



COSAC prepares for sampling and *in situ* analysis of cometary matter from comet 67P/Churyumov–Gerasimenko



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ABSTRACT

The comet rendezvous mission Rosetta will be the first mission to encounter and land on a comet nucleus. After a 10-year journey Rosetta is set for rendezvous with Comet 67P/Churyumov–Gerasimenko. The mission goal is: to study the origin of comets; the relationship between cometary and interstellar material and its implications for the origin of the solar system. The Rosetta spacecraft with an overall mass of about 3000 kg was launched in March 2004 and brought into cometary orbit towards comet 67P/Churyumov–Gerasimenko with 4 gravity assist maneuvers. On its way Rosetta passed and observed two asteroids, (2867) Šteins in 2008 and (21) Lutetia in 2010, respectively. In June 2011 Rosetta entered into hibernation and woke up – as planned – on January 20, 2014. In November 2014 Rosetta's Philae lander and 10 science instruments will be deployed onto the surface of comet 67P/Churyumov–Gerasimenko. This will be followed by the first ever *in situ* investigation of a comet nucleus. Onboard Philae is the COmetary SAMpling and Composition experiment (COSAC), one of two evolved gas analysers that will investigate organic compounds within the material of the nucleus. Data from the COSAC instrument are expected to provide important insights into the early history of our solar system and contribute to our knowledge of small bodies that may have seeded the early Earth through impacts. In this paper we review recent developments in cometary science, including data on target comet 67P/Churyumov–Gerasimenko. We report on laboratory measurements and the calibration of the COSAC instrument as well as the preparation for operations on the nucleus of comet 67P/Churyumov–Gerasimenko.

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1. Introduction

The Rosetta mission is a planetary cornerstone mission of the European Space Agency's Horizon 2000 Program that will orbit in 2014 and land on a comet for the first time in history. The selected target comet 67P/Churyumov–Gerasimenko (67P) is a short-period comet (orbital period ~6.5 years) that measures about 4 km in

mean diameter. The Rosetta mission will follow the comet from the onset of activity (> 3 AU) through perihelion (1.24 AU). Eleven instruments onboard the orbiter will investigate the physical and chemical evolution of the cometary coma and plasma environment and 10 instruments on the Rosetta lander Philae will study *in situ* the properties of the cometary nucleus. On its way Rosetta passed 2 asteroids. Asteroid (2867) Šteins showed a chain of about 7 craters. Close-up images of the asteroid (21) Lutetia showed a primitive heavily cratered object with a giant bowl-shaped depression from a distance of 3162 km, revealing a violent impact history. During the Lutetia fly-by the COSAC instrument was switched on twice in

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sniffing mode, once three hours prior to the closest approach and once one hour afterwards, measuring for 126 s each time. The instrument performed well and obtained two mass spectra (Goesmann et al., 2012). The spectra displayed no sign of a gaseous exosphere at Lutetia. However, this experiment showed that COSAC was able to analyze the residual gas inside the instrument itself and the Philae lander environment. A change in the amount of water vapour present in the gas phase before and after closest encounter correlates nicely with the temperature of the instrument. The spectra also confirmed that the lower pressure limit of the COSAC instrument is within design specifications at $\sim 5 \times 10^{-9}$ mbar. Results of the COSAC measurements are in line with those of the other Rosetta instruments that were switched on during fly-by (Morse et al., 2012).

On 20 January 2014 the spacecraft timer successfully initiated the wake-up call for the hibernating mission and an active signal was transmitted before Rosetta started its final journey to comet 67P. Successful COSAC tests (commissioning) were performed April 15–23. The Philae lander with an overall mass of about 98 kg is made up of a carbon fibre/aluminium honeycomb structure, a power system based on primary- and secondary batteries and a solar generator, see Fig. 1. It uses the Rosetta orbiter as a

telecom relay (Ulamec and Biele, 2009). The descent and landing scenario for Philae will only be initiated after an intense observation period of the comet by remote sensing (Ulamec et al., 2013). After the cruise phase the lander Philae will be pushed off the mechanical support system and separated from the orbiter with a velocity that is adjustable to high accuracy. The descent time is estimated to be on the order of 2–5 h, strongly depending on the gravity of the comet nucleus and the selected descent strategy. A cold gas system will provide a downward thrust and two anchoring harpoons fixation to the ground. Philae will rest on a tripod landing gear on the cometary surface. Ice screws will be used for additional anchoring.

The COSAC instrument is designed for molecular and chiral analysis and will measure volatile organic and inorganic compounds in the nucleus material. COSAC consists of a gas chromatograph (GC) and a mass spectrometer (MS), see Fig. 2. The GC will separate the components in a mixture of volatile molecules. The MS will produce and analyse ions from the volatiles for their identification.

2. Recent comet observations

Comets are small solar system bodies that were formed in a range of environments within the protoplanetary disk and are now located in the so-called main cometary reservoirs such as the Kuiper Belt and the Oort Cloud. They are predominantly icy bodies that also contain silicates and refractory organics (Greenberg, 1998). Comets are considered to be the most pristine material in our solar system, and their composition is therefore key to our understanding of early solar nebula processes. They help us to unravel the mysteries surrounding the origin and evolution of our solar system and life on Earth. In the early history of our solar system small bodies, comets and asteroids and their fragments impacted frequently the young planets. It has been suggested that the Late Heavy Bombardment LHB phase was triggered by the

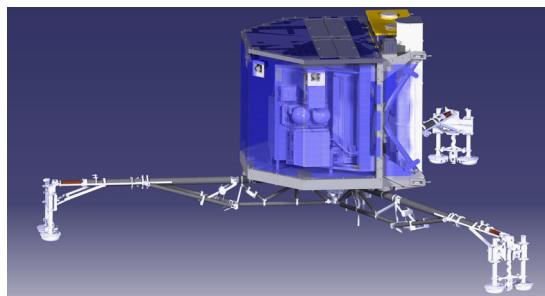


Fig. 1. The Philae lander, showing COSAC behind the hood with the solar generator.

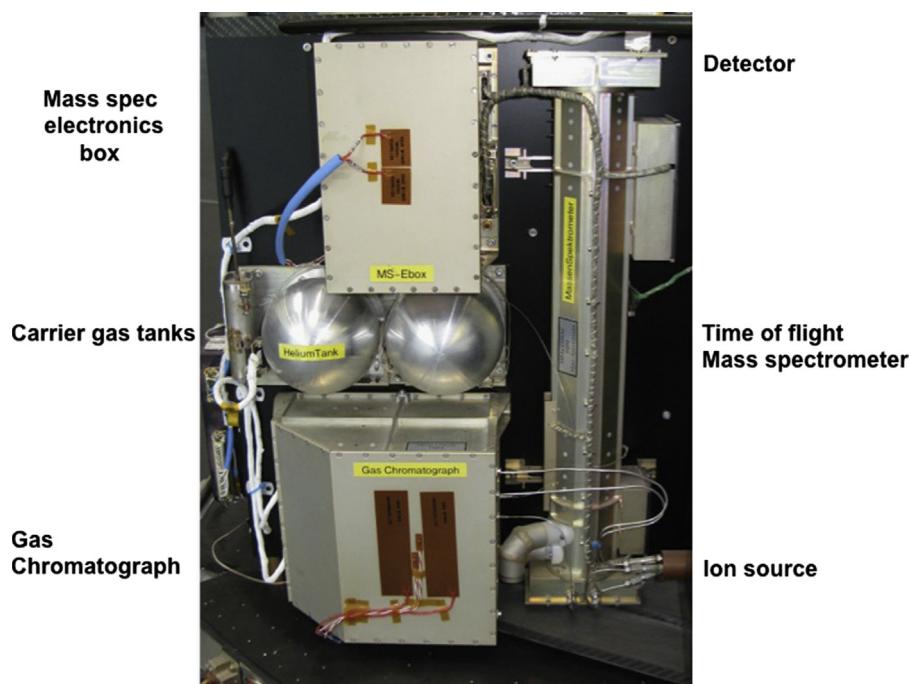


Fig. 2. Integrated COSAC instrument. The two spheres in the center are the carrier gas tanks. The white box above is the electronics box containing the data processing unit and MS electronics. The box below contains the electronic and pneumatic part of the GC. The long structure on the right is the ToF-MS with the ion source at the bottom and the detector at the top. The ovens and the tapping station are not visible in the image. They are located at the far right outside of the warm compartment.

rapid migration of giant planets (Gomes et al., 2005). Extraterrestrial material delivered to young terrestrial planetary surfaces during this period may have provided organic compounds and water, the necessary ingredients for the emergence of life (Chyba and Sagan, 1992; Ehrenfreund et al., 2002). Impacts of icy bodies could have also been responsible for the manufacture of complex organic molecules during the process of shock synthesis (Martins et al., 2013).

