COSAC, THE COMETARY SAMPLING AND COMPOSITION EXPERIMENT ON PHILAE

FRED GOESMANN[1,*], HELMUT ROSENBAUER[1], REINHARD ROLL[1],
CYRIL SZOPA[2], FRANCOIS RAULIN[3], ROBERT STERNBERG[3], GUY ISRAEL[2],
UWE MEIERHENRICH[4], WOLFRAM THIEMANN[5] and GUILLERMO
MUNOZ-CARO[6]
[1]*Max Planck Institute for Solar System Research, Katlenburg-Lindau, Germany*
[2]*Service d'Aéronomie du CNRS, Verrières-le-Buisson, France*
[3]*LISA, Laboratoire Interuniversitaire des Systèmes Atmosphériques, Créteil, France*
[4]*Université de Nice-Sophia Antipolis, Laboratoire Arômes, Synthèses et Interactions et Laboratoire de Chimie Bioorganique, Nice, France*
[5]*University of Bremen, Bremen, Germany*
[6]*Centro de Astrobiología, INTA-CSIC, Madrid, Spain*
*(*Author for correspondence: E-mail: goesmann@mps.mpg.de)*

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Abstract. Comets are thought to preserve the most pristine material currently present in the solar system, as they are formed by agglomeration of dust particles in the solar nebula, far from the Sun, and their interiors have remained cold. By approaching the Sun, volatile components and dust particles are released forming the cometary coma. During the phase of Heavy Bombardment, 3.8–4 billion years ago, cometary matter was delivered to the Early Earth. Precise knowledge on the physico-chemical composition of comets is crucial to understand the formation of the Solar System, the evolution of Earth and particularly the starting conditions for the origin of life on Earth. Here, we report on the COSAC instrument, part of the ESA cometary mission Rosetta, which is designed to characterize, identify, and quantify volatile cometary compounds, including larger organic molecules, by in situ measurements of surface and subsurface cometary samples. The technical concept of a multi-column enantio-selective gas chromatograph (GC) coupled to a linear reflectron time-of-flight mass-spectrometer instrument is presented together with its realisation under the scientific guidance of the Max-Planck-Institute for Solar System Research in Katlenburg-Lindau, Germany. The instrument's technical data are given; first measurements making use of standard samples are presented. The cometary science community is looking forward to receive fascinating data from COSAC cometary in situ measurements in 2014.

Keywords: rosetta, COSAC

1. Introduction

The cometary sampling[1] and composition experiment COSAC is one of the two evolved gas analysers (EGAs) on board Philae. Whereas the other EGA, Ptolemy, aims mainly at accurately measuring isotopic ratios of light elements (see article

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[1] The sampling drilling and sample distribution section of COSAC has been replaced by a separate experiment (SD^2) under Italian leadership in the course of the internationalisation of the ROSETTA LANDER project.

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on Ptolemy, this issue), COSAC is specialised in molecular and chiral analysis, in particular, in detection and identification of complex organic molecules.

2. Scientific Objectives

The nucleus of a comet can be regarded as a frozen record of the conditions and processes, which prevailed in the outer regions of our solar system in statu nascendi. As the principal formation processes were probably similar for other Sun-like stars and their planetary systems, the importance of studies of comets reaches far beyond the solar system. An overview on this subject is given in Goesmann *et al.* (2005).

The goal of the COSAC experiment is to contribute to the understanding of the processes that took place during the early stages of formation of the solar system by measuring the elemental, isotopic, chemical and mineralogical composition of surface and subsurface cometary material as derived from volatiles generated in the temperature range up to 600 °C. As these measurements will be performed as a function of solar distance as the comet approaches the Sun, we can hope to get more general information on the composition of a cometary nucleus than by a measurement of a singular point in time because it is known (Schulz *et al.*, 1998) that the composition of naturally evolved cometary volatiles changes as a function of solar distance; and, therefore, it is likely that the composition also changes as a function of subsurface depth.

The elemental composition, together with isotopic ratios, is important in so far as it proves or excludes the target comet's belonging to the solar system. With respect to the determination of *elemental* abundances, however, the COSAC experiment is not very powerful because many elements do not show up in volatiles at representative abundances. The COSAC instrumentation is better suited for determining *isotopic ratios*, which are interesting because they permit to draw some conclusions on the evolution of cometary matter composition since the time of its conglomeration in the early phase of solar system generation.

The main field for which the COSAC instrument is specially designed is probing the *chemical* composition of volatiles in the cometary matter. Special emphasis is put on the identification of organic molecules with high molecular mass numbers. Such molecules are of special interest because they might be the pre-biotic building blocks of life on Earth and other planets. This suspicion is based on the fact that all larger bodies in the solar system have – throughout their life times, but mainly shortly after their formation – been bombarded by comets. This bombardment may have been so heavy that a substantial part of the Earth's water was supplied this way. If this assumption was correct, also a huge amount of organic matter would have been transported to the young Earth by comets because their content of organic material is estimated to amount to approximately 30% (Greenberg, 1998).

A variety of small organic molecules in cometary matter haves been unambiguously identified already. However, many of the more complex molecules were detected in a more tentative if not speculative way (see, e.g. Cottin *et al.*, 1999).

For identification of molecules in a cometary coma by optical means, one of the main obstacles is the superposition of the spectra of all the molecules present, which both mixes the information and masks the rarer species. In addition, species present in trace amounts in the Earth's atmosphere make remote sensing of cometary species from ground difficult (Bockelée-Morvan *et al.*, 2004).

For the in-situ mass-spectrometric measurements (Huebner, 1987; Kissel and Krueger, 1987; Krueger and Kissel, 1987; Huebner *et al.*, 1989; Korth *et al.*, 1989; Krueger *et al.*, 1991) of the coma of comet Halley, the problems were firstly the low resolution and the low maximum molecular mass number limit of the instruments employed and secondly the nature of the samples: they were not only processed by evaporation from the comet but also by irradiation from the Sun and solar wind interaction. This increased the difficulties in determining the molecules originally present in the cometary matter. In order to overcome the above obstacles, the COSAC experiment will investigate material sampled directly from a cometary nucleus.

A speciality within the COSAC goals is the investigation of the *chirality* of potential pre-biotic molecules. If a deviation from a purely racemic distribution of organic compounds similar to the one observed in biotic matter on Earth were found, this could be an indication of a seeding function of cometary matter for life on Earth. Such enantio-enrichment was suggested to be induced into chiral cometary molecules by circularly polarized interstellar light (Meierhenrich *et al.*, 2005). Chiral organic molecules like amino acids were identified in laboratory simulations dealing with UV photo- and thermal processing of pre-cometary ice analogs (Muñoz Caro *et al.*, 2002).

3. The Instrument

COSAC comprises a gas – chromatograph (GC) and a mass-spectrometer together with the necessary infrastructure to operate such a system. Figure 1 shows the COSAC experiment during integration onto Philae. In the centre, one can see the two carrier gas tanks. On top is the black electronics box. At the right the mass-spectrometer is situated and may be identified by its white, spine-like harness. The box at the bottom houses the GC. The oven system is located outside the warm compartment of Philae. It is mounted at the far right and not visible in the image.

3.1. THE GAS CHROMATOGRAPH

A GC is an instrument to separate, identify and quantify the components of a mixture of volatile molecules. It is a standard tool in laboratory analyses and is commonly used to measure trace components.

Figure 1. The complete COSAC instrument (apart from the tapping stations) as integrated on Philae. It is approximately 400 mm wide and 500 mm tall.

In GC, a gaseous sample comprising a mixture of volatiles is looped into a constant stream of carrier gas and blown through long capillary tubes called chromatographic columns. The mixture interacts with the internal coating of the tubes (stationary phases), which leads to different transit times (retention times) for the different species and therefore to their separation. At the end of the columns, some detector monitors the composition of the exhaust gas. Under known operational conditions such as carrier gas flow, column temperature and columns length, etc., the retention time gives information about the nature of the compound in question and the size of the signal that can be used to quantify its amount.

