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Determination of linear alkylbenzensulfonates in aqueous matrices by ion-pair solid-phase microextraction–in-port derivatization–gas chromatography–mass spectrometry

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Abstract

Trace determination (low ng/ml) of linear alkylbenzensulfonates (LASs) in water was achieved by solid-phase microextraction (SPME) of ion-pairs formed with tetrabutylammonium. This ion-pairing reagent served two purposes. First, it allowed the extraction of LAS with the polydimethylsiloxane fiber by counterion association and second, the derivatization of the formed LAS ion pairs in the GC injection port at 300 °C to form the corresponding sulfonated butyl esters. The methodology developed allows the isomer specific determination of LAS at low detection limits (0.16–0.8 ng/ml), depending on the alkyl chain lengths of LASs with RSDs of 10–12%. Furthermore, the developed methodology was applied to urban wastewater and sea water and compared with a solid-phase extraction (SPE) method (e.g. C_{18} and strong anion-exchange sorbent) to obtain concordant values for urban wastewater. Moreover, the developed SPME methodology overcame the procedural blank and matrix-dependent recoveries found in the SPE methodologies at low LAS concentrations.

Keywords: Water analysis; Derivatization, GC; Environmental analysis; Alkyl benzenesulfonates, linear; Surfactants

1. Introduction

Anionic surfactants account for about 50% of surfactant use in the European Union (EU) and about 60% in the USA; their global production was 3.0×10^9 kg per year in 1998 [1,2]. Among anionic surfactants, linear alkylbenzensulfonates (LASs) are the most used class of anionic surfactants on the global market. Commercial LASs are composed of a linear alkyl chain consisting of 10-13 carbon atoms, a phenyl ring which is randomly distributed in all possible positions (except 1-phenyl) and a sulphonate group in *para* position. Although LASs are rapidly biodegraded under aerobic conditions, due to the large amount released, they are widespread in the aquatic environment varying in concentration range from low μg/l in pristine waters to tenths of mg/l in wastewater [3].

Species-specific determination of LASs in aqueous matrices is difficult owing to their being complex mixtures of both homologues and isomers. Although LASs can be determined directly by liquid chromatography (LC) without any derivatization step, partial resolution is obtained between isomers and the determination is usually carried out the homologue level using ultraviolet (UV) [4–6], fluorescence (FL) [7–9] and mass spectrometry (MS) [9,10] detection. Gas chromatography (GC) allows their isomeric

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resolution but owing to their lack of volatility, a derivatization step such as the formation of either sulfonyl chlorides [19] or alkyl esters is unavoidable [15,16,20–22].

LAS determination in water matrices usually involves a preconcentration step using solid-phase extraction (SPE) with C_8 [11,12], C_{18} [13,14], graphitized carbon [15,16], polymeric [17] and/or ion-exchange materials [11,18] prior to LC or post-derivatization GC determination.

Although solid-phase microextraction (SPME) has been successfully applied for a wide range of organic compounds [23], few papers related to SPME anionic surfactant determination and their degradation products have been published [24,25]. LASs determination by SPME–LC–FL was reported previously [26] in wastewater samples from a wastewater plant, but the method was unsuitable for quantification. The use of ion-pair (tetramethylammonium) SPME to convert long-chain fatty acids into their volatile methyl esters via in-injector derivatization was proposed by Pan and Pawliszyn [27]. Ion-pair extraction is a method for partitioning of ionic compounds with the aid of counter-ions of opposite charge [28]. A simple reaction of the tetrabutylammonium salt of sulfonates in the hot injection port of the GC to form the butyl esters has been used for quantitative determination of LASs [20–22].

The aim of this work was to develop a rapid, selective, sensitive and solvent-free method for the analysis of isomeric LASs in environmental aqueous samples by SPME. Direct SPME sampling has been used to preconcentrate LASs as ion-pairs. It allows the extraction of ionic analytes as hydrophobic species, thus increasing their fiber coating/water distribution coefficient, improving the efficiency of SPME that can be followed by post-derivatization GC for their quantitation.

