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Determination of linear alkylbenzenesulfonates in wastewater treatment plants and coastal waters by automated solid-phase extraction followed by capillary electrophoresis–UV detection and confirmation by capillary electrophoresis–mass spectrometry

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Abstract

Linear alkylbenzenesulfonates (LASs) were determined in wastewaters and coastal waters by solid-phase extraction, using two different sample preparation protocols depending on the sample treated, followed by capillary electrophoresis and ultraviolet detection (CE–UV). The linear range of the proposed method varied from 3 to 53 and from 25 to 495 μg/l, depending on the compound, with a limit of detection of 1 μg/l when 250 ml of coastal water was preconcentrated. $[M-H]^-$ ions were used for CE–MS confirmation after quantification by CE–UV. CE–MS diagnostic ions were the same ones used in LC–electrospray (ESI) MS and corresponded to *m/z* 297, 311, 325 and 339 for C_{10}, C_{11}, C_{12} and C_{13} LASs, respectively. LASs were determined in wastewater samples of the influent and effluent of three wastewater treatment plants (WWTPs), two of them using biological treatment with secondary settlement and receiving mainly domestic wastewaters whereas one of the plants was operated with physicochemical treatment and received mainly industrial wastewaters. LASs were also analyzed in two samples from coastal waters of the bay of Cadiz (Spain) receiving untreated domestic effluents. All samples were also analyzed by LC–ESI-MS and the results are compared with the CE–UV method developed in this work. The concentration levels of total LASs varied from 988 to 1309 μg/l in the influents of WWTPs, whereas in the effluents the concentrations varied from 136 to 197 μg/l. The levels of LASs in coastal wastewaters of the bay of Cadiz varied from 739 to 911 μg/l, indicating that the wastewaters discharged into the bay did not undergo any treatment at all.

Keywords: Water analysis; Environmental analysis; Surfactants; Alkylbenzenesulfonates, linear

1. Introduction

Linear alkylbenzenesulfonates (LASs) are the most commonly used anionic surfactants. From the $2.8 \cdot 10^9$ kg of surfactants produced in Europe in 1998, almost $0.42 \cdot 10^9$ kg correspond to LASs [1]. Commercially available LASs are mixtures of secondary isomers, with alkyl chain lengths of 10–13 carbon atoms. The formula of the commercial product is shown in Fig. 1. It corresponds to a mixture of homologues, most with chain lengths varying between 10 and 13 carbon atoms. Each of these homologues consists of a varying number of positional isomers.

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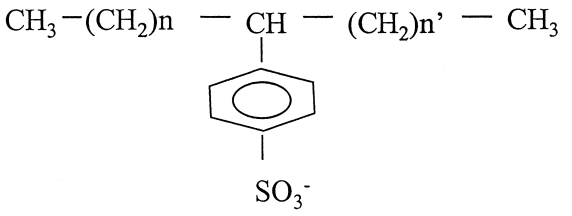

Fig. 1. General chemical structure of linear alkylbenzenesulfonates.

After use, LASs are discharged into domestic or industrial wastewaters. Routine determination of LASs in surface waters uses solid-phase extraction (SPE) followed by time-consuming and tedious derivatization prior to gas chromatography–mass spectrometry (GC–MS) [2,3]. Continuous flow fast atom bombardment MS was also developed and permitted the direct determination of LASs in wastewater and river samples [4].

Capillary electrophoresis (CE) is a good technique for the analysis of ionic compounds. Because of its high separation efficiency and low solvents costs, CE is appropriate for the analysis of many dyes and related compounds employed in the dye industry [5]. This efficiency of the CE technique can be additionally enhanced by an automated SPE including simultaneous sample enrichment and clean-up with elimination of interferences from wastewaters. An automated SPE method involving the ASPEC XL system, followed by CE–UV and CE–MS, was developed by our group for the determination of sulfonated azo dyes [6].

CE has been increasingly used for the analysis of LASs in environmental matrices in recent years [7–10]. For the separation of LAS homologues an organic modifier, like acetonitrile or γ-cyclodextrin is added to a phosphate or borate buffer [7,8]. Without adding organic solvents all LAS homologues and isomers produce only one peak in the electropherogram. This method is useful for the analysis of total LASs [9]. For the determination of isomeric compounds, CE has been suggested as one of the best methods available. Normally additives like sodium dodecyl sulfate (SDS) [7] or α-cyclodextrins [8] are used with a phosphate or borate buffer and acetonitrile as organic modifier, although some authors found a better resolution of some isomeric LASs using capillary zone electrophoresis (CZE) with no SDS present in the buffer [10].

