

COMPARING THREE ORGANIC EXTRACTION AND CHEMICAL DERIVATIZATION METHODS ON FIVE MARS ANALOGUE ROCKS FROM SVALBARD, NORWAY. K.E. Fristad¹, O. Botta², P.R. Mahaffy¹, J. Eigenbrode¹, A. Steele³, and the AMASE 2006 Team. ¹NASA Goddard Space Flight Center (Code 699, Greenbelt Road, Greenbelt, MD 20771; Kirsten.E.Fristad@nasa.gov), ²International Space Science Institute (Hallerstrasse 6, CH-3012 Bern, Switzerland) ³Geophysical Laboratory, Carnegie Institution of Washington, (5251 Broad Branch Rd, NW, Washington, DC 20015)

Introduction: The Sample Analysis on Mars (SAM) instrument containing a gas-chromatograph mass spectrometer (GCMS) system will be aboard the Mars Science Laboratory (MSL) rover launching in 2009 to search for organics on the surface of Mars. In addition to pyrolysis, SAM employs a chemical derivatization procedure involving silylation using (*N,N*-methyl-*tert*-butyl-dimethylsilyl-trifluoroacetamide (MTBSTFA) and simultaneous dimethylformamide (DMF) extraction to enable GCMS identification of amino acids and carboxylic acids [1] in rock and soil samples. To minimize complexity associated with sample processing, SAM will utilize a one-step extraction and derivatization procedure.

Historical Context: Organic geochemistry procedures have employed silylation using *N,O*-bis-trimethylsilyl-trifluoroacetamide (BSTFA) and multi-step extraction and derivatization procedures to identify organic compounds in rocks and soils [2]. To compare the simplified SAM extraction procedure to traditional extraction methods, three experiments were carried out; (1) SAM one step extraction and derivatization using MTBSTFA/DMF, (2) one step extraction and derivatization using BSTFA/DMF, and (3) multi step dichloromethane (DCM) and methanol (MeOH) extraction followed by MTBSTFA derivatization. By comparing these three analysis methods on five Mars analogue samples from Svalbard, Norway, we can establish a link between SAM and laboratory methods in order to better interpret GCMS data returned from the Mars Science Laboratory (MSL).

Mars Analogue Samples: Five Mars analogue samples collected during the Arctic Mars Analog Svalbard Expedition (AMASE) 2006 to Svalbard, Norway, were utilized in this extraction method study. The particular samples utilized range in relative organic content and species. Samples from the different locations were acquired using sterilized tools (chisel, scoop, spatula). In addition, one sample was acquired by the JPL CliffBot rover during its first deployment. The samples were collected in baked aluminium (500°C air, 4h) foil. Direct contact with the samples with non-sterilized tools was avoided at all times. To maximize the surface area for organic extraction, samples that were not in powder form were crushed using sterile, agate mortar and pestle.

The following samples were analyzed:

Diesel Dolomite. Organic-rich carboniferous dolomite collected from small outcrop within the Ebbadalen Formation in Ebbadalen.

Rover1. Evaporite precipitate crust on sandstone within the Ebbadalen Formation in Ebbadalen.

Stromatolite. 780 Ma stromatolite collected in Murchison Fjord.

Jotun Travertine. Travertine collected from Jotun hot springs in Bockfjorden containing endolithic microbes.

Olivine Sand. Weathered peridotite and olivine-bearing sand exposed to the surface on the lower slopes of Sverrefjell volcano in Bockfjorden.

Methods: 150 mg powdered samples from each of the five analogue rock samples were analyzed using the three described procedures. The samples were prepared in ashed amber vials with organically cleaned Teflon lids; lab procedures followed organically clean methods for instrument and tool use as described in [3]. The three organic extraction methods are as follows.

SAM: "One-step MTBSTFA" 30 μ L DMF and 90 μ L MTBSTFA were added to 150 mg of solid sample and the mix was heated at 75°C for 45 minutes. After the mixture was allowed to cool to room temperature, the supernatant was removed to a new ashed vial where 15 μ L pyrene in DMF at a concentration of 50 ng/ μ L was added. One microliter of supernatant was analyzed by GCMS.

