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Review

Ion mobility spectrometry in space exploration

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Abstract

Ion mobility spectrometry (IMS) has proven to be an effective tool for chemical detection and identification. Ion mobility spectrometers can be manufactured in small, rugged and portable designs and have been used in several mission critical circumstances from security screening and military preparedness. Perhaps most visible are the IMS analyzers that have been deployed in airports around the world to detect traces of explosives on passenger carry-on luggage. Intrinsic properties of ion mobility spectrometers make these analyzers suitable for both manned and robotic space exploration. In this review, we will discuss the utility, previous use and future use of ion mobility spectrometers in space environments.

Keywords: Ion mobility spectrometry; Space exploration; Mars; NASA; Organic compounds

Contents

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1. Introduction

An important aspect of past, present and future exploration of our solar system is the detection, identification, and quantitative determination of inorganic and organic molecules in human habitats and planetary environments. The motivations for such measurements are broadly two fold: (a) manned space exploration requires that the habitable environments be continuously monitored for harmful compounds that are routinely found aboard spacecraft as components of fuels or on-board experiments and (b) a detailed and accurate inventory of inorganic and organic species on Solar System bodies is one of the keystones to understanding the formation and evolution of our Solar System. Further, such an inventory will provide the best evidence of potential extant/extinct life elsewhere in the Solar System. Even if we learn that life in our Solar System is restricted to Earth, the discovery and characterization of pre-biotic chemistry elsewhere will help elucidate the origin of life and its evolution on Earth.

Human space flight and robotic missions undertaken by the National Aeronautics and Space Administration (NASA) and the European Space Agency (ESA) include particular requirements for analytical instruments. Instruments are needed for on-board air quality screening or monitoring for Space Shuttle, the International Space Station (ISS), and the family of Project Constellation Spacecraft that are being developed to replace the Shuttle fleet and eventually return men to the moon and possibly one day to Mars. In contrast, robotic space missions are designed to perform *in situ* or remote investigations of the geologic history, chemical nature and biological potential of planetary bodies such as Mars, Europa, Titan and other Solar System bodies.

Ion mobility spectrometers exhibit characteristics that are required of any instrument considered for manned or unmanned space flight missions. For example, complete analyzers are small, low mass, rugged, and mechanically simple with low power consumption; nonetheless, the instruments retain a high level of analytical capability providing knowledge of quantitative and qualitative composition of samples under investigation. Both the principles and practice of ion mobility spectrometry (IMS) have matured during the past 20 years with the support of NASA, and technology based on IMS has been recognized as an important tool for pursuing the exploration of space. Refinements of ion mobility spectrometers have occurred through various technology development programs at NASA including the Astrobiology Science and Technology Instrument Development and Mission Concept Studies program (ASTID), the Planetary Instrument Definition and Development program (PIDDP) and the Mars Instrument Development Project (MIDP). Moreover, ion mobility spectrometers have been developed and flown on the Space Shuttle to measure hydrazine vapors in the air-lock and aboard the International Space Station for the determination of volatile organic compounds in the air of the spacecraft.

A number of articles reviewing the use of gas chromatography [1] and mass spectrometry (MS) [2] in space applications provide some reference to IMS. However, a detailed discussion of the principles of IMS and demonstrated or planned uses for space exploration is warranted given the state of interest and maturity that IMS has attained. The purpose of this review is to highlight the potential uses and benefits of IMS in both manned and robotic exploration of the Solar System.

2. Review of ion mobility spectrometry

2.1. Principles of operation

Detailed descriptions of IMS including discussions of function, performance and applications can be found in recent reviews [3,4] and a recent text [5]. However, a brief overview of IMS is provided here for completeness. In IMS, substances are characterized as gas phase ions for drift velocity or mobility in a weak electric field (typically less than 200 V cm^{-1} at atmospheric pressure) often at ambient pressure in a purified air atmosphere. Ions as a swarm develop a speed, or drift velocity, v (cm s^{-1}), in an electric field, which is directly proportional to the electric field, E (V cm^{-1}) per Eq. (1):

$$v = KE \tag{1}$$

where K is the ion mobility coefficient. The mobility coefficient, which can be seen as drift velocity normalized to field, is characteristic of the ion, and is the basis of identification using IMS analyzers (see Fig. 1).

Mobility coefficients are dependent on a number of parameters including the charge and mass of the ion. Coefficients are affected by bulk properties of the supporting gas atmosphere such as the pressure, temperature, and mass. Further, the nature of the interaction between ions and the neutral gas species influ-

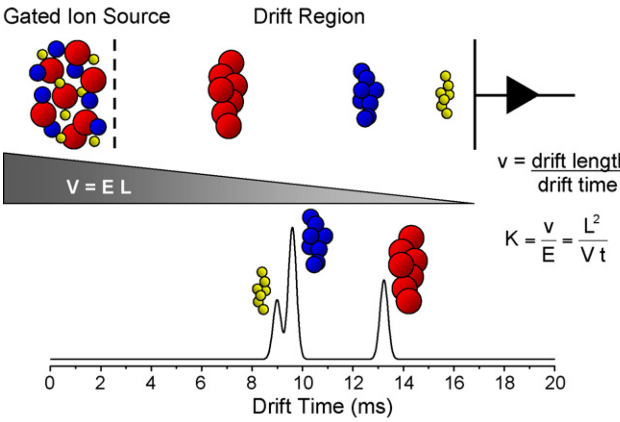

Fig. 1. Schematic showing the basic operating principles of IMS.

ence drift velocities through effects due to size and structure of both the ion and neutrals, as well as the polarizability of the neutral particles. A detailed theoretical description of the ion mobility constant can be derived from kinetic theory [5,6] yielding the following analytical form of the ion mobility coefficient

$$K = \frac{3q}{16N}\left(\frac{2\pi}{\mu kT}\right)^{1/2}\frac{1+\alpha}{\Omega} \tag{2}$$

where N is the number density of the drift gas atoms/molecules, q is the charge on the ion, μ is the reduced mass of the ion and drift gas atom/molecule, k is the Boltzmann constant, T is the effective temperature of the ion, Ω is the collision cross section, and α is a correction factor included to account for deviations from the otherwise first order approximation. The cross-section contains all the information regarding the ion-neutral interaction and is often written in terms of a dimensionless collision integral for diffusion, $\Omega^{(1,1)*}$, normalized to unity for rigid spheres with a summed radii of r_m:

$$\Omega = \pi r_\mathrm{m}^2 \Omega^{(1,1)*} \tag{3}$$

where r_m is the minimum in the ion-neutral interaction potential curve. Given the interaction potential, $\Omega^{(1,1)*}$ can be calculated as a function of temperature through three successive integrations over collision trajectories, impact parameters and energy. The collision cross section is responsible for the often referenced feature of IMS to characterize on the basis of "size and shape." The cross section dependence provides IMS with another important feature: isomers [7–12] and even enantiomers [H.H. Hill, private communication (2003)] can be separated.

A clarification of ion behavior and mobility can be made with Eq. (2) and a test with different ions (mass m) drifting in an identical gas atmosphere (mass M). For low mass ions, the reduced mass, $(1/m + 1/M)^{-1}$, is a fast changing function of ion mass leading to a strong correlation between the mass of the ion and its mobility. Indeed, IMS in the early 1900s was motivated by a desire to determine atomic and molecular masses prior to the wide availability of vacuum systems. The effect of the reduced mass term diminishes ($\mu \rightarrow M$) with increases in ion mass and the mobility becomes dominated by the collision cross section. As such, structural details of the ions become important and the degree of correlation between mass and mobility is reduced. The importance of ion structure is emphasized by the recovery of mass-mobility correlations among structurally similar compounds [13–16]. A particularly effective illustration of the dependence of mobility on structure is in amines where mobilities increase in the following sequence of structural categories: linear, branched, primary, secondary, tertiary, aliphatic compounds, and aromatic compounds [4].

