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SPECIAL FEATURE:
PERSPECTIVE

Ion trap mass spectrometry on a comet nucleus: the Ptolemy instrument and the Rosetta space mission

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In May 2014, the Rosetta spacecraft is scheduled to rendezvous with the comet Churyumov–Gerasimenko ('67P'). One of the instruments on board the 'Lander' which will descend on to the surface of the comet is a miniaturised GC/MS system that incorporates an ion trap mass spectrometer, specially developed for isotope ratio analysis. This article describes the development and optimisation of the ion trap for this unique application, and presents a summary of the range of pre-programmed experiments that will contribute to the characterisation of the solid and volatile cometary materials. Copyright © 2006 John Wiley & Sons, Ltd.

INTRODUCTION

At precisely 07:17 GMT on Tuesday, 2 March 2004, an Ariane-5 rocket carrying the Rosetta 'comet chaser' was launched at Kourou in French Guyana: the mission, to characterize the comet Churyumov–Gerasimenko, otherwise known as '67P'. One of the instruments with which this survey will be carried out is a mini chemical laboratory, MODULUS Ptolemy, which includes a GC/MS system incorporating an ion trap mass spectrometer specially designed for stable isotope ratio measurements. The purpose of this paper is to give an account of this highly unusual application of the ion trap and, in particular, to explore some of the technical and design considerations of a system that is fully automated, yet is not due to reach its target sample until 2014! While reading the description that follows, the reader may care to reflect on the fate of this lonely ion trap during its journey covering hundreds of million of miles. However, while the hardware design was effectively 'frozen in time' during 2000, the software and instrument control sequences continue to be developed while the mission is in progress. Most mass spectroscopists would expect to have utilised

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three or four new generations of instruments in a 20-year period, and would not normally have to wait two decades since their research project was initially conceived in order to (hopefully) see their first analytical mass spectrum! Nor would they expect to have to incorporate an age-distribution table into the initial funding application in order to demonstrate that at least some members of the original team, who know how to control the system and to interpret the data signals, will still be in place when the analyses are carried out!

THE ROSETTA MISSION

The name 'Rosetta' was taken from the 'Rosetta' stone, a slab of volcanic rock, now in the British Museum, that was found in the village of Rashid (Rosetta) in the Nile delta in Egypt by French soldiers in 1799. The stone is covered with carved inscriptions telling a story in Ancient Greek, together with the same tale told in both Egyptian Hieroglyphic and Demotic. Only Greek could be translated at the time and, by comparing the three sets of characters, scholars were able to decipher the meaning of the various symbols, thereby unlocking the secrets of 3000 years of ancient history. In the same way, this space mission seeks to unravel history by taking a range of physical and chemical measurements from a comet, which consists of the material left behind after the

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formation of the planets including Earth. Thus the comet holds a record of the conditions prevalent at the birth of our solar system, preserved in the deep freeze of space for 4600 million years. Hopefully, this 21st century endeavour will offer some of the answers to the questions of how the Earth evolved and even of how life on Earth started.

The Rosetta mission is the most ambitious cometary mission ever attempted. Previous missions to comets have primarily involved high speed fly-bys, such as the Giotto spacecraft that captured the first image of a comet nucleus (Halley), and Stardust that collected and returned to Earth samples of material from the tail of comet Wild 2. Even the recent Deep Impact experiment, in which a copper projectile was impacted with comet Tempel 1 under the gaze of cameras aboard the mother spacecraft, returned only 'snapshots' of comets during their orbits around the Sun. Still there remain fundamental questions regarding the chemical and physical nature of these ancient and important bodies, and how they interact with solar radiation to form their characteristic tails. Rosetta aims to address these questions by orbiting a comet nucleus for the first time, probing the nucleus as it approaches the Sun and starts to form its tail, and releasing a 'Lander' known as *Philae*, to perform *in situ* analyses. The Rosetta 'Orbiter' resembles a large box of dimensions $2.8 \times 2.1 \times 2.0$ m, and has two 14-m long solar panels with a total area of 64 m^2. On arrival at its destination in May 2014, Rosetta will orbit 67P in order to map the surface (which is approximately equal in cross sectional area to that of London Heathrow Airport!) in order to determine a suitable site for the Lander to target during its descent in November 2014. In addition to containing the main command and communications module, the Orbiter's payload includes the following 11 experimental probes, all controlled by different research groups.

An ultraviolet imaging spectrometer (ALICE), which will analyse gases in the coma and tail and measure the comet's production rates of water and carbon monoxide or dioxide. It will provide information on the surface composition of the nucleus.

A comet nucleus sounding experiment by radio wave transmission (CONSERT), to probe the comet's interior by studying radio waves that are reflected and scattered by the nucleus.

A cometary secondary ion mass analyser (COSIMA) utilising a time-of-flight secondary ion mass spectrometer with mass resolution up to 2000, which will analyse the characteristics of dust grains emitted by the comet, such as their composition and whether they are organic or inorganic.

A Grain impact analyser and dust accumulator (GIADA) to measure the number, mass, momentum, and velocity distribution of dust grains coming from the comet nucleus and from other directions (reflected by solar radiation pressure).

A micro-imaging dust analysis system (MIDAS), which will study the dust environment around the comet and provide information on particle population, size, volume, and shape.

A microwave instrument for the Rosetta orbiter (MIRO) to determine the abundances of major gases, the surface outgassing rate, and the nucleus sub-surface temperature.

An optical, spectroscopic, and infrared remote imaging system (OSIRIS), which is a wide-angle camera and a narrow-angle camera to obtain high-resolution images of the comet's nucleus.

