Fresenius J Anal Chem (2001) 371 : 479–485
DOI 10.1007/s002160101046

SPECIAL ISSUE PAPER

V. M. León · A. Gómez-Parra · E. González-Mazo

Determination of sulfophenylcarboxylic acids in marine samples by solid-phase extraction then high-performance liquid chromatography

Received: 22 February 2001 / Revised: 7 July 2001 / Accepted: 12 July 2001 / Published online: 12 September 2001

Abstract An analytical method is presented for the determination of sulfophenylcarboxylic acids (SPC) produced by the biodegradation of linear alkylbenzene sulfonates (LAS) in marine samples. Isolation and concentration of the compounds was by solid-phase extraction. The different factors affecting extraction efficiency – packing composition, pH, clean-up, ionic strength, and elution solvents – were studied and optimized. With the proposed method C_4–C_{13}SPC and C_{10}–C_{13} LAS recoveries varied between 65% and 105%, with standard deviations between 0.1 and 5, respectively, for 100-mL samples and 100 μg L^{-1} concentrations of each homolog. Detection limits within the range 0.5 g L^{-1} (for C_4SPC) to 1.0 g L^{-1} (for C_{12}SPC) were obtained by liquid chromatography with fluorescence detection. This method is the first to be proposed that enables the simultaneous determination of monocarboxylic SPC (C>3) and LAS homologs in marine samples by a simple, sensitive, and specific method giving high recoveries and reproducibility. SPC with from three to twelve carbon atoms in the carboxyl chain have been found in marine water samples.

Introduction

Surfactants are active ingredients in many cleaning products and are discharged in large quantities with domestic sewage. Of these surfactants, linear alkylbenzene sulfonates (LAS) (Fig. 1a) are among the most commonly used in the formulation of domestic detergent products, and their presence in the marine environment has been reported [1, 2, 3, 4]. Because LAS are highly biodegradable compounds [5, 6], the identification and quantification of their degradation intermediates, sulfophenylcarboxylic acids (SPC; Fig. 1b) are essential aspects of the study of the behavior of LAS in the environment.

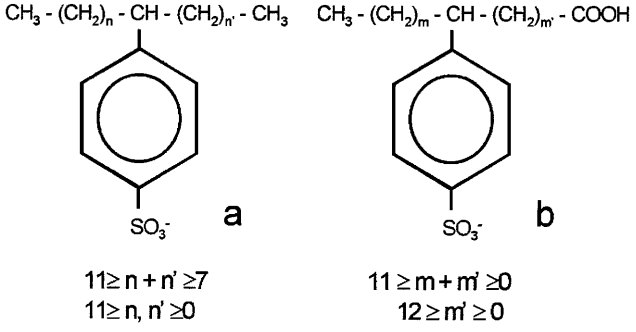

Fig. 1 General chemical structures of linear alkylbenzene sulfonates (**a**) and sulfophenyl carboxylate compounds (**b**)

Although HPLC is one of the most widely applied techniques for the analysis of LAS and SPC, and thus for the study of the environmental behavior of LAS [7, 8], the complexity of SPC mixtures and the lack of reference standards currently limit the applicability of HPLC with UV–fluorescence detection [9]. The identification of the longer-chain intermediates (C>7) for the first time in marine samples required the use of spectroscopic techniques [4], because reference standards were not available. An LC–MS technique has recently been used to characterize LAS biodegradation [10] and LAS and co-product intermediates generated in laboratory biodegradation tests [11] and in a sewage treatment plant [12].

For environmental samples it is necessary to perform initial concentration and isolation of the analyte before analysis. A method using solid-phase extraction has been developed specifically for marine samples [13]; it has good selectivity for LAS and percentage recovery is high over a wide range of concentrations. This method was used to study the distribution of LAS in water, suspended material, sediments, and interstitial water originating from a coastal zone in which untreated municipal waste waters have direct access to the sea. In addition, long chain-length SPC were identified by HPLC–MS [4] but those

V.M. León · A. Gómez-Parra · E. González-Mazo (✉)
Departamento de Química-Física, Facultad de Ciencias del Mar, Universidad de Cádiz.
Polígono Río San Pedro s/n, 11510 Puerto Real, Cádiz, Spain
e-mail: eduardo.gonzalez@uca.es

with short chains were not found. The failure to detect these could have only two possible explanations:

1. their average life is very short; or
2. these SPC are lost during treatment of the environmental samples before analysis, because of the polar nature of these intermediates.

