

APPLICATION OF SOLID-PHASE MICROEXTRACTION TO THE STUDY OF INTERACTIONS BETWEEN DISSOLVED ORGANIC MATTER AND ORGANIC CONTAMINANTS IN AQUATIC ENVIRONMENT

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Dissolved organic matter (DOM) in aquatic environments is a complex mixture containing only 20% of simple molecules and 80% of macromolecules difficult to characterize. Nevertheless, DOM is well known to play an important role in the fate of inorganic and organic pollutants. Indeed, DOM should bind these compounds modifying their distribution in aquatic environment, but also their bioavailability, biodegradation and subsequently their toxicity towards aquatic organisms (Haitzer *et al.*, 1998). Interactions between DOM and organic compounds depend on many factors such as DOM and contaminant characteristics (composition of DOM, size of molecules, polarity...) and physico-chemical parameters of the solution (pH, ionic strength...) (Akkanen and Kukkonen, 2003). In order to calculate the partitioning coefficient (K_{DOC}) of each pollutant to DOM, quantified by the dissolved organic carbon (DOC) content, it is necessary to analyse the free pollutant fraction separately from the DOM bound one. Few analytical techniques allow the measurement of only free compounds concentration: fluorescence quenching, solid-phase microextraction, equilibrium dialysis... Taking into account the variability of contaminants and DOM which can occur in the environment and the fact that most of the available techniques could modify the interactions during the analysis, the study of these interactions is a real challenge.

The goal of this study was therefore to develop a reliable technique that permits to quantify rapidly total and free organic pollutant concentrations: solid-phase microextraction coupled to gas chromatography-mass spectrometry (SPME-GC-MS) (Pörschmann *et al.*, 1998). Indeed, SPME fibre is introduced into the sample and only free pollutants are extracted according to their affinity with the fibre coating. After that, fibre is desorbed in the GC injector. A group of four Polycyclic Aromatic Hydrocarbons (PAH) (phenanthrene, fluoranthene, chrysene, benzo[a]pyrene) has been chosen for their different $\log K_{\text{OW}}$ (from 4.6 to 6.0) in order to model the behaviour of hydrophobic pollutants. During the development, Aldrich humic acid was used as DOM model. A series of tests was performed to optimize SPME parameters for the analysis of PAH (fibre coating, extraction time, injection system, desorption time...). After that, humic acid was added to calculate K_{DOC} values.

Preliminary results show that fibre coating such as polydimethylsiloxane (PDMS) seems to provide the best efficiency with a time of analysis of only one hour, low limits of detection (lower than 5 ng/L) and quite good reproducibilities (RSD lower than 25% but improved with the use of internal standards to 5%). K_{DOC} values calculated by SPME are in the range of the ones found in the literature (Akkanen and Kukkonen, 2003). Furthermore, a good linearity is observed between $\log K_{\text{DOC}}$ calculated by SPME and $\log K_{\text{OW}}$ of PAH, indicating the dominance of hydrophobic interactions between Aldrich humic acid and PAH (Pörschmann *et al.*, 1998). Thus, SPME seems to be a good tool to study the interactions between organic pollutants and DOM in complex aquatic environments.

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