In practice, the mobility coefficient is traditionally determined in time-of-flight measurements, where an ion swarm travels a fixed length, L, through a uniform electric field, E, at constant temperature and pressure, P. The mobility coefficient is obtained from the drift time:

$$K = \frac{L^2}{Vt} \tag{4}$$

where V is the potential drop across the drift region and t is the drift time. Since mobility coefficients are sensitive to temperature and pressure, values are routinely normalized to give reduced mobility coefficients (K_0) at standard atmospheric pressure and temperature per Eq. (5).

$$K_0 = \left(\frac{273\ \mathrm{K}}{\mathrm{T}}\right)\left(\frac{P}{760\ \mathrm{Torr}}\right)\frac{L^2}{Vt}. \tag{5}$$

Mobility and reduced mobility coefficients are both expressed in units of $\mathrm{cm^2\,V^{-1}\,s^{-1}}$.

2.2. Instrument basics

The essential component of an IMS instrument is the drift tube and the design of the drift tube ultimately defines the character of the electric field, the resolution of the instrument and other elements of performance such as memory effects. Drift tubes may be considered as two distinct regions: (1) the reaction region, including the ion source, where ionization and other ion chemistry take place and (2) the drift region where ion separation and detection occurs. This distinction is instructional only since the drift tube has traditionally been a single, strongly integrated device with regions sharing common gas atmosphere and electrical fields. The two regions are separated by an ion gate or shutter which is used to inject ions into the drift region in a temporally well-defined pulse. The ion pulse leads to an ion swarm which moves through the drift region with drift velocities characteristic of the component ions. At the end of the drift region, ions collide with a detector, which, in the simplest design, is a Faraday plate. The amplified ion current versus time, referenced to the ion shutter pulse, forms an ion mobility spectrum.

A conventional design for drift tubes is based upon stacks of ring-shaped electrodes held at fixed intervals with insulating spacers. A uniform electric field is created within the tube by applying potentials to each electrode in constant voltage drops. This can easily be accomplished with a high voltage power supply and voltage divider composed of precision resistors. In order to maintain the low field conditions required to assure the validity of Eq. (1), the ratio of electric field to neutral number density is generally kept below ~2 Td (i.e., $2 \times 10^{-17}\ \mathrm{V\,cm^2}$ or $E \sim 200\ \mathrm{V\,cm^{-1}}$ at 760 Torr).

2.3. Ion sources

Of all the components of an IMS instrument, the ion source defines the response, utilization, and possible applications of an IMS analyzer since the measurement of mobility may be regarded as a universal technique. The formation at ambient pressure of ions reflective of a sample has been both a historic strength and complicating feature of IMS technologies. A range of possible applications for IMS exist so long as the method of ion formation is favorably matched with target substance and potentially interfering matrix, if any. Additionally, source performance can be affected by physical parameters. An ion source that will operate at atmospheric pressure on a manned spacecraft will not necessarily function well at the reduced pressures on the surface of Mars. These considerations, along with the usual restrictions on mass, volume and power, must be incorporated into the evaluation of an ion source for space-based IMS instruments. Therefore, a somewhat detailed review of ionization techniques used in conjunction with IMS is provided below.

Gas phase chemical reactions at ambient pressure based on tritium, americium or, more commonly, a ^{63}Ni foil have been the traditional and most widely employed method of ionization in IMS applications [3,17,18]. A metal foil of ^{63}Ni spontaneously emits β particles, or high-energy electrons, with energies up to 67 keV [18]. Collisions between β particles and molecules such as N_2, H_2O, and O_2 yield positive (N_2^+, H_2O^+) and negative (O_2^-) ions which can be employed to ionize substances introduced into the reaction region of the drift tube. In the case of positive ions in air or nitrogen with moisture above 50 ppb, primary ions are rapidly converted to thermalized ions of hydrated protons [$(H_2O)_nH^+$], termed reactant ions. Collisions of reactant ions with a substance (M) can lead, through coulombic associations, to adduct ions, $MH^+(H_2O)_n$, which are stabilized through a third body collision and loss of water forming an ion from the substance, $MH^+(H_2O)_{n-1}$, also known as a product ion. This reaction has been called a *proton transfer reaction* though a better description would *be proton association* or *displacement reaction* since the term proton transfer is used in mass spectrometry with unclustered ions. Ionization chemistry in negative polarity is somewhat more complex than that for positive polarity and begins with an association to an intermediate $MO_2^-(H_2O)_n$ which can then proceed through charge exchange, hydride abstraction, fragmentation or adduct stabilization [19]. All reactions based upon collisions with reactant ions are governed by collision kinetics and the availability of reactant ions. Since the rate of product ion formation is faster at analyte concentrations of 10 to 1000 ppb than the formation of reactant ions, the supply of reactant ions can be seen as a quantitatively fixed reservoir which establishes an upper level and restricted range of response.

The benefits of ^{63}Ni metal foil ion sources are reliability [18,20], stability, simplicity, and low demand on utilities without any external power supply. Such features make ^{63}Ni foils attractive sources in chemical instruments for space-based applications. However, ^{63}Ni sources have disadvantages or limitations including the oxidation of the metal foil in air atmospheres at elevated temperatures and certain pragmatic constraints associated with transporting and handling ^{63}Ni-based analyzers with oversight by radiation authorities, and disposing of spent source material through procedures of the Nuclear Regulatory Commission (NRC). An implicit requirement of such a source is the need to deliver sample as a gas to the reaction region; hence, vapor pressures for analytes must be relatively high at the drift tube temperatures. This is well-suited for substances that are amenable to separations by gas chromatography (GC) where the column effluent is passed directly into the reaction region of the drift tube [21,22]. Analytes that are less electronegative than oxygen and those that have proton affinities lower than water are not suitable for ionization by the chemical reactions associated with ^{63}Ni metal foil ion sources and alternative methods for ion formation at ambient pressure have been developed for IMS analyzers.

Alternative ionization methods include photodischarge lamps [23,24], lasers [25], corona discharges (CD) [26–28], matrix assisted laser desorption ionization (MALDI) [29], and electrospray ion sources (ESI) [15,16,30–34]. Photoionization is accomplished with short wavelength ultraviolet (UV) light and is distinguished by relatively high response to those chemicals with low ionization potentials such as aromatic hydrocarbons and other molecules with delocalized π-electrons. The source is not limited by reactant ion density and has a comparatively large linear dynamic range. The limitations of photoionization with gas discharge lamps include finite and disappointingly brief operating lifetimes and comparatively high power requirements; these are both acute requirements for instrumentation intended for application with spacecraft and space exploration.

Corona discharges (CD) have been employed as ion sources with ion mobility spectrometers [17,26–28] bringing advantages of reaction chemistry found with ^{63}Ni foils together with high ion densities and some subtle variations in response. Bordsdorf et al. [17] reported that CD ion sources permitted improved response to non-polar hydrocarbons in positive mode over a ^{63}Ni foil or a photodischarge lamp. Such discharges are impeded by poorly described reaction pathways [17] some of which are known to be associated with ventilation of the reaction volume. Although positive ion chemistries are similar to that seen with radioactive foils [28], a serious complication arises when applying negative mode CD ionization in ambient air where nitrogen oxide ions and ozone suppress response to all chemicals with electron affinities below the high values of these reactant ions [28,35]. A pulsed corona discharge in a curtain gas of pure, non-electron attaching species such as nitrogen or helium, to separate the discharge region from the ionization region, was demonstrated and is an attractive design solution [35,36]. A simpler solution than these is to control gas flows where ventilation of the source can lead to exclusion of reactive neutrals from the source chemistry [37]. In this approach, response is restored to that seen with radioactive foils. As with radioactive foils, a pre-requisite for CD and photodischarge lamps is sufficient volatility of sample for delivery to the reaction region as a gas [17,23–25,28].

Non-volatile substances, when converted to gas phase ions, are suitable for evaluation by IMS as demonstrated with biomolecules and MALDI [29,38,39]. In MALDI, reactions between analyte and a source of charge are promoted through a laser-induced solid-to-gas phase transformation which is typified as a soft sampling method that produces singly charged ionic species. However, MALDI has several disadvantages. Dried, often acidic, organic matrices have to be prepared for the ionization process and this is a difficult task for an autonomous, robotic experiment.