2. Experimental

2.1. Materials

The following reagents were obtained from Sigma–Aldrich (Steinheim, Germany) and used as received: tetrabutylammonium hydrogensulfate (97%), glacial acetic acid (99.99%), Sea Salts and 4-octylbenzenesulfonic acid (97%). Water and methanol (LiChrosolvliquid chromatography grade), hydrochloric acid (25% for analysis grade) and LiChrolut columns for SPE RP-18 (500 mg) were from Merck (Darmstadt, Germany), lithium perchlorate from Hucoa-Erlöss (Barcelona, Spain). Commercial LASs with a low dialkyltetralin sulfonate (DATS) content (<0.5%) were supplied by Petroquímica Española in a single standard mixture with an approximate composition of the different homologues as follows, C_{10} 3.9%, C_{11} 37.4%, C_{12} 35.4% and C_{13} 23.1%. Polydimethylsiloxane (PDMS, 100 and 7 μm) fibers were from Supelco (Bellefonte, PA, USA), SPEC 3 ml strong anion-exchange (SAX) columns from ANSYS (Irvine, CA, USA).

LAS standard solution and 4-octylbenzenesulfonic acid (used as surrogate) were diluted in water to prepare a working standard solution of 1807 μg/ml (as total LASs) and 1844 μg/ml, respectively. Tetrabutylammonium hydrogensulfate was diluted in water at a final concentration of 0.5 *M*. Artificial sea water was prepared, diluting 1.75 g of sea salt in 50 ml of water. Stock and working solutions were stored at 4 °C.

Influent (following a septic sedimentation tank) and effluent urban wastewater samples from a constucted wetland serving 200 inhabitants (Les Franqueses, Catalonia, Spain) were analysed without any previous treatment. Samples were stored in polypropylene screw cap vials of 50 ml and frozen (−20 °C) after sampling. Sea surface microlayer samples from the Barcelona coastal area (Spain) were collected using a metal screen sampler device [29], and their corresponding underlying seawater were collected and stored under refrigerated conditions (4 °C) in Pyrex borosilicate brown glass bottles prior to analysis.

2.2. Instrumental analysis

2.2.1. Gas chromatography–mass spectrometry (GC–MS)

GC–MS analysis was carried out using a Trace GC–MS 2000 (Thermo Finnigan, Manchester, UK) system with Xcalibur software-based data acquisition. A BPX5 (30 m×0.25 mm I.D.) column with 0.25 μm film thickness (SGE, Ringwood Australia)

was used. The gas chromatographic conditions were as follows: the initial oven temperature was 110 °C for 3.0 min, then programmed to 200 °C at 20 °C/min, and then from 200 °C to 310 °C at 5 °C/min with a final hold time of 1.0 min. The injector temperature was 300 °C, in the splitless mode (3 min) and desorption time for the SPME fiber was 3 min. The MS ionization potential was 70 eV, the ionization current 350 μA, the ion source temperature 200 °C and the transfer line temperature 280 °C. Scans from 50 to 350 m/z at 1.0 scan s^{-1} were acquired in order to establish the homologue LASs retention time $[M\text{-}55]^+$ (i.e. n-C_8-LAS $m/z = 271$, C_{10}-LAS $m/z = 299$, C_{11}-LAS $m/z = 313$, C_{12}-LAS $m/z = 327$, C_{13}-LAS $m/z = 341$) (Fig. 1). LASs quantification was carried out in the single ion monitoring (SIM) mode using the fragment ions at m/z 91, 171, 172, 185 and 271 with 0.08 s dwell time from 7 to 25 min. Quantitation of LASs was based on the sum of the ion currents corresponding to m/z 171, 172, 185 and 271. LAS calibration curves were computed as a ratio between the LAS standard area to C_8-LAS surrogate. The correlation between total, individual homologue, and isomeric

