9

AN ION TRAP TOO FAR? THE ROSETTA MISSION TO CHARACTERIZE A COMET*

9.1. INTRODUCTION

At precisely 07:17 Greenwich mean time (GMT) on Tuesday March 2, 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. Although this event captured the fleeting attention of the media at the time, what was not particularly apparent is that one of the instruments with which this survey will be carried out is a mini–chemical laboratory, MODULUS,

*The authors are greatly indebted to Simeon J. Barber, of the Planetary and Space Sciences Research Institute, Open University, Milton Keynes, United Kingdom, for his considerable help in preparing the material for this chapter.

that includes a GC/MS system incorporating an ion trap mass spectrometer specially designed for isotope ratio measurements.

The purpose of this chapter 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 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 millions of miles, effectively frozen in time since the earliest stages of the development program began in 1994! Most mass spectroscopists would expect to have utilized three or four new generations of instruments in a 20-year period and would not normally have to wait two decades 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.

9.2. 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 in ancient Greek, together with 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 take a range of physical and chemical measurements from a comet that is 4600 million years old, even older than the planets in our solar system, in order to try and find clues as to how our Earth was formed. Both the Rosetta project and the Rosetta stone provide the key to unravelling history by comparing the known with the unknown. Hopefully, this twenty-first-century endeavor will offer some of the answers to the question of how life on Earth started.

Rosetta resembles a large aluminum box of dimensions $2.8 \times 2.1 \times 2.0\,\text{m}$ and has two 14-m-long solar panels with a total area of $64\,\text{m}^2$. It comprises two main components: an Orbiter and a Lander. On arrival at its destination in May 2014, Rosetta will orbit 67P in order to map the surface (which is approximately equal in 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 experiments, all controlled by different research groups.

- The *Ultraviolet Imaging Spectrometer (ALICE)* will analyze 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.

- *Comet Nucleus Sounding Experiment by Radiowave Transmission (CONSERT)* will probe the comet's interior by studying radio waves that are reflected and scattered by the nucleus.

- The *Cometary Secondary Ion Mass Analyser (COSIMA)* will analyze the characteristics of dust grains emitted by the comet, such as their composition and whether they are organic or inorganic.

- The *Grain Impact Analyser and Dust Accumulator (GIADA)* will 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).

- The *Micro-Imaging Dust Analysis System (MIDAS)* will study the dust environment around the comet and provide information on particle population, size, volume, and shape.

- The *Microwave Instrument for the Rosetta Orbiter (MIRO)* will determine the abundances of major gases, the surface outgassing rate, and the nucleus sub-surface temperature.

- The *Optical, Spectroscopic and Infrared Remote Imaging System (OSIRIS)* is a wide-angle camera and narrow-angle camera that will obtain high-resolution images of the comet's nucleus.

- The *Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA)* will determine the composition of the comet's atmosphere and ionosphere, the velocities of electrified gas particles, and reactions in which they take part.

- The *Rosetta Plasma Consortium (RPC)* 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.

- *Radio Science Investigation (RSI)*, 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.

- The *Visible and Infrared Mapping Spectrometer (VIRTIS)* will map and study the nature of the solids and the temperature on the surface of the nucleus as well as identify comet gases, characterize 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 fiber. Some of the instruments and subsystems are beneath a hood that is covered with solar cells. An antenna transmits data from the surface to Earth via the Orbiter. The Lander carries the following further nine experiments, including a drilling system to take samples of subsurface 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," will detect α particles and X-rays that will provide information on the elemental composition of the comet's surface.

