

**ELECTROSPRAY IONIZATION/ION MOBILITY SPECTROMETER/CYLINDRICAL ION TRAP MASS SPECTROMETER SYSTEM FOR IN-SITU DETECTION OF ORGANIC COMPOUNDS** I. Kanik<sup>1</sup>, L. W., Beegle<sup>1</sup> R. G. Cooks<sup>2</sup> and H. H. Hill<sup>3</sup>, <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, Ca 91109, [ikanik@pop.jpl.nasa.gov](mailto:ikanik@pop.jpl.nasa.gov), [Luther.Beegle@jpl.nasa.gov](mailto:Luther.Beegle@jpl.nasa.gov), <sup>2</sup>Department of Chemistry Purdue University West Lafayette In, 47907-0393, [cooks@purdue.edu](mailto:cooks@purdue.edu) <sup>3</sup>Department of Chemistry, Washington State University, Pullman Washington 99164, [hhill@wsu.edu](mailto:hhill@wsu.edu)

The potential of an Electrospray Ionization/Ion Mobility Spectrometer/Cylindrical Ion Trap Mass spectrometer (ESI/IMS/CIT-MS) as analytical instrument for analyzing material extracted from rock and soil samples will be demonstrated. This instrument will be able to identify volatile compounds as well as resident organic molecules on the parts-per-billion level as part of a suite of instruments on the proposed 2009 Mars Science Lander (MSL). By obtaining an inventory of chemical species on the surface of Mars a chemical inventory of volatiles of surface chemistry and astrobiology will be preformed.

**Description of ESI, IMS, and CIT:**

*ESI* is a powerful ionization method. A great advantage of ESI is its ability to provide soft ionization resulting in the ionization of large, fragile organic molecules without fragmentation [1]. Liquid samples are introduced to the ionizer via a capillary which is held at a fixed potential above a reference grid. Organics are ionized as the charged droplets evaporate while drifting in a high pressure environment, here ~ 300 torr.

*IMS* operation is analogous to that of Time-of-Flight (TOF) mass spectrometers except that IMS can operate at the same pressure that the ESI operates. This is advantageous because no differential pumping is required when the ions go from ionizer to analyzer. When an ion is placed in an electric field it migrates along in the direction of the field until it collides with another molecule. At that point it begins to accelerate again until it suffers another collision and so forth. This results in each species having an average drift velocity, which is proportional to the applied electric field and the ion mobility (K). The mobility itself is related to size and shape of the ion imparting a second dimension which enables IMS to separate isomers such as leucine and isoleucine [2]. Ion mobility spectrometers have been demonstrated to be very sensitive in detecting organic compounds [3,4,5], and are currently the instrument of choice for field detection of explosives and chemical/biological warfare agents [6].

*CITs* are mass spectrometers which determine the m/z ratios of ions. They consists of three simple plates with holes in the center and an electron multiplier at the end of one plate. Ions are stored in the trap using a radio frequency (rf) of low amplitude. The ions are then expelled from the trap by their sizes (starting from

the lowest mass ions) by increasing the amplitude of the rf potential. In spite of their mechanical simplicity, miniature ion traps (as with the larger laboratory-based instruments) are extraordinary instruments which have striking advantages over other mass analyzers [7]. The ability to perform multiple stages of mass analysis (MS<sup>n</sup>) [8] in a single analyzer, without modification except in applied voltages, is a major advantage when dealing with complex samples or mixtures which in situ samples undoubtedly will be. Ion traps also have the advantage that ions of specified mass-to-charge ratios can be accumulated before being mass analyzed. Ion traps can operate pressures at least 3 orders of magnitude higher than any other type of mass analyzer, such as quadrupole and time-of-flight mass spectrometers. This greatly reduces the pumping requirements and therefore the overall mass and power of the instrument. For the same resolution achieved by the CIT, the pumping speed for a conventional MS can easily reach several hundred l/s [9].

**The combined ESI/IMS/CIT instrument**

Rock, soil or chips from a drill will be introduced into a "beaker" where volatiles will be extracted by submerging them in a low boiling-point solvent (such as water, acetonitrile, methanol etc.). The solution with extracted volatiles will be delivered via a tube (fused silica is commonly used, while PEEK<sup>TM</sup>, Teflon etc can also be utilized.) into a metal capillary at the rate of <1  $\mu$ L/min. The metal capillary will be held at a fixed voltage (~ 1000 V) above a grid. As the liquid passes through the capillary the droplets will ionized. The evaporation of solvent will take place in the desolvation region between grid and gate (see Fig 1) where any molecules in the droplets will become ionized. The desolvation region and drift cell consists of metal rings at discrete intervals with different voltages applied to them making a smooth electronic field within the two regions. Once the ions pass through the grid they will be collected immediately before the IMS gate. The gate will be pulsed at discrete intervals and the ion drift time will be calculated by detection on a faraday cup at the end of the drift region. The Faraday cup will have a small aperture (~30 microns) which allows ions to be collected in the CIT. The CIT will continue to collect ions until a sizable number are trapped and then the voltage will be ramped with the ejected ions detected by a simple electron multiplier.