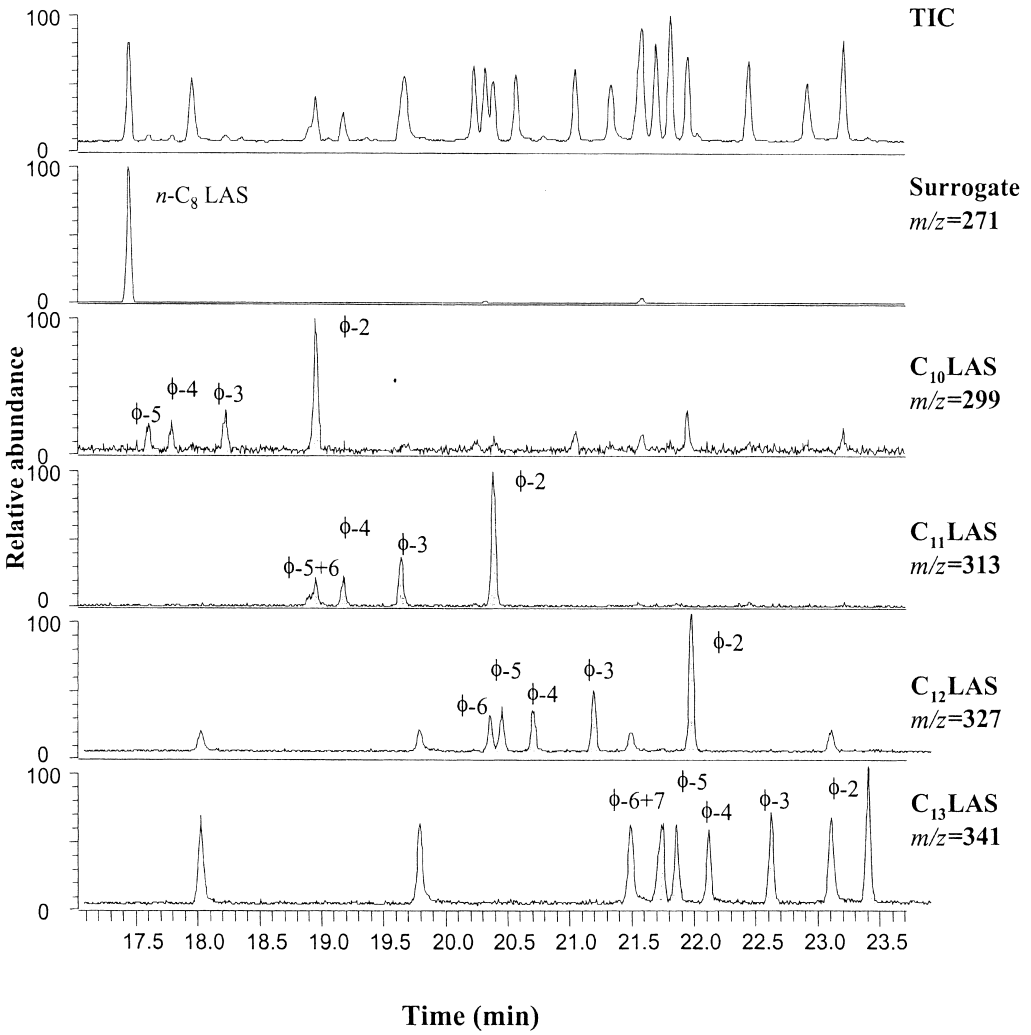

Fig. 1. LAS ion-pair SPME–in-port derivatization–GC–MS chromatogram (total ion chromatogram, TIC) of a LAS standard solution and n-C_8-LAS (surrogate), showing selected ion chromatograms for LAS homologues $[M\text{-}55]^+$.

LAS concentration was determined by linear regression with typical r^2 values of 0.987–0.995. The SPME holding device was purchased from Supelco Spain.

2.2.2. Liquid chromatography (LC)

LC with UV/fluorescence detection was used for comparison with SPME–GC–MS. LC separations were performed with a liquid chromatograph (Shimadzu, Kyoto Japan) equipped with a Rheodyne high-pressure injection valve (Rhonert Park, CA, USA) and 20 μl loop. The system consisted of a LC-10AT pump, an SPD-10AV dual UV detector ($\lambda = 193$, 223 nm), a SpectraSystem (Thermo Separation Products, San Jose, CA, USA) FL3000 fluorescence detector (high-purity quartz flow cell, 8 μl volume), SCL-10A controller and Class-VP software. The fluorescence detector was operated at 226 and 296 nm of excitation and emission wavelengths, respectively. Chromatographic separation was done using a reversed-phase C_8 column Hypersil BDS C_8 5 μm, 150×2 I.D. mm (Shandon, UK) at ambient temperature with a flow-rate of 0.4 ml/min. Gradient elution was performed with a methanol–water (80:20) mobile phase with 1% of $LiClO_4$. All solvents were filtered through a 0.4 μm membrane.

