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Journal of Chromatography A, 889 (2000) 211–219

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Handling of marine and estuarine samples for the determination of linear alkylbenzene sulfonates and sulfophenylcarboxylic acids

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Abstract

Due to the physicochemical properties of linear alkylbenzene sulfonates (LAS), an anionic surfactant, it is difficult to obtain representative samples from sampling sites. Further, the high biodegradability of these compounds makes it necessary to study their biodegradation intermediates, sulfophenylcarboxylic acids (SPC) that do not have a surfactant character and show a different behavior. A procedure for determining and quantifying LAS and SPC in different environmental matrices by Soxhlet and solid-phase extractions and high-performance liquid chromatography is presented. The recoveries varied in the range from 85 to 102% for the water samples, and from 75 to 105% for sediment samples, with a standard deviation of between 1 and 7, and 2 and 11, respectively. Detection limits obtained were in the range from 5 to 10 $\mu g\ kg^{-1}$ for sediment samples (10 g) and from 0.2 to 0.4 $\mu g\ l^{-1}$ for water samples (250 ml). The method was applied to the simultaneous determination of LAS (C_{10}–C_{13}) and SPC (C_4–C_{13}) homologues in water, sediment and interstitial water collected from different areas of Spain.

Keywords: Water analysis; Environmental analysis; Extraction methods; Marine sediments; Surfactants; Alkylbenzene sulfonates, linear; Sulfophenylcarboxylic acids; Carboxylic acids

1. Introduction

Today linear alkylbenzene sulfonate (LAS) is the anionic surfactant most widely used in the formulation of detergents and other cleaning products. The annual world consumption of LAS is approximately $2 \cdot 10^9$ kg per year [1]. The commercial product is a mixture of homologues, most of them with chain lengths of between 10 and 13 carbon atoms (Fig. 1a). Each of these homologues consists of a varying number of positional isomers.

Many studies have been conducted aimed at understanding the distribution of LAS among the various environmental compartments to which it has access [2–5]. In recent decades, much research has been conducted to develop new analytical techniques for the quantification of this surfactant and its degradation intermediates (Fig. 1b) sulfophenylcarboxylic acids (SPC). Although there have been relatively few studies of LAS in marine environments, its behavior is known generally [5–7], since

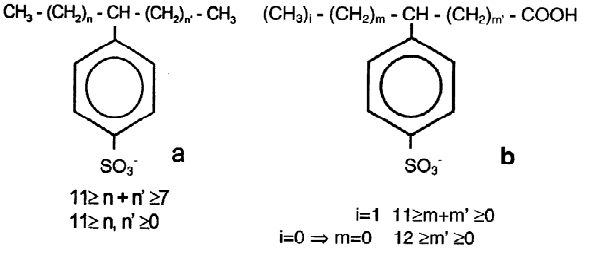

Fig. 1. General chemical structures of the linear alkylbenzene sulfonates (a) and the sulfophenyl carboxylate compounds (b).

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0021-9673/00/$ – see front matter
PII: S0021-9673(00)00569-0

the question of the analysis of its different homologues and isomers has been resolved using solid-phase extraction [8,9] followed by liquid chromatography (LC) [3,7,10–12], coupled with a variety of detection systems. The same cannot be said for its degradation intermediates, mainly for the following reasons:

(i) Studies carried out in wastewater treatment plants and in fresh water have confirmed rapid degradation kinetics for LAS [2,13]. This means that the half-life of the degradation intermediates is short.

(ii) Few techniques exist for marine origin samples (water, interstitial water and sediment), which provides high recovery rates for all the SPC homologues [14–16].

(iii) Detection by fluorescence is very sensitive and specific for LAS [8,17,18]. However, the complexity of SPC mixtures and the lack of reference standards currently limit the applicability of HPLC with UV-fluorescence (FL) detection methods [3].

Various studies are currently being conducted in the Bay of Cádiz (SW Spain), a zone where untreated municipal waste waters have direct access to the marine medium. LAS show a non-conservative behavior due to intense biodegradation, to sorption and the settling of material in suspension [5]. In these studies, the longer chain degradation intermediates (C>7), for which reference standards were not available, have been identified for the first time in the marine medium [19], using spectroscopic techniques. Therefore, it would be necessary to develop a sampling, extraction, purification and concentration procedure that permits the accurate quantification of LAS and SPC in all the environmental compartments to which they have access, including those of complex composition (of marine origin). This method must be adequate for samples which show considerable heterogeneity for the following reasons (i) the high variability in expected LAS and SPC concentrations as a consequence of their different degrees of exposure to surfactants and the variations in the affinity for this compound shown by each of the phases; and (ii) the wide range of salinities found in estuarine samples.

