IN-SITU MONITORING OF COMPOUNDS IN PLANETARY ATMOSPHERES USING A MINATURISED FIELD ASYMMETRIC ION MOBILITY SPECTROMETER

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ABSTRACT

Owlstone Ltd., a spin-out company from the University of Cambridge, has overcome the limitations associated with traditional chemical sensors with the development of a ground-breaking solid-state sensor whose operational parameters can be fine-tuned to detect a wide range of volatile chemicals in extremely small quantities. The Field Asymmetric Ion Mobility Spectrometer (FAIMS) outperforms conventional Ion Mobility Spectrometer detectors in the critical areas of size and weight, reliability, sensitivity, response speed, power consumption, versatility and cost of manufacture.

Owlstone Ltd. are collaborating with the Planetary and Space Sciences Research Institute at the Open University to evaluate the analytical suitability of the sensor and the specific design of the sampling interface for its possible use for planetary science. Owlstone Ltd. have funded a matched PhD studentship for Andrew Morris, which began in October 2007. The development of a fast Gas Chromatography (GC) interface, further enhancing the selectivity of the sensor, will be a primary focus of the project.

The theory behind the technology and proposed future developments will be discussed along with its potential application for planetary exploration.

1. INTRODUCTION

The application of Ion Mobility Spectrometry (IMS) has previously focused on the detection of chemical and biological agents found on a battlefield [1-3]. Over the past decade however the technology has undergone significant development so that it now has the capability to be an extremely effective analytical tool beyond the battle arena and homeland defence. One path of development has led to Field Asymmetric Ion Mobility Spectrometry (FAIMS) [4] which has the capability of detecting trace amounts of a specified analyte down to parts per trillion. It has been proposed by the Planetary and Space Sciences Research Institute (PSSRI) to work with Owlstone Ltd., a company whom have developed a FAIMS device, to consider markets beyond the conventional. To accomplish this the two institutions are co-funding a PhD with the aim of investigating the feasibility of matching the new technology to the new emerging markets [5]. The project is to develop protocols for a variety of applications and develop any additional required technology. The intellectual rights and developed technology are shared between the research institute and co-funding company.

1.1 Ion Mobility Spectrometry

In the mid to late 1800's it was discovered the conductivity of air changed due to the formation of ions because of ionisation from the exposure to x-rays. Soon afterwards, in 1895 Ernest Rutherford was able to characterize ions by their mobility. A period of high interest into ion mobility thus followed. The legacy of this early period of research was: the theoretical treatment of ions within a carrier gas, pulsed injection of ions into an IMS through the use of an electromagnetic gate and the work into understanding the effects of gas pressure and electric fields upon the mobility of ions within gases [1]. After this initial burst of research the detection of ions at ambient pressure fell out of favour until during the Second World War.

There are anecdotal references to a device implemented aboard allied Shackleton reconnaissance ships [6] to detect the diesel fuel being expelled from submerged vessels such as the Nazi U-Boat. This ionization detector was called Autolycus and from accounts had some success. A major issue however was the ability to distinguish between the detected diesel fumes of an aggressor and a friendly craft.

This was a useful and practical use of an ionization detector but the technology found greater acclaim after James Lovelock's studies detecting ions in ambient conditions [7]. He demonstrated a device which could be used to detect extremely low airborne vapour concentrations of organic vapours released by industry. The device was then used to make the first measurements of Chlorofluorocarbons' (CFC's) and their affect upon ozone which exists in the stratified regions of the Earth's atmosphere. In light of Lovelocks work interest in IMS once again grew as new applications and improvements on the premise were pursued.

Since the 1950's groups from universities have primarily developed IMS as an analytical tool for use within laboratories, while commercial organisations have pursued the application of IMS to the detection of hazards upon the battlefield, homeland security or for use by first responders to an accident site where harmful compounds may be present. These two commercial applications have been the dominant use of IMS technology throughout its modern history.

1.2 Underlying principles of IMS

Ion Mobility Spectrometry uses an ions characteristic mobility to separate it from other ion species so that a spectrum of ion species can be obtained. If we treat each species of ion as a swarm we can say each ion swarm has a drift velocity through the Ion Mobility Spectrometer of v_d where [1, 8, 9];

$$v_d = KE \qquad (1)$$

v_d = velocity of ion swarm [cm s^{-1}]
K = mobility coefficient [cm^2 V^{-1} s^{-1}]
E = electric field strength [V cm^{-1}]

This is only valid for a swarm and not individual ions since individual ions will undergo unique interactions within the instrument due to the presence of a carrier gas at ambient pressure. It is a framework to understand the propagation of the average ion of that ion swarms properties. It is often useful to be reminded that equation 1 is representative of diffusion (therefore the result of many collisions) as opposed to being directly a result of the Lorentz force.