2.3. SPE procedure

An off-line SPE was used for cleanup and preconcentration of the water samples prior to LC–UV/FL determination. A portion (25 ml) of unfiltered, acidified (pH 3, HCl 25%) water sample was previously spiked with C_8-LAS as surrogate (500 μl, 10 μg/ml). Samples were extracted and concentrated by SPE using, consecutively, hydrophobic SPE RP-18 (500 mg) and SAX minicolumns, following the previoously described procedure [30]. Recoveries, determined by spiking a known amount of LASs into water matrices ranged from 71 to 94% depending on the LASs homologue. Procedural blanks were obtained for the whole analytical procedure and were below 2.5 ng/ml.

2.4. SPME procedure

The main parameters that affect the SPME process (i.e. fiber selection, extraction time profile, desorption time and temperature, and ionic conductivity) were optimized using GC–MS. Before the initial analysis, fibers were conditioned for 60 min at 250 °C for the 100 μm PDMS and 3 h at 320 °C for the 7 μm PDMS. After the conditioning process, a fiber blank was run to confirm that not extraneous peaks co-eluted with the analytes. Samples for method development were prepared by adding 5 ml of HPLC water or ''artificial'' seawater into a 7 ml vial, sealed with a PTFE septum, stirred with a 10×3 mm stir bar at 1100 rev./min. Microliter amounts of the working standard solution of analytes were spiked into the extraction vial to obtain the following respective concentrations, total LASs (180 ng/ml) and C_8-LAS as surrogate (184 ng/ml). A total of 100 μl of tetrabutylammonium hydrogensulfate (0.5 M) was added. The absorption time profile was obtained by exposing the fiber to the water solution for 10, 20, 30, 40 and 60 min. Desorption times were 1, 2, 3 and 5 min. The linearity was evaluated from 1 to 2500 ng/ml for total LASs. Detection (LOD) and quantitation (LOQ) limits were calculated from low concentration value calibration curves by considering the peak area corresponding from three ($LOD = 3\sigma$) to ten ($LOQ = 10\sigma$) times the signal-to-noise ratio of a procedural blank.

3. Results and discussion

3.1. Optimization of the SPME procedure

3.1.1. Fiber selection

Fiber selection was limited by the desorption temperature during the in-port derivatization step (see below). Among the commercial fibers available, only PDMS (7 μm), polyacrylate (85 μm) and Carboxen–PDMS fibers can withstand temperatures above 300 °C. Polyacrylate fiber was dismissed due to lack of stability of the fiber itself [23]. Carboxen–PDMS fiber was also not considered because it is only suitable for small volatile compounds and its pore size excludes the analytes to be determinated. Furthermore, molecules larger than C_{12} are strongly retained on the Carboxen surface, and their desorption is difficult [23]. In a previous work [26], quantitative determination of LASs by SPME–LC–

FL was carried out using a Carbowax–template resin fiber (CW–TPR). This fiber is not suitable for the analytical approach developed in this study (used for LC). The Carbowax phase is oxidized in the presence of air, oxygen, and co-extracted organic matter at elevated temperatures (i.e. max. temperature 265 °C), reducing the life-time of the fiber. The PDMS fiber has proved to be the most suitable phase for LAS-ion pair species (Fig. 1). The LAS-ion pair formation reduces the polarity of LASs and improves the extraction itself. PDMS has been demonstrated to be the most robust fiber and it is able to withstand high injector temperature, up to 300 °C, a mandatory requirement for in-port LAS derivatization. PDMS (7 μm) fiber has been tested successfully for LAS determination but it is limited by its low capacity compared to the PDMS (100 μm) fiber. The maximum recommended temperature for the PDMS (100 μm) fiber is 280 °C, which is lower than the optimum temperature for LAS in-port derivatization (see below). However, more than forty determinations with the same PDMS (100 μm) fiber have been done at 300 °C in the injector port, without any fiber damage. This can be achieved due to the robustness of the fiber, by avoiding contact with oxygen at high temperature and the short residence time of the PDMS (100 μm) fiber in the injector port (3 min). Following the recommendations cited above, maximum operating temperature can be increased to 300 °C for PDMS (100 μm) fiber. Then, this fiber is suitable for trace analysis of LASs (μg/l) and the PDMS (7 μm) fiber for more contaminated samples (mg/l).

