

LIQUID CHROMATOGRAPHY ORBITRAP MASS SPECTROMETRY STUDY OF SYNTHETIC AND CHONDRITIC ORGANIC MIXTURES.

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Introduction: Meteorites show a high level of complexity of their organic matter content[1]. To try to understand its origin, an experimental approach consists in conducting laboratory synthesis experiments in well-constrained environments and compare the products with natural samples. Any feature of the final mixture shared with an extraterrestrial material will designate its synthesis conditions to be comparable to those at the origin of the extraterrestrial sample.

We postulate that the molecular complexity is a good indicator at the whole sample level. We highlight a method that uses the stoichiometry and functional complexity of the samples to propose an origin for natural samples. Liquid chromatography coupled to Orbitrap mass spectrometry is a technique of choice to describe both stoichiometries - thanks to the high mass resolution - and functionality - thanks to the time separation due to chemical interactions[2-3].

Methods: We evaluate here the differences between molecules produced in the laboratory by plasma irradiation in the gas phase[4,5] and those present in the carbonaceous chondrite soluble organic matter extracts[6]. The gas phase experiments aim at reproducing the protosolar nebula environment that is supposed to be at the origin of the extraterrestrial organic matter. A starting material of around 1mg is enough to perform all the described analyses.

The proposed analysis workflow is based on two analytical instruments and a home-made data-treatment software. A direct infusion (without chromatographic separation) measurement with an ESI-LTQ-Orbitrap™ mass spectrometer (Thermo Scientific) is performed to obtain mass spectra of the samples in both positive and negative mode, from m/z 50 to 300u and from 150 to 500u. The double polarity acquisition mitigates an ESI-Orbitrap bias that would discriminate some acido-basic functions in one mode over the other.

Along with the direct infusion, samples are analyzed by HPLC with Orbitrap™ detection (m/z from 50 to 350) with a ZIC-pHILIC column (Merck Millipore) where the retention is based on a hybrid behavior with both hydrophilic partitioning, ionic and hydrogen bonding interaction. The elution gradient is adapted from a metabolomic method[7] and consists in an acetonitrile/carbonate buffer (20mmol/L, pH 9.2) starting from 80/20 (%vol) to 60/40 in 10 minutes, followed by a plateau during 30 minutes, and then washing and equilibration of the column for a total run of 80 minutes. The home-made HPLC data-analysis starts from raw data of mass vs. time and generates an 'Ion Map' that is a 2D representation of mass vs. time with intensity color code. This allows us to do peak isolations and mathematical modelisations to extract for each chromatographic peak a couple of mass and retention time. This couple of values can then be attributed and compared to standard compounds or even predicted retention times[7].

Results: In direct infusion mass spectrometry, meteorites and analogues show a large amount of CHNO-bearing molecules, with a specific distribution based on carbon chain families[8]. Even if these samples present some differences, the stoichiometry only cannot discriminate them. The chromatographic analysis reveals that analogue samples present some mass and time correlation whereas extraterrestrial samples do not present this correlation. This indicates that the molecules' polarity inside extraterrestrial samples presents an homogeneous distribution compared to the discrete and separable polarity distribution that can be seen in synthetic samples.

References: [1] Schmitt-Kopplin P, et al. (2010) *Proceedings of the National Academy of Sciences* 107(7):2763–2768. [2] Yamashita Y, Naraoka H (2014) *Geochemical journal* 48(6):519–525. [3] Naraoka H, et al. (2017). *ACS Earth and Space Chemistry* 1(9):540–550. [4] Bekaert DV, et al. (2018) *The Astrophysical Journal* 859(2):142. [5] Hörst SM, et al. (2018) *Nature Astronomy* 2(4):303–306. [6] Orthous-Daunay F-R, et al. (2019) *Geochemical Journal* 53(1):21–32. [7] Creek DJ, et al. (2011) *Analytical Chemistry* 83(22):8703–8710. [8] Orthous-Daunay F-R, et al. (2019). this conference