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Pressurized liquid extraction followed by liquid chromatography-mass spectrometry for the determination of major surfactants in marine sediments

PABLO A. LARA MARTÍN, ABELARDO GÓMEZ PARRA and EDUARDO GONZÁLEZ MAZO*

Departamento de Química Física, Facultad de Ciencias del Mar y Ambientales, Universidad de Cádiz, Av. República Saharaui s/n, 11510 Puerto Real, Cádiz, Spain

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A simple and fast method is described for the determination in marine sediments of the anionic and non-ionic surfactants most commonly used worldwide. This group of compounds includes linear alkylbenzene sulfonates (LAS), alkyl ethoxysulfates (AES), nonylphenol polyethoxylates (NPEOs) and alcohol polyethoxylates (AEOs). The proposed method involves the extraction of 5 g of dry sediment with methanol by using an accelerated solvent extraction unit (ASE), preconcentration and purification by means of an octadecyl-bonded silica (C_{18}) mini-column and analysis by high-performance liquid chromatography coupled to mass spectrometry (HPLC-MS). The recoveries varied in the range of 51–109%, with a standard deviation between 4 and 11. Limits of detection were in the range of 1–5 μg/kg for sediment samples. This method was applied to the determination of these surfactants in a sediment core collected in the Bay of Cadiz (SW of Spain), with concentration values up to 637 μg/kg for LAS, 401 μg/kg for NPEOs, 861 μg/kg AEOs and 125 μg/kg for AES.

Keywords: Marine sediments; Anionic surfactants; Non-ionic surfactants; Extraction methods; Pressurized liquid extraction

1. Introduction

Coastal ecosystems receive large quantities of a wide range of organic contaminants from urban wastewater which are discharged either treated or untreated. Among these contaminants, surfactants constitute the main proportion of the total; these are a group of chemicals that are widely used, both industrially and domestically, in quantities above 15 million tonnes per year [1]. Their surface-active properties are the reason for this extensive usage as well as their wide variety of applications, mainly as ingredients in laundry and cleaning products, cleaners for hard surfaces, and shampoos.

*Corresponding author. Fax: +34-956-016040. E-mail: eduardo.gonzalez@uca.es

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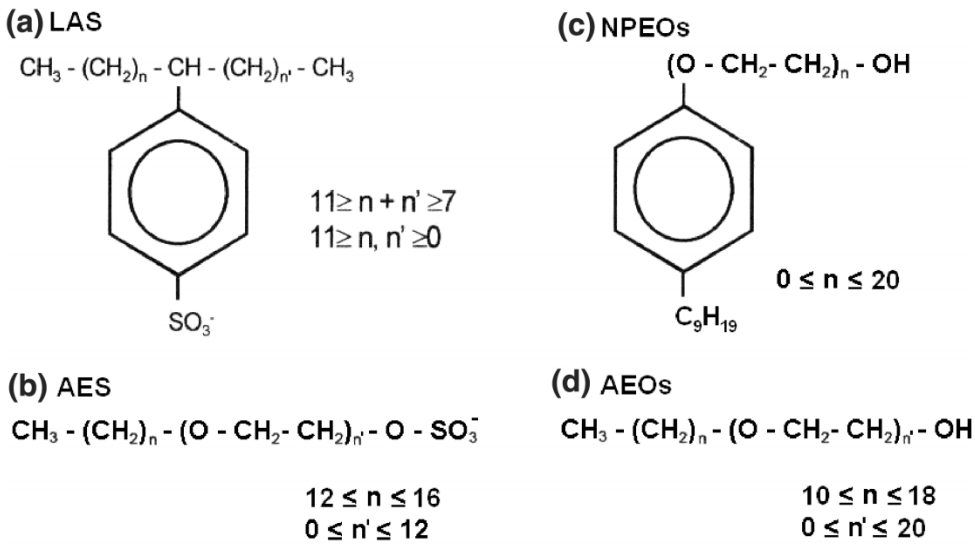

Figure 1. General chemical structures of (a) linear alkylbenzene sulfonate (LAS), (b) alkyl ethoxysulfate (AES), (c) nonylphenol polyethoxylates (NPEO) and (d) alcohol polyethoxylate (AEO) compounds.