The Rosetta orbiter spectrometer for ion and neutral analysis (ROSINA), which utilises a complementary pair of mass spectrometers to determine the composition of the comet's atmosphere and ionosphere, the velocities of electrified gas particles, and reactions in which they take part. A double focusing magnetic mass spectrometer with a mass range 1–100 Th and a mass resolution of 3000 at 1% peak height is optimised for very high mass resolution (ability to resolve CO from N_2 and ^{13}C from ^{12}CH) and large dynamic range. A reflectron-type time-of-flight mass spectrometer with a mass resolution better than 500 at 1% peak height is optimised for high sensitivity over a broad mass range from 1 (hydrogen) to 300 Th (organic compounds).

The Rosetta Plasma Consortium (RPC), which will measure the physical properties of the nucleus, examine the structure of the inner coma, monitor cometary activity, and study the comet's interaction with the solar wind.

The radio science investigation (RSI) probe, which using shifts in the spacecraft's radio signals, will measure the mass, density, and gravity of the nucleus, define the comet's orbit, and study the inner coma.

A Visible and Infrared Mapping Spectrometer (VIRTIS), which will map and study the nature of the solids and the temperature on the surface of the nucleus. It will also identify comet gases, characterise the physical conditions of the coma, and help to identify the best landing sites.

The Lander structure consists of a baseplate, an instrument platform, and a polygonal sandwich construction, all made of carbon fibre. Some of the instruments and subsystems are beneath a hood that provides a 'warm' compartment (i.e. temperature in the range from -40 to $+50\,°C$); others are mounted on an external balcony to be subjected to temperatures ranging from -140 to $-50\,°C$. The hood itself is covered with solar cells to recharge the Lander's batteries. An antenna transmits data from the surface to Earth via the Orbiter. The Lander carries the following further nine experimental systems, including a drilling system to take samples of sub-surface material; the payload of the Lander is about 21 kg.

The alpha proton X-ray spectrometer (APXS). When lowered to within 4 cm of the 'ground', APXS will detect α-particles and X-rays, which will provide information on the elemental composition of the comet's surface.

The Rosetta Lander imaging system (ÇIVA/ROLIS). This is a CCD camera to obtain high-resolution images during descent and stereo panoramic images of areas sampled by other instruments. Six identical micro-cameras will take panoramic pictures of the surface, and a spectrometer will

study the composition, texture, and albedo (reflectivity) of samples collected from the surface and sub-surface, some of which will then be subjected to further analysis by COSAC or MODULUS Ptolemy (given below).

The CONSERT system. CONSERT will probe the internal structure of the nucleus: radio waves from CONSERT will travel through the nucleus and will be returned by a transponder on the Lander.

The cometary sampling and composition (COSAC) system. This analyses the comet surface and sub-surface samples using a gas chromatograph/time-of-flight mass spectrometer to detect and identify complex organic molecules from their elemental and molecular composition.

The evolved gas analyser (MODULUS Ptolemy). The subject of this paper, this instrument utilises a gas chromatograph-isotope ratio ion trap mass spectrometer to obtain precise measurements of stable isotope ratios of the light elements H, C, N, O in their various forms within the material sampled from the comet's sub-surface, surface, and near-surface atmosphere.

The multi-purpose sensor for surface and sub-surface science (MUPUS). This will use sensors on the Lander's anchor, probe, and exterior to measure the density as well as the thermal and mechanical properties of the surface.

Rosetta Lander magnetometer and plasma monitor (ROMAP). This is a magnetometer and plasma monitor that will study the local magnetic field and the comet/solar wind interaction.

The Sample Drill and Distribution system (SD2). This will drill more than 20 cm into the surface, collect samples, and deliver them to different ovens for evolved gas analysis by COSAC and Ptolemy and microscope inspection by ÇIVA/ROLIS.

Surface electrical, seismic and acoustic monitoring experimental (SESAME) system. These three instruments will measure the properties of the comet's outer layers: the cometary acoustic sounding surface experiment will measure the way sound travels through the surface; the Permittivity Probe will investigate its electrical characteristics; and the dust impact monitor will measure dust falling back to the surface.

Integration of this total of 20 very different experiments into a single operation is clearly a highly complex matter. Each separate system must be capable of functioning under automated control, and of being brought into or out of use according to a strictly pre-determined schedule when the cometary encounter commences (see also below). Furthermore, communication with the instrumentation has to be co-ordinated through a scientific command centre and then through mission control using special software, which cannot be carried out directly by the individual research groups from their own institutions. In the case of MODULUS Ptolemy (which receives its instructions via the command systems on the Lander, which in turn is instructed from the Orbiter), the scientists in their laboratories at the Open University at Milton Keynes in the UK are some five steps removed from direct control of their mass spectrometer and associated equipment. Added to this complexity, the

Table 1. Time-sequence for the Rosetta Mission

Date	Event
2 March 2004	Launch of Rosetta
March 2005	First Earth gravity assisted fly-by
February 2007	Mars gravity assisted fly-by
November 2007	Second Earth fly-by
November 2009	Third Earth fly-by
May 2014	Comet Churyumov–Gerasimenko rendezvous manoeuvre
November 2014	Landing on the comet; *in situ* analysis by Lander instruments
December 2014 – November 2015	Orbiter escorts comet; remote sensing analysis by Orbiter instruments
December 2015	End of mission

transfer time for signals over the 500 million miles separation between Earth and Rosetta at the time of the encounter will be of the order of 50 min!

Following the launch into a tightly specified flight path, the timeline for the mission is as summarized in Table 1. The fly-by stages are a means by which the space module gains speed, rather like a child swinging round a lamp post when running down a street, so that Rosetta will eventually reach the velocity of the comet (up to 135 000 km/h). The landing process itself will present some significant hazards to the mission: because the comet is so small, and hence its gravitational field so weak, there is a danger that the Lander will simply bounce off the surface. The legs of the Lander contain a damping system to absorb most of the kinetic energy on contact, and a harpoon will be fired into the surface in order to anchor the system.

