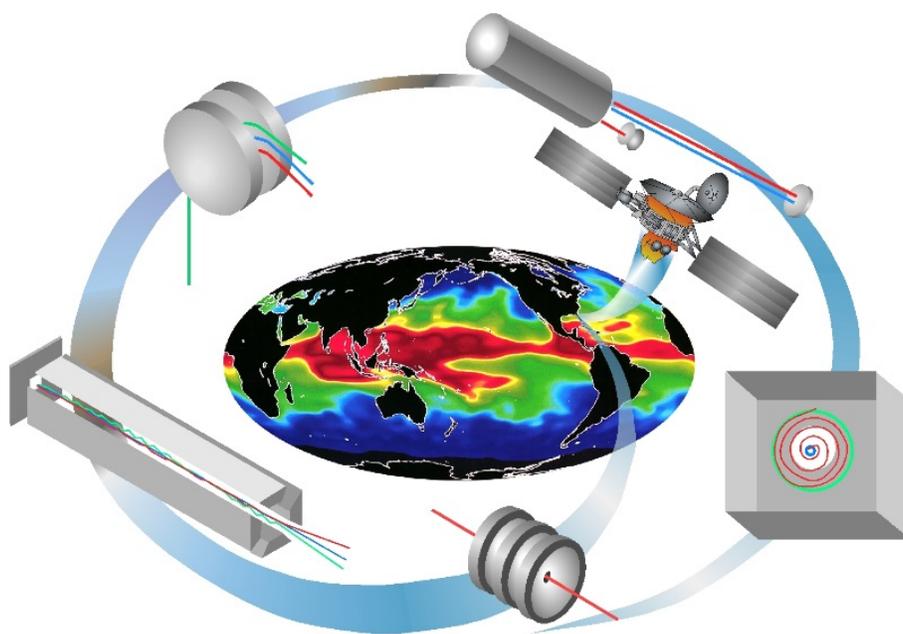


13th WORKSHOP ON
**HARSH-ENVIRONMENT
MASS SPECTROMETRY**



September 16–19, 2019
Myrtle Beach, South Carolina

Welcome!

On behalf of the Organizing Committee and HEMS Board, I am pleased to welcome you to the 13th Workshop on Harsh Environment Mass Spectrometry (HEMS). We are pleased to have you with us.

This year we continue our tradition of sharing the latest developments in both technology development and applications of mass spectrometry in harsh environments, and have a contribution from the ion mobility spectrometry community as well. Since our last meeting, industry and Government agencies have continued to express interest in deploying field-portable chemical detection systems and have supported development with program funding through various agencies. Domestically, we are seeing multiple opportunities from the Department of Homeland Security, the Department of Defense, NASA, and various industries, and many of our Workshop participants are key players in these programs. We also continue to see opportunities in extraterrestrial applications, with the emerging missions to the moon, lunar gateway, and long-duration Mars missions. Several mass spectrometry and ion mobility-based systems are already in use or test on the International Space Station.

This year's Workshop follows last year's first ever European HEMS meeting, which helped us highlight more of our European colleagues' innovations. Many thanks to Ken Wright for organizing the workshop and making it a success.

I also thank our corporate sponsors, whose support helps make the Workshop and the HEMS student scholarships possible. Many of our sponsors have been with us for many years, and while their corporate names have changed over time, they provide consistent help and essential technology for our work. Thank you very much for your support.

Finally, we are pleased that Myrtle Beach and our hotel were spared from the destruction of hurricane Dorian, which passed our way only two weeks ago. We strive to be all inclusive and make the most of our meetings, but having a harsh environment at the Harsh Environment Workshop was more than we had planned.

Welcome again. We hope you have a rewarding experience this week.

Sincerely,

Ben Gardner
President, HEMS
Chairman, 13th HEMS Workshop Organizing Committee

THANK YOU TO OUR SPONSORS!



The World's Sixth Sense™



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

The 10th Harsh-Environment Mass Spectrometry Workshop

September 13-16, 2015; Baltimore, Maryland

Presented by OI Analytical

The 11th Harsh-Environment Mass Spectrometry Workshop

September 18-21, 2017; Oxnard, California

Presented by UTC Aerospace Systems

The 12th Harsh-Environment Mass Spectrometry Workshop - EuroHEMS

October 16-18, 2018; Cologne, Germany

Presented by Inficon, Inc.

For programs, proceedings, and participants please visit:

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

Student Award Winners

Tanouir Aloui, Duke University

Kathleen Horvath, Duke University

Camila Anguiano Virgen, University of North Texas

PROGRAM

Mon, 9/16	Travel Day
5:30 p.m. - 7:30 p.m.	Registration and Welcome Reception Coastal Grill Bar - Manager's Reception
Tue, 9/17	HEMS Workshop
7:00 a.m.	Set-up of vendor tables and registration
8:30 a.m.	Welcome Remarks
8:40 a.m.	Technical Session I:
8:40 a.m.	On-site Applications of MIMS and the Importance of Interface Design as Exemplified by Highly Unusual "Fragments" in MIMS Mass Spectra of Chloramines and Bromamines Frants R. Lauritsen
9:30 a.m.	Designing a Coded Aperture Cycloidal Mass Analyzer to Detect Perfluorocarbon Tracers Kathleen L. Horvath, 2019 Student Award Winner
10:00 a.m.	Mid-morning Break
10:30 a.m.	Technical Session II:
10:30 a.m.	Development of Micro-Time-Of-Flight Mass Spectrometer with Orthogonal Injection for <i>In situ</i> Gas Analysis Frédéric Progent
11:00 a.m.	The Dragonfly Mission to Titan and the Enabling Technologies of the DraMS Mass Spectrometer Onboard R. M. Danell
11:30 a.m.	Evaluation of Aperture Materials for Coded Apertures Used in a Portable Cycloidal Miniature Mass Spectrometer Tanouir Aloui, 2019 Student Award Winner
12:00 p.m.	Lunch Provided Palladium Terrace
2:00 p.m.	Technical Session III:
2:00 p.m.	Vendor Presentations
2:00 p.m.	Vendor Presentations
2:30 p.m.	Vendor Presentations
3:00 p.m.	Vendor Presentations
3:30 p.m.	Poster Presenter Lightning Round
4:00 p.m.	Poster/Vendor Session , Refreshments served during poster session Palladium Foyer
7:00 p.m.	Evening Free

