

SEA SURFACE MICROLAYER: FRACTIONATION AND ANALYSIS

S. Frka Milosavljević¹*, C. Guigue², M. Goutx², Z. Kozarac¹, B. Cosovic¹, B. Gasparovic¹

¹ Division for Marine and Environmental Research, Ruder Boskovic Institute, Bijenicka c. 54, 10002 Zagreb, Croatia - frka@rudjer.irb.hr

² Laboratoire Microbiologie, Géochimie & Ecologie Marines, CNRS-UMR 6117, Université de la Méditerranée, Marseille, France

Abstract

The sea surface microlayer (SSM) as a key interface for exchange of gases, material and energy between the ocean and the atmosphere, consists of a wide variety of organic chemical substances. The SSM was studied as *ex-situ* reconstructed films after previous extraction by different organic solvents using phase sensitive ac. voltammetry, which offers a direct analytical possibility to investigate physicochemical characteristics and interactions in natural films. The electrochemical results will be compared with Iatroscan (TLC/FID) analysis of microlayer lipid material.

Keywords : Interfaces, Surfactants, Electrochemistry, Organic Matter, Chemical Analysis.

The sea surface microlayer (SSM) is a thin layer between the ocean and the atmosphere with special physical, chemical and biological properties that either affects or is affected by global climate change. Actually, it hosts the main exchange processes of organic and inorganic matter, gases, water vapour, heat and energy between those two departments. Moreover, some other boundary processes develop in this thin layer including the transformation of dissolved organic material into a dispersed state, the transformation of compounds from low- to high- molecular and photochemical transformation. The SSM is also known to concentrate many chemical substances that originate from both the air and seawater, with particular preference to those that are surface active and show particularly strong interfacial affinity. The environmental significance of surface microlayer is widely accepted, although there are still many gaps in our understanding of the morphology and chemical composition affecting the mechanisms of exchange processes.

During the three-year period, the SSM has been sampled in different marine environments in different seasons and weather conditions. Due to the fact that the SSM is complex mixture of organics as polysaccharides, proteins, lipids and their products of condensation and degradation, fractionation of microlayer material was performed by extraction using organic solvents of different polarities (n-hexane and dichloromethane). The extracts were evaporated to dryness in a rotary evaporator and dissolved again in preparatory solvent.

The capacitance of different *ex-situ* reconstructed films was estimated by a.c. voltammetry (*out-of-phase* signal) after transferring organic extracts of natural microlayers spread onto electrolyte from the air-water interface to the mercury surface by vertical dipping the electrode through the film (1). The capacity minimum values as well as the shape of capacitance curves and the position of desorption peaks of different films will be compared with those of model surfactants and their mixtures relevant for natural samples. The method will also offer a direct analytical possibility to investigate the structure, morphology and interactions in natural films, analysing the effect of potential organic pollutants such as polycyclic aromatic hydrocarbons present as solutes in the aqueous phase.

Additional characterization of the structure of natural films was carried out by ac. voltammetry (*in-phase* signal) using an electrochemical probe. The cathodic process of cadmium, as potential pollutant in natural waters, was chosen as an indicator of the permeability of adsorbed microlayers at the mercury electrode. The influence of transferred *ex-situ* microlayers on the reduction of cadmium was followed through the change of the peak current (I) relating to peak current (I₀) of pure cadmium. Fractionation of original SSM by extraction using solvents of different polarity enabled the selection of specific material which adsorbed to the mercury surface have different effects on the electrode process of cadmium.

The highest inhibition was noticed for almost all dichloromethane films.

Further, by using the Iatroscan, which combines thin layer chromatography (TLC) and flame ionisation detector (FID) technique, it would be possible to separate and quantify classes of lipids present in the SSM (2). Each lipid class will be identified and quantified against authentic standards. Although lipids are not the most abundant group of compounds in SSM, the study of these compounds is extremely important, since due to their reactivity they are essential in the processes of formation and stabi-

lization of the microlayers. The Iatroscan results would be compared with electrochemical responses of different *ex-situ* films and would add a new dimension to physicochemical characterization of natural surface films.

References

- 1 - Kozarac Z., Čosović B., Frka S., Moebius D., Hacke S., 2003. Complex methodological approach to the studies of natural microlayers at the air/water interface. *Colloids and Surfaces A: Physicochemical and engineering aspects*, 219: 173-186.
- 2 - Parrish C. C., 1998. Determination of total lipid, lipid classes, and fatty acids in aquatic samples In: Arts M.T., Wainman B.C., (ed.), *Lipids in freshwater ecosystems*. Springer-Verlag, New York, pp 4-20.