IN-SITU LIQUID EXTRACTION AND ANALYSIS PLATFORM FOR MARS AND OCEAN WORLDS.

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Introduction: Mars, Europa, Enceladus and Titan are particularly auspicious worlds to search for signatures of past or present alien life in our Solar System. Here we present a compact, integrated sample extractor and analysis unit that could be used to support robotic missions seeking these chemical signatures of life on these destinations. In a first step, inorganic and putative organic compounds are automatically extracted from approximately 1 cm^3 of regolith or ice/soil mixtures by subcritical water extraction (SCWE) at 175 - 250°C and elevated pressures [1]. Following the extraction, miniaturized electrochemical probes quantify the eluate's pH, redox potential and electrical conductivity to better understand the sample (ice or soil) chemistry and mineralogy. Colorimetric measurements by flow injection analysis (FIA) in a fully integrated microfluidic manifold (MicroFIA) furthermore allow additional assessment of the soil's ionic composition [2]. Besides the evaluation of the potential for past or present biology, this system can be employed as a front-end instrument for subsequent, more sophisticated organic analyzers such as capillary electrophoresis (CE) or mass spectrometer (MS) systems, to put these down-stream measurements in context [3].

Approach: The presented sensor platform consists of two sub-systems, comprising a SCWE and a MicroFIA unit. *SCWE* uses liquid water as extraction solvent at temperatures above the atmospheric boiling point of water (273 K, 0.1 MPa), but below the critical point of water (647 K, 22.1 MPa). At elevated temperatures, the permittivity, viscosity, ionization constant and surface tension of water are decreased, whereas its diffusion rate increases, making it a powerful solvent for extraction of both polar and non-polar compounds.

The presented automated and multiplexed SCWE system (Figure 1 and 2) allows for four independent extractions. The crucibles are mounted on a rotary holder and automatically moved by a stepper motor to four positions, where: 1. the sample is ingested and filled into the extraction crucible via the sample funnel, 2. the extraction crucible is capped and hermetically sealed by a linear motor and, 3. engaged with liquid interface to inject the extraction solution. At the 4. position, the crucible is heated up to 250°C by the cell's internal heater to initiate the extraction. After concluding the extraction, the crucible engages again with the liquid interface to release the extract to the MicroFIA system for downstream compositional analysis.

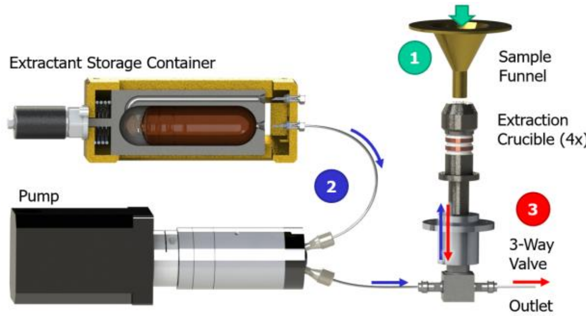

Figure 1: The solids enter one of the four extraction crucibles through the sample funnel (1). Thereafter, the crucible is hermetically sealed by a linear motor and pre-pressurized with the extractant by a high pressure pump (2). Subsequently, the temperature of the crucible is increased up to 250°C by an internal resistive heater, initiating the extraction of the compounds. The extraction is concluded by releasing the eluate via a 3-way valve (3).

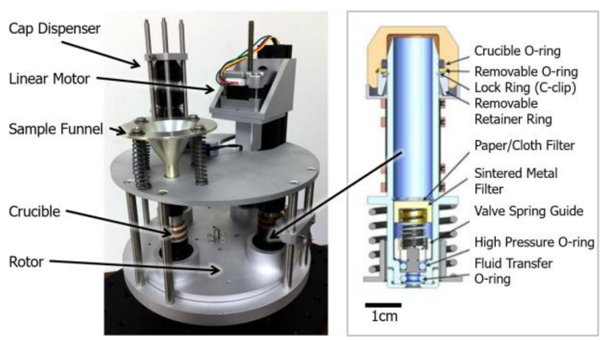

Figure 2: SCWE system (left) and cross-section of a sealed extraction crucible (right) [4].

FIA is a technique where a liquid sample is injected into a moving carrier stream. The two liquids form a reaction plug, which is transported toward a detector that continuously measures changes in e.g. absorbance and electrode potential. FIA is a powerful but simple tool to measure ion concentrations, pH, ORP and electrical conductivity of a liquid sample, such as the extract from the SCWE unit. The general concept of the presented MicroFIA platform is graphically depicted in Figures 3 and 4.