Surfactants may be divided into several classes, with anionic surfactants being produced in greater quantity than the non-ionics. Among the first group, linear alkylbenzene sulfonates (LAS) are the main ones, comprising a mixture of homologues with chain lengths of between 10 and 14 carbon atoms in commercial formulations (figure 1a). Each of these homologues consists of a varying number of positional isomers. Alkyl ethoxysulfates (AES) are included in the same group as LAS. Their chemical structure (figure 1b) in commercial products comprises an alkyl chain length of 12–16 carbon units joined to an ethylene oxide (EO) chain of one to 12 EO units with a terminal sulfate group. Also, AES mixtures typically contain various proportions of alkyl sulfates (AS), with no EO units. The second group, non-ionic surfactants, is mainly represented by nonylphenol polyethoxylates (NPEOs) and alcohol polyethoxylates (AEOs). Both of these present a long ethylene oxide chain, with more than 20 EO units in some cases (figures 1c and 1d). The use of NPEOs has been banned or restricted in some countries in Europe because their breakdown products are toxic and oestrogenic to aquatic organisms [2]. AEOs are currently the most important non-ionic surfactant in economic terms.

Because of their widespread use, source specificity and environmental persistence in many cases, surfactants are used effectively as molecular markers for the contamination of sediments by human activities [3]. A considerable number of studies have been conducted aimed at understanding the distribution of LAS and NPEOs in the marine environment to which they have access [4–8]. In contrast there are relatively few published papers about AEOs [9] in this environment and on the recent discovery of AES in marine sediments [10]. The main reason for this situation is the limitations of existing analytical techniques. Therefore, the lack of UV absorbance of AEOs and AES has constituted one of the main problems in trying to detect them by means of high-performance liquid chromatography with UV-fluorescence detection

(HPLC/UV-FL) as with LAS and NPEOs [11, 12]. Also, analysing them by gas chromatography coupled to mass spectrometry (GC/MS) requires the development of other methods because of the non-volatility of most of these surfactants and the consequent unavoidable derivatization [13–15]. By solving these issues, the use of HPLC/MS has today become the most effective means of analysing surfactants in environmental samples, and even enables them to be determined simultaneously [16–18].

Another limiting step in the development of analytical procedures for the study of surfactants in solid matrices such as soil, sediment or sludge is the extraction. Soxhlet and ultrasonic extraction have been the most commonly used techniques, with pure methanol or mixtures with acetone or dichloromethane as common solvents. Although recoveries are high in most cases, each sample requires several hours for extraction and the use of a considerable amount of solvent. Nowadays, less time- and solvent-consuming and more environmentally friendly techniques are preferred, such as supercritical fluid extraction (SFE) and accelerated solvent extraction (ASE). Unfortunately, these are still being developed, so few studies describing their use with surfactants have been published [19–23].

Therefore, it is considered necessary to develop a procedure that permits a fast but accurate identification and quantification of the major surfactants mentioned above (LAS, AES, NPEOs and AEOs) to allow their monitoring after being discharged into the marine environment. The aim of the work reported here is to develop an improved method for the screening of LAS, AES, NPEOs and AEOs in sediments by using ASE and HPLC/MS techniques. Also, the effectiveness of the method is demonstrated by means of the determination of the homologues and ethoxymers of these surfactants at the ppb level in several sections from an actual sediment core.

2. Experimental

2.1. *Materials*

Methanol, triethylamine and acetonitrile were of chromatography quality and purchased from Scharlau (Barcelona, Spain); acetic acid, sodium acetate and sodium sulfate were purchased from Panreac (Barcelona, Spain); and water was Milli-Q quality. The solid-phase extraction (SPE) mini-columns used (500 mg) were supplied by Varian (Bond Elut C_{18}).

