Integrated End-to-End Sampling System with Real Time Inorganic and Organic Biomarker Analyzer.
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Introduction: The search for a signs of a Second Genesis and evidence of extinct or extant life on Mars is the central driving theme for Mars Exploration. There is much debate and little consensus within the AstroBiology community as to what would constitute incontrovertible evidence of life on Mars. Furthermore, the scale of the number of possible sites to explore is daunting and many chemical considerations of the long term survivability of organic compounds suggest that subsurface exploration will be a necessity. It is unlikely that this question will be easily resolved by a few robotic missions that can analyze a limited area or by a single sample return effort. Life detection will also be the key objective of future Human Exploration of Mars. Human and robotic exploration will need to detect trace levels of organic compounds in real time and will need to characterize reactive, oxidative and toxic characteristics of the Martian regolith. *We are developing an end-to-end sample acquisition and analysis system based on a microfluidic lab-on-a-chip approach which can quantitatively resolve and detect soluble inorganic and organic species present in a solid sample to support in situ robotic missions and be implemented as a hand-held instrumental tool for Astronaut exploration of the Martian surface.*

The Urey Instrument: This system builds on the approach pioneered by the Urey Instrument that underwent technical development for the ExoMars Mission. Urey accepted powdered samples from the ExoMars drill/crusher system, performed a powerful liquid phase extraction on the sample capturing trace organic compounds and then analyzed the extractant for chiral organic compounds with detectivity at the subfemtomolar level. The flight version of Urey would have weighed about 8 kg. including all power supplies, detectors, sequencing electronics and consumables needed to support the analysis of up to 30 samples. The microfluidic lab-on-a-chip analyzer at the core of the Urey instrument accomplished the chromatographic separation of the target molecules with capillary zone electrophoresis. Detection was accomplished by chemical derivitization of target compounds followed by laser-induced fluorescent analysis. All of the required chemical steps for analysis, including dilution, buffer formation, mixing and derivitivization were accomplished on the 4-inch multilayer microfluidic chip. The microfluidic system is far lighter and significantly less complex than a GC/MS system while providing higher sensitivity for the target biomarkers.

Integrated End-to-End Chemical Analysis: With the cost limitations imposed by future landed robotic missions, we embarked on a development program to reduce the size and weight of the Urey Instrument while simplifying its extraction system, increasing the range biomarker compounds detected, increasing the number of samples that could be analyzed and adding a dedicated sample acquisition system. These goals were to be accomplished without reducing the sensitivity of the instrument. *The resulting End-to-End Analyzer (dubbed the AstroBioNibbler) consists of a miniaturized powder sampler, a low pressure driven transport tube, and a multilayer microfluidic analyzer that does on chip extraction of the powdered sample, all dilution and mixing operations, together with chromatic separation and detection of all soluble inorganic and organic compounds present. The flight version with supporting power supplies, electronics and consumables will weigh 3 kg.* The component systems are described in the following.

Solid Sampler: The integrated analyzer uses a powder sampling device developed by JPL's Nondestructive Evaluation and Advanced Actuator Technology Laboratory. This 1.5 inch long, 40 gram, ultrasonically-actuated miniature sampler generates 0-5 micron diameter particles that are transported from cutting head to the microfluidic extraction system by low pressure (vacuum) flow in a flexible metal tube. The sampling head can be placed several feet distant from the analyzer package. This dedicated sampler can be chemically cleaned to remove all measurable carbon compounds before flight to ensure that no false positives due to terrestrial contamination will occur. The prototype and the transport system have been tested using Atacama Desert rock samples. The powder sampler is shown in Figure 1a.

On-Chip Liquid Phase Extraction: The powdered sample is delivered to a holding cell where aqueous slurry is formed. A filtered aliquot of this liquid is sent to the inorganic analysis channel and the concentration of all anions and cations present in the solution is determined as described below. The organic compounds in the remaining slurry are extracted using a previously developed microfluidic analytical chemical sample preparation strategy called the H-Filter [1] which involves diffusional transfer of small molecules from one solvent to another while they run parallel down a single microfluidic channel. The dual stream flow configuration creates a laminar flow diffusion interface (LFDI) and the flow of two solvents in a

