Short communication

Determination of linear alkylbenzenesulfonates and their degradation products in water samples by gas chromatography with ion-trap mass spectrometry

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Abstract

A method was developed for the analysis of linear alkylbenzenesulfonates (LAS) and their degradation products, sulfophenylcarboxylic acids (SPC), in samples of sewage effluent and river water. This method involved extraction of the samples by graphitized carbon black cartridge, esterification by a two-step thionyl chloride–trifluoroethanol derivatization procedure, and separation, identification and quantitation by ion-trap GC–MS with EI and low pressure CI modes. High selectivity with few signals was observed in the low pressure CI mass spectra of LAS and SPC. Enhanced sensitivity with protonated molecular ion chromatograms of homologous C_{10}–C_{13} LAS by CI-MS permit the determination of LAS and SPC at trace concentrations in environmental samples. Recovery rates of LAS and SPC in spiked water samples ranged from 75 to 112% with R.S.D. values from 3 to 26%. The limit of quantitation for both LAS and SPC was estimated to be 0.01 μg/l in 100 ml of water sample. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Linear alkylbenzenesulfonates (LAS) are the most commonly used anionic surfactants in detergent formulations and surface cleaners. In Taiwan, more than 52 000 metric tons of LAS are consumed every year [1]. Theoretically, these surfactants can be degraded by chemical, physical and biological processes in wastewater treatment plants and these methods remove an average of 80, 27 and 98% of influent surfactants, respectively [2]. However, less than 5% of all wastewater is treated by wastewater treatment plants in Taiwan. Large quantities of these

surfactants in wastewaters are discharged into the rivers and ocean directly. The impact of surfactant pollution on the aquatic environment is very significant. Although serious river pollution problems in Taiwan are well known, no studies have reported the distribution and concentration of LAS residues and their degradation products in the aquatic environment.

For the specific characterization and quantitation of individual LAS and their degradation products in environmental samples, the application of GC–MS with derivatization of LAS and sulfophenylcarboxylic acids (SPC) to the corresponding ester derivatives is effective [2–7]. In previous studies, quantitation was based on the characteristic ions or molecu-

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lar ions of the LAS derivatives in electron ionization (EI) mode. However, to establish characteristic ion chromatograms of individual LAS isomers is laborious when the matrix is complicated. Quantitation based on molecular ion chromatograms of the LAS derivatives is effective, but the abundance of LAS molecular ions in EI mass spectra is low; sometimes the molecular ion is not detected in EI-MS of environmental samples. Chemical ionization mass spectrometry (CI-MS), however, provides a high abundance of quasi-molecular ions of LAS derivatives [5–7]. An inexpensive benchtop ion trap GC–MS system with low pressure CI capability was developed for quick switching between EI and CI scans without compromises in spectral quality. This technique has been applied to many environmental analyses routinely [8–10]. The ion-trap MS system accumulates reagent ions and holds them for reaction periods of 1–120 ms. During this period, a low reagent gas pressure is sufficient to produce a large population of sample ions. In comparison, a conventional CI source in a quadrupole or magnetic MS system, requires high reagent gas pressure, of the order of 1 Torr, in order to generate sufficient reagent ions in very short time frame, about 10^{-5} s. In addition to the quick switching between EI and CI scans, the low pressure CI of an ion-trap MS system does not need an expensive vacuum pumping system to handle the large amount of reagent gas, and provides very good CI sensitivity in the full-scan mode.

Because of the low concentration of LAS residues and SPC in environmental water samples, a preconcentration step is necessary. Procedures for extraction and concentration of LAS residues and their degradation products by graphitized carbon black (GCB) solid-phase extraction (SPE) have been reported elsewhere [11]. That study showed that a single GCB cartridge can be used to extract nonylphenol polyethoxylates (NPEOs), LAS surfactants and their degradation products simultaneously and to separate them by differential elution.

The aim of this work was to develop an improved method for the routine determination of LAS residues and SPC in water samples by using GCB-SPE and ion trap MS in CI mode. The effectiveness of the method was then demonstrated for the determination of analytes at low ppb levels in environmental samples.

2. Experimental

2.1. Samples and chemicals

Samples of secondary effluent (specific conductance 400 μS/cm) were collected from a municipal wastewater treatment plant located in Taipei, Taiwan. Samples of surfactant polluted river water (specific conductance 850 μS/cm) were obtained at the Chung-Jen bridge in Chung-Li city. Here, municipal wastewater from the city is discharged into the river directly. Blank surface water samples (specific conductance 250 μS/cm) were collected from an unpolluted river in a remote mountain area of Tao-Yuan County, upstream of a drinking water reservoir.