Further details of Rosetta's journey may be found at http://www.esa.int/export/esaMI/Rosetta/, and information about the actual launch is available at http://www.arianespace.com/site/news/mission_up_153.html. It should, perhaps, be noted that originally it was intended that Rosetta would target another comet, 46P/Wirtanen, in 2011, with a launch date in January 2003. However, because of the failure of the preceding Ariane-5 flight in December 2002, the operation was delayed and the precise time-window required for the trajectory was thereby missed. Consequently, a new target (i.e. 67P) was chosen and the whole project re-programmed.

THE MODULUS PTOLEMY EXPERIMENT

The name 'MODULUS' stands for Methods Of Determining and Understanding Light elements from Unequivocal Stable isotope compositions. It was concocted by Professor Colin Pillinger, FRS, and his co-investigators at the Planetary and Space Sciences Research Institute at the Open University in the UK in honour of Thomas Young, the English physician turned physicist, who was the initial translator of the Rosetta Stone and whose name is best known by the measure of elasticity, 'Young's Modulus'. In the original research plan it was intended to develop two versions of the MODULUS instrument, Ptolemy and Berenice: as noted above, the

former is part of the package of experiments on the Lander, while the latter was intended to examine (and thus provide a comparison with) the volatile species surrounding the comet as part of the research conducted by the Orbiter. In the event, only Ptolemy ultimately flew, and elements of the proposed Berenice science were incorporated into the Ptolemy instrument. Genealogists – those who study descent and ancestry – may be interested to note that Berenice and Ptolemy were subjects of the inscriptions on the Rosetta stone.

Stable isotope ratio measurements for light elements

The underlying aim of the Ptolemy experiment is to determine the degree of isotopic enrichment (or depletion) of D (i.e. ^{2}H), ^{13}C, ^{15}N, ^{17}O, and ^{18}O in cometary samples relative to specified standard reference materials. These measurements will yield data on the respective degrees of isotopic fractionation that have occurred, which should in turn provide information about the temperature regime within which the samples were formed, as well as give indications of the sources from which the samples were derived. To determine the relative isotopic abundances, samples of solid material taken by the SD2 system, mentioned earlier, from the body of the comet (which has been described as being like a dirty snowball) will be subjected to stepped pyrolysis and/or combustion in ovens according to pre-programmed protocols so as to generate evolved gases at pre-determined temperatures that will then be converted (if necessary) chemically into compounds such as H_2, O_2, CO, CO_2, and N_2. The resulting mixtures will then be separated and isotopically assayed by GC/MS using an ion trap mass spectrometer.

The isotope ratios are measured as the differential values according to the 'delta' notation of Urey:[1]

$$\delta(\text{rare isotope}) = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 1000\text{‰} \qquad (1)$$

where R is the ratio of intensities for (D/H), (^{13}C/^{12}C), (^{15}N/^{14}N), (^{17}O/^{16}O), (^{18}O/^{16}O), etc. As a result, all the determinations on the sample data must be directly compared with contemporary measurements on appropriate standard 'on-board' reference materials that have been calibrated to an agreed international standard. In this way, compensation can be made for any systematic fractionation effects in the instrumentation in order to maximise the accuracy and precision of the data.

The ion trap mass spectrometer as the instrument of choice

The mass spectrometer for Ptolemy serves two main purposes: firstly it must operate as a detector for gas chromatography, identifying and quantifying sample gases eluting from the GC column (this is a routine application of commercial ion traps); the second and more unusual objective is its operation as an isotope ratio mass spectrometer. Here the challenge is to measure precisely the relative abundance of an ion $M^{+\bullet}$ of m/z m, and that of its isotopic form of m/z $(m+1)$. Normally, in order to obtain the most precise

light element stable isotope ratio measurements on a single gaseous compound, one would choose a magnetic sector instrument, preferably with a dual inlet system designed for contemporaneous assays of the sample and of the standard reference material, thereby allowing results to be expressed in the delta notation format described in Eqn (1). However, since the total payload and physical space available were severely limited, and given all the other instrumentation being carried by Rosetta and the associated power requirements, alternative analyser types had to be considered. The small size and simplicity of construction of the ion trap, the fact that it functions on the basis of a single parameter control (i.e. the amplitude of the r.f. drive potential), and that in principle the ion accumulation time can be adjusted in order to allow the build-up of ions from the minor isotopes, thereby increasing the precision of their measurement, made this mass analyser an obvious candidate for consideration. Its tolerance to moderately high pressures (*ca* 10^{-3} mbar) of helium (which is employed as the GC carrier gas as well as for the actuation of the pneumatic valves of the GC injection valves) is a further advantage. Conveniently, the working pressure of the ion trap is of the same order as the maximum value anticipated in the region of the comet: at initial encounter the ambient pressure is expected to be around 10^{-7} mbar, but this is predicted to rise to *ca* 10^{-3} mbar at point of closest solar approach. This reduces the pumping requirements for the instrument, which in turn saves mass, power, and volume. These advantages were counterbalanced by the fact that at the time of design (1995–1998) there were no literature reports on the use of the ion trap for stable isotope ratio determinations at natural abundance levels. An intensive programme was therefore undertaken, to fully characterise and to evaluate this novel application;[2,3] what follows below is a distillation of the pertinent findings with respect to the use of an ion trap for stable isotope ratio mass spectrometry.