3.1.2. Desorption temperature

Injector temperature is an important parameter to be optimized in LAS SPME analysis coupled with the in-port derivatization process. Different desorption temperatures (260–320 °C) were evaluated and Fig. 2 shows the LASs response as a function of derivatization temperature. LAS derivatization yield increases until 300 °C in concordance with previous work [20–22] on off-line LASs in-port derivatization. No improvements in the derivatization yield is obtained by increasing the injector temperature above 300 °C.

3.1.3. Desorption time

Different desorption times (2.0, 3.0 and 5.0 min in splitless mode) were evaluated, with re-injection of the fiber for check carryover, confirming that 3 min was sufficient for quantitative desorption of the analytes at low concentrations. Using the PDMS (100 μm) fiber at high LAS concentrations (>2 ng μl^{-1} as total LASs), a carryover effect was detected (less than 5% of the previous injection) but employing PDMS (7 μm) fiber this problem was not detected.

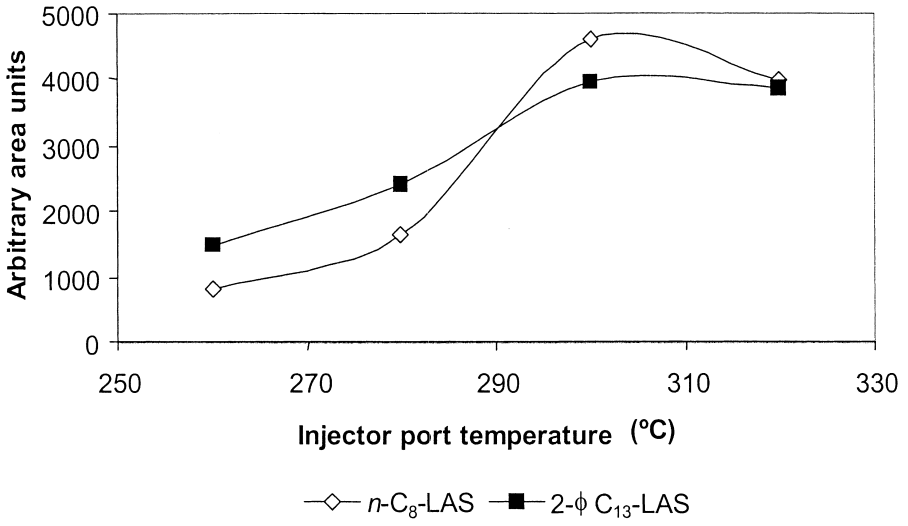

Fig. 2. Effect of injector temperature on the response factor for some LAS isomers in the ion-pair SPME–in-port derivatization procedure.

Table 1
LOD and LOQ values obtained by SPME–in-port derivatization–GC–MS for LAS isomeric determination with PDMS fiber (100 and 7 μm) evaluated in HPLC water and sea water matrices

PDMS	Isomer[a]	HPLC water		Sea water	
		LOD (ng/ml)	LOQ (ng/ml)	LOD (ng/ml)	LOQ (ng/ml)
100 μm	$C_{10\text{-}2}$	0.80	2.40	1.00	3.00
	$C_{11\text{-}3}$	0.70	2.10	0.90	2.70
	$C_{12\text{-}2}$	0.35	1.05	0.67	2.01
	$C_{13\text{-}3}$	0.16	0.48	0.45	1.34
7 μm	$C_{10\text{-}2}$	4.00	12.00	5.00	15.00
	$C_{11\text{-}3}$	3.50	10.50	1.50	13.50
	$C_{12\text{-}2}$	1.75	5.25	3.35	10.05
	$C_{13\text{-}3}$	0.80	2.39	2.23	6.70

[a] Isomeric notation C_{x-y} as follows: x, the total carbon number and y, the carbon number where phenyl is substituted.