The 99% pure C_{16} LAS internal standard and the commercial LAS mixture were supplied by Petroquimica Española (PETRESA), with the following homologue distribution for the commercial mixture: C_{10} (10.9%), C_{11} (35.3%), C_{12} (30.4%), C_{13} (21.2%) and C_{14} (1.1%). The commercial AES mixtures were supplied by KAO Corporation (KAO) and Procter and Gamble (P&G). Their proportional compositions of the various homologues are C_{12} (68.5%), C_{14} (29.8%) and C_{16} (1.7%) for the KAO standard and C_{12} (17.5%), C_{13} (28.2%), C_{14} (32.1%) and C_{15} (22.2%) for the P&G standard. Their average numbers of EO units are 3.4 and 4.2, respectively. The commercial NPEOs and AEOs mixtures were supplied by KAO, each with an average number of EO units of 12.2 and 11.5, respectively. The AEO homologue distribution is: C_{12} (53.4%), C_{14} (32.6%) and C_{16} (14.0%).

2.2. *Sampling pretreatment and spiking*

The study was carried out in a salt-marsh environment in the interior part of the Bay of Cadiz (southwest Spain). The sediments were collected with a gravity aluminium core sampler, transferred to the laboratory at 4°C and frozen until their analysis. In the laboratory, the frozen core was sectioned taking slices of 2 cm along its length (50 cm). Each slice was dried, kept in a heater at 85°C until constant weight, and later milled and strained through a 0.63 μm sieve.

Recovery studies were performed by spiking non-polluted sediments with 1, 5 and 10 mg/kg of commercial standards of AES, AEOs and NPEOs (supplied by KAO) and LAS (supplied by PETRESA). For this purpose, 100 g of wet sediment was mixed with 100 mL of seawater containing the surfactants, using a mechanical arm during 24 h. The entire mixture was rendered toxic with 1 g of $HgCl_2$ and kept in the dark to prevent surfactant degradation. Finally, fractions of 5 g were treated in the same way as the sediment samples and analysed in triplicate to calculate the recovery values of the method.

2.3. *Extraction procedure*

Surfactants were extracted from the sediment samples using an ASE unit from Dionex. Quantities of dried and sieved sediment samples (5 g) were packed into the ASE extraction cells (22 mL) and mixed with 15 g of sodium sulfate to fill the cells. Methanol was passed through the heated (100°C) and pressurized (1500 psi) cells during three cycles of 5 min each. Subsequently, the methanolic extracts were evaporated until dry in a rotavapor, and the dried residue was re-dissolved in 50 mL of water in an ultrasonic bath.

These extracts were purified and preconcentrated by solid-phase extraction (SPE) using mini-columns of the hydrophobic C_{18} type in an automated SPE Auto Trace unit (Zymark). These C_{18} mini-columns were rinsed with 10 mL of methanol and 5 mL of water prior to passing the 50 mL of sediment extracts. Then, they were washed with 5 mL of water and eluted with 10 mL of methanol. Finally, the elution was evaporated until dry and redissolved in 1 mL of a methanol/water 1 : 1 solution containing 1 μg/mL of C_{16} LAS as internal standard and 50 μM of sodium acetate.

2.4. *HPLC-MS analysis*

The HPLC system consisted of Spectrasystem liquid chromatograph and an autosampler with the volume injection set to 100 μL. The chromatographic separation was performed using a reversed-phase C-18 analytical column (LiChrospher 100 RP-18) of 250 × 2 mm and 3 μm particle diameter from Merck. The detection was carried out using an LCQ ion-trap mass spectrometer (Finnigan), equipped with an atmospheric pressure ionization source with an electrospray interface (ESI). All extracts were analysed using the ESI full-scan positive ion mode to determine NPEOs and AEOs and full-scan negative ion mode to determine LAS and AES, scanning the mass/charge (m/z) range of 200–1100 and 75–800, respectively.