Photometric and spectroscopic surveys of more than 100 comets have enabled the taxonomy of comets (Mumma and Charnley, 2011). More than 50 molecules have been identified in cometary comae (Crovisier et al., 2009; Di Santi and Mumma, 2009). About 20 species are identified as primary, coming from the comet nucleus, in contrast to molecules that are produced in the inner coma; others may be both primary and product in origin (e.g. H₂CO, CO) (Mumma and Charnley, 2011). Some organic molecules observed in cometary comae probably originate wholly or partially from the decomposition of larger molecules or particles, which suggests the presence of large polymers such as polyoxymethylene and HCN-polymers (e.g. Ehrenfreund et al., 2004; Cottin and Fray, 2008).

Our current knowledge of comets from ground- and space-based observations is mainly focused on material and processes in the cometary coma. However, past and recent space missions have also greatly contributed to our understanding of cometary nuclei and what we can expect upon landing on comet 67P. Rosetta's target is assigned to the Jupiter Family of comets that originate from the Kuiper Belt and are characterized by orbital periods of less than 20 years.

2.1. ICE, Vega 1, Vega 2, Suisei, Sakigake, Giotto, Extended Giotto Mission

NASA's ISEE 3 mission, which was renamed the International Cometary Explorer (ICE), became the first spacecraft to encounter a comet when it was re-targeted to intercept 21P/Giacobini-Zinner and flew through the tail of that object on 11 September, 1985. *In situ* measurements of energetic particles, waves, plasmas and fields were implemented and it was established that the interaction of the solar wind with comets provides a rich source of plasma physics phenomena (Von Rosenvinge et al., 1986).

An armada of spacecraft encountered comet 1P/Halley in 1986 including: two Russian spacecraft (Vega 1 and Vega 2); two Japanese spacecraft (Suisei and Sakigake) and ESA's Giotto spacecraft (Reinhard and Battrick, 1986).

In the course of the above encounters, only Giotto penetrated the contact surface of the comet and traversed the magnetic cavity (Neubauer et al., 1986). Energetic water group ions with $E > 260$ keV and less than 3.5 MeV were recorded in the cavity by the EPONA instrument, together with charged dust particles (McKenna-Lawlor et al., 2014). The Ion and Neutral Mass Spectrometers (resp. IMS and NMS) confirmed the detection of molecules already observed remotely (Cottin et al., 1999 and references therein). They also showed the presence of extended sources (Eberhardt, 1999) that can partly be attributed to the degradation of polyoxymethylene (POM) in the coma (Huebner et al., 1987). The PIA experiment (onboard Giotto) and the PUMA experiment (onboard Vega 1), both of which were dust impact mass spectrometers, revealed the presence of complex organic materials in grains collected in the cometary dust tail. More particularly, numerous organic ions with m/z values up to about 160 were reported to be present (Kissel and Krueger, 1987), only few of which can have been strictly identified. All of these investigations indicate the presence of large amounts of organic molecules at the surface of Comet 1P/Halley. On 10 July 1992 during the Extended Giotto Mission, an encounter with comet 26P/Grigg-Skjellerup allowed comparisons to be made, using the same suite of particle and field

instruments, between the characteristics of a comet having a low gas production rate ($Q = 7.5 \pm 1.5 \times 10^{27}$ water group mol s⁻¹—26P/Grigg Skjellerup) and those of a highly active comet 1P/Halley ($Q = 6.9 \times 10^{29}$ water group mol s⁻¹) (McKenna-Lawlor, 1999).

2.2. Recent missions to comets: Deep Impact, Stardust, EPOXI

The Deep Impact mission drove a 370 kg copper impactor into comet 9P/Tempel 1 (A'Hearn et al., 2005). The impact created a 100 m wide crater and the spacecraft observed the ejected material (e.g. Sunshine et al., 2007). Properties of the dust cloud caused by the Deep Impact experiment have been investigated and there is no evidence in the data of an enhancement in sub-micron particles in the ejecta compared to the typical dust distribution in active comets (Jorda et al., 2007).

NASA's Stardust comet sample return mission captured cometary dust intact at a collection velocity of 6.1 km s⁻¹ at a distance of about 300 km from the nucleus of comet 81P/Wild 2. The data provided evidence for the radial transport of large solid grains from the center of the solar nebula to the Kuiper belt (Brownlee et al., 2006). Laboratory analyses of returned material from the Stardust mission showed presence of the amino acid glycine (Elsila et al., 2009) as well as methyl and ethyl cyanide (Glavin et al., 2008).

The coordinated flyby of 103P/Hartley 2 during the EPOXI mission (renamed from Deep Impact after the Tempel 1 experiment) and the world-wide observing campaign during its recent near-Earth approach have provided remarkable images of the nucleus at radar (Harmon et al., 2011) and optical wavelengths, along with much new information on the composition and heterogeneity of this Jupiter-family comet (A'Hearn, 2011; Meech et al., 2011).

The results of NASA's successful Deep Space-1, Stardust, and Deep Impact exploration missions of comets 19P/Borrelly, 81P/Wild 2 and 9P/Tempel 1 have revealed an unexpected diversity of surface morphology on these low density, icy objects. However, investigations on the cometary surface of comet 67P will be crucial to reveal the true properties of a comet nucleus and the solar nebula conditions during comet formation.

2.3. The most recent comet ISON C 2012 S1

Comet ISON (official name comet C/2012 S1 but later renamed ISON to recognize the *Russian International Scientific Optical Network* used to discover it on 21 September, 2012), was a sun-grazing comet composed of components that included water, ammonia, methane and carbon dioxide. Images of ISON obtained by the Swift and Deep Impact spacecraft during January and February 2013 showed the comet to be active with an extended tail.

Measurements were made from April–May, 2013, using The Hubble Space Telescope (HST), of ISON's size, and of the color, extent, and polarization of its emitted dust (hubblesite.org/go/ison). Observations of the comet with HST at 3.8 AU showed jet-like features (Hines et al., 2014). On 13 June observations made using the Spitzer Space Telescope, when the comet was at a distance of about 500×10^6 km from the Sun, indicated that CO₂ out-gassing was of the order of 10^6 kg per day, while, contemporaneously, 54.4×10^6 kg of dust were emitted. Spectra obtained at, among other sites, the University of Hertfordshire showed in October, 2013 lines attributable to emissions from cyanogen and diatomic carbon.

ISON was initially suspected to have suffered complete dissolution on the day of its perihelion passage (28 November 2013) due to solar heating and tidal forces. However, a coma-like feature observed late on that day by members of the *Comet ISON Observing Campaign/CIOC* suggests that a small fragment may, in actuality,

have survived perihelion. On 2 December 2013 CIOC announced that comet ISON had fully disintegrated.

In summary, although exciting space missions and ground-based observations have strongly enhanced our knowledge concerning the nature of several comets, the detailed properties and composition of their nuclei is largely unknown. Thus *in situ* investigation of the cometary surface of comet 67P can provide a breakthrough; in particular COSAC will allow a detailed assessment of its organic inventory.