Wed, 9/18	HEMS Workshop
8:30 a.m.	Technical Session IV:
8:30 a.m.	Electric Field Fragmentation of Mobility Selected Ions Using Tandem Ion Mobility Spectrometry at Ambient Pressure with Molecular Identification through Neural Network Analysis Gary A. Eiceman
9:00 a.m.	Chemical Ionization of Xenon and Detection Utilizing a High Precision Digital Ion Trap (DIT) Timothy Vazquez
9:30 a.m.	Portable Mass Spectrometer for Explosives and Narcotics Detection Vadym Berkout
10:00 a.m.	Group Photo / Mid-morning Break
10:30 a.m.	Technical Session V:
10:30 a.m.	Detection and Analysis of Simulated Chemical Warfare Agents using Portable Mass Spectrometry Camila Anguiano Virgen, 2019 Student Award Winner
11:00 a.m.	Use of Computational Sensing Techniques to Improve the Performance of Mass Spectrometers in Harsh Environments Jason J. Amsden
11:30 a.m.	SIMION Beyond Ion Simulation: Field Analysis, Synthesis, and Harmonic Analysis for MS Design Robert H. Jackson
12:00 p.m.	Lunch on your own
1:30 p.m.	Technical Session VI:
1:30 p.m.	Spacecraft Atmosphere Monitor (S.A.M.) First Operational Data Stojan Madzunkov
2:00 p.m.	The Future of Linear Ion Trap Mass Spectrometer Systems for Planetary Exploration D. A. Kaplan
2:30 p.m.	Onsite Analysis of Illicit Drugs by Portable Ion Trap Gas Chromatography-Mass Spectrometry (GCMS) Charlie Schmidt
3:00 p.m.	Mid-Afternoon Break
3:30 p.m.	Technical Session VII:
3:30 p.m.	Membrane Inlet Mass Spectrometry for Ocean Worlds R. Timothy Short
4:00 p.m.	Evolution of a Compact TOF Mass Spectrometer from Space Exploration to the Internet of Things D. Lasi
4:30 p.m.	Development of a Low-Cost, Low-Power, Miniature Sector Mass Spectrometer with IonCCD Detection Noah Christian
7:00 p.m.	Workshop Dinner Lands End

Thu, 9/19	HEMS Workshop
9:00 a.m.	Technical Session VIII:
9:00 a.m.	Smart City Initiatives and Where HEMS Can Play a Role Guido Verbek
9:30 a.m.	LUVMI Rover to Characterize Volatile Content in Lunar Polar Regions Simon Sheridan
10:00 a.m.	Mid-morning Break
10:30 a.m.	Technical Session IX:
10:30 a.m.	Low-Pressure ICP-MS for Planetary Trace Elemental Analysis Mazdak Taghioskoui
11:00 a.m.	QIT-Mass Spectrometer for Lunar and Planetary Applications Frank Maiwald
11:30 a.m.	Closing Remarks
12:00 a.m.	Workshop Ends

ABSTRACTS

Evaluation of Aperture Materials for Coded Apertures Used in a Portable Cycloidal Miniature Mass Spectrometer

Tanouir Aloui[†], Raul Vyas[†], Kathleen Horvath[†], Charles B. Parker[†], Roger P. Sperline^{*}, M. Bonner Denton^{*}, Michael E. Gehm[†], Jeffrey T. Glass[†], Jason J. Amsden[†]

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Performing mass spectrometry in harsh environments requires robust small mass spectrometry instruments. However, mass spectrometer miniaturization requires surmounting a throughput vs. resolution trade-off. Spatially coded apertures have been proven to increase the throughput by an order of magnitude without any loss in resolution thus enabling miniaturization with minimal loss in performance. Our group has fabricated a prototype cycloidal coded aperture miniature mass spectrometer for detection of natural gas and volatile organic compounds in the mass range of 10 – 130 amu. We found that for ions of <40 amu, aperture imaging is satisfactory to achieve a good spectral reconstruction. However, for $m/z > 40$ amu, the aperture imaging degrades significantly. A potential cause for aperture image degradation at high m/z is accumulation of charges on the edges of the aperture slits preventing ions from being in the tolerated range of angular dispersion once they exit the ion source. Thus, the coded-aperture material and surface treatment are critical parameters to define the initial state of ions at the entrance of the cycloidal mass analyzer. In this study we report comparative results of different aperture materials as well as multiple surface treatments and cleaning procedures in order to quantify the impact of the aperture properties on the final data collected with a cycloidal mass spectrometer.

The information, data, or work presented herein was funded in part by the Advanced Research Projects Agency-Energy (ARPA-E), U.S. Department of Energy, under Award Number DE-AR0000546 and the National Science Foundation under Award Number 1632069. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Use of Computational Sensing Techniques to Improve the Performance of Mass Spectrometers in Harsh Environments

Jason J. Amsden,[†] Philip J. Herr,[†] Tanouir Aloui,[†] Raul Vyas,[†] Kathleen Horvath,[†] Charles B. Parker,[†] Adam D. Keil,[@] James B. Carlson,[‡] Maria Luisa Sartorelli,[^] Justin Keogh,^{*} Roger P. Sperline,^{*} M. Bonner Denton,^{*} Brian R. Stoner,^{‡,†} Michael E. Gehm,[†] and Jeffrey T. Glass^{†,^}

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Measurements from analytical instruments are a convolution of the instrument response and the spectrum. In a conventional instrument, the system is designed to make the instrument response a delta function so that measured spectrum is equivalent to the actual spectrum and thus straightforward to interpret. However, the design choices required to make the instrument response a delta function actually limit system performance. In a computational sensor, the system response does not have to be a delta function. The system response can be designed to maximize parameters of interest (such as throughput and resolution). Using the computational sensing technique of spatially coded apertures, one can increase the instrument throughput while maintaining resolution after spectral reconstruction, thus enabling miniaturization without loss in performance. This paper describes the challenges in the application of spatially coded apertures to a cycloidal mass analyzer and the design, fabrication and performance of a 15 x 20 x 8 inch 40 lb prototype cycloidal coded aperture miniature mass spectrometer building on the proof of concept demonstration described previously (Amsden, J. J.; et al., *J. Am. Soc. Mass Spectrom.* 2018, 29, (2), 360-372.). This paper will describe changes to the proof of concept instrument that improved alignment, electric field uniformity, and depth of focus that resulted in improved coded aperture imaging and better spectral reconstruction. The improved instrument also includes a flow through membrane inlet system for environmental analysis of natural gas and other volatile organic compounds.

