ChemPlusChem

Research Article
doi.org/10.1002/cplu.202200116

Chemistry Europe
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COSAC's Only Gas Chromatogram Taken on Comet 67P/Churyumov-Gerasimenko

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In memory of Helmut Rosenbauer († 05 May 2016) who designed and developed the scientific program of Rosetta's lander Philae

The Philae lander of the Rosetta space mission made a non-nominal landing on comet 67P/Churyumov-Gerasimenko on November 12, 2014. Shortly after, using the limited power available from Philae's batteries, the COSAC instrument performed a single 18-minutes gas chromatogram, which has remained unpublished until now due to the lack of identifiable elution. This work shows that, despite the unsuccessful drilling of the comet and deposition of surface material in the SD2 ovens, the measurements from the COSAC instrument were executed nominally. We describe an automated search for extremely small deviations from noise and discuss the possibility of a signal from ethylene glycol at *m/z* 31. Arguments for and against this detection are listed, but the results remain inconclusive. Still, the successful operations of an analytical chemistry laboratory on a cometary nucleus gives great hope for the future of space exploration.

Introduction

After the non-nominal landing of the Philae lander of the Rosetta space mission on comet 67P/Churyumov-Gerasimenko (67P) on the 12th of November 2014, it soon became clear that the spacecraft would not be able to sufficiently recharge its batteries with its dedicated solar arrays.[1] Expecting this would be the one and only chance to sample and analyze the comet's nucleus in situ, on the 14th of November the Sampler, Drill and Distribution System (SD2) attempted to forage the surface and deliver a sample to different analytic instruments onboard the lander.[2] One of those instrument was the COmetary SAmpling and Composition (COSAC) experiment that included a Gas Chromatograph (GC) linked to a Mass Spectrometer (MS).[3,4] Philae's final position made drilling difficult, as it was resting on its side, not anchored and in an undefined altitude relative to the local surface.[5] It is therefore believed that the drill did not penetrate the surface, although it did deploy successfully at 560 mm. For a comprehensive explanation of the landing and operations events see Ulamec et al.[1] and references therein.

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Still, there is the possibility that a small amount of surface material stuck to the drill from the ambient gas, as we expect volatile materials and dust between COSAC's chamber and the surface of the comet. COSAC then proceeded to analyze this sample with its only chiral chromatographic column (Chirasil-Dex CB 10 m×0.25 mm; 0.25 μm thick film, Varian-Chrompack, Middelburg, the Netherlands), using the limited power available from Philae's batteries. This measurement was never published as no clear signal is distinguishable from noise, so no molecules have been identified.

The Ptolemy instrument, another gas chromatograph on Philae, could not receive a sample from SD2 due to insufficient power supply. It still tried to analyze dust from the touchdown impact that may have become lodged inside one of its ovens, but the unavailability of the helium carrier gas due to the circumstances could not be compensated by the sample gas pressure which was too low to have anything flow through the column.[6] COSAC was given the priority due to its higher mass range and ability to identify more complex organics, including chiral compounds.

We describe here, for the first time, the only gas chromatogram taken by COSAC on the surface of comet 67P. These data are referred to as the First Science Sequence (FSS), while the blank run that was taken when still in cruise phase (about 7 months prior to landing on the 18th of April 2014) using the same GC-MS parameters is referred to as the Post-Hibernation Commissioning (PHC). We compare these measurements to try and find any disparity between the two that could represent a molecule found and identified on the comet. We propose the hypothesis of the detection of ethylene glycol as a very faint peak at 10 minutes for mass/charge ratio (*m/z*) 31 in the FSS measurement.

During this analysis, housekeeping data was taken approximately every 12 seconds (mean of one every 11.83 seconds) starting 22 minutes before the first mass spectrum was taken (defined here as T = 0). Housekeeping data refers to the real-time measurements of various instrumental parameters that are important for real-time assessment of COSAC's operational performance.[7]

Based on different important housekeeping data and on the 421 mass spectra that were obtained, we show that the COSAC instrument performed this historical analysis and operated nominally (Figure 1). We then carried out both automated and manual searches for any significant difference between FSS (data) and PHC (blank) mass spectra. We reproduced the experiment on a flight spare column in the laboratory to see