The mobility coefficient is often normalized to standard conditions to aid in comparisons.

$$K_0 = K\left(\frac{273}{T}\right)\left(\frac{P}{760}\right) \qquad (2)$$

K_0 = normalized mobility coefficient [cm^2 V^{-1} s^{-1}]
T = temperature [K]
P = pressure [Torr]

The units above differ from the more familiar SI designation, where by torr is used to quantify pressure. This is a result of much of the work on IMS being carried out in the United States.

To further the discussion on underlying principles it is useful to first describe a simple drift tube Ion Mobility Spectrometer, Figure 1 is a depiction of such an instrument.
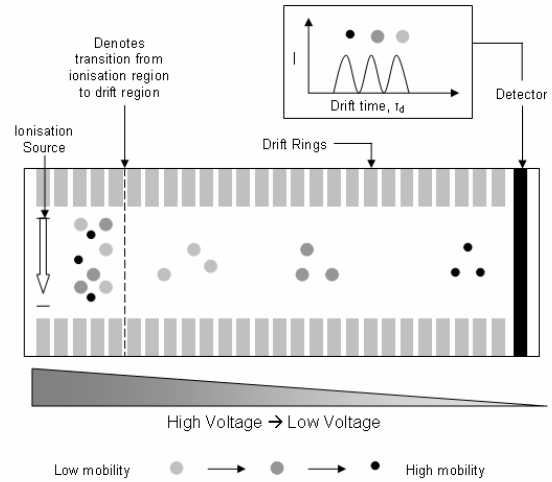

Figure 1. Ion Mobility Spectrometer drift tube showing ions in both the ionisation region and drift region

There are three main regions to a traditional IMS. These are the ionisation region, drift region and detection region. Figure 1 shows ions in both the ionisation region and drift regions, this has only been done to illustrate the premise of the IMS. If a continuous stream of ions was allowed into the drift region it would make it impossible to measure the drift time of the ions and therefore impossible to discover their mobility values. For example if a continuous input of ions was allowed through the detector high mobility ions could be detected after lower mobility ions which had entered earlier. This result would completely invalidate the method of ion mobility spectrometry. It is from trying to restrict this sequence of events that a pulsed entrance of ions into an IMS was developed in its early history to enable the successful identification of ions. This was accomplished by the use of 'gates' [1] which at user defined times allowed the passage of ions and at others restricted it. A gate is situated on the boundary between the ionisation region and the drift region. Within an IMS the gate speeds have to be very fast, 10 to 300 μs. The ideal shutter would allow all the ions in a sample into the drift region when open and no ions when closed. Allowing the maximum amount of ions into the drift region when open increases the IMS' sensitivity while not allowing any ions when closed increases the instruments achievable resolution. The practical way of providing the speed required is through varying the potential across the ionisation/drift barrier. This is accomplished through the Bradbury and Neilson and Tyndall design of gate [1].

The method by which the ions are formed generates some selectivity within Ion Mobility Spectrometers. This is to say that depending upon the method of ionisation some species are preferentially ionised compared to others. This can lead to a bias in the final achieved spectrum. A very common method of

ionisation is through the use of a ^{63}Ni (β source) but there are a variety of options. Table 1 is replicated from *Ion Mobility Spectrometry, G. A. Eiceman and Z. Kapras* with amendment from this author.

Table 1. A list of ionisation sources and their characteristics

Source of Ionisation	Type of Chemicals	Maintenance	Cost	Preferential compounds	Comments
Radioactive	Universal	Low	Medium/Low	High proton affinity	Licensing required
Coronal Discharge	Universal	High	Medium	High proton affinity	Maintenance required
Photoionization (UV)	Selective	Medium	Medium	Aromatics	Low efficiency
Surface Ionization	Nitrogen Bases	High	Medium	Nitrogen Bases	Complex
Electrospray	Liquids	Medium	Medium	Non specific	Long clearance
MALDI	Solids	High	High	Must be affixed within matrix	Laboratory use
Flame	Selective	Medium	Low	Mass dependent	Molecular structure lost

One of the major advantages of IMS over similar analytical techniques is its ability to operate at ambient pressure. Mass Spectrometry (MS) for example requires a good vacuum for successful operation which then leads to greater technical challenges that must be overcome. The disadvantage of IMS systems working at ambient pressure is the requirement for a carrier gas of non analyte material to be present within the instrument. This is to enable a continual flow of material through the instrument and mitigate the loss of detectable ions due to diffusion. The carrier gas is fed through the instrument and enters the same ionisation region as the sample. With so many ions being created at ambient pressure the carrier gas and sample often undergo chemical reactions prior to entering the drift region so it is actually the product of this interaction that is being detected by an IMS. This then means that the carrier gas entering the IMS must be well understood so that the ion spectrum produced can then be deconvoluted to infer which ions were present in the original sample to produce the detected results.

