

ADVANCED MASS SPECTROMETER TECHNIQUES FOR AGNOSTIC SURVEYS FOR MARTIAN BIOSIGNATURES. P. R. Mahaffy¹, R.D. Arevalo², W.B. Brinckerhoff¹, J.E. Cook¹, R.M. Danell³, S.A. Getty¹, H.V. Graham^{1,2}, S.S. Johnson⁴, M.G. Trainer, and X. Li^{1,5}, ¹NASA Goddard Space Flight Center, Solar System Exploration Division, 8800 Greenbelt Rd, Greenbelt, MD 20771 Paul.R.Mahaffy@NASA.gov, ²U. MD, College Park, MD, ³Danell Consulting, Winterville, NC, ⁴U. Georgetown, Washington DC, ⁵U. MD, Baltimore CO, MD.

Introduction: Recent discoveries in ancient Gale crater mudstones of chlorinated hydrocarbons [1], sulfur containing organic compounds [2], fragments of macromolecular carbonaceous material [1] as well as seasonal variations of atmospheric methane [3] motivate a vigorous ongoing and future search for signatures of extant or extinct life. Mass spectrometer based techniques are among the essential tools needed to search for carbon chemistry based biosignatures revealed in molecular structure and patterns.

An agnostic approach assumes that while these features may not be identical or even similar to those expressed by terrestrial life they will nevertheless be distinct from the randomness that is characteristic of organic compounds produced by abiotic processes such as radiation in space environments. Among the attributes identified in the recent National Academies astrobiology strategy report [4] and in previous studies [5] that mass spectrometers can probe are chirality and structural isomeric preferences as well as molecular weight patterns in homologous chemical series and chemically complex virus-like structures.

Organics Extraction, Derivatization, and Separation Methods: A broad search for molecular biosignatures will require sampling of a range of volatile and refractory compounds and a range of molecular polarities across a wide range of molecular mass values. Thermal or solvent extraction of organics will be necessary for some analysis methods. The Sample Analysis at Mars (SAM) instrument [6] presently operational in Gale crater and the Mars Organic Molecule Analyzer (MOMA) instrument [7] to be integrated into the ExoMars rover both employ gas chromatograph mass spectrometer (GCMS) and chemical derivatization (CD) techniques. GCMS enables a definitive identification of nonpolar compounds; CD with GCMS can identify more polar biotic or prebiotic compounds such as amino acids and lipids, and can quantify the stereo chemistry of targeted molecules.

Complex Molecules and Tandem Mass Spectrometry: The MOMA ion trap mass spectrometer additionally incorporates a powerful laser desorption ionization (LDI) technique [8] to introduce nonvolatile, higher-molecular weight molecules into the analyzer. This technique helps mitigate the potential combustion or degradation of organic compounds that may complicate their analysis using pyrolysis tech-

niques. Furthermore, the linear ion trap enables tandem mass spectrometry (or MS/MS) that by isolation and then collisional fragmentation of selected ions in the trap provides additional information regarding chemical structure.

An Orbitrap for Ultra-high Mass Resolution: Unambiguous determination of molecular stoichiometry and removal of isobaric interferences can be realized with an Orbitrap™-based mass analyzer [9] derived from recent substantial advances [10] with wide commercial impact. When integrated with a pulsed UV laser source, mass resolutions of $m/\Delta m \geq 120,000$ have been realized with ~ 3 ppm of mass accuracy [9]. Detection and identification of ≤ 1 pmol/mm² have been recently demonstrated [9] and with these advances this technology is rapidly moving toward spaceflight readiness.

Laboratory for Agnostic Biosignatures (LAB): LAB [11] is a recently-formed Network for Life Detection (NFoLD) team led out of Georgetown University (Fig. 1). Its advanced mass spectrometry studies are relevant to LAB's molecular complexity focus



Figure 1. LAB led by Sarah Johnson of Georgetown University brings together diverse disciplines and technologies to address extraterrestrial biosignatures without assumptions of a particular biochemistry.

where MS/MS analyses of a range of biotic and abiotic standards are implemented to explore the utility of Pathway Complexity biosignature measures [12].

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