SENSITIVE AMINO ACID COMPOSITION AND CHIRALITY ANALYSIS WITH THE MARS ORGANIC ANALYZER (MOA). Alison M. Skelley[1], James R. Scherer[1], Andrew D. Aubrey[2], William H. Grover[1], Robin H. C. Ivester[1], Pascale Ehrenfreund[3], Frank J. Grunthaner[4], Jeffrey L. Bada[2] and Richard A. Mathies[1], [1]Department of Chemistry, University of California, Berkeley, CA, 94720, USA; [2]Scripps Institution of Oceanography, University of California at San Diego, La Jolla, CA, 92093, USA; [3]Astrobiology Laboratory, Leiden University, 2300 RA Leiden, The Netherlands; [4]Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA, 91109, USA

Introduction: Detection of life on Mars requires definition of a suitable biomarker and development of sensitive yet compact instrumentation capable of performing *in situ* analyses. Our studies are focused on amino acid analysis because amino acids are more resistant to decomposition than other biomolecules, and because amino acid chirality is a well-defined biomarker. Amino acid composition and chirality analysis has been previously demonstrated in the lab using microfabricated capillary electrophoresis (CE) chips [1, 2]. To analyze amino acids in the field, we have developed the Mars Organic Analyzer (MOA), a portable analysis system that consists of a compact instrument and a novel multi-layer CE microchip.

Microfabricated Device and Portable Instrument: The heart of the MOA is the microchip that contains the CE separation channels as well as microfabricated valves and pumps [3] for sample handling (Figure 1). The pneumatic microfabricated valves are created by combining an etched displacement chamber, an actuated PDMS membrane layer, and a discontinuous fluidic channel structure. A microfabricated pump is created by combining three individually-addressable valves in series. These membrane valves and pumps are integrated with the glass electrophoretic separation channel using a novel multilayer design in which sample enters the top fluidic layer for routing and is directed to the bottom glass layers for CE separation and analysis.

The microfabricated device is operated by the portable instrument (Figure 2) that contains pressure/vacuum pumps and solenoids for controlling fluidic valves, electronics for performing electrophoresis, a thermoelectric cooler and temperature sensor, a 15 mW 400 nm diode laser, confocal detection optics and filters, and a fiber-optic coupled photomultiplier for fluorescence detection. The device has a mass of ~ 11 kg and a peak power consumption of ~15 W.

The MOA was characterized in the lab by determining the limit of detection using different injection schemes [4]. The "regular injection" consisted of a cross injection from sample to waste, presenting an unbiased population in the plug, followed by analysis. Alternatively, the regular injection can be enhanced by injecting different lengths of plug directly toward the cathode in a 2-step process. A 2 s direct injection resulted in a 10 x increase in signal over the cross injection alone; a 10 s direct injection resulted in a 100 x increase although some amino acid resolution was lost. The limits of detection of fluorescamine-labeled amino acids were in the nM to pM range corresponding to part-per-trillion sensitivities in soil samples (Figure 3).

Field Testing of the MOA: The MOA, in combination with the Mars Organic Detector (MOD) [5], was successfully field tested on soil samples rich in jarosite from Panoche Valley, CA. Jarosite is a key mineral indicating that liquid water was once present on the surface of Mars. Amino acids from jarosite samples were sublimed by MOD and deposited onto a fluorescamine-coated cold finger. The microfabricated pumps were used to direct buffer through the MOA sipper to dissolve the sample, and then to return the dissolved sample for analysis. The jarosite sample (Figure 4) was found to contain low levels of methyl and ethylamine (5 ppb), alanine/serine (0.4 ppb), glycine (0.2 ppb), glutamic (0.07 ppb) and aspartic (0.1 ppb) acid as well as a higher concentration of valine (~100 ppb) [4]. These results clearly demonstrate that amines and amino acids can be extracted from sulfate-rich acidic soils such as jarosite and analyzed using the MOA. The MOA is part of the Mars Astrobiology Probe (MAP) which is in development for the Pasteur payload on the European Space Agency ExoMars mission (http://astrobiology.berkeley.edu).