- The *Rosetta Lander Imaging System (ÇIVA/ROLIS)* is a charge-coupled device (CCD) camera that will obtain high-resolution images during descent and stereo panoramic images of areas sampled by other instruments. Six identical microcameras will take panoramic pictures of the surface, and a spectrometer will study the composition, texture, and albedo (reflectivity) of samples collected from the surface.
- *Comet Nucleus Sounding Experiment by Radiowave Transmission (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.
- *Cometary Sampling and Composition experiment (COSAC)* is one of two evolved gas analyzers. It will detect and identify complex organic molecules from their elemental and molecular composition.
- The *Evolved Gas Analyser (MODULUS Ptolemy)* is the second evolved gas analyzer and will obtain precise measurements of stable isotope ratios of the light elements H, C, N, and O in their various forms within material sampled from the comet subsurface, surface, and near-surface atmosphere.
- The *Multi-Purpose Sensor for Surface and Subsurface Science (MUPUS)* will use sensors on the Lander's anchor, probe, and exterior to measure the density and thermal and mechanical properties of the surface.
- The *Rosetta Lander Magnetometer and Plasma Monitor (ROMAP)* 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)*, which will drill more than 20 cm into the surface, will collect samples and deliver them to different ovens for evolved gas analysis by COSAC and Ptolemy and microscope inspection by CIVA/ROLIS.
- The *Surface Electrical, Seismic and Acoustic Monitoring Experiments (SESAME)* use three instruments to measure 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 these 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 predetermined schedule when the cometary encounter commences (see also below). Furthermore, communication with the instrumentation has to be coordinated through a scientific command center and then through mission control using special software and 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 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 United

TABLE 9.1. Time Sequence for Rosetta Mission

Date	Event
March 2, 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 maneuver
November 2014	Landing on comet
December 2015	Escorting comet; end of mission

Kingdom are almost five steps removed from direct control of their mass spectrometer and associated equipment. Added to this complexity, the 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 9.1. The fly-by stages are a means by which the space module gains speed, rather like a child swinging around 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 harpoons 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 reprogrammed; the additional cost of the delay has been estimated at 70 million Euros!

9.3. 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 Colin Pillinger and his coinvestigators of the Planetary and Space Sciences Research Institute at the Open University in the United Kingdom in honor 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 may be interested to note that Berenice and Ptolemy were subjects of the inscriptions on the Rosetta stone.

9.3.1. 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 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 in ovens according to preprogrammed protocols so as to generate evolved gases at predetermined temperatures that will then be converted (if necessary) chemically into compounds such as H_2, O_2, 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]:

$$\delta(\text{rare isotope}) = \left[\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right] \times 1000\%o \qquad (9.1)$$

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), and so on. As a result, all the determinations on the sample data must be directly compared with contemporary measurements on appropriate standard "onboard" 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 maximize the accuracy and precision of the data.

