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Simultaneous extraction and determination of anionic surfactants in waters and sediments

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Abstract

A new method has been developed for the simultaneous determination of the most frequently used anionic surfactants – linear alkylbenzene sulfonates (LAS), alkyl ethoxysulfates (AES) and alkyl sulfates (AS) – in aqueous and sediment samples. Preconcentration and purification of water samples are carried out by means of solid-phase extraction (SPE). The efficiency of two different extraction methods for the analysis of sediments – Soxhlet extraction and pressurized liquid extraction (PLE) – has been compared. Identification and quantification of the target compounds is performed using a liquid chromatography – mass spectrometry (LC–MS) system equipped with an electrospray interface (ESI) in negative ion-mode. Homologue recoveries are 85–123% for SPE, 94–112% for Soxhlet extraction and 81–125% for PLE in the case of LAS, and 60–94% for SPE, 61–109% for Soxhlet extraction and 55–99% for PLE in the case of AES, whereas the limits of detection are 0.1–0.5 ng ml^{-1} in water and 1–5 ng g^{-1} in sediment. This method has been applied to the determination of anionic surfactants in the Guadalete estuary (SW Spain), and LAS concentration levels from 538 to 1014 ng g^{-1} in sediments and from 25.1 to 64.4 ng ml^{-1} in waters have been found. AES values from 168 to 536 ng g^{-1} in sediments and from 4.5 to 11.9 ng ml^{-1} in waters are reported for the first time in European rivers.

Keywords: Sediments; Waters; Anionic surfactants; Extraction methods; Pressurized liquid extraction; Mass spectrometry

1. Introduction

More than 15 000 million kg of surfactants are manufactured yearly [1], which means that they have one of the highest production and consumption rates among the organic synthetic compounds due to their wide variety of uses, mainly in detergent formulation but also as emulsifiers, pesticide adjuvants and wetting agents. Approximately 65% of this production corresponds to the subtype classified as anionic surfactants according to their ionic charge. Linear alkylbenzene sulfonates (LAS) are the main component of this group, with an annual European production estimated at 400 million kg [2]. The alkylbenzene is the hydrophobic moiety which is derived from petroleum distillates and sulfonated prior to use. These compounds typically have 10 to 14 carbon units, each of these homologues consisting of a varying number of positional isomers in the alkyl chain; they are generally used in household detergents and surface cleaners. European production of alkyl ethoxysulfates (AES) and alkyl sulfates (AS) together reaches 378 million kg per year [3,4] so they are placed second in the production volume ranking after LAS by a narrow margin. These chemicals are derived by sulphation from alcohol ethoxylates (AEs) which are composed of a long-chain fatty alcohol with an ether linkage to a chain of ethylene oxide (EO) units. In the case of AES, the EO group typically has an average number of 3–4 units (zero for AS) while the alkyl chain length range between 12 and 16 carbon units. It includes both even and odd numbers of homologues or else only even homologues, in the cases of alcohols derived from petroleum or vegetable sources, respectively. Main applications for AES and AS include use in shampoos, hand dishwashing liquids, laundry detergents and cosmetic care products.

Although their removal in wastewater treatment plants (WWTPs) is efficient [5,6], many aquatic ecosystems may receive quantities of these compounds both from WWTPs effluents and from untreated urban wastewater discharges. Due to this, several studies have been conducted in recent decades in order to obtain a better understanding of the distribution, behavior and fate of anionic surfactants in the environment; these are

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summarized in a recent review presented by Ying [7]. However, almost all these studies concern the determination of LAS in water and sediment [8–12], and only a few recent papers deal with the environmental presence of AES [13,14]. One of the reasons that may explain this absence is the limitations of the analytical techniques until the last decade. Although the analysis of both these anionic surfactants in environmental samples has been possible during the 1980's using gas chromatography (GC) coupled to a flame ionization detector or with mass spectrometry (MS) [15–17], derivatization is unavoidable. High performance liquid chromatography – fluorescence detection (HPLC-UV) has been preferred during in the 1990's because it offered an easier way to quantify LAS [18–20]. The lack of a chromophore group of AES similar to the benzene in LAS makes it impossible to determine them by means of HPLC-UV. After some attempts with fast atom bombardment [21], this issue has been resolved during the last ten years as a result of the development of the electrospray (ESI) and atmospheric pressure chemical ionization (APCI) interfaces in liquid chromatography – mass spectrometry (LC–MS) [22–24]. Therefore the use of LC–MS has nowadays become one the most powerful tools for surfactant analysis in environmental samples because of its specificity, unequivocal identification of homologues and ethoxymers and capability of the determining several surfactants together [25,26] without the interferences that limited the use of HPLC-UV.