Unless noted otherwise all high purity chemicals and solvents were purchased from Aldrich, Tedia and Merck, and were used without further purification. 4-Octylbenzenesulfonic acid (C_8-LAS) as surrogate was purchased from Aldrich (Milwaukee, WI, USA), which was chosen as a surrogate because it dose not occur in commercial LAS mixture and is therefore suitable for evaluating the efficiency of LAS extraction and esterification. The commercial LAS mixture was provided by Taiwan Surfactant (Taiwan) and was used as received. The composition of the LAS mixture includes four alkyl chain homologs: C_{10}-LAS (13%), C_{11}-LAS (27%), C_{12}-LAS (48%) and C_{13}-LAS (12%). 2-Sulfophenylbutyric acid (2-SPC4), one of the LAS biodegradation intermediates, was synthesized as described by Marcomini et al. [12].

2.2. Sample extraction and preparation

The procedures used for sample extraction by graphitized carbon black (GCB or ENVI-carb, trade name from Supelco, USA) and derivatization were the same as reported elsewhere [6,11], with minor modifications. For recovery studies, a total of 100 μg/l of the LAS mixture, 10 μg/l of 2-SPC4 and 20 μg/l of C_8-LAS were added to water samples, and allowed to equilibrate for 2 h. Next the spiked water samples were acidified to pH 3 with concentrated HCl, and the LAS and SPC were extracted by passing the water sample through the ENVI-carb cartridge at a flow-rate of about 10–20 ml/min with the aid of vacuum. After the extraction, cartridge was

dried completely by drawing air through it for 2 min. The LAS and SPC were eluted from the cartridge with 7 ml of methylene chloride–methanol (9:1, v/v) eluent modified with 10 mM tetramethylammonium hydroxide·5H$_2$O (TMAOH) ion pair reagent.

After completion of the elution process, the extract in the reaction vial was completely evaporated to dryness by a stream of nitrogen. The residue was redissolved in 200 μl of thionyl chloride (SOCl$_2$) and reacted at 95°C for 1 h. The volume of the reaction mixture was reduced to 10 μl by evaporation, and then 200 μl of pyridine and 200 μl of 2,2,2-trifluoroethanol were added to the reaction vial, and the vial was left to react another 10 min. This procedure converts the thionyl chloride LAS into 2,2,2-trifluoroethyl ester LAS. The mixture was reduced by evaporation to about 50 μl and then another 100 μl of chloroform was added. The solution was passed through an alumina oxide column and eluted with hexane–ethyl acetate (1:1, v/v). The eluate was completely evaporated to dryness by a stream of N$_2$. The final residue was redissolved in 1 ml of chloroform containing 10 ng/μl of 2,2,2-trifluoroethyl-p-toluenesulfonate (C$_2$-LAS) as internal standard. Acidified 100 ml samples of river water and sewage effluent were prepared using the extraction and derivatization procedures described above.

2.3. GC–MS analysis

Analyses were performed on a Varian 3400CX gas chromatograph equipped with a 1078 injection port and a Saturn 2000 ion trap mass spectrometer (Varian, USA). A 1-μl volume of sample extract was injected splitless at a temperature of 250°C on a DB-5MS capillary column (30 m×0.25 mm I.D., 0.25 μm film, J&W, USA). The GC temperature program was as follows: 60°C for 2 min, temperature ramp at 8°C/min to 180°C, then from 180 to 230°C at 3°C/min, finally from 230 to 250°C at 10°C/min, hold for 10 min. The transfer line was set at 250°C. Full scan data were acquired under the following conditions: mass range 50–500 m/z, scan time 1 s, solvent delay 10 min, manifold temperature 120°C, emission current 10 μA, automatic gain control (AGC) target 25000 (represents as the target total ion current value). For CI mass spectral analysis, methane was used as CI reagent gas in the selected

ejection chemical ionization mode (SECI). Reagent ions were ionized for a variable duration set by automatic reaction control (ARC) of the instrument. ARC parameters for methane were as follows: ARC ionization time, 0.1 ms; CI maximum ionization time, 2.0 ms; CI maximum reaction time, 40 μs; CI ionization storage level, 5 m/z; CI reaction storage level, 13 m/z; CI background mass, 45 m/z, and reagent ion eject amplitude, 9 V. The autotune program was used to set most instrument parameters with target 5000 (represents as the target total ion current value in CI mode. This value was calculated from the target value found for EI, as described in the GC–MS operating manual [13]). The pressure of reagent gas in the ion trap was approximately $2 \cdot 10^{-5}$ Torr.