This paper describes the various different sampling techniques for the different compartments (water, interstitial water and sediment column); treatment of samples (by Soxhlet and solid-phase extractions); and the analysis of LAS and SPC by LC–FL in samples collected from different areas of Spain. The objectives of this study are:

(i) To establish the distinctive sampling techniques necessary for a complete study of the environmental behavior of LAS and SPC in the marine and estuarine environment.

(ii) To develop a procedure for the quantification of LAS and SPC in samples with wide variability in the expected concentrations of these compounds and with different salinities (water, interstitial water and sediment).

2. Experimental

2.1. Chemicals

Methanol was of chromatography quality, purchased from Scharlau (Barcelona, Spain), and water was Milli-Q quality. Tetraethylammonium hydrogensulfate (TEAHS) was purchased from Sigma–Aldrich (Steinheim, Germany). Sodium chloride was purchased from Scharlau and potassium dihydrogenphosphate from Panreac (Barcelona, Spain). The commercial LAS mixture was supplied by Petroquimica Española, with the following homologue distribution: C_{10} (3.9%), C_{11} (37.4%), C_{12} (35.4%), C_{13} (23.1%) and C_{14} (0.2%). Our research group has collected a complete set of monocarboxylic SPC standards (C_2–C_{13}-SPC), with the exception of C_7-SPC, some have been donated and the rest synthesized at the University of Cádiz. When the phenylcarboxylic acids were available, they were synthesized by sulfonation [10]; the others were synthesized by a five-stage procedure: a Wittig reaction [20], conversion to methyl esters, which were subsequently reduced and hydrolyzed to obtain the corresponding carboxylic acids, and finally these were sulfonated [10]. After synthesis, in all cases, the purity was higher than 96%. The structure of the compounds was confirmed by ^{1}H and ^{13}C NMR. The overall yield of the procedure was estimated at around 20 to 30%, depending on the length of the alkyl chain. The solid-phase extraction (SPE) minicolumns used (500 mg) were supplied by Varian (Bond Elut C_{18}) and Supelco (SAX). The Sterivac-GP10 filters (0.22 μm particle size) were purchased

from Millipore (Molsheim, France) and GF/F type filters from Whatman (Maidstone, UK).

2.2. Sampling and pretreatment of the samples

The water used for the preparation of the standard solutions was taken in the open sea, at least 16 km from the coast. The ocean water was free of surfactants and other contaminants, as confirmed by analysis. It was passed through filters of 0.22 μm particle size (Sterivac-GP10 from Millipore), prior to further filtration by GF/F type filters (Whatman). The standard solutions were prepared using this water spiked with LAS and SPC at environmentally-representative concentrations.

The marine samples were taken from Cadiz Bay in the Southwest of Spain. In this zone there is an untreated urban wastewater discharge from a population of 100 000 inhabitants. Three sampling stations (A, B and C) were established in order of increasing distance from urban wastewater discharge points. The estuarine samples were taken at three stations (X, Y and Z) from the Suances estuary (Santander), situated in the north of the Iberian Peninsula. These points are in order of increasing salinity conditions.

The water column sampling was performed by taking surface microlayer samples (between 0 and 3–5 mm depth), using a surface sampler (Hydro-Bios, Kiel, Germany), and at different depths with Ruttner bottles (Hydro-Bios). The samples were conserved by adding formaldehyde (2%) and then kept in the dark at 4°C until their analysis. The sediments were sampled with a gravity core sampler, transferred to the laboratory at 4°C and frozen until their analysis. In the laboratory, the frozen cores were sectioned taking portions at different depths (0–30 cm). Every portion was centrifuged at 35 000 *g* for 30 min obtaining the interstitial water, which was then frozen again. The rest of the sample (solid-phase) was dried, kept in a heater at 85°C for 48 h, and later milled and strained through a 160 μm sieve.

