

PTOLEMY – AN INSTRUMENT TO MEASURE STABLE ISOTOPIC RATIOS OF KEY VOLATILES ON A COMETARY NUCLEUS*

I.P. WRIGHT¹, S.J. BARBER^{1,**}, G.H. MORGAN¹, A.D. MORSE¹, S. SHERIDAN¹,
D.J. ANDREWS¹, J. MAYNARD¹, D. YAU¹, S.T. EVANS¹, M.R. LEESE¹,
J.C. ZARNECKI¹, B.J. KENT², N.R. WALTHAM², M.S. WHALLEY², S. HEYS²,
D.L. DRUMMOND², R.L. EDESON², E.C. SAWYER², R.F. TURNER²
and C.T. PILLINGER¹

¹*Planetary and Space Sciences Research Institute, Open University, Walton Hall, Milton Keynes,
MK7 6AA, England*

²*Space Science Department, Rutherford Appleton Laboratory, Didcot, Oxford,
OX10 0QX, England*

(**Author for correspondence: E-mail: s.j.barber@open.ac.uk*)

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Abstract. A fundamental goal of cometary studies is to determine the exact relationship between these bodies and the Solar System – the question(s) can be summarised as follows: did comets originate during the same events that spawned the Sun and planets, are they more primitive bodies that record a pre-solar history, or are they interstellar materials collected in relatively more recent times? Now, whatever the origin of comets, it is entirely possible that they could, in part, contain interstellar or pre-solar components – indeed, it seems rather likely in light of the fact that primitive meteorites contain such entities. These particular components are likely to be refractory (dust, macromolecular organic complexes, etc.). Of more relevance to the issues above are the volatile constituents, which make up the bulk of a comet's mass. Since these materials, by their very nature, volatilise during perihelion passage of a comet they can, in some instances, be detected and measured spectroscopically. Perhaps the most useful species for isotopic investigations are C₂, HCN and CN. Unfortunately, spectroscopic measurements can only currently be made with accuracies of ± 10 to $\pm 20\%$. As such it is very often not practical to conclude anything further than the fact that isotopic measurements are compatible with "solar" values, which tends to imply an origin from the margins of the solar accretion disk. But there is another problem with the spectroscopic measurements – since these are made on gaseous species in the coma (and relatively minor species at that) it is impossible to be certain that these represent the true nuclear values. In other words, if the processes of sublimation, active jetting, and photochemistry in the coma impart isotopic fractionation, the spectroscopic measurements could give a false impression of the true isotope ratios. What is required is an experiment capable of measuring isotopic ratios at the very surface of a comet. Herein we describe the *Ptolemy* instrument, which is included on the *Philae* lander as part of the *Rosetta* mission to 67P/Churyumov-Gerasimenko. The major objective of *Ptolemy* is a detailed appraisal of the nature and isotopic compositions of all materials present at the surface of a comet.

Keywords: Rosetta, Philae, comets, stable isotope ratios, gas chromatography, mass spectrometry, ion trap

*This paper is dedicated to the memory of Professor Ray Turner, whose tireless efforts at the early stages of the project laid the foundations for the successful delivery of the *Ptolemy* instrument.

1. Introduction

There are currently just a handful of stable isotope ratio measurements of comets and cometary materials. Some would argue that perhaps the most important of these are the measurements made in the laboratory on cosmic dust collected from the Earth's atmosphere (e.g. McKeegan *et al.*, 1985; McKeegan, 1987) – there is a good case for claiming that at least some of this material is cometary in origin (e.g. Brownlee, 1985; Bradley and Brownlee, 1986; Thomas *et al.*, 1993). Despite valiant efforts to relate the results from laboratory studies to specific comets (Messenger and Walker, 1998) it is unlikely that, in general, it will ever be possible to make unequivocal connections. Notwithstanding this, many useful chemical measurements of comet p/Halley grains were made in situ in 1986 by the PIA and PUMA mass spectrometers on board *Giotto* and *Vega* (Grün and Jessberger, 1990). Indeed, these include carbon isotope ratio measurements of individual grains, which were shown to range from about $^{12}\text{C}/^{13}\text{C} = 1$ to 5000 (Solc *et al.*, 1987; Jessberger, 1989; Grün and Jessberger, 1990). Studies of the samples returned to Earth following the *Stardust* spacecraft's fly-by of p/Wild-2 will undoubtedly advance our knowledge of the refractory grains present in comets. However, no amount of high precision measurements of dust particles collected from the atmosphere, low-Earth orbit, or during sample-return, can help in the quest to derive the overall isotopic compositions of the major volatile species. In this regard, ground-based spectroscopic measurements of coma volatiles, or remote in situ investigations during fly-by or rendezvous missions remain the best hope of satisfactorily resolving questions about cometary origins. We note here in passing the ambitious objectives of *Champollion*, which was originally proposed as part of *Rosetta* (Kerridge *et al.*, 1997; Neugebauer and Bibring, 1998), and which, in a re-cast version of the mission aimed to return to Earth a sample of cometary volatiles for analysis in the laboratory (Weissman, 1997). Unfortunately, the community still awaits the coming of such a daring mission.

Considering firstly the genealogical issue surrounding comets, the most useful measurements that could be made are those that relate to the bulk of cometary matter. In the case of carbon, this means CO and CO₂. Unfortunately it is not possible to determine spectroscopically the lines due to ^{13}CO or $^{13}\text{CO}_2$ ($^{13}\text{CO}^+$ or $^{13}\text{CO}_2^+$) – indeed, for carbon isotope measurements the only lines that can be satisfactorily resolved are at either 473.7 or 474.5 nm ($^{13}\text{C}_2$ Swan bands), 388.3 nm (0-0 B-X band of ^{13}CN), or 345.3398 GHz (six hyperfine components of the HCN(4 – 3) line). Even these are observationally difficult. Previous carbon isotopic measurements based on the C₂ species have been summarised in (amongst others) Wyckoff *et al.* (1989) – these measurements all have fairly generous errors but are considered to be compatible with a Solar System origin for the comets concerned. In the case of CN, notwithstanding a preliminary measurement that appeared to demonstrate a non-solar origin for p/Halley (Wyckoff *et al.*, 1989), it appears that the best estimates of $^{12}\text{C}/^{13}\text{C}$ for p/Halley are 89 ± 17 (Jaworski And Tatum, 1991) and 95 ± 12 (Kleine *et al.*, 1995). There are now data from HCN lines from Hale-Bopp which show