For the determination in positive ion mode, samples were injected in the HPLC/MS system using methanol (A) and water (B) as mobile phase. The following solvent programming was used: initial conditions 80% A, linearly increased to 100% A in 40 min and kept isocratic for 5 min. In negative ion mode, the following mobile

Table 1. Mass/charge (m/z) relations scanned for the identification of LAS, AES, NPEOs and AEOs homologues (also, m/z ranges are shown for AES, AEOs and NPEOs ethoxymers, with 44 m/z units of difference between each consecutive ethoxymer).

Homologue	m/z	Homologue	m/z
C_{10} LAS	183, 297	NPEOs $n_{EO}=1$–19	287–1079 (±44)
C_{11} LAS	183, 311	C_{12} AEOs $n_{EO}=1$–18	253–1001 (±44)
C_{12} LAS	183, 325	C_{13} AEOs $n_{EO}=1$–18	267–1015 (±44)
C_{13} LAS	183, 339	C_{14} AEOs $n_{EO}=1$–18	281–1029 (±44)
C_{12} AES $n_{EO}=0$–12	97, 265–793 (±44)	C_{15} AEOs $n_{EO}=1$–18	295–1043 (±44)
C_{13} AES $n_{EO}=0$–11	97, 279–763 (±44)	C_{16} AEOs $n_{EO}=1$–18	309–1057 (±44)
C_{14} AES $n_{EO}=0$–11	97, 293–777 (±44)	C_{18} AEOs $n_{EO}=1$–18	337–1085 (±44)
C_{15} AES $n_{EO}=0$–11	97, 307–791 (±44)		
C_{16} AES $n_{EO}=0$–10	97, 321–761 (±44)		

phase was used: acetonitrile/water 80 : 20 (A) and water with 5 mM acetic acid and 5 mM triethylamine (B). Addition of acetic acid was used to decrease the pH value to improve the interaction between triethylamine and the surfactant homologues for a better separation along the HPLC column. The elution gradient started with 47% A and was linearly increased to 100% A in 40 min and kept isocratic for 5 min. The flow rate in both cases was 0.15 mL/min. Other MS parameter values were: ion fragmentation energy 40 V, needle tip voltage 4.5 kV, gas stealth flow 60 mL/min and ion source temperature 220°C.

Table 1 shows the fragments used for the identification of the target compounds. Identification of each homologue of LAS and ethoxymers of AES was carried out by monitoring their quasimolecular ions $[M–H]^-$ and their specific fragment ion with m/z 183 and 97, respectively. In the case of NPEOs and AEOs, each ethoxymer was identified by monitoring its adduct ion $[M+Na]^+$. Surfactants concentrations were determined by measuring the peak areas of the quasimolecular ions for the anionics and adduct ions for the non-ionics, using external standards solutions (0.1–10 mg/L) of LAS, AES, NPEOs and AEOs prepared in methanol/water 1:1 and C_{16} LAS as internal standard (1 mg/L). Clean sediment extracts and a methanol/water 1:1 solution were spiked with 1 mg/L of LAS, AES, NPEO and AEO standards to check the influence of ion suppression (suppression of the analytes signals caused by high concentrations of matrix components) on the MS detection of target compounds.

3. Results and discussion

3.1. *Separation, calibration graphs and limits of detection*

The separation of NPEOs and AEOs is illustrated in figure 2. This chromatogram clearly shows an increase in retention time for AEOs homologues with a longer alkyl chain length. Under the HPLC conditions used, all the ethoxymers in NPEO and AEO homologues appear under the same chromatographic peak, although a small shoulder can be observed before the top of each peak. The reason for this is the existence of two kinds of ethoxymers for these surfactants, depending on whether the alkyl chain is linear or branched. Therefore, the main peaks would correspond to the linear ethoxymers, with the higher percentage in the supplied standards, being overlapped by