3. Target 67P/Churyumov–Gerasimenko (67P): Recent observations and modelling

Comet 67P/Churyumov–Gerasimenko (67P) was discovered in 1969 and has been observed between 1969 and now from Earth on several approaches to the Sun. Its estimated diameter is ~ 4 km with a surface albedo of ~ 0.04 . Comet 67P was at 4 AU when Rosetta arrived at the comet in June 2014. The Rosetta spacecraft will follow comet 67P for several months and study its evolution through perihelion out to 2 AU. Comet 67P will reach perihelion at 1.24 AU in August 2015. Observations have shown that comet 67P is unusually active for a short period object and it is classified as a dusty comet.

The peak dust production rate in 2002/2003 was estimated to be approximately 60 kg s^{-1} , although values as high as 220 kg s^{-1} were reported in 1982/1983 (Agarwal et al., 2010). The gas to dust emission ratio is approximately 2. HST's images showed that the nucleus measures five by three km and has an ellipsoidal shape. The comet rotates once in approximately 12 h.

Thermal evolution models for 67P were computed by De Sanctis et al. (2005, 2010) and compositional and physical results have been reported by Schleicher (2006). The evolution of the activity and composition of the coma of 67P was studied along its post perihelion orbit from 2.29 AU to 3.22 AU (Schulz et al., 2004).

Comet 67P was observed twice from the WISE spacecraft on previous passages at distances of 3.32 and 4.18 AU, respectively. Dust production rates reported are of the order of 10^4 g s^{-1} and production rates for CO_2 emission at 3.32 AU of $5 (\pm 2) \times 10^{25} \text{ molecules s}^{-1}$ have been measured as well as a mean dust grain size of 1 mm (Bauer et al., 2012).

A large number of studies have been performed on comet 67P in recent years to optimize the future scientific investigation of the Rosetta target. Earth-based observations have required extensive image processing due to the position of the comet in a rather bright area of the Milky Way. A well calibrated light-curve has been recently published by Snodgrass et al. (2013) which can be used to measure a brightness-distance relationship and to predict the future brightness of the comet.

Previous activity data of 67P were measured at a pre-perihelion distance from the Sun of 4.3 AU. These data suggest that only a small fraction (1.4%) of the surface was active and the comet shows a higher dust-to-gas ratio than average. The shape model and thermophysical analysis of the comet strongly imply a broad nucleus shape and a low thermal inertia of $< 15 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-1/2}$ indicating a surface regolith finer than lunar surface material (Lowry et al., 2012).

Several dust jets have been observed by Lara et al. (2011) indicating an activity that is not isotropically distributed on the surface but rather regional. Spin and activity of comet 67P have shown 3 active regions localized at -45° , 0° , and $+60^\circ$ of latitude (Vincent et al., 2013) that remained similar in two appearances indicating no changes in activity.

The Microwave Instrument MIRO on the Rosetta orbiter conducted its first observations of water vapour in June 2014. Observations in June 2014 of Rosetta's target comet with the OSIRIS camera showed no more an extended dust cloud around the nucleus and a significant drop in its brightness. Images from

July 2014 revealed a two-fold shape of comet 67P which represents a challenge for the forthcoming landing maneuver.

4. Rosetta landing

During 2014, Rosetta will characterize the nucleus of 67P with the orbiter instruments in a stepwise approach. Several Phases have been defined (Ulamec et al., 2013, Accomazzo and Biele, 2013):

- Near Comet Drift (NCD) and Far Approach Trajectory (FAT): distance to the comet about 100 km.
- Close Approach Phase (CAP): Pyramid-like trajectories will lead the spacecraft as close as about 50 km (towards the end of this phase) to the comet nucleus. Digital Terrain Models (DTMs), which are essential for landing site selection and the definition of a landing strategy, will be generated.
- Global Mapping Phase (GMP): global mapping of the surface of the comet from 20 km bound orbits.
- Close Observation Phase (COP): the aim is to fly orbits as close as possible to the surface of the comet (currently 10 km radius, i.e. ca. 7.5 km altitude); during this phase the selected landing site can be chosen after obtaining high resolution images.

The selection of the landing site is driven by the observations necessary to characterize the comet (Biele and Rosetta Working Group WG1, 2010; Accomazzo and Biele, 2013). At the end of the CAP phase, about 80 days prior to landing five potential landing sites will be identified. These will be reduced to two 60 days prior to landing, and the nominal site will be confirmed one month before landing. The final timeline for the lander will be up-loaded 5 days before separation. The nominal day for landing is November 11th, 2014, when comet and spacecraft are exactly 3 AU from the Sun.

Philae will be pushed off the Rosetta Orbiter with an adjustable ejection device, based on three lead screws which allow separation velocities to be between 5 cm s^{-1} and 50 cm s^{-1} , see Fig. 3. The Lander will descend ballistically to the surface of the comet, stabilized by an internal fly-wheel, on a pre-calculated trajectory. At touch-down, two harpoons will be fired to anchor Philae to the ground. An Active Descent System (cold gas system, ADS) will be activated to minimize any possible—bouncing. The landing gear is designed to dissipate most of the impact energy; screw devices in the feet will allow additional fixation to the surface material. After landing and anchoring, the landing gear allows rotation of the Lander main body, which gives flexibility in choosing the exact location for drilling and sample acquisition.

The on-comet operations of Philae are separated into two phases: a First Scientific Sequence (FSS), based on the energy in the primary battery, lasting for about 50 h and allowing all instruments (including COSAC) to operate at least once. After this, Long Term Science (LTS) starts, relying on the power generated by the solar generator and ideally lasting for several months. During LTS, instruments can operate only every 2–3 days (depending on the actual power generated at the particular landing site). COSAC science will be in competition with the other instruments aboard the lander.

5. COSAC measurements

5.1. First *in situ* inventory of volatile compounds from a cometary surface with COSAC

Remote spectroscopic observations of active comets are today the primary source of information about the cometary content of volatile compounds. They already revealed the presence of more

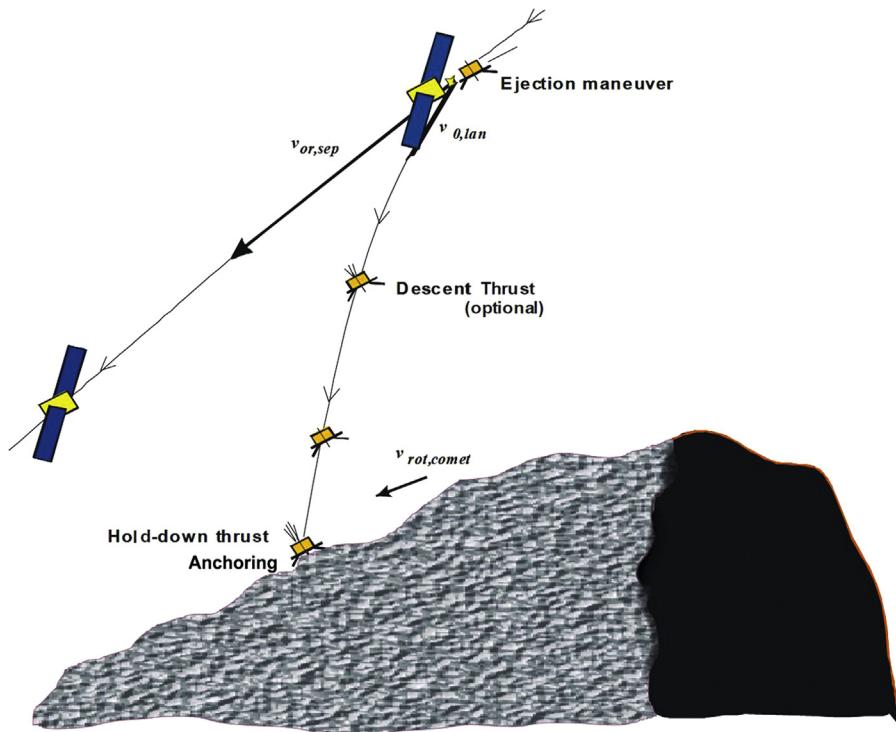


Fig. 3. Landing sequence (Ulamec et al., 2006).

than 50 species in cometary comae (Crovisier et al., 2009; Di Santi and Mumma, 2009).