3. Results and discussion

3.1. Full-scan EI and CI mass spectra of LAS and SPC

Fig. 1 shows the full-scan EI mass spectra of the trifluoroethyl derivatives of 5-phenyl and 3-phenyl C$_{12}$-LAS isomers found in a river water sample. The ion at m/z 408 is the molecular ion of C$_{12}$-LAS. The characteristic fragment of the 5-phenyl isomer (Fig. 1a) is the ion at m/z 309 (310), representing the benzylic cleavage of the seven-carbon alkyl chain [M−C$_7$H$_{15}$]$^+$ ([M−99]$^+$). This ion also represents the loss of the trifluoroethyl ester group [M−OCH$_2$CF$_3$]$^+$ ([M−99]$^+$) from the molecular ion. The ion at m/z 351(352) represents the loss of the four-carbon alkyl chain on the other side of the phenyl group of the 5-phenyl isomer. The relatively abundant signals at m/z 310 and 352 may be due to the hydrogen rearrangement and loss of the corresponding alkenes, which is commonly observed for alkylbenzene compounds when the alkyl side chain is propyl or longer [14]. The characteristic fragment of the 3-phenyl isomer (Fig. 1b) is the ion at m/z 281, representing the loss of the nine-carbon alkyl chain [M−C$_9$H$_{19}$]$^+$ ([M−127]$^+$). The analogous loss of C$_9$H$_{18}$ for the ion at m/z 282 is also observed due to the hydrogen rearrangement. Here, the ion at m/z 309 represents the loss of the trifluoroethyl ester group [M−99]$^+$ from the molecular ion. The ions at m/z 253 and 267 are the ions produced by the loss of
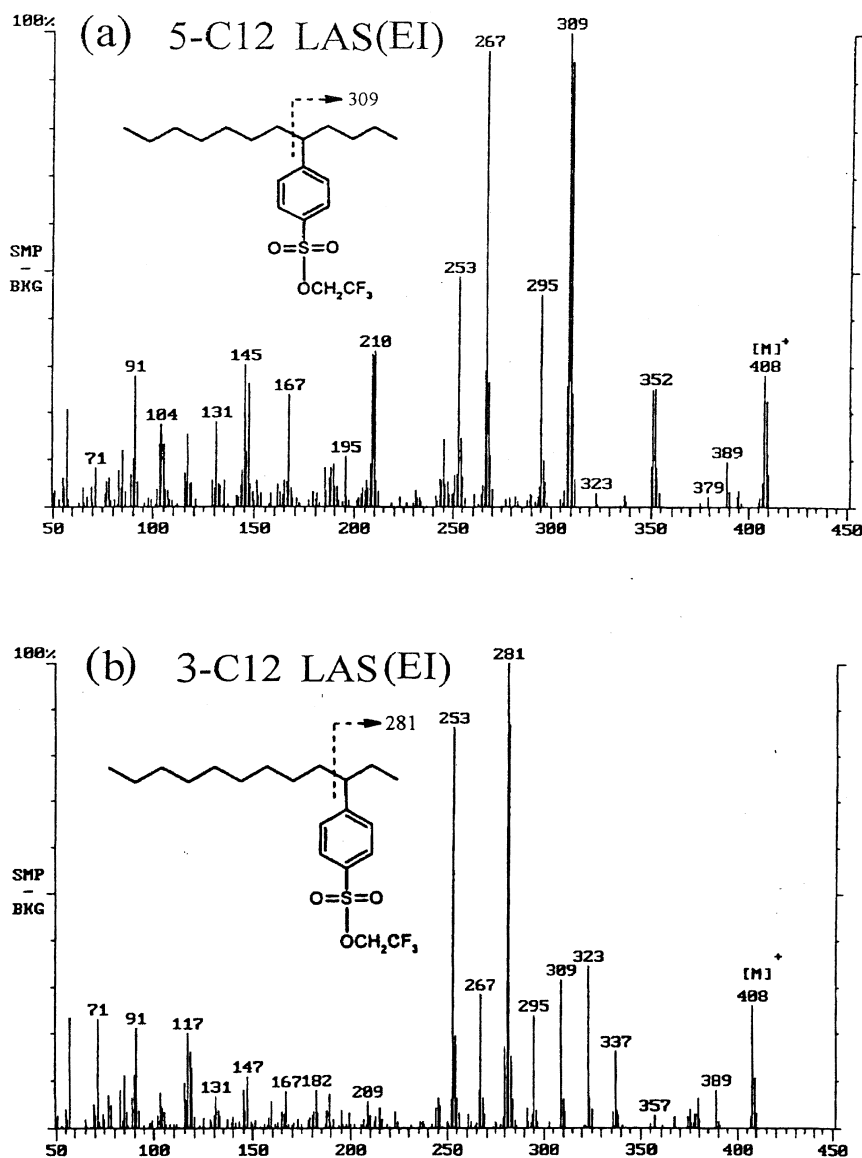
Fig. 1. Full scan EI mass spectra of the trifluoriethyl derivatives of (a) 5-phenyl and (b) 3-phenyl C_{12}-LAS isomers found in a river water sample.

the remaining two-carbon alkyl chain from the benzylic carbon of the characteristic fragment. The phenyl group attached to the 2, 4 and 6 positions of C_{12}-LAS give major characteristic ions at 267, 295 and 323, respectively.