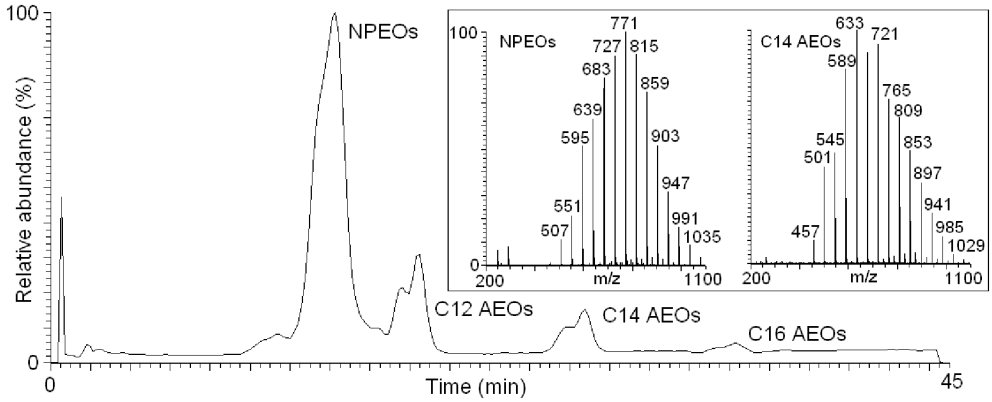

Figure 2. Full-scan HPLC/MS ESI positive ion chromatogram showing the separation between NPEOs and AEOs homologues in a standard solution. Also, mass spectra of NPEOs and C_{14} AEOs are presented, showing the adduct ions $[M+Na]^+$ of the different ethoxymers. Chromatograms and mass spectra were obtained under specific analytical conditions described in Section 2.4.

the branched ones, with a lower retention time due to their weaker interaction with the octadecyl-silica of the chromatographic column. Figure 2 also shows the NPEOs and C_{14} AEO mass spectra as examples, where the adduct ion $[M+Na]^+$ of each ethoxymer is present, allowing their identification and quantification.

In the case of LAS and AES, the separation, shown in the total ion current chromatogram in figure 3, is not so effective as with the non-ionics. LAS and AES have homologues with the same length of the alkyl chain, and it is not possible to achieve a complete separation between them with the octadecyl-silica column. However, as shown in the mass spectra in figure 3, the use of the HPLC/MS technique allows us to distinguish them because of their specific fragment ions, m/z 183 for LAS [24] and m/z 97 for AES [25], and quasimolecular ions $[M–H]^-$. Also, under the HPLC conditions used, it is possible to make an approach to indentify separately the internal and external isomers in each LAS homologue, the internal ones being eluted first in the sequence, followed by the external ones, which appear as two separate peaks per homologue, as can be observed in the m/z 183 chromatogram in figure 3. Separation of the ethoxymers of each AES homologue also occurs (m/z 97 chromatogram in figure 3), particularly between AS (with $n_{EO}=0$) and the AES with 1 and 2 EO units, these latter being the most relevant ones in marine sediments due to their higher concentration [10]. These ethoxymers appear successively as individual peaks, with the rest of the longer ethoxymers (3–10 EO units) appearing as a single peak with a longer retention time.

Unfortunately, individual ethoxymer standards for AES, AEOs and NPEOs were not available at the time of the study. Commercial mixtures with a known average number of ethoxymers were used instead, as in previous studies [7,9,16,18] to obtain an approximation. The calibration curves were obtained for each homologue of the studied compounds assuming the same response for all the AES, AEOs and NPEOs ethoxymers and LAS isomers. The shortest ethoxymers like NP_1EO or NP_2EO are in a very low proportion in the standards, so they were not quantified. The behaviour of all compounds was linear in a range of 0.1–10 mg/L, with r^2 values above 0.999