Prior to analysis by any of the techniques related above, it is necessary to isolate the anionic surfactants from their environmental matrices. Extraction from water is usually carried out by means of solid phase extraction (SPE). In the case of LAS, octadecylsilica mini-columns (C_{18}) have been the type most widely employed for this [18–20,23,26,28–30], although graphitized black carbon (GBC) [25], strong anion exchange resins (SAX) [23,27,28] and C_8 [17] have been also tested with satisfactory results. Similar SPE procedures are employed for the isolation of AES from aqueous matrices [13–15,22]. For the analysis of LAS in sediments, sludges and soils, the protocol most frequently used is methanol, alone or mixed with other solvents such as acetone or dichloromethane, in Soxhlet [14,27,28] and ultrasonic extractions [17,19,26]. Pressurized liquid extraction (PLE) [29–33] and supercritical fluid extraction (SFE) [33,34] are less time- and solvent-consuming new techniques that have emerged during the last decade and these have been also employed to extract LAS from soils, sludges and sediments. There are few papers about AES and AS extraction from solid matrices. They have been extracted from sludges by SFE [34] but a protocol has not yet been optimized in the case of PLE.

Therefore, the main aim of this work is the development and optimization of a procedure that permits the simultaneous extraction, purification, identification and quantification of the anionic surfactants LAS, AES and AS in waters and sediments, as a prerequisite for studying their distribution and fate in aquatic ecosystems, especially in the case of the last two because there is little environmental information available. To achieve this objective a three-stage methodology is presented that includes isolation of the target compounds using SPE, Soxhlet extraction and PLE and identification and quantification by means of LC–MS. The methodology has also been validated by determining LAS and AES homologues concentrations at ppb level in several water and sediment samples taken from an estuary located at the southwest of Spain.

2. Experimental

2.1. Materials

Methanol, triethylamine and acetonitrile were of chromatography quality, purchased from Scharlau (Barcelona, Spain). Acetic acid, $HgCl_2$, sodium sulfate and formaldehyde 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 2ΦC_{16} LAS internal standard and the commercial LAS mixture were supplied by Petroquimica Española (PETRESA), with the following homologue distribution for the latter: C_{10} (10.9%), C_{11} (35.3%), C_{12} (30.4%), C_{13} (21.2%) and C_{14} (1.1%). Commercial AES mixtures derived from vegetable and petroleum sources were supplied by KAO Corporation (KAO) and Procter and Gamble (P&G), respectively. 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 ethoxylated chains have an average number of 3.4 and 4.2 EO units, respectively.

2.2. Sampling and spiking

The samples were collected on an ebbing tide along the final stage of the estuary of the river Guadalete, which is located in the salt-marsh environment of the Bay of Cadiz (in the southwest of Spain). Three sampling stations were selected: A, located at the mouth of the estuary, and B and C, 6 and 12 km far away from A, respectively. A WWTP which treats the wastewaters of a town of 200 000 inhabitants discharges into the river 2 km upstream from C. Superficial waters were taken using 2.5 l amber glass bottles and adding 4% of formaldehyde. The top 10 cm of the sediment bottom were sampled from a boat by means of a Van Veen grab. All samples were kept at 4 °C during their transport to the laboratory and frozen until their analysis. In the laboratory sediment was dried in a heater at 75 °C until constant weight, and later milled and strained through a 0.63 μm sieve.

