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FLIGHT INTEGRATION AND TEST OF THE MARS ORGANIC MOLECULE ANALYZER (MOMA).

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Introduction: The Mars Organic Molecule Analyzer (MOMA) investigation [1] on the 2020 ExoMars rover [2] will examine the molecular composition of crushed samples acquired from depths of up to two meters below the martian surface, where organics may have been protected from radiative and oxidative degradation [3,4]. MOMA combines pyrolysis-gas chromatography/mass spectrometry (pyr-GCMS), both with and without chemical derivatization, and laser desorption mass spectrometry (LDMS), in coordination with the other investigations in the rover's Pasteur Payload, particularly the Raman [5] and MicrOmega [6] instruments. With its two modes, MOMA detects compounds over a wide range of molecular weight, volatility, and mineralological association.

Implementation of GCMS and LDMS Modes: GCMS mode is operated analogously to the Sample Analysis at Mars (SAM) investigation on Curiosity. Samples are sealed into ovens and heated to 850 C. Analyte gases, entrained in He, flow through the GC system to the MS. The GC includes two cooled hydrocarbon traps (Tenax and Carbosieve) that are opened after major water evolution (above 100 C) but prior to organic thermodesorption (from ~300 C up to > 500 C). Trapped organics are injected onto one of four columns and eluted over a temperature ramp to the MS electron ionization (EI) source. GCMS analyzes compounds of high-to-moderate volatility (enthalpies of vaporization $\Delta H_V \leq 50$ kJ mol^{-1}) such as alkanes, amines, and lighter carboxylic and amino acids and aromatic species. Derivatization agent present in some ovens enables detection of the higher ΔH_V and polar species over the full GCMS m/z range of 50-500 Da.

In LDMS mode, molecules are desorbed and ionized directly from powder samples with a pulsed UV laser (266 nm, 1 ns duration) at Mars ambient pressures. Parent molecular cations, and their fragments, enter the MS through a fast aperture valve that closes after ions are trapped, permitting the ion trap pressure to reduce to $<10^{-3}$ Torr where the detectors can be operated. LDMS mode is designed to analyze compounds of moderate-to-low volatility ($\Delta H_V \geq 40$ kJ mol^{-1}) such as heavier carboxylic acids, aromatic species, chain-like compounds, and macromolecular organics. The pulsed LDMS mode is not strongly affected by the potentially oxidizing effects of heat-evolved perchlorates, simplifying analysis of nonvolatile organics [7].

Flight System Intergration and Test: All flight models (MS, laser, electronics, pyrolysis, GC) have been individually tested, qualified, and delivered to the MOMA system integration and Mars thermal-vacuum facility at GSFC (Fig. 1), maintained under stringent contamination and planetary protection controls.

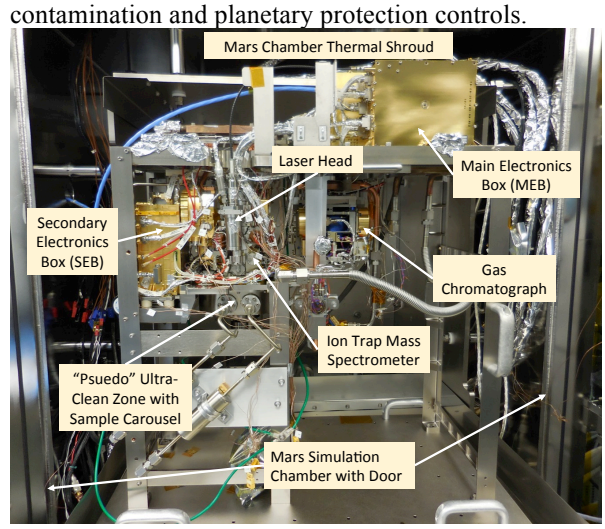

Fig. 1 Flight mass spectrometer and electronics assemblies with laser and GC in Mars environment simulation chamber to match mechanical, thermal, pressure, and contamination conditions that MOMA will experience on the ExoMars rover. End-to-end "test-as-you-fly" operations over more than a dozen full thermal cycles verify all performance and reliability requirements as well as MOMA science calibration.