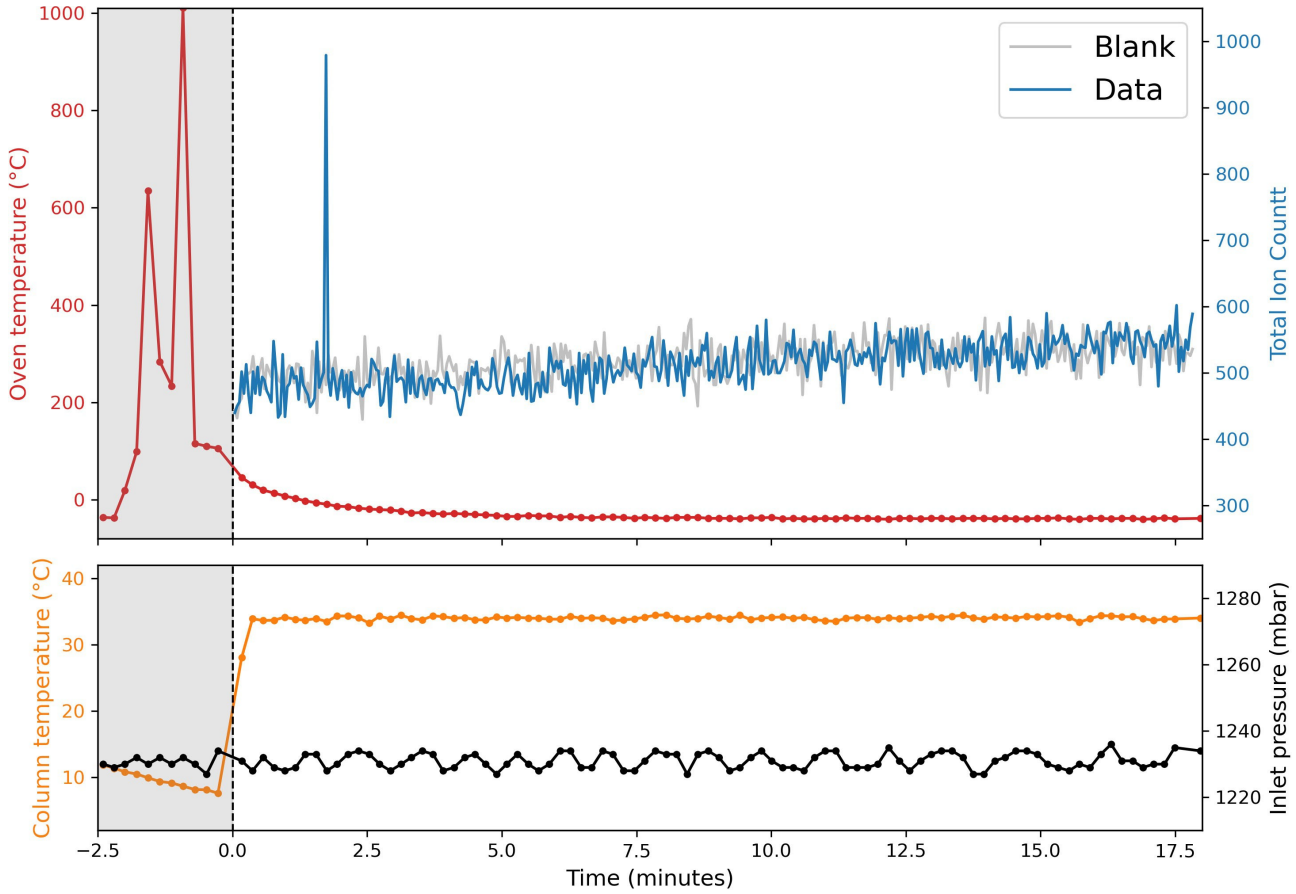

Figure 1. Monitoring of different relevant housekeeping parameters: oven temperature (top, red), column temperature (bottom, orange) and inlet pressure (bottom, black). On the top plot, the total ion count from the FSS mass spectra (Data) over time is shown in blue while in light grey we show the mass spectra from the gas chromatogram taken during PHC (Blank) under the same conditions. The data "peak" at around 2 minutes is a noise spike and should be disregarded.

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what molecules would be in the chromatographic space of this measurement, and we put forward the possibility of a very faint signal from ethylene glycol in the chromatogram taken on the cometary nucleus. We detail the arguments for and against this detection.

Before results from the Rosetta space mission on 67P, ethylene glycol was identified for the first time in comet C/1995 O1 (Hale-Bopp) as one of the most abundant organic molecules in cometary ices.[8] Since then, it has also been found in comets C/2012 F6 (Lemmon) and C/2013 R1 (Lovejoy),[9] as well as in comet 46P/Wirtanen,[10] the original target of the Rosetta mission.

Ethylene glycol has been shown to be very efficiently made from pure methanol ice irradiation.[11] This suggests that the presence of ethylene glycol is a tracer of a relatively high and segregated methanol concentration in the cometary ice.

In addition, in the gas phase, two CH_2OH radicals will efficiently form ethylene glycol $(CH_2OH)_2$.[12,13] This has been corroborated by its detection in star-forming regions,[14,15] and the fact that it is one of the largest molecules that has been identified in the interstellar medium.[16]

Results and Discussion

Starting at T-10 minutes (before the first mass spectrum was taken), a stable helium inlet pressure of 1230 mbar was set. During this time, after the non-nominal drilling from the SD2 instrument, potential material adsorbed on the drill was fed to a COSAC high temperature oven.

At T-120 seconds, the oven started heating the sample up to more than 600 °C within the next 2 minutes. The oven heater's last ON position was around T-15 seconds after which the column heater is turned ON, since both could not be working concurrently due to power constraints. We can then see the oven temperature decrease due to diffusion (see