Portable Mass Spectrometer for Explosives and Narcotics Detection

Vadym Berkout, David Joiner

Smiths Detection, 2202 Lakeside Blvd., Edgewood, MD 21040

The portable mass spectrometer is based on a linear ion trap (LIT) analyzer with an atmospheric pressure (API) interface. A novel ion funnel design is implemented to achieve efficient ion transmission using a small vacuum system. TSA screeners and other security professionals currently conduct sample collection using swab sampling. A thermal desorber (TD) is interfaced to the LIT analyzer to liberate sample from the swab surface. Desorbed sample vapors are ionized using a dielectric-barrier discharge (DBD). The TD-MS prototype system has been evaluated by depositing explosive and narcotic standards directly onto swabs.

Spectra were recorded and post-processed using detection algorithms developed in-house. The detection algorithm was designed for detection of threats in real-time, using dynamic thresholds that adjust to changes in the environment during continuous sampling. Threat peak windows contained within a library are monitored, and the peak amplitudes are compared against dynamically calculated thresholds to determine if peaks in these windows are statistically significant compared to the background spectral features. Scores are calculated based on the degree of significance and are accumulated over time. Once the score exceeds a pre-defined alarm threshold, an alarm is generated. Analytical figures-of-merit, including sensitivity and selectivity, will be presented to demonstrate the capability of the system for detecting trace levels of target explosives in an aviation security environment.

Development of a Low-Cost, Low-Power, Miniature Sector Mass Spectrometer with IonCCD Detection

Noah Christian (1) and Gottfried Kibelka (2)

(1) Leidos; 10260 Campus Point Dr, San Diego, CA 92121

(2) CMS Field Products; Xylem Inc, 2148 Pelham Parkway, Bldg. 400, Pelham, AL 35124

Under the Intelligence Advanced Research Projects Activity (IARPA) Molecular Analyzer of Efficient Gas-phase Low-power INTERrogation (MAEGLIN) program, Leidos developed technology for low cost chemical detection and identification using a compact magnetic sector mass spectrometer. This mass spectrometer incorporates several innovations for low-power, including a low power non-thermionic ionization system based on electron tunneling of field emitters, permanent magnet magnetic sector that does not use any power for mass separation, and an arrayed detector using an IonCCD for simultaneous detection of all ions. The short ion path length facilitates operation at higher pressures than typically required for a sector field instrument, further lowering power and improving fieldability. Because all ions are collected simultaneously on an arrayed detector, there is no loss of signal that would normally occur from a scanning or pulsed instrument, such as a conventional magnetic sector, electric/magnetic sector, time-of-flight, ion trap, or a quadrupole instrument. Our system underwent government testing and results of the final development and testing will be presented.

The research is based upon work supported by the Office of the Director of National Intelligence (ODNI), Intelligence Advanced Research Projects Activity (IARPA), via Air Force Research Laboratories contract FA8650-17-C-9103, and work supported by Leidos Exploratory Research and Development Funding. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the ODNI, IARPA, or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright annotation thereon.

The Dragonfly Mission to Titan and the Enabling Technologies of the DraMS Mass Spectrometer Onboard

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NASA's recent selection of the *Dragonfly* mission under the New Frontiers Program signals a return to investigate the surface of Titan, Saturn's largest moon, and one of the Ocean Worlds of primary interest to NASA. Titan is a complex planetary body with a dense atmosphere that is primarily composed of nitrogen, climate and weather patterns similar to those on Earth, a subsurface layer of (possibly ammonia-rich) liquid water, and surface lakes or seas of methane and ethane.

The density and complexity of the atmosphere and surface of Titan, combined with solar radiation and energetic particles from Saturn's magnetosphere, create an environment primed for extensive organic chemical synthesis. Simulations of this chemistry have produced a variety of organic molecules based on C, N and H atoms, from pre-biotically important molecules such as amines to amino acids. This complexity presents both a challenge and an opportunity for the chemical investigation of the surface of Titan, one of the major goals of the mission.

Dragonfly is a rotorcraft lander (a dual-quadcopter), which will enable aerial flight for transport between different locations on the surface of Titan. The low gravity and dense atmosphere make rotary flight favorable on Titan. *Dragonfly* will contain four different instruments, a camera suite, a geophysics and meteorology package, a Gamma-ray and neutron spectrometer, and a mass spectrometer. The *Dragonfly* Mass Spectrometer (DraMS) will perform both Laser Desorption/ionization Mass Spectrometry (LDMS) and Gas Chromatography Mass Spectrometry (GCMS), similar to the approach demonstrated by the Mars Organic Molecule Analyzer (MOMA). This presentation will discuss the key LDMS and GCMS techniques, operation schemes and instrument augmentations that will allow *in situ* analysis of materials collected at Titan's surface while also preparing for the complexity that is expected from these samples.

Electric Field Fragmentation of Mobility Selected Ions Using Tandem Ion Mobility Spectrometry at Ambient Pressure with Molecular Identification through Neural Network Analysis

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A tandem ion mobility spectrometer with a reactive stage at ambient pressure produced fragment ions from protonated monomers and established a foundation for molecular identification with ambient pressure technology. Fragmentation of alcohols was used a model compounds to examine the formation of fragment ions in strong electric fields of mobility isolated ions with carbon numbers three to nine. Protonated monomers of individual alcohols were mobility isolated in a first drift region and were fragmented to carbocations at 64 to 128 Td and 45 to 89°C. Precursor and fragment ions were mobility characterized in a second drift region. Enthalpies for fragmentation of ROH_2^+ to primary carbocations were calculated as 76 to 97 kJ/mole and enthalpies for subsequent charge migration to 2° carbocations were -49 to -58 kJ/mole. Spectra were also treated using backpropagation neural networks with training and testing of familiar and unfamiliar compounds. Findings suggest that much of the identification process could be attributed to memorization an about 30% learning on fragment ion patterns. In a bounded set of chemicals and five chemical families, classification and identification (both described as average adjusted values from the neural network) were greater than 0.95. Classification of unfamiliar compounds (those substances not used in any training or test of a network) showed rates over 0.5 for some compounds and others between 0.3 and 0.5. Increases of E/N to 150 to 200 Td should increase the amount of fragmentation and aid classification of unfamiliar compounds.

