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Competence evaluation of COSAC flight spare model mass spectrometer: In preparation of arrival of Philae lander on comet 67P/Churyumov–Gerasimenko

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ABSTRACT

The Cometary Sampling and Composition (COSAC) experiment onboard the Philae lander is a combined Gas Chromatograph–Mass Spectrometer targeted to determine the organic composition of the nucleus of comet 67P/Churyumov–Gerasimenko. The COSAC flight-model mass spectrometer (FM-MS) was scheduled to sample volatile organic species from 67P's coma prior to Philae's detachment from the Rosetta orbiter in November 2014. It was again scheduled to sample subsequent to Philae's touchdown but prior to drilling operations, thereby retrieving measurements of volatiles from the surface of an unperturbed nucleus. This article evaluates the competence of COSAC mass spectrometers in identifying volatile organic species in both cometary and laboratory-simulated environments. The evaluation was conducted on an operationally optimized COSAC flight spare model mass spectrometer (FS-MS) maintained in ultra-high vacuum. The FS-MS obtained analytical measurements by "sniffing" several organic molecule mixtures of diverse chemical functional groups and molecules with broader molecular masses introduced into the vacuum vessel housing the instrument. The results demonstrate that COSAC produces mass fragmentation patterns of organic species similar to those in calibration standard mass spectra; it is able to identify various organic species within mixtures present at low concentrations (100 ppm); and it can identify fragmentation patterns of non-introduced unknown species and those with high molecular masses within organic mixtures. These observations successfully substantiate the potential of the FM-MS to make qualitative measurements of organic species both in the rarefied environment of the coma and in the relatively enriched nucleus surface.

1. Introduction

The Rosetta spacecraft was launched in March 2004 on an Ariane 5 launch vehicle from Guiana Space Center, in Kourou, French Guiana. After approximately ten years of flight duration Rosetta arrived at its destination the comet 67P/Churyumov–Gerasimenko in August 2014. In one of the most crucial phases of the mission the Rosetta orbiter deployed the Philae cometary surface probe in November 2014 successfully. The foremost purpose of Philae is to perform in situ physico-chemical investigations of the cometary nucleus (Glassmeier et al., 2007; Meierhenrich, 2014).

The Cometary Sampling and Composition (COSAC) experiment is a Gas Chromatograph Time-of-Flight Mass Spectrometer (GC–MS) instrumental suite onboard the Philae Lander primarily designed to analyze the organic composition of comet 67P's nucleus. It can be operated in two individual operational modes – the GC–MS 'coupled' mode and the MS-only 'sniffing' mode. The technical specifications of COSAC have been meticulously outlined in Goesmann et al., 2007, 2009. The 'coupled mode' is precisely targeted to perform compositional analyses of nucleus samples delivered by the Sample Drill and Distribution System (SD2) payload (Ercoli Finzi et al., 2007). The sample will presumably be a solid organic mixture of unknown chemical composition, which when pyrolysed by either medium-temperature (maximum oven

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temperature 180 °C) or high-temperature ovens (maximum oven temperature 600 °C) will emit volatile organics. These species will then be GC-separated under continuous supply of a chemically inert carrier gas, Helium, and subsequently identified by the MS based on their mass fragmentation pattern (Goesmann et al., 2007, 2009, 2014). The process of separation first and identification of masses based on their evolving times later will assist in enhanced chemical characterization of native cometary organics.

The coupled mode is exclusively dependent on the SD2 for samples. It involves energy intensive operations: oven heating, operations of pneumatic valves for controlled flow of sample from oven to chromatography columns and flow of Helium carrier gas, long duration GC separation (2–17 min), and generation of many real-time mass spectra during the GC separation. These elaborate operations will be performed only after landing during the dedicated penultimate First Science Sequence (FSS) and the ultimate Long Term Science (LTS) phases of the mission. The coupled COSAC mode applies chiral stationary phases and aims for the separation, identification, and quantification of chiral molecules (Meierhenrich et al., 1999; Thiemann et al., 2001) including amino acids (Thiemann and Meierhenrich, 2001) in cometary ices.

At the same time the MS 'sniffing mode' permits analyses independent of the power-intensive GC operations, that they are of comparatively shorter duration, it does not target evolved volatile species, including the above mentioned chiral species, and does not rely on the sampling of solid nucleus surface material. This mode is devised to analyze organic species outgassed from the nucleus, by mass spectrometry only and relies on passive accumulation of volatiles into the MS ionization chamber (Goesmann et al., 2012). The sniffing mode can operate over a broad range of concentrations of organic compounds. The FM-MS was scheduled to sniff volatile species in the coma before its detachment from the Rosetta orbiter, during FSS in an unperturbed (undrilled) and less active nucleus, and finally during LTS when the nucleus has been perturbed (drilled) and when it becomes increasingly active as 67P approaches its perihelion.

