

**CONCEPT FOR REMOTE CHEMICAL ANALYSIS OF ENCELADUS AMINO ACID CHIRALITY.** J. P. Kirby<sup>1</sup>, M. L. Cable<sup>2</sup>, S. M. Jones<sup>2</sup>, A. G. Davies<sup>2</sup> and P. A. Willis<sup>2</sup> <sup>1</sup>Planetary Science Institute (1700 E. Ft. Lowell, Suite 106, Tucson, AZ 28519, jpkirby@psi.edu), <sup>2</sup>NASA Jet Propulsion Laboratory.

**Introduction:** A concept for an astrobiology science instrument is described here in the context of a future mission to Enceladus [1]. Water jets from the south polar region of this moon form a plume and supply material to the Saturn e-ring [2, 3]. By utilizing remote chemical analysis of free amino acid chirality, the Enceladus Amino Acid Sampler (EAAS) is designed to address the fundamental astrobiology science question, “is there life outside of Earth [4]?” The EAAS instrument concept expands from the capabilities demonstrated by the Ion and Neutral Mass Spectrometer (INMS) instrument on the Cassini spacecraft [5, 6]. The INMS instrument is currently exploring Enceladus’ plume and the atmosphere of Titan with the capability to detect small amino acids, such as glycine and alanine [7]; however, INMS was not designed with the capability to determine the extent of the chirality of alanine. Remote chemical analysis with the EAAS approach employs an aerogel sampler for collecting ice dust while in flight onboard a spacecraft [8], mitigating breakdown of molecules on impact with instruments like the Cometary and Interstellar Dust Analyzer on the Stardust mission [9]. Automation of sample analysis with EAAS is envisioned as a means of expanding the discovery of the identity, inventory *and* chirality of free amino acids from a potentially habitable subsurface ocean postulated to be present on Enceladus [10, 11, 12]. Remote chemical analysis with an EAAS science instrument is compatible with either an orbiter [1] or sample return spacecraft platform [13].

**5 Science Tiers for Enceladus Exploration with EAAS:** A flow chart illustrating the science instrument concept for the operation of EAAS is shown in Figure 1. The foundation of the instrument is a mass spectrometer (MS) that supports 5 science tiers, described as follow:

*Science Tier 1: Enceladus Encounter.* A spacecraft equipped with the EAAS instrument has a rendezvous with the plume or jets of Enceladus. During the encounter the MS operates to collect data in a similar fashion to Cassini’s INMS [5, 6].

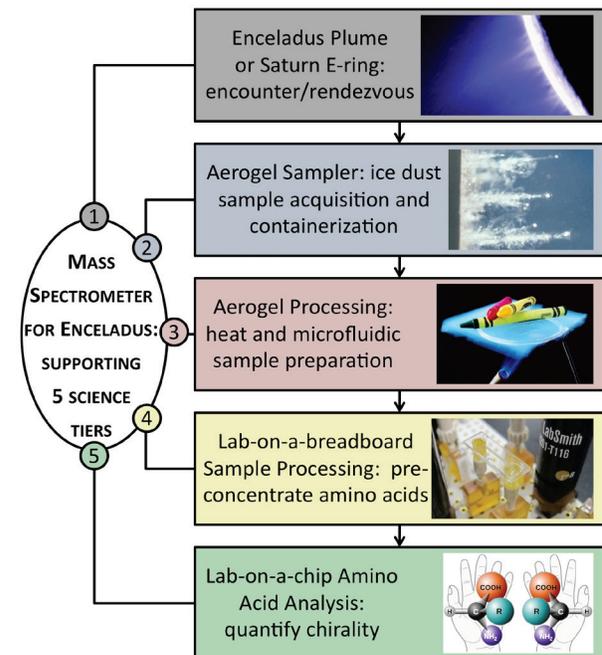
*Science Tier 2: Aerogel Sampler.* Also during the encounter, an aerogel sampler decelerates and entrains ice dust particles [13]. Volatiles liberated upon capture of the ice dust particles by the aerogel are analyzed by the MS.

*Science Tier 3: Aerogel Analysis of Captured Volatiles.* By enclosing the aerogel container after the encounter, heat can be applied, thermally desorbing

molecules from the aerogel for analysis with the MS. Additionally, a liquid or carrier gas can be introduced to the aerogel container with controlled heating to transfer a sample to the MS, or to deliver a sample from the aerogel to a lab-on-a-breadboard for further sample processing.

*Science Tier 4: Amino Acid Inventory Determination.* Sample pre-concentration is performed by a lab-on-a-breadboard subsystem amplifying the amino acid concentration by ~4 orders of magnitude or more. Pre-concentrated samples are then delivered to the MS for analysis or are delivered to a lab-on-a-chip subsystem for further processing [14].