It was found that residual water vapour molecules inherent in the vacuum system of a commercial ion trap undergo reactions with trapped $CO_2^{+\bullet}$, $CO^{+\bullet}$, and $N_2^{+\bullet}$ ions to produce the species MH^+ (where M = CO_2, CO, or N_2), which are isobaric with target isotope peaks and therefore render meaningless attempts to measure natural abundance stable isotope peaks at m/z $(m+1)$. It was of crucial importance that the mechanism for formation of MH^+ was demonstrated to be through reaction of a trapped *sample ion* with a *neutral water* molecule. Thus all the unique capabilities of the ion trap with regard to selective storage and ejection of ions cannot be utilised to eliminate the effects of these neutral water molecules. A radical approach was therefore adopted to allow isotope ratios to be measured in a space flight ion trap instrument: rather than attempt to preclude ion/molecule reactions, a technique named *ion/molecule reaction-aided isotope ratio analysis* (IMRAIRA) was developed in which the phenomenon could be exploited. A supplementary hydrogen make-up gas flow was introduced into the ion trap and was allowed to react with the stored sample ions through the hydrogen abstraction reaction:

$$M^{+\bullet} + H_2 \longrightarrow MH^+ + H^\bullet$$

$$(\Delta_r H < 0 \quad \text{for} \quad M = CO_2, CO, N_2) \qquad (2)$$
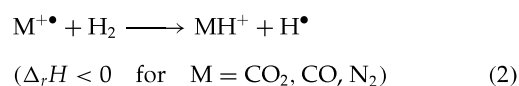
Owing to the favourable thermodynamics of the reactions involving CO_2, CO, and N_2, the reactions proceeded to near-completion. Thus isotope ratios could be measured, for instance, for CO_2 through the m/z ratios 46/45 and 47/45.

The precision or reproducibility of the measurements was estimated through the zero enrichment (ZE) technique, whereby many repeat measurements are made of the same isotopic ratio and then Eqn (1) is applied to each pair of consecutive ratios, in which the nth ratio is taken as being $R_{standard}$ with respect to the $(n + 1)$th ratio as R_{sample}. Ideally, the value of $\delta(ZE)$ should be zero. Thus for, say, 50 repeat measurements of R one would obtain 49 values of $\delta(ZE)$, and the precision can be evaluated from the standard error of the mean of the set of consecutive measurements. For 50 repeat analyses of CO_2 with hydrogen, each analysis consuming 47 nmol of CO_2, the precision was approximately $\pm3.7‰$ for m/z 46/45 and $\pm4.9‰$ for m/z 47/45. This level of performance is adequate for the intended space flight application (in which current uncertainties in isotopic compositions of comets are of the order plus or minus a few percent or tens of percents); full characterisation of the performance of the Ptolemy instrument as a whole is now underway using the Ptolemy 'qualification model' (given below), essentially a replica of the instrument currently *en route* to the comet.

In the flight model (FM) of the system, hydrogen gas from a reservoir cylinder is added to the helium buffer gas stream when nitrogen, carbon monoxide, and carbon dioxide are being assayed. Because of their lack of reactivity towards hydrogen, isotopic measurements using oxygen ions are carried out on the non-hydrogenated $O_2^{+\bullet}$ species.

So far this account has not included reference to the fourth element of interest to the Rosetta mission, namely, the determination of isotopic ratios in hydrogen; this is, of course, a measurement that is of special importance in characterising cometary water. Normally, in a terrestrial laboratory using magnetic sector instruments for isotopic work, the ratio D/H is found by converting the water into hydrogen gas, and then measuring the intensities of the m/z 2 and 3, corresponding to $H_2^{+\bullet}$ and $HD^{+\bullet}$, respectively. However, the sensitivity of the ion trap falls off at low values of m/z; furthermore, hydrogenation reactions of the kind noted above lead to the facile formation of H_3^+, causing an isobaric interference with target isotope peaks at m/z 3. Further, the IMRAIRA technique is not a practical option: although the forced conversion of $H_2^{+\bullet}$ and $HD^{+\bullet}$ to H_3^+ and H_2D^+ through introduction of supplementary hydrogen has been demonstrated, this is not a practical solution for Ptolemy due to isobaric interferences from residual helium buffer gas ions at m/z 4 (i.e. $^4He^{+\bullet}$). An alternative implementation of IMRAIRA was therefore investigated for the analysis of the D/H ratio in hydrogen gas. In this instance, the supplementary hydrogen make-up gas is switched off, and sample H_2 is allowed to react with stored $Ar^{+\bullet}$ ions and the D/H ratio determined through the ratio m/z 42/41 corresponding to ArD^+/ArH^+. The detailed assessment of the efficacy and precision achievable with this technique is another objective of the ongoing laboratory calibration programme utilising the Ptolemy qualification model.

Ptolemy instrument design: ion trap and associated hardware

Ion trap

The Ptolemy ion trap is housed in a moderately gas-tight aluminium box, which also incorporates the r.f. generator, high voltage, and ion detection electronics in order to minimise the mass and electromagnetic emissions of these supplies (Fig. 1(a) and (b)). The Ptolemy instrument utilises a non-stretched ion trap ($r_o = 8.0$ mm; $2z_o = 11.3$ mm) having grounded end-cap electrodes, operating at a nominal r.f. drive frequency of 0.6 MHz and the amplitude variable between approximately 25 and 300 $V_{(0-pk)}$. The reduction of these values from those of standard commercial instruments (for instance, the Finnigan MAGNUM instrument, used in our original isotope ratio experiments, employed $r_o = 10.00$ mm, with $2\pi\Omega = 1.05$ MHz) allows significant reduction in volume and voltage (and hence power and energy) requirements in Ptolemy.

