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The Mars Organic Analyzer (MOA): A field-tested instrument for sensitive amino acid composition and chirality analysis

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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 the dominant chemical component of carbon-based life on earth, they are very resistant to decomposition, and amino acid chirality is a well-defined biomarker. Amino acid composition and chirality analysis has been demonstrated in the lab using microfabricated capillary electrophoresis (CE) chips [1, 2]. To move this analysis to the field, we have developed the Mars Organic Analyzer (MOA), a portable organic amine 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 a 100 mm-diameter, 4 mm-thick microchip that contains the CE separation channels as well as microfabricated valves and pumps for sample handling. The microfabricated valves are created by combining an etched displacement chamber, a pneumatically actuated PDMS membrane layer, and a discontinuous fluidic channel structure [3]. Microfabricated pumps are 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 lower two-layer sandwich for CE separation and analysis.

The microfabricated device is operated by the portable instrument that contains pressure/vacuum pumps and solenoids for controlling pneumatic valves, high-voltage 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 $\sim$ 11 kg and a peak power consumption of $\sim$15 W [4].

The MOA was characterized in the lab by determining the limit of detection using different injection schemes [4]. The "regular injection" consists of a cross injection from sample to waste, presenting an unbiased population in the plug for 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; 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.

Analysis of Atacama Soil Samples: The MOA instrument was next characterized in the lab by analyzing aqueous extracts from Atacama Desert soils. The Atacama Desert is known for its highly oxidized soils with extremely low levels of bacterial life [5] and thus is an excellent Mars analog site for evaluating instrumentation. In the northern and mid-latitude samples, low but significant levels of alanine/serine, glycine, glutamic and aspartic acid (10 to 70 ppb) were detected above the serpentine blank with a 2 s direct injection. In the southern-most sample, several amino acids were present, including valine/γ-ABA, alanine/serine, glycine, and glutamic and aspartic acid (40 to 600 ppb) [4]. The increase in amino acid concentrations observed correlates with the trend in CFU/g previously reported [5] and indicates that the MOA is able to detect amino acids in samples from the most arid, Mars-like environment found on earth. We suggest that the ability to detect organics in these representative samples should be a pre-requisite for *in situ* Mars instrumentation.

Field Testing of the MOA: The MOA, in combination with the Mars Organic Detector (MOD) [6], was successfully field tested on jarosite samples from the 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 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 ($\sim$100 ppb) [4]. These results clearly demonstrate that significant and detectable concentrations of amines and amino acids are preserved in sulfate-rich acidic soils such as jarosite and that they can be extracted and analyzed using the MOA. The MOA is part of the Mars Astrobiology Probe (MAP, http://astrobiology.berkeley.edu) which is in development for the Pasteur payload on the European Space Agency ExoMars mission.

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