Electrospray ionization (ESI) sources have been successfully adapted for IMS determinations of non-volatile or biological macromolecules [7,15,16,29,31–34,40–50]. Large organic or biological molecules, when heated, often decompose rather than vaporize, frustrating any intent to form molecular ions [42]; in constrast, intact gaseous ions are formed in ESI directly

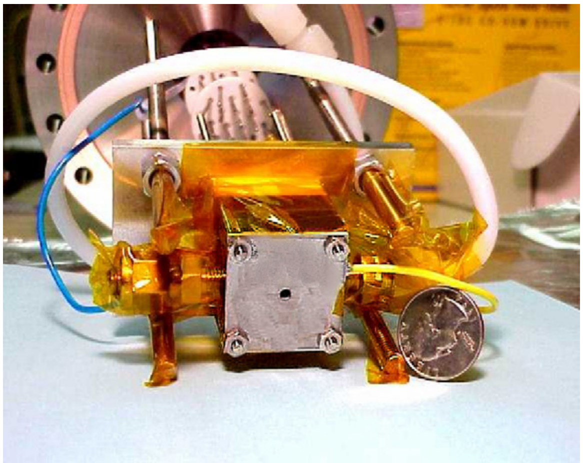

Fig. 2. Photograph of the Hollow Cathode Ionizer developed at JPL for atmospheric ionization on Mars.

from a solution preserving the composition and structure of the analyte. This distinctive advantage of ESI has allowed the characterization of shapes and sizes of various biomolecules from monomeric molecules to macro size proteins. Several groups have reported mobility and conformational studies of macro ions including clusters (oligomers) [43–45], peptides [49,50] and proteins [33,40,46,47] using ESI. In addition, ESI-IMS studies of amino acids [7,15], carboxylic acids [16], dinucleotides [48], and other organic molecules [51,52] have been reported.

Researchers at JPL have recently developed a hollow cathode ionizer (HCI) [53,54], which is compatible with IMS and was designed to function specifically under ambient Martian atmospheric conditions (Fig. 2). The HCI consists of a cylindrical hollow cathode and anode which sustain a discharge plasma with a fall voltage of ∼400 V at Martian surface pressures (∼5 Torr). The ionizer produces a stream of $(H_2O)_nH^+$ ions from gas phase H_2O molecules that are introduced into the discharge region from a reservoir. These ions react with volatile species in the reaction region via proton based reactions. All of the major constituents of the Martian atmosphere have proton affinities lower than that for H_2O [55]. Therefore, the HCI is able to ionize species of interest without ionizing the constituents of the Martian atmosphere. The abundances and proton affinities of the major Martian atmospheric constituents and a few potential organic molecules are shown in Table 1. Comparison of these values can illustrate the utility of this ion source in the intended application.

The ion sources described above illustrate that no universal ion source for IMS analyzers exists and that a preliminary understanding of the sample and matrix must be combined with a configuration suitable for the application. The selectivity intrinsic in this feature of IMS analyzers has been both a strength in flexibility and adaptability and simultaneously, a complication necessitating a level of preparation for a prospective user.

2.4. Ion gates

The ion gate, or ion shutter, is one of the most defining components of an IMS drift tube establishing performance in peak shape and width in mobility spectra. The ion gate blocks ions from flowing into the drift tube and then admits them into the drift region in a brief (10 to 300 μs) pulse which is initiated by a user or which automatically samples the reaction region at frequencies of 1 to 10 Hz. The ideal gate will maximize the number of ions admitted into the drift region during the injection time while perfectly excluding leakage of ions through the gate at all other times. The quality of the gate in terms of the former will affect the overall sensitivity of the instrument while the latter will set a limit on the achievable resolution. The two most common ion shutters or ion gate designs used in IMS instruments are the Bradbury-Nielsen shutter grid and the Tyndall gate [39].

Table 1
Proton affinities (PA) and abundances of common components in Martian atmosphere and PAs of some common organic molecules

Compound	Abundance (%)	PA ($kcal\,mol^{-1}$)
CO_2	95.46	130.9
N_2	2.7	118.2
Ar	1.6	88.6
O_2	0.17	100.9
CO	0.07	141.9
H_2O	**0.03**	**166.5**
HCN	Unknown	171.4
CH_2O_2	Unknown	177.3
C_6H_6	Unknown	181.9
NH_3	Unknown	204.1

The Tyndall gate operates by interrupting the uniform, linear potential between the ionization and drift regions of the spectrometers [56]. This is accomplished with two adjacent, yet electrically isolated ring electrodes, coaxially located with the ionization and drift regions, with thin wires or wire mesh suspended across the open area of the rings. By raising the potential on the first electrode or grid, with respect to the potential in the ion/drift tube, ions are prevented from entering the drift region and flow with the gradient between grids, and are eventually removed from the measurement by collision on a wire. Ions can be passed into the drift region when the grid is restored to the potential associated with the voltage gradient in the spectrometer. Meanwhile, the second grid is set to the potential associated with its position within the drift cell.

The Bradbury-Nielsen shutter functions much like the Tyndall design but consists of a plane of repeating parallel wires with potentials alternating above and below an average potential [57]. In IMS applications, this gate is arranged so that the plane of the wires is perpendicular to the ion flow with an average grid potential chosen to coincide with the potential associated with its position within the ion/drift tube arrangement, V_0. When potentials of $V_0 \pm \Delta V$ are alternately applied to adjacent wires of the shutter, ions approaching the wires are diverted by the electric field created by the alternating potentials on the interdigitated wires. The shutter is opened by setting the potentials on all wires of the grid to V_0.

Of these two designs, the Bradbury-Nielsen grid is generally considered the best in performance though more complicated to construct. In order to optimize performance, the wires in the grid must be kept parallel, closely spaced and thin.

In order to avoid the need for wire meshes and grids when constructing ion gates, Blanchard et al. [58] investigated using field gradient ion barriers (FGIB) or ion wells as the gating mechanism. In this scheme, the ring shaped electrodes of the standard IMS design are used to create a potential well along the radial direction of the flight tube by applying appropriate potentials. Ions are then released by replacing the potentials on the gate electrodes so the well is replaced with a smooth potential gradient. Although attractive in simplicity, ion motion in this injector is dynamic and refinements in the control and design of this approach are needed [58].

2.5. Utilities for analyzer operation

The drift tube is the central element in an IMS measurement and must be provided with certain utilities to form a complete analyzer. As with any chemical instrument, a few parameters must be controlled, often within a range of values, for reliable operation of the analyzer. In a mobility spectrometer, the critical parameters are moisture, temperature and purity of the supporting gas atmosphere; both ion formation and ion behavior in the drift region will be repeatable in a well-engineered instrument. Control of these can be found in any commercial IMS analyzer in levels of sophistication. Although analytical IMS is now over 30 years old, no standard conditions for these exist, perhaps due to suitable performance over a wide range of these parameters.

The gas atmosphere in a drift tube is usually exchanged continuously with a flow of gas (the drift gas) from 100 to 300 ml min^{-1} of air or nitrogen pre-treated over molecular sieves to remove impurities and provide a level of moisture governed by the amount, history, and age of the adsorbant. In commercial instruments, the adsorbants are found in cartridges that are replaceable, with lifetimes of months in a routine service schedule. Purity of the gas atmosphere inside the drift region is essential and any impurities or diffusion of sample vapors into the drift region will render response of an analyzer confusing or irreproducible or both. This can be prevented through careful control of flows inside the analyzer and two arrangements exist. Flows of purified gas can be introduced at both ends of the drift tube with sample introduced into the flow entering the ion source and reaction region. Purified gas, entering at the detector (the drift gas), and the gas flow from the reaction region are removed on the source side of the ion shutter. An alternative and robust design is where purified gas is introduced only at the detector and pushed through the entire drift tube, including the reaction region, and is vented to a trap or ambient air. Sample introduced in the reaction region, is swept with the drift gas flow through the ion source to vent. This design was intended as a detector for capillary gas chromatography [21] where high speed clearance from the drift tube was desired.