Testing of the GCMS mode on both engineering unit and flight instrumentation using calibration gases has demonstrated as-expected functional performance for resolution, acquisition rate, sensitivity, and fragmenta-

tion patterns. Analysis of a concentration series of volatile hydrocarbons was used to determine limits of detection for the mass spectrometer within expected MOMA sample volumes and analysis times. Benzene was readily detected at concentrations as low as 15 fmol s^{-1}, or approximately 0.06 parts-per-billion by weight (ppbw) equivalent, depending on Mars pressure (which modulates effective gas split ratios), when separated on a flight-level Restek CLP GC column. Subsequent testing of a broader mixture of gases using the MXT Chirasil column has provided intial data on GC separation for closely-spaced peaks under Mars conditions (Figure 2). The pentane/pentene/pentyne and hexane/hexane/hexyne triplets were individually resolved by monitoring precise retention times combined with single ion count (SIC) data in the ITMS. The chiral compound D,L-3-methylhexane was clearly identified; the separation of enantiomers was observed to increase dramatically with GC temperature (inset). The relatively high acquisition speed of the ion trap permits multiple full mass spectra across each GC peak, enabling accurate identification and quantification even in the presence of overlapping species.

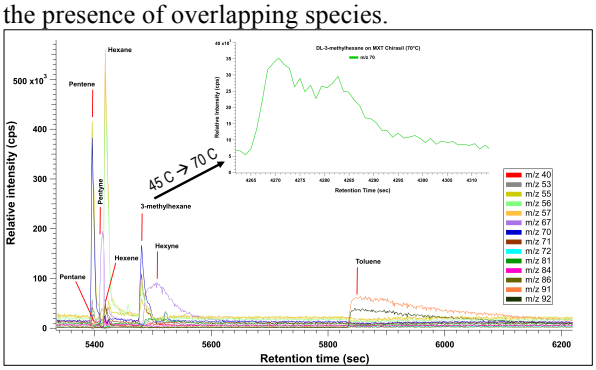

Fig. 2 MOMA GCMS chromatograms as captured by MS single ion chromatograms show separation and identification of hydrocarbons in He. Chiral D,L-3-methylhexane serves to test the GC enantiomeric separation over temperature.

The mass spectrometer including the flight model of the pulsed laser has now been tested, verifying ion transmission, sensitivity, resolution, and accuracy requirements over the mass range up to 1000 Da. A calibration target of solid CsI will be delivered to Mars with MOMA and used to track and correct any drift of m/z position or mass bias of sensitivity. Only trace-level (fmol) concentrations of selected organics are used to perform critical ground-test verification of the MOMA limit of detection for nonvolatile compounds in the FM. These have been demonstrated to leave zero residual background in the MS. Recent work has focused on operating the LDMS mode with (i) automatic "gain control" of laser and inlet focusing parameters to achieve optimal ion trap loading per spectrum, and (ii) stored waveform inverse Fourier transform (SWIFT) modes for ion isolation, concentration, and tandem MS (MS/MS) which permits structural analysis. Figure 3 demonstrates the successful application of SWIFT for MS/MS analysis of a phosphorous-bearing test target, which produces clusters with peak series of P (31 Da), P2 (62 Da), and P4 (124 Da) upon selective isolation and fragmentation. A substantial additional benefit of precise ion isolation is the enormous increase in signal-to-noise ratio for a narrow mass band due to suppression of ion trap space charge effects during the analytical ramp. Further work on increasingly complex and realistic analog target samples will enable incorporation of automated LDMS protocols to maximize the benefits of neutral-loss identification of organics

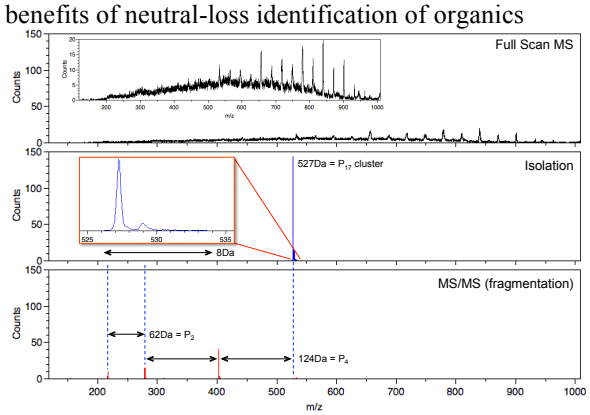

Fig. 3 The SWIFT mode of LDMS operation isolates a selected narrow m/z range around the P_{17} cluster, increasing SNR (middle) and enabling MS/MS identification (bottom).

Path Forward: Following final Mars thermal-vacuum testing and data review, the MOMA instrument is scheduled for delivery to ExoMars rover integration in March, 2018. It will be installed on the flight ultra-clean zone, containing the rover's sample processing and distribution system (SPDS), under extremely tight contamination and planetary protection constraints. Abbreviated end-to-end testing of both GCMS and LDMS modes to verify critical functionality under rover-level Mars conditions will precede delivery to higher levels of I&T and launch in 2020.

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