Determination of the Presence of Biological Compounds in Aerosol Particles with a Linear Ion Trap

Nathan Grimes, Theresa Evans-Nguyen

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Locations such as Enceladus and Titan are prime targets for astrobiological research due to the presence of water and organic species. Many of the methods of ionization employed on the space craft used to explore these regions involve high speed impacts which can be potentially destructive to any fragile organic species. The development of a flight-practical instrument capable of analyzing these organic species without destroying any higher order structures is crucial in the search for extraterrestrial life.

Herein the current development of an aerosol particle linear ion trap capable of determining the presence of biological compounds with fluorescence detection is discussed. The electrode geometry of the instrument is sourced from the mass analyzer of a commercial mass spectrometer and uses trapping waveforms from an external digital electronics system. Once validation of trapping efficacy has been done, the implementation of an aerosol generation device, a fluorescence excitation source, and detection device will be performed. Aerosol particles found in water plumes evolving from the surface of Enceladus or in the high altitude regions of Titan's atmosphere are the target of this device. It would collect natively charged aerosols in the potential well of the trap as a spacecraft transversed the area of interest. Multiple wavelengths from an excitation source oriented axially with the trap would be used to induce fluorescence in amino acids, nucleic acids, coenzymes, and chlorophylls contained in any of the trapped aerosol particles that could be observed by an orthogonally placed detector.

Designing a Coded Aperture Cycloidal Mass Analyzer to Detect Perfluorocarbon Tracers

Kathleen L. Horvath,[†] Tanouir Aloui,[†] Raul Vyas,[†] M. Luisa Sartorelli,[†] Yuriy Zhilichev,[†] Justin Keogh*, Roger P. Sperline,* M. Bonner Denton,* David Koester,[‡] Patrick Keelan[^], Jeffrey T. Glass,[†] Jason J. Amsden,[†] Jesko A. von Windheim[‡]

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High voltage transmission cables (HVTCs) exist buried underground as part of the electrical utility grid. These HVTCs degrade over time and the petroleum-based dielectric fluid can leak into the surrounding environment posing a safety, economic, and environmental concern. Current HVTC leak detection methods involve detecting perfluorocarbon tracer (PFT) molecules injected into the dielectric fluid with a truck mounted custom modified gas chromatograph. The gas chromatograph is extremely sensitive, but suffers from poor dynamic range, high cost, and limited portability. Duke University is collaborating with PFT Technology to develop a cycloidal coded aperture portable mass spectrometer capable of detecting PFT molecules for locating leaks in HVTCs in the field. This work presents a preliminary design and finite element analysis simulations of the proposed cycloidal mass analyzer including a 0.7 T NdFeB magnet, aluminum electric sector, electron ionization source, and focal plane capacitive transimpedance amplifier array detector. The mass analyzer is designed to detect fragments of PFT molecules in the mass range of 59-160 amu with a resolution of 0.5 amu. The anticipated footprint of this mass analyzer is 30 cm x 27 cm x 11 cm and will weigh ~ 40 kg.

The information, data, or work presented herein was funded in part by the National Science Foundation's Partnerships for Innovation Program Building Innovation Capacity (BIC), under Award Number 1632069. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

SIMION Beyond Ion Simulation: Field Analysis, Synthesis, and Harmonic Analysis for MS Design

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The problem of harsh environment mass spectrometer design very often involves considerable compromises to the nearer ideal designs made for the laboratory, in order to accommodate space, power constraints, cost, etc. Most of us engaged in the design of mass spectrometer technology have made use of some version of the SIMION™ ion optics simulation software somewhere along the way. However, over the past decade we have seen an explosion of computing power and added capabilities in SIMION, all controlled by the LUA scripting language and leading the release SIMION 8.2. To be sure the exploration of all of these capabilities defies most researchers time constraints, so this presentation will show examples using these capabilities with the goal of motivating a deeper look at what can be done with SIMION and how the user can expand the software to address many of the problems of Mass spectrometer design and optimization. We show that it is now possible within SIMION to analyze and mathematically characterize the fields created by the structures we design in order to understand the observed simulated ion motion and thereby the instrument performance. In order provide a very quick tutorial we utilize non-ideal ion traps and show how to grasp quickly and directly in SIMION the non-linear behavior and the effects on your instrument using spatial Fourier characterization of the mathematical form of the fields. We then show how new designs can be synthesized by modifying these fields and how to generate new electrode structures. It is hoped that the methods in these examples capture enough of the new capabilities to provoke the imagination of the audience with the further hope of generating interest in a SIMION user group or possibly a more general mass spectrometer simulation interest group.

The Future of Linear Ion Trap Mass Spectrometer Systems for Planetary Exploration

D. A. Kaplan^{1,2}, R. M. Danell^{1,3}, A. Grubisic¹, F. H. W. van Amerom^{1,4}, X. Li^{1,5}, M. Castillo^{1,6}, W. B. Brinckerhoff¹

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The Mars Organic Molecule Analyzer (MOMA) onboard the 2020 Rosalind Franklin Rover incorporates the first linear ion trap (LIT) mass spectrometer that will be deployed into space. The fundamental technology developed for MOMA will enable a family of instruments employed in space exploration over the coming decades. Several key features of the LIT, as well as enabling portability developments, allow this mass analyzer to be applied to a variety of targets across the solar system.

The MOMA instrument suite is capable of Gas Chromatography Electron Ionization (GC-EI) as well as Laser Desorption Ionization (LDI), with the two ionization approaches enabling detection of molecular species across the volatility spectrum in support of the overarching mission science goals to seek evidence of past and/or present life at Mars. However, other planetary targets (i.e. Ocean Worlds such as Europa or Enceladus) likely require other modes of ionization in order to best suit the anticipated sample composition and target analytes. Very sensitive detection of trace amino acids has been demonstrated through the use of fluorescent tagging combined with capillary electrophoresis (CE) but coupling this to a mass spectrometer is desirable to maintain broad chemical analysis capability. As such the design of a nano-electrospray ionization (nESI) source, compatible with the requirements of operation on Europa will be discussed, specifically addressing the issues of gas load and consumption as it impacts a portable instrument.