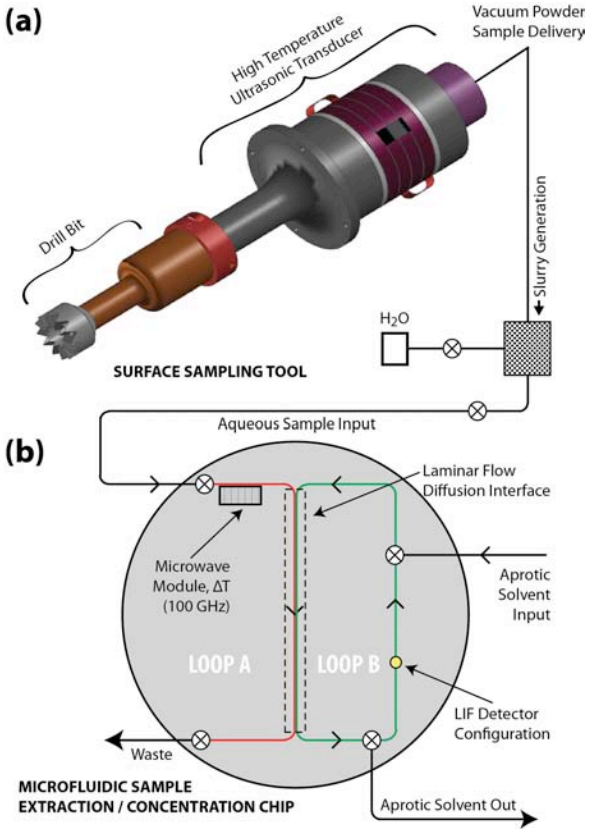

Figure 1. End-to-end sampling and extraction system: (a) ultrasonic drill and (b) solid phase extraction microfluidic chip.

single microfluidic channel allows for diffusive exchange across the LFDI without the influence of turbulent dynamics. This technique is particularly effective for the isolation of small organic molecules into an organic solvent from an aqueous stream or slurry. Upon diffusion into the organic stream, the target compounds are concentrated by solvent extraction and then directed to the organic analysis channels of the microfluidic chip. In order to accelerate the liberation/capture of bound organics, the water-based slurry is heated into the subcritical regime using a 100GHz microwave module immediately before being introduced into the parallel laminar flow channel. The microwave module consists of a solid state CW source operating at approximately 100 GHz with an output power that can be varied from 1 to 100mW. The extraction system is illustrated in Figure 1b.

Chemical Separation and Analysis: The traditional approach for microfluidic organic compound analysis (as used by Urey) consists of adding a derivitivization reagent in excess to the target solution. The reagent reacts with the organic compounds of interest forming a fluorescent adduct. This adduct fluoresces when excited by a laser at the appropriate wavelength. In the case of Fluorescamine, only the adduct is fluorescent. The sample is then injected into a flowing buffer solution as a spatially defined plug of liquid. As the plug flows over the channel length, different compounds flow at different rates and over distance, individual molecules are spatially separated and fluorescently detected. AstroBioNibbler uses this approach to detect trace levels of organics including amines, carboxylic acids, nucleic acids and bases as well as polycyclic aromatic hydrocarbons [2].

Anion and Cation Detection: For the analysis of anions and cations, we reverse the typical detection approach. Here, the buffer solution is fluorescent and the sample solution is injected without further reaction. The chromatic injection and flow process is carried out as before, but now, the separated presence of an anion (or cation) actually dilutes the background fluorescence of the buffer. Thus compound detection results in a loss of fluorescent intensity. This method is completely general and can be used to separate very complex ionic mixtures. In Figure 2, we give the analysis of perchlorate in the presence of nitrate, sulfate and chloride. The inset shows the separation of several different oxychloro species. These results far exceed the capability of the MECA ion specific electrode approach and enable the separation of complex oxidizing species as well as toxic inorganic materials with analysis times of several minutes.

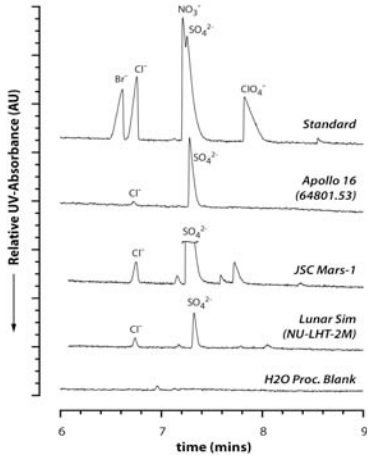

Figure 2. Indirect photometric detection (IPD) of anions in aqueous natural sample extracts using UV-detection. Bromide, chloride, nitrate, sulfate, and perchlorate are included in a standard in comparison to aqueous components of Apollo 16 Lunar regolith and Mars and Lunar Simulants. Perchlorate was undetectable in these samples above 1 ppm.

Summary and Implications: We are developing a comprehensive lightweight chemical analyzer as an end-to-end system that can capture a soil/rock sample, extract all soluble species including trace biomarkers and report concentrations without interferences. It can be a battery powered tool for Human Exploration or robotically mounted at a mass of just 3.0 kg.

References:

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[2] Stockton, A. *et al.* (2009) Astrobiology 9, 823-831.

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