One litre of seawater was spiked to 100 ng ml^{-1} and 100 grams of non polluted sediments with 1, 5 and 10 mg kg^{-1} by using commercial standards of LAS (supplied by PETRESA) and AES (supplied by P&G and KAO). For the spiking, wet sediment was mixed by means of a mechanical arm for 24 h with 100 ml of seawater containing the surfactants. The entire mixture was sterilized with 1 g of $HgCl_2$ and kept in darkness to avoid surfactant degradation. Finally amounts of 5 g of these spiked sediments as well as aliquots of 100 ml of spiked seawater were treated in the same way as the environmental samples and analyzed by triplicate to calculate the method recovery values.

2.3. Extraction procedure

Surfactants were extracted from the sediment samples using Soxhlet extraction and pressurized liquid extraction (PLE) by means of an accelerated solvent extraction ASE 200 unit from Dionex. Quantities of dried and sieved sediment samples (5 g) were packed into cellulose thimbles in the case of Soxhlet and mixed together with 15 g of sodium sulfate into steel cells (22 ml) in the case of PLE. Methanol was used as solvent for both types of extraction method, passing through the heated (50, 100 and 125 °C) and pressurized (1500 psi) PLE cells during three cycles of 5 min each and through the Soxhlet thimbles during 5 h. Subsequently the methanolic extracts were evaporated until 1 ml and re-dissolved in 100 ml of water in an ultrasonic bath.

These extracts and the water samples 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 100 ml of sediment extracts. They were then washed with 5 ml of water and eluted with 10 ml of methanol. Finally, the elution was evaporated to dryness and redissolved in 1 ml of a methanol/water 8:2 solution containing 1 mg l^{-1} of C_{16} LAS as internal standard.

2.4. LC–MS analysis

The HPLC system consisted of a Spectrasystem liquid chromatograph with autosampler, with the volume injection set to 100 μl. The chromatographic separation was done using a reversed-phase C-18 analytical column (LiChrospher 100 RP-18) of 250 mm × 2 mm and 3 μm particle diameter from Merck. The detection was carried out using a LCQ ion-trap mass spectrometer (Thermo), equipped with an atmospheric pressure ionization source with electrospray interface (ESI). All extracts were analyzed using ESI full-scan negative ion mode in order to determine LAS, AES and AS, scanning the mass/charge (*m/z*) range between 75 and 800. The following mobile phase was used: acetonitrile/water 80:20 (A) and water with 5 mM acetic acid and 5 mM triethylamine (B). The elution gradient started with 47% A and was increased linearly to 100% A over 40 min and kept isocratic for 10 min. The flow rate was 0.15 ml min^{-1}.

Table 1
Mass/charge (*m/z*) ratios (expressed as 'specific fragment, quasimolecular ion') scanned for the identification of LAS, AES and AS homologues

Homologue	*m/z*	Homologue	*m/z*
C_{10} LAS	183, 297	C_{12} LAS	183, 325
C_{11} LAS	183, 311	C_{13} LAS	183, 339
C_{12} AES n_{EO} = 1–10	97, 309–705 (±44)	C_{12} AS	97, 265
C_{13} AES n_{EO} = 1–10	97, 323–719 (±44)	C_{13} AS	97, 279
C_{14} AES n_{EO} = 1–10	97, 337–733 (±44)	C_{14} AS	97, 293
C_{15} AES n_{EO} = 1–10	97, 351–747 (±44)	C_{15} AS	97, 307
C_{16} AES n_{EO} = 1–10	97, 365–761 (±44)	C_{16} AS	97, 321

The *m/z* ranges are also shown for AES ethoxymers, with a difference of 44 *m/z* units between each consecutive ethoxymer.

Values of other MS parameters were: ion fragmentation energy 40 V, needle tip voltage 4.5 kV, gas stealth flow 60 ml min^{-1} 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, AES and AS and ethoxymers of AES was carried out by monitoring their quasimolecular ions $[M-H]^-$ and their specific fragment ion at *m/z* 183 and 97, respectively. Surfactant concentrations were determined by measuring the peak areas of the quasimolecular ions using external standard solutions (0.5–50 mg l^{-1}) of LAS and AES prepared in methanol/water 1:1 and C_{16} LAS as internal standard (1 mg l^{-1}). In the case of AES, every ethoxymer area corresponding to the same homologue was summed to the others in order to obtain the overall AES homologue concentration. Clean sediment extracts and a methanol/water 1:1 solution were spiked with 1 mg l^{-1} of LAS and AES standards to check the influence of ion suppression (suppression of the analyte signals caused by high concentrations of matrix components) on the MS detection of target compounds.