Owing to the temperature-dependence of the frequency at which maximum r.f. drive circuit resonance occurs (resonance being desirable as it produces the maximum amplitude of r.f. drive and hence the greatest attainable upper m/z limit), the exact frequency to be operated during any one Ptolemy experiment will be determined *in situ* by a self-tune feature. These parameters typically offer a mass/charge ratio range of 12 to 150 Th, allowing both general sample characterisation (e.g. from water to xenon) and isotope ratio measurement. The scan function is under software control, and is built up segment by segment, allowing the scientist to tailor scan functions for each of the planned analyses. In order to reduce complexity and power demands and, indeed, mass, there is no provision for d.c. isolation or resonant excitation experiments. Similarly, though the ionisation time is pre-selectable in the range 0.1 to 5 ms, there is no provision for automatic gain control.[4] Although this may appear to suggest a very basic ion trap system, reminiscent of the original Finnigan ITD 700 instrument,[4] compared to current state-of-the-art instruments, it should be remembered that this is a highly specific application upon which considerable research effort has been expended in terms of determining the precise operating conditions, sample amounts, etc. in order to achieve the desired level of performance. It should also be noted that the Ptolemy ion trap is operating at rather low m/z values (isotopic analyses are conducted at m/z <50) compared to laboratory instruments targeted at organic analyses. And finally, of course, this instrument must operate remotely on a mass and power budget of 4.5 kg and 10 W, respectively. Perhaps, it is therefore not surprising that the optimum design for fulfilling this unique application did not follow conventional wisdom derived from a knowledge of analytical organic mass spectroscopy.

The electrodes are fabricated from aluminium, cut away to reduce the mass, and the overall external dimensions of the analyser are 60 mm diameter × 70 mm height (Fig. 2). In order to minimise power consumption and provide some redundancy in this vital area, ionisation is effected by a beam of electrons generated from a 3 × 2 array of microstructures etched from a silicon wafer, each of the micro-fabricated units comprising an array of 40 × 40 nanotips.[5] Ion detection
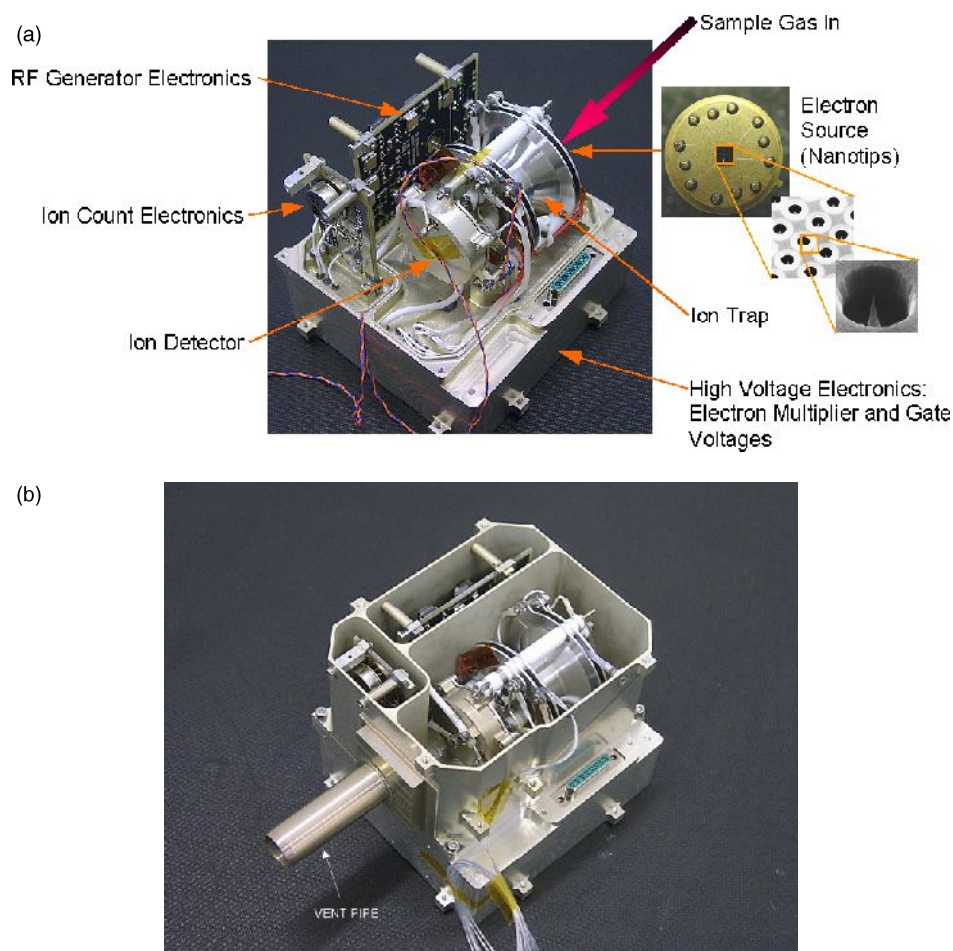
Figure 1. (a) Isometric photograph of the flight model (FM) of the Ptolemy ion trap with its associated electronic circuits, but with the shielding container removed. (Copyright CCLRC Rutherford Appleton Laboratory reproduced with permission.) (b) Isometric photograph of the flight model (FM) of the Ptolemy ion trap with its associated electronic circuits, showing the lower half of the shielding container and gas vent pipe. (Copyright CCLRC Rutherford Appleton Laboratory, reproduced with permission).

is accomplished in the pulse-counting mode using an electron multiplier developed by the Max-Planck-Institüt-für Sonnensystemforschung (MPS), Lindau, Germany, in which a spiral amplification channel is formed within a ceramic disc. The device is rugged and therefore compatible with rocket launch vibrations, and its shape is ideally suited to the geometry of the ion trap structure. The mass of the analyser assembly (electrodes plus ion source and detector) is 75 g; including electronics and structural items the ion trap weighs less than 500 g. The flight version of the ion trap with its associated ioniser, detector, and electronic circuits is shown in Fig. 1(a) and (b).

