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LABORATORY SECONDARY ION MASS SPECTRA OF COMETARY ANALOG MATTER. M. Hilchenbach¹, C. Brioso², H. Cottin³, C. Engrand⁴, K. Hornung⁵, J. Kissel¹, H. Krüger¹, H.J. Lehto⁶, K. Lehto⁷, J. Silen⁸, L. Thirkell², K. Varmuza⁹, ¹Max-Planck-Institut für Sonnensystemforschung, Max-Planck-Str.2, 37191 Katlenburg-Lindau, Germany (hilchenbach@mps.mpg.de), ²Laboratoire de Phys. Chim. de L'Environnement, 3 Av. de la Recherche Scientifique, 45071 Orleans, France, ³LISA, Universites Paris 12 Paris 7, Faculte des Sciences et Technologie, 61, Avenue du General de Gaulle, F-94010 Creteil Cedex, France, ⁴Centre de Spectrometrie Nucleaire et de Spectrometrie de Masse, Centre National de la Recherche Scientifique- Université Paris-Sud, Batiment 104, 91 405 Orsay Campus, France, ⁵Institut für Strömungsmechanik und Aerodynamik, Fakultät für Luft-und Raumfahrttechnik, Universität der Bundeswehr München, Werner-Heisenberg-Weg 39, 85577 Neubiberg, Germany, ⁶University of Turku, Department of Physics and Astronomy, Tuorla Observatory Väisäläntie 20, 21500 Piikkiö, Finland, ⁷Department of Biochemistry and Food Chemistry, University of Turku, FIN-20014 Turku University, Finland, ⁸Finnish Meteorological Institute, Department of Geophysics, rik Palmenin aukio 1, FI-00560 Helsinki, Finland, ⁹Institut für Verfahrenstechnik, Umwelttechnik und Techn. Biowissenschaften, Technische Universität Wien, Getreidemarkt 9,1060 Wien, Austria

Introduction: Secondary ion mass spectrometry (SIMS) is a laboratory surface analyzing technique and, with the COSIMA instrument onboard ROSETTA, it will be applied to in-situ measurements of cometary grains, once Rosetta reaches its target comet, 67P/Churyumov-Gerasimenko, in the year 2014 [1]. Furthermore, the elemental abundances of STARDUST samples have been measured with SIMS laboratory instrumentation [2].

SIMS ion mass spectra are a complex mixture representing the elements and molecules on the surface area analyzed by the primary ion beam. The interpretation of the spectra requires knowledge of the stable molecular ions as well as statistical methods analyzing and comparing mass spectra. The spectra are taken from cometary analog and reference samples analyzed with the laboratory reference instrument of COSIMA [3,4].

In this study, we are focusing on pure and mixed organic samples, and apply the multivariate curve resolution (MCR) method, designed for the recovery of pure components from a multi-component mixture, when little or no prior information is available [5,6].

Methods and Materials: The COSIMA instrument is a high resolution, reflectron type, time-of-flight mass spectrometer using a liquid metal indium ion source for the primary 8 keV ion beam and a single ion counting detection technique resulting in mass resolution of about 1700@100 amu [1]. The statistical analysis was carried out with the Unscrambler X software package (CAMO Software AS, Norway).

Organic compounds are cytosine, purine, L-cysteine, L-isoleucine, L-threonine, 4-aminopyrimidine and L-proline. The organics are dissolved in a water-ethanol solvent (9:1) with a final concentration of 0.05 mol/l except for L-proline and 4-aminopyrimidine with 0.1 mol/l. Lithium fluoride (LiF) was added as a tracer with a concentration of 0.01 mol/l.

For sample carrier or target we use blank silver sheet (area 1 cm²). All chemicals and the silver sheets have been acquired from Sigma-Aldrich Corporation, Germany. Multiple samples are applied to the target in 4 dilution steps up to 1:16. Additionally, one sample each is applied without the LiF salt tracer, another one is mixed with pyroxene grains (diameter range 25-100 um) and finally 8 samples constitute mixtures of up to 3 organic samples. The samples are transferred to

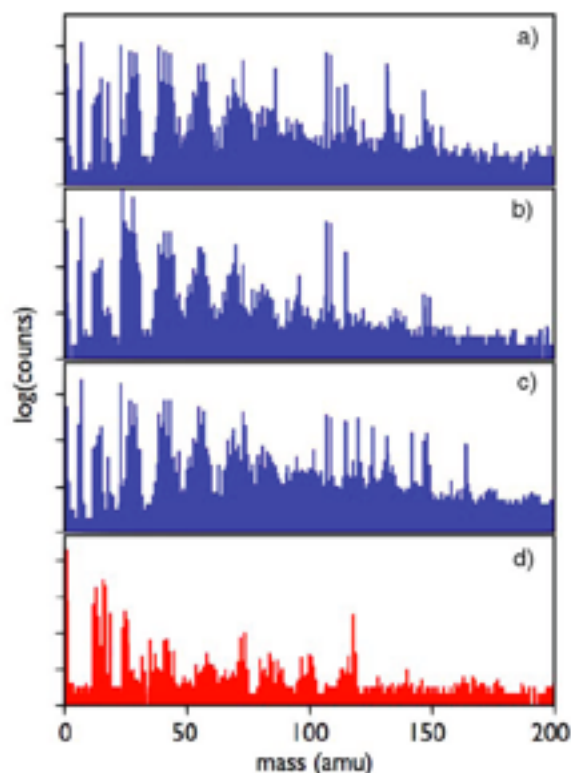


Fig.1: Examples of positive SIMS mass spectra: a) mixture of L-isoleucine, L-cysteine and cytosine, b) LiF and enstatite c) L-threonine and negative SIMS mass spectra: d) L-threonine.

the target with Eppendorf pipette tips (0.1 - 2 ul, Eppendorf AG, Germany). Each sample spot diameter is less than 1 mm. In total, 54 samples are applied to the target. The re-crystallization upon drying is not further controlled by any means and therefore the dried samples cover a wide range of surface morphologies.

