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Analysis of alcohol polyethoxylates and polyethylene glycols in marine sediments

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ABSTRACT

Alcohol polyethoxylates (AEOs) are the most commercially important type of nonionic surfactants, used in a wide variety of products such as household cleaning detergents, industrial cleaners, textiles, adjuvants in pesticides, wetting and dispersing agents, and emulsifiers. Our main objective in this work was to develop a methodology for the extraction, isolation and analysis of these compounds and their main degradation products and precursors (polyethylene glycols, PEGs) in solid environmental matrices. First, analytes were extracted by pressurized liquid extraction (PLE) using methanol at 120 °C as solvent and 3 cycles (5 min per cycle). Clean-up and concentration of the extracts were carried out by solid-phase extraction (SPE), using Oasis HLB cartridges and a mixture dicloromethane/methanol 1:1 as eluting solvent. Recovery percentages were usually between 54% and 106% for most compounds. Identification and quantification of analytes were performed using a liquid chromatography–mass spectrometry (LC–MS) system equipped with an electrospray interface (ESI) operating in positive ionization mode. Water content, cone voltage and adduct formation were optimized to this end. Limits of detection were usually below 50 ng g^{-1}, being higher for some shorter ethoxymers (>100 ng g^{-1}) because of poor ionization. Finally, the protocol proposed here was applied to the determination of the concentration of AEOs and PEGs in selected surface sediment samples collected in Mar Menor Lagoon (Murcia, Spain). In this sense, this paper presents some of the first data relative to the occurrence of these analytes in coastal sediments, showing relatively high concentrations of PEGs (up to 9000 ng g^{-1}) compared to those measured for AEOs (<100 ng g^{-1}).

1. Introduction

Nowadays, alcohol polyethoxylates (AEOs) are the main nonionic surfactants produced in Europe (e.g. 300,000 t/year just for household cleaning products [1]). This is in part due to relatively recent restrictions in the use of alkylphenol polyethoxylates (APEOs) in household detergents as a consequence of the estrogenic properties shown by their metabolites [2]. Widely used in domestic and industrial applications (e.g., detergents, emulsifiers, wetting and dispersing agents, industrial cleaners, textile, pulp and paper processing [1]), commercial AEOs consist of a mixture of several homologs of varying carbon chain length and degree of ethoxylation. Polyethylene glycols (PEGs), which have been described as the main degradation metabolites of AEOs [3], are an important group of nonionic synthetic water-soluble polymers of ethylene oxide that are also used in a wide range of applications. This includes the production of cosmetics, plastics, water-soluble lubricants, pharmaceuticals and nonionic surfactants including APEOs and AEOs [4]. In fact, the annual production of PEGs is estimated to be several millions of tons worldwide [4].

After their use, surfactant residues are discharged into aquatic ecosystems in treated or untreated wastewaters, and enter in various environmental compartments such as surface waters, sediments and biota [5]. Polyethoxylated surfactants and their metabolites are often found in wastewater effluents, receiving waters and sediments at very high concentrations compared to other targeted analytes [6], in spite of the high removal efficiencies (between 93% and 99%) in wastewater treatment plants (WWTPs). Total effluent concentrations range from 0.92 to 15.6 μg L^{-1} for NPEOs (nonylphenol polyethoxylates, which are the main type of APEOs) and AEOs [7,8]. Available studies on the presence, environmental behavior and distribution of these compounds are mainly focused on NPEOs, due to their potential adverse effects, showing concentrations between <0.2

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and 2 μg L^{-1} in surface waters [9,10] and between <10 and 28,500 ng g^{-1} in sediments [11–13] all over the world. On the other hand, data concerning to the presence of AEOs and PEGs are rather limited. Concentrations of AEOs in sediments can be comparable to those found for NPEOs [9,12,13], showing levels ranging from 40 to 12,200 ng g^{-1}. The occurrence of PEGs has recently been reported in the U.S. East Coast [14], where concentrations in surface sediments were generally higher (up to 1490 ng g^{-1}) than those for other classes of targeted surfactants detected in the same zone. Also, some authors have found concentrations between <0.1 and 49 μg L^{-1} for AEOs [9,11,12] and PEGs [14] in surface waters. Additionally, and although they do not act as endocrine disruptor compounds, AEOs have proven to be toxic for certain aquatic species [15].

For several years now, NPEOs and AEOs have been extracted from sediments and sludges using Soxhlet or ultrasonic extraction with methanol [14,16] or mixtures containing nonpolar solvents (e.g. dichloromethane [17]). Later, extracts are often preconcentrated and purified by means of solid-phase extraction (SPE) [14,17–21]. Different SPE cartridges such as octadecylsilica (C18) [17] or various polymers (e.g. HLB [14], Porapak Rdx [22]) have been tested with satisfactory results for these compounds, while elution is performed with solvent mixtures containing methanol, dichloromethane, hexane and/or acetonitrile. More recently, new extraction methods have been developed not only to save time, but also to reduce solvent consumption without losing efficiency. Pressurized liquid extraction (PLE) is used to improve the extraction process, as the solvents remain in their liquid state at high temperatures (100–200 °C) and pressures (about 150 atm). There are some recent protocols for performing PLE of AEOs and NPEOs from sediments [7,23,24] and soils [21], using methanol, hexane or acetone as solvents in most cases. Supercritical fluid extraction (SFE) is another relatively modern extraction technique that uses water instead of organic solvents to carry out the extraction of nonionic surfactants (NPEOs and AEOs) [25] within 15 min.