This number of molecules is significantly lower than the number of molecules detected in interstellar clouds (<http://www.astro.uni-koeln.de>). Comets have retained a part of the composition of the cloud that formed the solar system. Therefore it can be expected that many molecules detected in the interstellar medium will also be found in cometary material. Through measurements at the cometary surface, COSAC can monitor volatile species that may be of interstellar nature or perhaps were produced through processing in the primitive solar nebula. Among the parameters that play a role in the composition of cometary volatiles, the temperature of formation is probably the most critical one. An inventory of noble gases and light inorganic and organic species would give a result in order to estimate the thermal history of 67P. Of prime interest is the detection of organic species directly linked to thermal effects in interstellar or cometary ices, such as hexamethylenetetramine (Briani et al., 2013; Vinogradoff et al., 2013), which could bring important complementary information.

Comets are thought to have delivered various materials to the Earth. Recent measurements of the oxygen isotopic ratio of water contained in a Jupiter family comet, 103P/Hartley 2 (Hartogh et al., 2011) seems to prove that comets could have been the major source of the water on Earth. Unlike PTOLEMY (Wright et al., 2007) or ROSINA (Hässig et al., 2013) COSAC is not specifically devoted to achieve this type of measurement. However, COSAC can provide estimates of the isotopic ratios to support discussions on the relationship between cometary and Earth volatiles.

Cometary organic material could have made a significant contribution to the organic inventory present on the primitive Earth (Chyba and Sagan, 1992). An inventory of organics of the comet nucleus measured by COSAC will greatly advance our knowledge on how comets contributed to the prebiotic chemistry on Earth. The identification of building blocks of life such as nucleic acids and amino acids (see Section 5.3) will be exciting. But also the presence of simple molecules that can be at the origin of chemical reaction chains producing more complex molecules of

biological interest, such as HCN or HCHO (Cottin et al., 2003) will represent important findings.

Finally, organic polymers are suspected to be present in comets especially when considering a few extended sources such as CO, which could partly originate from polyoxymethylene (Cottin et al., 2004). The detection of polymers is challenging and complementary analytical techniques are needed to assess their presence in a comet nucleus. For instance, the combination of measurements performed with COSAC at the cometary surface, and of grains sampled in the coma by COSIMA (Le Roy et al., 2012) could lead to the formal detection of polymers.

5.2. Desorption and irradiation of pre-cometary ice analogs to test the performance of COSAC

Dedicated laboratory experiments under high-vacuum conditions, dealing with the deposition of gas mixtures onto a cold surface at 10 K, containing up to five different molecular components (water, ammonia, methanol, carbon monoxide and carbon dioxide), were performed. Water was generally the dominant ice component to mimic the composition of ice mantles in inter- and circumstellar environments.

The formed ice samples were photo-processed by vacuum-UV radiation and later warmed up to room temperature, leading to the synthesis of an organic refractory residue. A slow warm-up of the ice mixtures without irradiation did not lead to formation of a residue. First, the results obtained in ice irradiation experiments will be presented below. Second, we will introduce the results from temperature programmed desorption (TPD) experiments of non-irradiated ice mixtures.

During ice irradiation at 10 K, new simple molecules, fragments, and radicals form, which react during warm-up leading to more complex species. In addition to the compounds identified by chromatographic techniques, other species were detected *in situ* by infrared spectroscopy; these include hexamethylenetetramine $[(\text{CH}_2)_6\text{N}_4, \text{HMT}]$, ammonium salts of carboxylic acids, $[(\text{R}-\text{COO}^-)(\text{NH}_4^+)]$, amides $[\text{H}_2\text{NC}(=\text{O})-\text{R}]$, and esters $[\text{R}-\text{C}(=\text{O})-\text{O}-\text{R}']$ (Bernstein

et al., 1995; Muñoz Caro and Schutte, 2003; Muñoz Caro et al., 2004; Muñoz Caro and Dartois, 2009, 2013).

So far, the most characteristic infrared fingerprints of these organic refractory residues, i.e. those absorbing in the 3.4 μm region with peaks at 3.42 and 3.48 μm , were not observed in the space environment (Muñoz Caro and Dartois, 2009). But, as it was earlier suggested (Oró, 1961), some comets are probably the best candidates to host in relatively high abundances complex organic species of interest for prebiotic chemistry (Muñoz Caro and Dartois, 2009, 2013, and references therein). If, as it is commonly thought, comets were formed by accretion of tiny dust particles covered by ice mantles, it is important to study the role of processing in pre-cometary ice analogs to explain the presence of organic refractory matter (also called CHON particles based on their elemental composition), first detected during the Halley missions (Kissel et al., 1986a, b).

For instance, a thin ice sample in the laboratory cannot reproduce the expected continuous desorption of the more volatile species like CO, which emerges from deeper (and thus colder) layers in the comet nucleus. In order to serve as a benchmark for the interpretation of the COSAC sniffing mode data, temperature programmed desorption (TPD) experiments of ice mixtures with 5 molecular components were recently performed, using infrared spectroscopy and quadrupole mass spectrometry (Martín-Doménech et al., 2014), see Fig. 4. Desorption of all species at temperatures similar to those in the pure ice form was observed when their relative-to-water abundances were above 3%. In addition, desorptions at higher temperatures were observed for all the species except water, indicating entrapment of molecules within the water ice structure. Analog to the well-known co-desorption of other molecules with water near 165 K, it was found that methanol, a molecule that makes hydrogen bonds in the ice with a strength slightly lower than that of water, also led to entrapment and co-desorption (starting at 140 K) of species like CO, CO₂, and NH₃.

5.3. Organic molecules

A wide range of organic compounds can be expected in the comet nucleus produced from the chemical evolution of its main constituents. In addition to the small volatile compounds described in Section 5.2 the reaction products of any photochemical or other ice processing remain trapped in the comet nucleus. These products include a number of organic chemical compounds that are not necessarily biomolecules themselves, but can serve as building blocks for biomolecules and can thus be found in many living systems. Finding any of these molecules on a comet would indicate an available pool of complex precursor molecules that could have been delivered to the early Earth through impacts. Starting with the results of an experiment with a pre-cometary ice analog composed only of methanol and ammonia (Nuevo et al., 2010), a number of substances have been identified that could be good targets for the COSAC experiment.

In an ice mixture composed of methanol:ammonia (1:1) exposed to vacuum ultraviolet radiation from an H₂-discharge lamp for ~44 h, six simple, water soluble organic molecules were found after slowly warming the sample to room temperature. These were urea, glycolic acid, hydroxyacetamide, glycerol, glyceric acid, and glycerol amide.

As these molecules are all condensed from methanol, it is not surprising to see that they exhibit so many C–O subunits. On the comet, however, the C-sources for a synthesis should be more versatile, so it is expected to find other, similar molecules as well. Here, a systematic list of other substances will be compiled. In a first step, we see that, when methanol is added to glycolic acid, glyceric acid is formed (Fig. 5, middle column). If, however only a methyl radical is added, the formed product is lactic acid.

The same is applicable to amides (Fig. 5, right-hand column) to yield lactamide. In a second step, not only the carboxylic acids, but lower oxidation states are considered, too. Here we have 2-hydroxy propanal and 2-hydroxy propanol (also called propylene glycol), which are derived from glycolic acid, and glyceraldehyde (between glyceric acid and glycerol).

Since we do not know, which specific chemical pathways were/are open for organic synthesis on a comet or their precursor materials, we need to assume that the described ice experiments do not yield exactly the same compounds present on the comet. What we can be sure of, however, is that compounds with a certain size and composition can be formed. It is therefore proposed that all structural isomers of the substances described above and shown in Figs. 5 and 6, are suitable targets for the COSAC instrument. These isomers are listed in Table 1.