The CI mass spectra of trifluoroethyl derivatives of 5-phenyl and 3-phenyl C_{12}-LAS isomers are shown in Fig. 2. Few signals were observed in the

ion trap low pressure CI mass spectra. The spectra predominantly show protonated molecular signals $[M+H]^+$ at m/z 409, and characteristic ions that depend on the position of phenyl group (m/z 309 and 281). These spectra show less fragmentation than spectra obtained by using a conventional CI source in a quadrupole or magnetic MS system [5,6]. The signal at m/z 389 is due to the loss of hydrogen
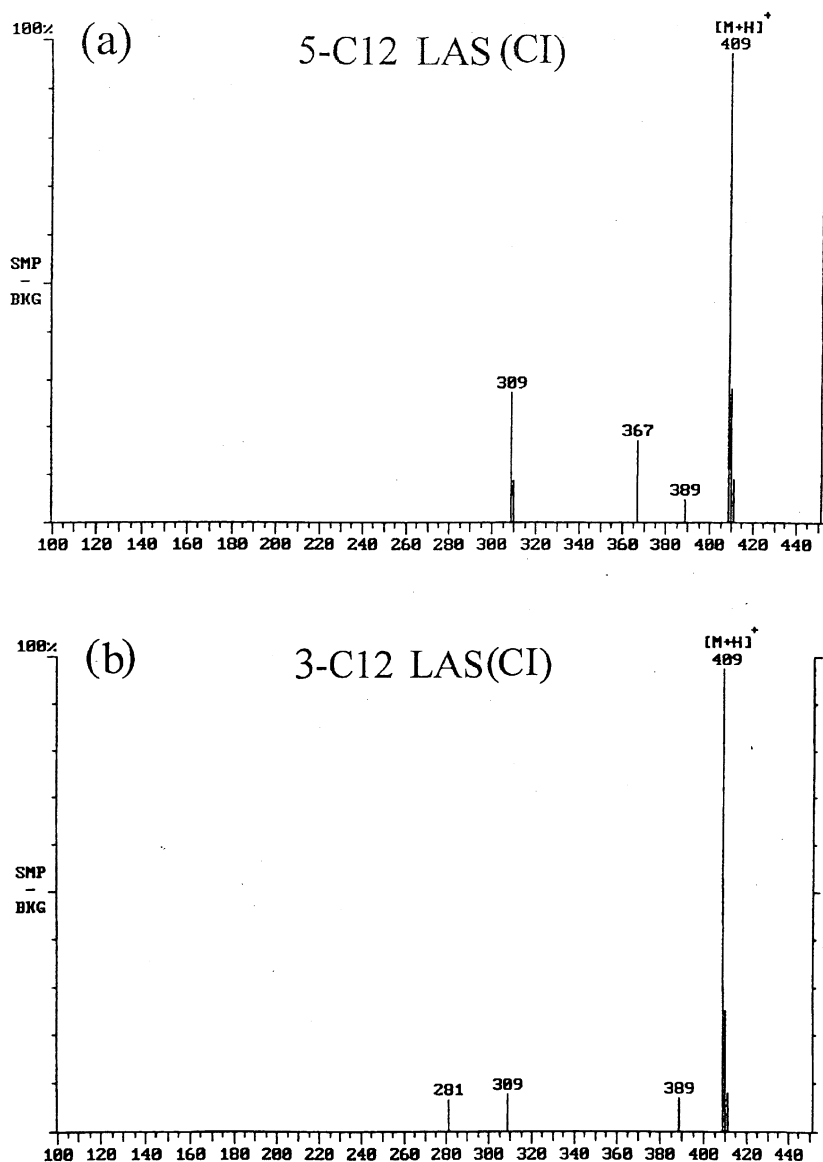
Fig. 2. CI mass spectra of the trifluoroethyl derivatives of (a) 5-phenyl and (b) 3-phenyl C_{12}-LAS isomers found in a river water sample.

fluoride from $[M+H]^+$. The ion at m/z 309 represents the loss of the trifluoroethyl ester group $[M+H-HOCH_2CF_3]^+$ from the protonated molecule. Generally, the signal intensities of the quasi-molecular ions in CI ($[M+H]^+$) are 10–50 times higher than the intensities of the molecular ions in EI. Similar CI spectra are obtained for all isomers and homologs of LAS.

