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# In Situ Analyses Of Tholins Using DMF-DMA Derivatization For DraMS Instrument Onboard The Future Dragonfly Mission

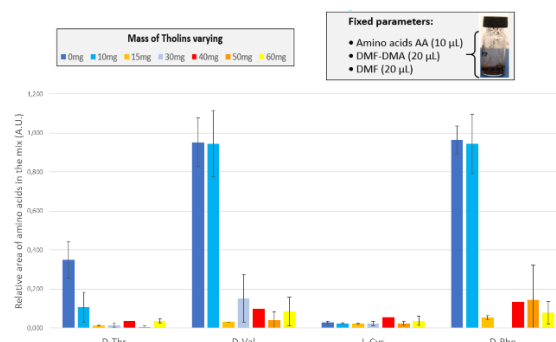
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**Introduction:** To prepare for the future mission *Dragonfly* [1,2], and the *in situ* analyses of Titan samples with the Dragonfly Mass Spectrometer (DraMS) instrument [3], laboratory sample preparation and analysis with Gas Chromatographic – Mass Spectrometry (GC-MS) has to be developed and optimized. For this astrobiologically focused mission, one of the objectives is the detection and quantification of heavy and complex organics relevant for prebiotic chemistry [2]. For instance, amino acids are one of the targets as they constitute proteins necessary for life [4]. One of the reagents that is carried within DraMS, called dimethylformamide dimethyl acetal (DMF-DMA), will help to volatilize refractory and polar organic molecules in order to be analyzed by GC-MS [5,6]. To prepare the derivatization experiment, we have investigated the analysis of Titan analogs [4,7,8] and the efficiency of the DMF-DMA reagent to derivatize low volatility organics under DraMS-like conditions. DMF-DMA will also be used to preserve the chiral conformation of derivatized organics [5] – separated on a chiral column – to enable the detection of an enantiomeric excess. Enantiomeric excess of amino acids, for example, represents a potential biosignature if found on the surface of Titan [9].

**Ex situ derivatization:** To optimize for the DraMS *in situ* derivatization on Titan organics, we applied a DMF-DMA pre-treatment on both a standard solutions of amino acids and a mixture of amino acids with analogs of Titan aerosols (tholins) to optimize the volume of reagent as a function of the mass of tholins. The efficiency of DMF-DMA derivatization of organic molecules was tested in a concentration range from trace to high abundance in the initial sample with *ex situ* experiments. The preliminary results show good efficiency in derivatizing most of the studied amino acids and tholin organic molecules (both alone and as a mix). This chemical process produces organics with moderate (*e.g.* Threonine, Cysteine), or high (*e.g.* Phenylalanine, Valine) mass spectrometer sensitivity. Thus, all derivatized trace abundances of astrobiologically relevant molecules, such as amino

acids, were detected and quantified in a 120mg sample using only 40 $\mu$ L of DMF-DMA (see Figure 1) – presenting a final ratio of 3:1 for the mass of tholins (or sample) to the DMF-DMA reagent volume.



**Figure 1:** Relative area of detected amino acids derivatized in presence of 0 to 60mg of tholins (derivatized too).

**In situ derivatization:** To optimize this ratio and test the DMF-DMA pre-treatment in DraMS conditions, the studies are repeated using the *in situ* derivatization process. The corresponding results and the comparison of the *ex situ* and *in situ* derivatization will be presented with a focus on the method and results of this last DraMS-like GC-MS analyses. This comparison and the *in situ* experiments will guide the determination of DraMS instrument requirements such as the mass of sample that DrACO should deliver to DraMS, and the reagent volume to be stocked in capsules to sufficiently derivatize all trace molecules of astrobiological interest that may be present on sampled surfaces.

**References:** [1] Barnes, J.W. et al. (2021) Planet. Sci. J. 2, 130. [2] Lorenz, D. (2021) Planet. Sci. J. 2, 24. [3] Grubisic, A. et al. (2021) Int. J. Mass Spectrom. 470, 116707. [4] Brassé, C. et al. (2017) Astrobiology 17, 8–26. [5] Freissinet, C. et al. (2010) J. Chromatogr. A 1217, 731–740. [6] Goesmann, F. et al. (2014) Planet. Space Sci. 103, 318–330. [7] Neish, C.D. et al. (2010) Astrobiology 10, 337–347. [8] Poch, O. et al. (2012) Planet. Space Sci. 61. [9] Neveu, M. et al (2018) Astrobiology 11, 1375-14.