3. Results and discussion

3.1. Extraction efficiency

By spiking seawater and sediments as indicated above, recoveries have been calculated and shown in Table 2. In the case

Table 2
Recovery percentages (%) and standard deviations (SD) (*n* = 3) obtained for water and sediment spiked with LAS and AES after SPE, Soxhlet + SPE, and PLE + SPE[a]

	SPE	Soxhlet			PLE		
	100 ppb	1 ppm	5 ppm	10 ppm	50 °C	100 °C	125 °C
C10 LAS	123 ± 14	89 ± 18	104 ± 17	82 ± 18	51 ± 2	109 ± 8	125 ± 15
C11 LAS	103 ± 12	103 ± 13	112 ± 12	78 ± 11	51 ± 6	93 ± 8	119 ± 11
C12 LAS	89 ± 13	105 ± 14	109 ± 9	74 ± 8	58 ± 1	82 ± 7	114 ± 10
C13 LAS	85 ± 11	82 ± 7	94 ± 9	65 ± 11	24 ± 3	62 ± 5	81 ± 8
C12 AES	84 ± 8	98 ± 6	81 ± 7	65 ± 9	–	64 ± 6	74 ± 5
C13 AES	94 ± 6	75 ± 9	109 ± 9	82 ± 10	–	–	–
C14 AES	60 ± 4	49 ± 2	61 ± 4	45 ± 5	–	60 ± 7	99 ± 4
C15 AES	70 ± 3	49 ± 9	66 ± 7	62 ± 4	–	–	–
C16 AES	25 ± 2	–	–	–	–	51 ± 8	55 ± 12

[a] Sediments were spiked with 5 ppm of LAS and AES in the case of PLE + SPE.

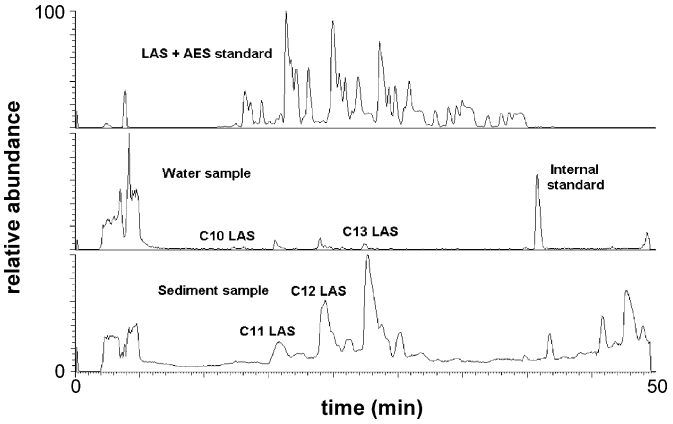

Fig. 1. Full-scan LC/ESI/MS negative ion mode chromatograms corresponding to an LAS + AES standard, a water sample after SPE and a sediment sample after PLE + SPE. Chromatograms were obtained under the specific analytical conditions described in Section 2.4.

of the aqueous samples, SPE employing C_{18} mini-columns has been shown to be a reliable technique for preconcentrating and purifying LAS and AES simultaneously. After spiking seawater with a mixture of commercial LAS (PETRESA) and vegetable (KAO) and petrochemical (P&G) origin AES in order to reach a concentration of 100 ng ml^{-1}, the recovery values varied in the range from 85 to 123% for LAS homologues and from 60 to 94% for AES homologues, with a standard deviation of between 11 and 14 and between 2 and 8, respectively. Lower recoveries (25%) are observed in the case of the C_{16} AES, the homologue containing the longest alkyl chain and, hence, the most hydrophobic one. These values for LAS are very similar to those reported by previous authors employing similar SPE conditions [20,28] but they are also comparable with others presented in previous papers which use a methodology specifically designed for the analysis of AES by means of SAX [15] or C_2 [22] mini-columns.