A range of carrier gasses have been traditionally used. To aid in understanding of the earliest systems non-polar and reasonably un-reactive carrier gases were used so as to help in the understanding of what was producing the detected ions.

However, in later systems a consideration when choosing the correct carrier gas is that only certain carrier gases permit the formation of both positive and negative ions. The ability to form both species enables the construction of a more universal detector. As a result air is often used in contemporary designs since Nitrogen ions can go on to form positive molecular ions with a sample and Oxygen can produce negative ions. The humidity levels within the air carrier gas must also be monitored, since water reacts with the recently formed molecular ions to form a molecular ion cluster. Air is also one of the most abundant and easily accessible carrier gases for the majority of applications therefore a system will not always require an additional reservoir of carrier gas for operation.

2. FIELD ASYMMETRIC ION MOBILITY SPECTROMETRY

The principle difference in operation between a FAIMS device and a traditional IMS is the electric field that is imposed upon the ions within the drift region. As described above IMS uses a constant electric field to force separation of the different ion species. Within a FAIMS device an asymmetric field is used [3]. The ideal waveform consists of a short period of high electric field and a longer period of electric field of opposite polarity. The magnitude of the product of electric field and period should be equal for both regions as included within Figure 2.

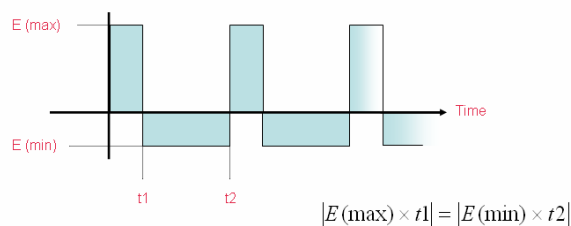
$$|E(\max) \times t1| = |E(\min) \times t2|$$

Figure 2. A diagram depicting the ideal waveform for use within a FAIMS device

The requirement that the two regions equal one another is to ensure there is no overall net electric field which would force the ions and that any affect on the propagation of the ions exclusively exists through the characteristic of the ions mobility.

FAIMS instruments take advantage of the fact that when ions are exposed to high electric fields its mobility is no longer constant.

The field dependence of the mobility coefficient K(E) is now represented by a series expansion of even powers of E/N [10] to include the low and high field regimes [3].

$$K(E) = K(0)\left[1 + \alpha_1\left(\frac{E}{N}\right)^2 + \alpha_2\left(\frac{E}{N}\right)^4 + ...\right] \quad (3)$$

Where K(0) is the coefficient of mobility of the ion in a weak electric field, and α_1, α_2 etc are coefficients of the expansion. The power series can be simplified to equation 4 if α(E/N) is taken as an effective coefficient of the entire power series.

$$K(E) \approx K(0)\left[1 + \alpha(E/N)\right] \quad (4)$$

It can be inferred from equation 4 that there are three situations under high electric field conditions that could be observed. These three situations are: α > 0, α < 0 and α ≈ 0. Under low electric field conditions the equation 4 will reduce to equal simply K(0). An example of how ions may vary with each class of α value dependent upon electric field strength is shown within Figure 3.
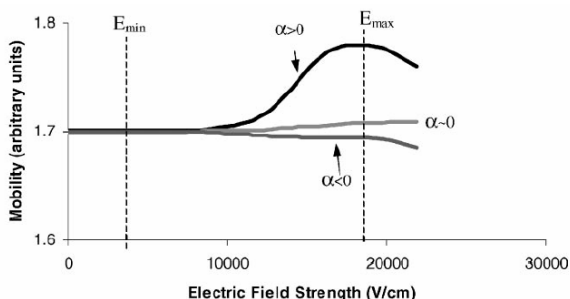

Figure 3. Mobility dependence on electric field for three different ion species, figure originally from Miller, R.A., et al., *A MEMS radio-frequency ion mobility spectrometer for chemical vapor detection*