Heat for the analyzer is another utility that factors in engineering constraints and analytical response and is governed by the thermal mass of the analyzer and the operating temperature. Temperatures need to be above that where condensation of sample occurs. For volatile organic compounds below carbon numbers often to fifteen, temperatures of 150 °C are suitable and lower temperature may be used with degraded clearance of sample from the analyzer through surface adsorption. High temperatures have a direct though often unintended effect on susceptibility of a measurement to variations in moisture in the gas atmosphere. Increases in temperature tend to decluster ions of adducts of water or other polar or polarizable molecules found in the drift gas. Thus, small variations in moisture that might change ion mobility coefficients slightly, are minimized or eliminated. However, high temperature in a drift tube is costly in power and has secondary effects with ion fragmentation and unwanted reactivity.

At temperatures above 125 °C, product ions for some alcohols may undergo dehydration reactions and product ions for all alcohols are totally decomposed to fragment ions at 175 °C. Similar reactions occur for other organic compounds though temperatures of decomposition are characteristic of chemical families [59,60]. Thus, control of temperature is a compromise of performance with a broad optimum in analytical response between temperatures too high where ions decompose and too low where sample vapors condense. Heat can be provided to a drift tube with a resistive heater placed in an insulating shell surrounding the drift tube.

3. IMS in manned space flight

The only sustained application of IMS in space exploration to date has been air quality monitoring aboard the Space Shuttle and the International Space Station. The environments on manned spacecraft are inherently susceptible to contamination by harmful compounds; a problem that is exacerbated by the semi-closed nature of these environments. Therefore, all spacecraft employ systems which clean and re-circulate the air in conjunction with air quality monitoring to ensure astronaut safety. Among the sources of contamination that may pollute spacecraft environments are human metabolites (e.g., CO, CO_2, NH_3, and H_2S), offgassing from materials on board, thermal degradation by products, and containment breaches of payload and utility chemicals (fuels, coolants, on-board experiments). The importance of environmental monitoring on manned spacecraft is emphasized by studies of archived Space Shuttle air samples which have shown the presence of over sixty volatile organic compounds (VOCs) [61].

The dangers and risks associated with environmental contamination are substantially increased with the duration of a mission. Not only does the total amount of contaminant released into the environment increase with time, but so does the probability of incidents or mishaps. Since astronauts are continuously exposed to this semi-closed environment over the life of a mission, the problem is compounding in effects. This is reflected in the NASA standards, termed Spacecraft Maximum Allowable Concentrations (SMACs) of contaminants, which give decreasing exposure limits with increasing mission duration. Therefore, the need for sensitive and reliable monitoring systems are essential on extend flights so that crew members can be alerted to dangers and respond before any adverse effects on health and performance are suffered. As NASA follows its “vision for space exploration” toward manned missions to the moon by 2020 and eventually to

Table 2
Compounds targeted for detection and quantification by the VOA on the ISS [2,121] along with the expected concentration ranges of each

Compound	Concentration ($mg\,m^{-3}$)	Compound	Concentration ($mg\,m^{-3}$)
Methanol	0.1–1.5	Ethanol	0.2–3.5
1-Butanol	0.3–4.0	2-Methyl-2-propanol	0.1–2.0
Ethanal	0.1–1.2	Benzene	0.1–1.5
m,*p*-Xylene	0.4–5.0	Chlorodifluoromethane	0.3–5.0
o-Xylene	0.2–2.7	1,1,1-Trichloroethane	0.1–1.6
Toluene	0.2–2.6	1,1,2-Trichloro-1,2,2-trifluoroethane	0.2–2.5
Dichloromethane	0.1–1.2	Hexane	0.2–2.4
Acetone	0.1–1.2	Pentane	1.0–12
2-Butanone	0.1–1.5	2-Methyl-1,3-butadiene	0.4–5.0
Ethyl acetate	0.2–2.4	Trifluorobromomethane	0.1–2.2
2-Propanol	0.2–3.2		

Mars, the demands on air quality control and monitoring can be expected to increase.

3.1. The International Space Station Volatile Organic Analyzer (VOA)

Development of the Volatile Organic Analyzer (VOA) dates to the planning of Space Station Freedom (SSF; the American predecessor to the International Space Station). The vision of a space station housing a large number of experiments, which would require the long term storage of chemical wastes with an overall projected life of 30 years, spurred the development of the VOA and related technologies. Although the SSF project was eventually cancelled, development of the VOA as a risk mitigation experiment on the Space Shuttle continued to a full-time presence on the ISS. The role of the VOA is to monitor the cabin air for contaminants of concern and to track the effectiveness of decontamination efforts. A list of compounds that the VOA was developed to detect aboard the ISS is given in Table 2.

Originally, the development of a VOA was based on gas chromatography–mass spectrometry (GC–MS) in order to capitalize on the proven analytical capabilities, wide acceptance and the heritage of GC–MS in space flight, e.g., the Viking landers. A modified commercial version of the Viking GC–MS was at one point the prime candidate for a VOA development. However, the growing refinement of IMS hardware for on-site applications such as battlefields and airport security screening points led to a reconsideration of IMS and eventually a decision to develop GC-IMS as the VOA. The primary advantage of GC-IMS over GC–MS is that IMS operates at ambient atmosphere without vacuum pumps. Therefore, a considerable advantage in size, mass, power, cost and reliability was achieved by eliminating a vacuum system. The development of the VOA was an example of technology development initiated and sustained by NASA. These efforts led to the first construction of a GC-IMS with the capabilities of a benchtop gas chromatograph and a heated drift tube in a fully integrated instrument. Though this pioneering endeavor was contemporary with the development of a hand-held GC-IMS [62] derived from military analyzers, the requirements for operation and measurements with the VOA were unprecedented.

A schematic of the VOA system in Fig. 3 shows the instrument consisting of two independent GC-IMS analyzers with a common timing cycle and shared sampling inlet. Ambient air, containing VOCs if any, is drawn into the inlet over a period and diverted into pre-concentrators which are multi-sorbent bed traps. Volatile organic compounds retained by the traps are released from the traps when heated and are passed to the GC columns as a concentrated sample. Different columns are used in each of the two analyzers providing a dimension of selectivity through retention of analytes on two stationary phases. Effluent is introduced into the ion source of the drift tube where mobility spectra are generated throughout the temperature ramp for the columns. Further description of the GC-end of the instrument is beyond the scope of this review; however, a detailed description is given by Limero et al. [61].

The ion source for the VOA is the conventional radioactive foil of ^{63}Ni. Both positive and negative ions are generated simultaneously; however, only ions of one polarity can be determined at a time in a single drift tube with the time-of-flight configuration. Thus, each drift tube could be operated in either positive or negative polarity for each of the stationary phases making the VOA capable of large flow of analytical information. In practice, the calculated mobility values (or $1/K_0$) and retention time for a chromatographic peak allows reliable identification of constituents in the air sample. Intensities of the product ion peaks in the IMS spectra permit quantitative determinations with precision considered high even for a laboratory grade analytical instrument. Fig. 4 shows the results of a GC-IMS analysis taken as part of a prototype VOA risk mitigation experiment (VOA-RME) flown on the Space Shuttle mission STS-89. Here, the

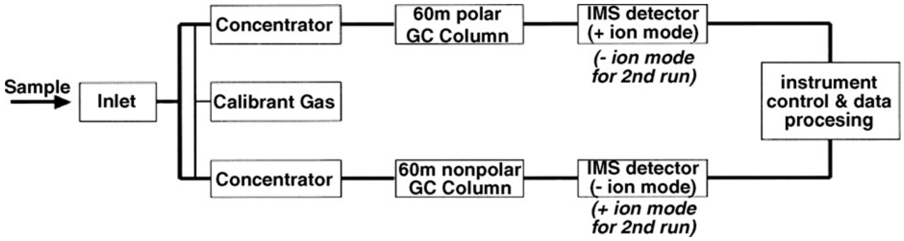

Fig. 3. Schematic diagram of the GC–IMS based VOA developed for monitoring VOCs on the ISS (Reprinted by permission of Elsevier from Mass Spectrometry in the U.S. Space Program, by Peter T. Palmer and Thomas F. Limero, Journal of the American Society for Mass Spectrometry, 12, 656–675, Copyright 2001, by the American Society for Mass Spectrometry).