Mass	15 kg
Power (Max)	20 Watts
Operating power	15 watts
Mass Range (CIT)	1,000 daltons
Mass Range (IMS)	Unlimited
Volume	10cmx10cmx50cm
Voltage Maximum	1000 volts max
Vacuum requirements (IMS)	NONE
Vacuum requirements (CIT)	10 <sup>-4</sup> torr

The ESI's favor is its utility in the analysis of biologically important molecules because it can extract fragile organic species from solution intact, ionize them and transfer them into the gas phase where they can undergo analysis by a spectrometer. This allows one to be able to detect very large biological compounds, ones with masses up to several million amu including proteins and DNA, as necessary [10]. In addition, molecules can be ionized with multiple charges so they can be detected by analyzers which have a maximum  $m/z$  value on the order of 10,000 daltons. Both detectors described here can detect molecules with masses over 10,000 daltons, which is why the ESI/IMS/CIT marriage works.

The data output will include: a) Pressure and temperature of the IMS cell, b) Faraday cup current as a function of drift time, c) EM current as a function of extraction voltage. From these three values, the mobility and  $m/z$  will be determined for each ion. These values will give a unique identification of each molecule extracted from a sample since no two molecules have the same mobility and mass.

Finally it is possible to determine the chirality of smaller organics, such as amino acids in the CIT [11]. The determination of the chirality of organic molecules is one of the most important astrobiological measurements that can be made. Our method is based on gas phase metal ion-bound cluster ions, which are formed in an electrospray ionization source, mass selected, and then subjected to collision-induced dissociation (CID) to undergo competitive ligand loss. We are currently working on ice core material to determine chiral ratios of the organics present when microorganisms decay after biologic activity ceases.

#### Conclusions

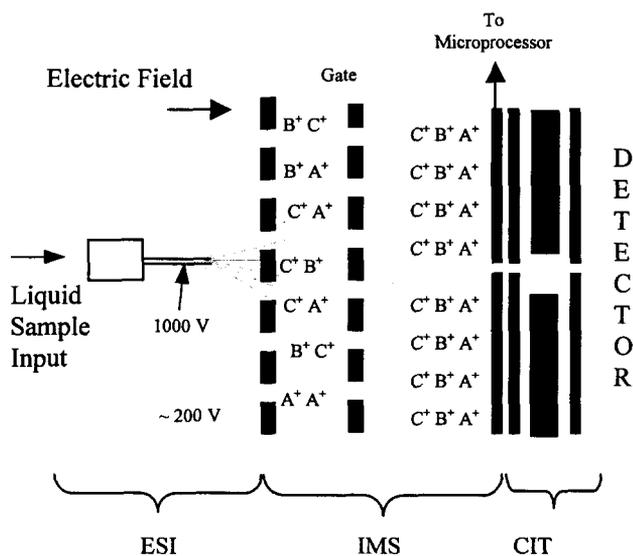
The high-resolution ESI/IMS/CIT technique, in our opinion, has a great potential to fulfill NASA requirements for detecting and accurately analyzing volatile compounds *in situ*. A small, self-contained ESI/IMS/CIT instrument would be able to quickly detect and correctly identify organic compounds (such as biotic amino acids [2], Abiotic amino acids [4],

peptides[3], etc.) as part of an *in situ* experiment on the surface of a planetary body such as Europa. Furthermore, it possesses ppb detection sensitivity and free from any fragmentation problem owing to a soft ionization method (ESI). A miniature, low-power stand-alone ESI/IMS/CIT detector, which contains no moving parts and is very economical to construct, would be ideal for a small rover searching for specific organic molecules as part of a suite of instruments on the 2009 MSL platform.

#### Acknowledgment:

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**References:** [1] McEwen, C. N. and Larsen, B. S., in "Electrospray Ionization Mass Spectrometry, Fundamentals, Instrumentation and Applications", John Wiley and Sons Inc. pp 177 (1999). [2] Beegle L W et al. (2001) *Anal Chem* 73, 3028. [3] Beegle L W et al. (2002) *J. Mass Spec.* 216, 257 [4] Kanik, I. (2003) *J. of Chrom.*, to be submitted [5] Beegle, L W et al. (2003) *Anal. Chem.*, to be submitted. [6] Baumbach J I and Eiceman G A, (1999) *App Spec* 53, 338A. [7] March (2000) *Ion trap Mass Spectroscopy in the Encyclopedia of analytical chemistry.* [8] Johnson R.C. et al. (1999) *Chim Acta* 395, 239 [9] DeHoffman E. et al. (1996) in *Mass Spectroscopy: Principals and Applications* [10] Banks J.F. and Whitehouse C.M. (1997) *I J Mass spec* 162, 163 [11] Tao WA, et al (2000) *J Am Chem Soc* 122 10598



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**Table 1. Specifics of the ESI/IMS/CIT-MS**

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