9.3.2. The Ion Trap Mass Spectrometer as the Instrument of Choice

Normally, to obtain the most accurate and precise 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. However, since the total payload and physical space available were severely limited, given all the other instrumentation being carried by Rosetta and the associated power requirements, alternative instruments 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 RF drive potential), and its tolerance to moderately high pressures ($\sim 10^{-3}$ 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) made this the obvious mass analyzer of choice. Fortuitously, 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 $\sim 10^{-3}$ mbar at point of closest solar approach. A further advantage is that the ion accumulation time can be adjusted to allow the buildup of ions from the minor isotopes, thus increasing the precision of their measurement. In the final design, a nonstretched ion trap ($r_0 = 8.0$ mm; $2z_0 = 11.3$ mm) having grounded end-cap electrodes has been employed, operating at a nominal RF drive frequency of 0.6 MHz and amplitude variable between approximately 25 and 300 $V_{0\text{-p}}$; the exact frequency will be determined by a self-tune feature, which selects the most appropriate frequency depending upon the ambient temperature and hence tuning of the RF circuit. These parameters offer a mass/charge ratio range of 12–150 Th, allowing both general sample characterization (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. To reduce complexity and power demands and indeed mass, there is no provision for DC isolation or resonant excitation experiments. Similarly, though the ionization time is preselectable in the range 0.1–5 ms, there is no provision for AGC (see Chapter 3). Although this may appear to suggest a very basic ion trap system, reminiscent of the original Finnigan ITD 700 instrument, 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, and so on, to achieve the desired level of performance. It should also be noted that the Ptolemy ion trap is operating at rather low mass/charge ratios (isotopic analyses are conducted at $m/z < 50$) compared to laboratory instruments targeted at organic analyses. 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 aluminum, cut away to reduce the mass, and the overall external dimensions of the analyzer are 60 mm diameter $\times$ 70 mm height (see Figure 9.1). To minimize power consumption and provide some redundancy in this vital area, ionization is effected by a beam of electrons generated from a 3×1 array of microstructures etched from a silicon wafer; each of the microfabricated units comprises an array of 40×40 nanotips [2] and ion detection is accomplished
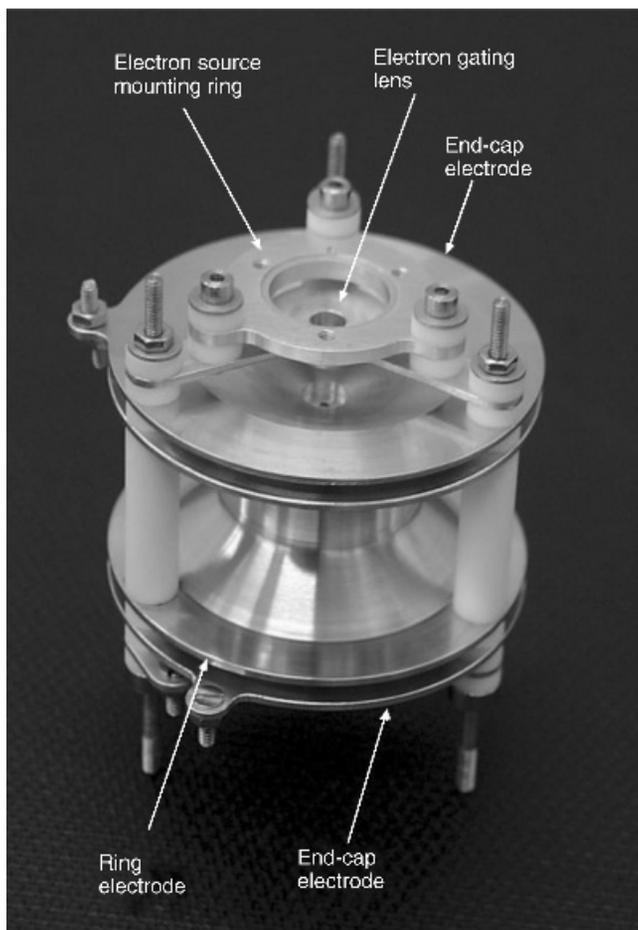
Figure 9.1. Photograph of assembled electrodes of flight model (FM) of Ptolemy ion trap. The electrodes are fabricated from aluminum; the electron source and detector are each mounted on supports, one of which is shown above upper end cap. Total mass of electrode assembly together with ion source and detector is 75 g. (Copyright The Central Laboratory of the Research Councils, reproduced with permission.)

using a novel type of spiral ceramic electron multiplier operating in the pulse-counting mode and developed by the Max-Planck-Institut für Aeronomie (MPAe), Lindau, Germany. The mass of the analyzer assembly (electrodes plus ion source and detector) was 75 g; including electronics and structural items the ion trap weighed less than 500 g. An illustration of the flight version of the ion trap with its associated ionizer, detector, and electronic circuits is shown in Figures 9.2*a* and *b*.

The supply of helium, used variously as the carrier gas, actuator for the pneumatic valves, and 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
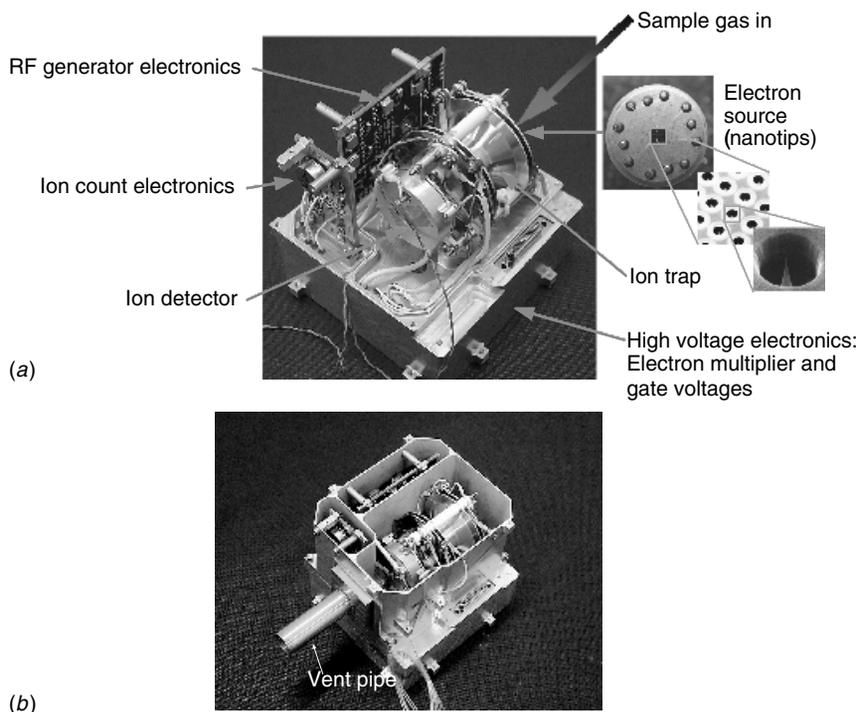
(a)