The first possibility is unlikely, bearing in mind that laboratory results have confirmed that the short-chain intermediates are more persistent [14]. The second hypothesis would, in contrast, be in accordance with the findings of Altenbach and Giger [15] and of Di Corcia et al. [16].

In this paper we describe a method specially developed for quantitative analysis of samples of marine origin. It is based on solid-phase extraction then HPLC with fluorescence detection, and enables the highly sensitive, specific, and reproducible simultaneous determination of monocarboxylic SPC (C>3) and LAS homologs. Because the quantification of these monocarboxylic acids had not yet been achieved, the purpose of the work was:

1. to develop a solid-phase extraction method that affords good recoveries of SPC;
2. to determine the optimum analytical conditions for the determination, separation, and quantification of all the LAS and SPC homologs by HPLC with fluorescence detection; and
3. to apply the method to a variety of marine water samples.

Experimental

Chemicals

The solvents used as chromatographic mobile phases in the experiments were water and methanol, both of chromatography quality, purchased from Scharlau (Barcelona, Spain). Tetraethylammonium hydrogen sulfate (TEAHS) was purchased from Sigma–Aldrich (USA). Sodium chloride was purchased from Scharlau and potassium dihydrogen phosphate from Panreac. Commercial LAS was supplied by Petroquímica Española; the homolog distribution was: 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 a complete collection of monocarboxylic SPC standards (C_2–C_{13}SPC), with the exception of C_7SPC; some of these have been donated, the rest were synthesized in Cadiz University. When the phenylcarboxylic acids were available, the compounds were synthesized by sulfonation. The others were synthesized by a five stage procedure – Wittig reaction [17], conversion to the methyl esters which were subsequently reduced and hydrolyzed to obtain the corresponding carboxylic acids, and finally sulfonation of these. The purity of all the synthesized compounds was >96%. The structures of the compounds were confirmed by ^{1}H and ^{13}C NMR. The overall yield of the procedure was estimated to approximately 20% to 30%, depending on the length of the alkyl chain. The solid-phase extraction minicolumns used were supplied by Supelco (Bellefonte, PA, USA; C_{18} and quaternary amine-SAX), Varian (Zug, Switzerland; BondElut C_{18}), and Merck (Darmstadt, Germany; LiChrolut EN – ethylvinylbenzene–divinylbenzene copolymer,).

Sample preparation

Water used for the preparation of the standard solutions was sampled in the open sea, at least 10 miles from the coast. It was confirmed by analysis that this water was free from surfactants and other contaminants. Water was passed through a 0.22-µm pore-size filter (Sterivac GP1, from Millipore) before further filtration through a GF/F filter (Whatman). Sea water was also sampled near an urban waste-water discharge point in a salt-marsh area to the south of the Bay of Cadiz in southwest Spain; they were preserved by addition of formaldehyde (2%) and stored in the dark at 4 °C until they could be analyzed.

Recovery studies

Solid-phase extraction of 100-mL solutions was performed in an Adsortex SPU unit with 24 channels. The solid-phase extraction method proposed by González-Mazo and Gómez-Parra [13] was evaluated, by analysis of the different fractions obtained (A, B, C, F; Fig. 2). Fractions A (100 mL) and B (6 mL) were neutralized with NaOH and subsequently passed through an SAX column. The experiments were performed in triplicate.

Different types of mini-column were used (C_{18}, LiChrolut EN, BondElut C_{18}, and SAX), to study the effect of packing composition, and different pretreatment conditions were tested (pH, clean-up, ionic strength, and elution solvents) to optimize the extraction method.

Recoveries of SPC (C_2–C_{13}) and LAS (C_{10}–C_{13}) were evaluated by use of standard solutions (ocean water spiked with LAS and/or SPC, using environmentally representative concentrations of each homolog).