2. Qualifying conditions for COSAC-MS sniffing mode

The most abundant molecular species emitted from comet nuclei are water and carbon monoxide, which have often been observed in the sub-millimeter region at ~557 GHz and ~576 GHz respectively (Gulkis et al., 2007). While sample gases have been detected, the relative abundance of any accompanying organic molecules is still in doubt. A coarse rule of thumb estimation of the molecular proportion would be (Krankowsky et al., 1986; Combes et al., 1988; Bockelée-Morvan et al., 2005),

H_2O:CO:organics = 100:15:1

The heliocentric distance of 67P/Churyumov–Gerasimenko at the time of SDL will be about 3 AU (Biele et al., 2009). For a heliocentric distance of 2.9 AU the production rate of water was estimated to be around 3×10^{26} molecules/s and 2.4×10^{24} molecules/s at a distance of 4.5 AU (de Almeida et al., 2009). Recently the Microwave Instrument for the Rosetta Orbiter (MIRO) reported detection of water line at 556.9 GHz, when the spacecraft was at a distance of ~360,000 km from the comet and when the heliocentric distance of the comet was 3.93 AU. Initial estimates based on the MIRO measurements suggest water production rates between 0.5×10^{25} and 4×10^{25} molecules/s (Gulkis, 2014). While still not very accurate measurements, they agree with previous estimated production rates (Table 1). If these rates are accurate then organics would be expected at the 1% range, which is in the order of 0.5×10^{23}–4×10^{23} molecules/s. This assessment seems reasonable given the ratio of organics to water in well studied comets like 1P/Halley and C/1995 O1 Hale–Bopp (Bockelée-Morvan et al., 2005). This would mean that the flux of organic volatiles produced should be well within the detection limits of FM-MS when it makes measurement after touchdown.

3. COSAC FS-MS: operating conditions

The laboratory analytical experiments to simulate COSAC's flight analyses mentioned in this paper were conducted on the FS-MS, which has been maintained at the Max Planck Institute for Solar System Research in Göttingen, Germany. The FS-MS is kept in a vacuum vessel with essential electrical and pneumatic connections. The pressure in the vacuum vessel is maintained at ~10^{-7} mbar and at ambient temperature (20–25 °C). Both these physical conditions are representative of the COSAC environment inside the Philae lander, during its operations on the comet. The FS communicates the generated data via the Control and Data Management System (CDMS) hardware identical to the one on the Philae Lander. Both the FS-MS and FM-MS are high resolution time-of-flight mass spectrometers with an electron impact ionization source. The major difference amongst them is that detector used in the FM-MS is a multi-sphere-plate secondary electron multiplier detector, whereas the FS-MS is fitted with a micro-channel-plate detector. For further COSAC mass spectrometer specifications please refer to Goesmann et al., 2007, 2009.

The samples used in the experiments (below) were in gaseous state to streamline their introduction into the vacuum vessel. The volatile samples were pressurized in separate empty gas cylinders (1 L). During the analyses of the respective samples these cylinders

Table 1
Water production rates of comet 67P/Churyumov–Gerasimenko at various heliocentric distances.

Heliocentric distance (AU)	Water-production rate (molecules s^{-1})	Nature of measurement
4.5	2.4×10^{24}	Theoretical calculation (de Almeida et al., 2009)
3.93	0.5×10^{25}–4×10^{25}	Rosetta MIRO detection (Gulkis, 2014)
2.9	3×10^{26}	Theoretical calculation (de Almeida et al., 2009)

Table 2
Sample mixtures studied and their characteristic molecular features addressed for evaluating COSAC-MS performance.

Analyzed sample mixtures	Characteristic functional groups	Targeted molecular feature of mixtures
Unknown concentration of residual gases in the vacuum vessel	–	–
3-methylheptane (100 μL)+1 bar He	Alkane	High molecular mass (u=114), branched chain aliphatic hydrocarbon
n-propane+n-butane+n-pentane+n-hexane+benzene (100 ppm each)+1 bar He+3-methylheptane (unknown trace volume)	Alkane+benzene derivative	Low concentration volatile aliphatic and aromatic hydrocarbon mixture
2-propanol (100 μL)+benzene (100 μL)+1 bar He+perfluorotributyl amine (unknown trace volume)	Hydroxyl+benzene derivative +perfluoroalkyl amine	Multiple functional group mixture with high molecular mass species (u > 671)