(b)

Figure 9.2. (a) Isometric photograph of the FM of the Ptolemy ion trap with its associated electronic circuits but with shielding container removed. (Copyright The Central Laboratory of the Research Councils, reproduced with permission.) (b) Isometric photograph of the FM of the Ptolemy ion trap with its associated electronic circuits, showing the lower half of shielding container and gas vent pipe. (Copyright The Central Laboratory of the Research Councils, reproduced with permission.)

for the inclusion of argon is twofold: first, it is used to aid mass calibration of the ion trap (providing a well-defined signal at m/z 40) and, second, it is employed in the measurement of D/H ratios (see below). The helium/argon supply is contained within two independent gas tanks of a "sealed-for-life" design fabricated from titanium using an all-welded construction. Each tank has an internal volume of 30 cm^3 and is filled to a pressure of 50 bars, giving a total volume of gas of 30 liters at standard temperature and pressure (STP). Once Ptolemy arrives on site, the gas will be released in 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. Although under the conditions of use there will be no need for conventional vacuum pumping (see earlier), chemical "getter" pumps will be employed, for example, calcium oxide to remove carbon dioxide. The entire Ptolemy instrument, comprising the sample collection system,
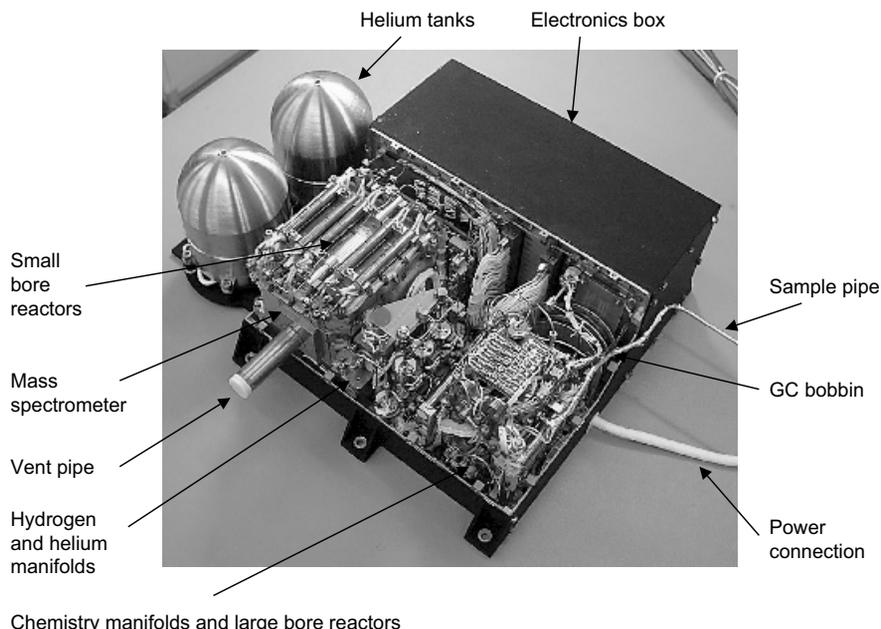
Figure 9.3. Isometric photograph of the FM of the complete MODULUS Ptolemy system with one cover removed to reveal the components of the "mini-laboratory." The complete system (with cover) has mass of 4.5 kg and consumes less than 10 W of power. (Copyright The Central Laboratory of the Research Councils, reproduced with permission.)

gas-handling and sample-processing units, gas chromatograph, ion trap mass spectrometer, electronic units, and control/data management system, occupies a volume of approximately $250 \times 330 \times 110$ mm, weighs 4.5 kg, and consumes less than 10 W of electrical power. Figure 9.3 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 of -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 preprogrammed 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 reprogrammed in flight prior to the encounter or between experimental periods should this be necessary (see also 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 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 to ensure that the correct instructions are being transmitted.