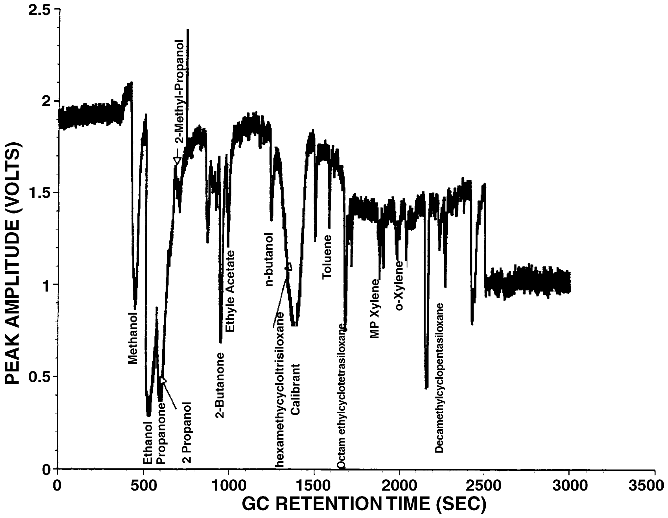

Fig. 4. Results of a GC-IMS analysis taken as part of a prototype risk mitigation experiment on board Space Shuttle mission STS-89. Here, the reactant ion peak is plotted as a function of GC retention time. (Reprinted by permission of Elsevier from Mass Spectrometry in the U.S. Space Program, by Peter T. Palmer and Thomas F. Limero, Journal of the American Society for Mass Spectrometry, 12, 656–675, Copyright 2001, by the American Society for Mass Spectrometry).

reactant ion peak is plotted as a function of GC retention time. The chromatogram illustrates the chromatographic performance and response to a range of chemical classes.

Metal oxide or Metox canisters are reusable scrubbers used to clean the recirculated air inhaled by astronauts during "space walks" or "extravehicular activities" (EVAs). In these canisters, CO_2 and trace contaminants are removed with a combination of metal oxide and charcoal filters. Canisters are regenerated by passing a flow of ISS cabin air through the canister when heated. The contaminants and the rate released during this process are equivalent to that generated by an additional crew member and can be easily accommodated by the Environmental Control and Life Support System (ECLSS) [63]. In Table 3, results are shown from the real time analyses of the air quality in the ISS using VOA during the regeneration of a Metox canister in April 2002. Also shown are GC–MS results of archival air samples taken during the regeneration and returned to Earth for analysis in grab sample containers (GSCs). The ground based analysis affirmed the performance and utility of the VOA as a real time air contaminant monitor and the implications of speed and convenience of the VOA are understood in contrast to the delays and costs of returning samples to Earth for analyses.

Table 3
Comparison of grab sample container (GSC) analysis and real-time VOA data from the April 2002 Metox canister regeneration on board the ISS [63]

Target compound	VOA (mg m^{-3})	GSC (mg m^{-3})
Methanol	0.23	0.29
2-Propanol	0.13	0.10
2-Methyl-2-propanol	0.05	Trace
Ethanal	0.06	0.16
Ethanol	~2.3	2.50
1-Butanol	0.11	0.09
m,*p*-Xylene	Trace	Trace
o-Xylene	0.12	0.23
Toluene	Trace	Trace
Isoprene	Trace	0.00
2-Butanone	Trace	Trace
Ethyl ethanoate	Trace	Trace
Propanone	0.09	0.20
Benzene	0.00	Trace
Dichloromethane	0.10	0.20

Table entries of "Trace" indicate that the compound was identifiable but not quantifiable by the method of detection.

3.2. Hydrazine detection

Hydrazine (N_2H_4), monomethylhydrazine (N_2H_3–CH_3), and unsymmetrical dimethylhdrazine (N_2H_2–CH_3–CH_3), often abbreviated as HZ, MMZ and UDMH, respectively, are common components as fuels for spacecraft, rockets and satellites. Hydrazines are hypergolic fuels (i.e., they combust upon contact with an oxidant without an external ignition source), are highly toxic and are known or suspected carcinogens. The American Conference on Governmental Industrial Hygienists has set the threshold limit values for these compounds at 10 parts-per-billion (ppb) while NASA has established 2 ppb as its maximum allowable concentration in spacecraft. A particular concern with Shuttle missions is the accidental introduction of hydrazines into the atmosphere of the Shuttle following EVAs. In an EVA, hydrazines might be absorbed on spacesuits through malfunction of Shuttle thrusters, also powered with hydrazines, and the contamination would be volatilized upon re-entry into the Shuttle environment. Thus, the valuable role hydrazines have in spacecraft flight and the dangers of human contact with hydrazines mean that human exposure should be prevented through monitoring of the on-board spacecraft environment (and perhaps on-ground during spacecraft servicing) with highly selective, sensitive and fast analyzers.

A particular challenge in developing an IMS analyzer for hydrazines was the resolution of ammonia, hydrazine and MMH in a hand-held military grade instrument operated at ambient temperature. Laboratory studies at New Mexico State University demonstrated that when the supporting atmosphere was modified with a 1 ppm vapor level of a ketone, 5-nonanone, the ion clusters of each of these could be reliably determined with low ppb detection limits [64]. A military grade IMS analyzer termed an Airborne Vapor Monitor (AVM) for commercial markets from Graseby Ionics Ltd. (Watford, Herts, U.K.) was modified with 5-nonanone in the internal gas supply and was flown in April 1991 on the Space Shuttle Atlantis mission STS-37. This exercise demonstrated the feasibility of operating IMS technology in space and details of the instrumentation are summarized in Table 4. The analyzer was calibrated for HZ and MMZ at the Kennedy Space Center both before and after the Shuttle mission spanning nearly 6 months including the launch, use on flight, landing and prolonged storage after landing before final calibration. Results of these calibrations are summarized in Table 5 illustrating from similarity of the pre- and post-flight calibrations the inherent rugged and stable character of the AVM. There were clearly no obvious failures due to the extremes experienced during the mission, including launch.

Table 4
Instrumentation details of the Graseby Ionics, Ltd. AVM which flew on the Space Shuttle Atlantis in April 1991 (STS-37) [64]

Experimental parameter	Value
Methylsilicone inlet membrane	75–150 μm thick
Ionization source	10 mCi ^{63}Ni
Drift length	12 mm
Electric field strength	244 V cm^{-1}
Drift gas flow rate	200 mL min^{-1}
Inlet sample flow rate	0.5 L min^{-1}
Shutter pulse width	180 μs
Shutter repetition rate	40 Hz
Drift tube temperature	Ambient

Table 5
Hydrazine calibration results of the Graseby AVM which flew on the Space Shuttle Atlantis in April 1991 (STS-37) [64]

Concentration (ppb)		Peak Height (mV)		Difference in percent relative
		Preflight	Postflight	
HZ	0	0	0	0
	40	6.3	4.6	−27
	96	14.8	13.7	−7.4
	296	33.3	39.2	17
	601	61.5	60.8	−1.1
				Average 13.1
MMH	0	0	0	0
	9	26	18	−31
	42	63	64	1.6
	94	118	120	1.7
	304	438	440	0.46
	617	805	772	−4.1
				Average 7.8

Though successful, this hydrazine based analyzer was limited by the size and shape of the AVM making use inside the air lock uncomfortable and unwieldy. Clearly a smaller package with similar performance would have been an attractive detector for hydrazines. A second limitation of the AVM was a subtle engineering compromise. The device used to deliver vapor of 5-nonanone to the drift gas was based upon a permeation tube originally developed for another reagent for military applications. This design and the vapor pressure of 5-nonanone caused the release of poorly controlled and excessive levels of ketone vapor into the analyzer, necessitating tens of minutes for stabilization after power on and a frequent maintenance schedule. A more sophisticated vapor delivery system would have solved both of these issues in a single iteration but was unavailable in the early 1990s. The story of ion separation of hydrazines by mobility in ketone rich atmospheres was recently clarified and completed with IMS/MS studies [65].