Fig. 3 shows the full-scan EI and CI mass spectra

of the bis(trifluoroethyl) derivative of a sulfophenylbutyric acid isomer found in a sewage effluent sample, as well as the EI and CI mass spectra of the bis(trifluoroethyl) derivative of synthesized 2-SPC4 (Fig. 3b and d) for comparison. In the EI mass spectrum of sewage effluent sample (Fig. 3a), the ion at m/z 389 probably represents $[M-F]^+$, in analogy to the LAS derivatives spectra and no molecular ion shows up. The significant base
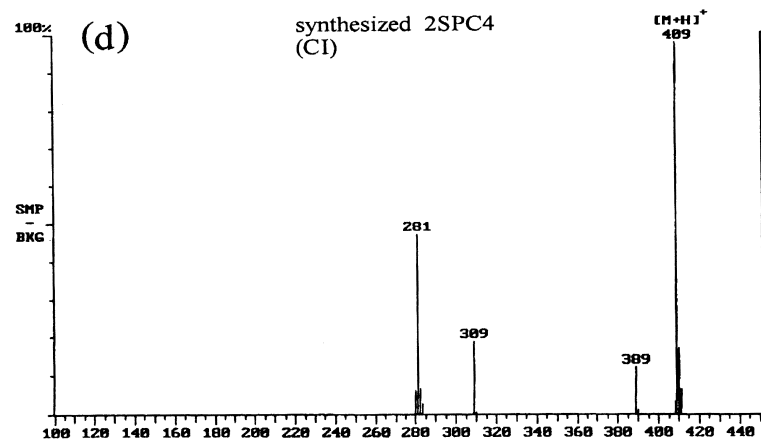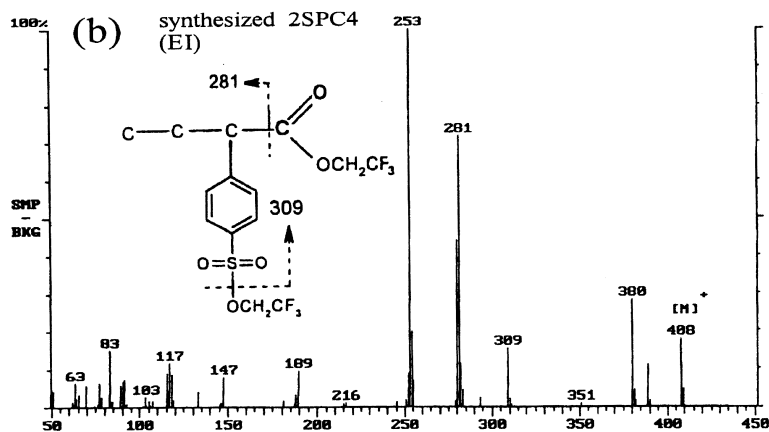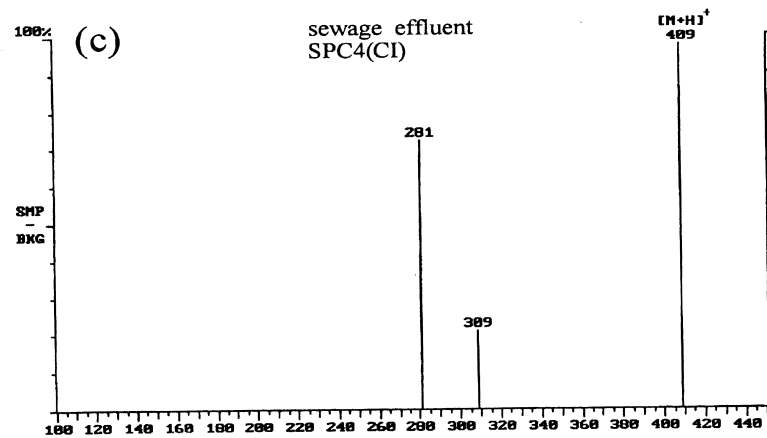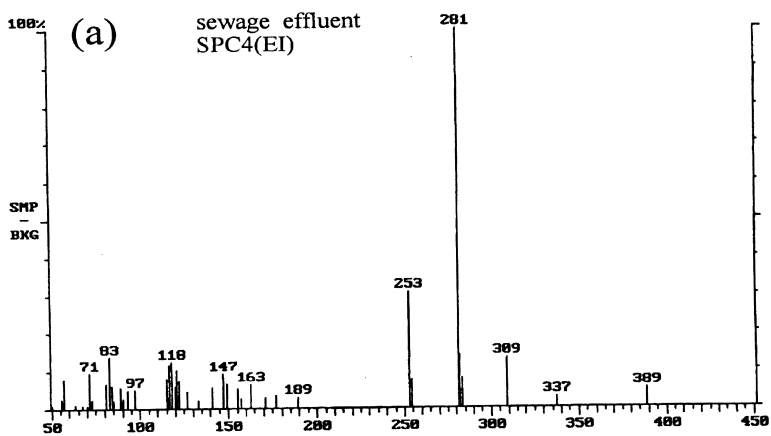
Fig. 3. (a) EI and (c) CI mass spectra of the bis(trifluoroethyl) derivative of a sulfophenylbutyric acid isomer found in a sewage effluent sample; (b) EI and (d) CI mass spectra of the bis(trifluoroethyl) derivative of synthesised 2-sulfophenylbutyric acid (2-SPC4).