9.3.3. Sample Processing and Isotope Ratio Measurements

9.3.3.1. Ion Trap Operation   From the preceding discussion we have seen that early in the planning stage it was determined that the QIT mass spectrometer offered considerable advantages over other alternative analyzers, for example, magnetic-sector, time-of-flight, and quadupole mass filter. However, at this time (1995–1998) there were no literature reports on the use of the ion trap for isotope ratio determinations. An intensive program was undertaken, therefore, to fully characterize and evaluate this novel application [3, 4].

Key figures of merit in relation to isotope ratio determinations are the abundance sensitivity, accuracy, and precision associated with the measurements. The *abundance sensitivity* is a measure of the extent to which the mass spectral peak tail from a lighter major isotope contributes to the height of the adjacent peak arising from the minor isotope, for example, the contribution made by the peak at *m/z* 44 (^{12}C $^{16}O_2^+ \cdot$) to the peak at *m/z* 45 (^{13}C $^{16}O_2^+ \cdot$) in carbon dioxide. Ideally, for a minor isotope of 1% abundance, the contribution to the measured intensity from the major isotope should be <0.01%. This parameter is clearly determined by the resolution of the mass spectrometer. The *accuracy* is a measure of the ability of the instrument to determine the "true" isotopic ratio of the sample. In the present application, this factor is not regarded as being highly critical since, as noted above, comparisons are being made contemporaneously with calibrated reference samples. Of much greater importance is the *precision*, which is determined by the reproducibility of the measurements. This parameter may be determined by the zero-enrichment (ZE) technique, whereby many repeat measurements are made of the same isotopic ratio and then Eq. (9.1) is applied to each pair of consecutive ratios, in which the *n*th ratio is taken as being $R_{standard}$ with respect to the (*n*+1)th ratio as R_{sample}. Ideally the value of δ(ZE) should be zero. Thus for, say, 50 repeat measurements of R one would obtain 49 values of δ(ZE), and the precision can then be evaluated from the standard error of the mean of the set of consecutive measurements. While with a terrestrial magnetic-sector isotope ratio mass spectrometer one would hope to achieve precisions corresponding to one standard deviation of much better than ±1‰, for the Rosetta mission a precision of ±5‰ was specified as being acceptable. Hence the characterization and optimization of the ion trap mass spectrometer were carried out with ±5‰ as the target level of performance.

The initial experiments were carried out with a standard Finnigan MAGNUM ion trap combined with a Varian Model 3400 gas chromatograph equipped with a Model 1075 split/splitless injector. "Pure" samples of gases were admitted via a "sniffer" system at a rate of approximately 1 nmol/s, and the peak intensity ratios determined for mass/charge ratio values 29/28 for nitrogen, 33/32 and 34/32 for oxygen, and 45/44 and 46/44 for carbon dioxide. Numerous experiments were carried out to explore the effects of helium buffer gas pressure and space charge on the quality of the data obtained, but essentially the measured isotope ratios showed extremely low accuracy, with some values being in error by more than 100% compared to the

expected values! The problem appeared to stem from at least three fundamental issues: insufficient resolution of the QIT, insufficient number of digital steps (DAC steps) controlling the RF drive amplitude across the mass spectral peaks, and the occurrence of ion/molecule reactions within the ion trap.

To overcome the first two, instrumental inadequacies, a new instrument control system and associated software were developed, called ACQUIRE (Advanced Control of the Quadrupole ion trap for Isotope Ratio Experiments); this allowed the scan speed to be reduced to 2000 Th/s (i.e., about three times slower than that of the standard trap) and the number of DAC steps to be increased from around 8 to 23 for each "mass unit."