5.4. Amino Acids as COSAC's target compounds

When preparing for the 2014 COSAC investigations on comet 67P based on the Greenberg cometary core-grain model (Greenberg, 1982), pre-cometary interstellar/circumstellar ices were simulated in the Sackler laboratory at Leiden Observatory by subjecting condensed volatile molecules such as water, ammonia, methanol, carbon monoxide and carbon dioxide under low temperature and low pressure conditions to ultraviolet irradiation. 16 Amino acids were identified in the interstellar ice analogues (Muñoz Caro et al., 2002) and new detection techniques revealed the presence of 20 amino acids and 6 diamino acids (Meinert et al., 2012a). Similar experiments performed by a team at the NASA Ames center also showed the presence of amino acids in the material produced from the irradiation of simulated interstellar ices (Bernstein et al., 2002). Therefore, amino acids are key targets for revealing cometary chemistry, and they have to be investigated in detail by the COSAC instrument (Thiemann and Meierhenrich, 2001).

The list of 12 chiral (see Section 5.5) and 12 non-chiral substances serves as a guideline for compounds that could be found on the comet nucleus. These are all stable molecules that should be very easily identifiable by GC/MS since they are all carboxylic acids, amides or alcohols. For these groups of substances analytical protocols, including derivatization by dimethylformamide dimethylacetal (DMF-DMA), are available and established.

From the analytical point of view, amino acids and carboxylic acids require a chemical derivatization step in order to be transformed into volatile species that can be analyzed using gas chromatographic techniques. The COSAC gas chromatograph will apply chemical derivatization using DMF-DMA (Meierhenrich et al., 2001a). Derivatization also allows to perform high quality chromatography on volatile polar molecules. In addition to amino acids, N-heterocycles and amines were identified in the refractory residues of interstellar/circumstellar ice analogues (Meierhenrich et al., 2005) in preparation for the COSAC 2014 investigations (Meierhenrich et al., 2001b).

5.5. Chirality investigations by COSAC

Terrestrial biomolecules are all one-handed, or homochiral, e.g. nucleic acids are made of all-D sugars, and the code for proteins is made of all-L amino acids, in contrast to non-living material, which is normally racemic. Any deviation from the racemic state in nature would be most unusual, and could indicate either biological activity (unlikely in a comet) or else pre-biotic chemistry in the process of going homochiral, perhaps due to some external chiral influence.

So far enantiomeric excesses (e.e.) of extraterrestrial origin have been the excesses of L-amino acids found in various carbonaceous chondrite meteorites (Cronin and Pizzarello, 1996; Glavin and Dworkin, 2009). An important goal of the COSAC instrument is

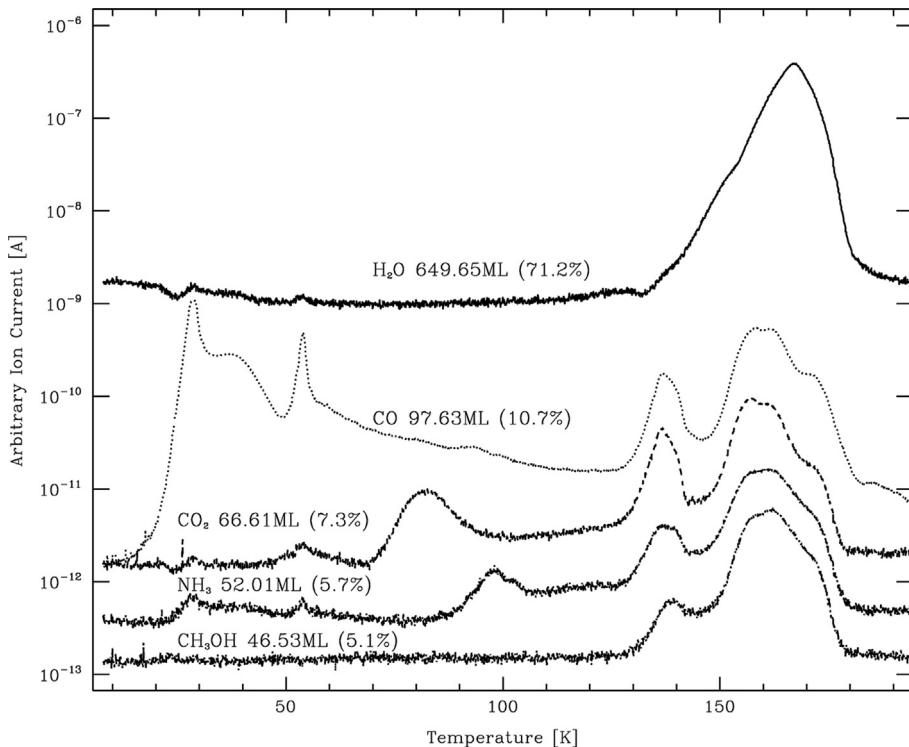


Fig. 4. Displayed are the results of the temperature programmed desorption (TPD) experiment of an ice mixture, deposited at 8 K, warmed up at a rate of 1 K min^{-1} . The relative abundances and number of monolayers (ML, one monolayer is defined as a column density of $1 \times 10^{15} \text{ molecules cm}^{-2}$) of each component is displayed. The presented data were obtained with a quadrupole mass spectrometer (QMS), which detects molecules in the gas phase desorbing from the ice. The peaks below 110 K are similar to those in pure ice experiments. Co-desorptions of the more volatile species (CO, CO₂, and NH₃) with CH₃OH and H₂O were observed around 140 K and 165 K, respectively. The data curves are offset in the y-axis for clarity. The data are adapted from Martín-Doménech et al. (2014). The TPD curves of a pre-cometary ice analog, taking into account the estimated heating rate of the comet surface, indicate that water molecules could already be detected in the cometary coma during the first approach of the Rosetta mission in July 2014, when the mean temperature of the cometary surface should be about 140 K.

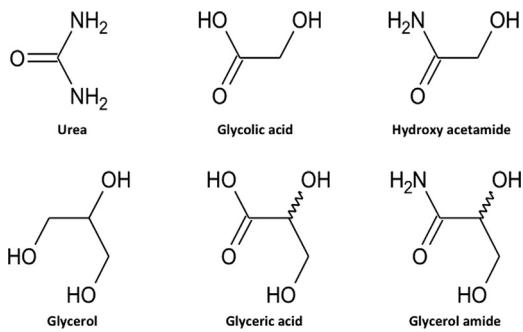


Fig. 5. The six molecules identified in a pre-cometary ice analog composed of methanol:ammonia (1:1) and VUV-irradiated for 44 h. Looking at the chemical structures of these products, a certain pattern can be seen and missing molecules can be identified that should form in analogous reactions with different starting materials.

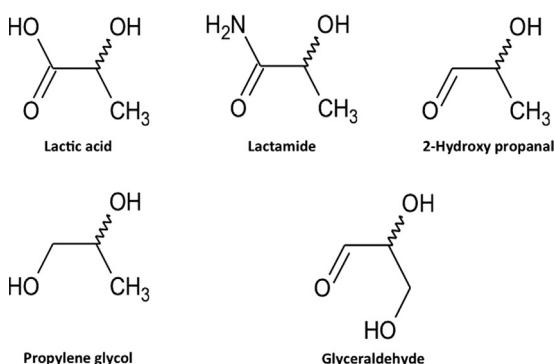


Fig. 6. Chemical structures derived from those in Fig. 5.

to reveal whether such enantiomeric excesses are also present in comets.

The broken symmetry of biomolecules has attracted immense scientific interest for decades (Jones, 2012; MacDermott, 2012), and although it is clear that homochirality is essential for an efficient biochemistry, the particular choice of the natural L-amino acids over their “unnatural” D mirror images has remained unexplained. Various physico-chemical models have been developed in order to explain biomolecular symmetry breaking. The enantiomeric excesses in meteorites suggest an attractive photochemical model in which the initial symmetry-breaking event occurs in interstellar space. The detection of circularly polarized light (CPL) in the OMC-1 star formation region of Orion (Bailey et al., 1998) and more recently in NGC 6334-V (Kwon et al., 2013) suggests that the asymmetric photochemical interaction of CPL with racemic organic molecules might result in enantiomeric enhancements of interstellar and cometary chiral molecules (Meinert et al., 2011). The interaction of CPL with amino acids does indeed produce circular dichroic features (Meinert et al., 2012b) that were shown to induce asymmetries of up to 4.2% enantiomeric excess in the amino acid alanine (Meinert et al., 2014). The CPL-initiated synthesis of interstellar ice analogues starting with water, methanol, and ammonia (2:1:1) resulted in the formation of amino acids showing enantiomeric excesses in the 1% range (De Marcellus et al., 2011).