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peak at m/z 281 represents the loss of the carbonyl trifluoroethyl ester group $[M-C(O)OCH_2CF_3]^+$ ($[M-127]^+$) on the alkyl chain. The loss of the trifluoroethyl ester group from molecular ion (i.e., m/z 309) and the loss of the two-carbon alkyl chain from the benzylic carbon of the m/z 281 fragment (i.e., m/z 253) are also observed. The CI mass spectrum (Fig. 3c) shows the major protonated molecular signal $[M+H]^+$ at m/z 409. The ions of m/z 309 and 281 probably represent the ions of $[M+H-HOCH_2CF_3]^+$ and $[M+H-HOCH_2CF_3-CO]^+$, respectively. The synthesized 2-SPC4 derivative displays the similar fragments in its EI and CI spectra. Fragments of $[M+H]^+$, $[M+H-HOCH_2CF_3]^+$ and $[M+H-HOCH_2CF_3-CO]^+$ were observed for SPC4 through SPC6 in the samples of sewage effluent and river water by CI-MS. The characteristic fragment of $[M+H-HOCH_2CF_3-CO]^+$ in CI mass spectrum can be used to distinguish between LAS and SPC species of the same $[M+H]^+$.

3.2. Extracted ion chromatograms

Fig. 4 shows the partial molecular ion chromatograms and characteristic ion chromatograms of the trifluoroethyl derivatives of LAS isolated from a river water sample by EI-MS. Clear isomers distributions of each homolog of LAS were observed in molecular ion chromatograms (Fig. 4a). The numbers shown above the peaks indicate isomer position. The C_{11} 5- and 6-phenyl isomers coelute, as do the C_{13} 6- and 7-phenyl isomers. Fig. 4b shows the characteristic ion chromatograms of the $C_{10}-C_{13}$ LAS isomers and homologs. The use of these ions can help to distinguish the coeluting peaks, such as the peaks of C_{11}-LAS 5- and 6-phenyl isomers, as well as the peaks of C_{13}-LAS 6- and 7-phenyl isomers as indicated in the corresponding characteristic ion chromatograms. However, in the m/z 267 ion chromatogram, the characteristic peaks of 2-phenyl of C_{10}-LAS and C_{11}-LAS derivatives interfered with those of the C_{11} 5- and 6-phenyl isomers, and C_{12} 5- and 6-phenyl isomers, respectively. In general, small signal-to-noise ratios for these peaks were obtained in the characteristic ion chromatograms due to the relatively high background from complex sample matrix, which reduced the quantitation capability and reliability.

Fig. 5 shows the partial ion chromatograms of protonated molecules from CI-MS of LAS derivatives obtained from a river water sample. Comparison of the signal-to-noise ratios indicates a 10–20-fold higher sensitivity of detection with CI as compared to EI. Quantitation with CI is more reliable than with EI, because the CI provides the relatively higher signal-to-noise ratio of quasi-molecular ions and the CI baseline shows much less interference. Fig. 6 demonstrates the detection of ppt level of LAS in blank surface water by CI-MS. These components could not be detected by EI with either the molecular ion or the characteristic ion chromatograms.

3.3. Recovery study

The recovery study for GCB-SPE and derivatization procedures were firstly performed by spiking known amounts of the commercial LAS mixture and 2-SPC4 in deionized water. Three replicate 100-ml deionized water samples were spiked to give a total of 100 μg/l of LAS mixture, 10 μg/l of 2-SPC4, and 20 μg/l of C_8-LAS. The recoveries of LAS and 2-SPC4 were estimated by comparing the response factors of the standard mixture and that of the deionized water samples. Table 1 summarizes the average percent recoveries of $C_{10}-C_{13}$-LAS and 2-SPC4 in 100 ml of deionized water. Recovery rates in the deionized water ranged from 84 to 104% with R.S.D. values from 1 to 13%, even with some of the LAS isomer being present at concentrations only 1 μg/l or less.