Quantities of dried sediment samples (≅10 g) were placed in Soxhlet extraction cartridges, previously washed with methanol, and the compounds were extracted over 12 h with methanol. Subsequently the methanolic extracts were evaporated until dry in a rotavapor, and the dried residue was re-dissolved in 200 ml of hot water (50–55°C) in an ultrasonic bath. The recoveries of Soxhlet extraction procedure were determined using a marine sediment spiked with LAS (C_{10}–C_{13}) and SPC (C_4, C_8 and C_{11}) homologue standards. The tested concentrations for each homologue were: experiment A: 50 ppb SPC+ 50 ppb LAS; experiment B: 200 ppb SPC+5 ppm LAS and experiment C: 500 ppb SPC+25 ppm LAS. The LAS concentrations used are higher than for SPC because the latter are more polar and have less affinity for the sediment.

2.3. Solid-phase extraction

The process of solid-phase extraction was performed in an Adsortex SPU unit of 24 channels, employing two minicolumns: a Bond Elut C_{18} and an SAX. Both minicolumns were previously activated by washing with methanol (10 ml) and water (10 ml). Sodium chloride at an ionic strength of up to 5 *M* and potassium dihydrogenphosphate (0.05 *M*) were added to the samples (water: 250 ml, interstitial water: 25 ml and sediment extracts from Soxhlet extraction: 200 ml) according to the procedure of Sarrazin et al. [21] for fresh water. Subsequently the samples were acidified by adding orthophosphoric acid (pH 1.5) and were passed through a Bond Elut C_{18} minicolumn at a flow-rate of 2 ml min^{-1}. The clean-up was performed using 1 ml water (neutral pH) and the compounds were subsequently eluted with 10 ml MeOH. These 10 ml of the obtained extract were mixed with 90 ml of HPLC-quality water and then passed through the SAX minicolumn. The clean-up was performed using 1 ml of water with 2% AcH and the elution with 3 ml MeOH (2 *M* HCl). The final extract, 3 ml of methanol (2 *M* HCl), was evaporated with N_2 and heat (below 50°C) and re-eluted with 1 ml MeOH–water (80:20). The recovery efficiency of the solid-phase extraction stage was determined using standard solutions (sea water spiked with LAS and SPC), at environmentally-representative concentrations (10, 50, 100, 200 and 450 ppb of each homologue). Each spiked sample was prepared with the same concentration of each SPC and LAS homologue. The assays were performed in triplicate.

The treatment of higher volumes could be necessary for determining LAS and SPC in samples with

Table 1
Gradient regime used for the separation of LAS and SPC homologues. Flow-rate=1 ml min^{-1}

Time (min)	A[a] (%)	B[b] (%)
0	10	90
5	36	64
9	50	50
16	60	40
20	67	33
35	70	30
45	90	10
51	100	0
55	100	0
60	10	90

[a] A: MeOH–water (80:20) with 1.25 m*M* of tetraethylammonium hydrogensulfate.
[b] B: Water.

Table 2
Recoveries and standard deviations (n=3) for LAS and SPC homologues in spiked sediment samples using Soxhlet extraction with MeOH

Compound	Recovery (%)±SD		
	A[a]	B[b]	C[c]
C_4-SPC	56±9	54±11	48±5
C_8-SPC	89±6	75±5	53±9
C_{11}-SPC	105±10	102±8	95±2
C_{10}-LAS	89±7	85±10	72±4
C_{11}-LAS	91±7	91±9	75±6
C_{12}-LAS	101±5	90±9	73±5
C_{13}-LAS	90±8	91±11	74±3
C_{14}-LAS	102±5	95±9	71±4

[a] A: 50 ppb for each SPC+50 ppb for each LAS.
[b] B: 200 ppb for each SPC+5 ppm for each LAS.
[c] C: 500 ppb for each SPC+25 ppm for each LAS.

low contamination. A study of breakthrough volumes in the solid-phase extraction stage was conducted. For this, standard solutions were prepared using the seawater taken in the open sea. The same quantity of each of the standards (5 μg) was added to samples of different volumes (100, 250 and 500 ml), and this assay was also performed in triplicate.