The instrument described here differs in many ways from the standard laboratory equipment mainly because of the two boundary conditions. One is the complexity of the task: It is reasonable to assume a wide range of possible molecules. This means that the instrument had to be designed to be able to identify many different species with widely varying properties, which could only be achieved by using a multiple column system. Another is the strict limitation of resources. Mass, power and volume are scarce. Strict miniaturisation of the components like valves and detectors as well as careful use of consumables (carrier gas) and other resources had to be performed.

Therefore, the instrument is described in some technical detail. Firstly, the flow of the carrier gas is illustrated, and secondly the sample path is described.

3.1.1. *The Gas Flow*

The carrier gas in COSAC is helium, which is used as it is chemically inert, likely not a cometary compound, and has a thermal conductivity much larger than any organic molecular species, so that the thermal conductivity of the exhaust may be used for chemical detection. Figure 2 shows the gas unit of COSAC. It comprises three containers: one cylinder at the left for calibration gas, two spheres for helium carrier gas. One of the helium tanks is equipped with a single shot valve. The size of the tanks is about 330 cm^3 each and are filled to 40 bar. The He-tanks, the single shot valve and the mounting plate were procured by the Service d'Aeronomie in Verrieres-le-Buisson, Paris, France. Additionally, it comprises a pressure regulation system.

Figure 2. The carrier gas unit of COSAC. The tanks have a diameter of 90 mm.

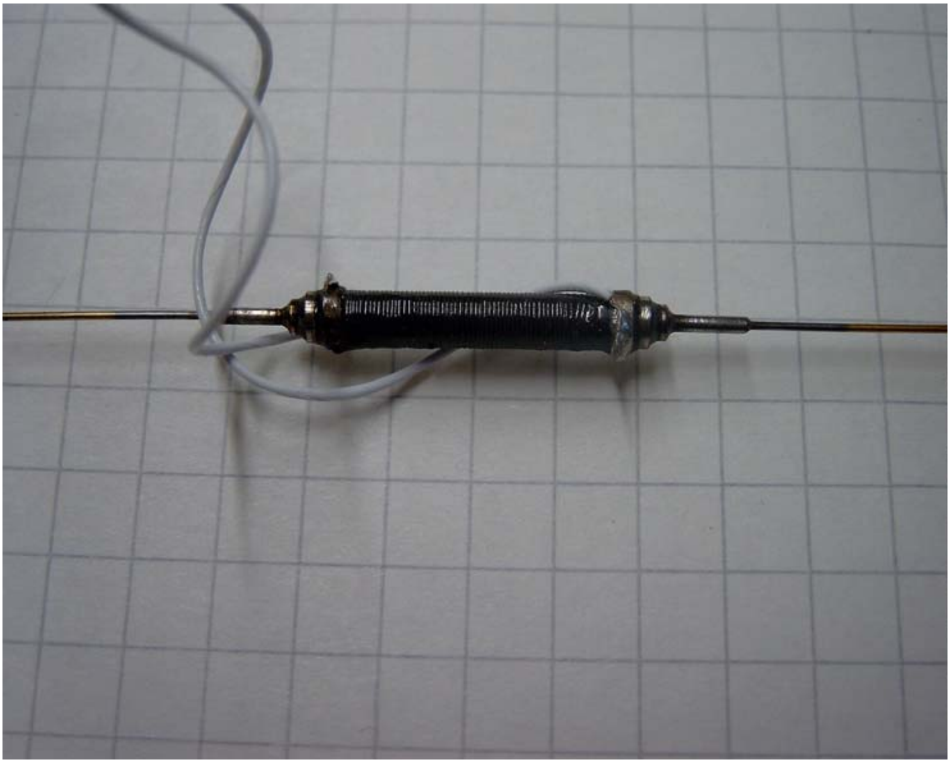

Figure 3. The pressure reduction valve as used in COSAC depicted on 5 mm graph paper.

The pressure regulation is achieved by means of thermally operated valves. These patented valves, developed and produced at the MPS, exploit the idea of differential thermal expansion. The whole valve is heated and due to careful choice of construction materials it opens continuously from a temperature limit upwards. For helium, the signal of a KPY pressure sensor from Siemens is used in a feedback loop to control the column head pressure for the GC. An actual valve depicted on millimetre graph paper is shown in Figure 3.

The central components of the gas distribution system in the GC are on–off switching valves especially developed and produced for this project. A schematic cross section of such a valve and an actual valve depicted on millimetre graph paper are shown in Figure 4. The operation of the valve is based on electrostatic attraction of two opposing plates of which one is suspended by springs. The valve is open by default and closes when a voltage of about 200 V is applied between the two plates. The insulating layers on the silicon plates prevent discharge so that the valve does not draw any current. The valve itself weighs 1.6 g and can be operated in a temperature interval between -60 and $+200\,^{\circ}$C. Typical leak rates are around 10^{-6} mbar l/sec (millibar litre per second is a commonly used unit in leak detection),

TABLE I
Columns used in the COSAC gas chromatograph.

No. of columns	Column	Inner diameter (mm)	Thickness of stationary phase (μm)	Length (m)
1	CarboBond	0.25	10	15
2	MXT U-PLOT	0.18	1.0	10
3	MXT 1701	0.18	1.2	15
4	MXT 20	0.18	1.0	15
5	MXT 1	0.18	0.1	10
6	Chirasil Dex CB	0.25	0.25	10
7	Chirasil L Val	0.25	0.12	12.5
8	Cyclodextrin G-TA	0.25	0.125	10

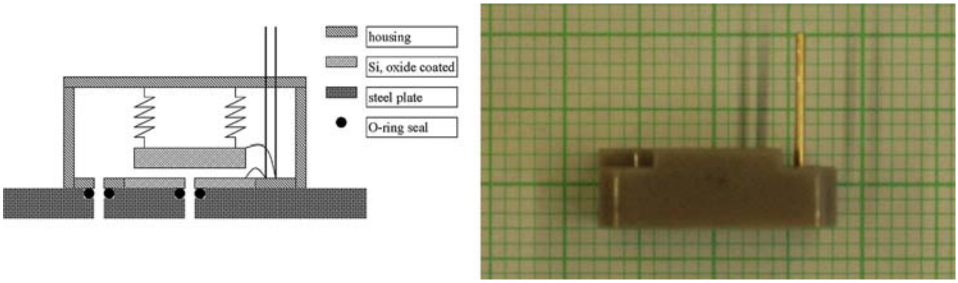

Figure 4. The operational principle and the actual hardware of an on-off switching valve on mm graph paper. Twenty-eight of these valves are integrated in the gas distribution manifold of the GC.

flow rates for an open valve around 10 sccm/min (standard cubic centimetres per minute, a unit frequently used for flow rates in gas-chromatography) at 20 mbar pressure difference and 1 bar absolute pressure. Twenty-eight of these valves were used within COSAC.

For the analysis the carrier gas has to flow through a system of chromatographic column and detector. Figure 5 gives an overview of a column unit. The image shows a prototype of a unit of chromatographic column, detector, heater and temperature sensor. Heater and column are joined into a spool using epoxy glue which leads to a rigid structure and good thermal contact between heating wire and column. Column packet and detector are mounted to a common piece of stainless steel. Eight such sub-units form the set of chromatographic columns of COSAC. The general columns (1–5) were selected and procured by the Laboratoire Interuniversitaire des Systèmes Atmosphériques, Paris, France; the chiral columns (6–8) were selected by the University of Bremen, Germany (Meierhenrich *et al*., 1999; Szopa *et al*., 1999).

The columns and their properties are listed in Table 1.