3.4. Application to samples of sewage and river waters

The recoveries of LAS and SPC from environmental samples were evaluated by means of a standard addition experiment. Three replicate 100-ml samples of blank surface water, surfactant polluted river water and sewage effluent samples were used to perform the studies. The background concentrations of LAS and SPC in the environmental samples were determined in duplicate. Concentrations of LAS and
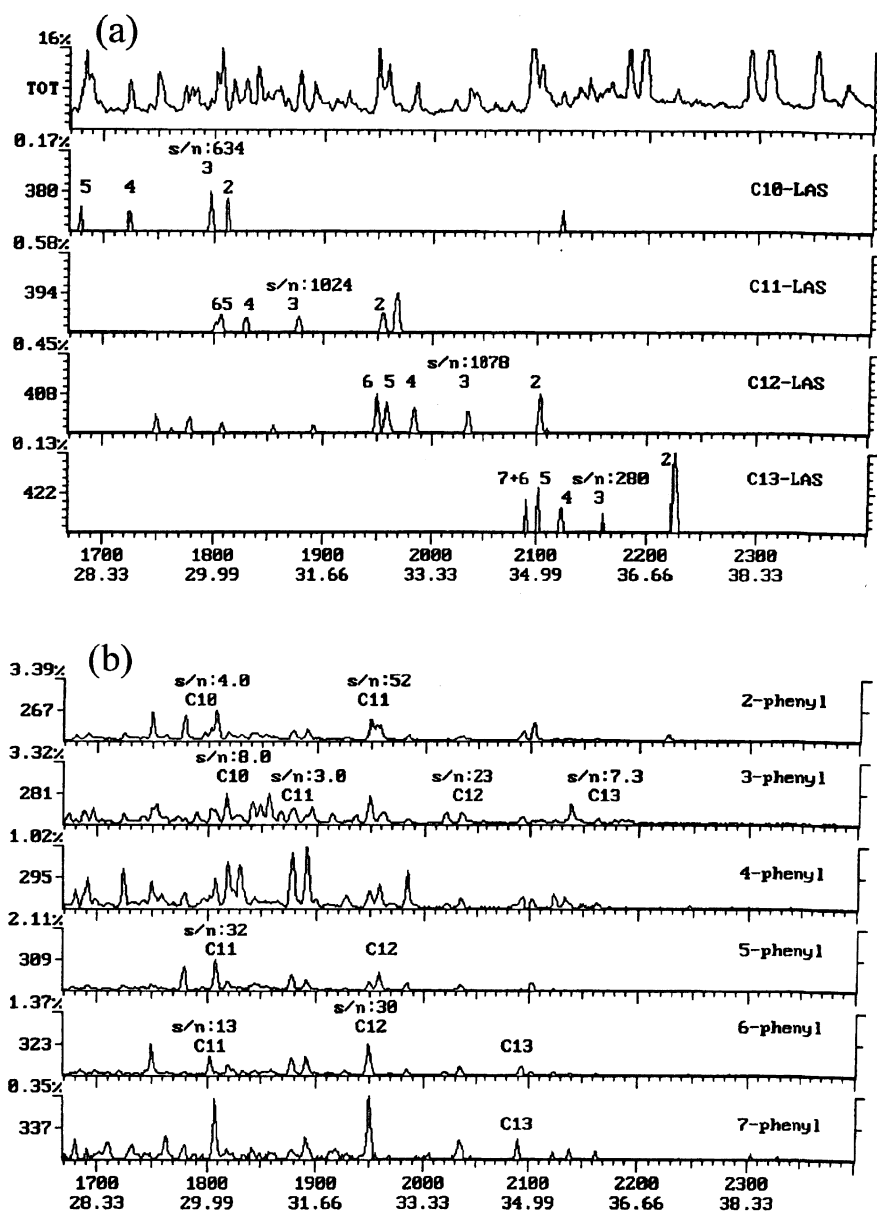
Fig. 4. (a) Partial molecular ion chromatograms and (b) characteristic ion chromatograms of the trifluoroethyl derivatives of LAS isolated from a river water sample and analysed by EI-MS. Signal-to-noise ratios of 3-phenyl in each LAS homolog is displayed for comparison.

SPC isomers in environmental samples were determined semi-quantitatively by relating the individual LAS isomer CI quasi- molecular ion ([M+H]$^+$) to the internal standard (C$_2$-LAS). Thus, the calculated concentrations were based on the assumption that the response factors for the internal standard and the analyte were the same. Table 1 summarizes the average percent recoveries of C$_{10}$–C$_{13}$ LAS and 2-SPC4 in the samples of river water and sewage effluent, as well as their average background concentrations in the samples. Recoveries for environmental samples were from 75 to 112% with R.S.D.
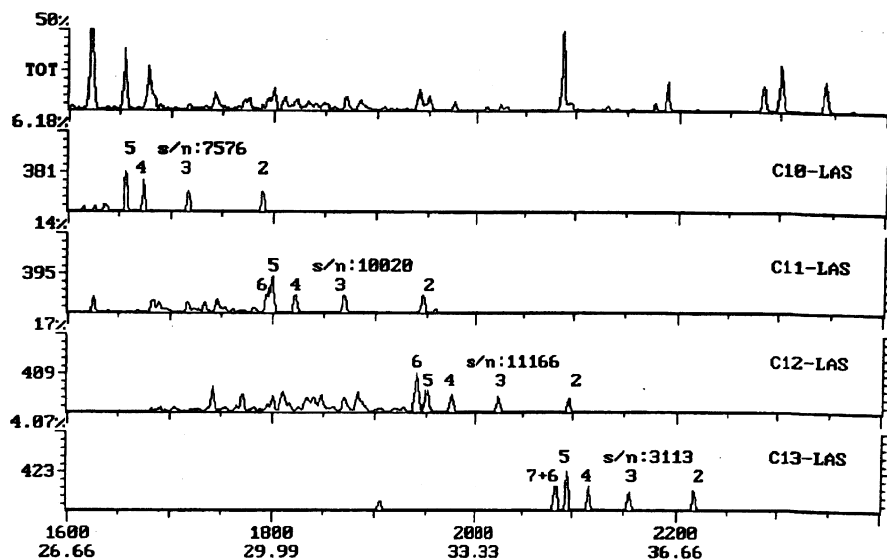
Fig. 5. Partial ion chromatogram of protonated molecules from CI of LAS derivatives obtained from a river sample. Signal-to-noise ratios of 3-phenyl in each LAS homolog is displayed for comparison.