Chromatographic conditions

The LAS and SPC were determined by high-performance liquid chromatography (Hewlett Packard 1050) with fluorescence detection (λ_{exc}=225 nm, λ_{em}=295 nm). The different homologs were

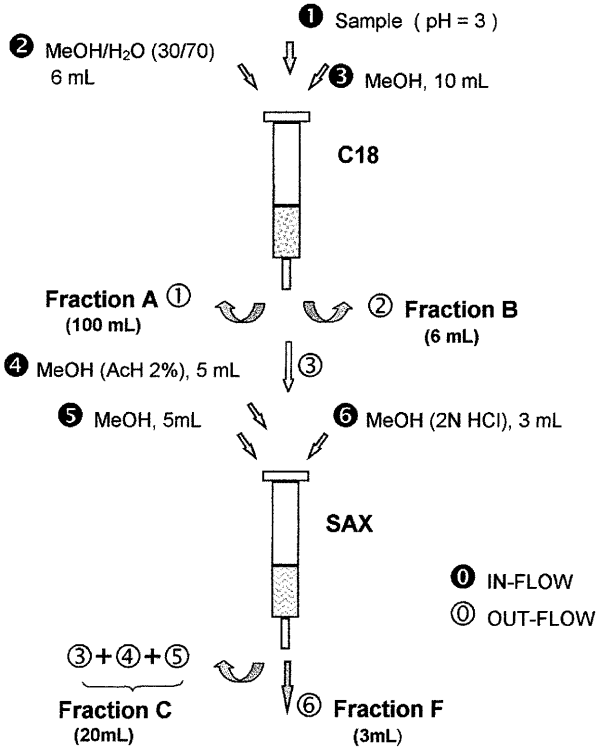

Fig. 2 Different fractions (*A, B, C,* and *F*) analyzed after use of the solid-phase extraction method proposed for determination of LAS by González-Mazo and Gómez-Parra [10]

Table 1 Mobile-phase gradient used to separate LAS and SPC homologs. The flow rate was 1 mL min^{-1}

Time (min)	A (%)	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 is 80:20 MeOH–H_2O containing 1.25 mmol L^{-1} tetraethylammonium hydrogensulfate; B is H_2O

separated by use of a 250 mm×4.6 mm i.d., 10 μm particle size, LiChrospher RP-8 column (Teknokroma) with the mobile phase gradient shown in Table 1. The injection volume for all the samples was 100 μL. The external standard solutions used for quantification (5 to 500 μg L^{-1} of each homolog) were treated in the same way as the samples.

Results and discussion

Recovery studies

Table 2 shows the amounts (%) of the different compounds obtained in each of the four fractions (A, B, C, F) corresponding to Fig. 2 (solid-phase extraction method designed for LAS). Recovery increases as the non-polar character of the compounds increases (fraction F), and short chain-length SPC (<6 carbon atoms) are lost. Because the amounts of these SPC obtained in fraction C are very low, the compounds must have been lost from fractions A or B, as is shown by the data in Table 2. The more polar SPC are weakly retained by the C_{18} and even clean-up of this cartridge with 30% MeOH (fraction B) was enough to elute up to 30% of the SPC of intermediate chain length.

Total percentages for the four fractions (A+B+C+F) were not 100%. The percentages obtained for fractions A and B must be higher than those shown (Table 2), because both fractions were subsequently passed through an SAX column, where losses have also been detected (fraction C). The next operation was to optimize the two solid-phase extraction steps separately – firstly the conditions for the non-polar minicolumn, and subsequently the conditions for the polar minicolumn.

Non-polar minicolumn: effect of clean-up, pH, packing composition, and ionic strength

As stated above, use of 30% MeOH to clean the column resulted in elution of SPC with less than seven carbon atoms (fraction B, Table 2). Thus two different clean-up steps without methanol were tested for the C_{18} minicolumn – 1 mL H_2O of neutral pH and 1 mL H_2O of pH 3 (adjusted with HCl). The retained compounds were eluted with 10 mL MeOH and the extracts were evaporated with a stream of N_2 flux at a temperature below 50 °C. Although recoveries of C_2 to C_6 SPC were always higher than for the experiment described above (data not shown), they were still below 50%, and so other conditions had to be optimized. The pH of the sample was adjusted to 2 with HCl and the results were compared with those obtained at pH 3. Although recoveries of short-chain SPC were higher at pH 2, they were still not sufficient; similar results were obtained when another type of minicolumn (LiChrolut EN) was used at pH 2.

