass spectrometer with two modes of operation: laser desorption ionization (LDI) at Mars ambient conditions (5-7 Torr of mainly CO₂) and electron ionization (EI) of gas chromatograph effluent. Three laboratory prototypes have been used to optimize key aspects of the flight instrument design and to assess our capability for meeting critical performance requirements. An engineering test unit is currently under construction to reach a final, flight-like form and function. The prototypes are being operated with a mixture of commercial and custom electronics as well as breadboard electronics of the flight circuit designs. Experience gained building previous mass spectrometers for space, especially SAM, is being leveraged for MOMA.

Design of a Prototype Digital Ion Trap for High Resolution Ion Trap Analysis

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Digital ion trap frequency scanning methods, where scanning is achieved by ramping the frequency of a square waveform with fixed amplitude, have attracted wide attention from high mass protein analysis to ultra-high mass nano particles research. Here, a quadrupole ion trap driven by a digital waveform has been studied, where a high speed, 990 Hz, continuous frequency scan was applied to obtain 990 mass spectra per second over a mass range of 500 amu. In high speed continuous injection mode of operation, ions are injected into the trap continuously during the mass scan, which enables mass scan in ultra-high repetition rate. Automatic gain control could be realized by control of the EI source current, which shows its impact in mass resolution in the experiments. Both mass selective instability scan and resonance ejection mode were tested. Although mass resolution is compromised in exchange for high repetition rate, specific applications might benefit from this mode of operation, for example, when high volume fast scanning is needed for very specific application, such as for airport screening of explosives or for ultra-fast GC/MS coupling.

The Application of Coded Aperature Spectroscopy to Magnetic Sector Mass Spectrometers

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Coded apertures have been widely used in multiplexed optical spectroscopy systems for higher signal to noise ratio and improved throughput without sacrificing resolution.[1,2]. For this work we apply the concept of using coded apertures to mass spectrometry for the first time. We designed a series of different coded aperture patterns including 2D Hadamard arrays and 1D Hadamard slit arrays. We have shown that the use coded apertures can improve ion throughput by 15x in comparison to a single slit without sacrificing mass resolution. One of the major obstacles in development of miniature sector mass spectrometers is the reduction in throughput when reducing the size. This research indicates that the addition of coded apertures can help alleviate this tradeoff.

Acknowledgments

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The Trace Organic Gas Analyzer (TOGA) - An Airborne Fast Gas Chromatograph Mass Spectrometer for Atmospheric Chemistry Measurements

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Recently an airborne gas chromatograph mass spectrometer (GC-MS) was developed for atmospheric chemistry research performed with the NSF Gulfstream V (GV) aircraft. The instrument is denoted TOGA-GV (Trace Organic Gas Analyzer) and is an airborne fast GC-MS capable of measuring a suite of volatile organic compounds (VOCs), including: oxygenates (OVOCs), non-methane hydrocarbons (NMHCs), halocarbons, and nitrogen and sulfur containing species. The compounds are diverse in their range of sources (anthropogenic, biogenic, or a combination thereof), of atmospheric reactivity with OH (minutes (isoprene, terpenes) to years (CFCs)), of loss to photolysis (days (acetaldehyde) to negligible (NMHCs)), and of solubility ($k_H \sim 150$ to 10^{-4}) and toxicity (formaldehyde, benzene, etc.). The TOGA-GV measures these organic compounds with high accuracy, precision, and low detection limits (~ 10 ppt to < 1 ppt) at a sampling rate of 2 minutes or less. The instrument is usable throughout the troposphere and lower stratosphere to an altitude of approximately 45k feet.

We will describe a number of the design issues involved in the TOGA instrument development and will show data from recent experiments where the instrument was used to measure the movement of boundary layer atmospheric chemicals to the upper troposphere via convective storms.