CE–UV is the preferred method for analysis of LASs. In environmental analysis the use of MS detection has been demonstrated to be an indispensable tool because it can overcome the large number of interfering substances and thus can avoid overestimation as compared to less sensitive detectors like UV. In CE–MS additives like SDS cannot be used because of sensitivity problems. Moreover, the separation and determination of isomers in environmental water samples with CE is difficult although it is not essential to know LAS isomeric distribution in wastewater samples for risk assessment.

Taking into account these facts the objectives of this work were: (1) to develop a methodology for the trace determination of the four commonly used LAS homologues by SPE, using two different protocols depending on the sample treated (coastal waters receiving untreated domestic effluents from the bay of Cadiz or industrial wastewaters from influent and effluent of water treatment plants from Catalonia, Spain), followed by CE–UV. (2) To compare the former methodology with the reference liquid chromatography–electrospray mass spectrometry (LC–ESI-MS) methodology. (3) To use CE–MS for confirmation purposes of CE–UV environmental traces.

2. Experimental

2.1. Study area of the bay of Cadiz and sample pretreatment

The study area and sample pretreatment are the same as those described in a previous paper [11]. Coastal marine water samples receiving untreated wastewater discharges from the bay of Cadiz, in the southwest of Spain, were analyzed with the method developed in this work. Water samples (250 ml) were acidified to pH 3, then purified, and concentrated by SPE using a C_{18} hydrophobic-type mini-column and eluted with methanol onto a SAX strong anionic exchanger. The second elution was carried out with 3 ml of 2 *M* HCl in methanol. The eluate was evaporated until dryness and was re-dissolved with 1

Table 1
Recoveries and standard deviations ($n=6$) for LASs using two-stage SPE (C_{18} and SAX)[a]

Compound	Average recovery (%)	SD (%)
C_{10} LAS	94	2
C_{11} LAS	96	1
C_{12} LAS	98	2
C_{13} LAS	94	1

[a] A 200-ml volume of water spiked with a final concentration of 50 μg/l (LAS mixture) was preconcentrated.

ml of water. Table 1 shows the recoveries obtained with this method.

2.2. Treatment plants and sample preparation

Sample collection took place at three wastewater treatment plants (WWTPs). Two of the plants carry out biological treatment (WWT1D and WWT2D) which receive domestic effluents. The third one (WWT3I), consisted of primary settlement involving only physicochemical treatment, which received industrial effluents from various types of industries the major discharges (around 60%).

Water samples from the influent and effluent were collected corresponding to 24-h composite samples. The 24-h composite samples were obtained by the treatment plant operators. All water samples were collected in glass bottles. Samples were transported to the laboratory and were stored at 4°C prior to the analysis that took place within 1–2 days. Before analysis, the pH values of the samples were adjusted to the neutral range and samples were filtered when necessary.

Disposable 6-ml cartridges packed with 200 mg Isolute ENV+ (International Sorbent Technology, UK) were attached to the ASPEC XL system (Gilson, Villiers-le-Bel, France) which is fitted with an external Model 306 LC pump and connected with a Model 817 switching valve for the selection of samples. The SPE cartridges were conditioned with 7 ml methanol followed by 3 ml water (pH 3) with a flow-rate of 1 ml/min. After the spiked groundwater samples (200 ml) were dispensed with a flow-rate of 5 ml/min through the cartridge columns, a clean-up step with 1 ml water (1 ml/min, pH 7) was performed. Subsequently a drying step was introduced, which took about 30 min by using a Baker Spe 12G combined with a vacuum system (15 p.s.i. negative pressure; 1 p.s.i.=6894.76 Pa). The target compounds were eluted with two aliquots of 5 ml of methanol with a waiting time of 5 min between the two elution steps. The eluate was evaporated under gentle stream of nitrogen at 25°C. The samples were reconstituted in 1 ml water. Table 2 shows the recoveries of the different LASs obtained with this SPE method.