3.1.4. Extraction temperature

Extraction temperatures at 25, 30 and 40 °C were evaluated. Extraction efficiency of LASs decreased dramatically at elevated temperatures. Therefore, room temperature (25 °C) was selected.

3.1.5. Salting out effect

Salt addition decreases the extraction efficiency of LASs under the optimum conditions. However, an artificial sea water matrix was tested in order to determine if LASs determination can be carried out in sea water samples (Table 1).

3.1.6. Extraction profile

The extraction time profile for different LAS-ion pair isomers for PDMS (100 μm) fiber is shown in Fig. 3. As illustrated, LASs extraction reached equilibrium at 30 min. Most papers described the effectiveness of high stirring rates during SPME extraction procedure. Therefore, a stirring rate of 1100 rev./min was chosen for all experiments. The extraction equilibration time is adequate for GC analysis (28 min) allowing a new extraction while the GC run is carried out, reducing the total analysis time. The LAS ion-pair PDMS extraction profile reached the equilibrium faster than LAS CW–TPR where 120 min was necessary [26].

3.1.7. Figures of merit of the analytical procedure

Once the SPME–in-port derivatization–GC–MS

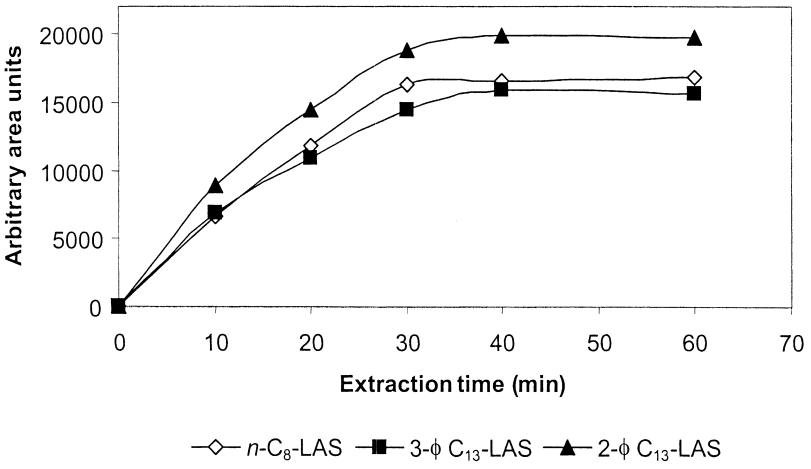

Fig. 3. Extraction time profile of some LAS isomer-ion pairs using PDMS (100 μm) fiber.

procedure was optimized, the analytical quality parameters (i.e. LOD, LOQ, precision, linearity, reproducibility and repeatability) were evaluated. The linearity of the response in the SIM mode was acceptable from 0.5 to 2.4 ng/ml (depending on LAS isomers) to 200 ng/ml with $r^2 = 0.990–0.998$ for each isomeric LAS. Table 1 shows the LOD and LOQ for the isomeric LASs evaluated. When the alkyl chain length of LASs was increased, their extraction improved, yielding the lowest LOD for the C_{13} LAS isomers (0.16 ng/ml). HPLC water and artificial sea water were used as solvents for the calibration curves, and no traces of LASs were found. This blank level cannot be achieved for LAS trace analysis when off-line SPE is used as preconcentration step [31,32]. RSD was 11.0% for interday analysis ($n = 10$) and the repeatability as RSD value was 8–10.0% ($n = 5$). When urban wastewater and sea surface microlayer were analyzed, the RSD value ($n = 3$) was similar, 10–12%. An external calibration (without using surrogate) gave an unacceptable correlation coefficient ($r^2 \leq 0.75$) for all the analytes evaluated. These evidences point out the need for the use of a surrogate for quantitative analysis of LASs with SPME–in-port derivatization–GC–MS. This approach avoids exhaustive extraction, clean-up steps, solvents, etc. diminishing significantly the total analysis time compared to conventional methods. The same PDMS fiber was used to perform more than 40 analyses without any significant damage.