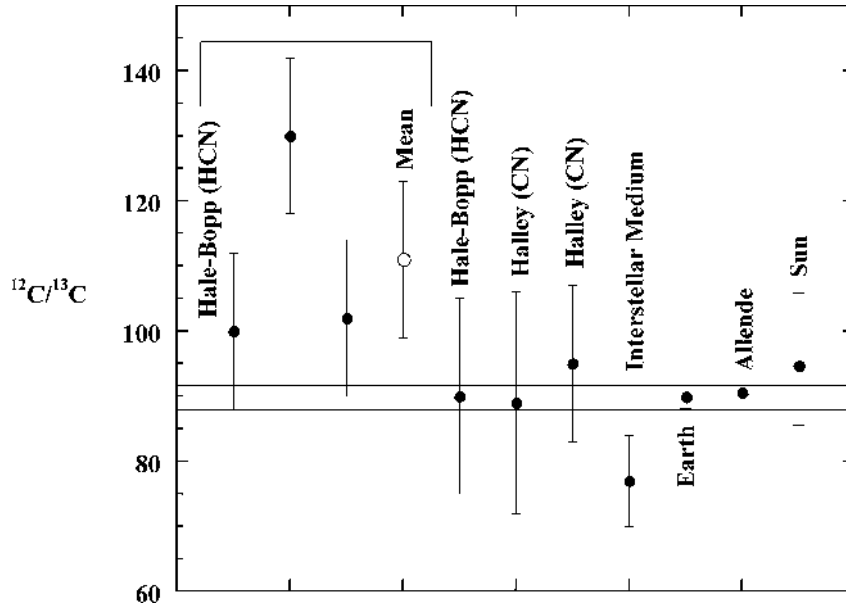


Figure 1. Comparison of carbon isotope ratios measured in comets, compared with data from the interstellar medium, the Sun, Earth and a primitive carbonaceous chondrite (Allende).

$^{12}\text{C}/^{13}\text{C}$ of 90 ± 15 (Lis *et al.*, 1997) and 111 ± 12 (Jewitt *et al.*, 1997). The $^{12}\text{C}/^{13}\text{C}$ data for p/Halley and Hale-Bopp are shown in Figure 1, along with an assessment of the equivalent ratio in the interstellar medium, or ISM (Wilson and Rood, 1994) and further spectroscopic measurements of the Sun's photosphere (Hall, 1973). Also plotted is the typical range of $^{12}\text{C}/^{13}\text{C}$ for materials found on Earth and the value for a bulk carbonaceous chondrite (Allende); in these cases the measurements have been made in laboratories on Earth using mass spectrometry, where individual ratios have uncertainties of $\pm 0.01\%$ (thus, the international reference material, PDB which has a $^{12}\text{C}/^{13}\text{C}$ value of 88.99, could theoretically be measured to an accuracy of ± 0.09 ; in practice isotopic measurements have even smaller uncertainties).

Some conclusions present themselves immediately – firstly some of the cometary data overlap with the value obtained for the ISM. However, since errors are large it is not possible to distinguish these same data from typical solar values. When just the mean value of 3 measurements from the most recent HCN data for Hale-Bopp are considered, it could be concluded that this particular comet shows evidence for a distinctly different $^{12}\text{C}/^{13}\text{C}$ ratio (i.e. being relatively ^{12}C -enriched) from either the solar or ISM values. It should be pointed out that the authors of the Hale-Bopp work (Jewitt *et al.*, 1997) consider that when due account is taken of the errors on the data then no distinction should be made between the $^{12}\text{C}/^{13}\text{C}$ ratio of HCN and

typical solar values. And herein lies the problem – current spectroscopic data are not accurate enough to constrain unambiguously the origins of comets.

There exists an opportunity to rectify the current situation with the *Rosetta* mission. One of the instruments on *Rosetta* aims to address explicitly the question of isotopic compositions – MODULUS (Methods Of Determining and Understanding Light elements from Unequivocal Stable isotope compositions) is a gas sampling device for the analysis of stable isotope ratios at high precisions and accuracies (Wright and Pillinger, 1998), the target isotope ratios being $^{12}\text{C}/^{13}\text{C}$, $^{14}\text{N}/^{15}\text{N}$, $^{16}\text{O}/^{18}\text{O}$, $^{16}\text{O}/^{17}\text{O}$ and D/H. Since MODULUS was originally proposed in three different forms, i.e. on the orbiter, and one on each of the two landers that were originally proposed (see Verdant and Schwehm, 1998, for details of the mission at an earlier stage of development, when it still had 46P/Wirtanen as the target), the three separate instruments were distinguished by different names i.e. *Ptolemy*, *Cleopatra* and *Berenice*, these being some of the cartouches used by Thomas Young and Champollion in deciphering the Rosetta Stone. For various reasons only the variant on the *Philae* lander remains on the mission – the name of the instrument is *Ptolemy*, the operating principle is MODULUS.

The overall *Ptolemy* experiment comprises a suite of analytical channels designed so as to establish the identity, abundance and isotopic compositions of major, minor and trace components. The operational protocol of MODULUS allows determination of the isotope ratios of interest on gaseous species either via direct sampling of the nucleus/coma, or by converting more refractory materials (polymeric organic compounds, dust etc.) to the requisite gas using various thermal and chemical techniques. The isotope ratios are then measured using a novel design of a small mass spectrometer. The ratios will be measured as differential values according to the delta formulation (δ) (Urey, 1947) and referenced to well established and internationally recognised standard materials (e.g. SMOW, PDB, and AIR). It is probably not necessary to make an excessive number of measurements – rather, the most complete exposition is obtained by studying the light elements in all their settings (e.g. volatiles, ices, grains, etc.). In arriving at the above scientific goal, it will therefore be necessary to make some or all of the following measurements: (1) Major volatiles (CO , CO_2 , H_2O , NH_3 (?) etc.), i.e. overall chemical abundances to a few % precision, and isotopic abundances, i.e. $\delta\text{D}_{\text{SMOW}}$, $\delta^{13}\text{C}_{\text{PDB}}$, $\delta^{15}\text{N}_{\text{AIR}}$, $\delta^{17}\text{O}_{\text{SMOW}}$, and $\delta^{18}\text{O}_{\text{SMOW}}$, to precisions of ± 0.5 to 5%, dependent upon the species measured and the sample size (≥ 20 nmol of gas admitted to the mass spectrometer); (2) Minor/trace volatile species (CH_3OH , CH_4 , etc), i.e. chemical abundance to a few % and isotopic abundances where possible; and (3) involatile/refractory species (CHON , silicates, dust, etc), i.e. abundance measurements. The investigations proposed for *Ptolemy* are entirely complementary to the other forms of mass spectrometry on the orbiter of *Rosetta* (viz. ROSINA – Balsiger *et al.*, 1998; COSIMA – Verdant and Schwehm, 1998).