2.4. LAS and SPC analysis

The LAS and SPC homologues were analyzed simultaneously in a HP 1050 high-performance liquid chromatograph equipped with a fluorescence detector (FL, λ_{ex}=225 nm, λ_{em}=295 nm). The different homologues were separated using a LiChrosorb RP-8 column of 250×4.6 mm I.D. with a particle size of 10 μm (Teknokroma), and an elution gradient shown in Table 1. The injection volume for all the samples was 100 μl. For the quantification external standard solutions were used (ocean water spiked with LAS and/or SPC standards); these were treated in the same way as the samples.

3. Results and discussion

3.1. Soxhlet extraction

The percentage recoveries for the Soxhlet extraction procedure for sediment samples (10 g) spiked with different LAS and SPC homologue concentrations are shown in Table 2. LAS homologue recoveries were higher than 90% for concentrations lower than 25 ppm.

The recovery decrease until 70% for higher concentrations (experiment C) probably due to the saturation of the minicolumn. Anyway these concentrations, used in case C, were higher than those registered in highly contaminated sediments. The C_{11}-SPC recoveries were higher than 95% in all cases. The C_8-SPC percentage recoveries were higher than 75% for the experiments A and B, and for the C_4-SPC were around of 50% in all cases. Di Corcia et al. [22] have demonstrated that when the samples contain appreciable quantities of fulvic acids, this could have a considerable effect on the retention of the weak organic acids which include SPC. These considerations could explain the recovery decrease obtained for the shorter carboxylic chain SPC homologues.

3.2. Solid-phase extraction

The results for the recovery of LAS and SPC homologues for different standard solutions (10–450 ppb) are shown in Table 3. The recoveries were generally good for all the compounds tested, apart from C_2- and C_3-SPC, these suffer lower retentions as a result of their greater polarity. However, for the higher concentrations of each compound (200 and 450 ppb), the recoveries are lower as a consequence of the saturation of the minicolumn. This effect is

Table 3
Recoveries and standard deviations (n=3) for LAS and monocarboxylic acids obtained for the proposed method and different concentrations of each homologue (10, 50,100, 200 and 450 $\mu g\,l^{-1}$)

Compound	Recovery (%)±SD concentration ($\mu g\,l^{-1}$)				
	10	50	100	200	450
C_2-SPC	3±1	2±0	3±1	1±1	1±1
C_3-SPC	20±1	15±2	20±2	11±2	5±1
C_4-SPC	84±2	89±5	92±3	48±8	20±1
C_5-SPC	100±3	108±2	105±1	84±4	80±1
C_6-SPC	103±3	109±3	102±3	91±1	84±2
C_8-SPC	105±5	103±2	104±1	83±5	77±2
C_9-SPC	104±7	135±2	108±9	102±7	97±5
C_{10}-SPC	95±5	103±3	101±2	91±3	75±3
C_{11}-SPC	101±6	99±1	96±2	89±3	77±2
C_{12}-SPC	99±8	95±3	90±5	87±4	79±4
C_{13}-SPC	108±7	94±4	79±5	79±6	73±1
C_{10}-LAS	91±7	91±7	69±5	65±4	55±3
C_{11}-LAS	102±10	71±5	65±5	64±4	59±2
C_{12}-LAS	108±5	57±3	64±3	60±2	56±1
C_{13}-LAS	72±7	35±3	47±1	48±3	45±4

particularly sharp for the longer-chain compounds. In any event, these concentrations are much higher than those found in the natural environment, even in highly-contaminated zones; for these, if it were necessary, minicolumns with larger quantities of adsorbent could be used.

In Table 4 the recovery percentages obtained using different volumes of standard solution are shown. The recoveries were good for the various cases, except for C_2- and C_3-SPC. The 250 and 500 ml samples presented similar recoveries, slightly lower than the 100 ml samples; however, the standard deviation increased with the volume.

3.3. Calibration graphs and limits of detection (LOD)

The calibration curves obtained for SPE of 100 ml sea water spiked with 10, 50, 100, 200 and 450 ppb of each homologue of LAS and SPC are shown in Table 5. The behavior of all the compounds was linear, including at higher concentrations than those actually detected in highly contaminated zones, except for the SPC shorter than four carbons.