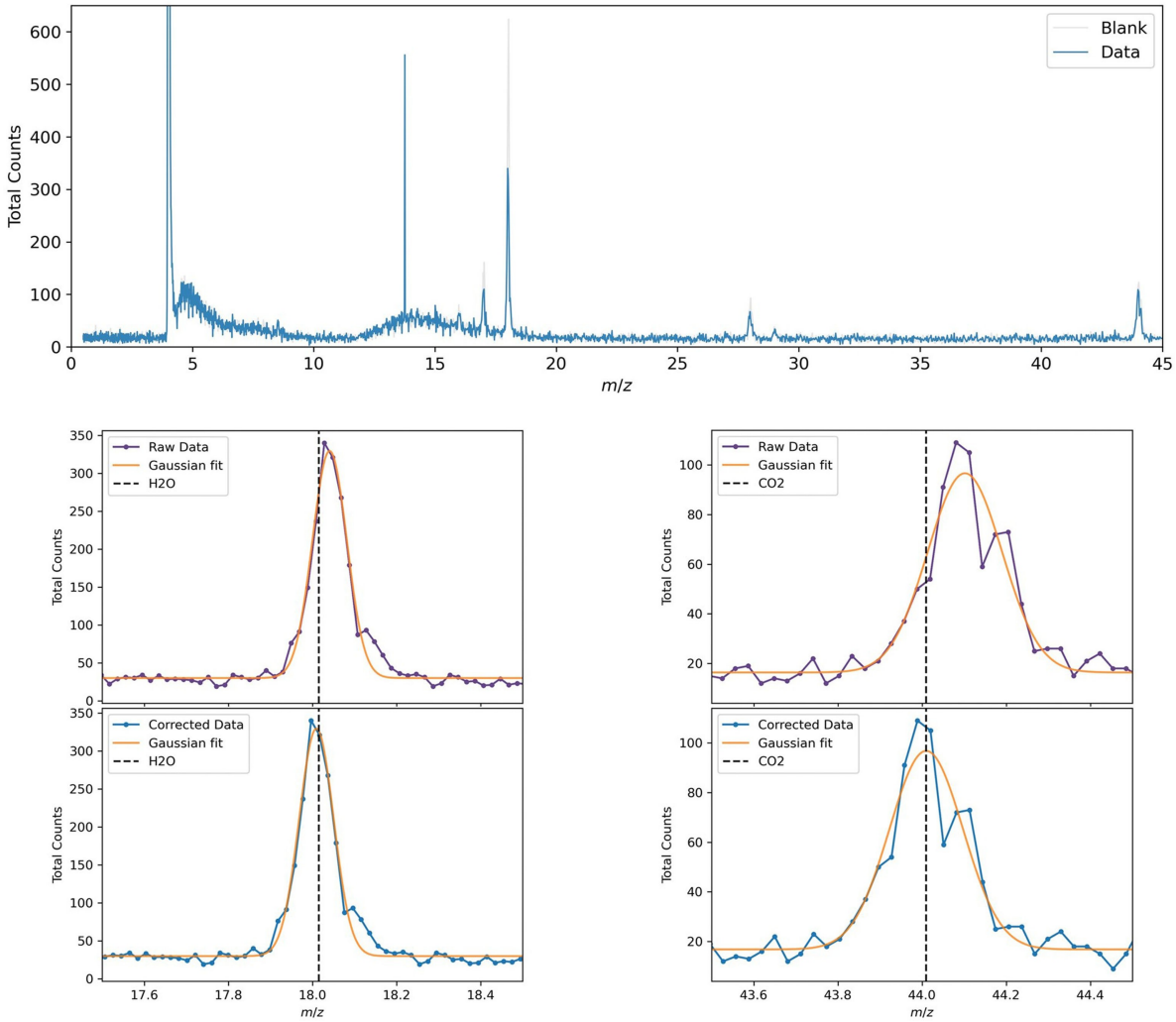

Figure 2. Top: Mass spectrum of the full FSS (Data) and PHC (Blank) gas chromatograms, where 7 peaks are discernible from noise: *m/z* 4, 16, 17, 18, 28, 29, 44. The data "peak" at *m/z* 14 is a noise spike and should be disregarded. The helium peak at *m/z* 4 is truncated for easier visualization; the maximum count is 18512 and 19579 for the blank and data respectively. **Bottom**: Comparison between raw and corrected mass scale of the FSS total mass spectrum for the *m/z* 18 (bottom, left) and 44 (bottom, right) peaks. A gaussian fit of each peak is shown in orange, and in vertical dashed lines is the exact mass of the ionized fragment the signal at this *m/z* is expected to come from. The corrected mass scale was the one used for the rest of the research.

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Figure 1). The highest oven temperature reading of 1011 °C is likely on open circuit phenomenon, as it is also the value received when there is no oven in the tapping station (0x1FFF). The actual oven temperature at that time should therefore be between the 2 readings around it (50–100 °C).

Due to the non-nominal sampling, the COSAC team decided to use an injection time of 6 seconds to maximize chances to have a signal from what was expected to be very little material. This value was found to be optimal after tests using the flight spare model of the instrument.[17]

Starting at T = 0, a mass spectrum was taken every 2.54 seconds during the 17.8 minutes gas chromatogram, resulting in 421 individual mass spectra with a scan range of 1–330 *m/z*. The Time-Of-Flight (TOF) MS was operated in "low resolution", where each bin in mass space are time windows of 4 ns. This results in a mass resolution of about 0.01 amu at *m/z* 4 up to 0.1 amu at *m/z* 330. This is in contrast with the "high resolution" mode that was used for the MS "sniffing" where time windows have a width of 2 ns.[18]

The inlet pressure was 1231 ± 2 mbar for the duration of the measurement, while we assume vacuum in the mass spectrometer in equilibrium with the comet's environment. The column temperature was kept at an isothermal 34.0 ± 0.3 °C during the chromatogram. These values, coupled with the dimensions of the column, induce a helium flowrate of about 2.1 mL/min.

Figure 2 (top) shows the total mass spectrum, that is the sum of the 421 individual mass spectra over the 17.8 minutes. The helium peak at *m/z* 4 is truncated for easier visualization, but the maximum count is 18512 and 19579 for the blank and data respectively. More than 95% of the counts are due to the helium carrier gas flow. While we lose the time component, we can see that there is also an expected constant flow of different contaminants (mainly water), already present in the column. These are *m/z* 16 (O^+), 17 (OH^+) and 18 (H_2O^+) all consistent with water's fragmentation pattern, *m/z* 28 (CO^+) and 44 (CO_2^+) from outgassing, and *m/z* 29 (CHO^+) coming from the column's cyclodextrins degradation. All these peaks (except for helium) are slightly higher in the PHC measurement which is not surprising considering it was done 7 months prior which would have flushed out some of the contamination.

The "peak" seen on the FSS at around 1 min 30 s (Figure 1) and *m/z* 14 (Figure 2, top) is an anomaly as it is due to a single bin with a count of 516 in the 40th mass spectrum while all the adjacent bins are at the local background. This value should therefore be disregarded.