While these modifications gave substantially improved mass spectral resolution and peak shapes, they did not address the remaining serious problem, namely the fact that the ions being studied were effectively "changing mass" through the occurrence of ion/molecule reactions with background gases, especially water, within the ion trap. For example, the $CO_2^{+\cdot}$ ion will react with H_2O according to

$$CO_2^{+\cdot} + H_2O \rightarrow CO_2H^+ + OH^\cdot \tag{9.2}$$

with an ergicity $\Delta_r H = -65\,kJ/mol$ [5]. As a result, depending upon the degree of conversion, the ion peak at m/z 45 will contain unknown proportions of $^{12}CO_2H^+$ and $^{13}CO_2^{+\cdot}$. Inevitably, without being able to resolve the "doublet" at m/z 45, the "measured" proportion of ^{13}C in the sample will be significantly exaggerated. In analogous reactions with H_2O, $CO^{+\cdot}$ forms COH^+ ($\Delta_r H = -137\,kJ/mol$) and $N_2^{+\cdot}$ forms N_2H^+ ($\Delta_r H = -186\,kJ/mol$). On the other hand, the corresponding reaction of $O_2^{+\cdot}$ with H_2O is not thermodynamically favorable ($\Delta_r H = +224\,kJ/mol$).

One possible solution to this problem in the Ptolemy instrument would be to attempt to remove all hydrogen-containing species from the trap. But given that the major constituent of the comet is ice, this was regarded as being impractical. The alternative approach, which was adopted in the flight system, has been to attempt to force complete protonation of each of the isotopic species by adding hydrogen gas to the helium buffer gas stream. Isotope ratios may then be measured on the protonated ions, thereby eliminating the isobaric interferences.

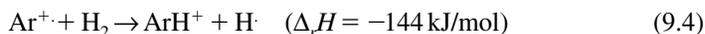Reactions analogous to those described in reaction (9.2) with H_2O occur with H_2:

$$M^{+\cdot} + H_2 \rightarrow MH^+ + H^\cdot \tag{9.3}$$

for $M^{+\cdot} = CO_2^{+\cdot}$ ($\Delta_r H = -128\,kJ/mol$), $CO^{+\cdot}$ ($\Delta_r H = -200\,kJ/mol$), and $N_2^{+\cdot}$ ($\Delta_r H = -249\,kJ/mol$); with $O_2^{+\cdot}$ the reaction is again thermodynamically unfavorable ($\Delta_r H = +161\,kJ/mol$).

In the initial investigations using the modified MAGNUM ion trap mass spectrometer controlled by the ACQUIRE system [3], pure hydrogen was used in place of helium as the buffer gas at a flow rate of ~1 ml/min. Substantially improved isotope ratio data were obtained: isotope ratios within +18‰ for (m/z 46)/(m/z 45) and −55‰ for (m/z 47)/(m/z 45) of the "theoretical" values for CO_2 were obtained using 47-nmol amounts of sample, with precisions determined by the ZE technique of ±4‰ and ±5‰, respectively.

In the flight model 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 toward hydrogen, isotopic measurements using oxygen ions are carried out on the nonhydrogenated $O_2^{+\cdot}$ species. To conserve both power and space, the dimensions and frequency of the RF drive potential were reduced from the standard values employed on the MAGNUM instrument ($r_0 = 10.00\,mm$, $2\pi\Omega = 1.05\,MHz$) to those noted above (8.00 mm and 0.6 MHz, respectively).

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 characterizing cometary water. Normally, in a terrestrial laboratory using magnetic-sector instruments for isotopic work, the ratio of 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 $H_2^{+\cdot}$ and $HD^{+\cdot}$, respectively. However, the sensitivity of ion traps falls off at low mass/charge ratios; furthermore, hydrogenation reactions of the kind noted above lead to the facile formation of H_3^+ and H_2D^+ at m/z 3 and 4, respectively. Since the helium buffer gas will also yield ions at m/z 4 (i.e., $^4He^{+\cdot}$), there is clearly scope for considerable inaccuracies in such measurements, and an alternative approach must be adopted when using the ion trap mass spectrometer.

