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Determination of alcohol sulfates and alcohol ethoxysulfates in marine and river sediments using liquid chromatography–tandem mass spectrometry



C. Fernández-Ramos, O. Ballesteros, R. Blanc*, A. Zafra-Gómez, F.J. Camino-Sánchez, A. Navalón, J.L. Vilchez

Research Group of Analytical Chemistry and Life Sciences, Department of Analytical Chemistry, University of Granada, Campus of Fuentenueva, E-18071 Granada, Spain

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ABSTRACT

A novel and successful method has been developed for the identification and quantification of alcohol sulfates (AS) homologues and alcohol ethoxysulfates (AES) ethoxymers in marine and river sediment samples. The method involves the extraction of 5.00 g of dry sample with methanol using pressurized liquid extraction (PLE) and liquid chromatography–tandem mass spectrometry (LC–MS/MS). 2-Octylbenzene sulfonic acid sodium salt (2OC₈-LAS) was used as internal standard. The analytical methods were applied to marine sediments collected from the coast of Almeria (South-east Spain) and river sediments collected from the Monachil river (Granada, South-east Spain). For AS homologues, the found limits of detection were 0.04–0.08 $\mu\text{g g}^{-1}$ for marine and river sediments. For AES ethoxymers, the found limits of detection were 0.03–0.09 $\mu\text{g g}^{-1}$ and 0.06–0.22 $\mu\text{g g}^{-1}$ for marine and river sediments, respectively. The highest concentrations of AS and AES were found in river sediment samples. Significant differences were also observed between the behavior of short-chain compounds (C₁₂) and long-chain compounds (C₁₄ to C₁₈). The influence of the physic-chemical properties of water on the occurrence of these compounds was also evaluated, and differences between long- and short-chain compounds were also observed. Additionally, principal components analyses were carried out in order to study the relationship between variables and to evaluate the sources of data variability and behavior patterns. Finally, important conclusions were drawn regarding the environmental behavior of AS and AES.

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1. Introduction

Surfactants are active ingredients in detergent formulations, cleaning and personal care products, emulsifiers, pesticides, adjuvants and wetting agents. These compounds are produced and consumed in large quantities. In 2010, total consumption (not including soaps) in Europe was 2.94 million tons [1]. Two of the most abundant anionic surfactants, especially in household detergents and surface cleaners, are alcohol sulfates (AS) and alcohol ethoxysulfates (AES). These products are high production volume (HPV) chemicals, and as a result many of these chemicals are ultimately released into the environment (at ng L^{-1} to $\mu\text{g L}^{-1}$ levels) [2].

Over the last few years, due to the increasing public concern over environmental safety, laws regarding the use of these compounds have become stricter because of their potential to

produce adverse effects on ecosystems and the wildlife that live in them [3]. Coastal ecosystems are the receptors of large amounts of surfactants from urban wastewaters that are discharged, either treated or untreated, directly into the sea or estuary, or indirectly via rivers or groundwater [4]. Surfactants are chemicals that typically contain hydrophobic and hydrophilic groups. The hydrophobic domain is usually a hydrocarbon whereas the hydrophilic group can be non-ionic, positively or negatively charged, or amphoteric. These characteristics give them specific physical and chemical properties. Because of the low solubility and great ability to associate with particles, surfactants are always present in sediments. Marine sediments act both as reservoirs and as potential sources of these chemicals and can adversely affect sediment-dwelling organisms by causing direct toxicity or altering benthic invertebrate community structure [5,6]. In addition, the aqueous ionic composition also influences the sorption of ionizable organic contaminants, since processes such as ion exchange or ion pair formation are directly influenced by the composition of the medium [7,8]. Consequently, the sorption of these pollutants is different in fresh and sea water. In general, sorption coefficients of

* Corresponding author. Tel.: +34 958 240799; fax: +34 958 243328.
E-mail address: mrbanc@ugr.es (R. Blanc).

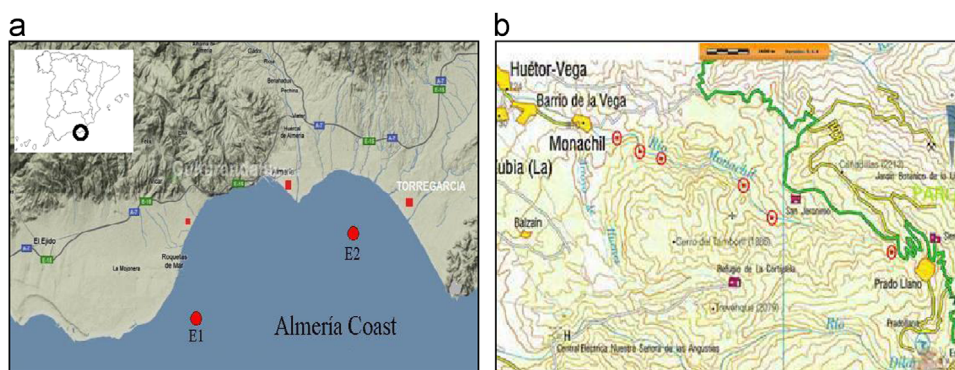


Fig. 1. Maps with sampling sites in (a) the coast of Almeria and (b) the Monachil river.

contaminants in marine environment are higher than in fresh water media [9]. Some of these contaminants are persistent in the environment, and the cumulative effects in coastal environments are expected to be considerable.