2.3. CE–UV conditions

CE was carried out with a Beckman P/ACE 5000 CE system (Beckman Instruments, Palo Alto, CA, USA). The UV detector operated at a wavelength of 214 nm. The separation was performed in a 47 cm (40 cm effective length to detector)×75 μm I.D. fused-silica capillary (Beckman Instruments). The electrophoresis buffer solution was 50 m*M* ammonium acetate in water at pH 5.6 and with an organic modifier of 30% isopropanol. The capillary was regenerated subsequently with 0.1 *M* NaOH (15 min), water (5 min), and working buffer solution (10 min) before each analysis. The temperature of the capillary column was set at 25°C. After a pressure injection (0.5 p.s.i.) over 5 s, a voltage of 20 kV was applied across the capillary. Data analysis was performed by System Gold software.

The pH of the electrolyte and the spiked water samples was adjusted by adding ammonia and acetic acid, respectively and it was measured with a Model 691 pH meter (Metrohm, Herisau, Switzerland) connected with pH glass electrode containing 3 *M* KCl and silver chloride. In order to optimize the separation several parameters were tested. Different

Table 2
Mean recoveries and standard deviations (SDs), for LASs using Isolute ($n=4$)[a]

Compound	Mean recovery (%)	SD (%)
C_{10} LAS	78	3
C_{11} LAS	93	4
C_{12} LAS	82	3
C_{13} LAS	77	3

[a] A 200-ml volume of water spiked with a final concentration of 50 μg/l (LAS mixture) was preconcentrated.

percentages of organic modifier were used (20, 30 and 40%) with different buffer concentrations (ammonium acetate, 10, 25, 50 and 80 m*M*). Finally, several pH values from 5 to 9 were tested. Acetonitrile instead of isopropanol was also used as organic modifier (20, 30 and 40%) with ammonium acetate in water as buffer system. The most significant advantage of acetonitrile is the reduction of the analysis time (analytes could be analyzed in less than 10 min) but resolution was not as good as with isopropanol and, in some real sample analysis, there were some interferences coeluting with the target compounds. Due to the fact that the number of samples in this study was not high, the separation with isopropanol was chosen.

2.4. CE–MS conditions

For CE–MS operation the voltage applied was 20 kV and the capillary length was 80 to 100 cm in order to extend it to the probe tip through the stainless steel sheath capillary.

The CE system was connected to a VG Platform mass spectrometer from Micromass (Manchester, UK) equipped with a CE probe and an ESI interface. The design of this probe consists of a triaxial flow arrangement whereby the CE eluent is mixed with a suitable make-up solvent at the probe tip, and then nebulized using nitrogen gas. The CE capillary extends fully to the probe tip through the stainless steel sheath capillary, which carries the make-up solvent. Around the sheath capillary is the nebulizer capillary through which the nitrogen gas flows to the probe tip. The make-up solvent performs two functions: to supplement the CE flow to a level adequate for electrospray operation (the CE electroosmotic flow is in the range of 10 nl/min and is too low for ESI operation without make up solvent) and to make electrical contact between the CE buffer and the probe tip. The nitrogen gas that flows through the probe tip maximizes the efficiency of the nebulization. The design of the source is not different from the system used in the normal megaflow ESI operation which has been previously described by our group [12].

The make-up solvent, consisting on isopropanol–water (80:20) with 0.1% of ammonia, was delivered at a flow-rate of 10 μl/min by a gradient system used in isocratic condition from a Waters 616 pump controlled by a Waters 600S Controller from Waters–Millipore (Milford, MA, USA).

The MS instrument was tuned by filling the capillary with the studied compounds and monitoring the signal corresponding to the mass of the tuning ion while the voltage of the CE was applied to introduce the sample into the MS system. The operating parameters were adjusted in order to achieve maximum sensitivity (with the consequent loss of fragmentation and structural information). In this study a nebulizer gas of 25–30 l/h was used and the drying gas was set at a low value (in the order of 50 l/h or less). The source temperature was set at 75°C. The cone voltage was set at 20 V in order not to produce fragmentation and achieve the best sensitivity.

The instrument control and data processing utilities included the use of the MassLynx application software installed on a Digital DEC personal computer 466.

The operational parameters of the LC–ESI-MS method are explained in a former paper [13].

3. Results and discussion

3.1. Calibration graphs

The linearity of the system with UV detection was studied by external calibration carried out by quantification of spiked groundwater with different concentrations of the LASs in the range from 3 to 500 μg/l depending on the compound. This was followed by SPE preconcentration.