2. Instrument Description

2.1. SYSTEM OVERVIEW

What follows is an overview of the workings of the main elements of *Ptolemy*; a more detailed description of individual components is given in the following section. The essential components of *Ptolemy* are shown in Figure 2. At the front end of the experiment lies SD2, which is the lander's sample drilling and distribution system. Once down on the comet SD2 will be used to obtain a small core of ice/dust from both the near-surface and sub-surface environments (up to 20 cm depth). Solid samples collected in this way will then be delivered to an oven (supplied by MPS, the Max-Planck-Institut für Sonnensystemforschung, Lindau) mounted on SD2's rotatable carousel. Then the carousel rotates to a position whereby a device colloquially referred to as a "tapping station" (supplied by MPS) is used to connect the oven to the inlet of the *Ptolemy* gas processing and distribution system. At this point sample volatiles can be released into the analytical system by heating the oven.

Once gases have been transferred to the gas processing system they are quantified, purified and chemically reacted, where necessary, to produce a relatively simple gas mixture. Gas movement in this part of the system involves diffusion into previously evacuated pipework and volumes. The pressure differential for this process is provided by the localised high pressures accompanying the substrate degassing, and other parts of the gas management system which have been exposed to ambient conditions (i.e. near-cometary space). Although *Ptolemy* does not include a pump, in the conventional sense of the word, the gas management system is able to purge residual gases using chemical pumps such as calcium oxide (which removes CO₂) and getters (which remove most "active gases").

Gases can be passed to the analytical part of the system, which is centred around an ion trap mass spectrometer, either directly or through one of three analytical channels comprising gas chromatography (GC) columns and additional chemical processing modules ("reactors"). For experiments requiring gas chromatography a constant supply of helium (the "carrier gas") is delivered by a regulated supply, which ensures maintenance of the necessary pressure and flow-rate. The helium is used to force the cometary gas mixture through the selected column and associated reactors in order to effect further separation, reaction and purification.

In either mode of operation (direct, or chromatography) the ion trap mass spectrometer is set to perform continuous sweeps over the mass range of interest (which can be anywhere between m/z 12 and 150). The way the device works is to ionise gases as they flow into the chamber which contains the mass spectrometer. Non-ionised gases and excess helium flow to an external vent tube while ionised species become trapped within the electrode structure of the mass spectrometer. Through a combination of rapidly applied radio frequency (RF) potentials to the electrodes the ions are sequentially ejected according to mass-to-charge ratio and detected by an

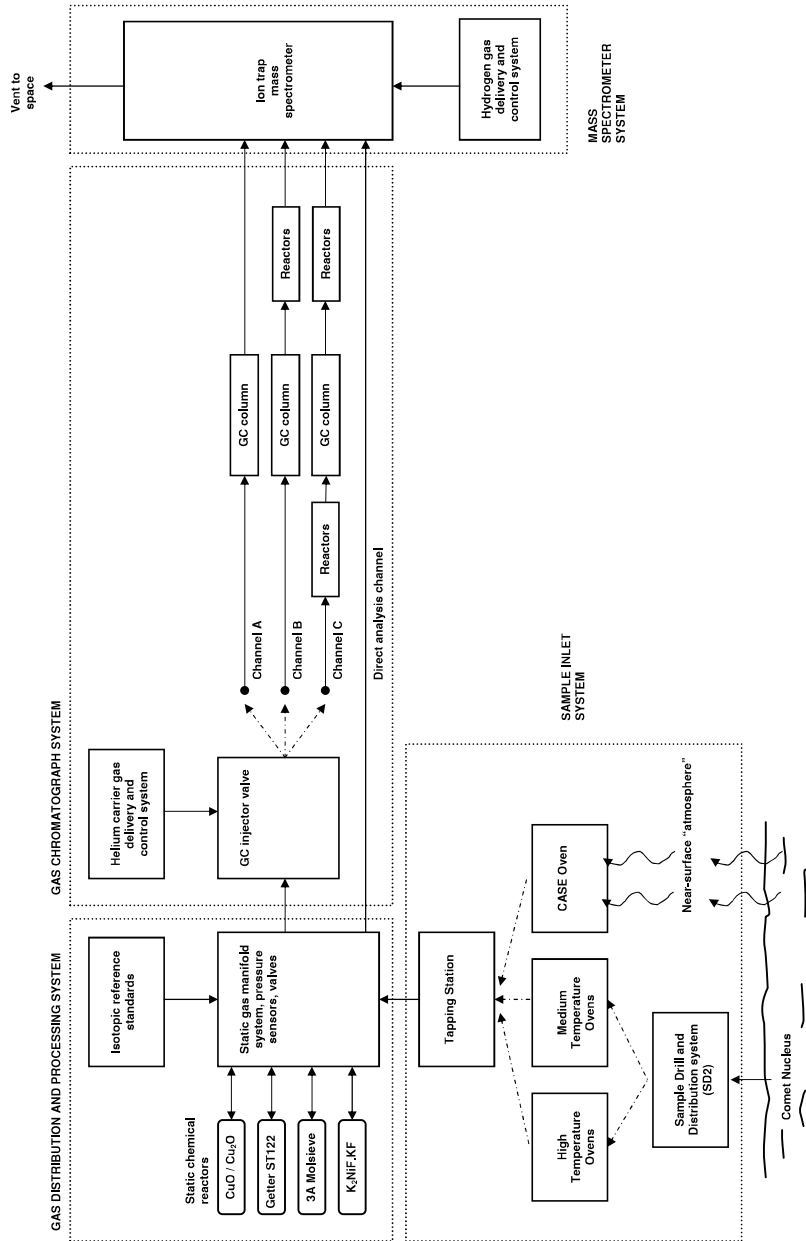


Figure 2. Ptolemy functional diagram.

electron multiplier. The cycle of ionisation, trapping and ejection is then repeated many times; the duty cycle is typically 10 ms.

The ion trap has two main functions: to determine qualitative analytical data (i.e. assess what gases are present in any particular sample) and to measure stable isotope ratios. With the ion trap in a qualitative analytical mode it would be anticipated that the instrument may operate over quite a large mass range (e.g. m/z 12 to 100, 40–150, and so on). In contrast, during isotope ratio determination the mass range will be quite restricted (for instance, $m/z = 43$ to 47 for measurements of $^{12}\text{C}/^{13}\text{C}$ on CO_2 gas, and so on). In either case the ion beam measurements made by the electron multiplier are integrated over a number of consecutive mass sweeps and the appropriate information recorded digitally for subsequent analysis. Since MODULUS aims to obtain isotope ratio measurements of the highest possible precisions, the ion trap instrument will be calibrated in situ during the same period of time over which the cometary analyses are made. For this, equivalent analyses will be made of a reference gas taken from Earth to the comet (and delivered to the instrument through the gas management system). In this way analogous isotope ratio data will be acquired from the reference gas. With knowledge of the actual isotope ratio of the reference it will then be possible to correct the measured cometary data in order to obtain an absolute value for the ratio of interest, through use of the delta notation (Urey, 1947).