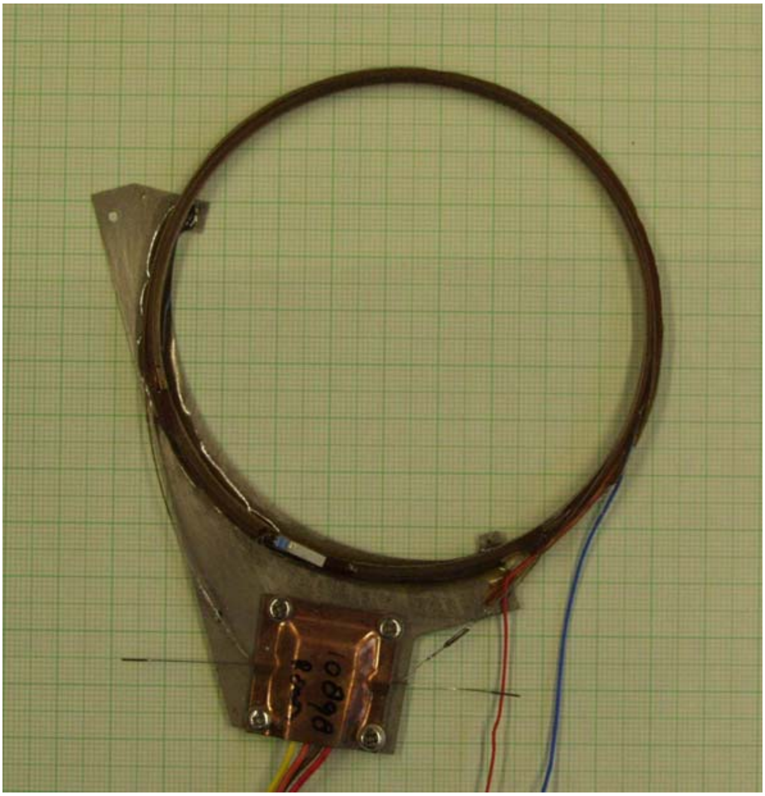

Figure 5. A prototype of a column detector unit of the COSAC GC on mm graph paper. The inner diameter of the column coil is 100 mm.

Micro-machined thermal conductivity detectors (TCDs) from Varian were used on each column. Figure 6 shows a schematic overview of a TCD. In principle it is a Wheatstone bridge of four filaments which are cooled by two flows of gas. It is entirely symmetrical. Under normal operating conditions both gas tubes are fed with comparable flows of carrier gas from a common source. One channel acts as a constant reference, the other one monitors the output of a chromatographic column. The filaments are supplied with a constant voltage. A signal is caused by the usually lower thermal conductivity of the analytes as compared with the pure carrier gas. This causes a higher temperature in the filaments of the measurement channel which due to the temperature coefficient of the filaments' resistance leads to an output voltage.

In COSAC the TCDs are used slightly differently in two ways: Firstly the detectors are switched. For every value to be measured they are switched on for several Milliseconds, a value is taken and converted to digital format, and switched off again. This helps to save electric energy. Secondly the reference channel is not fed with an extra gas flow but much rather connected according to Figure 7. The gas

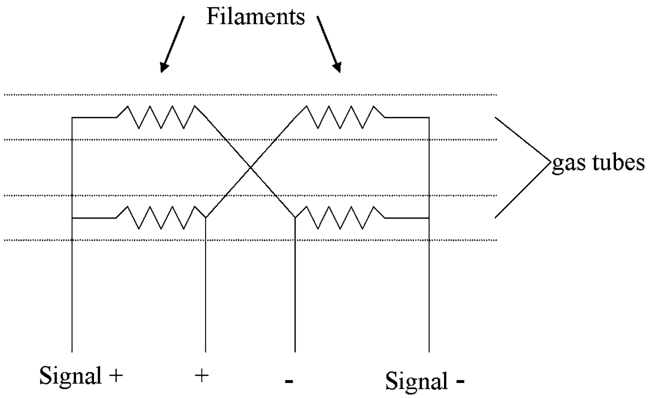

Figure 6. Operational principle of the thermal conductivity detector.

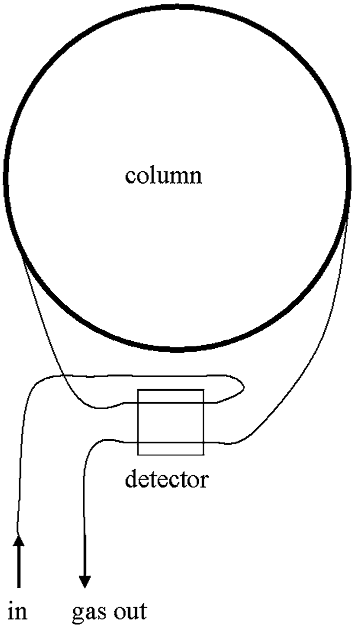

Figure 7. Principle of the gas flow in a column detector unit.

from the injector is passing the detector twice: firstly before entering the column and secondly after the column passage. This helps to save carrier gas. Connecting the detector in such a way has advantages and disadvantages. An advantage is that the sample passes the detector twice. So the sample leaves a negative and short signal on its way into the column which can be used (a) to estimate the total amount of the sample entering the system and (b) to serve as a starting signal for the retention time in the GC spectrum itself. A disadvantage is that the detector is

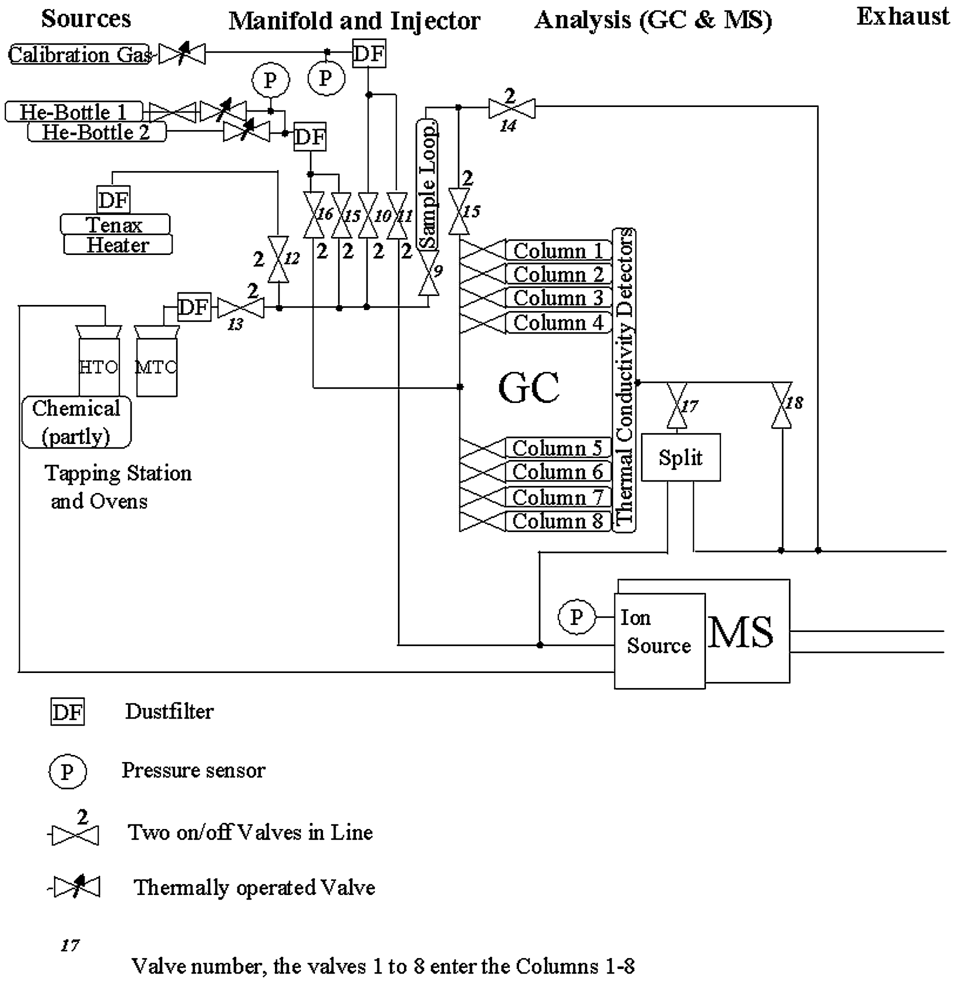

Figure 8. The complete gas distribution manifold of the GC. The image is more of a logical representation of the pneumatic system than a sketch of the hardware.

used out of balance. The pressure between the two channels in the detector differs by the pressure drop along the column. In order to tune the detector back to zero signal under nominal operating conditions of column head pressure and column temperature, a resistor is added in parallel to one filament, for example between supply-plus and signal-minus.

Figure 8 shows the pneumatic part of the GC. On the left a schematic overview of the gas flow system is given. It represents the logical gas flow rather than its physical implementation. It is not intuitively understandable.