Calibrations were performed by a five-point calibration curve over the concentration range. The linear regression equations with slopes and correlation coefficients are summarized in Table 3. Repeatability varied between 2 and 5% for an average of six injections in the same day and reproducibility between 6 and 12% for one injection in six different days. The relationship between the concentration of each compound and its peak area was found to be linear, as indicated by correlation coefficients between 0.9807 and 0.9952. The minimum detectable amount (limit of detection, LOD) was about 1 μg/l at a signal-to-noise ratio of 3 for the four LASs.

Table 3
Calibration data obtained with CE–UV at 214 nm

Compound	Calibration equation	r^2	Linear range (μg/l)
C_{10} LAS	$y=0.000282x-0.000737$	0.981	3–53
C_{11} LAS	$y=0.000255x-0.00517$	0.995	25–495
C_{12} LAS	$y=0.000245x-0.00592$	0.992	23–469
C_{13} LAS	$y=0.000232x-0.00531$	0.984	15–306

Table 4
Concentrations of LASs found in several coastal water samples from the bay of Cadiz and influent (Inf.) and effluent (Eff.) wastewaters of several wastewater treatment plants by CE–UV

	Concentration (μg/l)			
	C_{10} LAS	C_{11} LAS	C_{12} LAS	C_{13} LAS
WWT1D Inf.	271	721	359	139
WWT1D Eff.	12	57	99	53
WWT2D Inf.	275	839	406	110
WWT2D Eff.	31	134	102	41
WWT3I Eff.	9	92	69	58
Cadiz 1	162	622	321	75
Cadiz 2	188	663	291	146

Table 5
Concentrations of LASs found in several coastal water samples from the bay of Cadiz and influent (Inf.) and effluent (Eff.) wastewaters of several wastewater treatment plants by LC–ESI-MS

	Concentration (μg/l)			
	C_{10} LAS	C_{11} LAS	C_{12} LAS	C_{13} LAS
WWT1D Inf.	194	536	385	194
WWT1D Eff.	41	66	25	4
WWT2D Inf.	121	399	319	149
WWT2D Eff.	47	75	73	31
WWT3I Eff.	35	87	38	6
Cadiz 1	118	347	306	140
Cadiz 2	118	310	232	79

3.2. Environmental samples

The concentrations obtained for the samples from the influent and effluents of the wastewater treatment plants and the bay of Cadiz are summarized in Table 4. These samples were also determined by LC–ESI-MS in order to compare the CE–UV method with the previously reported one and the results are shown in Table 5.

From the data reported in Tables 4, 5 and 6 we can conclude that although the samples analyzed were the same with both systems, the concentrations do not fully agree. Differences of 27% average were found. There are two explanations for such disagree-

Table 6
Comparison of concentrations of total LASs (by combining the data of Tables 4 and 5) found in several coastal water samples from the bay of Cadiz and influent (Inf.) and effluent (Eff.) wastewaters of several wastewater treatment plants by LC–ESI-MS and CE–UV

	Concentration (μg/l)		Discrepancy (%)
	CE–UV	LC–MS	
WWT1D Inf.	1490	1309	9
WWT1D Eff.	221	136	34
WWT2D Inf.	1630	988	35
WWT2D Eff.	308	197	31
WWT3I Eff.	228	167	22
Cadiz 1	1180	911	18
Cadiz 2	1288	739	38

ment. First, the cases of overestimation that CE–UV shows can be attributed to coeluting substances, whereas LC–MS is much more selective. However, for individual LASs, some samples show lower concentration values in CE–UV than in LC–ESI-MS, so in that case it cannot be attributed to coelution. In this case the explanation can be found in the existence of positional isomers of each one of the four individual LASs which are a complex mixture of 20 possible isomers. If not all the isomers of each individual LAS homologue coelute in one peak, this can affect on the quantification and can be an explanation of the observed disagreement. In MS detection, all the isomers of each homologue are quantified together because they have the same m/z value. However, when comparing total LAS concentrations with both methods then this problem does not exist. This hypothesis can be confirmed by data in Table 6, where the comparison between total LASs determined with two methods gives overestimation of the CE–UV method in all cases.