Similarly to how the LIT is finding applications on multiple missions, the development of algorithms and techniques for one scenario can often be applied to many others. A common challenge for small, resource-constrained ion traps is the need to deal with samples that have a wide range of concentration of analytes. During MOMA development as well as during the development of a second-generation MOMA-like LIT instrument recently field-deployed to the Atacama

Desert, a range of techniques such as SWIFT, selective accumulation, broad band isolation and high dynamic range lens gating have all been investigated to address the challenges of a complex sample. The application of these techniques to Mars analog samples, including those studied in the Atacama desert, as well as future expected ESI data will be presented and discussed.

Evolution of a Compact TOF Mass Spectrometer from Space Exploration to the Internet of Things

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(2) University of Bern, Physics Institute, Sidlerstrasse 5, 3012 Bern (Switzerland)

We present a new compact time-of-flight (TOF) mass spectrometer for the Internet of Things (IoT), which builds upon the heritage of three generations of similar instruments for space and stratospheric missions^{1,2,3}.

After an overview of the evolution of the reflectron-TOF architecture for ESA space missions, from RTOF/Rosetta to NIM/JUICE, we summarize the key design patterns that led to achieving a unique mix of performance, dimensions, and resources utilization (mass and power): reliance on electron-impact ionization using low-power ($\sim 1\text{W}$) thermionic emitters, extraction and an optional mass blanking with fast ($\sim 2\text{-}3\text{ ns}$) high-voltage pulsers, use of integrated metal-ceramic screen-printed ion optics, extreme optimization of fast ($\sim 0.5\text{ ns}$) custom-build impedance-matched Micro-Channel Plates (MCP) detectors, and use of automated particle-swarm optimization algorithm to maximize the instrument performance⁴. Examples of implemented designs together with some key performance results are used to expose the key tradeoffs behind these design choices.

We then discuss how some key lessons learned and design patterns from the development of these space instrument's development have been implemented in a novel commercial IoT mass spectrometer by a spin-off from the same group. This new device is based on orthogonal-extraction reflectron TOF architecture and is compact (sensor: $\sim 300\text{ mm}$; electronics $238 \times 165 \times 105\text{ mm}$). Early tests with residual and calibration gases showed $720\text{ M}/\Delta\text{M}$ (at 44u , CO_2) mass resolution and 10^5 dynamic range, but 950 and 10^6 are at reach with further optimizations, considering SIMION results and achievable noise level targets ($\sim 1\text{mV rms}$ white noise).

Contrary to its predecessors, this commercial instrument has been designed for manufacturability and cost, yet with the advantage of using state-of-the-art electronics, such as high-performance FPGAs and commercial Systems-in-Package (SiP) that provide for higher flexibility, performance, and reduced development times. Moreover, an HTTP API make it a true IoT device, allowing real-time control and data visualization via web browser and data storage to InfluxDB time-series database, allowing to envision new ConOps based on distributed system-of-systems architectures, for example in drinking water quality monitoring.

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On-site Applications of MIMS and the Importance of Interface Design as Exemplified by Highly Unusual “Fragments” in MIMS Mass Spectra of Chloramines and Bromamines

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This talk will give an overview of MIMS applications for analyzing gaseous, liquid and solid samples for both volatile and very low volatility analytes. The focus will be upon the different interface designs needed for the different sample types and a number of industrial on-site uses will be presented using a MIMS instrument that can simply and in the field be shifted from one type of interface to another.

The talk will in detail discuss an example, where a “standard” flow through MIMS system previously used with success for analyzing volatile organic compounds in hundreds of applications behaved in an un-acceptable way with a new type of analytes. Under certain ion source and interface setups the analysis of haloamines (monochloramine, dichloramine, monobromamine and dibromamine) gave rise to mass spectra, where unusual “fragment” ions corresponding to pick up of 1 or 2 atomic hydrogen radicals ($H\bullet$). Most prominent were the “fragment” ions at m/z 52 $[NH_3^{35}Cl]^+$ and m/z 54 $[NH_3^{37}Cl]^+$ from dichloramine ($NHCl_2$) and at m/z 96 $[NH_3^{79}Br]^+$ and m/z 98 $[NH_3^{81}Br]^+$ from dibromamine ($NHBr_2$).

Spacecraft Atmosphere Monitor (S.A.M.) First Operational Data

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We will present the first results and status from the Spacecraft Atmosphere Monitor (S.A.M.) instrument recently deployed to International Space Station (ISS) and powered on August 8th. S.A.M. is mass spectrometer based on Jet Propulsion Laboratory's Quadrupole Ion Trap Mass Spectrometer (QIT-MS). Its function on ISS is to measure the major constituents of the ISS's atmosphere. This spectrometer is a Technology Development Unit (TDU) #1 with low mass (9kg), minimized power (max. 45W with heater bulb on), and on-board data processing capability houses within 9" cube.

S.A.M is a fully automated unit. After power-up on the ISS the received telemetry showed nominal operation. S.A.M. takes 100 full mass spectra each second which are processed by automated algorithms to extract the major constituent's abundances (N₂, O₂, CO₂, CH₄) which are then reported on a per second basis. We will also report on the interesting correlation between measured ion count (from integrated mass spectra) and the Earth's magnetic field intensity.

QIT-Mass Spectrometer for Lunar and Planetary Applications

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The Planetary Mass Spectrometer group at the Jet Propulsion Laboratory has developed a compact Quadrupole Ion Trap Mass Spectrometer (QIT-MS) with potential usage for multiple missions. One proposed implementation is to combine the QIT-MS with a JSC-built Linear Energy Transfer Spectrometer (LETS) for multi-day lunar surface exospheric and radiation investigations. Both subsystems primary science goals are to determine the density, composition, and time variation of the lunar volatiles and atmosphere, and correlate these with the local solar wind environment. Another application is to use the QIT-MS as a mass analyzer coupled to an electrospray ionization (ESI) source, in order to analyze ionizable species present in liquid samples.