To improve the interaction of SPC with C_{18} the ionic strength of the sample was increased in accordance with the methodology proposed by Sarrazin et al. [18, 19] for analysis of fresh-water samples on BondElut C_{18}. Natural sea water (salinity=36) has an ionic strength equivalent to 0.7 mol L^{-1} NaCl solution. When sodium chloride was added to the marine water samples to bring the concentration to approximately 5 mol L^{-1}, recoveries better than 90% were obtained for SPC with more than three carbon atoms, and for LAS (data not shown). Good recoveries were not, however, obtained for C_3SPC (<40%). Because of the long time needed to evaporate the solvent with ice and a stream of N_2 [18], we tried evaporation at moderate temperatures (<45 °C) and substituting the acetone by MeOH as organic solvent in the treatment. Similar recoveries of short-chain SPC were obtained by both treatments, and no significant differences were observed. We therefore selected treatment with MeOH as organic solvent and moderate-temperature evaporation. When this treatment was applied to samples of oceanic seawater spiked with LAS and SPC the chromatograms obtained were free from interference and easy to quantify. When, however, we treated real samples, particularly those taken from coastal systems (with complex matrixes), the chromatograms showed the presence of interferences which made accurate quantification impossible. Further purification of such samples was necessary, and use of an SAX minicolumn after the BondElut C_{18} was proposed, as described elsewhere for analysis of LAS [13].

Table 2 Amounts (%) of SPC homologs, and standard deviations (n=3), obtained for different fractions by use of the method proposed by González-Mazo and Gómez-Parra [13]

Fraction[a]	Recovery (%)							
	C_2SPC	C_3SPC	C_4SPC	C_5SPC	C_6SPC	C_8SPC	C_{10}SPC	C_{11}SPC
A	51±9	48±7	45±8	25±16	1±1	n.q.	1±1	n.q.
B	1±1	5±5	9±5	30±5	24±7	n.q.	3±5	n.q.
C	1±1	3±3	n.q.	n.q.	22±16	2±2	12±14	n.q.
F	n.q.	n.q.	4±3	10±1	44±4	68±4	73±4	72±6

[a]As shown in Fig. 2
n.q. – detected but not quantified

Polar minicolumn (SAX): influence of clean-up and the proportion of organic solvent in the sample

The loss of SPC in the quaternary amine minicolumn (SAX) could be because MeOH was used to elute the sample from the C_{18} adsorbent. To correct this, the eluent (MeOH) was diluted with H_2O (90 mL) before passage through the SAX. Recoveries from SAX treatment were evaluated separately by use of 100-mL standard solutions (10:90 MeOH–H_2O). Three different clean-up steps for this minicolumn were also tested:

1. 1 mL H_2O (neutral pH);
2. 1 mL H_2O containing 2% AcOH; and
3. 5 mL MeOH containing 2% AcOH+5 mL MeOH.

Elution was performed with 3 mL MeOH (containing 2 mol L^{-1} HCl). The eluate was evaporated (at 45 °C, maximum) to dryness and then redissolved in 1 mL 80:20 MeOH–H_2O. These experiments were extended to the other SPC and to all the LAS homologs. Complete results are given in Table 3.

In general, recovery was improved, indicating that re-dilution of the extract with water effectively promotes interaction of the SPC with the SAX minicolumn. The best recoveries were obtained for the clean-up steps performed with water (A and B), especially when the clean-up was performed with water at acid pH (B). Table 3 also shows the effect of the organic content of the solvent used to re-dissolve the dried extract (condition B). The best results were obtained when the eluate was evaporated to dryness then re-dissolved in 1 mL 80:20 MeOH–H_2O ((column B). When the proportion of MeOH was reduced to 50:50 MeOH–H_2O (B′) or 10:90 (B″) recoveries of the LAS and SPC homologs decreased, especially for the long-chain compounds.

The differences between the two evaporation processes (cold and with moderate heat) were also studied for the full set of homologs and were not significant (data not shown); evaporation was therefore performed with moderate heating.