Alternatively, the universal weak nuclear force might have transferred its inherent asymmetry to biomolecules (Yamagata, 1966; MacDermott, 1995, 2012). The weak force could exert its chiral influence through either the weak charged current (WCC) or the weak neutral current (WNC).

The WCC produces an excess of left-handed electrons in beta-decay, which could in turn produce an enantiomeric excess in chiral

Table 1

List of structural isomers of molecules identified in pre-cometary ice experiments.

# C	# N	# O	Formula	Substances
1	2	1	CH ₄ N ₂ O	Urea
2	0	3	C ₂ H ₄ O ₃	Glycolic acid
2	1	1	C ₂ H ₅ NO	Acetamide, <i>N</i> -methyl-formamide
2	1	2	C ₂ H ₅ NO ₂	Hydroxy acetamide, glycine, carbamic acid-methylester
2	2	0	C ₂ H ₁₀ N ₂	1,2-Diamino propane*, 1,3-diamino propane
3	0	2	C ₃ H ₆ O ₂	2-Hydroxy propanal*
			C ₃ H ₈ O ₂	Propylene glycol*, 1,2-propanediol*
3	0	3	C ₃ H ₆ O ₃	Lactic acid*, glyceraldehyde*, methoxy-acetic acid
			C ₃ H ₈ O ₃	Glycerol
3	0	4	C ₃ H ₆ O ₄	Glyceric acid*
3	1	1	C ₃ H ₉ NO	1-Amino-2-propanol*, 2-amino-1-propanol*
3	1	2	C ₃ H ₇ NO ₂	Lactamide*, (β)-alanine(*), urethane, <i>N</i> -methylglycine
3	1	3	C ₃ H ₉ NO ₂	3-Amino-1,2-propandiol*, 2-amino-1,3-propandiol
			C ₃ H ₇ NO ₃	Glycerol amide*, serine*, isoserine*, <i>N</i> -hydroxy urethane

*Denotes chiral molecules.

molecules (the Vester–Ulbricht process), either by direct interaction of spin-polarized electrons (Darge et al., 1976) or via chiral Bremsstrahlung (Ulbricht and Vester, 1962). Such processes could be of particular importance in early cometary environments in which ²⁶Al contributed to thermal heating of cometary nuclei, providing a considerable flux of chiral positrons that might have interacted with cometary racemic organic molecules (Meierhenrich, 2008).

The WNC produces a small parity violating energy difference between enantiomers (MacDermott, 2012; Quack, 2002) and the resulting tiny enantiomeric excess could be amplified by autocatalytic polymerization reactions (Sandars, 2003). To verify the above hypotheses based on CPL and the weak nuclear force, it was proposed to investigate the chirality of organic molecules of cometary, interplanetary, and interstellar origin (MacDermott et al., 1996). The COSAC instrument is the first ever device launched into space capable of distinguishing between chiral molecules. The COSAC instrument was designed to include a ‘Chirality-Experiment’ by employing enantioselective stationary phases for the resolution of enantiomers (Thiemann et al., 2001).

If enantiomeric excesses are detected in organic molecules (Evans et al., 2012), we will be able to apply anisotropy spectroscopy (Evans et al., 2013) of the molecules under investigation including amino acids and diamino acids (Bredehoft et al., 2007) in order to deduce whether the enantiomeric excess was induced via asymmetric photochemistry or other chiral driving forces.

6. COSAC instrument performance

A detailed presentation of the COSAC instrumental suite can be found in Goesmann et al. (2007). In order to meet the Philae Lander’s dimension requisites, COSAC has been substantially miniaturized as compared with commercial bench-top gas chromatography-mass-spectrometry GC-MS suites.

The main COSAC components are the GC capillary columns packed in a pneumatic hardware box, a time-of-flight MS, carrier gas containers and the allied electronics box that assists in the payload’s remote operations, see Fig. 7. The miniaturization translates in the first instance into a decreased total mass; a mere 4.5 kg. Second the power dissipation of the entire payload peaks at 20 W. These modifications separate COSAC from performance equivalent to those of bench-top instruments that can have desired power supplies, equipment mass, and data processing software. COSAC nevertheless is designed to conduct significant compositional analyses, even under harsh environmental conditions, on the comet nucleus. Any results, qualitative or quantitative, yielded by COSAC will have pioneering status.

6.1. Challenges for the COSAC-GC

The GC performance was investigated using the flight spare model in a vacuum chamber. The results are described in Szopa et al. (2007). The challenges for the gas chromatograph of COSAC stem from its miniaturized design and the environment in which it has to operate.

The GC hardware is subjected to extremely cold cometary nucleus temperatures. The ovens, oven-to-columns transfer tube, the thermally operated valves, and the eight chromatographic columns are the only hardware that can be heated. The high temperature oven and the medium temperature oven, mounted on the carousel, can heat the sample to a maximum of 600 °C and 180 °C, respectively. The oven temperature value can be commanded in 255 steps. The exact translation into actual temperature is not easy and depends on the initial temperature of the oven (Philae balcony environment) and the COSAC electronics temperature. The range is approximately between 0 °C and 600 °C.

The evolved gas, generated from sample heating in the oven, moves from the tapping station to the GC via a stainless steel transfer tube. The transfer tube can be heated, but in a rather coarse way. The heater can be commanded ON or OFF and the tube temperature can be monitored in the housekeeping data. Housekeeping data refers to the real-time measurements of various instrumental parameters that are important for real-time assessment of COSAC’s operational performance. It assists in smooth acquisition of scientific data but is itself not of imminent scientific relevance. Owing to the potentially high amount of water ice in the sample, evolved gas containing water vapour is another cause of concern for the performance of the tube and GC columns.

After the transfer of the first sample from the tapping station to the tube, when the heated tube and columns will cool down, there is a possibility of vapour condensation on the inner periphery of the tube and columns. Eliminating this condensed vapour from the tube will be demanding due to restricted power supplies on the lander. Also the oven and the transfer tube cannot be heated concurrently due to power constraints. To overcome this, the tube will be heated prior to the oven; and this prior tube heating inhibits the condensation in the tube of evolved gases. During the actual oven heating, the tube heater is off, but it is switched on again afterwards. In addition the heating of the GC column is interrupted during oven heating, but resumed thereafter.

The temperature and pressure of the COSAC-GC columns are maintained at a constant value unlike its commercial counterparts whose temperature and pressure values can be ramped under constant flow conditions. The injection system also differs largely from commercial solutions.