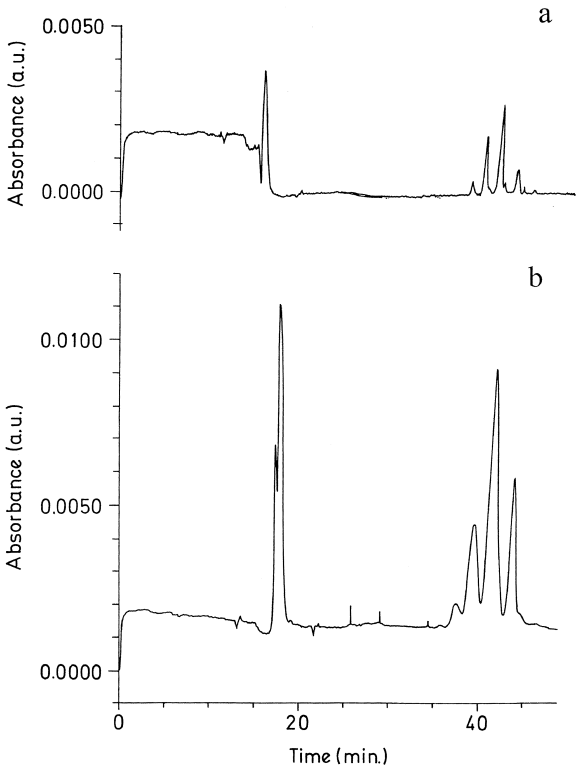

Fig. 2. CE–UV (214 nm) electropherogram of a water extract from an effluent (a) and influent (b) of WWT2D (Ripoll, Girona, Spain).

More agreement was also found in some samples as compared to other ones. This can be attributed to the instability of the LC–ESI-MS system, that can lead to reproducibilities of 15–20%. In some cases the signal has much more fluctuations than with CE–UV, and consequently, will affect quantification. Fig. 2 shows an electropherogram of the analysis of the influent and effluent of WWT2D by CE–UV.

3.3. Confirmation with CE–MS

In the previous section, the disagreement between the CE and the LC data has shown the need for the MS detection with the CE methodology. For this reason the confirmation with MS for the samples analyzed by CE–UV has been developed. The parameters of the mass spectrometer were optimized in order to get the maximum sensitivity. By changing the cone voltage it is possible to induce fragmentation in the source region, and consequently, to obtain structural information (but at the expense of sensitivity). Due to the low amounts injected in CE (nl) the sensitivity is a serious drawback of this technique. This is the reason why we needed to use low cone voltages (20 V) in order to avoid fragmentation and achieve the highest detection limits. All the compounds studied were detected as anions and the negative mode of ionization in time-scheduled selected ion monitoring (SIM) conditions was used for all of them. The ions employed to detect the compounds by SIM conditions were the deprotonated molecular ions, which give the best signal-to-noise ratio for each compound and corresponded to m/z 297 for C_{10} LAS, 311 for C_{11} LAS, 325 for C_{12} LAS and 339 for C_{13} LAS.

Fig. 3 shows an electropherogram of a water extract from the influent and the effluent of WWT2D (Ripoll, Girona, Spain). In Fig. 4, the selected ion electropherograms of the influent of the same sample of Fig. 2 are shown. No positional isomers are apparent in the CE–MS chromatographic trace, but this could be attributed to the lower sensitivity of CE–MS versus CE–UV. So, we cannot discount the existence of coeluting positional isomer peaks in the CE–UV analysis being a problem for the quantitative analysis of LASs.