Table 3 Recovery (%), and standard deviations (n=3), obtained for treatment with the SAX minicolumn by use of different clean-up conditions (A, B, C) and organic solvent used of different compositions for re-dilution of the dried extract obtained under conditions B

Homolog	Recovery (%)±S.D.				
	A	B	C	B′	B″
C_2SPC	87± 5	87± 2	55± 4	74± 1	66± 4
C_3SPC	90± 6	89± 3	84± 5	84± 2	86± 2
C_4SPC	95±11	94± 2	101±11	95± 1	94± 2
C_5SPC	90±10	90± 3	97±15	86± 1	85± 1
C_8SPC	88±10	89± 4	79± 6	77± 1	55± 6
C_9SPC	90±12	89±11	84± 8	96± 5	54± 5
C_{10}SPC	75±14	76± 1	94±13	70± 6	26± 8
C_{11}SPC	74± 7	74± 7	82±10	69±14	26± 4
C_{12}SPC	79± 4	80± 3	82± 4	54± 2	12± 4
C_{13}SPC	86± 2	85± 5	90± 7	25± 1	7± 4
C_{10}LAS	86±21	95±12	94± 9	49± 2	18± 7
C_{11}LAS	78± 4	85± 8	84± 9	87± 3	27±16
C_{12}LAS	82± 3	83±10	82±13	42± 2	13± 6
C_{13}LAS	87± 4	96±10	85±17	39±15	20± 8

A is H_2O at neutral pH, B is 2% AcOH in water at 2% C.
Clean-up was as proposed by González-Mazo and Gómez Parra [13].
For B′ the sample was re-eluted with 50:50 MeOH–H_2O; for B″ the sample was re-eluted with 10:90 MeOH–H_2O; for A, B, and C the samples were re-eluted with 80:20 MeOH–H_2O

Proposed treatment for LAS and monocarboxylic SPC

Considering all the results described here, the final procedure used to isolate and preconcentrate LAS and SPC simultaneously was based on solid-phase extraction on BondElut C_{18} and SAX minicolumns. Sample (100 mL) adjusted to 5 mol L^{-1} NaCl and 0.05 mol L^{-1} $KHPO_4$ (pH 1.5, adjusted with H_3PO_4) were passed through a BondElut C_{18} minicolumn previously activated with

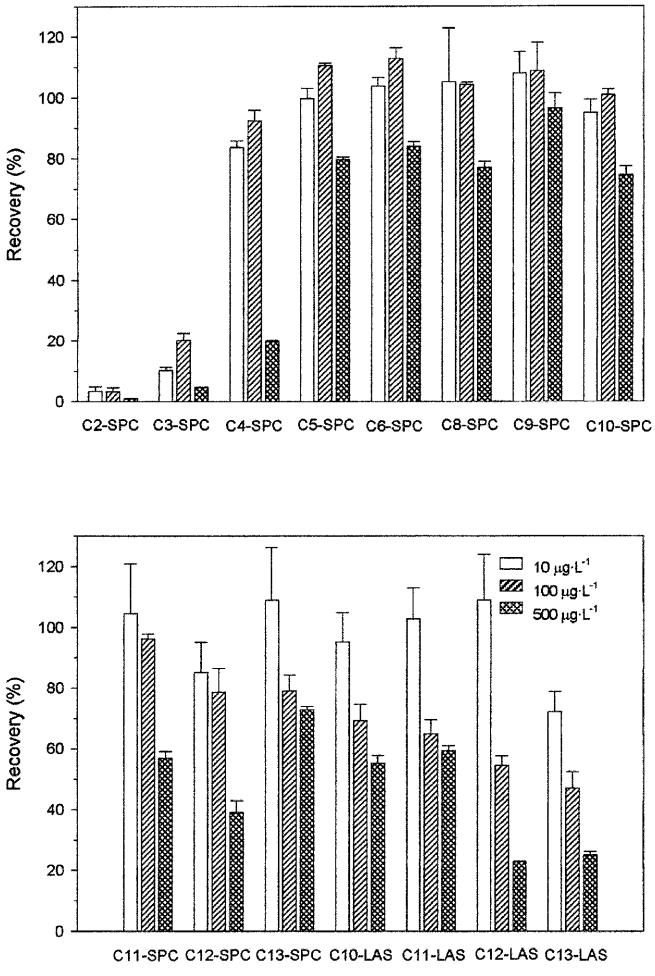

Fig. 3 Recoveries (%) of LAS and monocarboxylic acids, and standard deviations (n=3) obtained by use of the proposed method for different concentrations of each homolog (10, 100, and 500 µg L^{-1})