The detection limits obtained for samples from different environmental compartments, based on a signal-to-noise ratio of 3:1, are shown in Table 6. Values were similar for LAS and SPC homologues, ranging from 0.2 to 0.4 for 250 ml of water and from 5 to 10 for 10 g of sediment. The method was shown to be slightly less sensitive for C_{12}-SPC and C_{13}-LAS, due to the existence of small irregularities in the baseline at its retention time (gradient regimen conditions) and the lower recovery obtained for this type of compound. The problem with the treatment of interstitial water samples is the small volume that

Table 4
Recoveries and standard deviations (n=3) for LAS and SPC homologues in spiked seawater samples with different volumes (100, 250 and 500 ml)

Homologue	Recovery (%)±SD		
	100 ml	250 ml	500 ml
C_2-SPC	24±6	16±1	7±2
C_3-SPC	44±6	13±8	6±5
C_4-SPC	96±4	86±3	69±3
C_5-SPC	93±5	88±3	90±5
C_8-SPC	95±7	84±4	87±8
C_9-SPC	106±4	108±1	102±5
C_{10}-SPC	95±6	84±5	85±6
C_{11}-SPC	99±4	93±5	98±8
C_{12}-SPC	100±2	84±7	87±1
C_{13}-SPC	83±1	81±5	74±6
C_{10}-LAS	102±1	97±4	100±6
C_{11}-LAS	103±3	93±4	94±11
C_{12}-LAS	94±2	89±7	90±15
C_{13}-LAS	73±3	70±11	69±15

Table 5
Calibration data obtained for SPE of 100 ml spiked sea water, concentration range: 10–450 $\mu g\,l^{-1}$

Homologue	Calibration curve	r^2
C_2-SPC	$y=0.035+0.501x$	0.558
C_3-SPC	$y=6.665+2.747x$	0.504
C_4-SPC	$y=-7.640+40.000x$	0.997
C_5-SPC	$y=70.000+43.478x$	0.995
C_6-SPC	$y=65.227+45.454x$	0.996
C_8-SPC	$y=50.400+40.00x$	0.992
C_9-SPC	$y=24.176+13.513x$	0.971
C_{10}-SPC	$y=55.909+45.454x$	0.993
C_{11}-SPC	$y=8.003+2.873x$	0.986
C_{12}-SPC	$y=245.936+21.276x$	0.920
C_{13}-SPC	$y=1.764+18.182x$	0.988
C_{10}-LAS	$y=9.524+47.667x$	0.976
C_{11}-LAS	$y=19.667+41.667x$	0.982
C_{12}-LAS	$y=215.461+76.923x$	0.970
C_{13}-LAS	$y=32.182+15.151x$	0.912

Table 6
Detection limits for LAS and SPC homologues in marine/estuarine samples obtained using HPLC–FL

	Detection limits			
	C_4–C_{11}- and C_{13}-SPC	C_{12}-SPC	C_{10}–C_{12}-LAS	C_{13}-LAS
Water ($\mu g\ l^{-1}$)	0.2	0.4	0.2	0.3
Sediment ($\mu g\ kg^{-1}$)	5	10	6	7

can normally be obtained, and as a consequence the sensitivity of the method for this kind of sample is lower.

3.4. Marine and estuarine water samples

Fig. 2 shows a comparison between the chromatograms obtained from sea water spiked with LAS and SPC and from water column sample (panels a and b, respectively). The procedure followed produces chromatograms that show efficient separation of each LAS and SPC homologue as a unique peak, under which all the positional isomers are eluted. In this water sample (from station X), all the SPC homologues from two to 11 carbon atoms in the carboxylic chain have been detected, the intermediate length chains being the most abundant. The identification of the C_7-SPC, for which no standard is available, was performed by HPLC–MS, following the procedure described by Gonzalez Mazo et al. [19]. It was quantified in an approximate way, based on that of C_8-SPC.