Figure 9 shows the pneumatic set-up of the GC of COSAC. It is a single-piece aluminium frame into which the gas connection interface, the manifold and the

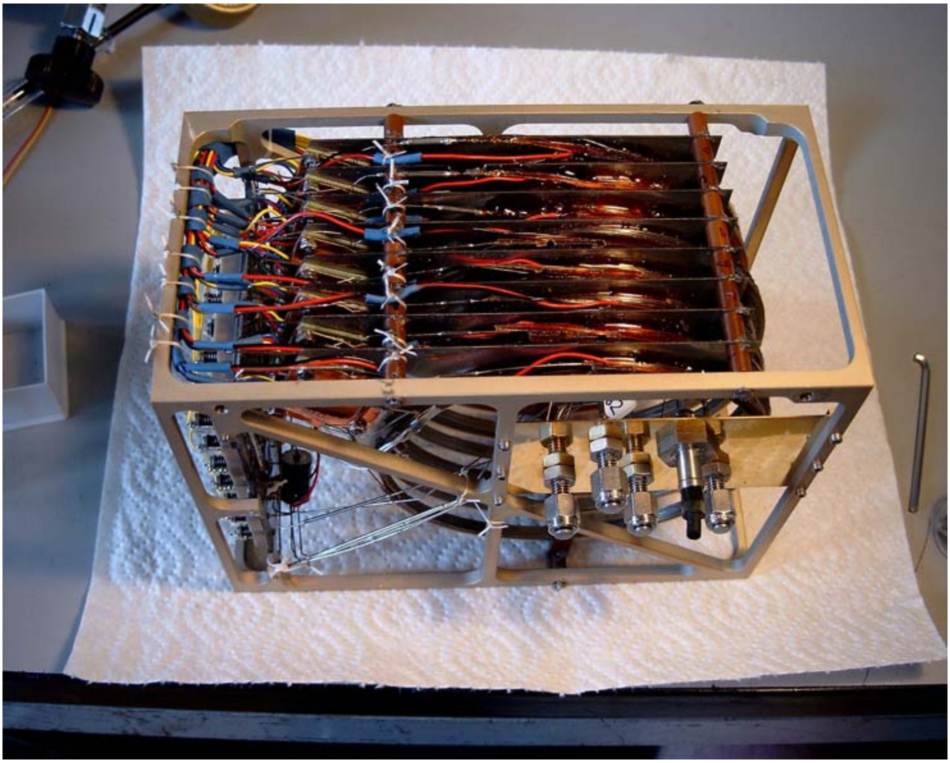

Figure 9. The pneumatic hardware of the GC. For a detailed description see text. The mounting frame is 80 mm wide, 120 mm long and 105 mm tall.

GC columns with their heaters and detectors are mounted. At the front there is the interface plate comprising connectors for helium , calibration gas , oven pipe , exhaust and transfer pipe to MS. The tubes from the interface plate lead down to the left where the manifold is mounted. It contains the tubing on the right and the valves and their electrical connections on the left. At the top tubes lead across to the eight column-detector units. The electrical connections are grouped into three parts: heaters and control, valves and detectors. The electrical harness is mounted at the rear of the aluminium structure.

3.1.2. *The Sample Flow*

Soil samples from the cometary nucleus will be delivered into ovens which are then closed, heated and the evolving gaseous species are transferred to the GC. The travel route of the samples is described in the following paragraphs.

Two types of ovens are available for COSAC. One type allows infra-red and visible sample inspection by the CIVA instrument through a bottom window and can be heated to approximately 180 °C. These are called medium temperature ovens (MTO). Another does not have a window but can be heated to 600 °C, therefore

Figure 10. A high temperature oven (HTO) of Philae. Such ovens may be connected to Ptolemy or COSAC.

called high temperature oven (HTO). Figure 10 shows an image of an HTO on millimetre graph paper. It is made of platinum. The heating is achieved by a resistive platinum wire heater enamelled onto the oven. For temperature monitoring a type K (Chromel-Alumel) thermocouple is integrated into the bottom of the oven. The four connections (heater in and out, thermocouple + and −) are made via four Pt plates visible at the bottom.

The MTOs are identical as far as the electrical and pneumatic interfaces are concerned. The difference is that they have an optical window at the bottom of each oven allowing infra-red inspection of the samples.

The pneumatic and electrical connection between oven and COSAC is done by the tapping station. Figure 11 shows the COSAC tapping station in frontal view. The ovens would be located on a carousel in front. After a loaded oven was positioned in the open tapping station it can be closed in the following way. Firstly the oven is supported from underneath by a Vespel anvil. For the electrical connection spring contacts visible at the bottom of the tapping station are pushed against the Pt plates at the ovens. The transfer tubes between COSAC and the oven end in a sphere made

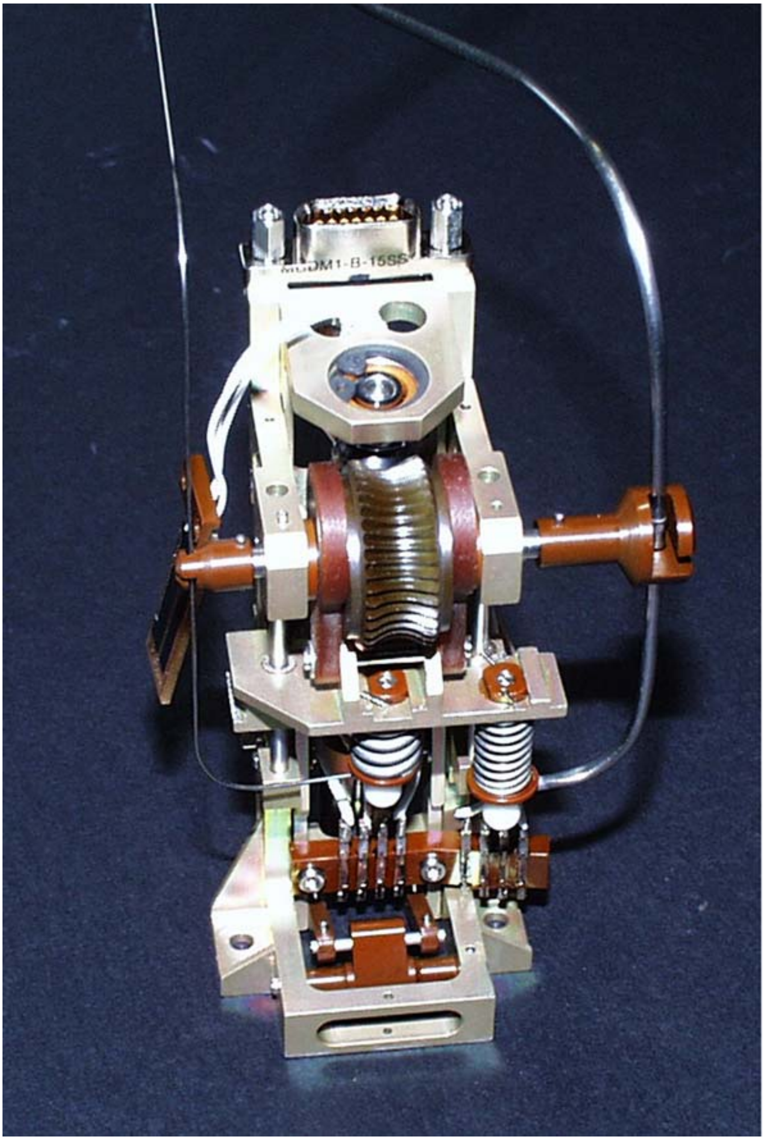

Figure 11. The COSAC tapping station. The sphere in the middle and its tube are connected to the GC; the one at the side is connected to the MS. The overall height is 90 mm.

from zirconia mounted to a stainless steel holder. So the actual seal is between the soft Pt rim of the oven and the hard polished zirconia surface. The COSAC tapping station has two such positions. The central position is connected to the GC; the side position is connected to the mass spectrometer.