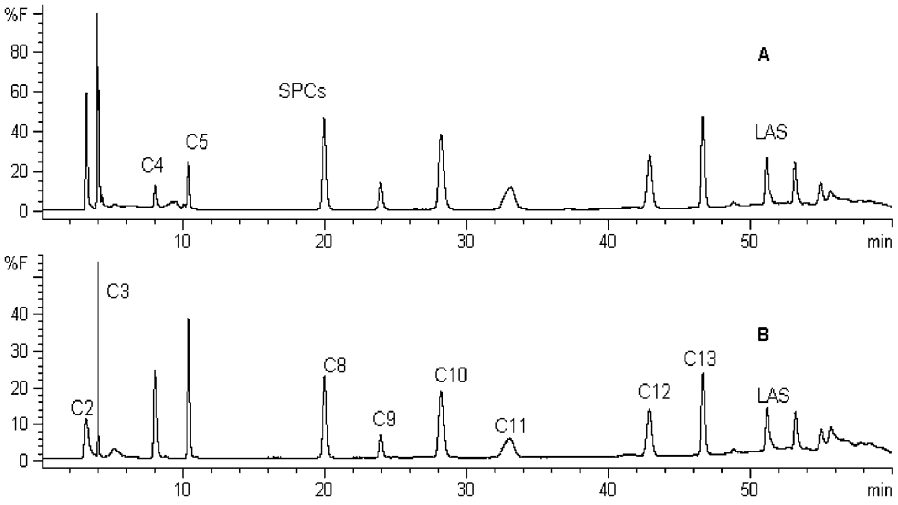

Fig. 4 HPLC–FL chromatograms obtained from sea water spiked with LAS and SPC homologs, by use of the proposed method: **A**, final extract 80:20 MeOH–H_2O; **B**, final extract 8:92 MeOH–H_2O

10 mL methanol then 10 mL water. This minicolumn was washed with 1 mL H_2O (neutral pH) and the compounds were subsequently eluted with 10 mL MeOH. The 10 mL eluent was mixed with 90 mL H_2O and the mixture was then passed through a previously activated SAX minicolumn. Clean-up was performed with 1 mL H_2O containing 2% AcOH and the compounds were eluted with 3 mL MeOH (containing 2 mol L^{-1} HCl). The eluate was evaporated to dryness (at 45 °C, maximum) and then redissolved in 1 mL 80:20 MeOH–H_2O.

Recoveries from standard solutions (sea water spiked with LAS and SPC at environmentally relevant concentrations – 10, 100, and 500 μg L^{-1} of each homolog) are shown in Fig. 3. Recoveries were very good for low concentrations (10–100 μg L^{-1}), except for C_2 and C_3SPC. Recoveries were lower for higher concentrations (500 μg L^{-1}) as a consequence of saturation of the minicolumn.

Table 4 Calibration data obtained for LAS and SPC

Homolog	Calibration curve	r^2
C_2SPC	y=–0.071+1.996x	0.558
C_3SPC	y=–2.426+0.364x	0.504
C_4SPC	y=0.191+0.025x	0.997
C_5SPC	y=–1.610+0.023x	0.995
C_6SPC	y=–1.435+0.022x	0.996
C_8SPC	y=–1.260+0.025x	0.992
C_9SPC	y=–1.789+0.074x	0.971
C_{10}SPC	y=–1.230+0.022x	0.993
C_{11}SPC	y=–2.785+0.348x	0.986
C_{12}SPC	y=–11.559+ 0.047x	0.920
C_{13}SPC	y=–0.097+0.055x	0.988
C_{10}LAS	y=–0.200+0.021x	0.976
C_{11}LAS	y=–0.472+0.024x	0.982
C_{12}LAS	y=–2.801 + 0.013x	0.970
C_{13}LAS	y=–2.124+0.066x	0.912

Analytical separation of LAS and SPC homologs

HPLC with a mobile phase gradient resulted in elution of the different isomers of each homolog as a single peak. This gradient used (Table 1) was based on that used in methods reported elsewhere [4, 20], although with some modifications (the methanol was substituted by acetonitrile, the concentration of the tetraethylammonium ion was reduced, and the eluent proportions were changed).

