EPSC Abstracts
Vol. 13, EPSC-DPS2019-1520-1, 2019
EPSC-DPS Joint Meeting 2019

EPSC
EPSC-DPS Joint Meeting 2019
15–20 September 2019 | Geneva, Switzerland

Direct Laser Desorption of Amino Acids using LIMS

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Abstract

Laser desorption studies of amino acids are presented using a miniature time-of-flight mass spectrometer designed for in situ operations on planetary surfaces. A variety of amino acids were investigated, ranging from Glycine to Tyrosine, at different concentrations down to the sub-µM level. The measurements conducted allowed the mass spectrometric identification of specific amino acids signatures that do not show isobaric interferences with signatures of other amino acids. The latter is of high importance in case a mixture of amino acids is investigated. The demonstrated figures of merit will be of high importance for future space exploration missions devoted to the detection of life, past or present, on planetary surfaces.

1. Introduction

In situ detection of life, past or present, on planetary surfaces other than Earth is extremely challenging. A positive detection depends on a number of parameters, ranging from appropriate field site selection for material sampling, to the operation of sensitive instrumentation that allows the identification of the biosignature, if present. Various biosignatures exist and most of them can be identified at the micrometre level. Biomolecules such as amino acids, lipids, hydrocarbons are prominent biomarkers, and under certain environmental conditions, they can survive billions of years. For future exploration missions novel and sensitive measurement strategies providing the chemical fingerprint with high spatial resolution are of interest. In this contribution, we present the direct and sensitive detection of amino acids with concentrations down to the sub-µM level.

2. Experimental

2.1 Sample Preparation

Amino acid solutions of Gly, Ala, Ser, Glu, Meth, His, and Tyr of different concentrations (100 µM down to nM), and solutions containing a mixture of them, were prepared and drop casted (1 µl) at atmospheric condition and at room temperature into shallow cavities (0.2 mm x Ø 3 mm) on sample holders made out of stainless steel. Before introducing the sample holder into the instrument, the water was removed by evaporation at the air, giving a dry biofilm on the sample holder surface.

2.2 LIMS Measurements

The system used for the laser desorption studies consists of a compact time-of-flight mass analyser (160 mm x Ø 60 mm) connected to a nanosecond pulsed laser system (pulse width ~3 ns, wavelength λ = 266 nm, pulse repetition rate = 20 Hz) [1-4]. The principles of operation [1] and figures of merit are discussed in earlier publications [e.g., 2-4]. In the following, only a short description is given.

The mass analyser is installed within a small vacuum chamber (operating at the mid 10^{-8} mbar level). The laser system is operated outside the vacuum chamber and an optical system is used for beam delivery towards the mass analyser. Laser pulses are focussed through the mass analyser towards the sample surface. In this study, the sample is positioned outside the laser focus, which allows a gentle laser desorption of the analyte (laser spot size ≥ 20 µm). Each laser pulse induces laser desorption and ionisation. Only positively charged species can enter the ion optical system of the mass analyser. The ions are first accelerated, confined and focussed towards the field free drift path, and at the ion mirror, they are subsequently reflected backwards to the detector system, by passing a second time the field free drift tube. The ions arrive in time sequences at the detector system (time-of-flight measurement principle), and a quadratic equation is used for the conversion of the time-of-flight spectra to mass spectra.

For the laser desorption studies, measurement campaigns for each amino acid at various laser pulse energies were conducted (laser fluence campaigns). To investigate the limit of detection of each amino acid a series of different concentration was measured at optimal instrumental parameters. In each campaign, the biofilms were sampled spot-wise by applying up to 100 laser shots per position before moving to the next biofilm position (up to 40 positions).

3. Results and Discussion

Laser fluence measurement campaigns on each single amino acid allowed the identification of amino acid specific signatures. Within the investigated amino acids, no isobaric interferences were detected which is of high importance for the analysis of amino acids mixtures. In Figure 1 unique features of the amino acids Tyr, His, Glu and Ala are shown. In case of Ala the parent peak could be detected.

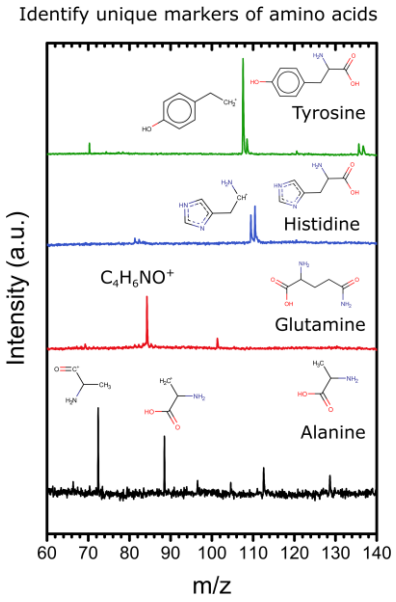

Figure 1: Laser desorption studies of singly drop casted amino acids.

At optimal instrument settings, which concerns mainly the applied pulse energy, the preliminary analysis reveals limits of detection (LOD) down to the sub-µM level. Currently, the LOD is limited by interfering mass peaks coming from the substrate, which can be minimised by e.g., the application of another substrate, cleaner bulk sample holder material, among others. In this contribution, the LOD of various amino acids will be discussed in detail.

4. Summary and Conclusions

Laser desorption studies with our miniature LIMS system were conducted on various amino acids that matter to life. The measurements allowed the identification of unique amino acid biomarkers. No isobaric interferences of these biomarkers were observed, which is fundamental for the analysis of amino acids mixtures. Furthermore, these unique biomarkers are traceable down to the sub-µM concentration, which was not limited by the amino acid concentration, but rather to the background residuals on the sample substrate. This study is of significant importance for future space exploration missions devoted to the detection of life, if present.

Acknowledgements

AR acknowledges the support from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska- Curie grant agreement No. 750353. PW acknowledge the support by the Swiss National Science foundation (SNSF).

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