2.2. SUB-SYSTEM DESCRIPTION

The *Ptolemy* Flight Model (FM) occupies a volume of approximately $250 \times 330 \times 110$ mm, consumes 10 W average power and weighs 4.5 kg (Figure 3). The instrument may be considered as comprising the following basic elements: a sample inlet system, a gas distribution and processing system, a Gas Chromatograph (GC) system, a Mass Spectrometer (MS) system, and associated control electronics and software.

2.2.1. Sample Inlet System

Ptolemy can analyse both solid samples extracted from the comet surface and sub-surface by SD2's drilling system, and also gaseous samples collected from the tenuous near-comet atmosphere, this being known as the Comet Atmosphere Sampling Experiment – CASE. In either mode, the sample is contained within an “oven”, a small platinum cylinder 6 mm long by 3 mm diameter, wrapped with fine-scale platinum resistance wire (encased in glass). High temperature ovens (HTOs) are designed to achieve the maximum temperature of order $>800^\circ\text{C}$; medium temperature ovens (MTOs) include a window to allow optical analysis of samples by the ÇIVA/ROLIS instruments, but this limits the operation temperature to less than 300°C . The CASE oven is based on an HTO, but includes a small canister containing a small quantity of CarbosphereTM. The interface with *Ptolemy* is via a spherical seal made out of zirconium oxide (i.e. a ball of 4 mm diameter), through

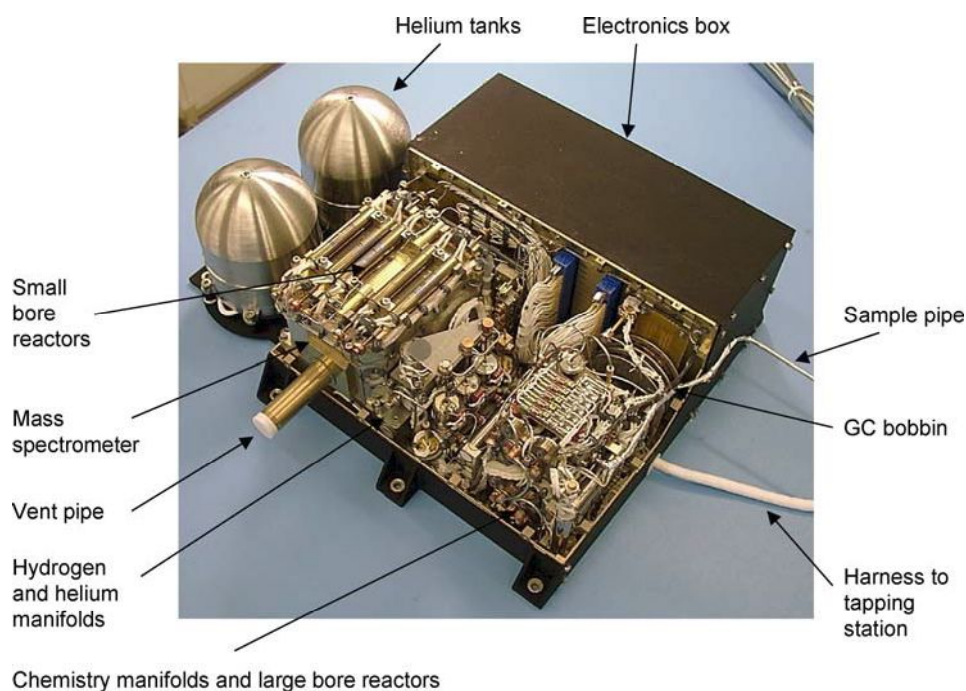


Figure 3. The *Ptolemy* Flight Model—details of the sub-components and overall dimensions are given in the text (image is copyright by the Council for the Central Laboratory of the Research Councils, reproduced with permission).

which is routed the *Ptolemy* sample inlet pipe; the oven is pressed against the zirconium oxide ball by the tapping station. For details of the tapping station and ovens, see Goesmann *et al.*, 2006; the *Ptolemy* tapping station differs only in that it has a single, rather than dual, interfacing ball and pipe. The ovens and their associated carousel and tapping station are, by necessity, located on the cold balcony of the lander; the pipe from the sealing ball is connected to the gas management system (which is in the warm enclosure of the lander) via ~ 150 mm of heated stainless steel pipe. Since the pipe is of the order of 1.6 mm outside diameter, it is sufficiently flexible to allow the movement which accompanies the operation of the sealing mechanism.

2.2.2. Gas Distribution and Processing System

The gas distribution and processing system is based around two lightweight stainless steel manifolds, upon which are mounted various shut-off valves, chemical “reactors” and pressure transducers. The ten shut-off valves are an in-house modification of a commercially available solenoid valve. The reactors are essentially ceramic tubes containing solid-state chemical reagents. A resistance element is coiled around the tube, and a series of outer shields provide thermal insulation. The reactors are capable of heating the contained reagents to ca. 1000 °C using

10W of power. One of the reactors contains Asprey's salt ($K_2NiF.KF$), a source of fluorine gas, so the valves to isolate this reactor are fluorine-tolerant. Everything on the manifolds is optimised so that the interconnections are of the shortest possible length, which not only improves efficiency, but also minimises mass.

The gas manifolds allow the pressure of gas to be manipulated within various parts of the manifold, and allow the sample gases to be chemically reacted to form gaseous species appropriate for subsequent analysis. The manifolds are operated in the "static" sense, in that gases are manipulated through diffusion and expansion into previously evacuated volumes. By contrast, the GC and mass spectrometer sections of the instrument operate in the dynamic mode, in which sample gases are transported in a flowing stream of carrier gas.

2.2.3. Gas Chromatograph System

The GC system comprises the GC columns themselves, with associated pre- and post-column flow-through chemical reactors, plus injection valves and a carrier gas storage and delivery system. The GC injector valves (derived from commercially available portable GC instruments) form the interface between the static gas manifolds and the dynamic GC system. The injector valves are pneumatically operated, and allow a small portion of the gases contained within the manifolds, to be "injected" into a flowing carrier gas stream, and transferred into one of the three GC columns for separation. The columns have been selected to carry out the necessary chromatographic separations; these are explained more fully in the functional description below (Section 3).

The carrier gas flow and the pneumatic supply used to operate the injection valves is provided by the carrier gas supply system, the requirements of which are quite demanding, with design criteria that include the ability to survive several years of the cruise phase in the vacuum of space. To this end a new design of gas tank has been completed. The gas tanks are of a "sealed-for-life" design, in which the carrier gas is sealed within a primary vessel of all-welded construction. On *Ptolemy* there are two identical, independent titanium alloy gas tanks, each of which has an internal volume of 300 cm^3 and is filled with carrier gas to a pressure of 50 bar, giving a total volume of carrier gas of 30 litre at S.T.P. The carrier gas is grade 6 helium (i.e. 99.9999% pure) admixed with grade 6 argon to a dilution ratio of 100 ppm (Ar/He). The reason for inclusion of argon is 2-fold: firstly it is used to aid mass calibration of the ion trap (providing a well-defined signal at m/z 40), and secondly it is implicated in the measurement of D/H ratios (see below).