Soxhlet extraction was performed by spiking sediments with LAS and petrochemical origin AES at three different concentrations. Recovery values between 65 and 112% for LAS and 45 and 109% for AES are reported in Table 2. There are no significative differences between the three spiked concentrations; however the intermediate concentration (5 mg kg^{-1}) appears to show slightly higher values and so this was selected to spike sediment with a mixture of LAS and vegetable origin AES and to extract these surfactants using pressurized liquid extraction (PLE). Data are also presented in Table 2 and the effect of the alkyl chain length in the extraction can be observed for both techniques; the lower recoveries of the longer homologues are probably due to their more hydrophobic character and, consequently, their retention in the sediment as well as in the SPE mini-column. A preliminary test carried out at 50 °C has shown that recovery efficiency for LAS is rather low, with values from 24 to 58%. These results are in accordance with those reported previously by González et al. [29], who also employed this low temperature in PLE to extract LAS from sediments avoiding nonylphenol volatilization. Therefore we decided to increase the extraction temperature to 100 °C in order to obtain a higher recovery. The homologue values from 62 to 109% obtained in a 15 min extraction can be compared with that previously determined by Ding and Fann [32] in a 40 min extraction using laboratory-made PLE equipment instead of a commercial ASE 200 unit. Finally 125 °C was found to be the optimal temperature for extracting LAS from sediments, giving recovery values from 81 to 125%. In the case of AES there are no previous studies on the optimization of their extraction from sediments, but it can be observed from the data summarized in Table 2 that there is also an increase in their extraction efficiency values from 51 to 64% at 100 °C to 55–99% at 125 °C.

Overall the Soxhlet extraction with methanol during 5 h and the use of the same solvent in an ASE unit at 125 °C and 1500 psi during 15 min have proved to constitute reliable, efficient and reproducible methods for the extraction of anionic surfactants in sediments. For a large amount of samples, however, PLE should be preferred since it is a less time- and solvent-consuming technique.

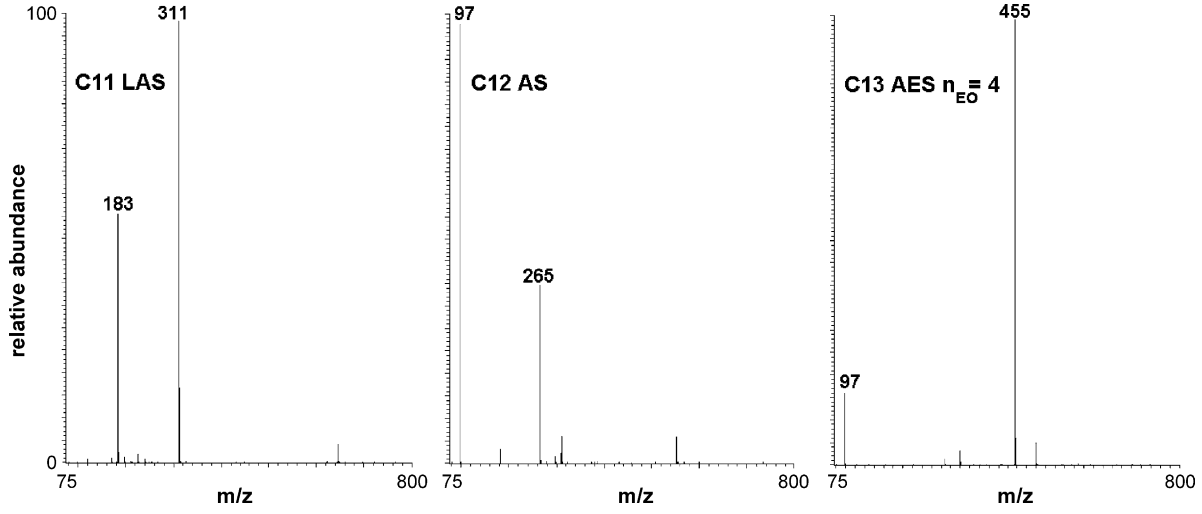

Fig. 2. Full-scan LC/ESI/MS negative ion mode mass spectra of C_{11} LAS, C_{12} AS and C_{13} AEOs with $n_{EO} = 4$. Mass spectra were obtained under the specific analytical conditions described in Section 2.4.