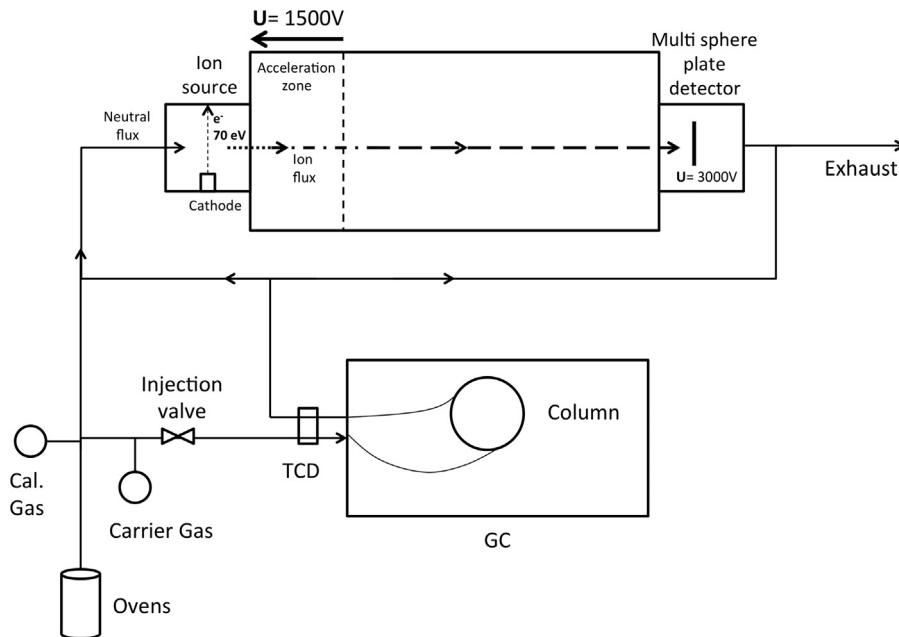


Fig. 7. Schematic outline of the sample flow within COSAC (for a more detailed version see [Goesmann et al., 2007](#)). In GC–MS mode gas produced by heating a soil sample in the oven is guided into the GC where it is injected into a carrier gas stream and separated into components in the GC columns (only one depicted). It passes the two channels of a thermal conductivity detector on the way into the column as well as on the way out. The effluent can be routed to the ToF-MS where the molecules are ionized (and fractured), accelerated, and detected. In addition a direct flow oven – MS or GC – exhaust can also be routed. The MS can also be operated without oven or GC (sniffing mode).

It is based on switching valves and described in [Goesmann et al. \(2007\)](#). Column conditioning can be conducted at column temperature of 70 °C, while the column temperature during a chromatographic run will be approximately 30 °C.

6.2. Advantages of the COSAC-GC

Despite all the above hardware limitations, the operational settings can be chosen for many parameters. As mentioned above, the ovens and transfer tube temperatures can be chosen as required. The chromatogram injection time for the evolved gas can be set via telemetry command from zero to 65,000 ms in a step width of 1 ms.

The effect of injection time has been observed to affect the sensitivity in terms of peak dimensions. An injection time below 2 s produces hardly any signal. Greater injection times, above 10 s increases the sensitivity but widens the peaks. An injection time of 6.5 s has been considered optimum, since it curbs peak overlapping and maintains practical resolution ([Szopa et al., 2007](#)).

The column head pressure can be set via telemetry command in 255 steps. The standard value for which the time to digital converters (TCDs) were tuned, is 221 which corresponds to a pressure of about 1.3 bar absolute. The column run time can also be set via telemetry command from 1 min to 17 min with a step width of 1 min. The GC allows two columns to be operated with simultaneous injection; this is known as the dual channel mode. Some of the columns in the COSAC-GC have affinity for same families of organic analyte species, for example MXT 20 and MXT 1701, but they tend to have varying elution times with regard to species. The dual channel mode can yield a two-dimensional signal that will confirm the existence of particular analyte species ([Szopa et al., 2004](#)).

6.3. Operational parameters of the COSAC-MS

The COSAC mass spectrometer is a multi-pass Time of Flight (ToF) spectrometer. It is designed as a linear spectrometer, with the ion source on one side, and the detector at the end. Once

volatile molecules injected in the MS are ionized they are all accelerated at the same energy of 1500 eV. Their time of flight within the spectrometer thus depends only on the square root of the mass-to-charge ratio of these ions (light ions travel faster than heavy ones). The detector is a multi-sphere plate secondary electron multiplier (SEM) coupled to a time to digital converter (TDC) for signal and flight time registration. The SEM is operated routinely at a voltage of 3000 V.

Ions are detected in 16,000 constant time bins of 2 ns for high resolution mode (8000 ns for low resolution mode). Emission current for the ion source and voltage for the detector parameters can be adjusted via telemetry command. So far only conservative values have been used in order to stress the flight unit as little as possible.

The in-flight COSAC-MS was operated several times during flight. The last operation was during the flyby of the main-belt asteroid 21 Lutetia in 2010 ([Goesmann et al., 2012](#)). This allowed the performance of the spectrometer to be estimated. The mass calibration of the time axis done by the Electrical Ground Support Equipment software appeared to be quite satisfactory and needed only minor corrections. The raw data as delivered by COSAC are ion count versus detector arrival time. This is converted into ion count versus mass per charge using a simple equation of the sort $m/q = (A \times \text{time} - B)^2$ where the parameters A and B, as determined during the instrument ground tests, are commonly used. The values are precise enough for a preliminary evaluation, i.e. allow for single mass accuracy. Some fine tuning is required depending on the operational condition. In GC–MS mode (high pressure in the MS due to GC gas load) they differ slightly from sniffing mode (low pressure in the MS). Mass spectra acquired during the Lutetia flyby presented noise. This noise most probably corresponds to actual ions coming from the ionization source ([Goesmann et al., 2012](#)).

6.4. Advantages of the COSAC-MS

By default the COSAC MS is used in low-resolution mode, ions follow only a single path (~37 cm) in the spectrometer before reaching the detector. The spectrometer resolution in this

configuration is $m/\Delta m = 350$ at m/z 70. Ionization is performed by electron impact at a standard energy of 70 eV (emission current of approximately 200 nA). This ionization energy is advantageous as it allows comparison with existing spectral databases (such as the NIST-MS database).

The comparison should only be qualitative (ions generated) but not quantitative (the intensity ratios are different). For redundancy purpose, the MS has three thermal electron cathodes that can be used alternatively. The mass range of the spectrometer in standard conditions (low resolution mode) goes from $m/z=1$ to 330. This range can be extended up to $m/z \sim 1500$. The total measurement time can be adjusted from 2 to 32 s in increments of 2 s. This is especially useful in GC-MS mode when data transmission gets volume critical. This offers the option of balancing chromatographic resolution versus data volume.

An originally envisaged high-resolution mode allowed multi-turn by using two grid-less reflectors on both sides. This mode can be commanded but it did not live up to expectations; it is operationally difficult and did not improve mass resolution. Two different procedures can be used to improve the signal-to-noise ratio of the COSAC MS. The first one is to command spectrum accumulation so that, instead of transmitting multiple spectra with little content, they can be added up internally. This is useful for long sniffing measurements where the ion count rate is expected to be low. A second possibility is numerical post-treatment of the data with binning of the channels. This supports an increase in the signal-to-noise ratio, but leads to a loss of information, especially regarding the mass resolution of the peaks.

7. Selected test results on volatiles, complex and chiral organic molecules

Because of the wide diversity of compounds and chemical families, which are expected in the cometary nucleus (e.g. Szopa et al., 2003), molecular analysis of this environment requires the use of several complementary gas chromatographic columns.

Eight different GC capillary columns connected in parallel are used to achieve the required gas chromatographic separation (Goesmann et al., 2007, 2009). They include five GC columns for general separation and three GC columns devoted specifically to chiral separation.

The five general columns use stationary phases selected to target four main groups of compounds (Szopa et al., 2003). A Carbobond column (Agilent) is devoted to the analysis of noble gases and very low molecular weight hydrocarbons (C1–C2). A MXT U column (Restek corp.) is used for separating low molecular weight organics and inorganics. A MXT 20 and a MXT 1701 are used to operate the separation of organic compounds, having up to about 6 carbon atoms of different chemical families.

The fifth generalist column, a MXT1 GC column, is optimized for the separation of heavier molecular weight organics, having more than 6 carbon atoms, including alkylated aromatic compounds and small PAHs. Several tests and calibrations have been achieved on these 5 columns (Szopa et al., 2001, 2002a,b, 2004). In particular their robustness for space application has been studied (Szopa et al., 2002a, 2014, in revision). Several examples of typical chromatographic analyses have been published previously (see Szopa et al., 2003, and references therein). In Fig. 8 we present a typical chromatogram obtained with the COSAC spare model using the MXT 20 column. It shows the capability of this column to separate organic compounds of interest for the study of comets, under operational conditions similar to those that will be used by the flight model.