The leak-tight nature of the primary vessel ensures minimal gas leakage during the long cruise phase. Adjacent to the primary vessel is a secondary manifold, containing a one-shot rupture device developed by CCLRC Rutherford Appleton Laboratory (RAL), which serves to release the carrier gas prior to operations. The rupture device consists of a shape memory alloy metal strip, which when resistively heated reverts to its "memorised" shape and in doing so breaks a hollow titanium

tube, thus releasing the carrier gas into the secondary manifold. In this way energy is required to cause only the initial opening of the tank; after that, helium has the potential to flow continuously from the tank until it is empty.

The flow of helium into the instrument is controlled by thermally-operated valves of a type designed and supplied by H. Lauche (MPS). These thermal valves operate upon the principle of differential thermal expansion: when cold, two stainless steel pipes seal against a sapphire ball and thus prevent gas flow. In contrast, when heated, differential expansion allows carrier gas to flow. In fact variation of the temperature can be used to control the flow rate. During normal operation the thermal valve is heated (typically 0.5 W power) and the carrier gas flows into a plenum chamber and associated pressure sensor. Feedback from the pressure sensor allows for precise setting of the thermal valve heater, and thus the pressure in the plenum chamber can be maintained within $\pm 1\%$ of its target value of 4–6 bar. Gas in the plenum chamber is used to control the operation of the pneumatic GC injector valves, and via a flow restrictor comprising a 0.025 mm I.D. tube provides a constant flow of approximately $1 \text{ cm}^3 \text{ min}^{-1}$ of carrier gas through the GC columns.

2.2.4. Mass Spectrometer System

The ion trap mass spectrometer consists of three electrodes (2 “end caps” and a central ring) constructed from aluminium, along with an ionisation device and an electron multiplier ion detector (Figure 4). The diameter of the trapping volume, which is bounded by the internal dimensions of the central ring, is 16 mm; the height of the volume, bounded by the extremities of the end caps, is 11.3 mm. The overall dimensions of the outer structure of the ion trap assembly are 60 mm diameter by 70 mm height. The mass of the analyser assembly (electrodes plus ion source and detector) was 75 g; together with electronics and structural items the mass spectrometer weighed less than 500 g. Ionisation is via the field effect which can be generated from a 3×2 array of microstructures etched from a silicon wafer; each of the microfabricated units (produced by RAL) comprises an array of 40 by 40 nanotips. Ion detection is accomplished using a novel type of spiral ceramic electron multiplier supplied by H. Lauche (MPS), operated in pulse-counting mode. The ion trap electrode structure is housed in an aluminium box, $80 \times 100 \times 55$ mm (Figure 5), which is vented to space via a tube exiting through the top of the lander. RF generator, high voltage and ion counting electronics are located beneath the analyser assembly; a further mass spectrometer-specific PCB is located within the *Ptolemy* electronics box. Under normal conditions the mass spectrometer is operated with the end caps grounded and the central ring electrode at a voltage between 25 and 300 V. The radio frequency signal applied to the ring is approximately 0.6 MHz.

A characteristic feature of ion traps in general is that ion-molecule reactions in the volume of the instrument are quite prevalent. Under normal circumstances this would be considered quite deleterious for a stable isotope ratio mass spectrometer

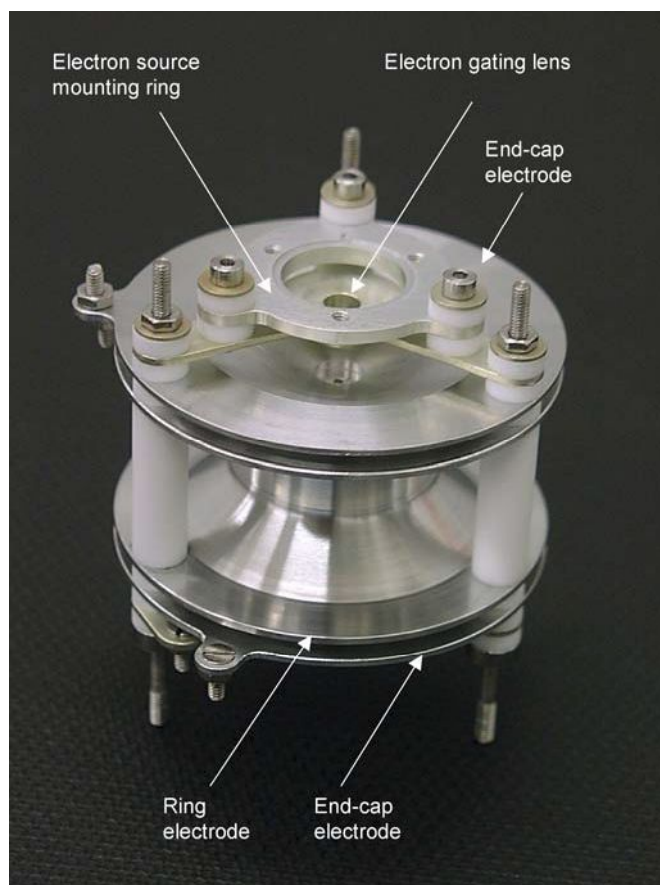
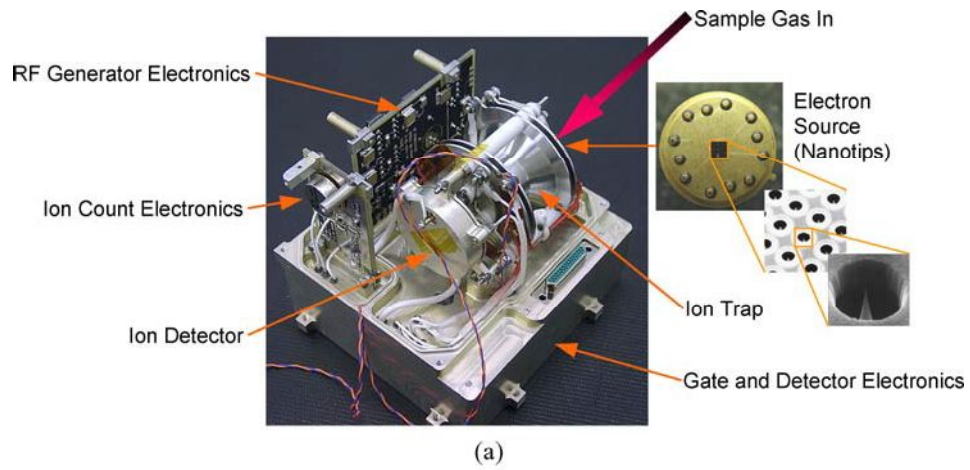
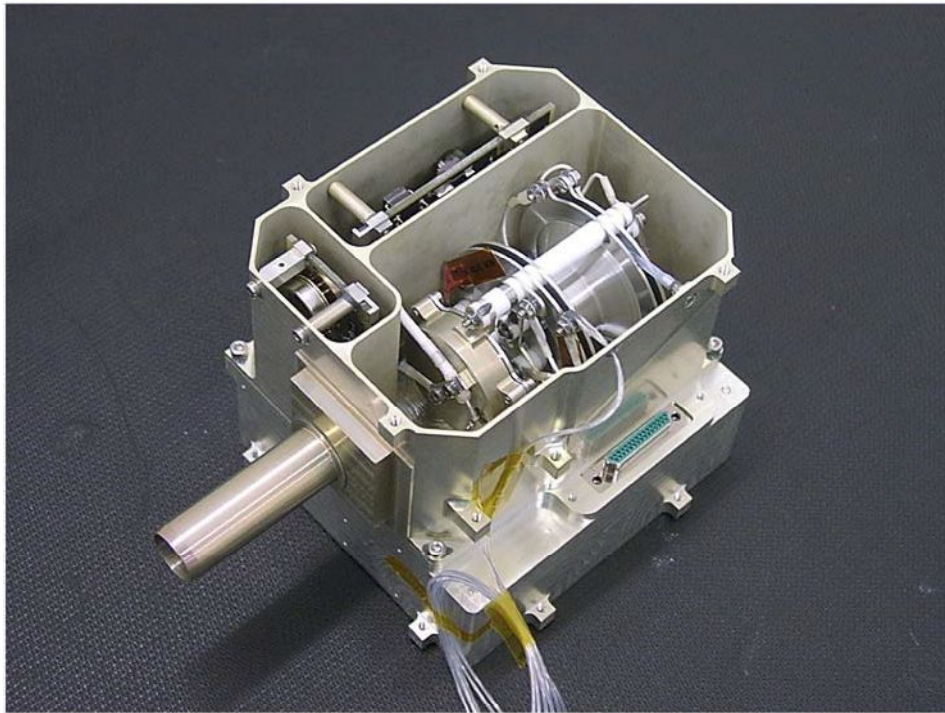


