Characterization of marine surface microlayer by ATR-FTIR spectroscopy, free amino acids analysis and chemometrics

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The surface microlayer (SML) of the ocean, a rather understudied system, represents the boundary layer between the atmosphere and the ocean surface body, having a typical thickness of tens to hundreds of μm [1]. It consists of a large variety of substances such as polysaccharides, transparent exopolymer particles (TEPs), polypeptides, lipid-like material, carbohydrates and amino acids, bacterioneuston and phytoneuston [2].

Coastal marine surface microlayer (SML) samples were collected from two sampling sites at Elefsis Gulf, during two different sampling periods (summer, winter). In order to calculate any potential enrichment of the SML in the parameters studied, paired samples of sub-surface water (SSW) at a depth of ~50 cm and 2 m below the sea surface were also obtained. SML samples were obtained with the glass plate of Harvey and Burzell [3], providing a thickness of 50 μm.

Samples were filtered using glass fiber (GF) filters. The infrared absorption spectra of filters were obtained by Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy by a Perkin Elmer Spectrum-Two spectrometer equipped with a Diamond ATR compartment. The free amino acids profiling of samples was conducted with the EZ:faastaminoacid derivatization technique for GC-MS (Phenomenex®, Torrance, CA, USA)

IR absorption spectra were significantly different between SML and SSW samples, as also demonstrated in the Principal Component Analysis (PCA) analysis carried out, which showed a complete discrimination between SML and SSW as well as between winter and summer samples. Eighteen free amino acids were determined, with glutamine (Glu) and glutamic acid (Gln) enrichment factors (EFs) being significantly higher than unity. Analysis data employing ATR-FTIR are for the first time reported in SML samples, since to the best of the authors' knowledge, no pertinent data are available in literature.

References:
1. Z. Zhang, L. Liu, C. Liu, W. Cai, *J. Colloid Interface Sci.* **264,** 148 (2003)
2. S. Karavoltsos, E. Kalambokis, A. Sakellari, M. Plavsic, E. Dotsika, P. Karalis, L. Leondiadis, M. Dassenakis, M. Scoullos, *Mar Chem* **173**, 234 (2015)
3. G. W. Harvey, L. A. Burzell, *Limnol. Oceanogr.* **17**, 156 (1972)