The supply of helium, used variously as the carrier gas, actuator for the pneumatic valves and the ion trap buffer gas, is 'Grade 6' helium (i.e. 99.9999% pure), admixed with argon (Grade 6) to a dilution ratio of 100 ppm (Ar/He). The reason for the inclusion of argon is two-fold: firstly, it is used in the IMRAIRA technique for the analysis of D/H (given above), and secondly, it provides a well-defined signal at m/z 40 thereby aiding mass calibration of the ion trap. The helium/argon supply is contained within two independent gas tanks of a 'sealed-for-life' design, fabricated from titanium alloy using an all-welded construction. Each tank has an internal volume of 300 cm^3 and is filled to a pressure of 50 bar, giving a total volume of gas of 30 l at STP. Once Ptolemy arrives at the comet, the gas will be released into the gas management system by puncturing each vessel using a frangible pillar and Shape Memory Alloy (SMA) actuator and in-line particulate filter, all built into the base of each pressure vessel.

The hydrogen required for the IMRAIRA technique is contained in a stainless steel canister (10 cm^3 at 50 bar) and is metered out through a thermal valve (Dr Hans Lauche, MPS, Lindau, Germany), which also acts as an ultra-low leak rate valve. The flow rate required to achieve full conversion of sample gases into their protonated counterparts is software-controlled through the use of a feedback loop incorporating a pressure sensor, the proportional thermal valve, and an outlet flow restrictor.

Although under the conditions of use there will be no need for conventional vacuum pumping (given earlier), chemical 'getter' pumps will be employed, e.g. calcium oxide to remove residual carbon dioxide, which is a product of the combustion of carbonaceous compounds (given below). Additionally, helium and spent sample gases will exit the ion trap box via a vent to space; this pipe produces an effective pumping speed of some 10 l s^{-1}.

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Figure 2. Photograph of the assembled electrodes of the flight model (FM) of the Ptolemy ion trap. The electrodes are fabricated from aluminium; the electron source and detector are each mounted on supports, one of which is shown above the upper end-cap. The total mass of the electrode assembly together with the ion source and detector is 75 g. (Copyright CCLRC Rutherford Appleton Laboratory, reproduced with permission).

Gas manifold system

The static gas manifold system contains a number of miniature solenoid-activated shut-off valves and pressure transducers, and is shown schematically in Fig. 3. These allow gases to be admitted into the system from the sample oven by diffusion into previously evacuated volumes, and then the samples can be chemically processed. The analytical procedures make use of a series of chemical reactors, which are essentially ceramic tubes containing solid-state chemical reagents, and have a heating element coiled round the outside capable of reaching 1000 °C using 5 W of power. The system is highly compact in order to minimise mass and to eliminate dead volumes. A reaction may typically be the oxidation of carbonaceous material to form carbon dioxide using a supply of oxygen generated on board by heating a mixture of CuO/Cu_2O; essentially this would take the form of a stepped combustion analysis to determine the isotopic compositions of organic materials, such as polymers and macromolecules. Other reactors contain adsorbent materials (given below), drying agents or reagents for generating fluorine (given below), and carbon dioxide.

Connected to the static manifold system are two sources of reference gases, one a gaseous mixture retained by a leak-tight thermal valve, the other solid calcium carbonate which when heated releases carbon dioxide of known isotopic composition. The reference gases can be processed by the analytical system in a manner analogous to sample processing, thereby enabling the sample-to-standard comparison analytical technique to be effected *in situ* on the comet.

Gas chromatography system

The interface between the static manifold and the ion trap is formed by the GC system, comprising a direct analysis channel that allows direct sampling by the mass spectrometer, and a three-channel gas chromatograph with associated injector valves. The operation of the three GC channels may be summarised as follows:

Channel (A): a Varian Chrompack Ultimetal CP-Sil 8CB column whose function is to provide separation of hydrocarbons and organic species;

Channel (B): a Varian Chrompack Ultimetal PoraPLOT Q column to separate gases such as CO_2, CO, CH_4, and N_2. Post-column oxidation by a flow-through reactor containing Rh_2O_3, and a reactor containing molecular sieve drying agent, allow conversion of CO and CH_4 to CO_2. A complex set of procedures allows their constituent carbon, oxygen, and nitrogen isotope ratios to be determined;

Channel (C): A Varian Chrompack Ultimetal Molsieve 5 Å column plus associated reactors, which is used to determine the isotopic composition of water. H_2O is converted to H_2 and CO, the CO gives the $^{16}O/^{17}O/^{18}O$ composition of water, and the H_2 provides the D/H ratio, as described above.

The Ptolemy instrument

The entire Ptolemy instrument, comprising the gas handling and sample processing units, GC, ion trap mass spectrometer, electronic units, and control/data management system, occupies a volume of approximately $250 \times 330 \times 110$ mm^3, weighs 4.5 kg, and consumes less than 10 W of electrical power. Figure 4 shows the flight model with the gas tanks fitted, but with the cover removed. As with all the instruments carried on Rosetta, Ptolemy has been vibration-tested and designed to withstand temperature variations from −55 to +70 °C during its flight to the comet. All the control routines for the entire operation of the mass spectrometer and associated analytical procedures are pre-programmed into EEPROMS, since once the measurements commence, there will be no opportunity for interactive real-time interpretation and response to the data being obtained. However, the EEPROMS can be re-programmed in flight prior to the encounter or between experimental periods, should this be necessary (given below).