After heating, the evolving gas is transferred from the central position to the GC through a heated stainless steel tube. The gas can be guided to the injection

TABLE II
Operational sequence of the injection system

	Valve state[a]				
Step	1	2	3 & 4	5	Duration
1	X	O	X	O	5 min
2	O	X	X	O	1 min
3	X	X	X	O	30 s
4	X	X	O	X	0.5–10 s
5	X	X	X	O	17 min
6	O	O	O	O	–

[a] O: open; X: closed

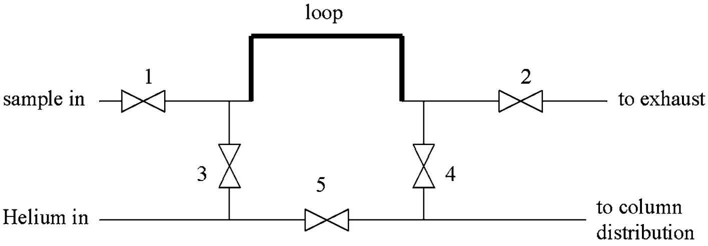

Figure 12. Operational principle of the COSAC GC injector.

system directly or to an absorbent capsule filled with TENAX material. From this capsule it may be liberated by heating later and then injected into the GC. The task of feeding the sample into the carrier gas stream is achieved by the so-called injector. In terrestrial systems commonly a syringe is used to inject a sample with several options (split, split-less injection; liquid injection onto hot surfaces, etc). For COSAC another concept had to be developed. The following paragraphs describe the injection procedure.

Figure 12 shows a part of the pneumatic manifold of COSAC which acts as an injector for the GC. It has four ports: the first is the input for the sample, the second is the exhaust, the third is the helium input and the fourth is the line leading to the columns. It also comprises an injection loop which stores the sample immediately prior to injection and five on-off valves which govern the flow of gases. A typical operational sequence is listed in Table 2 and explained in the text below:

Step 1: The GC is warming up. Helium flows from the gas unit through valve 5 to the columns. The loop is evacuated via valve 2. No sample is available. This takes 5 min typically.

Step 2: The sample is prepared. The helium flow remains constant. The exhaust is closed. Sample gas (calibration gas, something stored in the TENAX material or something evaporating from an oven) enters the loop. About 1 min duration is nominal.

Step 3: The sample settles in the loop. The loop is entirely locked.

Step 4: The sample is injected into the helium flow. Valve 5 is closed and simultaneously valves 3 and 4 are opened. The helium is forced to take a detour via the loop and to push some of the content into the columns. This may take between 0.5 and 10 s. The time can be freely programmed according to the amount of sample wanted or available.

Step 5: The measurement is running. Immediately after injection the valves are switched back so that the sample is pushed through the columns by the helium flow. A typical running time is 17 min. Any duration between 1 and 17 min can be chosen in 1 min steps.

Step 6: This describes the end of a measurement cycle. Once the measurement is over all valves are opened to clean the system.

It is possible to go back to step 2 directly after step 5 in order to investigate another sample.

After this procedure the sample is on its way through column and detector as described in the chapter for the carrier gas. Then the GC measurement is finished. If the exhaust gas of the GC are to be investigated by the MS a reduction of gas flow is necessary because otherwise the MS would receive too high apressure for operation. For this purpose a jet separator is used. Figure 13 shows a drawing of the

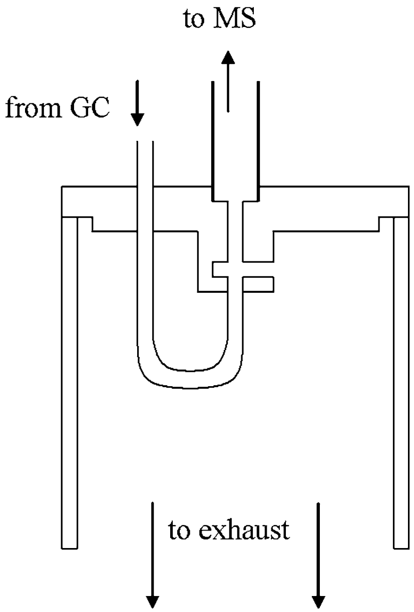

Figure 13. Operational principle of the jet separator (named split in Figure 8) in the line between column exhaust of the GC and entrance of the MS.

cross section of the system. The external diameter is 6 mm. The idea is that the gas flows from the GC to the MS passing a small slit which leads to the exhaust at low pressure. Some of the gas will escape; some will go straight on to the MS. Since the carrier gas is the lightest component in the gas stream it will escape preferentially and lead to some ‘de-richment’ of carrier gas in relation to the analyte.

3.2. The Mass Spectrometer

The MS is a high-resolution multi-pass TOF instrument, with an electron-impact ionisation source, a multi-sphere-plate secondary electron multiplier as detector and a time-to-digital converter (TDC) for signal and flight time registration. The instrument is of the linear reflectron-type with the ion source at one and the detector at the other end. For determining an m/q spectrum, all ions inside the source are accelerated into the flight path with principally the same energy. Therefore heavy ions will travel slower than that of the light ones. In the low resolution mode, only the single flight path of approximately 370 mm from the source to the detector is used. In this case, the $M/\Delta M$ is 350 for ions of mass 70. For achieving a higher mass resolving power, the MS can be used in the multi-turn mode. This mode is possible due to two gridless reflectors, one at the source side and the other at the detector side (Wollnik and Przewloka, 1990; Casares *et al.*, 1999).

An electron impact storage ion source is employed (Grix *et al.*, 1989). Three thermal electron emitters can be used alternatively, thus providing redundancy. The electron flux can be varied by telecommand. The storage capability allows to produce ions for $\sim 200\,\mu$s while the release pulse is only $\sim 1\,\mu$s. The ions are accelerated to 1500 eV at the source. An ion pulse is released every 1 ms or optionally every 250 μs. The ion travel time is more than sufficient to cover the envisaged mass range of 1–1500 amu, even in modes with a high number of passes.

The ions are post-accelerated in front of the detector to 4 keV to be registered with high probability in the multi-sphere-plate electron multiplier. The time of the output signal of the amplifier which is normally produced by a single ion is recorded with a resolution of 2 ns. This time resolution is realised by means of a 33 MHz clock, in connection with a switchable digital delay line of sixteen 2 ns elements. The time of the signal is transmitted to a fast FIFO memory. The FIFO can be read out asynchronously during the measurement. The times are then transmitted to another memory which serves also for spectrum integration. Usually, the measurements will be repeated 2^{16} times. That means that 65536 mass spectra will be taken in approximately 1 min. Resolution enhancement is possible by starting every other spectrum with 1 ns delay.

Figure 14 shows the MS during integration. At the right-hand side on the top one can see the two stainless steel inlet ports for the tubes direct from the tapping station and from the GC. The box also contains the ion source. Further to the left the two large exhaust pipes are located. The box at the left end contains the detector

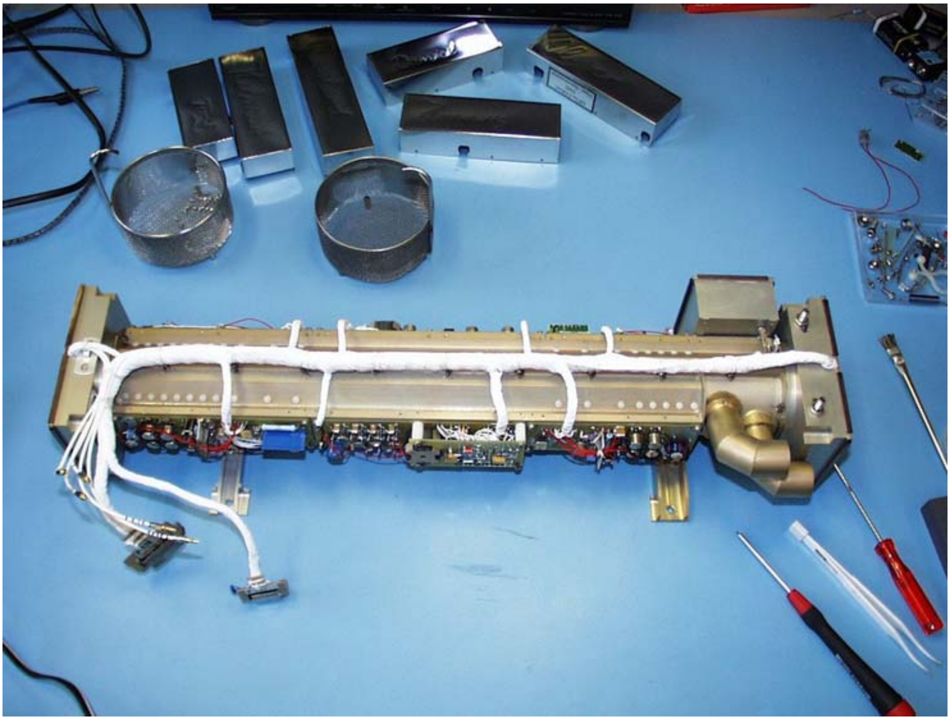

Figure 14. The MS during integration. The cover boxes of the electronics are not mounted. The total length of the instrument is 460 mm.

unit. The electronic circuit boards are still uncovered; the housing boxes are at the top of the image. The white structure connecting the different boards is the harness to connect the MS to the main electronic box.