Each ion species has its own unique α value and so every species will act differently from one another within the FAIMS instrument. For example, taking an ion species with a positive α value, during the large positive region of the applied electric field waveform the ion will migrate preferentially to one side of the drift region. When the waveform is switched in polarity it will migrate in the opposite direction but to a reduced magnitude since it is a lower field region and the additional term on the RHS of equation 4 no longer

has an effect. This pattern continues every time the waveform is repeated until the ions of that species collide with the wall of the FAIMS device and annihilates. A similar process occurs for ion species with a negative α value but the collision with the instrument wall occurs on the opposite wall as the positive α ions. When α ≈ 0 both the high and low electric field regions have an identical affect as one another and the ions are able to pass through the drift region unhindered and on to detection. These three situations are depicted within Figure 4.
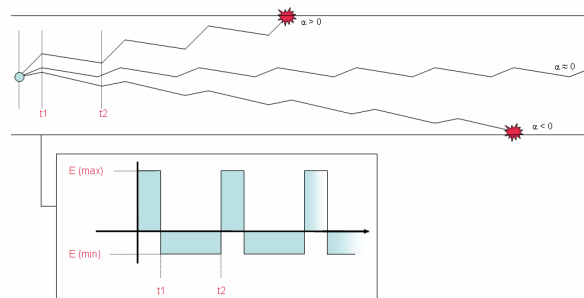

Figure 4. Cross section of a simple parallel plate FAIMS device being driven by an idealised asymmetric waveform

If this was how the situation was left a FAIMS device would only be able to detect the ion species where α ≈ 0 with all other species of ions being excluded from passing through the device. Changing the asymmetric electric field is not trivial and the resources required to do so are significant. To overcome this issue a Direct Current (DC) voltage is added which results in a constant electric field that acts upon the ions within the drift region. This is in addition to the asymmetric waveform and it has the affect of applying a force to the ions within the drift region. This 'compensation voltage' results in a force being equally applied to all the ions within the drift region and is equivalent to slightly modifying the entire asymmetric waveform. This will result in ions which would previously have been annihilated being able to pass on to detection and ions which previously would have been detected colliding with the instrument walls. Through tailoring of the compensation voltage any single species of ion can be isolated and detected. If the compensation voltage is cycled through a range then every species of ion within the device will at one point be detected at the exclusion of all others. This allows for a very sensitive and selective detector. Variation of the compensation voltage to generate a separate constant electric field and combining it with the asymmetric field is a lot less resource intensive than exclusively varying the asymmetric electric field.

The mobility coefficient is described as dependent upon both E and N (more specifically E/N) because the mobility of the ions is dependent on two processes which occur within the drift region. The first effect increases the mobility because of the magnitude of the electric field (E). The formations of ions within a FAIMS device is the same as that within an IMS so the ions within the drift region are clustered molecular ions as described within Section 1.2. This results in a large effective cross section of the ions. As the electric field increases these clustered ions splinter which decreases their effective cross section, which in turn increases the mobility coefficient and hence the mobility of the detected ions. The second effect is a negative one upon the ion's mobility and is due to both the electric field and the neutral number density within the drift region. As the electric field increases the ions are driven harder through the instrument. This leads to increased collisions with the neutral atmosphere and this detrimental effect is accentuated when the number density is increased. It is the combination of the ion's mobility and the effects of E and N which form the value of α and when any of the two latter effects become dominant or they equal one another the three situations of $\alpha > 0$, $\alpha < 0$ and $\alpha \approx 0$ occur.

Apart from the applied electric field the methods of ionisation and detection are identical to those used within IMS. There are also similar considerations concerning the carrier gas within a FAIMS device as that found within an IMS. For this reason FAIMS instruments can be tailored for the particular application they are to be applied to. An ion gate is not required for the successful operation of a FAIMS device if the timing of the operation and waveform are well controlled.

3. THE OWLSTONE SENSOR

The co-funding company for the PhD project have developed their own unique FAIMS device which is made using lithography techniques to produce a solid state detector. There are a number of benefits of having a solid sate detector which include low power, small size, low cost, low mass and reliability.

Owlstone Ltd. claims that their sensor also outperforms other similar models in the critical areas of sensitivity reduced false positives and speed.

The current iteration of the sensor can use any carrier gas with air preferentially used due to its ability to form both positive and negative ions. The total flow required is three litres per minute with the carrier gas being dry ($H_2O < 10$ ppm) and clean (VOC < 1 ppm). The sensor itself is housed within the Owlstone Tourist platform which is intended for laboratory qualification [11].

The ionisation source for the Owlstone sensor in its current configuration is a radioactive ^{63}Ni source and therefore preferentially ionises compounds with a high proton affinity. The system is flexible enough to accommodate other ionisation sources however such as an Ultra Violet (UV) source which preferentially excites aromatic compounds, allowing the Owlstone device to be tailored to a variety of applications. Detection of ions is through the use of a Faraday plate.