For the mission there are essentially three versions of Ptolemy: the actual flight model (FM) that forms part of the Rosetta package now in space, an identical 'qualification model' (QM) mounted in a high vacuum system (10^{-7} mbar) in the laboratory and upon which analytical procedures can be checked and replicated prior to sending signals to the FM
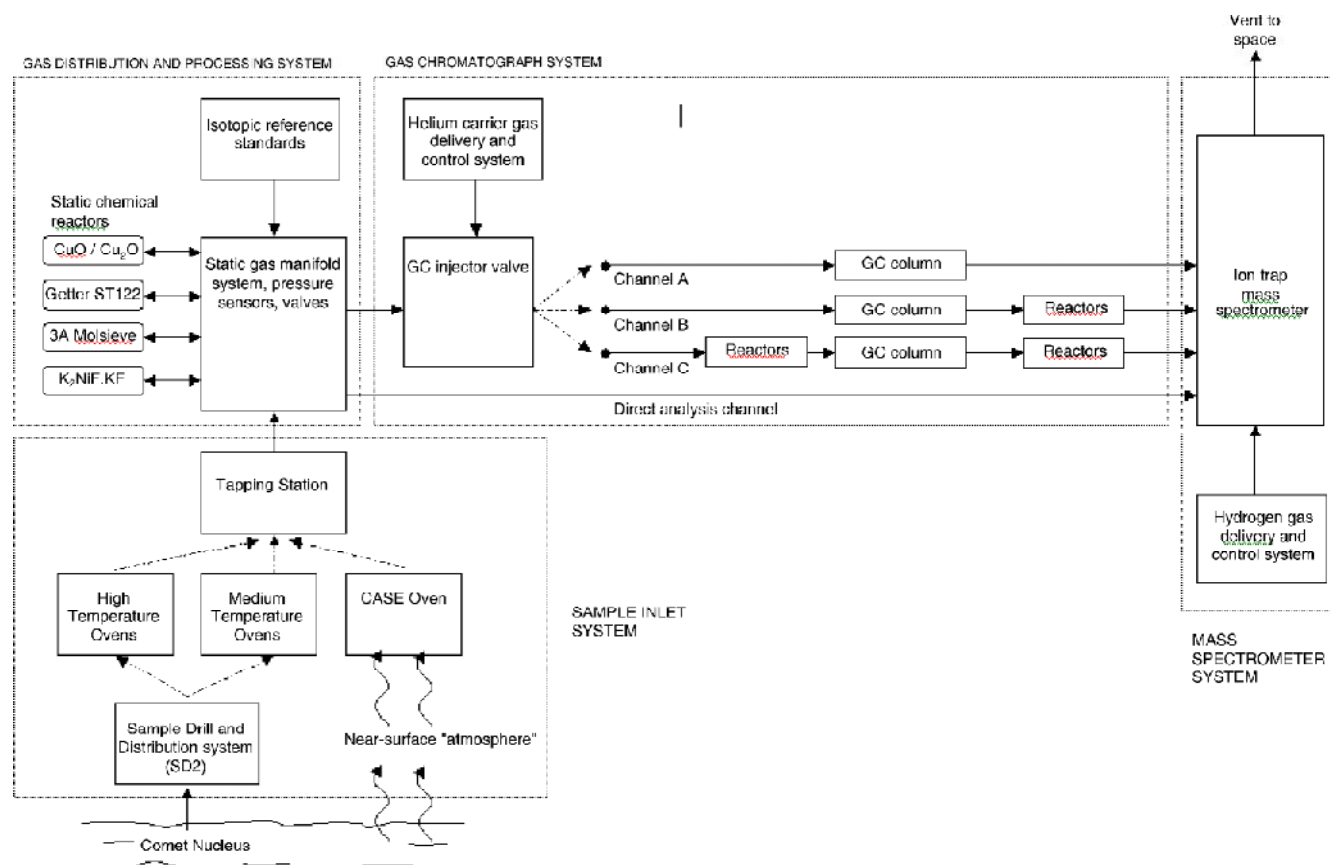
Figure 3. Schematic diagram of the MODULUS Ptolemy experimental system. (Copyright Open University, reproduced with permission).
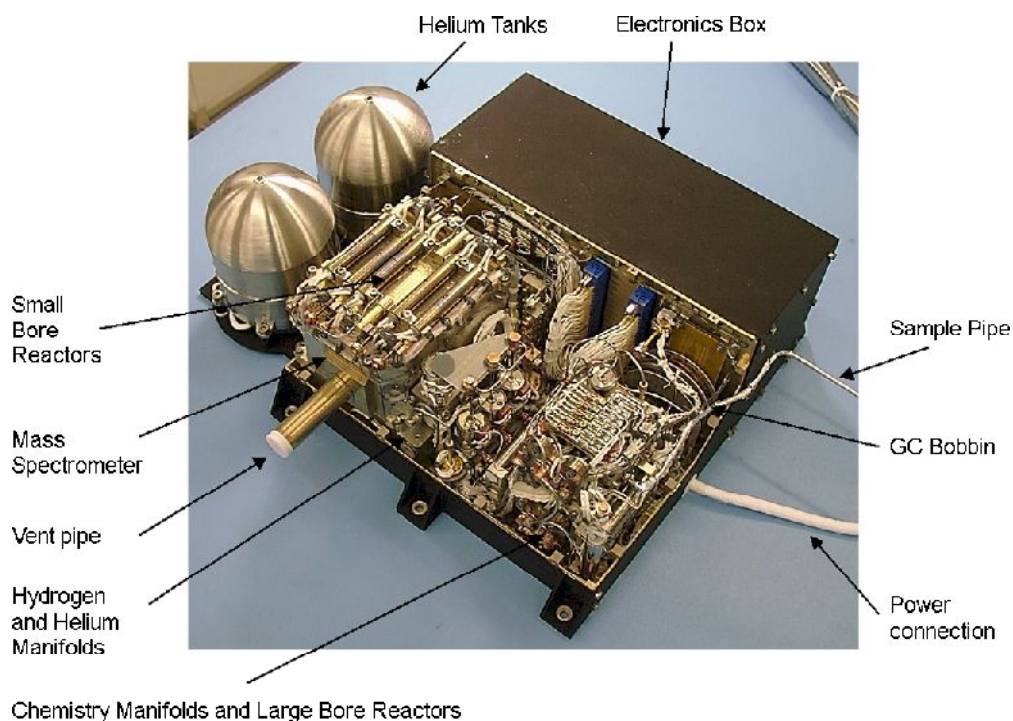

Figure 4. Isometric photograph of the flight model (FM) of the complete MODULUS Ptolemy system with one of the covers removed to reveal the components of the 'mini laboratory'. The complete system (with cover) has a mass of 4.5 kg and consumes less than 10 W of power. (Copyright CCLRC Rutherford Appleton Laboratory, reproduced with permission).

version in Rosetta, and a ground-based electronic simulator reference model with which one can test the transfer of signals prior to their being sent in order to ensure that the correct instructions are being transmitted.