Table 7
LAS and SPC homologue concentrations ($\mu g\ l^{-1}$) in estuarine water (station Z) at different depths and salinities[a]

	Depth			
	0–5 mm	0.25 m	1.5 m	2.5 m
C_4-SPC	2.4	1.0	n.d.	n.d.
C_5-SPC	n.d.	0.3	n.q.	n.d.
C_6-SPC	5.4	2.0	1.0	n.d.
C_7-SPC	1.0	0.9	0.6	n.d.
C_8-SPC	n.d.	n.d.	0.7	0.7
C_9-SPC	n.q.	n.d.	n.d.	n.d.
C_{10}-SPC	0.9	n.d.	n.d.	n.d.
C_{11}-SPC	1.7	n.d.	n.d.	n.d.
C_{12}-SPC	n.d.	n.d.	n.d.	n.d.
C_{13}-SPC	n.d.	n.d.	n.d.	n.d.
C_{10}-LAS	11.0	7.8	1.4	0.9
C_{11}-LAS	50.5	30.7	5.7	4.6
C_{12}-LAS	49.1	22.9	3.8	3.5
C_{13}-LAS	27.7	9.5	3.3	2.7

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

Table 7 shows the concentrations of LAS and SPC found at different depths in station Z (Suances Estuary). Different salinities were found for the samples (15.49, 15.50, 33.60 and 33.84 for 0–5 mm, 0.25 m, 1.5 m and 2.5 m depth, respectively), showing that this estuary was stratified at the time of the sampling. The highest LAS homologue concentrations were detected in the surface microlayer (around twice as high as at the depth next analyzed), showing a typical vertical profile of a surfactant-type molecule. Therefore, for an accurate quantification of LAS in the water column, samples must be taken at various depths. However, the SPC homologues (C_4–C_9) detected at very low concentrations did not show a similar behavior. Their distribution is homogeneous due to the loss of surfactant properties by the molecules.

3.5. Marine sediment

Table 8 shows the concentrations of LAS and SPC in sediment and interstitial water, for station B at different depths. The LAS concentrations found were three orders of magnitude higher than in their corresponding interstitial water and water column samples. All the homologues showed the same behavior, with concentration decreasing with depth, due either to the increase of detergent consumption or to the existence of degradation processes in this compartment. With respect to the SPC, the concentrations are similar in both phases, as a consequence of their greater polarity. From the values obtained, it is clear that samples must be taken at

