MARS END-TO-END MICROFLUIDIC ANALYZER (MEEMA) FOR SOLIDS, LIQUIDS, AND GASES

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Introduction:

We propose to develop a 3kg, 2W, flight-capable microfluidic lab-on-a-chip analyzer that is capable of injesting solid, liquid, or gas samples and performing a suite of chemical analyses with parts per trillion sensitivity. For gases or liquids, the system would be capable of actively acquiring samples via a needle inlet. Solids would have to provided by an external system in powder form and dumped into a funnel atop the unit. Our technology builds upon the foundation laid by the Mars Organic Analyzer systems conceived and developed at UC Berkeley. It would extend that technology in a number of critical aspects:

1) It would be completely autonomous.
2) It would have an expanded range of chemical targets.
3) It would handle samples in multiple forms.
4) It would have a reliable means for storing reagents.
5) It would operate at Mars ambient temperatures.

Background:

Quantitative compositional analysis of the organic material in Mars could could "fingerprint" the processes that have shaped Martian organic chemisty, as abiotic processes yield a statistical distribution of racemic organics, while biotic processes homochirally enrich organic molecules useful to life [1]. However, it is expected that only trace amounts of organics would be found in the topmost layers of Martian soil due to radiative damage [2], and the Viking mission was not able to detect any organics in the Martian regolith using GC/MS technology [3] despite an organic infall rate of 10^5 kg/yr [4]. Therefore, implementing instrumentation with the highest possible sensitivity may be of utmost importance for successful detection of organic chemical signatures of past or present life on Mars.

Mars Organic Analyzer (MOA) technology [5] that is the basis for MEEMA has proven to have extremely high sensitivity (sub-pptr to ppb) to multiple organic compound classes, including amines, amino acids [6], aldehydes, ketones [7], carboxylic acids [8], and polycyclic aromatic hydrocarbons [9]. This technology, developed at UCB (MOA) and under further maturity development at JPL (MEEMA), utilizes microchip capillary electrophoresis with laser-induced fluorescence detection. Laboratory prototypes using off-the-shelf parts inherently require low power (~15W) reagents (< 100 μL/analysis) and with low mass (~11 kg) and volume (< 14,000 cm^3).

Recent Enhancements in Chemical Analysis:

Because we cannot expect Martian life to evolve to use the same organic molecules that terrestrial life uses, the capability to quantitatively analyze a broad range of organic compound classes may be essential to fingerprint life. For example, thiols are a class of organic molecules that may have been implicated in the origin of life on Earth and can provide information on the biotic or abiotic chemical processes that have shaped an extraterrestrial location. We developed a MEEMA-compatible analytical method for thiols using the fluorescent probe Pacific Blue malemide. This method yielded pptr limits of detection, and enabled the quantitative compositional analysis of dissolved thiols in samples from geothermal pools at Hot Creek Gorge, CA [10].

We have also developed a new method for the analysis of long chain amines using microchip capillary electrophoresis. This method also yields pptr senstivitity and provides baseline resolution of chains differing by only 2 carbons for chains containing 18+ carbons. For this method however, we used a non-aqueous solvent, ethanol, which enabled analyses at significantly reduced temperatures. We demonstrated analyses down to -20°C, and expect to be able to conduct analyses at much lower temperatures (<-80°C), enabling analyses at Mars ambient temperature [11].

For any analytical method that relies on chemical reagents, there is concern about storage and stability of reagents. Hence we demonstrated that we can dehydrate and rehydrate reagents on MEEMA-compatible microdevices and obtain nearly quantitative recovery (~ 98%). We additionally characterized the hydrolysis rate of the Pacific Blue fluorescent probe, and found optimal storage conditions at pH 4, enabling usage of each aliquot of this reagent for approximately 4 Martian sols [12].

Recent Developments in Instrumentation:

In MEEMA technology, microfluidic manipulation is accomplished using pneumatically actuated monolithic membrane valves. Initial microchip demonstrations were accomplished using polydimethylsiloxane (PDMS), which exhibits good elasticity and adherence to glass. However, certain properties make it unsuitable for space-flight applications, including chemical and gas permeability, and the tendency to permanently bond to the discontinuity in the fluidic layer when not actuated for long time periods (months). Therefore, we developed methods to fabricate devices with Teflon®

and Fluorocur™ perfluoropolyether (PFPE) and successfully demonstrated these membranes in multi-wafer stack fluidic manipulation devices. These fluorinated membrane based devices maintain performance after repeated thermal cycling, exhibit good chemical resistance, and enable flight-ready devices [13,14].