Hence a second novel technique for utilizing ion/molecule reactions to aid isotope ratio measurements was proposed. Fortunately, the reactions

$$Ar^{+\cdot} + H_2 \rightarrow ArH^+ + H^\cdot \quad (\Delta_r H = -144\,kJ/mol) \qquad (9.4)$$

and

$$Ar^{+\cdot} + H_2O \rightarrow ArH^+ + OH^\cdot \quad (\Delta_r H = -81\,kJ/mol) \qquad (9.5)$$

are both thermodynamically permitted, so that deuterium and hydrogen can be assayed in terms of the ratio of the intensities of the ArD^+ and ArH^+ ions at m/z 42 and 41, respectively. It should be noted that ions from the minor isotopes of argon, namely $^{36}Ar^{+\cdot}$ and $^{38}Ar^{+\cdot}$, will form adducts with H and D at m/z 37, 38, 39, and 40, but these will not cause isobaric interferences with the measured ions at m/z 41 and 42. As mentioned above, in Ptolemy the source of argon used for these experiments is the high-purity helium/argon buffer gas mixture.

9.3.3.2. Sample Processing and Analysis

The analytical procedures make use of a series of chemical reactors connected by a compact manifold containing miniature solenoid-activated shut-off valves and pressure transducers. The reactors 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 minimize 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 (see below), drying agents or reagents for generating fluorine (see below), and carbon dioxide. Cylinders containing reference gases are also connected to the manifold. A schematic diagram of the experimental system is shown in Figure 9.4.

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, for example, selective removal of active gases using a "getter," and the remaining gases 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 pyrolyzed 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 that 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 Asprey's Salt, $K_2NiF \cdot KF$, 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.

As noted above, there are three GC channels whose operation may be summarized as follows:

Channel A: A Varian Chrompack Ultimetal CP-Sil 8CB column whose function is to provide general analysis of evolved gases.

Channel B: A Varian Chrompack Ultimetal PoraPLOT Q column in line with two reactors containing Rh_2O_3 reactor molecular sieve drying agent. This arrangement separates gases such as CO_2, CO, CH_4, and N_2, while CO and CH_4 are converted to CO_2; a complex set of procedures allows 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. The 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.
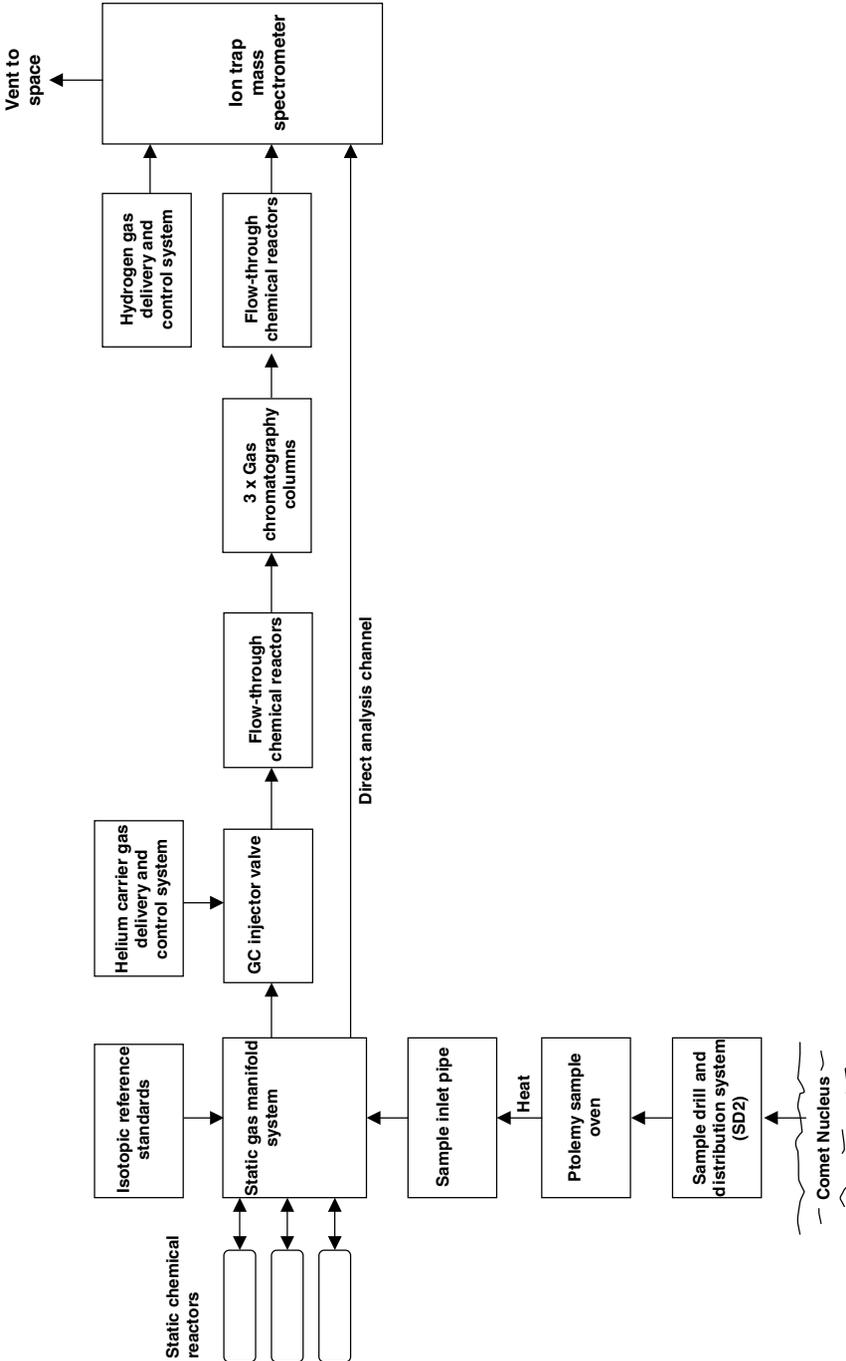
Figure 9.4. Schematic diagram of MODULUS Ptolemy experimental system. (Copyright by the Open University, reproduced with permission.)