SAM/BSTFA: "One-step BSTFA" 30 μ L DMF and 90 μ L BSTFA were added to the 150 mg solid sample and the mix was heated at 75°C for 45 minutes. After the mixture was allowed to cool to room temperature the supernatant was removed and placed into a new ashed vial with 15 μ L of pyrene in DMF at a concentration of 50 ng/ μ L. 1 μ L of supernatant was analyzed by GCMS.

SAM/DCM-MeOH Extraction: "Multi-step MTBSTFA" 150 mg of solid sample was sonicated for 5 minutes in 120 μ L of DCM/MeOH (3:1). The supernatant was pipetted off using glass Pasteur pipettes. The DCM and methanol extraction procedure was replicated three times per sample. All removed supernatant was dried down in a vacuum centrifuge. Then 30 μ L of DMF and 90 μ L of MTBSTFA are added and heated to 75 °C for 45 minutes. After cooling to room temperature, 15 μ L pyrene was added and 1 μ L analyzed by GCMS.

Each derivatized sample was analyzed using a Thermo-Finnigan UltraGC-TraceDSQ quadrupole mass spectrometer with a 100°C to 270 °C at 3 °C/minute programmed temperature ramp. An RXT-1701 column (Restek, 30 m, 0.25 mm ID, 0.12 µm film thickness) was used for sample analysis, and helium was used as the carrier gas. Chromatographic peaks were identified in Selective Ion Mass chromatograms using literature data [4] and the Xcalibur software package in connection with the NIST mass spectra library Mass Search 2.0.

Results and Discussion: SAM will use a one-step extraction derivatization procedure in order to minimize complexity associated with sample processing. This study explores how GCMS analysis of Mars analogue materials differs between one-step extraction and derivatization versus a multi-step extraction and derivatization procedure.

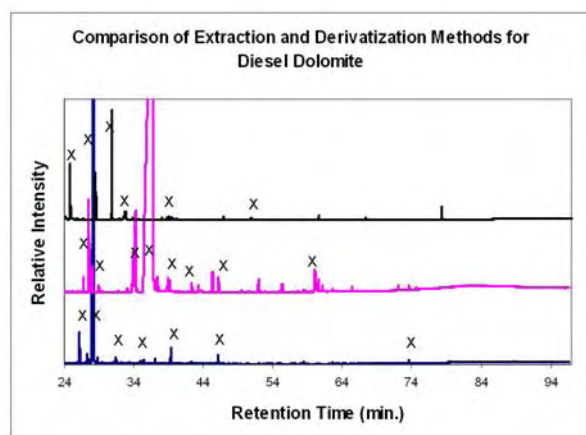


Figure 1. Total Ion Chromatograms for One-step MTBSTFA, One-step BSTFA, and Multi-step DCM-MeOH/MTBSTFA extraction and derivatization techniques for Diesel Dolomite stacked respectively up the y-axis. “X” marks indicate peaks due to solvent artifacts.

Extracted and derivatized organics from the Diesel Dolomite are shown in Figures 1 where One-step MTBSTFA, One-step BSTFA, and DCM-Methanol extraction with MTBSTFA derivatization are stacked from bottom to top respectively. Chromatographic peaks due to solvent artifacts are marked with an “X”.

MTBSTFA is a highly reactive species; when unbonded upon introduction to the GC, it will react with any existing species inside the GCMS (column, carrier lines, septum, etc.) creating a number of artifacts in the resulting chromatograms. Due to the increase in free MTBSTFA, artifacts are often increased in chromatograms of solvent blanks.

This study is important for understanding and interpreting derivatization data from the SAM GCMS

instrument as well as understanding the organic content of Mars analogue rocks. A comparison of the organics measured with the various extraction and derivatization techniques for each of the five Mars analogue samples will be presented.

References: [1] Mahaffy, P.R. et al. (2004) LPSC XXXV #1392. [2] Brocks, J. et al. (2003) Organic Geochemistry 34, pp.1161-1175. [3] Benning, L., Eigenbrode J., Steele A., et al. (in prep). [4] Hunt, J. (1995) Petroleum Geochemistry and Geology, W.H. Freeman Co., pp.743.

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