4. IMS in robotic space exploration

While no IMS has yet flown on an *in situ* robotic mission, there are mission opportunities where IMS may eventually be an integral part of the analytical payload. Such potential mission opportunities fall under the following mission categories. Flagship missions are large (cost cap of >$1 billion) directed missions that are sent to targets specifically chosen for their high scientific value as identified by NRC Decadal Surveys. Other potential mission opportunities are in the form of NASA Principal Investigator (PI) led peer-reviewed selections in the Mars Scout program (cost cap of <$500 million), Discovery program (cost cap of <$500 million) and New Frontiers program (cost cap of <$800 million). While the goals of these missions will, of course, be dependent on the destination, a number of objectives are common to many of the likely targets. These goals include understanding the chemical environment where the probe is exploring and to determine the past and present biological potential of these bodies. The determination of biological potential can include the direct search for biological molecules or furthering our knowledge of organic chemistry throughout the Solar System, both of which will help develop our understanding of the pre-biotic Earth.

In support of the search for life or the precursors to life throughout the Solar System, we offer the following arguments. On Earth, life emerged in or a relatively short period of time, early in its history [66,67]. Therefore, conditions suitable to the origin of life may only need to be present for a short period for pre-biotic chemistry or even life to develop. Further, the resilience of extant life on Earth indicates that life is capable of existing in remarkable array of varied environments. On Earth, life has been found to occupy virtually every environment where food and energy exist including so called ‘extreme’ environments where conditions would seem unsuitable for life. For example, life is now known to exist at great depths within the ocean near hydrothermal vents where pressures and temperatures were once considered too extreme for life [68]. A further example is in the dry valleys of Antarctica where extreme temperatures and high UV flux, at first glance, seem unfavorable to life [69]. However, various microorganisms, including lichens, algae and fungi, have evolved to live within porous rocks where they are protected from the UV and remain dormant except for short periods during the summer. Finally, one can point to the Earth’s subsurface biosphere (at depths >1 km) as an extreme environment where methanogenic bacteria are known to exist in a wide variety of locations [70–75].

4.1. Potential destinations for future in situ space missions

Here we discuss several potential destinations for robotic space missions which would benefit from having IMS as part of the payload. Given that IMS operates at elevated pressures, IMS naturally lends itself to Solar System bodies which retain an appreciable atmosphere (i.e., Mars, Titan, etc.). However, this does not preclude consideration of IMS instruments on scientific payloads to bodies with minimal, tenuous or no atmosphere (i.e., comets, Europa). In these cases, a sealed, pressurized drift cell would be a design requirement. In contemplating the utility of IMS in these situations, a careful cost-benefit analysis is needed to balance the benefits of IMS described here with the requirement of carrying a fixed amount of consumable drift gas. Mars, Europa and Titan are arguably the three most interesting solar system bodies from an astrobiological perspective. Given the application of IMS to astrobiological investigations for evidence of life in the form of organic compounds, these bodies have been singled out for individual attention.

4.1.1. Mars

There is direct physical evidence in the form of geomorphological, mineralogical and surface elemental abundances that at one time there were large amounts of liquid water on the surface of Mars. Images taken by orbiting spacecraft such at Mars Odyssey, the Mars Global Surveyor and the Mars Reconnaissance Orbiter, suggest that this water was present on the surface in sufficient quantities and on sufficient time scales to create river deltas, river beds with tributaries, lakes, and seas [76–80]. It has been suggested that at the time liquid water was present on the surface [81], conditions on Mars were similar to the conditions on the early Earth [82] (i.e., when life first appeared) and hence conducive to the origin of life. It is therefore possible that either life or the pre-cursor, pre-biotic chemistry that lead to life on Earth may have existed on Mars. If so, there may still be chemical evidence surviving within sedimentary rock formations on the surface. If life did arise on Mars, it is possible that it could still exist in protected niches such as sulfur-rich sub-surface areas for chemoautotrophic communities, rocks for endolithic communities, permafrost regions, hydrothermal vents, soil, or evaporate crystals [83].

The search for organic molecules as traces of extinct or extant life is an important scientific objective of future missions to Mars. In 1976, the two Viking landers performed the only *in situ* search for organics on Mars to date. However, the Viking GC–MS failed to detect organic molecules on the Martian surface. The two Viking landers took regolith samples into a pyrolysis oven where they were heated to 200, 350 and 500 °C for 30 s, respectively. The released gas phase materials were introduced into a GC–MS for detection and identification of volatilized species. There was no detectable organic material in the regolith analyzed at either landing site [84,85] except for the detection of the solvent used to clean the spacecraft. This result is not consistent with the estimated $\sim 2 \times 10^5$ kg of reduced carbon expected to be deposited on Mars each year through meteoric sources and through the accumulation of interplanetary dust particles (IDPs) [86]. Many forms of carbon found in these sources should have easily been detected given the capabilities of the Viking GC–MS [87,88]. This Viking null-result has been attributed to the oxidizing conditions on the surface of Mars which converts organics into carbon dioxide [84,85].

Recently, the Viking experimental results have come under some scrutiny. Benner et al. [89] have hypothesized that benzenecarboxylic acids would be stable in the highly oxidizing environment that Viking characterized. These carboxylic acid-salts would not have been detectable given the Viking GC–MS experimental parameters. In addition, Navaro-Gonzelze [90] has identified organic molecules in Atacoma desert samples using a pyrolysis–GC–MS technique, but needed to raise the temperature of the pyrolysis oven to over 700 °C before detectable quantities of organic material evolved from the samples. Finally, Viking only analyzed unconsolidated surface samples, not the interiors of rock samples. Meteorites have been shown to contain organic material under a protective outer shell while life has evolved to exist within rock interiors found in the Antarctic dry valleys. In aqueous environments evidence of life can be trapped in deposits as the material becomes lithified. Samples representing either of these scenarios have yet to be analyzed on the Martian surface.

For any analyzer (IMS, GC-MS, etc.) to be part of an *in situ* analytical laboratory on a future Mars mission, it must be able to analyze samples taken from rock interiors, or through subsurface drilling [91,92]. The samples can be prepared either through traditional pyrolysis or through liquid extraction and electrospray ionization. Analysis of the organic component of surface and sub-surface material is a priority for the understanding of the chemical nature of the surface. In the case of amino acids, the liquid extraction step would enable them to be analyzed as intact molecules, while they may become fragmented in pyrolysis. On a more cautionary note, the large presence of salts on the Martian surface must be carefully considered as large amounts of solvated ions can interfere with electrospray ionization of analytes.

4.1.2. Europa

Europa has recently generated increased interest in the planetary science community because of the ever increasing evidence for the existence of a liquid ocean buried beneath the water–ice surface. The possibility of an ocean's existence has been strengthened by observational data from the Galileo spacecraft [93–97]. Models of the Europan interior support the notion that liquid water can exist beneath the surface as a result of heating due to tidal interactions within the Jovian system [97]. Such tidal interactions, which are responsible for the spectacular volcanic eruptions of Io, make the existence of hydrothermal vents beneath the encapsulating ice layer a distinct possibility.