Figure 4. The *Ptolemy* Flight Model ion trap mass spectrometer electrode assembly. The electrodes are machined from aluminium; the electron source and detector are each mounted on supports, one of which is shown above the upper end cap electrode (image is copyright by the Council for the Central Laboratory of the Research Councils, reproduced with permission).

where ubiquitous H_2 and H_2O would react to produce hydride species, in addition to the ions of interest, giving erroneous ratio measurements. For example, $^{12}\text{C}/^{13}\text{C}$ measured on carbon dioxide through determination of m/z 44 ($^{12}\text{CO}_2^+$) and 45 ($^{13}\text{CO}_2^+$) would be considerably in error if the m/z 45 measurement also included a contribution from $^{12}\text{CO}_2\text{H}^+$. For this reason, ion traps have never been previously used to measure stable isotope ratios at natural abundance levels. In order to meet the performance requirements of the *Ptolemy* instrument, we have developed a new technique in which we actually exploit the phenomenon (Barber, 1998). Hence on *Ptolemy* FM we induce ion-molecule reactions by introducing hydrogen gas from a discrete supply, and establish conditions through which we ensure complete conversion of the analyte ion to its hydride counterpart. So, for instance, instead of



(a)



(b)

Figure 5. (a) The *Ptolemy* Flight Model ion trap mass spectrometer with shielding vacuum container removed, showing associated electronics circuits (image is copyright by the Council for the Central Laboratory of the Research Councils, reproduced with permission). (b) *Ptolemy* Flight Model ion trap mass spectrometer in its shielding vacuum container with gas vent pipe, with top lid removed (image is copyright by the Council for the Central Laboratory of the Research Councils, reproduced with permission).

measuring the $^{12}\text{C}/^{13}\text{C}$ ratio on m/z 44 and 45 (as above), we determine instead the ratio from m/z 45 and 46 ($^{12}\text{CO}_2\text{H}^+$ and $^{13}\text{CO}_2\text{H}^+$), and so on.

The process of ion-molecule reactions is also harnessed to make H/D measurements of cometary water. Traditionally in the laboratory the ratio is determined by converting the water to hydrogen gas and then measuring m/z 2 and 3, i.e. H_2^+ and HD^+ . This is a problematic measurement for an ion trap for two reasons: firstly, sensitivity of an ion trap drops off at low values of m/z , and secondly the helium in the carrier gas forms a relatively intense ion beam at m/z 4 ($^4\text{He}^+$), which tails into the region of interest at m/z 3 (and 2). In order to overcome this problem we allow cometary water to enter the ion trap, which in turn reacts with the argon in the carrier gas. We can then subsequently assess the H/D ratio in cometary water by measuring m/z 41 ($^{40}\text{ArH}^+$) and 42 ($^{40}\text{ArD}^+$).

The *Ptolemy* FM mass spectrometer contains a number of consumable items (including ionisation source and detector) and hence performance testing on the FM has been limited to ensure sufficient remaining operational lifetime at the comet. For this reason a full characterisation and calibration programme is underway in Open University laboratories using Prototype Model (PM) and refurbished Qualification Model (QM) instruments. Isotopic precision capabilities of the PM have been demonstrated using the zero enrichment technique to be of the order $\pm 0.5\%$ for 20 nmol quantities of reference gas for $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ (Barber, 1998). Precision for more difficult to analyse species i.e. ^{17}O and D/H may be an order of magnitude poorer by current estimates. Sensitivity of the *Ptolemy* QM has been assessed in a preliminary study. The field effect ionisation source was replaced for reasons of longevity by a standard filament source (operated at an output some one-sixth the design capacity of the FM field effect sources). A typical mass spectrum resulting from the analysis of 20 nmol of CO_2 is shown in Figure 6. Some 50,000 counts are obtained for the CO_2^+ ion at m/z 44, demonstrating that picomole level detection limits are feasible. A detailed calibration programme is underway to fully assess the capabilities of the *Ptolemy* instrument in isotopic and analytical modes.