Moreover, the efficiency of the GC coupling with the MS is demonstrated by the mass spectra regularly recorded during the

GC run. Fig. 8 shows that the overlap of butane and methanol peaks in the chromatogram, that usually prevents a direct identification of these molecules by pure chromatography, is resolved by the MS that clearly detects specific ions from the two species. Thus, through these calibrations in the laboratory the GC-MS mode is demonstrated to be fully operational.

A set of eight GC columns – identical to the flight columns – were kept under vacuum in the laboratory during the Rosetta cruise. Their chromatographic performances were tested before the Rosetta launch in 2003–2004, and at the end of the cruise, in 2012–2014. Three of the 8 stationary phases employ chiral selectants in form of chiral valine, β -, and γ -cyclodextrins embedded in liquid polydimethylsiloxane (PDMS) to chromatographically resolve enantiomers. In order to evaluate the robustness against space vacuum and potential loss of key monomers, volatiles, and chiral selectors, spare models of the three chiral stationary phases were exposed to vacuum conditions from 2004 to 2013, mimicking those conditions experienced in space. Before and after exposure to space vacuum environments the enantiomeric resolution capabilities were tested against three different chiral analytes.

Results show, that the resolution values confirm the presence of only slight variations in the range of chromatographic error bars and the authors concluded that the three enantioselective stationary phases maintained their resolution capacities throughout their journey (Meierhenrich et al., 2013). The chiral stationary phases for the COSAC instrument were selected in order to provide enantiomeric resolution for a wide variety of chiral organic compounds. They do not exclusively focus on the resolution of amino acid enantiomers (Giri et al., 2013). Chiral alcohols and diols (Meierhenrich et al., 1999) including 2-hexanol (Thiemann et al., 2001), as well as chiral branched aliphatic hydrocarbons (Meierhenrich et al., 2001c) including 3-methylhexane (Meierhenrich et al., 2003), carboxylic acids in the form of lactic, mandelic, malic, and tartaric acid (Meierhenrich et al., 2001a) as well as amino acids (Thiemann and Meierhenrich, 2001) will be resolved into enantiomers by the use of COSAC's enantioselective stationary phases and quantified for enantiomeric excess determination. A complete list of chiral organics as tested for the COSAC instrument is available at www.unice.fr/meierhenrich/COSAC.html.

For the five "generalist" columns, retention times, capacity factor, Van Deemter curves and behaviour related to low temperature conditioning were studied after 8 years under vacuum. The obtained results show, in general no significant degradation of the chromatographic performances of these five columns, except for the separation efficiency of the Carbobond column related to ethyne and that of the MXT-20 column related to propanal which decreased significantly.

8. Conclusion

During April 2014 the Post Hibernation Commissioning of spacecraft and payload was performed. In this phase all components of COSAC, electronics, mass spectrometer, carrier gas system, gas chromatograph, and tapping station were thoroughly tested. All tests were completed nominally. In particular the GC-MS run scheduled for the First Scientific Sequence was executed with identical operational parameters using the neighbouring oven on the carousel. This measurement will serve as reference and background information for the first soil measurement on the comet nucleus after landing. Keeping in mind that the instrument was assembled, tested, and delivered 12 years ago the system is in almost surprisingly good shape. The Deep Space hibernation phase does not seem to have had an impact on the hardware.

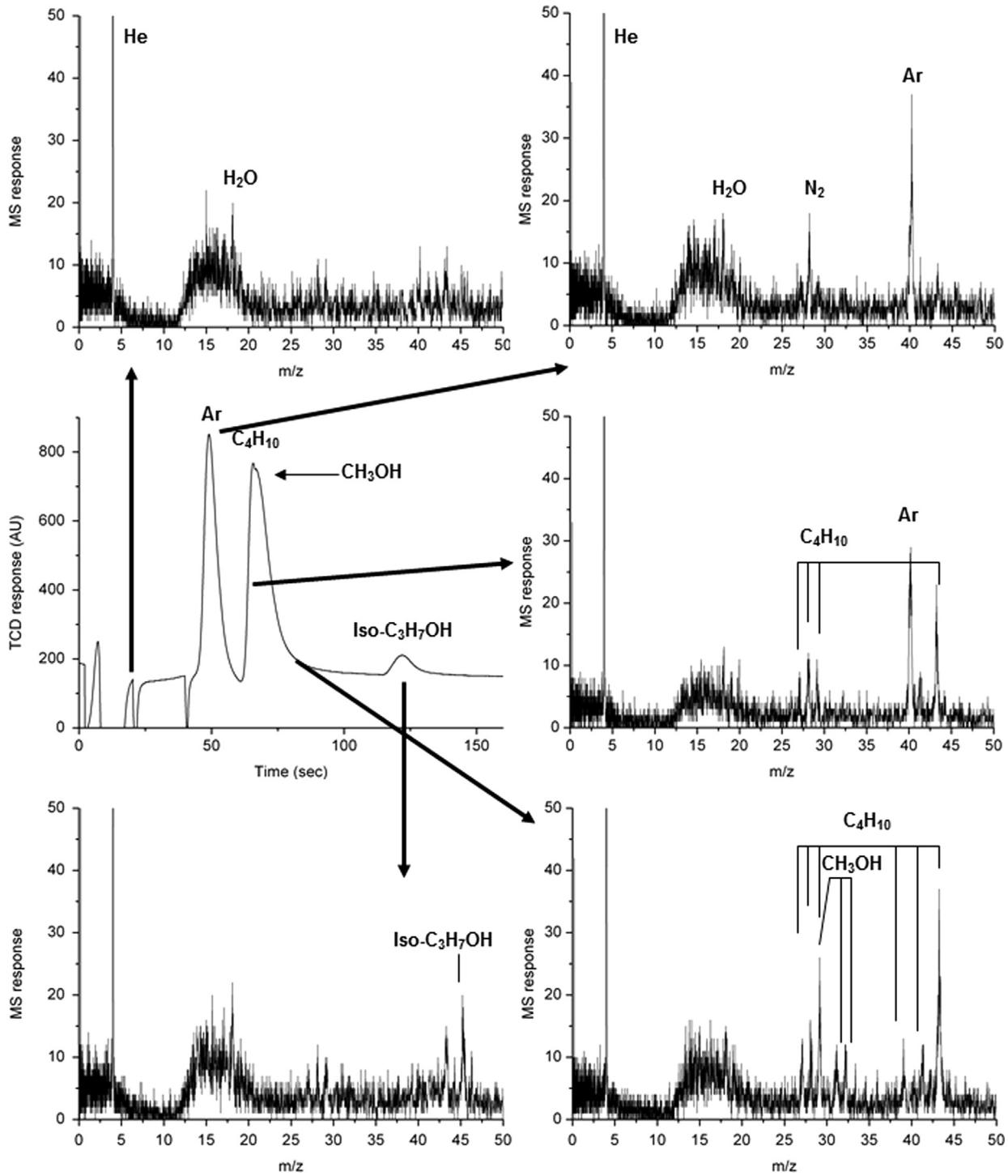


Fig. 8. Chromatogram and corresponding mass spectra obtained for the analysis of a simple mixture of organics with the MXT 20 column. The chromatogram (middle left panel) corresponds to the signal recorded from the thermal conductivity detector of the gas chromatograph. Each of the five mass spectra is recorded at specific elution times indicated by arrows on the chromatogram. On each mass spectrum, the peaks corresponding to the main fragments of the chemical species analyzed (from NIST databases) are indicated and also their corresponding molecules. Chromatographic conditions: GC inlet pressure = 1.3 bar, outlet pressure \sim 1 mbar; GC column temperature = 30 °C, injection duration = 10 s.

In summary, COSAC measurements will enhance our understanding of the composition of the comet nucleus and its organic inventory. The obtained data will be of utmost relevance to the origin of our solar system and the origin of life on Earth in a truly fascinating way. The measurements on 67P in November 2014 will be a result of almost ten years of development and about ten years of cruise. After the successful commissioning, showing that the instrument has survived cruise and hibernation very well and is

ready for operations on the comet, the team is eager to see the first scientific results in fall 2014.

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