It is generally thought that organic molecules were not originally incorporated into any of the Jovian satellites since temperatures in the circum-Jovian nebula were too high during the formation of the parent bodies [98]. Therefore, any organic material that is present must be explained by gravitational capture [99]. While the surface of Europa is relatively young, visual evidence on Callisto, along with the fate of Comet Shoemaker-Levy 9, suggests that Europa should have undergone heavy bombardment by comets and carbonaceous meteorites both of which contain relatively large percentages of organic material. Even though these impacting events cause a loss of the initial organic material through gravitational escape, it is reasonable to assume that a fraction would survive [100,101]. Blank et al. [102] have performed an experiment in which several amino acids (lysine, norvaline, aminobutyric acid, proline, and phenylalanine) were subject to shocks that simulate the entry of cometary material into the Earth's atmosphere (approximate equivalent of 200 kbars and 600 °C). They found that 40–70% of the amino acids survived; some of them paired to form dipeptides, the first step towards amino acid chains. In addition, the accumulation of IDPs, which have the highest proportion of organic material of any sampled objects in the Solar System [103], on Europa should be substantial due to the immense Jovian gravity well's ability to capture them. Although the amounts of exogenic organics delivered at any one time are relatively small, they would accumulate over time due to the increased number of impacts as a result of Jupiter's gravitational influence. This exogenic material can act as the input of organic material to the sub surface ocean. Given the possible existence of an internal energy source, it is within the realm of possibility that life may be present in the subsurface ocean.

If life exists on Europa, evidence of its existence such as organic material should be present in the ice and within the liquid ocean. Currently, there are plans to send an orbiter to Europa to study the surface and subsurface [122]. Because of the intense surface radiation, any probe to the surface must either have radiation shielding, or quickly get into the subsurface. A single instrument capable of identifying both small and large molecules, such as an IMS, would greatly reduce the required analytical payload and increase the feasibility of an *in situ* Europa mission.

4.1.3. Titan

Titan is the second largest satellite in the Solar System and is the only satellite with a significant atmosphere. In fact, the atmospheric pressure is ∼1.5 bar at the surface, more then 50% greater than on Earth. The atmosphere consists of predominantly nitrogen with ∼1.6% methane, and trace amounts of gases such as hydrocarbons (including ethane, diacetylene, acetylene, propane and over 10 other documented organic compounds), argon, carbon dioxide, carbon monoxide, cyanogen, hydrogen cyanide and helium. The rich hydrocarbon inventory of the atmosphere and surface [104] is formed when methane in the atmosphere is photodissociated by UV radiation and resulting chemical reactions with the radical species produced. This supply of radical producing UV radiation is augment by exposure to the strong solar wind as the satellite moves in and out of Saturn's magnetic field.

The lifetime of methane in the atmosphere is limited by photochemistry to the order of 10–100 million years [105,106]. The atmospheric ^{12}C/^{13}C isotope ratio measured by the recent Huygens probe indicates that a continuous or periodic replenishment of methane is ongoing [107]. In addition, the nitrogen isotopic ratio is enriched in ^{15}N suggesting that the early atmosphere was most likely 5 times denser then at the present time [123]. Finally, the low abundance of noble gases, especially argon, indicates that the atmosphere was most likely captured as ammonia gas instead of molecular nitrogen. Argon 40 was also detected at the surface and its presence indicates that Titan has in the past experienced, and is most likely still experiencing today, internal geological activity.

The surface temperature on Titan is about 94 K, right at the triple point of methane. This could lead to hydrocarbon lakes, where organic material may accumulate over time. Upon landing, the Huygens probe measured an increase of methane indicating that the surface is saturated with methane either as a liquid or solid and was evaporated as the cold surface was heated by the spacecraft. Finally surface material was found to be rich in organic material indicating a complex organic chemistry [123].

The organic material on Titan is usually referred to as Tholin. This term was coined by Carl Sagan to describe the highly refractory material created in a Miller-Urey type experiment on atmospheric gases resembling the known constituents of the atmosphere. The result of these series of experiments is a reddish-brown "goo" that is an analogue of the organic component of the planetary surface. This material can be considered to be an analogue of the material present on the early Earth. Identifying the chemicals present on the surface, in lakes and in the subsurface could indicate what molecules were present when life first started on the Earth. While no (new) *in situ* missions to Titan are currently planned in the near future, it is a high priority target in terms of understanding organic chemistry and potential prebiotic chemical pathways.

4.1.4. Other solar system bodies

Of course there are many other targets of investigation that might benefit from IMS based instrumentation. Among these are comets and other icy bodies in the outer solar system. In fact, as discussed in Section 4.2, GC–IMS instruments have been developed with comet investigations in mind. Of all the remaining bodies, perhaps Enceladus remains the most enticing.

On July 14, 2005, the Cassini spacecraft flew by Saturn's moon Enceladus and made what is likely to be the most unexpected discovery of the Cassini mission. Specifically, evidence from a variety of on-board instruments found plumes of water erupting for the 'tiger stripe' region near the South Pole. Currently, the presence of these vapor plumes has been attributed to trapped pockets of near surface liquid water. Given NASA's "follow the water" exploration strategy, Enceladus has quickly become a target of great interest.

4.2. IMS instruments

There have been a number of IMS instruments that have been developed and proposed as Astrobiology mission experiments and have been included in the proposed instrument payloads of unmanned, Solar System exploration spacecraft. Although none of these instruments has yet to fly on a space mission, the instruments in question were developed with a range of Solar System targets in mind. Unfortunately, most details of these instruments are held as proprietary information or are otherwise not available in the open literature. Therefore, we present only a brief summary and description of the evolution of these instruments.

The Comet Rendezvous Asteroid Flyby (CRAF) was a mission, proposed to launch in the early 1990's, to send an unmanned spacecraft to rendezvous with comet Tempel-2, fly in formation with it for 3 years and fire an instrumented penetrator into the comet's nucleus. Close flybys of two asteroids (Malautra and Hestia) were also planned to take place on its way to the comet encounter. The CRAF mission was to conduct detailed studies of the composition and physical properties of the comet nucleus and observe changes that occur as the comet approaches the sun. It was also to determine the size, shape and surface properties of the Malautra and Hestia asteroids. Amongst the proposed instruments was the GC–IMS Comet Ice and Dust Experiment (CIDEX).

The CIDEX instrument later evolved into a more advanced and streamlined version, the mini-CIDEX [108], that was included in the proposed Hummingbird (commentary) Discovery Mission. This instrument was to include an X-ray Fluorescence spectrometer to determine the composition of cometary dust grains and a GC–IMS to determine the molecular composition of dust and ices.

The mini-CIDEX then evolved to be included in the Titan Ice and Dust Experiment (TIDE) that was part of the Titan Orbiter Aerorover Mission (TOAM) [109] proposed to NASA's New Vision's program. The TOAM concept is to combine an orbiter and aerorover to conduct both *in situ* and remote sensing of Titan's surface, atmosphere, ionosphere and magnetospheric interaction. The TIDE instrument would obtain molecular and elemental assays of volatile organics in the atmosphere. For the TIDE application, a Micro-Mechanical System (MEMS) GC and mini-cell helium IMS have been developed to replace their respective mini-CIDEX components with similar to advanced analytical capability [110].

The latest evolution of this development effort is the Mars Geochemical Instrument (MARGI) which was proposed to be included (but not selected) in the science package aboard the Mars Science Laboratory which is set to launch in 2009. All of the above instruments incorporate sealed gas tight drift cells with dry helium as the drift gas due to its universal response and common use as a GC carrier gas [D.R. Kojiro (personal communication, 2006).

Currently, an IMS is part of an instrument package that is being developed to analyze inorganic and organic compounds from Martian surface and sub-surface samples and to search for biosignatures on Mars called the "Wet Chemistry Experiment at Mars (WetChem)" [111]. As its name implies, the experimental approach being developed utilizes wet chemical analysis and extraction. Specifically, WetChem consists of an integrated suite of instruments including the Robotic Chemistry Analysis Laboratory (RCAL) and an electrospray ionization-ion mobility spectrometer in tandem with a cylindrical ion trap mass spectrometer.