SPME–GC–MS of LASs exhibit advantages compared to the off-line procedure. Off-line LASs in-port derivatization is carried out in the split mode (split ratio 1:7) which worsened the LOD. The low selectivity achieved by chloroform extractions required a routine replacement of the inlet liners every 20–25 analyses. Moreover, injection of 1 μl of trifluoromethylphenylammonium hydroxide (0.2 *M*) was suggested to minimize any potential sample carryover into the next injected sample (increasing the analysis time) [20–22]. Off-line, large-volume LAS injection was reported [15] in order to improve LOD, but exhibited drawbacks similar to the ones cited above. The developed SPME methodology overcame these problems and achieved higher selectivity than the off-line procedure, by minimizing carryover, avoiding the use of glass wool and eliminating the need to replace the glass liner insert.

3.2. Real sample analysis

3.2.1. Application to urban waste water matrices

Urban waste water samples were analyzed applying the analytical methodology developed and compared with an established method (SPE–off-line LC–UV/FL). For this particular matrix, FL was used for quantitation because the analytical conditions were more selective than the ones used in UV. LAS SPME determination is in agreement with the SPE–LC/FL values after recovery corrections. The RSD for reproducibility of SPE–LC–FL was 18% ($n = 5$) and there was no statistical difference ($P = 0.02$) between the two methodologies. However, LAS homologue determination by SPE–LC–FL is strongly matrix-dependent yielding random recoveries [31,32]. SPME does not present this drawback because it is a non-exhaustive extraction. SPE–LC–FL analysis permits homologue LAS determination, but not isomer distribution, which is achieved only by GC. Knowledge of the actual chain length distribution is sometimes required, as in determination of biodegradability. It might be also important to know what portion of the LASs is the 2-phenyl isomer. The 2-phenyl isomer comprises about 27–30% of alkylbenzenes produced by $AlCl_3$-catalyzed alkylation, but only 15–24% of alkylbenzenes from HF-catalyzed alkylations (2-phenyl LAS isomers are more water soluble than the other isomers) [2]. The methodology developed allows an assessment of the LAS removal efficiency of the constructed wetland systems (see Fig. 4).

3.2.2. Application to sea surface microlayer/underlying seawater samples

The developed analytical methodology was applied to seawater samples in order to determine the LAS enrichment factor at the sea surface microlayer. As it is shown in Table 2, low LAS concentrations were found in both the sea surface microlayer and the underlying seawater. However, it was possible to determine the enrichment factors. The LAS concentrations reflect the heterogeneity of these samples