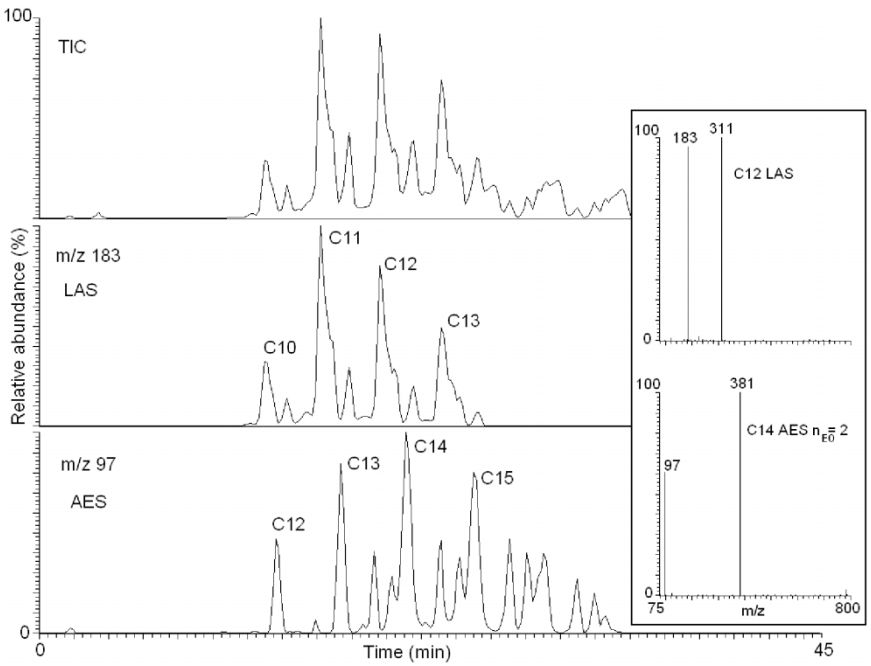

Figure 3. Full-scan HPLC/MS ESI negative ion chromatogram showing the presence of LAS and AES homologues in a standard solution. Also, two extracted ion chromatograms are presented, showing the separation between the homologues of these two surfactants by means of their specific fragment ions m/z 183, for LAS, and m/z 97, for AES. Mass spectra of C_{12} LAS and C_{14} AEOs with $n_{EO} = 2$ are presented as examples. Chromatograms and mass spectra were obtained under the specific analytical conditions described in Section 2.4.

Table 2. Recovery percentages and standard deviations (SD) ($n = 9$) obtained for sediment spiked with LAS, AES, NPEOs and AEOs.

Homologue	Recovery (% ± SD)	Homologue	Recovery (% ± SD)
C_{10} LAS	109 ± 8	C_{12} AES	64 ± 6
C_{11} LAS	93 ± 8	C_{14} AES	60 ± 7
C_{12} LAS	82 ± 7	C_{16} AES	51 ± 8
C_{13} LAS	62 ± 5	C_{12} AEOs	105 ± 8
NPEOs	60 ± 4	C_{14} AEOs	109 ± 10
		C_{16} AEOs	66 ± 11

for each homologue. The limit of detection was calculated using a signal-to-noise ratio of 3 : 1, being in the range of 1–5 µg/kg of each homologue in sediment samples. The influence of ion suppression was determined to be a reduction of less than 5% on the signal intensity for each analyte.

3.2. *Recovery study*

By spiking sediments as indicated before, recoveries were calculated and are shown in table 2. The values varied in the range of 51–109%, with a standard deviation of 4–11. The highest recoveries are obtained for LAS and AEOs, with an average value above 85%, being lower for NPEOs and AES, at around 60%.

Looking at each homologue recovery value, one can observe the effect of the alkyl chain length and how the lower recoveries of the longer homologues are probably due to their more hydrophobic character and, consequently, their retention in the sediment and in the SPE cartridge. The same trend has been reported by Kreisselmeier and Dürbeck in the case of LAS and NPEOs combining ASE and SFE with methanol as solvent [20], yielding similar recoveries. Recoveries are considerably better for NPEOs (65–93%) using 1 : 1 hexane:acetone as solvent in the ASE with the same temperature and pressure conditions [21]. This mixture improves recoveries for non-polar homologues like C16 AES or NP, but there is a considerable and unacceptable decrease in recoveries for shorter homologues like C10 LAS or C12 AES, as well as for other related compounds like sulphophenyl carboxilyc acids (SPCs) (data not shown).