As mentioned previously, unlike a mass spectrometer which returns the mass of the detected ion, FAIMS' do not provide fundamentally distinguishable characteristics of the ion detected. This means that for the successful identification of compounds a test must be run to characterize the fingerprint of a compound from which future results of an unknown compound can be compared. This is a result of the theory relating an ions mobility to high electric fields is still incomplete therefore true analytical analysis (as enjoyed by MS) is not yet available, requiring the use of spectral fingerprints.

The time taken for a typical full scan of a sample using the Tourist platform is three minutes. The system is then immediately able to perform another test. If the electric field is known for a particular analyte a scan for that particular compound can be completed within a second. Once again the system is immediately ready to perform another test.

4. APPLICATION IN PLANETARY SCIENCE

The existence of methane in the martian atmosphere, at the sub ppm level, is now commonly accepted. Ground-based spectroscopic measurements by Krasnopolsky and more Mumma [12], complemented by the results reported by Formisano [13], from the Planetary Fourier Spectrometer (PFS) onboard Mars Express, have all independently verified the presence of this simple, yet most interesting of hydrocarbon species. Whilst the presence of methane (proposed as a potential marker for the presence of extant life) is indisputable, the picture portrayed for the actual abundance levels and the global distribution of this gas is confused. The theories about the potential sources and sink processes are equally as disparate. The presence of formaldehyde, generated by one of the sink processes for methane, is even more controversial [14]. The Gas Analysis Package (GAP) [15], on Beagle2, had the capability of making direct measurements of the methane concentration on the surface. It is proposed, in collaboration with Owlstone Ltd, to evaluate the Owlstone sensor coupled with a GAP type instrument with respect to taking measurements of formaldehyde concentrations (ppbv) on the surface of Mars.

The principal investigator for the Planetary Fourier Spectrometer, Vittrio Formisano, states large quantities of Formaldehyde have been detected upon Mars with strong correlation to observed Methane [16]. Formaldehyde is produced through the oxidation of Methane and has a lifetime of 7.5 hours within the Martian atmosphere. This indicates an ongoing generative process of which Formisano has proposed three methods which could produce Formaldehyde upon Mars. These three methods are Hot Chemistry, Cold Chemistry and Life.

Hot Chemistry: Deep underground where the temperatures reach 400-500°C Methane could possibly form and with water would be slowly moving towards the surface since the equatorial ice table is unstable and must be refurbished. Formaldehyde could be formed in Methane percolating through dry soil on top of the ice table.

Cold Chemistry: The permafrost is continuously being bombarded by solar energetic particles and by cosmic rays. There is therefore a resemblance to a cometary environment. Comets host complex chemistry to the point they are considered precursors of life.

Life: To satisfy the overall picture resulting from the PFS instrument some sort of Biota should be present with methanogetic bacteria producing methane and methanthropic bacteria oxidising methane and eventually producing formaldehyde.

Formisano states that the amount he believes the PFS instrument has detected could only have been produced by life present upon Mars. The remainder of the PFS team express caution since inferring Formaldehyde is upon the limits of the PFS' capabilities.

Linked to the issue of Formaldehyde is the disagreement from different teams that have detected Methane upon Mars with respect to its abundance and distribution. Placing an *in situ* sensor that could both detect both Methane and Formaldehyde upon Mars would provide the results required to provide a much more detailed understanding of abundances in the locality of the sensor which would be made even more powerful if it was mounted upon a moving platform such as a rover or balloon.

5. SUMMARY

This document and presented poster are to introduce the new sensing technology currently being developed by interested parties and to demonstrate how the new technology could tackle ongoing investigations within planetary science. Due to the ability of FAIMS devices to be tailored for a wide range of applications the Owlstone sensor is also undergoing evaluation with respect to potable water safety, air quality and the detection of aldehydes within the manufacturing markets. FAIMS is an emergent technology which is finding markets well beyond the conventional detection of explosives and chemical warfare agents. The systems are generally, smaller, lighter, more reliable and more sensitive than competing equipment which can wok under the same conditions.

The aim of ongoing work is to investigate the feasibility of the Owlstone sensor to a range of applications including planetary science. As part of this work it is proposed to add a preliminary Gas Chromatography (GC) stage and determine the protocols required for the best detection for each application.

It is hoped that the Owlstone sensor will be well suited for a large range of terrestrial and planetary science investigations which will provide Owlstone Ltd. with a new market and myself with a host of new skills.

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