Once extracted from solid or aqueous matrices, separation, identification and quantification of AEOs, PEGs and other polyethoxylated compounds can be carried out by means of several methods based on the use of high-performance liquid chromatography coupled to ultraviolet and fluorescence detectors (HPLC-UV-FLU) [18,26], and gas chromatography with mass spectrometry (GC–MS) [16]. However, analysis of AEOs by these techniques is more challenging than that for APEOs due to their lack of UV absorbance, fluorescence and volatility, so prior derivatization is required in most cases [26]. Considerable progress has been achieved during the last decade, mainly due to the development of new interfaces such as electrospray ionization (ESI), allowing the determination of these surfactants by high performance liquid chromatography–mass spectrometry (HPLC–MS). This combination offers many advantages in terms of greater sensitivity, selectivity and the possibility to simultaneously measure multiple classes of compounds together. The application of HPLC–MS for the determination of AEOs and PEGs [22,27] is severely limited compared with the relatively large number of protocols developed for nonylphenolic compounds analysis over the last decades [10,19,20]. NPEOs and AEOs have been simultaneously measured in different environmental compartments [17,21,23,25] by means of HPLC-single quadrupole/ion trap (IT)-MS. More recently, tandem mass spectrometry (MS–MS) has been used for the analysis of organic pollutants, increasing sensitivity and selectivity when determining AEOs in aqueous matrices [28,29], as well as in marine sediments [13]. Less commonly used than other HPLC–MS instrumental approaches in the analysis of surfactants, liquid chromatography coupled to time-of-flight mass spectrometry (LC-ToF-MS) constitutes an alternative for the identification of surfactants and many other organic pollutants, due to the capability for estimating their elemental composition by accurate mass measuring of ions for confirmation purposes. So far, there are only a couple of papers dealing with LC-ToF-MS analysis of AEOs and PEGs in environmental samples [14,30].

In spite of the numerous methods presented above for the determination of nonionic surfactants in environmental samples, most of the work done has been focused on the extraction of APEOs and their degradation intermediates in soils, sediments and sludges. The environmental behavior of these compounds is therefore relatively well-known today, whereas information for AEOs is increasing and it is still really scarce on many other compounds such as PEGs. In order to help solving these deficiencies, we have developed and optimized a new method for the simultaneous extraction, preconcentration, purification, identification and quantification of AEOs and PEGs in sediment samples using a combination of ultrasonic extraction, PLE, SPE and HPLC-IT-MS. Additionally, this procedure has been applied to the determination of concentrations of both compounds in surface sediments from a coastal lagoon in the southeast of Spain, allowing for a comparative study on the environmental levels of AEOs and PEGs for the first time.

2. Material and methods

2.1. Chemicals and standards

Ethyl acetate (Acet), methanol (MeOH), water, acetone (Ace), dichloromethane (DCM) and hexane (Hex) were of chromatography quality, purchased from Scharlau (Barcelona, Spain). Acetic acid, sodium sulfate, sodium acetate and ammonium acetate were purchased from Panreac (Barcelona, Spain). The solid-phase extraction (SPE) mini-columns used (6 mL, 500 mg) were supplied by Varian (Bond Elut C18) and Waters (Oasis HLB).

The individual >98% pure polyethylene glycols (PEGs) having 1, 2, 3, 6 and 8 EO units, AEO ethoxymers (C_{12}, C_{14}, C_{16} and C_{18} homologs having 1, 2, 3, 6 and 8 EO units), and a PEG 300 mixture were purchased from Sigma-Aldrich (Milwaukee, USA). The ≥98% pure $C_{10}AEO_8$ internal standard used in positive ionization mode was also purchased from Sigma-Aldrich (Madrid, Spain).

Stock standard solutions containing individual species or mixtures of them were prepared by dissolving them in 100% methanol. Working standard solutions were made by further diluting with methanol.

2.2. Pressurized liquid extraction

Target compounds were extracted from the sediment samples using pressurized liquid extraction (PLE) by means of an accelerated solvent extraction ASE 200 unit from Dionex. Quantities of dried and sieved sediment samples (4 g) were mixed together with 16 g of sodium sulfate and placed into steel cells (22 mL). Extraction was optimized by testing several extraction solvents. Methanol was selected and passed through the heated (120 °C) and pressurized (1500 psi) PLE cells for three cycles of 5 min each. Subsequently the methanolic extracts were evaporated until 5 mL.

2.3. Ultrasound assisted-extraction

The extraction from dried sediment (0.5 g per sample) was performed for comparison with PLE using ultrasonic irradiation at 30 °C during 3 cycles (30 min each), and methanol/dicloromethane 1:1 (30 mL) after testing several extraction solvents. After extraction, solvent was separated from sediment samples by centrifugation and evaporated to 5 mL.