At the beginning of the HPLC gradient the mobile phase is 8:92 MeOH–H_2O; the final residue from the SPE is, however, 80:20, as a result of which some of the SPC analyzed (<6 carbon atoms) coelute at the beginning of the chromatogram, as shown in Fig. 4A. Because the proportion of MeOH in the samples injected for HPLC analysis should be less than 10%, the final extracts had to be diluted with Milli-Q water before injection (Fig. 4B), despite the loss of sensitivity which results.

Limits of detection were estimated for the various analytes studied under the experimental conditions used. For analysis of 100 mL of a treated spiked marine water, the limits of detection were:

- LAS homologs 0.6 μg L^{-1} except for C_{13}LAS (0.8 μg L^{-1})
- C_4–C_{13}SPC homologs 0.5 μg L^{-1} except for C_{12}SPC (1.0 μg L^{-1}).

Calibration curves

External standard calibration was used for quantification of the extracts after off-line SPE. Calibration was performed by plotting the amount injected (y, μg) against peak area (x). Calibration graphs were constructed by use of standard solutions (seawater spiked with 10, 50, 100, 200, or 500 μg L^{-1} of each homolog) that were treated in the same way as the samples (Table 4). The relationship between fluorimetric response and concentration was found to be linear for all compounds over all the ranges tested, except for SPC with fewer than four carbon atoms.

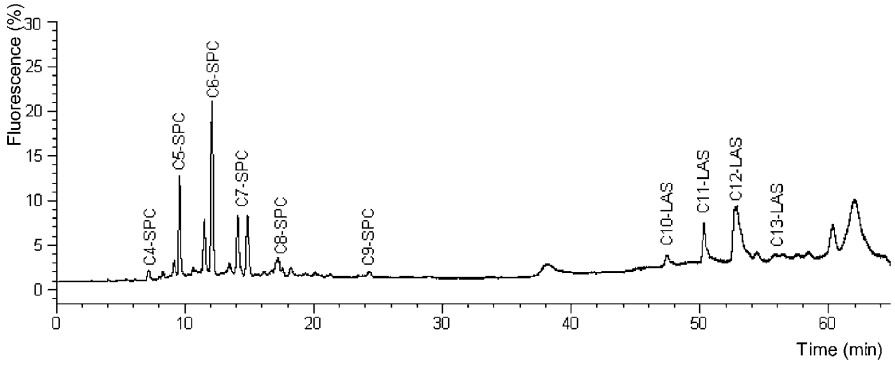

Fig. 5 HPLC–FL chromatogram obtained, by use of the proposed method, from a sea-water sample taken near a waste-water discharge point (B)

Table 5 LAS and SPC concentrations (μg L^{-1}) in marine samples with different exposure to non-treated waste-water effluent

Homolog	Concentration (g L^{-1})		
	Station A	Station B	Station C
C_3SPC[a]	7.8	n.q.	n.d.
C_4SPC	2.2	n.q.	n.q.
C_5SPC	5.5	7.4	n.q.
C_6SPC	7.7	19.4	1.5
C_7SPC	3.0	15.2	1.7
C_8SPC	3.0	4.3	1.0
C_9SPC	5.6	2.0	1.5
C_{10}SPC	n.d.	3.6	n.d.
C_{11}SPC	3.8	0.2	n.d.
C_{12}SPC	7.6	5.0	n.d.
C_{13}SPC	n.d.	n.d.	n.d.
C_{10}LAS	301.5	2.4	n.q.
C_{11}LAS	940.3	8.7	4.1
C_{12}LAS	853.5	12.3	8.2
C_{13}LAS	423.9	2.9	1.1

n.d. denotes not detected
n.q. denotes detected but not quantified
[a]Approximate concentrations (method not valid for this SPC homolog)

Environmental samples

The method was applied to samples from Bay of Cadiz (Spain). An example of a chromatogram obtained from a seawater sample is shown in Fig. 5. SPC homologs containing from four to nine carbon atoms in the carboxylic chain were separated. Identification of C_7SPC, for which a standard is not available, was achieved by HPLC–MS [4]. This homolog was quantified approximately, on the basis of the response to C_8SPC.

