THE STATE-OF-THE-ART IN CAPILLARY ELECTROPHORESIS AND MICROCHIP ELECTROPHORESIS INSTRUMENTATION FOR OCEAN WORLDS MISSIONS SEEKING SIGNS OF LIFE

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Introduction:

A reasonable assumption in the search for life on ocean worlds is that the limit of detection required of analytical instrumentation for dissolved organics is on the order of parts-per-billion, which is similar to the concentration of organics in extreme environments such as subglacial Lake Vostok in Antarctica [1]. This limit of detection requirement is challenging to meet using traditional, high-TRL instrumentation such as gas-chromatography mass spectrometry (GC-MS), which has been demonstrated to be capable of detecting organics such as amino acids and carboxylic acids at the parts-per-million level [2]. In order to increase the sensitivity of this gas phase technique to nonvolatile organics, one needs to develop methods and instrumentation for liquid-handling pre-processing steps prior to gas-phase separations. These steps include removal of interfering water or solids from samples, and reaction of the sample with molecules that create new molecular adducts having a significant vapor pressure, that can then be vaporized and analyzed by GC-MS. This was the general approach taken by the SAM instrument on Mars, although in that case no sample processing was performed [2].

Approach:

An alternative approach to achieve these same measurement goals with simpler sample handling is to leave the sample in the liquid state for the entire analysis. This approach is particularly attractive for ocean worlds missions where samples of interest will contain water and salts which could simply be melted/filtered prior to analysis. The techniques of capillary electrophoresis (CE) or microchip electrophoresis (MCE) can be then used to separate a liquid mixture into its components [3]. These techniques work by introducing nanoliter volume "plugs" of sample into microndiameter glass channels which are then subjected to an applied electric field between the channel entrance and exit. Different species inside the plug of sample material move at different speeds under this electric field and are separated from one another as they travel the length of the capillary. At the exit of the capillary, detection is performed using methods such as capacitively coupled contactless conductivity detection

(C⁴D), laser-induced-fluorescence detection (LIF), or mass spectrometry (MS).

But despite the obvious advantages of this approach, this TRL 5 technology has yet to be included as part of a spaceflight mission. In this presentation we will continue with our critical assessment of this technology, first published in 2015 [3]. We will summarize our recent work [4] in the development of the most promising new method for direct analysis of salty aqueous samples expected on Europa and Enceladus, and show how it is possible with these new methods to greatly increase the capabilities of this technique to identify three distinct biosignatures (both chiral and achiral) in amino acid samples. We will also summarize the most recent technical advances in this area and provide a critical assessment of the overall state of the art in this exiting research and development area, and provide a framework for the future TRL 6 development necessary for implementation on upcoming astrobiology missions to ocean worlds.

References:

[1] Christner, B. C.; Royston-Bishop, G.; Foreman, C. M.; Arnold, B. R.; Tranter, M.; Welch, K. A.; Lyons, W. B.; Tsapin, A. I.; Studinger, M.; Priscu, J. C., "Limnological conditions in Subglacial Lake Vostok, Antarctica" *Limnology and Oceanography* **2006**, *51* (6), 2485-2501.

[2] Stalport, F.; Glavin, D. P.; Eigenbrode, J. L.; Bish, D.; Blake, D.; Coll, P.; Szopa, C.; Buch, A.; McAdam, A.; Dworkin, J. P.; Mahaffy, P. R., "The influence of mineralogy on recovering organic acids from Mars analogue materials using the "one-pot" derivatization experiment on the Sample Analysis at Mars (SAM) instrument suite" *Planetary and Space Science* **2012**, *67* (1), 1-13.

[3] Willis, P.; Creamer, J.; Mora, M., "Implementation of microchip electrophoresis instrumentation for future spaceflight missions" *Analytical and Bioanalytical Chemistry* **2015**, 407 (23), 6939-6963.

[4] Creamer, J. S.; Mora, M. F.; Willis, P. A., "Enhanced Resolution of Chiral Amino Acids with Capillary Electrophoresis for Biosignature Detection in Extraterrestrial Samples", *Analytical Chemistry* **2017**, 89 (2), 1329-1337.