3. Functional Description

3.1. OPERATING PRINCIPLES

The principal mode of operation of *Ptolemy* is stepped heating of solid samples. A number of different approaches are available for the analysis of solid samples. The simplest is to heat the oven in discrete temperature intervals in a process known as *stepped pyrolysis*. Alternatively, pure oxygen gas (generated by the $\text{CuO}/\text{Cu}_2\text{O}$ reactor) can be admitted to the oven to initiate gas-phase oxidation (an example being the conversion of involatile graphite to gaseous carbon dioxide); as before

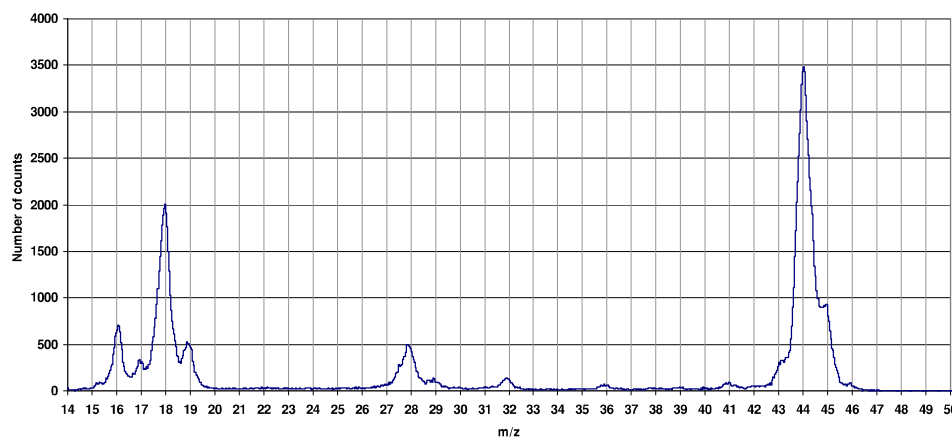


Figure 6. Mass spectrum obtained from *Ptolemy* Qualification Model for the analysis of 20 nmol of CO_2 . Some 55,000 counts are observed for CO_2^+ at m/z 44. Additional peaks due to residual vacuum tank gases and cracking are also evident (i.e. O^+ at m/z 16, OH^+ at m/z 17, H_2O^+ at m/z 18, N_2^+ and CO^+ at m/z 28, CO_2H^+ at m/z 45). The ion trap was operated in a standard state of tune. Improved mass spectral resolution could be readily achieved, if required, through simple software manipulation of the scan function that controls the instrument. Alternatively, a wider m/z range could be selected.

the oven would be heated in stages leading to a *stepped combustion* analysis. The benefit of the stepwise heating approach is that components of differing volatilities, or differing resistances to oxidation, can be analysed separately (e.g. carbon as carbon dioxide ice, organic compounds, or graphite, all liberate CO_2 at different temperatures). This process not only allows an assessment of the nature and relative abundance of the different components present, but also allows stable isotopic measurements to be made on each – this reduces the complexity and ambiguity that would otherwise be involved with the interpretation of bulk, “whole-sample” analyses. One of the main goals of the stepped combustion process will be to analyse the isotopic compositions of “refractory” organic materials (i.e. polymers and macromolecular materials).

Having acquired an appropriate solid sample from the cometary nucleus using the SD2 drill it is deposited in one of the ovens, which is then rotated to line up with the *Ptolemy* tapping station. At this point the oven is sealed and evacuated, and then heated to the first temperature step (with or without added oxygen) and held constant for 5 min. At the end of this interval the evolved sample gases are released into the gas management system, whereupon excess oxygen can be removed through exposure of the gases to the $\text{CuO}/\text{Cu}_2\text{O}$ reactor. The gases are then optionally exposed to the 3 Å molecular sieve reactor, which is a drying agent and acts to remove water. This may be desirable when trace volatiles are to be studied and it is necessary to remove the expected major species. The overall pressure inside the gas management system is measured by a small transducer and, if necessary, gases can be either exposed to a getter (selective removal of all active gases, except methane),

or vented to reduce pressure. The next stage of operation involves either letting gases flow directly into the ion trap mass spectrometer through the direct analysis channel (Figure 2) or injecting them into one of the GC columns. Following on from the admission of the sample gases into the GC and mass spectrometer, the sample oven is once again evacuated and the temperature raised to that of the next step. The procedure of gas processing is then repeated.

In addition to the stepped heating procedure, two further modes of analysis are possible: near-surface volatile measurement (CASE – see Section 2.2.1) and fluorination. For CASE one of the *Ptolemy* ovens contains within it a small quantity of Carbosphere™, a carbon molecular sieve that acts as a gas-trapping medium. By exposing this to the ambient cometary environment it should be possible to collect certain volatiles from the tenuous near-surface atmosphere. This “trapping” process is essentially passive, and relies on the high surface-area of Carbosphere™ coupled with the low temperatures experienced by the oven assembly. After a pre-defined collection period the relevant oven is rotated to the *Ptolemy* tapping station, at which point the cometary gases can be released into the gas management system and analysed according to one of the schemes outlined above. In the case of fluorination, a solid silicate-rich sample (most probably a sample that has already been analysed by stepped heating to some extent) will be reacted at 500 °C with fluorine to produce oxygen gas. This oxygen will then be analysed by the mass spectrometer in order to determine its stable isotopic composition ($^{16}\text{O}/^{17}\text{O}$ and $^{16}\text{O}/^{18}\text{O}$). Whilst it is highly unlikely that the analytical procedure will result in a quantitative yield of oxygen (and thus by default, will not give representative $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values), it is the relative difference between $^{16}\text{O}/^{17}\text{O}$ of the comet and the mean Solar System value that is important. Since this can be gauged by the following relationship, $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$, it is clear that the extent of conversion is unimportant. The dry fluorine gas is produced from an inert solid compound known as Asprey’s salt (K_2NiF_6), through a reversible reaction which is temperature-dependent. Although at first glance the presence of a fluorine generator on *Ptolemy* may be a cause for a certain amount of consternation, it should be noted and appreciated that Asprey’s salt, on a mass basis, contains relatively less fluorine (17%) than Teflon (76%), and has about the same thermal stability. When heated to 250 °C, Asprey’s salt breaks down to give F_2 , which can be admitted to one of the ovens (i.e. containing a sample) and used to displace [O] from silicate minerals to produce O_2 gas (fluorine being more oxidising than oxygen).