While initial chip designs enabled successful sample routing, the sample still had to be processed by hand before introduction to the microdevice. For Mars investigations, this is not possible. Hence we developed a microfluidic architecture that enabled automated sample labeling, serial dilutions, and autonomous analysis of fluidic laboratory standards containing amines and amino acids [15].

While the above device demonstrated fully autonomous fluidic sample processing and analysis of one compound class, a new design was required for the automated analysis of all compound classes in our chemical arsenal. To this end, we characterized device performance based on multiple factors including operational protocols and the fluidic resistance between microvalves and reservoirs [16]. We developed a set of design rules, and developed a novel, general purpose microfluidic processor based on these rules. This processor has a dense-packed network of microvalves at its core, is capable of automated analysis of all target compound classes, and can be reprogrammed in response to unexpected sample compositions.

Additionally, we have proof of concept for manipulating powdered solids on chip (Fig.1). We are developing this technology further to include liquid-based extraction of organic molecules from solid samples.

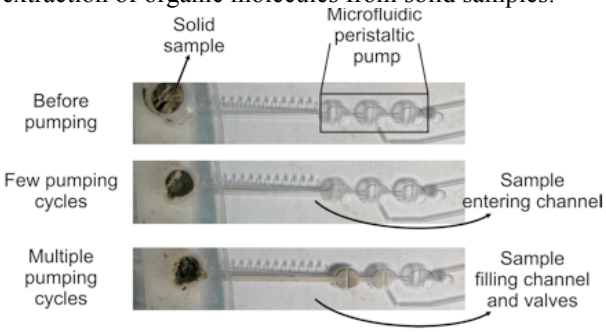

Figure 1. Photographs of on-chip transfer of powdered solid sample from a reservoir on the left using the three valves in series on the right hand side of the device. Slurries can also be manipulated on-chip.

To increase the TRL level of our chip-based technology, we sought to further miniaturize the packaging of all necessary off-chip instrumentation. To this end, we designed the "Chemical Laptop", a complete battery powered prototype that can operate our chip devices in order to perform fully automated analysis of all targeted compound classes on fluidic and solid samples. This instrument is the size and weight of a large laptop, and incorporates a touch-screen user interface to be compatible with a general user conducting astrobiological or other investigations in the field. A provisional patent is in place [17], and prototype development is underway via SBIR funding.

Proposed MEEMA Instrumentation:

We propose to repackage Chemical Laptop technology for Mars exploration. By removing the "user friendly" design constraint required for a commercial instrument, the system can be reduced to a <3 kg mass that can fit inside a 17.5 cm diameter, 9 cm tall cylinder (Fig.2) and uses a time average of ~ 0.5 W (2 W peak) power. MEEMA could take as inputs gas, liquid, or solid, and analyze with parts-per-trillion sensitivity the sample's amine, amino acid, short peptide, aldehyde, ketone, carboxylic acid, thiol, and polycyclic aromatic hydrocarbon content.

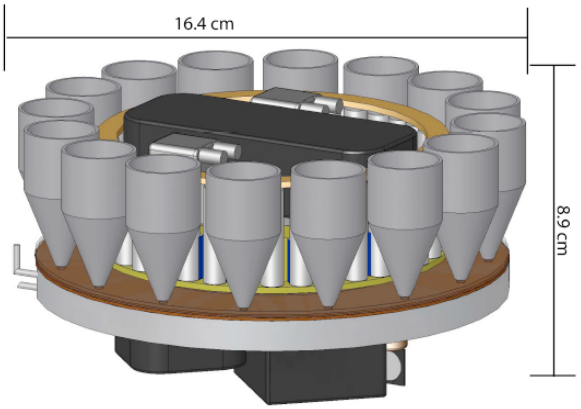

Figure 2. Design for MEEMA, a flight-build µCE instrument. Solid samples are delivered to the instrument via funnels and processed on-chip. This proposed instrument **could be built today** utilizing off-the-shelf, well-known components, utilizes a time-average of 0.5 W (2 W max) during operation, and weighs less than 3 kg.

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