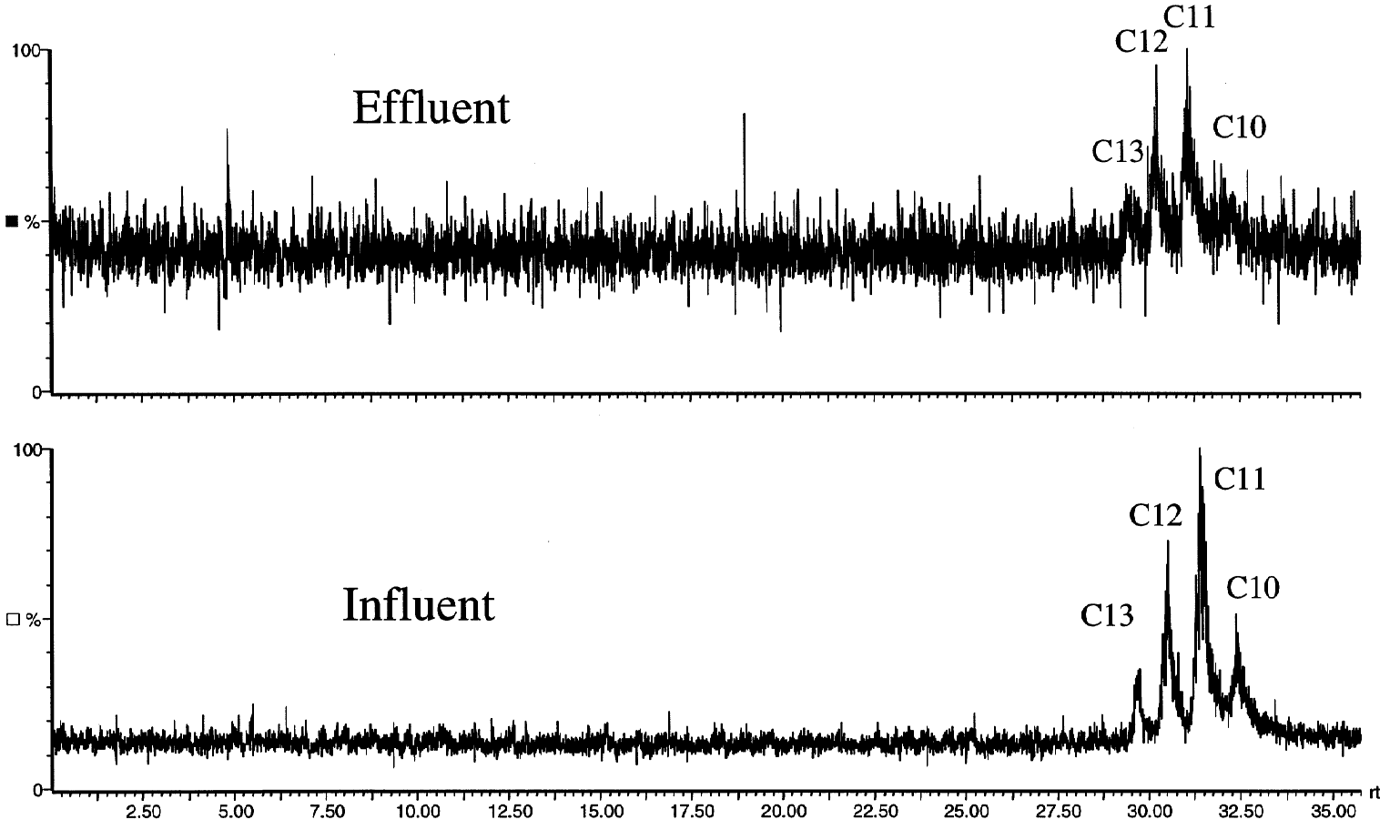

Fig. 3. CE–ESI-MS electropherogram of water extract from the influent and the effluent of WWT2D (Ripoll, Girona, Spain). Ions monitored corresponded to m/z 297 for C_{10} LAS, 311 for C_{11} LAS, 325 for C_{12} LAS and 339 for C_{13} LAS. x-Axis: migration time in min.