3.3. Control and Data Handling Unit

The instrument communicates with the control and data management system (CDMS) of the ROSETTA Lander through a DPU board including a Harris RTX 2010 processor, a PROM, an EEPROM, an SRAM and additional controllers. This board is housed inside the ROSETTA Lander Common Electronic Box. The data flow between the processor and the instrument is routed through an additional interface board which also hosts the mass memory of 3M × 16 bit, sufficient for storing the data collected during a measurement sequence in GC/MS coupling mode.

Most of the control logics is realised in a group of four Field Programmable Gate Arrays (FPGAs). In addition the FPGAs control the pyrolytic unit, the high voltages, the ion source, the time to digital converter, the MS spectrum accumulation and the main activities of the GC unit including heater, valve, injector switching and data registration.

The software for controlling the experiment is written in FORTH, the native programming language of the Harris RTX 2010, to take full advantage of the processor's internal stack-based structure.

The main tasks of the software are:

- control of the experiment during measurement cycles
- data formatting and pre-processing
- in-flight calibration
- collection of housekeeping data
- handling of data communication to and from the CDMS
- data compression

The algorithms for controlling the different measurement cycles are part of the flight software stored in the DPU's EEPROM. Several telecommands (TCs) were defined for uploading of new parameters for the fine-tuning of these onboard algorithms prior to measurements. Additional TCs are available for software maintenance tasks and debugging in case of a non-nominal behaviour.

3.4. DATA

In this chapter data produced by COSAC are described in three parts. The first chapter describes GC data; the second gives examples of MS data; in the third coupled GC-MS data are presented. The instrument providing these data is the flight identical spare instrument operated at MPS in a vacuum chamber.

Figure 15 shows a chromatogram where a mixture of argon, butane, methanol and isopropanol in helium was injected from the injector described above (6 s injection time) into two columns in parallel. The pink curve is the signal of the MXT 1701 column; the dark blue curve corresponds to the MXT 20 column. The first peak is caused by Ar and experiences no retention. The second peak is caused by butane. It is separated well from the third peak of methanol on the MXT 1701 column but less so on the MXT 20 column. The fourth peak is the one caused by isopropanol. The Height Equivalent Theoretical Plate (HETP) value for these peaks is around 5 mm. The HETP figure is commonly used to quantify the resolution performance of a GC system. This value is not particularly good compared to laboratory GCs. The wide peaks are mainly caused by the long injection time. But the chromatogram clearly shows that it is possible to inject a sample into more than one column in a single injection and to produce meaningful results.

The following chapter gives an indication of the performance of the MS of COSAC. In Figure 16 a mixture of water (H_2O) and heavy water (D_2O) in approximately even proportion was fed into the MS. One can clearly see the peaks corresponding to mass 1, 2 and 3 caused by H^+, H_2^+ and D^+, and HD^+. Mass 4

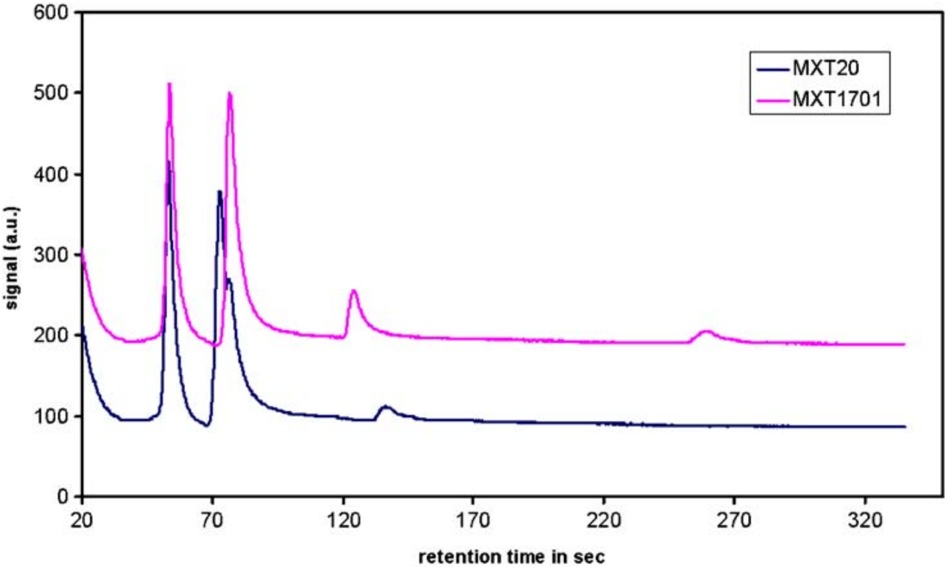

Figure 15. Chromatogram of a sample (see text) injected into two columns of COSAC in parallel and acquired simultaneously.

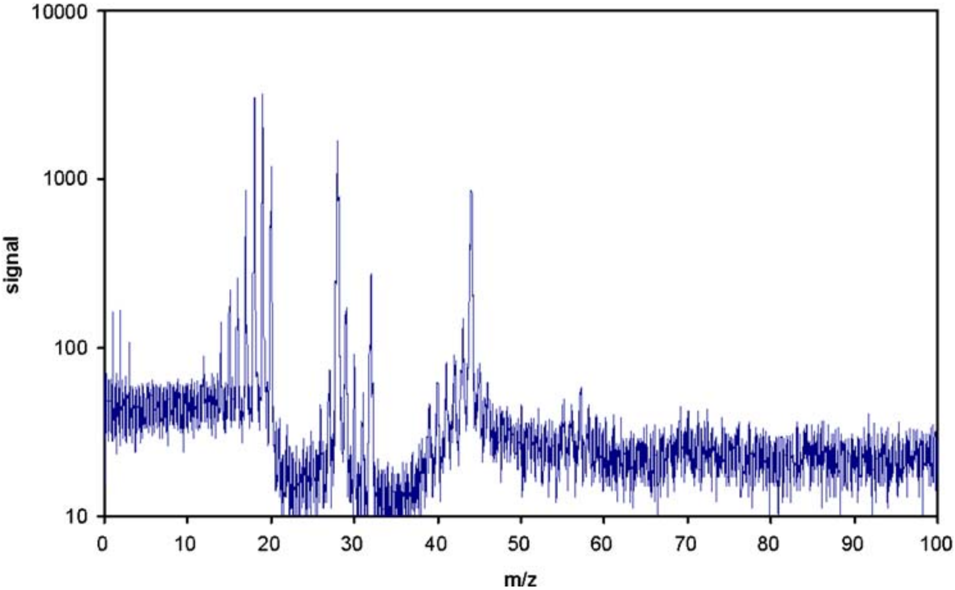

Figure 16. Accumulated MS spectrum of a mixture of H_2O and D_2O in approximately even proportion.