3.2. Separation, calibration graphs and limits of detection

Fig. 1 shows the chromatograms resulting from applying the optimized methodology described above to a mixture of LAS and AES standards and to water and sediment samples collected in the Guadalete estuary. Homologues from C_{10} to C_{13} LAS are easily detected in environmental samples in the total ion current chromatograms shown in this figure due to their higher abundance with respect to AES and to the efficiency of SPE and PLE extraction and isolation procedures. To differentiate all the target compounds is not feasible because LAS and AES have homologues with the same length of alkyl chain and it is not possible to achieve a complete separation between these two surfactants with the octadecyl-silica column employed. However, as shown in mass spectra in Fig. 2, the use of the LC/MS technique allows us to distinguish them because of their specific fragment ions, *m/z* 183 for LAS [14,23] and *m/z* 97 for AES [14,24], and quasimolecular ions $[M-H]^-$ represented in Table 1.

Fig. 3 shows several extracted chromatograms from a spiked sediment sample selecting LAS specific and quasimolecular ions, where an effective separation between C_{10} and C_{13} homologues can be observed. There are several peaks per homologue which contain different LAS isomers being eluted sequentially. Thus, the more hydrophobic isomers having the benzene closer to the end of the chain (known as external isomers and named as $2,3\Phi C_n$) show higher retention times than the rest (internal isomers $4,5\Phi C_n$). C_{16} LAS is the internal standard, a homologue containing one pure external isomer ($2\Phi C_{16}$ LAS) so only one peak appears. Separation of the AES and AS homologues is also feasible using their specific and quasimolecular ions. The extracted chromatograms presented in Fig. 4 show the efficiency of the HPLC conditions employed in separating the homologues from C_{12} to C_{15}. It can be observed that it is also possible to discriminate between $n_{EO}=1$ to $n_{EO}=10$ AES ethoxymers. These ethoxymers appear successively as individual peaks by scanning their corresponding quasimolecular ion.

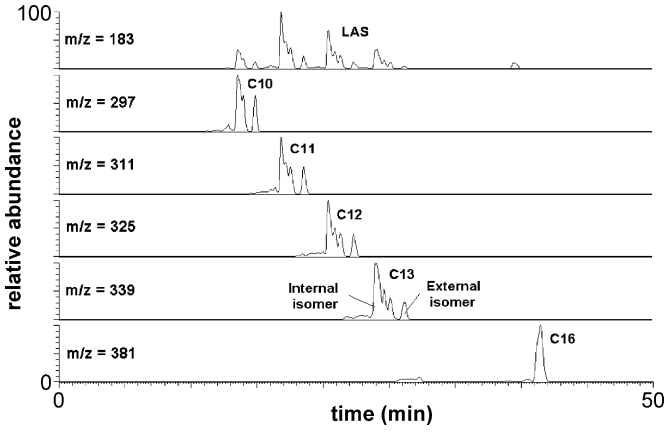

Fig. 3. Extracted LC/ESI/MS negative ion mode chromatograms showing the identification and separation of LAS homologues by means of their quasimolecular and specific fragment *m/z* = 183 in a spiked sediment sample after PLE + SPE. Chromatograms were obtained under the specific analytical conditions described in Section 2.4.

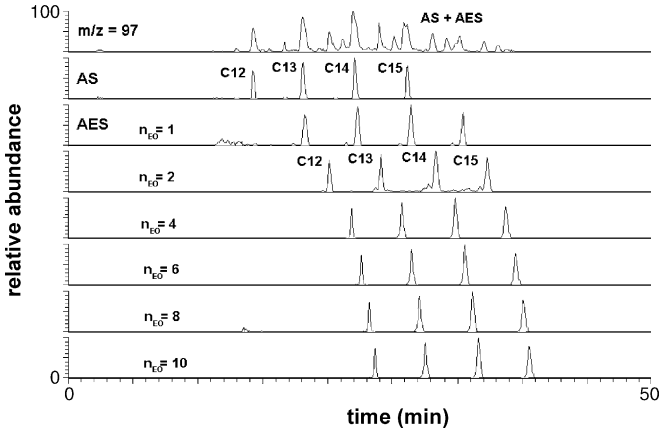

Fig. 4. Extracted HPLC/MS ESI negative ion mode chromatograms showing the identification and separation of AS homologues and AES homologues and ethoxymers by means of their quasimolecular and specific fragment *m/z* = 97 in a spiked sediment sample after PLE + SPE. Chromatograms were obtained under the specific analytical conditions described in Section 2.4.