Besides, comparing this study with previous ones [10, 26], where sediment was spiked and extracted by means of Soxhlet extraction, it can be seen that the ASE is less efficient in the case of the longer homologues using the same solvent (methanol). An increase in the extraction time or the use of another solvent would be required to achieve better recoveries with these compounds. However, the main objective of this paper is to develop a relatively simple and fast method that allows us to perform a screening of the major surfactants in marine sediments. Table 2 shows standard deviation values for the recovery tests. These SD values (4–11), together with the corrections performed using the internal standard C16 LAS, are low enough in a wide range of concentrations (1–10 mg/kg) to ensure a good reproducibility in the results. In any case, ASE has been proven to give a better reproducibility than Soxhlet extraction in the same study; this technique leads to better data quality and requires less time and solvent consumption, so this is a reliable and suitable method for routine analysis.

3.3. *Marine sediments*

Figures 4 and 5 show chromatograms obtained by applying the method described above to sediment samples. It can be observed that the procedure followed produces chromatograms showing an efficient separation of each surfactant homologue or ethoxymer without interference and with sufficient intensity to permit an accurate quantification in environmental samples. Also, identification of other related surfactants is possible. Figure 4 shows a chromatogram from a sediment sample at 17 cm where the presence of tetrapropylenebenzenesulfonate (TPS) is confirmed by means of its specific fragment ion m/z 197 and quasimolecular ion m/z 325 [27]. This surfactant, which was used commercially before LAS, has a similar structure when compared with C_{12} LAS but with a branched alkyl chain instead of a linear one, which made the compound very difficult to biodegrade. The TPS concentration at this depth has been estimated around 200 μg/kg according to the C_{12} LAS peak as they show very similar response factors. Figure 5 compares C_{14} AEOs ethoxymers from 10 to 13 in a standard versus a sediment sample, showing an increment in the proportion of branched alkyl chain ethoxymers due to their slower degradation, as with TPS and LAS in the case described.

Table 3 lists the concentrations of surfactants obtained in the sampled sediment core. Concentrations are up to 637 μg/kg for LAS, 401 μg/kg for NPEOs, 861 μg/kg AEOs and 125 μg/kg for AES, located in the surface (depth 1 cm). These values are in the same magnitude order as others shown in a previous study [9] in the Bay of Cadiz

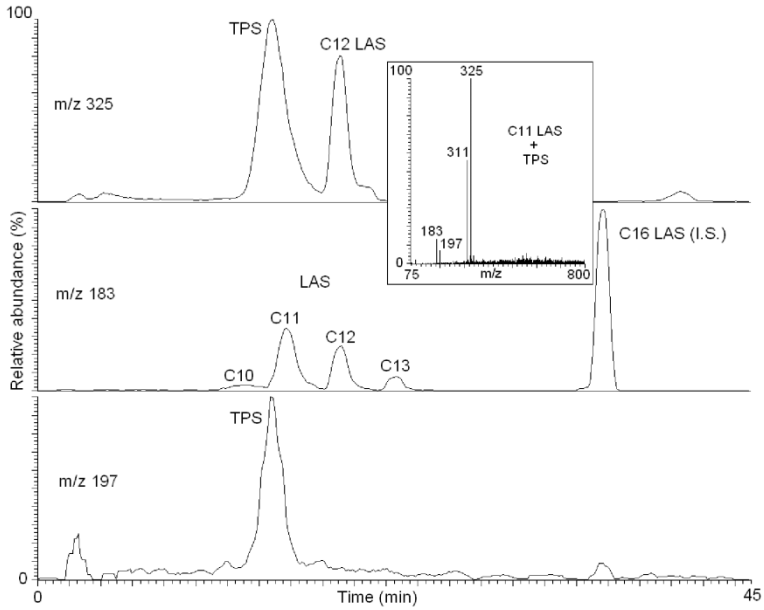

Figure 4. Extracted HPLC/MS ESI negative ion chromatograms showing the identification of tetrapropylenebenzenesulfonate (TPS) in a sediment sample among LAS homologues by means of its quasimolecular and specific fragments m/z 325 and 197, respectively. Also, a mass spectrum of TPS together with C_{11} LAS is presented. Chromatograms and mass spectra were obtained the under specific analytical conditions described in Section 2.4.