Figure 2 (bottom) zooms on the *m/z* 18 and 44 peaks and shows the loss of accuracy with increasing *m/z* coming from an imperfect calibration of the mass calculation from the TOF MS. Rescaling of the MS's TOF parameters using the exact mass of the lowest and highest evident *m/z* contributors (respectively helium for *m/z* 4 and CO_2 for *m/z* 44) as baselines yields the visible shift in *m/z* shown underneath. This was done for both data and blank. After this process, the exact mass of the expected molecular fragment at a unit *m/z* is within one local mass bin of the peak's maxima for both examples. This is true for all 7 discernible fragments in *m/z* space.

From these peaks, we can also calculate the standard deviation σ in mass space as a function of *m/z*. This is shown in Figure 3. We can then extrapolate σ for all unit *m/z* and look at the chromatograms of individual unit ions where the dominating variation of the helium signal is invisible.

A search was made using a simple algorithm that finds the biggest disparity between FSS and PHC counts over different time intervals, for each unit *m/z*. The searches were centered on the unit mass and the mass window was set to 3 σ. The threshold for alerts was fixed to a data count at least 3 times higher than blank count over a time interval of 8 mass spectra (or almost 21 seconds) at a given *m/z*, with a minimum data count in this interval of 12 (mean of 1.5 count per spectrum) and at least one count of 4 or higher. These numbers have been chosen after thorough testing and from the statistical distribution of the count number per mass spectrum per *m/z*.

Indeed, for *m/z* > 20 (and omitting all discernible peaks, see Figure 2) the mean count number per mass spectrum per *m/z* is 0.6, its median is 0 and its standard deviation 0.8. The method scanned all time intervals for all unit *m/z* (1–330). Catches from the algorithm were then visually inspected. This search resulted in 7 unique flagged *m/z* and time interval pairs, coming from only 2 peaks. These were found at *m/z* 31 and 10 minutes, and at *m/z* 42 at 4.5 minutes. The first is the largest disparity that was found by a significant margin with 17 counts in the FSS against 3 in the PHC.

The one at *m/z* 42 shows 12 data count against 2 blank count. A visualization of both peaks is shown in Figure 4.

Figure 5 shows us the decomposition of the FSS signal into smaller mass windows: 0–1, 1–2 and 2–3 σ. We can then compare the results to those predicted by a gaussian centered on the unit *m/z* which is what is expected for counts that are the result of an ionized molecular fragment being detected. If that is the case, the distribution should follow the 68–95–99.7

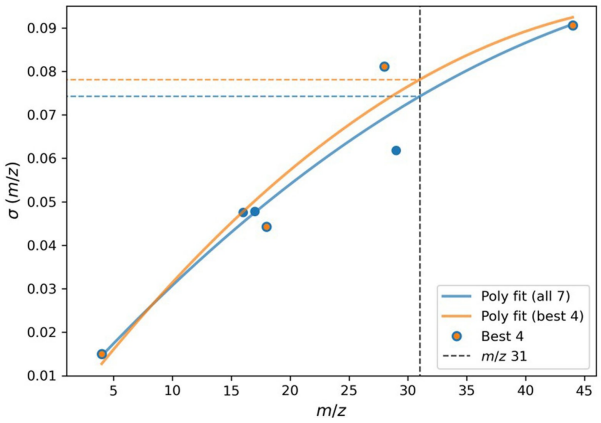

Figure 3. Standard deviation σ of the gaussian fits (Figure 2) as a function of *m/z*. The second-degree polynomial fits for all 7 visible peaks and a 4 "best" points subset is shown in blue and orange respectively. The 4 best points fit uses only the ones with the higher Signal over Noise Ratio (SNR) while covering the mass space homogeneously: *m/z* 4, 18, 28 and 44. Extrapolation to *m/z* 31 yields 0.074 and 0.078 *m/z* for the 7 and 4 points fit respectively, as is shown by the colored intercept lines. Similarly, extrapolation to *m/z* 42 yields σ = 0.089 and 0.091 (not shown). We always choose the highest of the two values to carry out our search with.

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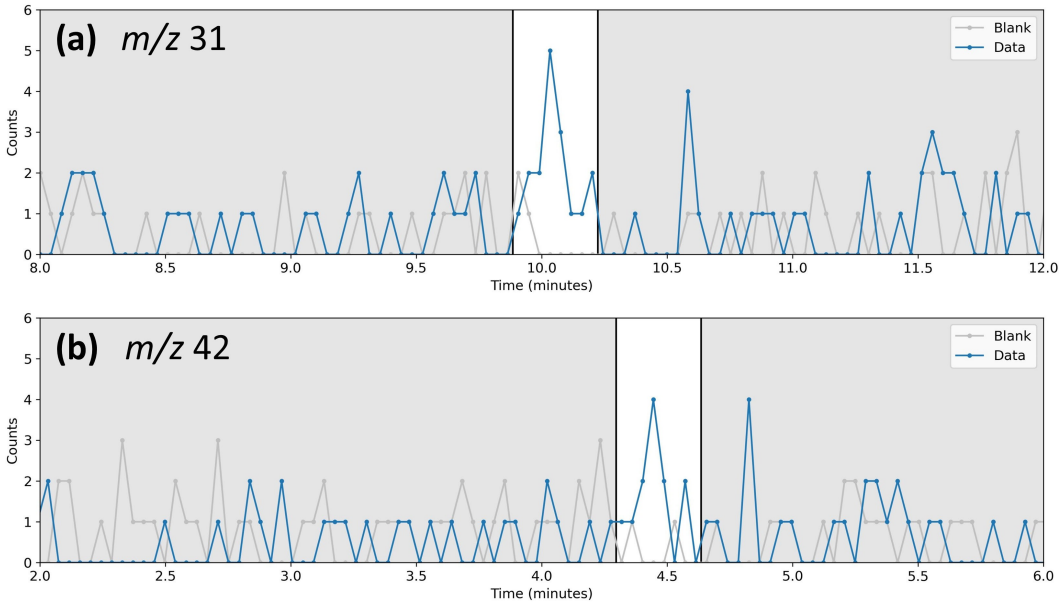

Figure 4. Visualization of the scanning process and of the 2 different peaks that were flagged by our algorithm. **(a)** *m/z* 31: the FSS (Data) shows 17 counts against 3 in the PHC (Blank) in the highlighted time window. **(b)** *m/z* 42: likewise, the FSS shows 12 counts against 2 PHC count.