Table 5 shows LAS and SPC concentrations measured at three sampling sites (A, B and C); the results are listed in order of increasing distance from an urban waste-water discharge point. The highest LAS concentrations (>2000 μg L^{-1}) were recorded at A. There was a sharp reduction in LAS levels with distance – at B (3 km from the discharge point) the concentration was 25 μg L^{-1}. This decrease might be a result of adsorption on particulate material (suspended solids and sediments) or biodegradation.

Although the occurrence of biodegradation has been demonstrated, this is the first time short-chain (C_3–C_6) SPC have been detected in the marine environment (Table 5). Higher concentrations of long-chain SPC concentrations were been found at station A. Shorter chain-length SPC, which are more persistent [14], predominate at short distances from the effluent (B), and far away (C); their concentrations also decrease, and biodegradation continues until mineralization. This is the theoretical distribution as a consequence of biodegradation based on consecutive chemical reactions.

Conclusions

The quality of the calibration curves and recoveries obtained by use of the method are indicative of high reproducibility and repeatability, except for C_2 and C_3SPC. It is, therefore, concluded that this method is suitable for determination of LAS and SPC in samples of marine origin. It is also applicable to other, less complex, systems, e.g. continental waters.

Acknowledgement We thank Francesc Ventura (Aguas de Barcelona) and Jennifer Field (Oregon State University) for supplying some of the SPC standards necessary for this work. This research was supported by the Environmental and Climate Program of the European Commission Pristine (Contract. No. ENV4-CT97–494) from Waste Water Cluster.

References

1. Amano K, Fukushima T, Nakasugi O (1992) Hydrobiologia 235/236:491
2. Takada H, Ogura N, Ishiwatari R (1992) Environ Sci Technol 26:2517
3. Prats D, Ruiz F, Vazquez B, Zarzo D, Berna JL, Moreno A (1993) Environ Toxicol Chem 12:1599
4. González-Mazo E, Honing M, Barceló D, Gómez-Parra A (1997) Environ Sci Technol 31:504
5. Swisher RD (1987) Biodegradation. Surfactant Science Series., Vol. 18. Marcel Dekker, New York, pp 1085
6. Larson RJ, Rothgeb TM, Shimp RJ, Ward TE, Ventullo RM (1993) J Am Oil Chem Soc 70:645
7. Linder DE, Allen MC (1982) J Am Oil Chem Soc 59:152
8. Marcomini A, Busetti S, Sfriso A, Capri S, La Noce T, Liberatiori A (1991) In: G. Angeletti and A. Bioset, Organic Micropollutants in the Aquatic Environment, Kluwer, Dordrecht, pp 294–305

9. Field JA, Leenheer JA, Thorn KA, Barber LB II, Rostad C, Macalady DL, Daniel SR (1992) J Contam Hydrol 9:55
10. Knepper TP, Kruse M (2000) Tenside Surf Deter 37:41
11. Di Corcia A, Casassa F, Crescenzi C, Marcomini A, Samperi R (1999) Environ Sci Technol 33:4112
12. Di Corcia A, Capuani L, Casassa F, Marcomini A, Samperi R (1999) Environ Sci Technol 33:4119
13. González-Mazo E, Gómez-Parra A (1996) Trends Anal Chem 15:375
14. Hrsak D (1995) Environ Pollut 89:285
15. Altenbach B, Giger W (1995) Anal Chem 67:2325
16. Di Corcia A, Marchese S, Samperi R. (1993). J Chromatogr 642:163
17. Greenwald R, Chaykosky M, Corey EJ (1963) J Org Chem 28:1128
18. Sarrazin L, Arnoux A, Rebouillon P (1997) J Chromatogr A 760:285
19. Sarrazin L, Wafo W, Rebouillon P (1999) J Liq Chrom Rel Technol 22:1511
20. Cavalli L, Cassani G, Lazzarin M (1996) Tenside Surf Deter 33:158