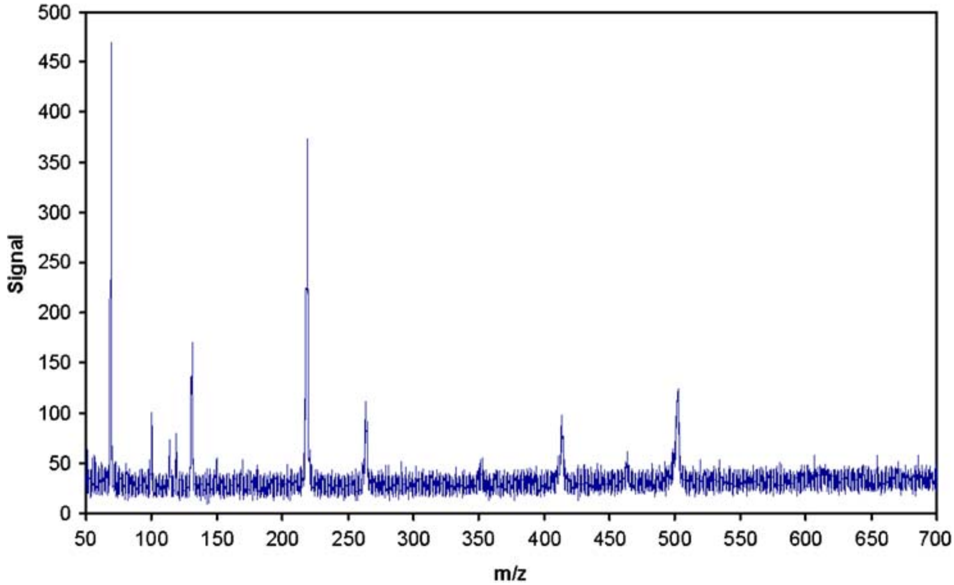

Figure 17. Accumulated MS spectrum of Perfluorotributylamine.

caused by D_2^+ (or possibly He^+) is not visible. These measurements are useful since COSAC is the only MS on Philae capable of measuring masses below 10 amu directly. The peaks from 16 to 20 amu are caused by the different H_2O/D_2O fragments. The peaks corresponding to mass 12, 14 and 15 were likely caused by the contamination of the vacuum vessel.

Figure 17 shows an accumulated mass spectrum of Perfluorotributylamine, a substance commonly used to check for performance at higher molecular masses. The weight of the complete molecule is 671 amu. The obtained spectrum corresponds well with the tabulated one in the NIST library.

The coupled mode of GC-MS delivers data of the following kind: A sample as described in the chapter on GC data (Figure 15) was injected into the MXT1701 column and the exhaust fed into the MS. Three figures visualise the result. In the chromatogram (Figure 18) the four peaks similar to the ones in Figure 15 of the GC chapter can be seen.

The chromatogram is displayed from the very beginning of data acquisition. Some pressure disturbance at the beginning is visible. Then a negative peak cut off at the zero line is shown. This is caused by the sample passing the reference channel of the TCD before entering the column as described in the chapter on the GC carrier gas flow. The clear information of the chromatogram is that at least four different components are present in the sample but their nature is not a priori obvious. The accumulated mass spectrum of all the GC exhausts is shown in Figure 19.

This would be the MS result without any chromatographic separation in advance. One can see a distinct peak at mass 4 for helium, the carrier gas. Then there is a

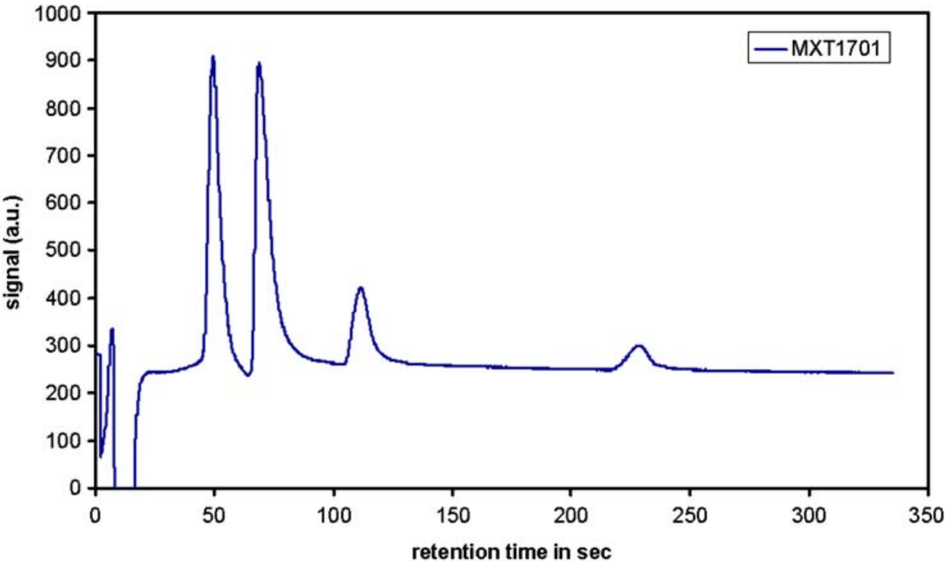

Figure 18. Chromatogram of a sample (see text) injected into one column.

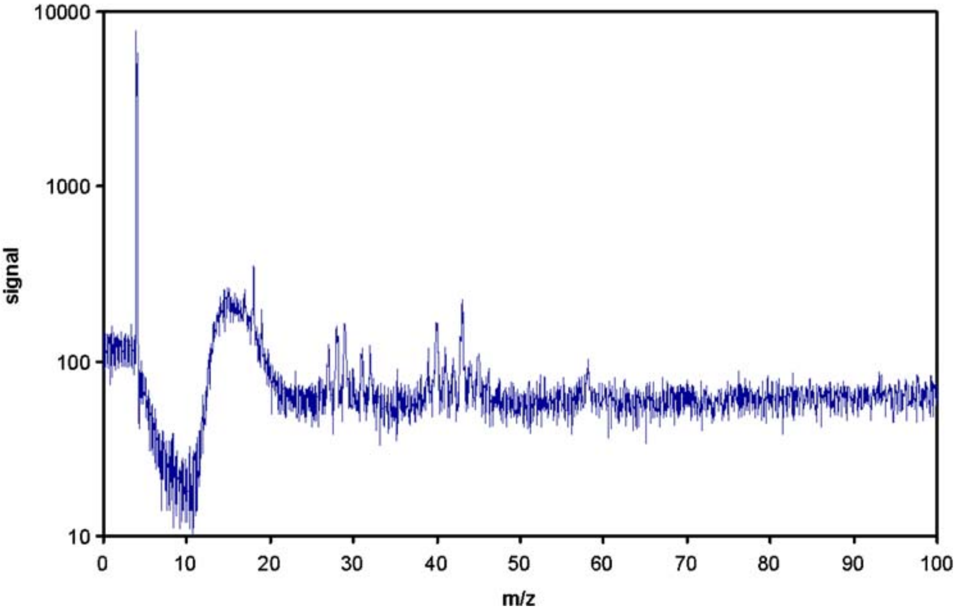

Figure 19. Accumulated MS spectrum of the same sample acquired from GC exhaust gases.

broad drop in background count and a rise again. This feature is probably due to a detector saturation caused by the comparatively large amount of helium. The peaks around 18 amu are caused by water. The following peaks arose from the mixture of sample constituents. All fragments of the molecules are visible but it