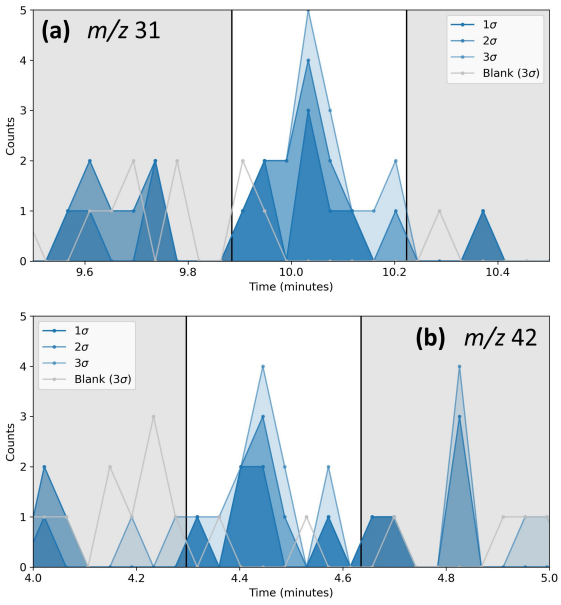

Figure 5. (a) Peak of interest at *m/z* 31, with overlayed the 1, 2 and 3 σ mass window shape of the FSS GC-MS. The PHC GC-MS result is shown only for 3 σ in grey. The 0–1, 1–2 and 2–3 σ ranges show 8, 5 and 4 counts respectively in the 9.9 to 10.2 minutes interval. σ = 0.078 *m/z*. **(b)** Same representation for the peak of interest at *m/z* 42. Following the same method, in the 4.3 to 4.6 minutes interval we have 6, 2 and 4 counts for the defined σ ranges. σ = 0.091 *m/z*.

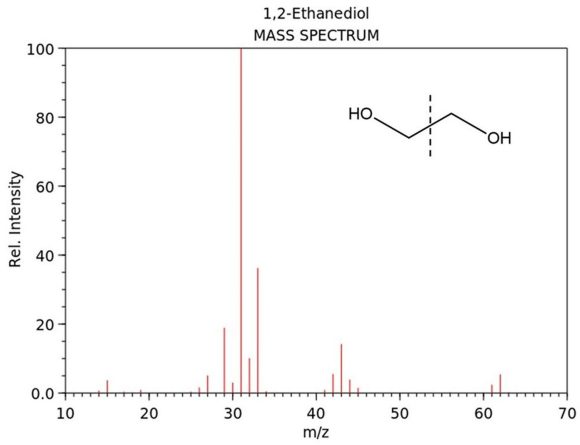

Figure 6. Electron Ionization (EI) mass spectrum of 1,2-ethanediol or ethylene glycol ($C_2H_5O_2$). The base peak is at *m/z* 31 and is significantly stronger than any other *m/z* as it represents the perfectly symmetric breaking of the molecule (shown on the top right corner), leaving 2 hydroxymethyl radicals of which either one can keep the positive charge induced by the electron impact. From NIST Chemistry WebBook (https://webbook.nist.gov/chemistry).

rule, which represent the percentage of values that lie within 1, 2 and 3 σ of the mean respectively. The 0–1, 1–2 and 2–3 σ are then populated by 68, 27 and 5% of the counts respectively.

For *m/z* 31, in the 9.9 to 10.2 minutes interval the 0–1, 1–2 and 2–3 σ ranges show 8, 5 and 4 counts respectively, representing 47, 29 and 24% instead of the expected 68, 27 and 5%. Still, even when removing all counts from the 2–3 σ interval, the peak holds a promising shape.

Doing the same thing for peak at *m/z* 42, in the 4.3 to 4.6 minutes interval we have 6, 2 and 4 counts, representing 50, 17 and 33% respectively. A variation of the value of σ between the two limits set by Figure 3 did not affect the results for both cases. Due to a lower peak and overall counts, worst results from the σ decomposition, and most importantly no realistic candidate molecule with a base peak at this *m/z*, our conclusion is that the *m/z* 42 peak most certainly is a noise anomaly.

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Arguments for detection

Ethylene glycol was already found as one of the 16 molecules in the analysis of the "sniffing" mass spectrum taken by COSAC,[18] and confirmed to be one of the most likely molecules detected within that spectrum by recent research.[19] It has also been detected in the coma of 67P by the ROSINA DFMS instrument onboard the Rosetta orbiter.[20]

Only very small molecules are expected to elute within the 18 minutes chromatogram with the oven kept at the low temperature of 34 °C. Methanol, ethanol, methyl formate and 1-propanol also have a base peak at *m/z* 31, but all of them are too volatile and elute even before the 1-minute mark in these conditions.

In addition, ethylene glycol is the only one for which its base peak constitutes more than half (55 %) of the intensity of all fragments. This could be an explanation for why it would be the only compound seen in this chromatogram.

Propylene glycol, with simply an added methyl group, shows a retention time of more than 20 minutes (out of view for this experiment). This further proves the very narrow chromatographic window we are dealing with, limiting possible candidates.