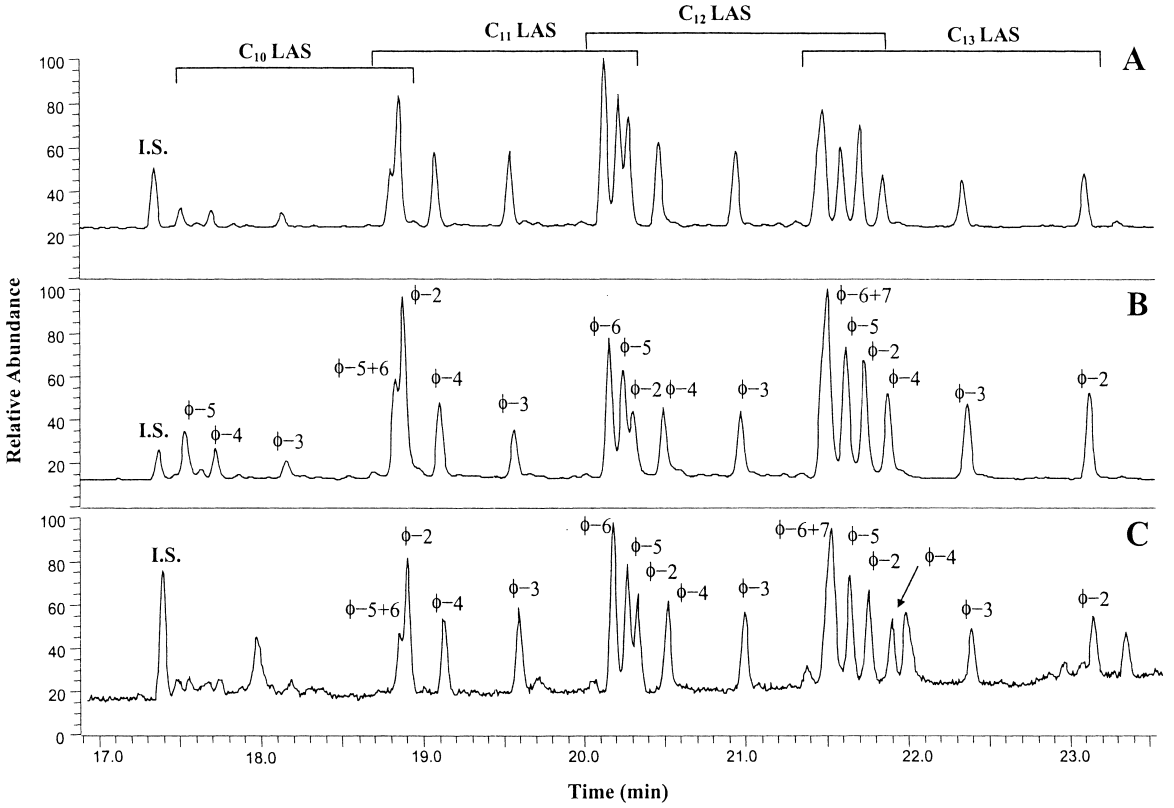

Fig. 4. SPME–in-port derivatization–GC–MS reconstructed selected ion chromatograms ($m/z = 171 + 185 + 271$) showing isomeric separation of (A) LAS standard (B) urban waste water and (C) sea surface microlayer samples. The surrogate n-C_8-LAS is indicated (I.S.). The notation ϕ-x means the carbon number where phenyl is substituted.

[33]. Currently, large amounts of sea surface microlayer are required to determine LASs, affecting the sampling process. The low LAS concentration present in sea water matrices requires a low procedural blank, which is difficult to attain with conventional procedures [31,32]. The methodology developed, improves conventional techniques in terms of sample volume (5 ml), analysis time and blank level.

4. Conclusion

LAS ion pair SPME–in-port derivatization–GC–MS has been demonstrated to be a reliable technique for determination of LASs isomeric in aqueous environmental samples at low concentration levels (i.e., 0.5 ng/ml for C_{13}-LAS). The methodology developed gave comparable results to conventional techniques such as SPE–LC–FL for wastewater samples. Moreover, SPME of LAS offered improved performance in comparison to conventional techniques in terms of procedural blank, analysis time, sample volume, recoveries and elimination of solvent usage during the analytical procedure. Moreover, it eliminates the drawbacks of off-line LAS ion-pair in-port derivatization methodology. Furthermore, it can be used as a rapid analytical methology to obtain detailed information about the sources, behavior and fate of LASs in environmental samples.

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Table 2
LAS isomer concentration distributions in surface microlayer (ML) and underlying (ULW) seawater samples by SPME–in-port derivatization–GC–MS

		Samples					
		I		II		III	
		ML (ng/ml)	ULW (ng/ml)	ML (ng/ml)	ULW (ng/ml)	ML (ng/ml)	ULW (ng/ml)
Isomers	$C_{11\text{-}2}$	9	ND[a]	ND	ND	ND	ND
	$C_{11\text{-}3}$	4	ND	ND	ND	ND	ND
	$C_{11\text{-}4}$	5	ND	ND	ND	ND	ND
	$C_{11\text{-}5+6}$	4	ND	ND	ND	ND	ND
	$C_{12\text{-}2}$	8	3	2	ND	3	3
	$C_{12\text{-}3}$	6	3	2	ND	3	3
	$C_{12\text{-}4}$	6	2	2	ND	3	3
	$C_{12\text{-}5}$	10	5	4	ND	7	4
	$C_{12\text{-}6}$	12	6	4	ND	7	5
	$C_{13\text{-}2}$	8	4	5	4	6	4
	$C_{13\text{-}3}$	7	3	5	4	5	5
	$C_{13\text{-}4}$	7	3	5	4	5	5
	$C_{13\text{-}5}$	9	6	5	5	6	7
	$C_{13\text{-}6+7}$	15	6	6	5	10	7
Homologues	C_{11}	22	ND	ND	ND	ND	ND
	C_{12}	42	19	14	ND	23	18
	C_{13}	46	22	26	22	32	28
LASs (total)		110	41	40	22	55	46
Enrichment factor			2.7		1.8		1.2

[a] ND = Not detected.

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