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► **To cite this version:**

Melissa Guzman, Cyril Szopa, Caroline Freissinet, A Buch, T Fornaro, et al.. Gas Chromatography-Mass Spectrometry Detection of Diagnostic Features of Molecular Bioindicators Adsorbed on Minerals Relevant to ExoMars's MOMA Instrument. Ninth International Conference on Mars, Jul 2019, Pasadena, United States. pp.LPI Contribution No. 2089, id.6167. insu-04445343

HAL Id: insu-04445343

<https://insu.hal.science/insu-04445343>

Submitted on 7 Feb 2024

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GAS CHROMATOGRAPHY-MASS SPECTROMETRY DETECTION OF DIAGNOSTIC FEATURES OF MOLECULAR BIOINDICATORS ADSORBED ON MINERALS RELEVANT TO EXOMARS'S MOMA INSTRUMENT.

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Introduction: The Mars Organic Molecule Analyzer (MOMA) experiment will travel to Mars onboard the rover of the joint ESA/Roscosmos ExoMars 2020 mission. MOMA is a miniaturized chemical laboratory specifically dedicated to analyzing the organic and inorganic content of samples collected by the rover at the martian surface and subsurface down to 2 meters deep [1]. MOMA will go a step beyond characterizing habitability of Mars and will search for traces of life, or biomarkers, including nucleobases and amino acids, fundamental building blocks of terrestrial life [2]. To reach that goal, MOMA includes a gas chromatograph (GC) and a mass spectrometer (MS). Coupled together, these instruments will respectively separate the volatile compounds produced from heating or chemical treatment of the samples, and provide a spectral signature of each compound. This combination allows the identification of organic molecules. In order to widen the detection capabilities for compounds of astrobiological interest using GCMS, MOMA carries onboard wet chemistry, used to produce controlled reactions to protect reactive groups of polar molecules. It is also known that the presence of perchlorates on Mars can cause potential problems for detection of organics by GCMS [3]. This study tests the capabilities of the GCMS technique to detect four potential representative organic bioindicators, adenosine 5'-monophosphate (AMP), L-glutamic acid (Glu), L-phenylalanine (Phe), and phthalic acid (PhA), which have been adsorbed on to a mineral, Montmorillonite, at three concentrations and with or without the addition of magnesium perchlorate.

Methods: The Montmorillonite (Mont) SAZ-1 (Clay Minerals Society) was treated to remove organics (0.112wt% C) so that the carbon content was below the detection limit of Isotope Ratio Mass Spectrometry (IRMS). Next, molecule-mineral complexes were prepared by mixing the mineral powder with an aqueous solution of the four molecules of interest, AMP, Glu, Phe, and PhA, for a time sufficient to reach equilibrium. Then, the suspensions were dried in mild conditions to simulate desiccation processes of liquid water bodies on Mars. Samples were prepared at 3 concentrations, i.e. 5%, 1%, and 0.1 wt%. Samples with perchlorates were treated with Mg-perchlorate at 1 wt% (Figure 1).

The samples were first tested under flash pyrolysis at 650°C, then under a MOMA-like pyrolysis program starting at 45°C and ramped up to 830°C at 200°C/min and held at the final temperature for 2 min. Derivatization was performed on the samples using *N,N*-methyl-tert-butyl-dimethyl-silylfluoroacetamide (MTBSTFA) and *N,N*-Dimethylformamide dimethyl acetal (DMF-DMA), two derivatization agents which are implemented in the MOMA experiment. For MTBSTFA derivatization, two techniques were explored for extraction of the organics from the mineral matrix: extraction by solvent (water+isopropanol at 1:1 by volume) and a MOMA-like derivatization where 15 µL of the derivatization reagent was applied directly to the sample. In the case of the extraction protocol, the sample was derivatized at 75°C for 15 min; for the direct derivatization the sample was heated at 140°C (DMF-DMA), 200°C (DMF-DMA) or 250°C (DMF-DMA, MTBSTFA) for 3 min. GCMS injection is by hand-held 1 µL SGE syringe, in contrast to the injection traps used on MOMA [1].



Figure 1: (Left) Montmorillonite samples spiked with organic molecules. Right) a sample sealed with 15 µL of MTBSTFA for MOMA-like derivatization.