The strongest argument for this detection is that ethylene glycol elutes precisely at the 10-minute mark when injected at a

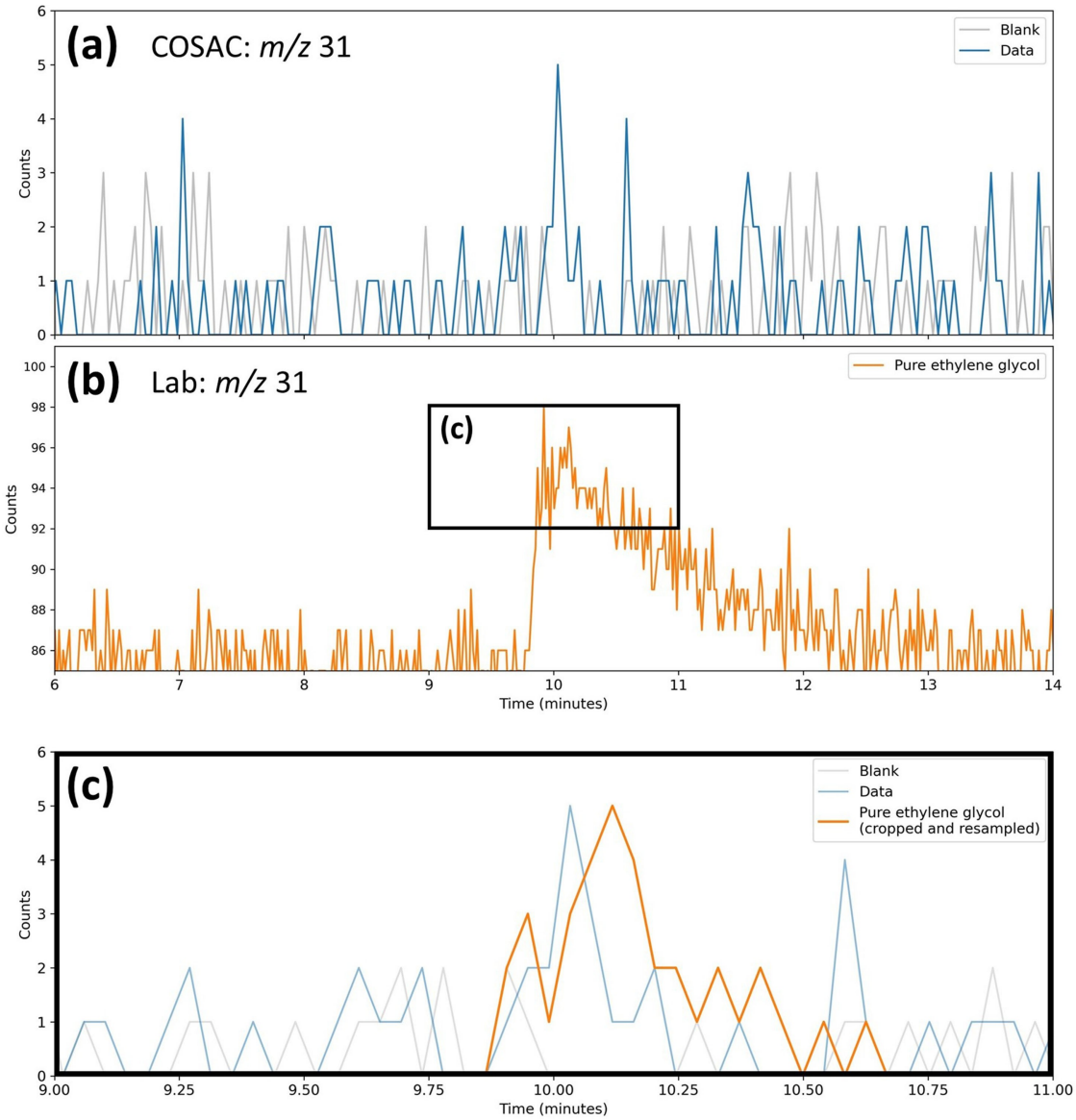

Figure 7. (a) Ion count over time of *m/z* 31 (with a mass window of $\pm 3\sigma$) in the FSS (Data) and PHC (Blank) gas chromatograms. **(b)** Ion count over time of *m/z* 31 in a laboratory injection of pure ethylene glycol (concentration 10^{-5} M in ethyl acetate) in a Chirasil Dex flight spare column with the same GC parameters. **(c)** Zoom in and resampling of the top of the elution peak to extrapolate on what the results could look like in the COSAC conditions of extremely low background contamination and analyte concentration. The laboratory data (orange) was resampled to match the frequency of measurement (2.54 seconds between 2 scans) from COSAC, and the FSS and PHC counts are shown in transparency for better comparison. Results from the *m/z* 31 peak were more promising and the best candidate molecule to cause this potential signal was found to be ethylene glycol ($C_2H_5O_2$). Ethylene glycol's mass spectrum is shown in Figure 6, with a large base peak at *m/z* 31.

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concentration close to the limit of detection in the laboratory with the same GC parameters as the FSS and PHC measurements (Figure 7bc). With the uncertainties on the inlet pressure and the column temperature from the housekeeping data, using the Agilent Pressure Flow Calculator we find 2.05 and 2.1 mL/min for the lower and higher bound of helium flowrate respectively (constant during the measurement as we are in isothermal and isobaric conditions). The shift in retention time due to a change in helium flow rate was found by doing the same injection several times with only varying the flowrate from 2.0 to 2.2 mL/min. In this range, the decrease in ethylene glycol's retention time has been found to be 10 ± 1 seconds per 0.05 mL/min increase in flowrate, leaving only a maximum 10 second ambiguity due to this effect.

Although the injection systems from COSAC and from our laboratory differ significantly, the start of each measurement is well-defined and allows for accurate retention time comparisons. For COSAC, the first mass spectrum (that we defined at $T = 0$) is taken right after the injection sequence finishes, that is after the sample has entered the column. In the laboratory, it is taken at the moment of injection, that is just before the sample enters the column. The time ambiguity between the two is then simply the COSAC injection time of 6 seconds.