Results and Discussion: Positive and negative SIMS mass spectra of the 54 samples are acquired sequentially and some examples are shown in Fig. 1. Silver, indium and poly-dimethyl-siloxane (PDMS), a common contamination compound, are present in all positive spectra. The protonated molecular mass - $(M+H)^+$ - of the organic compounds can be identified in the positive SIMS spectrum, for single compounds as well as for organic mixtures. Organic salts of Li and Na are identified, e.g. for L-threonine at ion mass 126, 142, 164 (Fig 1c). The de-protonated molecular masses - $(M-H)^-$ - are identifiable in the negative SIMS spectra (e.g. L-threonine, ion mass 118, Fig 1d).

The MCR analysis applied to the positive and negative spectra reveals as main components for all spectra (1) Na^+ , (2) O^- , (3) Li^+ , (4) OH^- , (5) K^+ , (6) cytosine, (7) CN^- , (8) PDMS $Si(CH_3)_3^+$, $Si_2O(CH_3)_5^+$, (9) Cl^- , Br^- , (10) Ca^+ and Si^+ , (11) Mg^+ and Si^+ , (12) CH^- , (13) Ag^+ , In^+ , (14) L-isoleucine, (15) L-threonine, (16) H^- , (17) L-proline, (18) $C_nH_{2n-1}^+$, $C_nH_{2n+1}^+$.

The MCR analysis separates negative and positive spectra. Four organic compounds, lithium, enstatite as well as diopside and the contaminations due to PDMS are well detached from each other. L-cysteine and purine are not identifiable by the applied analysis even so both are present in the SIMS spectra. The negative de-protonated ion mass peak of L-threonine (see Fig. 1d) is not eminent in the MCR results. 4-amino-pyrimidine is neither identified by individual SIMS mass spectra peak search nor the MCR analysis.

Conclusions: The analysis of SIMS mass spectra of captured dust grains of comet 67P/Churyumov-Gerasimenko will be a complex task, as the secondary ions of the organic and inorganic compounds present on the grain surfaces will be entangled in single mass spectra. For separation of the various compounds, a sufficient number of linear independent mass spectra must be collected. Only then statistical methods such as principal component analysis, random projection or the MCR method can be applied. The great advantage of MCR is that the resulting spectra can be interpreted with the known or expected chemistry and/ or mineralogy in mind. The spectra derived with MCR highlight potentially associated mass peaks. On the other hand, as with single mass spectra interpretation, statistically less significant peaks are not necessarily retrieved and the sensitivity threshold for single mass peaks seems to

be minor compared to the examination of individual mass spectra.

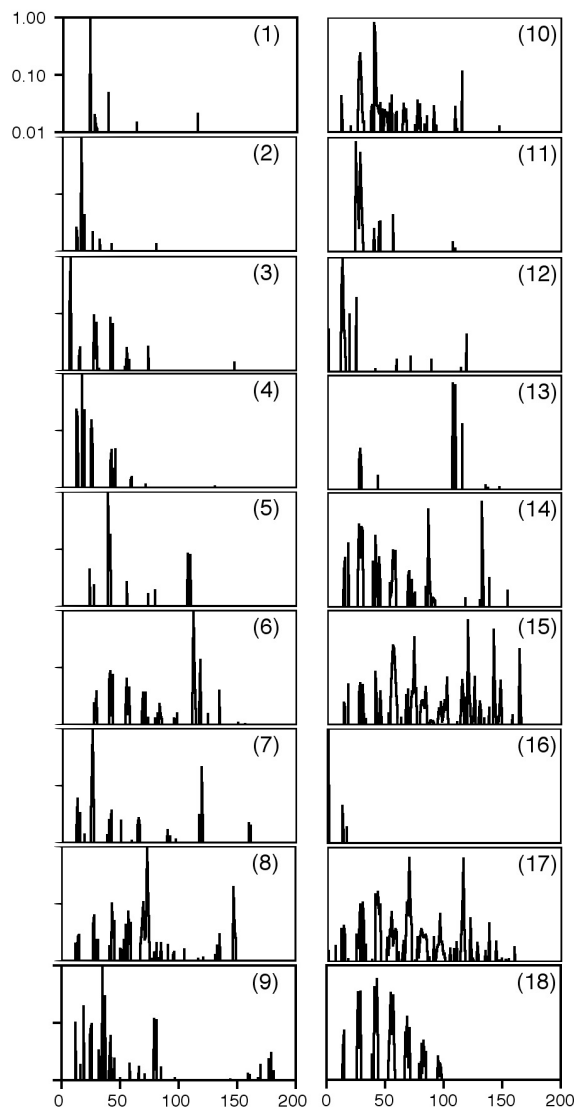


Fig.2.: Multivariate curve resolution (MCR) analysis of the positive and negative SIMS spectra. See text for details.

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