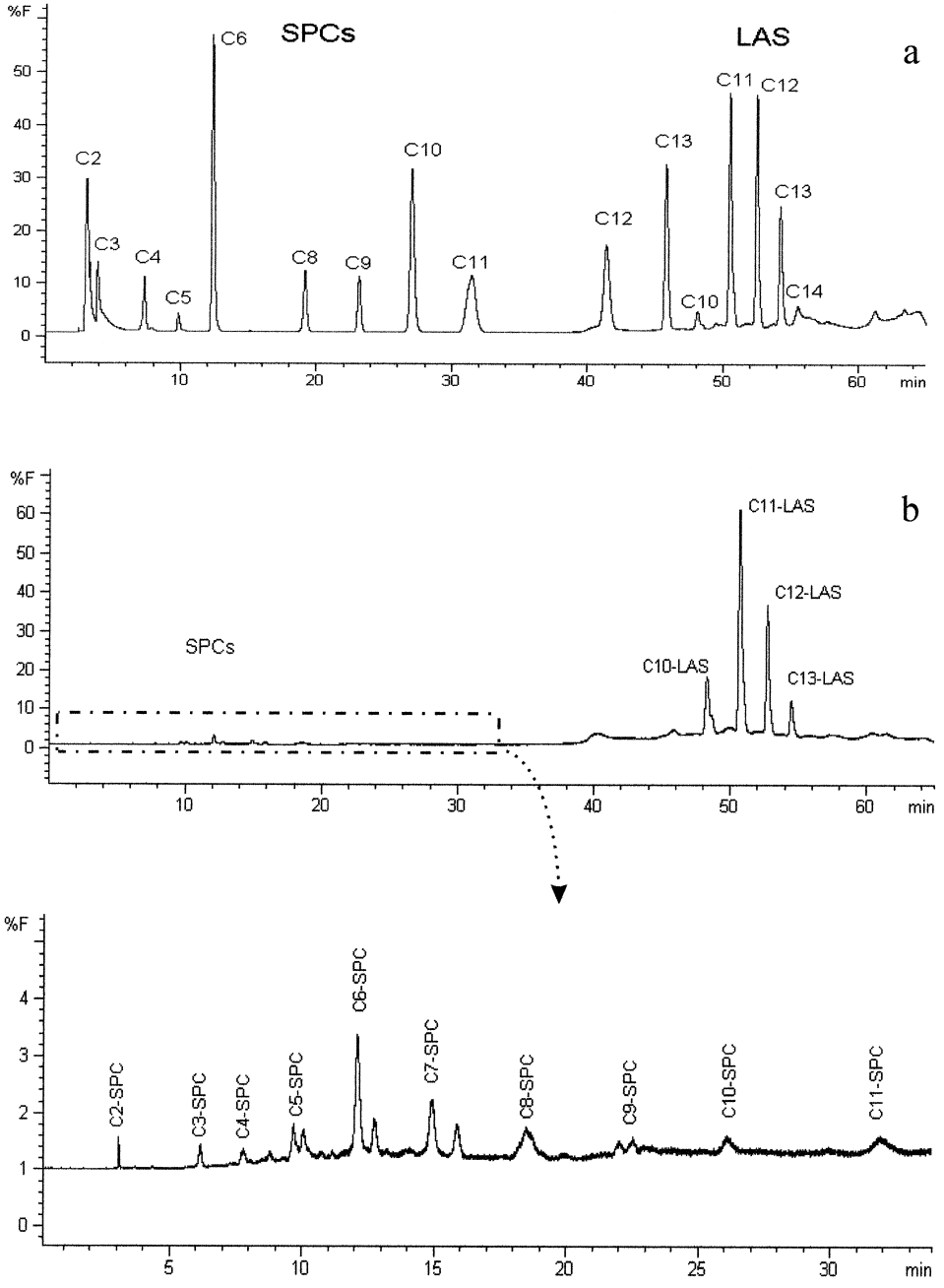

Fig. 2. HPLC–FL chromatograms obtained of (a) seawater spiked with LAS and SPC homologues and (b) estuarine water sample from the station Z. Chromatographic conditions: LiChrosorb RP-8 column of 250×4.6 mm (10 μm), flow-rate=1 ml min^{-1} fluorescence detection (λ_{ex}=225 nm, λ_{em}=295 nm), gradient regime (Table 1) and 100 μl of injection volume.

Table 8
LAS and SPC homologue concentrations detected in marine sediment and interstitial water (station B) at different depths[a]

Homologue	Sediment ($\mu g\ g^{-1}$)			Interstitial water ($\mu g\ l^{-1}$)		
	0.5 cm	10.5 cm	26.5 cm	0.5 cm	10.5 cm	26.5 cm
C_4-SPC	0.01	0.01	0.01	15.5	27.6	13.1
C_5-SPC	0.05	0.09	0.05	46.9	100.2	54.3
C_6-SPC	0.01	0.01	0.01	n.q.	2.9	1.4
C_7-SPC	n.q.	0.06	n.q.	11.3	45.3	3.8
C_8-SPC	0.02	0.06	0.02	13.6	165.8	4.4
C_9-SPC	n.q.	0.05	n.q.	10.0	138.5	39.9
C_{10}-SPC	n.d.	1.10	n.d.	5.5	47.7	60.3
C_{11}-SPC	n.d.	0.16	n.d.	3.4	10.1	17.0
C_{12}-SPC	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C_{13}-SPC	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C_{10}-LAS	0.31	0.13	0.10	2.7	2.8	1.8
C_{11}-LAS	3.18	1.03	0.82	20.2	10.8	7.1
C_{12}-LAS	8.21	1.54	1.18	25.4	17.8	10.4
C_{13}-LAS	14.79	1.89	1.33	9.0	3.0	1.7
C_{14}-LAS	0.33	0.14	0.14	n.d.	n.d.	n.d.

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

various depths in order to characterize this environmental compartment accurately.

4. Conclusions

The proposed method permits the simultaneous determination of LAS (C_{10}–C_{13}) and SPC (C_4–C_{13}) homologues in water, sediment and interstitial water from marine and estuarine origins, with high selectivity, recoveries and reproducibility. The concentrations found in water and sediment show the need for sampling at various depths, in order to obtain representative samples from the sampling sites, due to the physico–chemical properties of these compounds.

Acknowledgements

Our thanks are due to Francesc Ventura (Aguas de Barcelona) and to Jennifer Field (Oregon State University) for supplying some SPC standards without which this work could not have been done. This research has been supported by the Environmental and Climate Program of the European Commission PRISTINE (contract. No. ENV4-CT97-494) from Waste Water Cluster.

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