The column has been shown to retain its separating capabilities after the long (~10 years) interplanetary travel.[21]

Arguments against detection

The main argument against this detection is the extremely low SNR. What's more, no other fragments of ethylene glycol are seen. The second highest peak in its mass spectrum is at *m/z* 33 and represents about 20% of the total intensity (Figure 6). No significant surplus of counts is seen at 10 minute and *m/z* 33 in the COSAC data in the time window of interest.

Ethylene glycol, due to its two hydroxyl groups, tends to self-react and to be strongly adsorbed by the GC column stationary phase, which makes its analysis without derivatization difficult. This is evidenced by the strong tailing seen in Figure 7b, even when injected in trace amounts. This effect is not seen in the FSS sequence.

In addition, we expect that the 6 seconds ambiguity caused by the injection method on the COSAC instrument would lead to a larger spread of the peak compared to a laboratory measurement, but the inverse is seen here (Figure 7c). Although this could be counteracted by the lower concentration, it is still noteworthy.

The retention time is quite sensitive to the column temperature; indeed, additional injections were done with only varying the temperature to 33 and 35 °C which led to a shift of plus and minus 0.8 minute in retention time respectively.

While the peak holds its shape even after removing the 2–3 σ counts, it reduces even further the SNR of the signal in question.

Formamide, which has also been found in the published COSAC mass spectrum, was injected following the same protocol and eluted at around 6 minutes while showing less significant tailing. In theory there is therefore a better chance of detecting it in the chromatogram. Yet, nothing is found from its base peaks here.

While the data count in the time window of interest is one of the highest seen in the FSS, this is also a case of the blank count being extremely low which is at least partially due to chance.

Conclusion

We publish, for the first time, the COSAC data from its only chromatogram taken on comet 67P/Churyumov-Gerasimenko. We report that, even though the sampling of the cometary nucleus was not done in the expected conditions, the measurement made from the COSAC instrument was successfully downlinked to Earth using the final power remaining in Philae's batteries and usable for the scientific payload at the time. This GC-MS run represents the very first measurement of its kind on a comet.

From housekeeping data, we see that all tasks were performed nominally by the instrument. Although there is no clear molecule detected within this chromatogram owing to the extremely small amount of material that arrived in the GC oven due to the non-nominal drilling, we automated a search for signal to look for even the smallest deviations from background noise. We argue for and against the detection of ethylene glycol based on the largest difference found between data and blank over the entire dataset at *m/z* 31. The very low SNR does not allow us to confirm this detection, but the retention time of pure ethylene glycol on the flight spare column is a strong argument for a trace detection of the compound in these data. Still, our conclusion is that arguments for this detection do not outweigh significantly enough the ones against for the evidence to be sufficient.

Ethylene glycol has already been detected in several comets, including 67P in both its coma and nucleus by the ROSINA and COSAC MS instruments respectively.

The pioneering Rosetta space mission has brought incredible insight into the composition of the early Solar System, and raised open questions that future cometary missions will aim to answer in the next decades.[22] The successful operations of the complex COSAC analytical chemistry laboratory on a cometary nucleus gives great hope for the future of space exploration.

Experimental Section

All chromatographic analyses done in the laboratory were performed using an Agilent 6890N-5973N GC-MS system (Agilent, Santa-Clara CA, USA) equipped with a Varian-Chrompack (Middelburg, the Netherlands) Chirasil-Dex CB capillary column (10 m × 0.25 mm; 0.25 μm thick film). All compounds were analyzed following the same exact protocol. Any variation from the values below is clearly specified in the text when an injection is described.

The injected samples were solutions of concentration 10^{-5} M of the analyte in ethyl acetate. The injection volume was 0.5 μL with a split ratio of 10:1. The flow rate was a constant 2.1 mL/min of He

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(99.9995%) carrier gas. The injector temperature and the MS transfer-line were set at a constant 250 °C and 200 °C respectively. The oven temperature was set at an isothermal 34 °C. After a solvent delay of 1 minute, ions were detected within a 15–350 *m/z* range.

Acknowledgements

G.L and U.M acknowledge the financial support of the ANR (ANR-15-IDEX-01 and ANR-18-CE29-0004). T.G. acknowledges the financial support from the Programme National de Planétologie (PNP) of CNRS/INSU co-funded by CNES and of the ANR (ANR-20-CE49-0004-01). G.M.M.C. acknowledges the Spanish MICINN under project PID2020-118974GB–C21 (AEI/FEDER, UE) and the Unidad de Excelencia 'María de Maeztu' MDM-2017-0737 – Centro de Astrobiología (INTA-CSIC).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: comet · gas chromatography · mass spectrometry · Philae · Rosetta · trace analysis