The QIT-MS has the capacity of identifying and quantifying molecular species with abundances of ten (10) molecules/cm³, which has been verified for gaseous samples [1,2,3]. Currently, we are exploring the sensitivity of the QIT-MS with ESI inlet for molecular species that can be ionized in solution. In addition, the QIT-MS has an unprecedented combination of low mass (7 kg) and power (max 30 W with heater bulb on), with high sensitivity (0.003 counts/cm³/sec) as well as an ultra-high precision (0.5% for noble gas isotope ratios over 24 hours). These parameters yield 10× better than previously reported ion trap mass spectrometer, ex. [4].

The low mass, power, and data rate of the QIT-MS enable flexibility for the accommodation in different space missions with constrained resources. Moreover, the measured performance on breadboards and engineering demonstrators [3] show that high-value science return can be obtained without needing complex sample handling or mobility. The maturity (>TRL=7) and versatility of the QIT-MS enable tailoring for a wide range of flight opportunities of interest to NASA.

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Development of Micro-Time-Of-Flight Mass Spectrometer with Orthogonal Injection for *In situ* Gas Analysis

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CEA works on *in situ* gas field analyzers, especially on miniaturization of time of flight mass spectrometer. Such device has numerous applications covering a wide range of analyze fields such as environment, industry, space, homeland security, etc. In this regard, the device must have a small footprint, be lightweight, low power consuming and easily usable. CEA works therefore on Micro-Electromechanical System (MEMS).

CEA has developed a linear micro time-of-flight (μ -TOF) mass spectrometer on chip. Results on linear μ -TOF have been previously shown. Briefly, linear μ -TOF is composed of an ionization stage and a zone of extraction and focalization of the ions. Each part has been optimized. Electronic impact is used for ionization and ions are detected on a Micro Channel Plate (MCP), mass spectra are recorded with an oscilloscope.

This linear μ -TOF is used to investigate orthogonal injection. Currently, two devices of orthogonal injection are evaluated: the first one is composed of metallic electrodes, the second one is a MEMS to test orthogonal injection on a chip assemblage (Fig 1 A).

Metallic structures are used to explore geometric layout of electrodes and associated voltage setting. Using gas mixtures of rare gas in helium we were able to obtain limit of detection at 10 ppm. Results help on chip studies and provide guideline for voltage setting.

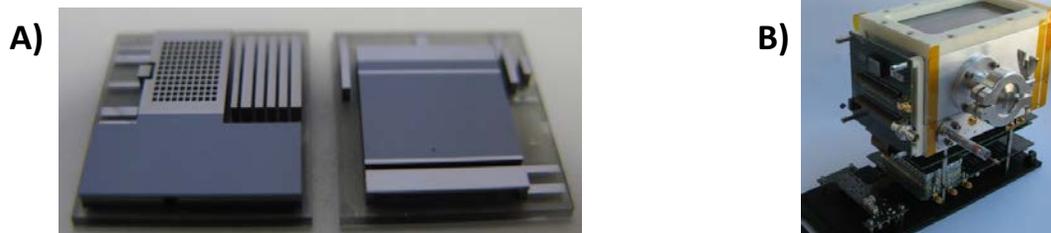


Fig. 1: A) Ion source and orthogonal injection chips; B) Electronic device

Furthermore, very significant efforts have been made to reduce size of electronics. A complete power supplies system has been designed and validated (Fig 1 B).

This work shows encouraging results and pulls the μ -TOF one step closer towards a fully integrated portable analytical system.

Onsite Analysis of Illicit Drugs by Portable Ion Trap Gas Chromatography-Mass Spectrometry (GCMS)

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False-positive results from on-scene illicit drug analysis using presumptive color tests have caused numerous wrongful arrests. In many states, forensic laboratories do not ever receive the substance for confirmative identification of the illegal substance unless the defendant goes to trial, which makes it impossible to know the severity of this problem. Additionally, some defendants take a plea deal, which can result in these defendants spending months or years in prison for a crime they did not commit. Improving the reliability of on-scene illicit drug testing by incorporating confirmatory methods capable of achieving very low limits of detection such as gas chromatography/mass spectrometry (GC/MS) into the field could help reduce these wrongful arrests.

In this research, over 50 common illicit drugs and 15 additives were used to create an ion trap GC-MS library. The instrument uses a toroidal ion trap, which has 3 major advantages over other ion traps (e.g., cylindrical ion traps): (1) its small size, (2) its durability, and (3) its higher operating pressure which lowers pumping requirements. Due to the potential for space charge and ion-ion interactions in ion-trap MS, a customized library for this type of field application is critical to prevent missed identifications (i.e., false negatives). In this research, many of the tested compounds had spectra different from that of the NIST MS database due to the presence of space charge and ion-ion interactions. The ion trap GC/MS library was then used to test the ability to detect and identify illicit substances and their additives in seized drug samples. In addition, results were compared with data generated from the same samples using a field-portable quadrupole GC/MS. It was concluded that with additional library development, portable ion trap GC/MS is a viable choice for the confirmatory identification of seized drugs in the field.

LUVMI Rover to Characterise Volatile Content in Lunar Polar Regions

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The low inclination of the lunar orbit allows areas in high and low latitudes to remain in eternal darkness. These Permanently Shadowed Regions (PSR) are never illuminated by sunlight and are some of the coldest places in the Solar System and could contain vast deposits of water and other volatiles. In-situ measurements are required as a 'ground-truth' measurement to determine the existence volatiles in these regions.

The LUnar Volatiles Mobile Instrumentation (LUVMI) is an autonomous, low mass, modular rover concept consisting of surface and subsurface sensing instruments with an in-situ sampling and analysis technology capable of depth resolved volatile extraction and characterisation. Volatile extraction from the lunar regolith will be carried out by the Volatiles Sampler (VS), which will sample the subsurface up to a depth of 20 cm, extract water and other loosely bound volatiles through heating. The design of the VS provides efficient volatile sample transfer and minimizes sample handling requirements. Evolved volatile characterisation will be performed by the Volatiles Analyser (VA) which is a miniature ion trap mass spectrometer based on the Ptolemy mass spectrometer instrument on-board Philae, the ESA Rosetta Lander. LUVMI-X (eXtended) will add the capability of allowing direct access to a PSR(s) via a miniature instrumented low velocity projectile that will be launched from the rover platform into areas of interest that are inaccessible to the rover.

We will discuss the LUVMI test campaign conducted in December 2018, the current LUVMI-X configuration, the design of the mass spectrometer extraction systems and recent laboratory results obtained with volatile doped regolith simulant.