The GC column used was a 30 m Restek Rxi-5ms, which is different in length and coating from the MOMA columns. This standard column was selected since we were interested in the GCMS analysis of the samples rather than separation performance of a given column. The GC column was held at 40°C for 1 min and then ramped up to 300°C at 10°C/min. The He carrier gas flow rate was 1.1 mL/min. An external standard of D8-naphthalene in DMF at 5×10^{-3} mol L⁻¹ was used as an external standard for quantification.

Results and Discussion:

Pyrolysis. No major qualitative difference was found between flash pyrolysis and MOMA-like ramp pyrolysis, with the exception of the PhA sample, in which more reaction products were observed after flash pyrolysis. There was no detection of pristine AMP, which is expected due to the high molecular weight of the nucleotide, nor of Glu and Phe, which is expected because these molecules rely on derivatization for GCMS detection.

There was no major difference between the perchlorate free and perchlorate samples, with the exception of additional oxygenated compounds detected in the perchlorates samples with Phe and some chlorohydrocarbons detected in the perchlorates samples with PhA. PhA is known to be a precursor of chlorohydrocarbons detected by Curiosity's Sample Analysis at Mars (SAM) instrument. These types of laboratory analyses will be important analog GC runs during MOMA operations on Mars in order to 1) predict and identify compounds of interest, including degradation and reaction products, in flight chromatograms, and 2) learn more about the martian parent mineral based on identified compounds in the chromatogram and in comparison to these types of analog samples.

Derivatization. Glu, Phe, and PhA derivatized with MTBSTFA were clearly detected at all three concentrations, while AMP was not detected at any concentration. Glu, Phe, and PhA at the highest concentration, 5 wt%, were harder to detect with DMF-DMA derivatization as the chromatographic response was close to the noise limit. This difficulty prompted some optimization of the derivatization temperature protocol for DMF-DMA, which was tested at 140°C (optimized for standards by [4]), 200°C, and 250°C.

No major qualitative difference was observed between the extraction by solvent versus the MOMA-like direct derivatization, nor between the perchlorate free and perchlorates samples. Using the 5 wt% sample of PhA without perchlorates and derivatized with MTBSTFA, the difference in chromatographic response of the extraction method was found to be about 6×10^8 counts/s higher than that of the direct derivatization method. The direct derivatization method is closer to the method to be utilized on Mars with MOMA.

We used the samples at 3 concentrations of Glu, Phe, and PhA to calculate the limit of detection (LOD) for each of these compounds after a MOMA-like derivatization with MTBSTFA. The detection limits are shown in Figure 2, illustrating that the GCMS technique enables detection of organics at concentrations of 0.01 wt% or below, the lowest detection limit of an ExoMars instrument for these samples to date.

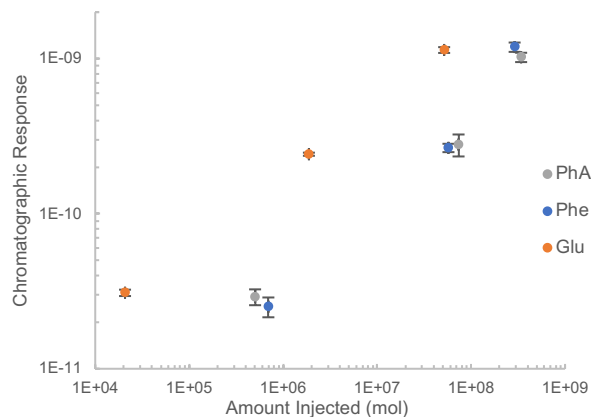


Figure 2: log/log scale response of the chromatogram (area of the peak) depending on the quantity of product injected (mol).

Conclusions: A martian analog mineral spiked with biomarkers of interest was tested in the presence of MOMA-like pyrolysis and derivatization. The effects of perchlorates and organic concentration are explored. The tests show positive detections of bioindicators of interest, such as amino acids, and the limitations of the technique to detect heavier weight compounds such as a nucleic acid under these run conditions. If preliminary biomolecules are detected on Mars, these data will help inform the trade space on whether to modify the GC run conditions in order to target higher molecular weight compounds.

References:

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