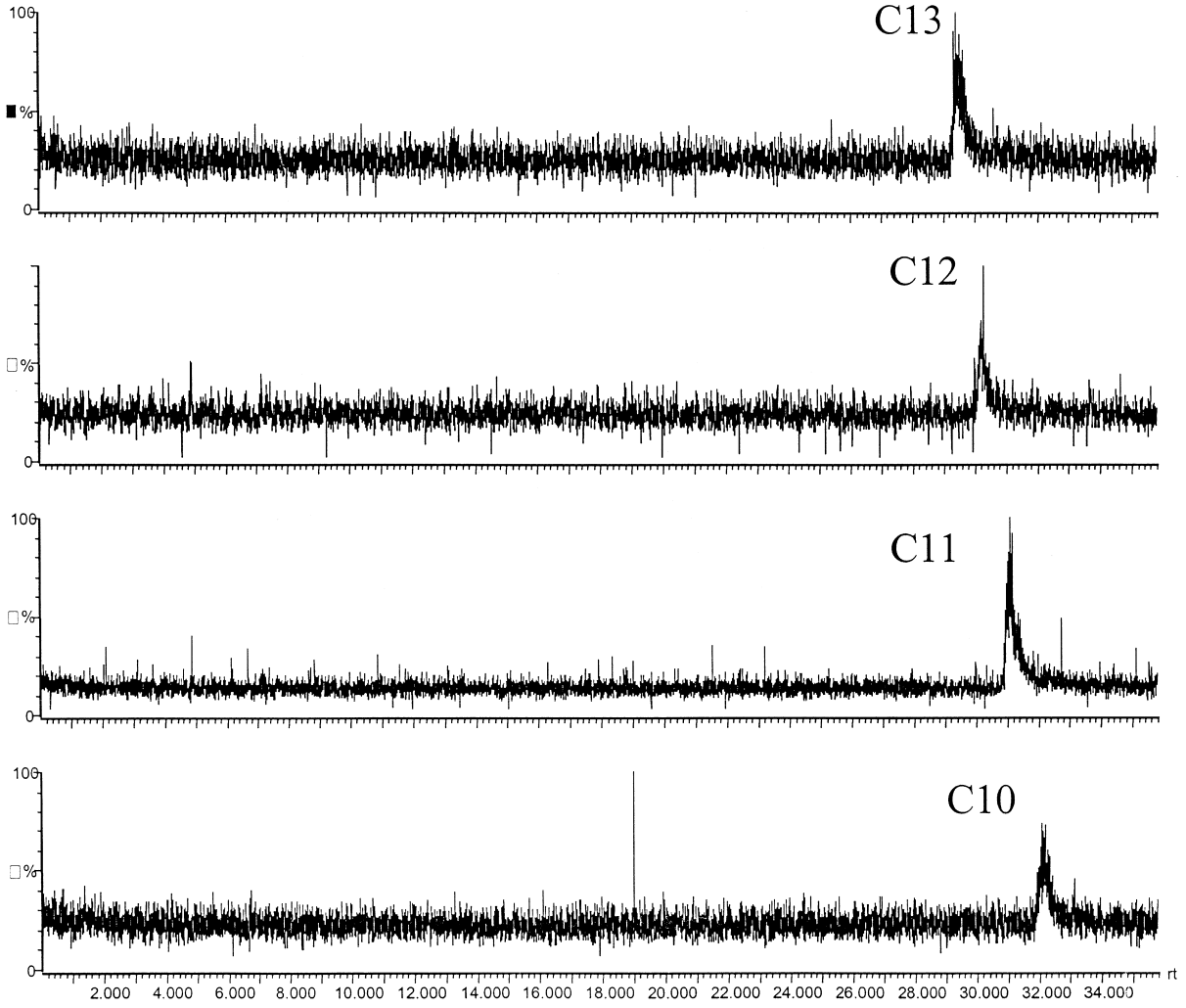

Fig. 4. Selected ion electropherograms of an extracted sample from the effluent of WWT2D (Ripoll, Girona, Spain), where no isomer peaks can be observed. Ions monitored corresponded to m/z 297 for C_{10} LAS, 311 for C_{11} LAS, 325 for C_{12} LAS and 339 for C_{13} LAS. x-Axis: migration time in min.

4. Conclusions

Overall, we have shown that the present method reported here allowed the determination of LASs in wastewaters and coastal waters by using CE–UV. By the use of CE–MS it was feasible to confirm the presence of the different analytes. It was not a problem to determine LASs by CE–UV since the LODs of the CE system are in the 1 ppb range and most of the samples had much higher values. CE–UV and CE–MS, having much poorer detection limits than LC–ESI-MS, are useful techniques in wastewater monitoring. They offer good selectivity and they permit the quantification of the different LASs. The use of CE–UV and CE–MS for other types of environmental matrices, such as groundwater or surface water samples, is more complicated because sensitivity is poorer as compared to LC–

ESI-MS. For the analysis of wastewater, the samples are much more concentrated with organic pollutants, so sensitivity is not a problem. In addition, CE offers good selectivity and low operating costs, which offer potential for environmental trace analysis. The need for MS detection in environmental applications for CE can be derived from the disagreement observed between CE–UV and LC–ESI-MS data. So further work to improve the stability of CE–MS is needed. Future work is planned in order to quantify LASs by CE–MS, so it will improve the quantitative data obtained by CE–UV in environmental samples. In the present work only qualitative data for confirmation could be obtained.

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