References

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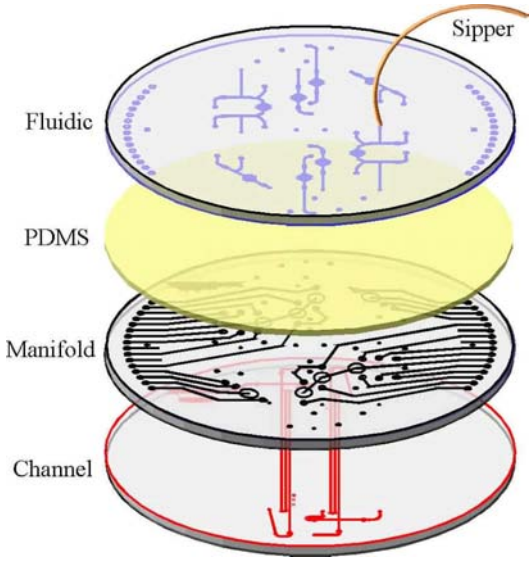

Figure 1. Microfabricated wafer for sample preparation and amino acid analysis. The 100-mm diameter microfabricated wafer stack is composed of a 4-layer sandwich of glass and PDMS to create electrophoresis channels and pumping structures.

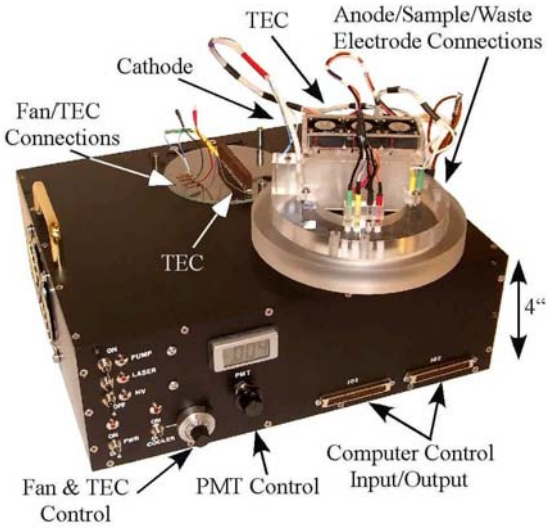

Figure 2. The Mars Organic Analyzer (MOA). The portable CE instrument, measuring 4" x 10" x 12", integrates all necessary pneumatic actuation, high voltage power supplies and confocal optics for laser excitation and fluorescence detection.

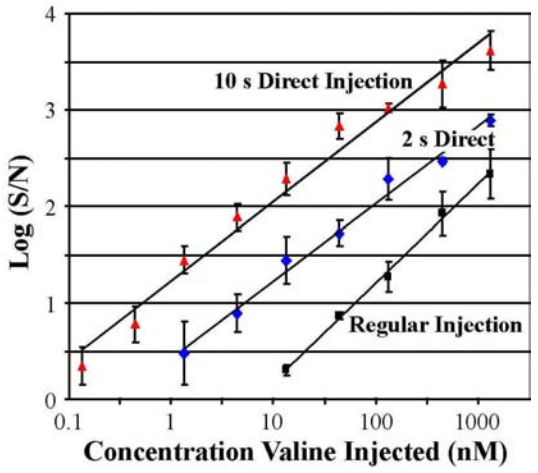

Figure 3. Limits of detection of the MOA system. The cross injection can detect down to 13 nM valine, the 2 second direct injection limits are 1.3 nM, and the 10 second direct injection limits are 130 pM.

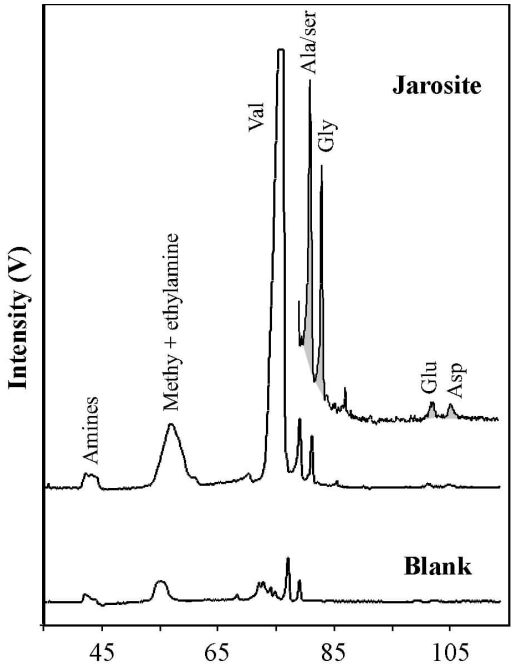

Figure 4. MOA field analysis in Panoche Valley, CA of a jarosite sample prepared by MOD. The peak identities were confirmed by spiking with standard samples.