9.3.3.3. 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 $T + 15$ min to $T + 12$ h, the second in the period from $T + 55$ h 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 (see 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 analyzed using the *Science* 1 mode (see 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. 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 summarized 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 and analyze CO, CO_2, and N_2.
  Heat oven to $+100°C$: Analyze H_2O and dry sample, 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 $+400°C$: Analyze CO_2.
  Heat oven to $+800°C$: Dry sample and analyze CO, CO_2, and N_2.
  Prepare oxygen, admit to oven, and heat to $+800°C$: Analyze 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 $+200°C$.
  Analyze N_2 isotopes.
  Analyze water isotopes.
  Dry sample.
  Analyze reference gas isotopes.

GC analysis.

Analyze isotopes of CO and CO_2.

9.3.4. Summary and Conclusions

The aim of this chapter has been to show how the ion trap mass spectrometer has been adapted to obtain precise stable isotope ratio measurements. Furthermore, the instrument has been combined with a miniaturized and ruggedized automated chemical laboratory capable of working entirely under automated control in the ultimate remote hostile environment. The world of mass spectrometry will watch with bated breath to see whether Ptolemy is successful in performing its mission; in the meantime much of the technological spin-off from this program must surely have an abundance of practical applications in real-world applications, where small-scale portable instruments have a vital role to play?

ACKNOWLEDGMENT

REFERENCES

1. H. C. Urey, The thermodynamic properties of isotopic substances, *J. Chem. Soc.* (1947) 562–581.

2. B. J. Kent, E. Huq, J. N. Dominey, A. D. Morse, N. Waltham, The use of microfabricated field emitter arrays in a high precision mass spectrometer for the Rosetta missions, paper presented at the Third Round Table on Micro/Nano Technologies for Space, ESTEC, May 15–19, 2000.

3. S. J. Barber, A. D. Morse, I. P. Wright, B. J. Kent, N. R. Waltham, J. F. J. Todd, C. T. Pillinger, Development of a miniature quadrupole ion trap mass spectrometer for the determination of stable isotope ratios, in E. J. Karjalainen, A. E. Hesso, J. E. Jalonen, U. P. Karjalainen (Eds), *Advances in Mass Spectrometry*, Vol. 14, Elsevier Science, Amsterdam, 1998.

4. S. J. Barber, Development of a quadrupole ion trap mass spectrometer for the determination of stable isotope ratios: Application to a space-flight opportunity, Ph.D. Thesis, Open University, Milton Keynes UK, 1998.

5. D. R. Lide (Ed.), *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 1995.