The liquid sample enters the 3D-printed MicroFIA manifold (Figure 5) and is routed via various 3-way valves. A liquid plug of reagent is injected into the carrier stream by switching one of the 3-way valves, accessing the reagent reservoir. The sample and reagent mix and react, leading to an absorbance change depending on the reagent and the concentration of the analyte of interest in the sample. These colorimetric changes and therefore the analyte concentration can be determined by a white-light LED and RGB photodiode. Custom-made, miniaturized electrochemical sensors additionally measure pH, oxidation reduction potential (ORP) and temperature of the liquid sample.

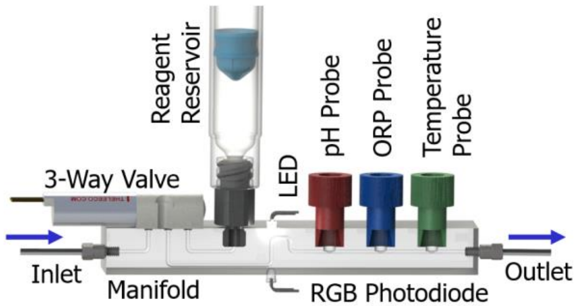

Figure 3: General MicroFIA concept: fluidic manifold, 3-way valve for liquid routing and reagent injection, colorimetric absorption cell and electrochemical sensors for in-line measurement of pH, ORP and temperature.

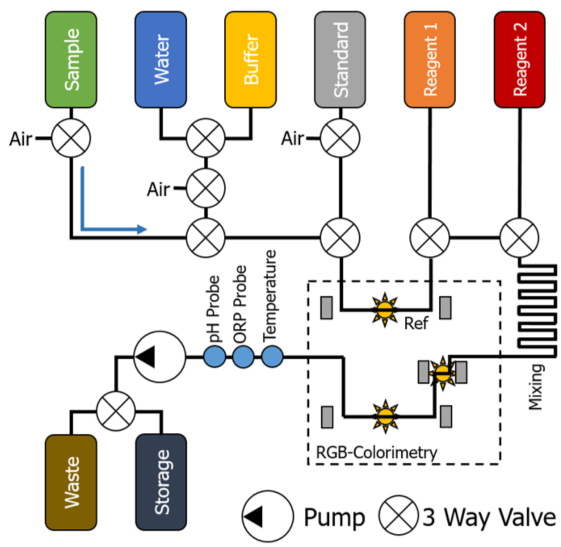

Figure 4: MicroFIA schematics: The liquid sample is pulled through the fluidic manifold by a pump mounted at the system's outlet. Controlled switching of the 3-way valves allows to inject different indicator reagents in the sample solution. Resulting color changes can be quantified in the colorimetric absorption cells.

The presented, fully automated MicroFIA system (Figure 6) allows to quantify up to six different analytes (such as, but not limited to, Mg^{2+}, PO_4^{3-}, Cu^{2+}, NH_3-N, H^+, and formaldehyde) by colorimetry, and pH and ORP by electrochemical sensors.

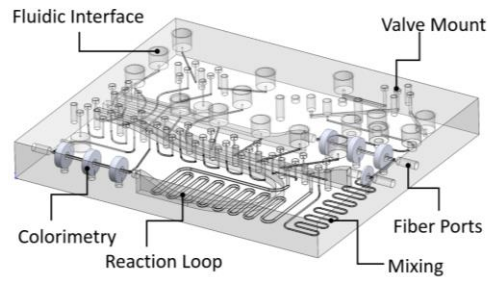

Figure 5: 3D printed MicroFIA manifold.

Outlook: After the prototype development and successful technology demonstration, extended measurement campaigns are planned to evaluate both efficiency of the extractor as well as limit of detection of the FIA system. In the near future, the two systems will be combined for an end-to-end analysis of Mars analogue samples. In 2017, a fully-integrated version will be installed on the K-Rex Rover (NASA Ames) for in-situ measurements in the Atacama Desert (Chile).

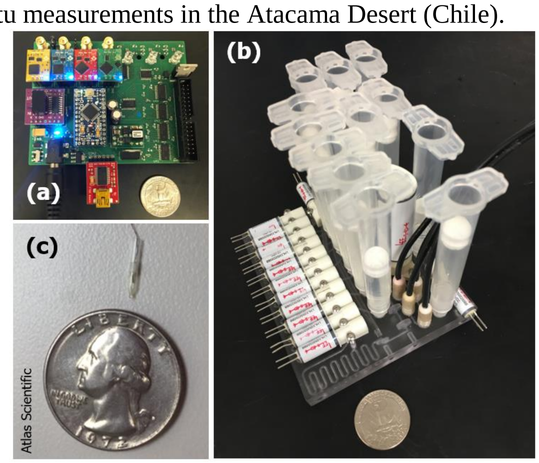

Figure 6: Photographs of (a) MicroFIA electronics, (b) assembled MicroFIA system, (c) miniature pH probe.

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