The calibration curves were obtained for each homologue of the studied compounds assuming the same response for every AES ethoxymer and LAS isomer. The behavior of all compounds was linear in a range between 0.1 and 50 mg l^{-1}, with r^2 values above 0.999 for each homologue. The limit of detection was calculated using a signal-to-noise ratio of 3:1, and was found to be in the range from 0.1 to 0.5 ng ml^{-1} of each homologue in water samples, and from 1 to 5 ng g^{-1} in sediment samples. The influence of ion suppression was determined as a reduction of less than 5% of the signal intensity for each analyte.

3.3. Estuarine samples

Table 3 shows the concentration values of anionic surfactants obtained for the water and sediment samples collected in the Guadalete estuary. Total LAS concentration ranges from 538 to 1014 ng g^{-1} in sediments and from 25.1 to 64.4 ng ml^{-1} in waters. These values are of the same order of magnitude as others previously reported in this area [9,14] and in others estuaries on

Table 3
LAS and AES + AS homologue concentrations detected in water (ng ml^{-1}) and sediment (ng g^{-1}) samples along the Guadalete estuary[a]

	Water			Sediment		
	A	*B*	*C*	*A*	*B*	*C*
C10 LAS	9.3	14.0	19.9	26	68	58
C11 LAS	8.9	16.1	26.6	126	265	236
C12 LAS	4.5	7.1	12.0	170	362	320
C13 LAS	2.4	3.5	5.9	216	319	339
ΣLAS	25.1	40.8	64.4	538	1014	953
C12 AES	2.7	4.3	7.4	30	71	196
C13 AES	n.q	n.q	n.q	52	66	105
C14 AES	1.8	2.7	4.4	85	172	225
C15 AES	n.d.	n.d.	n.d.	n.d	n.d	n.q
C16 AES	n.d.	n.q.	n.q.	n.q.	2	10
ΣAES	4.5	7.0	11.9	168	311	536

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

the Spanish coasts [10]. In the case of AES, information about their environmental levels is extremely scarce so it is not possible to compare their values found in sediments from this zone (from 168 to 536 ng g^{-1}) with other locations, although they seem to be close to those reported for LAS, probably due to their similar production rate nowadays [2–4]. AES concentrations in water are in the range from 11.9 to 4.5 ng ml^{-1}. In a previous study made by Pojana et al. [13] AES values were below detection limits, so this is the first time to our knowledge that AES have been detected in a European river by means of a specific methodology and their concentration values are reported. These data are comparable to those determined in several rivers of the U.S.A. [15,22].

An increase in the concentrations of both surfactants in water and sediment can be followed from the mouth of the estuary (sampling station A) to the last station C. This is most probably due to the wastewater discharges of the WWTP located up-stream as LAS and AES levels decrease down-stream due to dilution, sorption-precipitation and degradation processes [9]. It is also noticeable that there is an enrichment in longer alkyl chain homologues for LAS and AES in sediments when compared with standards and water samples due to their greater hydrophobicity and affinity for the organic matter of the sediment [9,14]. AES homologues with an alkyl chain with an even number of carbon atoms (those from vegetable sources) are occurring at higher concentrations than those with odd number (of petrochemical origin) because of their greater use in Europe (71% versus 31%, respectively) [3,4].

4. Conclusions

The proposed method permits the simultaneous analysis of the most used anionic surfactants (LAS, AES and AS) in water and sediment samples with high selectivity and reproducibility, in a simple and less time consuming way when compared with older specific methods for the determination of each surfactant separately. Further it is possible to differentiate among the various LAS, AES and AS homologues and AES ethoxymers. In this respect, the most recently developed techniques such as PLE and LC–MS have been demonstrated to be very useful as powerful tools for performing a faster and easier environmental monitoring of these compounds on which, in some cases like AES and AS, there is relatively little information available. LAS and AES concentration values found at environmental samples are comparable due to their similar production rates.

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