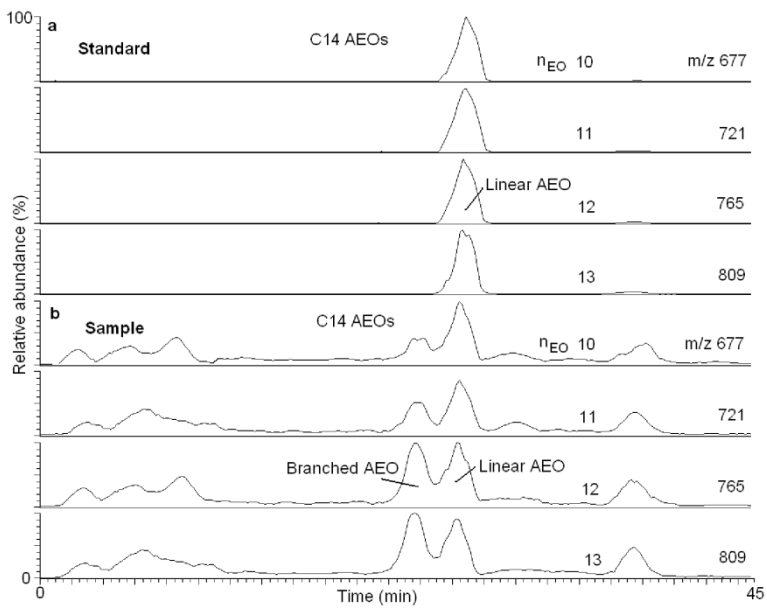

Figure 5. Extracted HPLC/MS ESI positive ion chromatograms showing the presence of linear and branched C14 AEOs ethoxymers with n_{EO} between 10 and 13 in (a) a standard solution and (b) a sediment sample. Chromatograms were obtained under the specific analytical conditions described in Section 2.4.

Table 3. LAS, AES, NPEOs and AEOs homologue concentrations (μg/kg) detected in marine sediment at different depths[a] in the sampled core.

Homologue	1 cm	17 cm	47 cm
C_{10} LAS	24	18	n.q.
C_{11} LAS	219	173	77
C_{12} LAS	199	120	46
C_{13} LAS	195	63	12
Total LAS	637	374	135
C_{12} AES	78	40	n.q.
C_{13} AES	10	n.q.	n.d.
C_{14} AES	21	15	n.q.
C_{16} AES	16	n.q.	n.d.
Total AES	125	55	n.q.
Total NPEOs	401	97	13
C_{12} AEOs	35	n.d.	n.d.
C_{13} AEOs	42	n.d.	n.d.
C_{14} AEOs	96	n.q.	n.d.
C_{15} AEOs	184	n.q.	n.d.
C_{16} AEOs	222	5	n.d.
C_{18} AEOs	282	29	n.d.
Total AEOs	861	34	n.d.

[a]n.d.: not detected; n.q.: detected but not quantified.

and in other bays on the Spanish coast (around 1000 μg/kg for LAS and 200 μg/kg for AEOs and NPEOs). The main trend along the sedimentary column, as described in other sampling areas [7, 28, 29], is towards a decrease in the concentration values of all these compounds with depth, with no detection or a non-possible quantification due to very low concentrations in most cases at 47 cm. Also, enrichment in longer alkyl chain homologues for LAS, AES and AEOs can be observed when compared with standards, due to their greater hydrophobicity and affinity for the organic matter of the sediment [6, 10].

4. Conclusions

The proposed method permits the determination of LAS, AES, NPEO and AEO homologues and ethoxymers in marine sediments with a high selectivity and reproducibility, in a simple and less time-consuming way compared with older specific methods for the determination of each surfactant. Also, it is possible to differentiate in a first approach between linear and branched ethoxymers in the case of NPEOs and AEOs and between LAS and TPS. This demonstrates the value of the most recently developed techniques such as ASE and HPLC-MS, as powerful tools for enabling the presence of these compounds in the environment to be monitored faster and more simply.

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