Membrane Inlet Mass Spectrometry for Ocean Worlds

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Detection of extant life and habitability assessment on Ocean Worlds is a high scientific priority for NASA. Gases, including light hydrocarbons and volatile organic compounds, are a relevant set of analyte species that can be occluded in water and ice as products of metabolism and indicators of habitability, and are expected to be present in a variety of planetary environments. Future missions to icy moons such as Europa and Enceladus may be engineered to penetrate ice and send autonomous payloads to oceans below, although initial missions to Ocean Worlds likely will only access the surface and near-surface ice. On Mars, recent discovery of liquid water ~1.5 km below the surface of the South Polar Layered Deposits may provide a more near-term opportunity to study liquid water and overlying ice on another planet. Consequently, we are investigating ways to employ variations of membrane inlet mass spectrometry (MIMS) for extraction of volatile analytes that have relevance to advancing the search for life and assessment of habitability on Ocean Worlds.

We are developing a low-power static (i.e., non-flowing sample) MIMS interface that obviates the need for power-hungry sample pumps and requires only limited volumes of water. The static MIMS interface is intended ultimately for in-situ analyses of gaseous, semivolatile, and water-soluble biosignatures from liquid or melted ice samples in lander missions with limited power budgets on Ocean Worlds. The MIMS interface receives small volumes (e.g., 1 mL) of liquid samples from which a large fraction of the volatile species are extracted and delivered to a linear quadrupole mass spectrometer. The interface will be coupled with a Goddard Space Flight Center (GSFC) gas processing system (GPS), which is based on the GPS incorporated into the Sample Analysis at Mars instrument currently operating on the Curiosity Rover on Mars. The GPS includes enrichment cells to concentrate volatiles of interest for analysis, and a scrubber cell to trap unwanted water vapor. We will present progress to date on individual work on the static MIMS probe at SRI International (SRI) and the GPS at GSFC and our initial integration of the two systems.

We will also present a concept to integrate two techniques, a Honeybee Robotics thermal ice probe and an SRI underwater MIMS system, to create MeltMIMS, a

novel instrument for in-situ analyses of dissolved gases and volatile organics in ice and ice-covered lakes. The GSFC team is providing expertise on in-situ planetary habitability and biosignature measurements for development of the concept. The MeltMIMS is proposed to ultimately allow us to determine concentrations of volatile analytes of biological relevance in the melt water with high spatial resolution as the thermal ice probe melts through, e.g., a Europa or Mars ice layer, and when it reaches a subglacial ocean or lake below.

Low-Pressure ICP-MS for Planetary Trace Elemental Analysis

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Inductively coupled plasma mass spectrometry (ICP-MS) is the gold standard for elemental analysis. However, due to rigorous size, power, and gas consumption constraints, ICP-MS techniques have not been employed for planetary exploration. Currently, the standard for elemental analysis during planetary exploration is laser desorption mass spectrometry (LDMS; e.g., MOMA onboard the ExoMars rover) or laser-induced breakdown spectroscopy (LIBS; e.g., ChemCam on the Curiosity rover). However, these techniques do not offer the detection limits required for accurate quantitation of trace elements at ppmw levels and below.

We are developing a mission enabling miniaturized ICP-MS system with an advanced quadrupole mass spectrometer based on the heritage design of SAM QMS space flight instrument. The ICP-MS system under development employs a reduced-pressure plasma that requires only a fraction of the power (<20W) and gas supply (<200 SCCM) of the conventional system. Our current and ongoing efforts will be presented that includes preliminary studies regarding reduced-pressure argon and helium plasmas, Langmuir probe studies, ion extraction with a two-lens system as the interface, and preliminary mass spectrometric measurements with a custom QMS system.

Overview of the MOMA Mass Spectrometer and Examination of Some Mineral Matrices as Learning Curve for MOMA Return Data

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The Mars Organic Molecule Analyzer (MOMA), a linear ion trap (LIT) mass spectrometer-based investigation of potential extinct or extant life on Mars, has been delivered in Europe and is installed inside the Rosalind Franklin rover in preparation for ExoMars launch in July, 2020.

The LIT is capable of measuring ion masses from m/z 50-1000 by making use of two distinct ion sources. For higher volatility molecules over m/z 50-500, an electron ionization (EI) source is implemented with front end based on pyrolysis of crushed drill samples taken from a depth up to 2 meters where cosmic radiation has not penetrated. Gas chromatography both with and without chemical derivatization is applied from any of four columns including one sensitive to molecular chirality. For lower volatility molecules over m/z 100-1000, a laser desorption/ionization (LDI) source is implemented directly on crushed particulate samples, delivered to a tray underneath a 266 nm laser capable of 140 uJ with 1 ns wide pulses.

At GSFC a second instrument duplicating the MOMA flight model is being installed into an environmental chamber to support Mars surface operations under identical conditions (5-7 Torr and temperatures from -45 to 0 °C). As this “flight spare” must maintain very low contamination levels to permit real-time diagnosis during the mission, an engineering test unit with full flight functionality is now available for testing of operating procedures and interpretation of Mars data based on analog analyses. This unit has been updated and cleaned to permit investigation of the complex LDI mass spectra produced by pulsed UV LDI of complex mineral mixtures with and without admixed organics, as to support development of advanced methods for detection and spectral interpretation. A discussion of the MOMA mass spectrometer will be presented and an initial examination of mineral matrix spectra will be discussed.

Chemical Ionization of Xenon and Detection Utilizing a High Precision Digital Ion Trap (DIT)

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Isotope ratio mass spectrometry (IRMS) is commonly used in space applications to perform radiometric dating, and in the sourcing of gas distributions on an extraterrestrial body. Typically, these measurements are taken utilizing instruments such as time-of-flight and magnetic sectors. Ion traps however, are not normally considered due to sensitivity and precision issues that arise from space charge effects. To improve sensitivity, xenon will undergo chemical ionization (CI) to improve ionization efficiency. Additionally, improvements to the y-axis resolution of the data acquisition (DAQ) will allow for higher precision measurements.