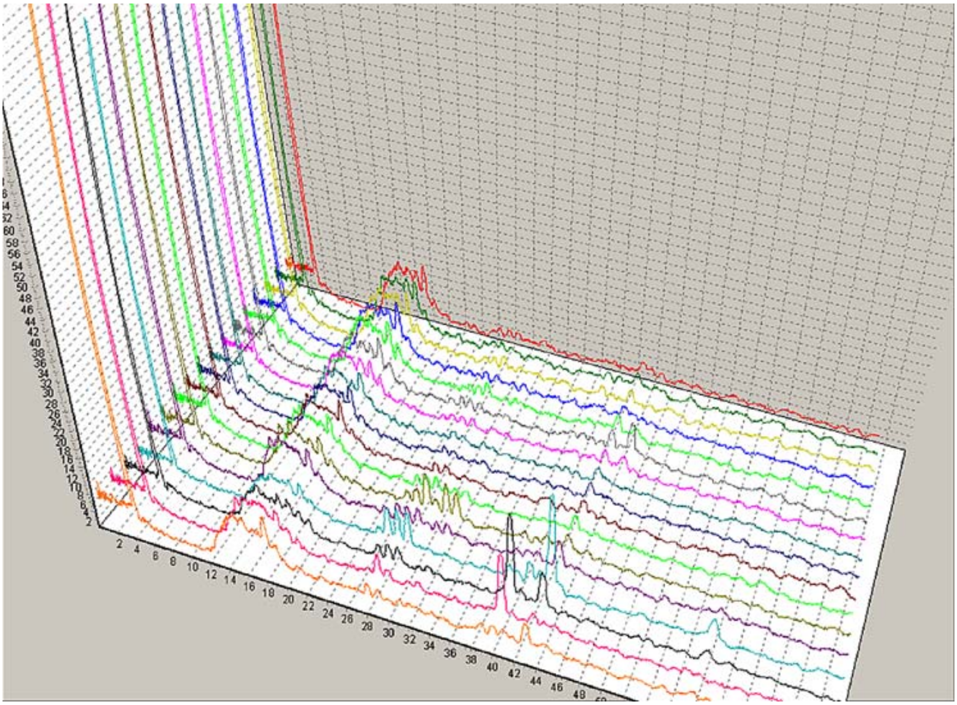

Figure 20. 3D view of the MS spectra as a time series. The mass scale is to be read from left to right; the intensity points upwards and the time series is to be interpreted from front to rear.

is almost impossible to decide which peaks belong to which compound. Figure 20 shows the set of mass spectra plotted versus the time when they were acquired. This image gives the resolved information. The accumulation time of the MS spectra was 16 sec. All spectra display the peak at mass 4 for helium and the water signal. The second (red) spectrum shows a clear peak at mass 40 for argon; the fourth displays the fragment pattern of butane (bluish-grey), while the third (black) is a transition between the two. The sixth spectrum (olive-green) shows the fragmentation pattern of methanol, the twelfth spectrum (light grey) the one of isopropanol. This figure therefore demonstrates the usefulness of the method itself as well as the functionality of the COSAC instrument.

4. The COSAC Project Team

The COSAC instrument was designed, developed, constructed, tested and calibrated by an international team.

The development of the GC was strongly supported by the team of the LISA (Laboratoire Interuniversitaire des Systèmes Atmosphériques), Paris. This group (with a large team) led by Francois Raulin and Robert Sternberg has selected and procured the columns for the chemical analysis and has also performed numerous tests to make the GC a well working and reliable instrument.

The helium carrier gas system was provided by the Service d'Aéronomie du CNRS, Verrières-le-Buisson. The team led by Guy Israel and Jean-Francis Brun has also executed several tests for column qualification.

Selection and tests of the columns for chirality investigation as well as the development of a novel process for derivatisation were contributed by the University of Bremen by Wolfram Thiemann and Uwe Meierhenrich. U.M. is now at the University of Nice-Sophia Antipolis, France.

The concept of the linear gridless multi reflection TOF MS for the mission was developed and tested by the University of Gießen by Hermann Wollnik and his team.

The following team has worked at the MPAe (renamed Max-Planck Institute for Solar System Research, MPS in 2004) in Katlenburg-Lindau, Germany:

Helmut Rosenbauer	Principal investigator
Reinhard Roll	Project manager
Fred Goesmann	Project scientist
Peter Hemmerich	Division manager
Reinhard Borchers	GC consultant
Hans Lauche	High-pressure valve development
Oliver Küchemann	Software development
Jan Schröder	Electronics development
Henning Fischer	Electronics development
Daniel Windler	Electronics
Antonio Casares	Mass spectrometer development
Alexander Kholomeev	Mass spectrometer electronics
István Héjja	Hardware development and tests
Steffen Ebert	Designer

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Alexandra MacDermott, University of Houston at Clear Water, TX, USA, was the main driver for chirality measurements at the beginning of the project. The University of Leiden with the late Majo Greenberg, and Pascale Ehrenfreund has supported the COSAC development by providing material and information on material expected at the comet. The task to develop a suitable high-resolution TOF MS had originally been taken on by Takekiyo Matsuo and his team at the University of

Osaka. The development of this deflection type multi-turn time of flight mass spectrometer for COSAC had, however, to be discontinued after the unexpected death of Professor T. Matsuo, whose engaged devotion to the project we miss sincerely. However, the prototype produced at Lindau has successfully been tested at Osaka. For reference see Matsuo *et al.* (1999); Toyoda *et al.* (2000). Arthur Ghielmetti has supported the development of the mass spectrometer by numerous calculations and discussions. We acknowledge all participants of the development of the COSAC experiment and would like to thank also E. Jessberger, H. Rauer, O. Eugster, S.A. Fuselier, S. Ulamec, and many unnamed contributors for the help with starting the project and the fruitful and pleasant cooperation. The financial support of the whole project by the German Federal Ministry of Education and Research (BMBF) via Deutsches Zentrum für Luft- und Raumfahrt (DLR) under project number 50 QP 9708 is gratefully acknowledged. CNES is also acknowledged for its financial support in the French participation.

References

Bockelée-Morvan, D., Crovisier, J., Mumma, M.J., and Weaver, H.A.: 2004, *Comets II*, Festou, M.C., Keller, H.U., and Weaver, H.A. (eds.), The University of Arizona Press, Tucson, pp. 391–423.

Casares, A., Kholomeev, A., Mankov, N., Roll, R., Rosenbauer, H., and Wollnik, H.: 1999, *Proceedings of the 47th ASMS Conference Dallas*

Cottin, H., Gazeau, M.C., and Raulin, F.: 1999, *Planet. Space Sci.* **47**, 1141–1162.

Goesmann, F., Rosenbauer, H., Roll, R., and Boehnhardt, H.: 2005, *Astrobiology* **5**(5), 622–630.

Greenberg, J.M.: 1998, *Astron. Astrophys.* **330**, 375–380.

Grix, R., Grüner, U., Li, G., Stroh, H., and Wollnik, H.: 1989, *Int I. Mass Spectr. Ion Proc.* **93**, 323–330

Huebner, W.F.: 1987, *Science* **237**, 628–630.

Huebner, W.F., Boice, D.C., and Korth, A.: 1989, *Adv. Space Res.* **9**(2), 29–34.

Kissel, J., and Krueger, F.R.: 1987, *Nature* **326**, 755–760.

Korth, A., Marconi, M.L., Mendis, D.A., Krueger, F.R., Richter, A.K., and Lin, R.P.: 1989, *Nature* **337**, 53–55.

Krueger, F.R., and Kissel, J.: 1987, *Naturwissenschaften* **74**, 312–316.

Krueger, F.R., Korth, A., and Kissel, J.: 1991, *Space Sci. Rev.* **56**, 167–175.

Matsuo, T., Ishihara, M., Toyoda, T., Ito, H., Roll, R., and Rosenbauer, H.: 1999, *Adv. Space Res.* **23**(2), 341–348.

Meierhenrich, U.J., Nahon, L., Alcaraz, C., Bredehöft, J.H., Hoffmann, S.V., Barbier, B., and Brack, A.: 2005, *Angew. Chem. Int. Ed. 44*

Meierhenrich, U., Thiemann, W.H.-P., and Rosenbauer, H.: 1999, *Chirality* **11**, 575–582.

Muñoz Caro, G.M., Meierhenrich, U.J., Schutte, W.A., Barbier, B., Arcones Segovia, A., and Rosenbauer, H.: 2002, *Nature* **416**, 403–406.

Schulz, R., Arpigny, C., Manfroid, J., Stüwe, J.A., Tozzi, G.P., Rembor, K., Cremonese, G. and Peschke, S. and .: 1998, *Astron. Astrophys.* **335**, L46–L49.

Szopa, C., Sternberg, R., Coscia, D., Cottin, H., Raulin, F., and Goesmann, F.: 1999, *J Chromatogr. A* **863**, 157–169.

Toyoda, M., Ishihara, M., Yamaguchi, S., Ito, H., Matsuo, T., and Roll, R.: 2000, *J. Mass Spectrom.* **35**, 163–167.

Wollnik, H. and Przewloka, M.: 1990, *Int. J. Mass Spectr. Ion Proc.* **96**, 267.