RCAL is the evolution of the Mars Environmental Compatibility Assessment (MECA) Wet Chemistry Lab (WCL) that was flight qualified for the Mars 2001 Odyssey Lander prior to its cancellation after the crash of the Mars 1999 Polar Lander [112]. MECA is now set to fly on the 2007 Mars Scout mission: the Phoenix Mars Lander. Like its predecessor, RCAL is designed to provide information on bulk salt content and to characterize the salts and minerals that are present in Martian soil using an array of electrochemical sensors. The sensor array consists mainly of potentiometric ion selective electrodes but also includes conductivity, and voltammetric microelectrodes for determination of heavy metals. In addition, RCAL will serve as the front-end instrument to extract volatiles, inorganic and organic compounds from Martian regolith to be fed to the ESI unit for further analysis of the samples by the IMS-MS instrument. As part of this development effort, a broad survey of types and abundance of carbon containing molecules including complex organic molecules is being performed in an effort to identify potential chemical biosignatures (i.e., amino acids, carboxylic acids) in solid phase materials using the IMS-MS system. Finally, a prototype instrument will be used to conduct field studies at evaporate sites in the Deep Springs Playa and the Death Valley Salt Pan which are considered to be extreme environments (i.e., very dry, highly alkaline with pH levels up to 11) and represent excellent analogs for putative Martian evaporites.

5. Current/future directions and development

5.1. IMS-MS (mass-mobility correlations)

Recently, the correlation between mass and mobility has been revisited with the intention of improving specificity in a tandem IMS-MS measurement. For years, mass and mobility were known to be well-correlated among structurally similar compounds. However, as reported by Johnson et al. [15], amino acids display a high degree of mass-mobility correlation despite the wide variation in amino acid structures. This led to the speculation that a common charge location on stable hydrogen bonded rings between the amine and carboxylic groups were the source of the correlation. A second study of carboxylic acids found similar correlations among structurally dissimilar compounds [16]. Here the analysis was expanded to include chemical modeling of the gas phase ion conformations which supported the assertion that charge location on stable hydrogen bonded ring structures is responsible for the degree of correlation between the mass and mobility of these compounds.

Ultimately, a tandem IMS-MS instrument, yielding both the mobility and mass of an ion, could locate an unknown ion on the mass-mobility plane. By comparing an ion's location on this plane with pre-determined regions characteristic of various compound classifications (i.e., known mass-mobility correlation curves), one could identify the family of compounds to which the unknown belongs. Such ability would be of tremendous value if a tandem IMS-MS system was used to analyze unknown samples in a complex chemical environment (e.g., WetChem on Mars). To this end, a JPL-Caltech group is currently working toward accurate theoretical predictions of mass mobility correlation curves [113].

5.2. Differential mobility spectrometers

Recently, a variation on traditional IMS was introduced as field asymmetric waveform ion mobility spectrometry (FAIMS) or differential mobility spectrometry (DMS) and is based upon the dependence of mobility on electric field. Planar microfabricated configurations of DMS are inherently amenable to spacecraft due to enhanced analytical capability, small size and weight, and low thermal mass. Configurations of GC-DMS analyzers are now routine in research laboratories [114–117] and available in a commercial package (CP-4900 Differential Mobility Detector, Varian Inc.).

In DMS, ions are characterized in an oscillating electric field with high frequency where mobility coefficients are no longer constant with respect to electric field but where K actually changes with the electric field. Plots of K versus E were known from the early part of the 1900s to be flat until a certain point after which the plot increased in ways characteristic for each ion. Thus, Eq. (1) is still valid in DMS except that K should be

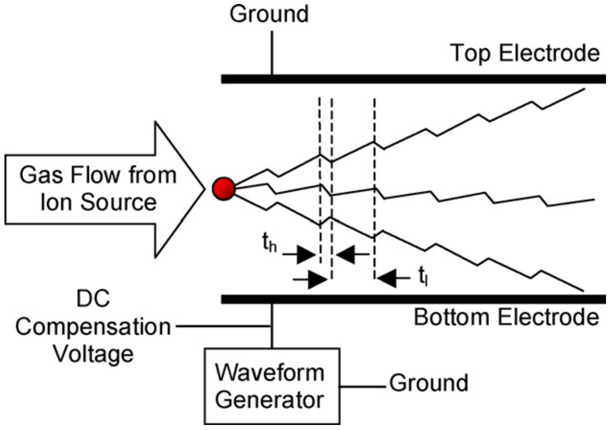

Fig. 5. Schematic diagram of a differential mobility spectrometer (DMS). The symbols t_l and t_h represent the time intervals associated with the low and high field portions of the applied waveform, respectively.

written as $K(E/N)$ where N is number density of molecules in the supporting atmosphere. The values for E where ions of organic compounds become field dependent are 20,000 to 30,000 V/cm so ordinary time-of-flight drift tubes are unworkable. Instead, ions can be characterized for field dependence and separated from a difference in such dependences by moving ions in a flow of gas between two parallel plates with one plate held at ground while a waveform $V(t)$ is applied to the other (see Fig. 5). The applied waveform consists of a high voltage component and a relatively long low voltage component of opposite polarity. During the high field component, ions travel a transverse distance of $K(E/N)_h E_h t_h$, where E_h is the applied electric (high) field and t_h is the period for with the high field is applied. Similarly, the ion will travel a distance $K(E/N)_l E_l t_l$ in the opposite direction over the time, t_l, that the low-field, E_l, is applied. Since the integration of each waveform cycle is zero, the relative values of K_l and K_h determine if the net transverse motion is zero (when $K(E/N)_h = K(E/N)_l$) or in one direction or the other (when $K(E/N)_h/K(E/N)_l \neq 1$). If so, then a DC voltage can be applied to compensate for the transverse drift to give zero net transverse displacement (i.e., the ion does not strike a plate). If the ions derived from different compounds do not have the same ratio of mobilities, then different compensation voltages are required to pass ions through the analyzer. Therefore, the DMS instrument acts as an ion filter which separates ions with different dependences of mobility on E/N. By scanning the compensation voltage, a differential mobility spectrum is generated and all ions in a mixture can be determined. All of the ion characterization and separation occurs in a distance of 13 mm or smaller in the micro-fabricated configurations [118] making the size of the analyzer very attractive for space applications.

The first demonstration of DMS was given by Buryakov et al. [119]. Since its inception, a new configuration with concentric cylinders have been described and commercialized [120]. However, the planar configuration has intrinsic advantages of low cost for manufacture. In either design, reliability is afforded through the simplicity of the drift tube without ion shutters and stacked ring assemblies. A last advantage of DMS which portends favorable development as a GC-DMS instrument for exploration with spacecraft is the simultaneous determination of ions of positive and negative polarity in a single analyzer. Since ions are carried by flow through the gap between the plates, positive and negative ions pushed with gas flow from the ion source are also pushed simultaneously through the analyzers. Ion characterization perpendicular to gas flow is independent of polarity and dependent only upon differences in $K(E/N)$ for an ion, positive of negative. At the end of an analyzer, detector plates for negative and positive ions are set to a slight DC bias yielding differential mobility spectra using parallel amplifiers and a common scan for compensation voltage.

6. Conclusion

Ion mobility spectrometers possess a number of properties which make then intrinsically well suited to space exploration (small, low mass, low power, rugged, etc.). As such they have been, and continue to be, developed for application in both manned and robotic space exploration. Indeed, IMS has a technical pedigree in space applications as part of the environmental monitoring on board the International Space Station. As NASA's "vision for space exploration" unfolds with manned missions to the moon expected by 2020 and planning for eventual manned missions to Mars, the need for reliable air quality monitoring is expected to increase with the duration and scope of these endeavors. Given its flight heritage and past success in this arena, IMS is likely to remain a key technology on board future manned spacecraft.

In terms of robotic exploration, IMS has so far been considered mainly with astrobiological objectives in mind. Despite not having flown on this type of mission to date, groups at NASA Ames Research Center and the Jet Propulsion Laboratory continue to investigate the utility of IMS instrumentation as part of the analytical payload on missions to study the chemical composition of comets, Mars, Titan and other solar system bodies. Given the size and scope of Mars exploration programs (both NASA and ESA), Mars is perhaps the most likely target for an IMS based *in situ* experimental investigation. For example, a mission such as the proposed Astrobiology Field Laboratory would benefit from IMS based assays of organic and chemical compositions of samples collected from protected environments such as rock interiors and subsurface environments.

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