Xenon gas is introduced into an external ion volume at a partial pressure of $\sim 1 \times 10^{-6}$ torr_{Xe} where it is ionized utilizing either an EI source or a CI source when introducing the appropriate reagent gas. Ions are then gated into a 3D – quadrupole ion trap operating in resonance ejection mode while utilizing digital square waveforms (DIT) for trapping and ejection. The ion trap operates with a constant 1 MHz frequency and 300 V_{0-p} on the ring electrode while the endcap electrodes are operated with a frequency sweep ranging from 1 MHz – 15 kHz at 2 V_{dc}. For signal acquisition, a variable y-axis resolution (8-16 bit) DAQ system was initially employed. Data obtained was compared to a previously used fixed y-axis (8-bit) resolution DAQ.

Upon taking measurements it was found that our fixed DAQ system provided per mille deviations of 18.8 ± 105.8 ‰ while the variable DAQ system provided 0.5 ± 1.0 ‰ resulting in ~ 2 orders of magnitude improvement. To obtain these results, the new DAQ was operated with 16-bit y-axis resolution and with an integrated low pass filter set at 23 kHz.

Smart City Initiatives and Where HEMS Can Play a Role

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With the wide concern regarding pollution and the presence of any harmful chemicals in the ambient air, air monitoring instrumentation, as well as trapped recycled air in buildings, has become of high interest and concern. In cities where various locations are major sources of pollutants or have the potential of releasing harmful chemicals into the air, the application of a mobile air monitoring system (land, water, air) would resolve the issue of having to set up individual monitoring systems in every location of concern. A vehicle mounted portable mass spectrometer, MS on air handlers, and Drone Effluent Stream Devices can be created to get a real-time picture of city's chemical issues. These Chemical Sniffing systems can be implemented to highly trafficked urbanized cities to monitor the concentrations of pollutants that can pose a threat to any and all vulnerable individuals that are in close proximity, such as patients or children in nearby hospitals and schools. This kind of analysis can help determine traffic trends in terms of which routes are commonly used by most drivers. The data obtained from traffic trends can then be used to direct commercial vehicles to less commonly used routes to reduce the amount of vehicular related pollutants produced in areas where vulnerable individuals are located. Apart from traffic related chemical releases, the mobile system will be able to monitor and detect any harmful chemical effluent streams that may be produced by nearby manufacturing companies that commonly use harmful chemicals to manufacture their products. New Smart City AI, Big Data, and Logistics cannot move forward properly without this critical chemical knowledge. Our groups' technology, and a description of how HEMS groups can plug into this space can be an initiative for us all to direct the narrative for Smart City proposals.

Detection and Analysis of Simulated Chemical Warfare Agents using Portable Mass Spectrometry

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There's been a significant demand for the development and improvement of technology used for the detection and identification of chemical warfare agents (CWA). Current government technology includes Fourier Transform Infrared (FTIR) and Lightweight Chemical Detector (LCD3) systems. While the systems are able to quantitate, they cannot perform an analysis in a short period of time nor identify the type of CWA. The U.S. Army Dugway Proving Ground's annual S/K Challenge provides the opportunity to assess the performance and reliability of prospective devices being developed by researchers worldwide to optimize their performance. To do so, trial testing of simulated chemical and biological warfare agents in both indoor and outdoor environments were performed, mimicking past attack scenarios. One of the major chemical simulants used throughout the trials is Methyl Salicylate (MeS), which is known for being a simulant for sulfur mustard gas. Other simulants used include: Trimethyl Phosphate (TMP), Triethyl Phosphate (TEP), Sulfur Hexafluoride (SF₆), and a TEP-Syloid complex.

Membrane Inlet Mass Spectrometry (MIMS) technology on a portable system was successful in performing a rapid analysis along with quantification and identification of each CWA simulant utilized for the trials. The MIMS system can detect and quantify low-mass (1-300 m/z) permeable compounds with high parts-per-trillion (ppt) limits of detection. This allows for analysis to be achieved in seconds after the initial time of exposure, which is significantly faster than that of the FTIR and LCD3 systems utilized at Dugway Proving Ground. The system's performance at the S/K Challenge along with previous successes in various other applications, proves its ability for the use of CWA detection and identification purposes. Further testing can be conducted leading to the minimization and prevention of exposure time experienced by areas that are at high risk of attacks.

A Comparison of Thermionic Filament and Carbon Nanotube Field Emitter Array-based Ion Sources in Coded Aperture Miniature Mass Spectrometers

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This work presents a comparative study of thermionic filament and CNT emitter array-based electron sources in a cycloidal-coded aperture miniature mass spectrometer (C-CAMMS). The use of spatially coded apertures in mass spectrometry enables miniaturization by improving throughput without sacrificing resolution. To enable the full advantages of spatial aperture coding, the ion source must produce a spatially and temporally uniform sheet of ions directed at the coded aperture. Carbon nanotube (CNT)-based electron ionization sources for mass spectrometers provide several potential benefits over conventional thermionic emitters, including low voltage and power operation, room temperature operation, long lifetime, and ability to operate in a pulsed mode. In this study, electron emission stability and coded aperture image (as a measure of ion signal stability) over time were compared for C-CAMMS containing a CNT-based, and a thermionic filament-based ion source. We found that the thermionic filament produced a much more stable coded aperture image than the CNT-based ion source. The greater fluctuations in the CNT-based source are a result of adsorption and desorption of molecules on the CNT surface that cause local work function changes. These work function changes lead to spatial and temporal fluctuations in the electron emission and ion signal. Possible solutions to the CNT spatial and temporal fluctuations are discussed.

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In-situ Measurements of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of Dissolved CO_2 using an Underwater Mass Spectrometer

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We present here novel high-resolution measurements of stable isotopic ratios of dissolved CO_2 ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) calculated from an underwater mass spectrometer. The isotopic composition of dissolved CO_2 can be diagnostic of the gas source and may enable identification of leaks around oil and gas sites. We show that current underwater mass spectrometers are able to measure masses 44, 45, and 46 in sufficiently high resolution to enable precise *in-situ* measurements of CO_2 isotopes in deionized water. There are also possible interferences at masses 45 and 46 in seawater, and their effects on our stable isotope calculations. We present data from both laboratory studies of CO_2 dissolved in seawater and measurements taken in the Gulf of Mexico with very high depth resolution. A high-resolution record of dissolved CO_2 isotopes would further our understanding of the oceanic carbon cycle and pave the way for *in-situ* isotopic measurements of other species of interest such as methane and ethane.