Some studies have been conducted to understand the distribution of major anionic surfactants in marine environments [10–14]; however, there are few papers on the determination of AS and AES in river [15] and marine sediments [16]. The main reason for this is the limitations of existing analytical techniques available over the last decade. The analysis of these compounds is complicated due to their structure, the complexity of the matrices and also because these compounds are generally found in very low concentrations. Therefore, it is necessary to develop new analytical methods to improve the isolation and extraction of these compounds. Different methods for the determination of AS and AES in environmental samples have been published in the scientific literature [2, 15–25]. For example, our research group has recently proposed a new procedure for the determination of AS in wastewater samples. The method includes an SPE procedure prior to a hydrolysis-derivatization procedure in one single step to directly convert AS into trimethylsilyl derivatives [18]. On the other hand, the lack of UV absorbance of AS and AES is one of the main problems when trying to detect these compounds using high-performance liquid chromatography with ultraviolet (HPLC-UV) or fluorescence detection (HPLC-FD). To overcome this problem, a derivatization reaction is required. These techniques could be an alternative to the determination of these surfactants in environmental matrices when LC-MS is not available. Beneito-Cambra et al. [19] proposed a method for the determination of fatty alcohol ethoxylates (FAE) and alkylether sulfates (AES) in industrial samples and seawater, where these compounds were extracted using a strong anionic exchanger (SAX), and esterification for FAE and transesterification of AES with a cyclic anhydride was performed. Finally, the separation of the derivatized ethoxymers was achieved using reversed phase (RP), RP-HPLC-UV and mass spectrometry (MS) detection. However, in the last decade, the use of liquid chromatography with mass spectrometry detection (LC-MS) or with tandem mass spectrometry (LC-MS/MS) has become the most powerful tool for surfactant analysis in environmental samples due to its specificity and unequivocal identification of compounds, even allowing their simultaneous determination [2, 15, 16, 19–25].

The aim of the present work was to develop and validate accurate and sensitive analytical methods for the determination of AS homologues and AES ethoxymers in marine and river sediments based on a pressurized liquid extraction (PLE) procedure, followed by a liquid chromatography–tandem mass spectrometric (LC-MS/MS) analysis. After validation, the methods were successfully applied to the analysis of sediment samples collected from the two major wastewater outfalls (at the points of discharge into

the Mediterranean Sea) of the coast of Almeria, and from the Monachil river (fed by Sierra Nevada, a mountain range in the province of Granada, Spain). Next, a monitoring and a statistical study, based on the correlation and multivariable analysis, for both AS and AES, were developed to compare the behavior of the compounds in these environmental compartments.

2. Experimental

2.1. Chemicals and reagents

All reagents were of analytical grade unless otherwise specified. Individual standard of sodium dodecyl sulfate (AS-C₁₂) (purity 99%) was supplied by Fluka (Madrid, Spain). Sodium 1-tetradecyl sulfate (AS-C₁₄), sodium *n*-hexadecyl sulfate (AS-C₁₆) and sodium *n*-octadecyl sulfate (AS-C₁₈) (purity 95–99%) were supplied by Alfa Aesar (Barcelona, Spain). The commercial mixture of AES (COSMACOL AES 70-2-24) was supplied by Sasol Italy S.p.A. (Milan, Italy) as an aqueous solution of the sodium salt with an AES (AES-C_nE_x content of 70.0% (w/w) with the following homologue distribution: AES-C₁₂ (55.0%) and AES-C₁₄ (45.0%) and an average numbers of ethoxylated units (EO) of 2.0. The internal standard, 2-octylbenzene sulfonic acid sodium salt (2OC₈-LAS; 81%, w/w) was supplied by Cepsa Química S.A. (Madrid, Spain). Stock solutions of AS and AES (100 µg mL⁻¹) were prepared in methanol. The solutions were stored at 4 °C in the dark, remaining stable for at least six months. Working standards were prepared immediately before use by dilution in methanol. Methanol and acetonitrile (both HPLC-grade) used as mobile phase were supplied by Merck (Darmstadt, Germany). LC-MS grade water, triethylamine, acetic acid and formaldehyde were supplied by Sigma-Aldrich (Madrid, Spain). Methanol (PAI grade) used in the extraction and clean up were supplied by Panreac (Barcelona, Spain). Water (18.2 MΩ cm) was purified with a Milli-Q plus system (Millipore, Bedford, MA, USA). Prior to injection into the LC system, the samples were filtered through regenerated non-sterile cellulose filters (pore size, 0.20 µm, and 4 mm in diameter) supplied by Sartorius (Goettingen, Germany).

2.2. Instrumentation and software

Pressurized liquid extraction (PLE) was made using a model 200 accelerated solvent extractor (ASE) from Dionex (Dionex Corp, Sunnyvale, CA, USA). A centrifuge, model Universal 32, from Hettich (Tuttligen, Germany) was used to separate solid and liquid phases. Analyses were performed using an Agilent 1200 series (Agilent Technologies Inc., Palo Alto, CA, USA) high-performance liquid chromatography system equipped with a binary pump, a vacuum membrane degasser, a thermostated

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