EXAMPLE OF PTOLEMY ANALYTICAL PROCEDURES

A great analytical advantage of Ptolemy is that it represents a miniature chemical laboratory, in which the scope of the analytical experiments that may be performed on cometary material is limited only by the imagination and skill of the operator remote on Earth (and in practical terms by the mission resources of battery power and Lander lifetime). Therefore new analytical procedures are still being developed in the laboratory, using the Ptolemy QM housed in a comet simulation chamber, and comet analogue samples. Below are described just some examples of the scope of analyses available.

A typical analytical procedure might be as follows: A solid sample acquired via the SD2 drilling system is placed in an oven, evacuated and heated (with or without added oxygen) to the first temperature step and held constant for 5 min. Evolved sample gases are released into the static gas manifold system, excess oxygen removed reactively, and the volatiles exposed optionally to a drying agent to remove water. Further treatments are possible, e.g. selective removal of active gases using a 'getter', and the remaining gases are then admitted directly to the ion trap mass spectrometer or passed into one of three parallel GC column systems for separation prior to isotope ratio analysis. Following this mass analysis step, the sample oven is once again evacuated and the temperature increased to that of the next step, and the above procedure repeated.

Two further modes of analysis are possible: near-surface volatile measurement and fluorination to release oxygen from silicate-rich material (possibly the remains of a sample that has been previously pyrolysed as above). For the measurement of the near-surface volatiles, ambient gases are 'trapped' using a carbon molecular sieve, Carbosphere, contained within one of the ovens, which is then heated to release the gases for analysis as indicted previously. For the fluorination experiments, a supply of fluorine is generated by means of the inert solid compound $K_2NiF \cdot KF$ (Asprey's Salt), which when heated to 250 °C yields F_2; this in turn is admitted to the oven containing the solid sample whereupon it reacts to displace [O] from the silicate to produce O_2.

OPERATIONAL SEQUENCE AT COMETARY ENCOUNTER

Shortly after landing, the Control and Data Management System (CDMS) on the Lander instructs Ptolemy to undergo a series of operational and survival checks before entering the *Safe Mode*. The time-sequence of the encounter is divided into two 'major mission phases', where the aim is to take those measurements judged to be of the highest levels of scientific priority.

During the *primary mission phase* immediately after landing, which corresponds to the period $T (= 0)$ to $T + 65$ h,

Ptolemy has been allocated two 6-h operational windows: the first in the period $T + 15$ to $T + 12$ h, and the second in the period from $T + 55$ to $T + 65$ h. The first time-window will be used to perform the highest priority science, namely, analysis of a cometary surface sample using a sequence called the *Science 1* mode (given below). The second time-window will be used for the second priority science project, that is, the analysis of the comet's atmosphere (using the *Science 2* mode). The detailed modes comprise a sequence of instructions in a look-up table stored within the Ptolemy software, and are outlined below.

The *secondary mission phase* corresponds to $T + 65$ h to $T + 100$ h, in which a sample will be taken at the greatest possible depth below the surface of the comet and analysed using the *Science 1* mode (given below). When all the other instruments on board the Lander have met their objectives, the *Science 3* mode will be implemented, namely, oxygen isotope analysis of silicates using the fluorination procedure mentioned previously (this experiment being left till the last owing to the perceived risk to other experiments, though in practice it is considered unlikely that fluorine gas would escape the Ptolemy instrument itself). Further experiments may then be carried out according to the nature of the initial results, and it is planned to continue the analysis of the cometary atmosphere at approximately weekly intervals, depending upon the rate of usage of helium from the storage tanks.

Typical operational modes are summarised as follows, although it is possible that the precise details of the experiments will be modified during the flight period as work continues on the QM version of Ptolemy based in the laboratory.

The *Science 1* sequence:
load sample into oven;
heat oven to −50 °C: dry sample, analyse CO, CO_2, and N_2;
heat oven to +100 °C: analyse H_2O; dry sample, analyse CO, CO_2, and N_2;
heat oven to +400 °C: dry sample, CO, CO_2, and N_2;
prepare oxygen, admit to oven, and heat to +400 °C: analyse CO_2;
heat oven to +800 °C: dry sample, analyse CO, CO_2, and N_2;
prepare oxygen, admit to oven, and heat to +800 °C: analyse CO_2.

The *Science 2* sequence:
a sample from the cometary atmosphere is adsorbed on to Carbosphere contained within one of the ovens;
heat oven to +200 °C;
N_2 isotope analysis;
water isotope analysis;
dry sample;
reference gas isotope analysis;
GC analysis;
isotope analysis of CO and CO_2.

SUMMARY AND CONCLUSIONS

This paper has described the miniaturisation and ruggedisation of a stable isotope analysis laboratory, to be operated

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remotely in one of the most distant and hazardous environments imaginable. Along the way, many new techniques have had to be developed, including the use of an ion trap for a new application, namely, the measurement of stable isotopes of light elements at natural abundance levels. While the world of mass spectrometry must wait until 2014 to see whether Ptolemy is successful in performing its mission, in the meantime much of the technological spin-off from this programme has an abundance of practical applications in real-world applications, where small-scale portable instruments have a vital rôle to play – these applications are already under development.

Acknowledgements

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