values ranging from 4 to 26%. Average recovery of the C_8-LAS surrogate was 99±3%, which indicated that the method performed satisfactorily despite the variable compositions of environmental samples. The limit of quantitation for individual LAS and SPC was estimated at a signal-to-noise ratio of 10. The quantitation limit for both LAS and SPC was estimated to be 0.01 μg/l in 100 ml of water sample.
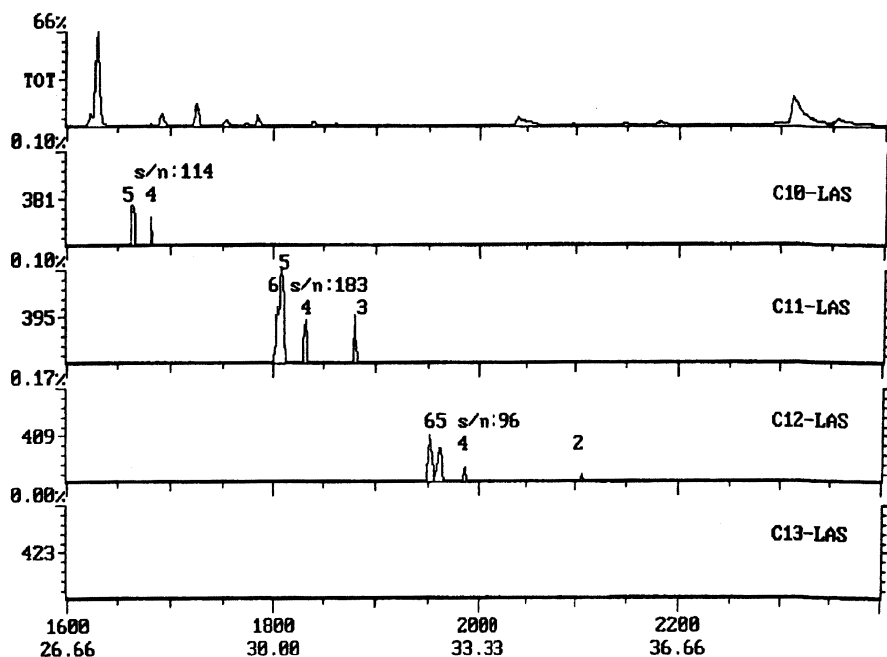

Fig. 6. Detection of sub-ppt level of LAS isomers in blank surface water by CI-MS.

Table 1
Background concentration and the recovery results of LAS and 2-SPC4 spiked into different water samples

Sample	LAS				Surrogate	Total
	C_{10}	C_{11}	C_{12}	C_{13}	C_8-LAS	SPC
Deionized water						
Spiked recovery (%)	95.3 (4%)	94.0 (4%)	104 (2%)	84.2 (13%)	103 (1%)	91.5 (8%)[a]
Blank surface water						
Average background conc. (µg/l)	0.01	0.07	0.06	N.d.		−
Spiked recovery (%)	75.0 (11%)	84.4 (4%)	88.1 (4%)	77.8 (7%)	96.4 (4%)	−
Polluted river water						
Average background conc. (µg/l)	26.3	50.1	47.9	10.9		0.5
Spiked recovery (%)	112 (26%)	112 (25%)	86.1 (18%)	92.9 (15%)	99.2 (10%)	89.8 (7%)[a]
Sewage effluent						
Average background conc. (µg/l)	8.8	15.8	15.1	3.0		3.2
Spiked recovery (%)	93.2 (16%)	79.4 (19%)	108 (7%)	102 (9%)	97.6 (10%)	81.5 (3%)[a]

Relative standard deviation is given in parentheses.
[a] Spiked 2-SPC4 for SPC recovery study.

4. Conclusions

The procedures used here indicate that trifluoro-ethyl esterification combined with ion trap GC–MS analysis in EI and CI modes is an effective approach for positive identification and quantitation of LAS and SPC. Compared to EI-MS, protonated molecular ion chromatograms of homologous LAS by CI-MS offers enhanced sensitivity to improve the quantitation of trace LAS and SPC in environmental samples. The results suggest that the ion trap GC–MS system in EI and the low pressure CI modes are reliable, offering a convenient analytical technique for determination of target compounds in complex environmental samples.

Acknowledgements

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