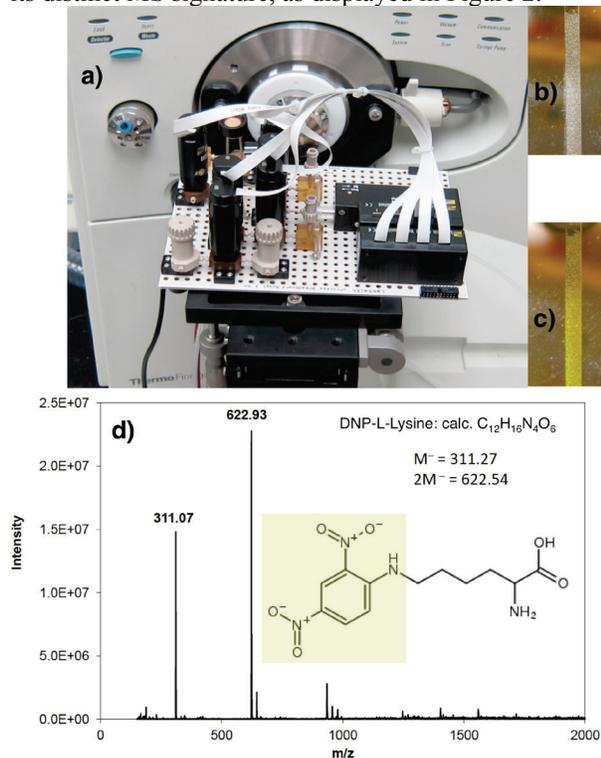
*Science Tier 5: Amino Acid Chirality Quantification.* The EAAS is an astrobiology science instrument capable of measuring amino acid chirality by utilizing lab-on-a-chip technology [15]. The identity of the chiral components of a sample at this stage of the analysis chain will also be verified using the MS.



**Figure 1.** Arrows indicate the science instrument system operational sequence. The lines leading to the MS illustrate how the core subsystem is utilized during 5 stages of EAAS instrument operation, creating 5 distinct science tiers.

**EAAS Science Instrument Automation:** Strategies developed for isolating amino acids from rare sources such as meteorites [8] and terrestrial extreme

environments [16] typically follow similar bench top procedures and protocols to isolate and quantify amino acids. The results presented here focus on the automation of sample preparation and pre-concentration, by adapting standard bench top techniques with automation for processing amino acids from environmental samples. To illustrate and monitor the timing of the various steps involved in the processes required for pre-concentration, a non-natural amino acid,  $\epsilon$ -3,4-dinitrophenyl-L-lysine (DNP-L-Lysine), is employed as a tracer molecule, due to its vibrant yellow color and its distinct MS signature, as displayed in Figure 2.



**Figure 2.** The above image **a)** displays a lab-on-a-breadboard mounted to a bench top MS to simulate a subsystem described by Science Tier 4. Highlighted are the 1-mm-wide microfluidic channels loaded with strong acid cation exchange resin beads before **b)** and after **c)** automated processing of a DNP-L-Lysine sample. Displayed in **d)** is the chemical structure, calculated and observed mass for detection by MS.

**Subsystem Prototype for EAAS Instrument.** Automation of the microfluidic pre-concentration process is facilitated by sample delivery directly into a MS for detection and characterization of individual amino acids. The EAAS design utilizes lab-on-a-breadboard components with a sample inlet, sample outlet, reagents, controllers, pumps, valves and pre-concentration column for the EAAS prototype assembled on a 5" by 7" breadboard. Scripting software is used to automate control of sample pre-concentration and delivery from

a microfluidic channel containing cation exchange resin beads for the highly selective sequestration of free amino acids from a sample in the liquid phase. The amino acids are immobilized into a resin bead located in the optically transparent channel of a microfluidic chip. This facilitates direct monitoring of the pre-concentration process or release of amino acids upon addition of a water-ammonia solution.

**Flow Cell Demonstration.** Rapid generation of scripting code allows for process automation due to its interactive real-time compiling and testing with a versatile graphical user interface. Development of the initial automation scripts allows testing of amino acid pre-concentration. The initial flow cell measurements employ water. The flow rates have been achieved as high as  $\sim 1.0$  mL/min with the assembled system displayed in Figure 2.

**Conclusions:** Initial demonstration of the EAAS concept is suitable for testing samples that simulate the conditions of Don Juan Pond, considered to be the Earth's coldest and saltiest body of liquid water, located in the Wright Valley of Antarctica [16]. This EAAS development is an important step toward a new type of astrobiology science instrument. Beyond Enceladus, this instrument architecture has broad reaching applications for solar system exploration, and represents a new instrument paradigm capable of providing unique remotes chemical analysis science data from a cruising or orbiting spacecraft.

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**References:** [1] Vision and Voyages for Planetary Science in the Decade 2013-2022 (2011) *The National Academies Press*. [2] Hansen C. J. et al. (2008) *Nature*, 456, 477-479 [3] C. J. Hansen, et al. (2006) *Science*, 311, 1422-1425. [4] Marais D. J. D. et al. (2008) *Astrobiology*, 8, 715-730. [5] Cravens T. E. et al. (2009) *Geophys. Res. Lett.*, 36. [6] Matson et al. (2007) *Icarus*, 187, 569-573. [7] Hoerst S. M. et al. (2012) *Astrobiology*, 12, 809-817. [8] Elsila J. E. et al., (2009) *Meteorit. Planet. Sci.*, 44, 1323-1330. [9] Kissel J. et al. (2004) *Science*, 304, 1774-1776. [10] Postberg F. et al. (2011) *Nature*, 474, 620-622. [11] Parkinson C. D. et al. (2008) *Origins Life Evol. B.*, 38, 355-369. [12] Nimmo, F. et al. (2007) *Nature*, 447, 289-291. [13] Tsou P. et al. (2012) *Astrobiology*, 12, 730-742. [14] Mora M. F. et al. (2012) *Electrophoresis*, 33, 2624-2638. [15] Mora M. F. et al. (2011) *Anal. Chem.*, 83, 8636-8641. [16] Cockell C. S. and Nixon S. (2013) *Astrochemistry and Astrobiology*, eds. Smith I. W. M. et al. Springer-Verlag Berlin Heidelberg, 211-241.