

ELECTROSPRAY IONIZATION/ION MOBILITY SPECTROMETER/CYLINDRICAL ION TRAP MASS SPECTROMETER SYSTEM FOR IN-SITU DETECTION OF ORGANIC COMPOUNDS

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The potential of an Electrospray Ionization/Ion Mobility Spectrometer/Cylindrical Ion Trap Mass Spectrometer (ESI/IMS/CIT-MS) as an analytical instrument for analyzing material extracted from rock and soil samples as part of a suite of instruments on the proposed 2009 Mars Science Lander (MSL) will be demonstrated. This instrument will be able to identify volatile compounds as well as resident organic molecules on the parts-per-billion (ppb) level. Also, it will be able to obtain an inventory of chemical species on the surface of Mars which will result in a better understanding of ongoing surface chemistry. Finally, questions relevant to biological processes will be answered with the complete inventory of surface and near surface organic molecules that the ESI/IMS/CIT is capable of performing.

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 non-volatile and fragile organic molecules with little fragmentation [1]. Liquid samples are sprayed into the ion source via a capillary which is held at a fixed potential above a reference. Charged droplets evaporate in a high pressure environment, are passed through a heated capillary and the ionized vapor phase organic molecules are injected into the mass analyzer.

IMS is a high-pressure time-of-flight (TOF) method based on elastic collisions of an ion with a buffer gas. It is advantageous over the other detection methods because it can operate at the same pressure as the *ESI* resulting in no differential pumping when the ions go from ionizer to analyzer. When an ion is placed in the electric field of the *IMS* it migrates 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_m). The mobility itself is related to the size and shape of the ion imparting a second dimension of selectivity which enables *IMS* to separate isomers such as leucine and isoleucine [2]. *IMS* has been demonstrated to be very sensitive in detecting organic compounds [3,4,5], and is currently the instrument of choice for field detection of explosives and chemical/biological warfare agents [6].

CITs are mass spectrometers and as such can provide complementary information (i.e mass-to-charge ratio) to ion mobility instruments. *CIT* consists of three simple plates with holes in the center and an external electron multiplier detector. Ions are stored in the trap using a radio frequency voltage (rf) of high amplitude. The ions are then expelled from the trap according to their mass/charge (m/z) ratio (starting from low mass) by ramping the amplitude of the applied rf. In spite of their mechanical simplicity, *CITs* are extraordinary instruments which have striking advantages over other mass analyzers [7]. The ability to perform multiple stages of mass analysis (MS^n) [8] in a single analyzer, without modification except in applied voltages, is a major advantage when dealing with complex samples 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 at pressures three orders of magnitude higher than any other type of mass analyzer, such as quadrupole and time-of-flight mass spectrometers [7]. This greatly reduces the pumping requirements and therefore the overall mass and power of the instrument.

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™, Teflon etc can also be used) into a metal capillary at the rate of $\approx 1 \mu\text{L}/\text{min}$. The metal capillary will be held at a fixed voltage ($\sim 1000 \text{ V}$) above a grid. The evaporation of solvent and associated ionization will take place in the desolvation region between grid and gate (see Fig 1). The desolvation region and drift cell consists of metal rings at discrete intervals with different voltages applied to them making a smooth electric field within the two regions. Once the ions pass through the grid, they will be trapped 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 which allows some of the ions to be introduced and then trapped in the *CIT*. The *CIT* will continue to collect ions until a sizable number are

Estimated Performance Specifics of the ESI/IMS/CIT-MS instrument. Including all command and control electronics and vacuum pumps.	
Mass	20 kg
Power (Peak)	40 Watts
Operating power	25 watts
Mass Range (CIT)	800 daltons
Mass Range (IMS)	Unlimited
Volume	10cmx10cmx50cm
Voltage Maximum	1000 volts max
Vacuum requirements (IMS)	NONE
Vacuum requirements (CIT)	10^{-4} torr

trapped. The rf voltage will then be ramped with the ejected ions being detected by an electron multiplier.

The ESI allows 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. This allows one to detect generate ions from large biological compounds, with masses beyond 10^5 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 in the range 1,000 - 10,000 daltons. Both analyzers described here can detect molecules with masses approaching 1,000 daltons, which is one reason why the ESI/IMS/CIT marriage works so well.

The data output will include: a) Pressure and temperature of the IMS cell, b) Faraday cup current as a function of drift time, c) electron multiplier 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 chemical compound extracted from a sample since no two compounds have the same mobility and mass.

Finally it is possible to determine the chirality of smaller organics, such as amino acids, utilizing the CIT [11]. The determination of organic molecule chirality is one of the most important astrobiological measurements. 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 [12].

Conclusions: The high-resolution ESI/IMS/CIT technique, has 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 accurately 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 Mars, Europa and Titan. Furthermore, it possesses ppb detection sensitivity and is largely free from any fragmentation problems owing to the soft ionization method (ESI). A miniature, low-power stand-alone ESI/IMS/CIT instrument, which contains minimal 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.

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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 W.A, et al (2000) J Am Chem Soc 122, 10598.[12] [4] Tsapin A. (2003) LPSC XXXVIII.

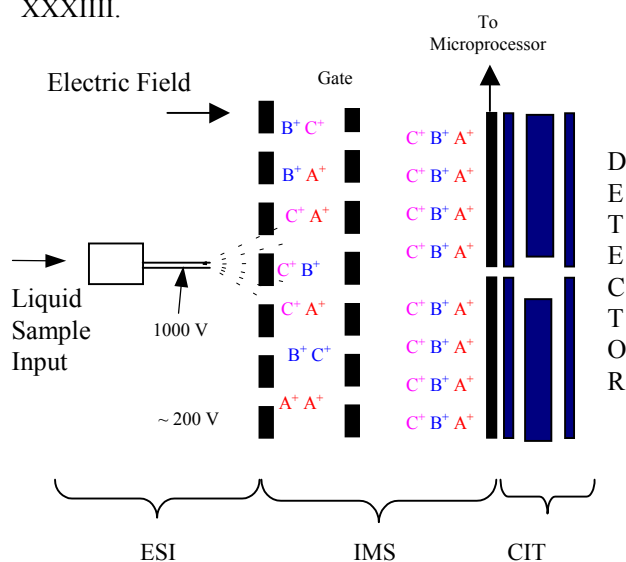


Figure 1. Schematic of the ESI/IMS/CIT instrument concept.