[1] S. Ulamec, C. Fantinati, M. Maibaum, K. Geurts, J. Biele, S. Jansen, O. Küchemann, B. Cozzoni, F. Finke, V. Lommatsch, A. Moussi-Soffys, C. Delmas, L. O'Rourke, *Acta Astronaut.* **2016**, *125*, 80–91.
[2] P. Di Lizia, F. Bernelli-Zazzera, A. Ercoli-Finzi, S. Mottola, C. Fantinati, E. Remetean, B. Dolives, *Acta Astronaut.* **2016**, *125*, 183–195.
[3] F. Goesmann, H. Rosenbauer, R. Roll, C. Szopa, F. Raulin, R. Sternberg, G. Israel, U. J. Meierhenrich, W. H.-P. Thiemann, G. M. Muñoz Caro, *Space Sci. Rev.* **2007**, *128*, 257–280.
[4] F. Goesmann, H. Rosenbauer, R. Roll, H. Böhnhardt, *Astrobiology* **2005**, *5*, 622–631.
[5] J. Biele, S. Ulamec, M. Maibaum, R. Roll, L. Witte, E. Jurado, P. Munoz, W. Arnold, H.-U. Auster, C. Casas, C. Faber, C. Fantinati, F. Finke, H.-H. Fischer, K. Geurts, C. Guttler, P. Heinisch, A. Herique, S. Hviid, G. Kargl, M. Knapmeyer, J. Knollenberg, W. Kofman, N. Komle, E. Kuhrt, V. Lommatsch, S. Mottola, R. Pardo de Santayana, E. Remetean, F. Scholten, K. J. Seidensticker, H. Sierks, T. Spohn, *Science* **2015**, *349*, aaa9816–aaa9816.
[6] A. D. Morse, D. J. Andrews, G. H. Morgan, S. Sheridan, S. J. Barber, I. P. Wright, *Acta Astronaut.* **2016**, *125*, 196–211.
[7] F. Goesmann, F. Raulin, J. H. Bredehöft, M. Cabane, P. Ehrenfreund, A. J. MacDermott, S. McKenna-Lawlor, U. J. Meierhenrich, G. M. Muñoz Caro, C. Szopa, R. Sternberg, R. Roll, W. H.-P. Thiemann, S. Ulamec, *Planet. Space Sci.* **2014**, *103*, 318–330.
[8] J. Crovisier, D. Bockelée-Morvan, N. Biver, P. Colom, D. Despois, D. C. Lis, *Astron. Astrophys.* **2004**, *418*, L35–L38.
[9] N. Biver, D. Bockelée-Morvan, V. Debout, J. Crovisier, J. Boissier, D. C. Lis, N. Dello Russo, R. Moreno, P. Colom, G. Paubert, R. Vervack, H. A. Weaver, *Astron. Astrophys.* **2014**, *566*, L5.
[10] N. Biver, D. Bockelée-Morvan, J. Boissier, R. Moreno, J. Crovisier, D. C. Lis, P. Colom, M. A. Cordiner, S. N. Milam, N. X. Roth, B. P. Bonev, N. Dello Russo, R. J. Vervack, M. A. DIsanti, *Astron. Astrophys.* **2021**, *648*, A49.
[11] Y.-J. Chen, A. Ciaravella, G. M. Muñoz Caro, C. Cecchi-Pestellini, A. Jiménez-Escobar, K.-J. Juang, T.-S. Yih, *Astrophys. J.* **2013**, *778*, 162.
[12] J. Enrique-Romero, A. Rimola, C. Ceccarelli, N. Balucani, *Mon. Not. R. Astron. Soc.* **2016**, *459*, L6–L10.
[13] T. Butscher, F. Duvernay, P. Theule, G. Danger, Y. Carissan, D. Hagebaum-Reignier, T. Chiavassa, *Mon. Not. R. Astron. Soc.* **2015**, *453*, 1587–1596.
[14] N. Brouillet, D. Despois, X.-H. Lu, A. Baudry, J. Cernicharo, D. Bockelée-Morvan, J. Crovisier, N. Biver, *Astron. Astrophys.* **2015**, *576*, A129.
[15] V. M. Rivilla, M. T. Beltrán, R. Cesaroni, F. Fontani, C. Codella, Q. Zhang, *Astron. Astrophys.* **2017**, *598*, A59.
[16] J. Li, Z. Shen, J. Wang, X. Chen, D. Li, Y. Wu, J. Dong, R. Zhao, W. Gou, J. Wang, S. Li, B. Wang, X. Zheng, *Astrophys. J.* **2017**, *849*, 115.
[17] C. Szopa, F. Goesmann, H. Rosenbauer, R. Sternberg, *Adv. Space Res.* **2007**, *40*, 180–186.
[18] F. Goesmann, H. Rosenbauer, J. H. Bredehöft, M. Cabane, P. Ehrenfreund, T. Gautier, C. Giri, H. Krüger, L. Le Roy, A. J. MacDermott, S. McKenna-Lawlor, U. J. Meierhenrich, G. M. M. Caro, F. Raulin, R. Roll, A. Steele, H. Steininger, R. Sternberg, C. Szopa, W. H.-P. Thiemann, S. Ulamec, *Science* **2015**, *349*, aab0689–aab0689.
[19] G. Leseigneur, J. H. Bredehöft, T. Gautier, C. Giri, H. Krüger, A. J. MacDermott, U. J. Meierhenrich, G. M. Muñoz Caro, F. Raulin, A. Steele, H. Steininger, C. Szopa, W. Thiemann, S. Ulamec, F. Goesmann, *Angew. Chem. Int. Ed.* **2022**, DOI 10.1002/anie.202201925.
[20] L. Le Roy, K. Altwegg, H. Balsiger, J.-J. Berthelier, A. Bieler, C. Briois, U. Calmonte, M. R. Combi, J. De Keyser, F. Dhooghe, B. Fiethe, S. A. Fuselier, S. Gasc, T. I. Gombosi, M. Hässig, A. Jäckel, M. Rubin, C.-Y. Tzou, *Astron. Astrophys.* **2015**, *583*, A1.
[21] U. J. Meierhenrich, J. R. L. Cason, C. Szopa, R. Sternberg, F. Raulin, W. H.-P. Thiemann, F. Goesmann, *Adv. Space Res.* **2013**, *52*, 2080–2084.
[22] N. Thomas, S. Ulamec, E. Kührt, V. Ciarletti, B. Gundlach, Z. Yoldi, G. Schwehm, C. Snodgrass, S. F. Green, *Space Sci. Rev.* **2019**, *215*, 47.

Manuscript received: March 31, 2022
Revised manuscript received: May 2, 2022
Accepted manuscript online: May 5, 2022

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