As explained previously, once sample gases have been manipulated within the static manifold, they can either be admitted directly into the ion trap via the direct analysis channel, or be injected into one of three channels containing GC columns. Channel A uses an analytical gas chromatography column (Ultimet CP-Sil 8CB 30 m \times 0.25 mm ID, supplied by Varian Chrompack), to allow qualitative measurements of whatever gases are evolved from the sample (these measurements being made in a traditional gas chromatography-mass spectrometry mode). Channel B contains an Ultimet PoraPLOT Q column (Varian Chrompack), 30 m long

× 0.25 mm ID, which acts to separate gases such as CO₂, CO, CH₄ and N₂. Carbon isotopic ratios will be determined either on CO₂ or CO, with a post-column Rh₂O₃ reactor being used to convert CH₄ to CO₂ and CO to CO₂. In order to determine the oxygen isotopic composition of CO₂ and CO, measurements are made in a two-stage process, the first as above, with the Rh₂O₃ reactor at ambient temperature, and the second using the Rh₂O₃ reactor heated so as to effect isotopic exchange of cometary oxygen with that on-board the spacecraft (i.e. from Earth). By measuring the appropriate ratios before and after exchange it is then possible to calculate the 3-isotope composition of oxygen (¹⁶O/¹⁷O, ¹⁶O/¹⁸O). Channel C contains an Ultimet 5Å molecular sieve column, 15 m × 0.25 mm ID (Varian Chrompack), and is primarily used to determine the oxygen isotopic composition of water. In the first instance, gases are passed over a pre-column reactor containing a mixture of platinum and carbon, which converts H₂O to H₂ and CO; measurement of CO gives the 3-isotope composition of oxygen in water whilst the H₂ is used in the process of determining the D/H ratio (see above).

It should be noted that in principle there are many other combinations of reactors and gas chromatographic column settings which can be used to gain information on further cometary volatiles.

3.2. OPERATIONS AT COMETARY ENCOUNTER

The *Ptolemy* instrument is designed to operate by selection of modes initiated by command and then function autonomously. At power on, *Ptolemy* will enter *Safe Mode* and await further commands from the lander Command and Data Management System (CDMS). In *Safe mode* all of the gas processing components (reactors, valves, mass spectrometer) are off, but *Ptolemy* can receive commands for onboard memory management or a command to enter *Standby mode*. In *Standby mode*, all gas-processing components are off, but can be enabled/disabled by commands from the CDMS. The CDMS can also command *Ptolemy* to begin any one of the 16 *Ptolemy* active modes. In detail the active modes consist of a sequence of instructions stored on a look-up table in the *Ptolemy* EEPROM. Each instruction is operated sequentially until the end of the look-up table, whereupon *Ptolemy* returns to *Standby mode*. The exact duration and power requirement of a mode will depend on local conditions as well as the sequence of instructions. At the end of a mode sequence, *Ptolemy* will enter *Standby Mode* to await further commands from the CDMS. Anomalous events will cause *Ptolemy* to enter *Safe Mode*. On entering *Safe Mode*, all gas processing commands are switched off and disabled so that they cannot be inadvertently switched on.

Many of the active modes are used during the cruise phase of the *Rosetta* mission or to prepare *Ptolemy* for science operations. There are five Science modes assigned to Science operations during the comet encounter:

In *Science 1* mode (ice core analysis) *Ptolemy* performs a complete isotopic analysis of a sample delivered to a *Ptolemy* high temperature oven by SD2. The sample is heated in steps and the gases analysed. The sequence is as follows:

Heat oven to -50°C : dry sample, analyse CO, CO₂ and N₂
 Heat Oven to $+100^{\circ}\text{C}$: analyse H₂O, dry sample, analyse CO, CO₂ and N₂
 Heat oven to $+400^{\circ}\text{C}$: dry sample, analyse GC4 trace, CO, CO₂ and N₂
 Prepare oxygen, admit to oven and heat to $+400^{\circ}\text{C}$, analyse CO₂
 Heat oven to $+800^{\circ}\text{C}$: dry sample, analyse GC4 trace, CO, CO₂ and N₂
 Prepare oxygen, admit to oven and heat to $+800^{\circ}\text{C}$, analyse CO₂

The *Science 2* mode (analysis of comet atmosphere) performs a complete isotopic analysis of a sample from the CASE oven containing the adsorbent phase. The sequence is as follows:

Heat oven to $+200^{\circ}\text{C}$: analyse N₂ isotopes, analyse water isotopes
 Dry Sample
 Analyse reference gas isotopes
 GC analysis
 Analyse CO, CO₂ isotopes

Science 3 mode is used for the fluorination of cometary silicates whilst *Science 4* performs measurements using so-called “medium temperature ovens”, which are available on the carousel, but not dedicated to *Ptolemy*. The *Science 5* mode has been set aside for, as yet, unplanned operational sequences.

During the primary mission phase of the lander (i.e. 0 to 65 h after landing) *Ptolemy* has been allocated two operational windows. The primary science for *Ptolemy* is the chemical and isotopic analysis of two comet samples, one from the surface and the second from a sample extracted by SD2 to the greatest possible depth. In the first operational window *Ptolemy* starts by performing a “survival evaluation” mode. If this is successful then *Ptolemy* will operate in various modes to prepare the GC carrier gas, condition the required sample ovens and analyse the reference gas so that the instrument is ready to receive the first sample. It is expected that SD2 will collect a sample from the comet surface and deliver this to one of the four *Ptolemy* high temperature ovens, which will be analysed by operating *Science 1*. *Ptolemy* will be switched off and it is expected that other instruments will be operating during this time. SD2 will then extract a sample from its maximum depth and deliver this to the next *Ptolemy* high temperature oven. This sample will then be measured using *Science 1* during the second allocated operational window. Finally *Ptolemy* will heat the CASE oven containing the adsorbent phase to prepare this oven to begin collecting any comet “atmosphere”.

After the primary mission phase, the main *Ptolemy* objective will be to analyse any trapped comet atmosphere (*Science 2*) and analyse samples using a medium

temperature oven (Science 4) so that ÇIVA can make observations of the sample before and after heating to 180 °C.

At this stage there will be one high temperature oven and several medium temperature ovens remaining. Any following experiments will depend on the results/discoveries from the main mission phase as well as constraints imposed by available power and *Ptolemy* resources such as helium supply and chemical reagents. The CASE oven will be used to sample the comet atmosphere to monitor any changes as the comet approaches perihelion. The duration of this phase depends upon the amount of helium usage from the gas tanks. There are many circumstances which will result in *Ptolemy* not being able to operate (pressure, temperature, available power, helium). It is hoped that after other instruments have met their objectives, *Ptolemy* will be able perform oxygen isotope analysis of silicates (*Science 3*).

4. Summary

Ptolemy is a complete instrument package designed for the analysis of cometary volatiles, refractory organic materials and silicates. Operating under the ethos of MODULUS the objectives for *Ptolemy* are to provide a complete description of the nature and distribution of elements such as H, C, N and O, as well as determining their stable isotopic compositions. *Ptolemy* aims to provide ground-truth measurements of those volatiles which are subsequently detected further out from the nucleus in the coma. By incorporating elements of the proposed *Berenice* orbiter analogue into the *Ptolemy* design, i.e. the CASE experiment, it may be possible to constrain not only the primary isotopic compositions of cometary volatiles, but also the secondary effects which are incurred during sublimation of ices, and gas-gas/gas-solid interactions in the near surface coma.

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