ELSEVIER

Determination of surfactants in surface water by solid-phase extraction, liquid chromatography and liquid chromatography–mass spectrometry

Simon D. Scullion[a], Malcolm R. Clench[a,*], Michael Cooke[a], Alison E. Ashcroft[b]

[a] Environmental Research Centre/Division of Chemistry, School of Science, Sheffield Hallam University, Pond Street, Sheffield S1 1WB, UK

[b] VG Organic, Tudor Road, Altrincham, Cheshire, UK

Abstract

Determination of surfactants in surface waters is required owing to their toxicity to aquatic micro-organisms and potential oestrogenic effects. We have investigated methods for the determination of two types of surfactants by solid-phase extraction with C_{18} and SAX cartridges. HPLC separation of anionic and non-ionic surfactants on a C_1 (TMS) column has been achieved and detection via both fluorescence and liquid chromatography–mass spectrometry (atmospheric pressure chemical ionisation interface) is reported. Recoveries are approximately 100% using the method developed with detection limits of 50 ng on column for detection by fluorescence. Alkylphenol ethoxylates have been detected in samples taken from the River Rother in South Yorkshire, UK, at levels of 5.6 μg l^{-1} using the described methodology.

Keywords: Water analysis; Liquid chromatography–mass spectrometry; Environmental analysis; Surfactants; Alkylphenol ethoxylate surfactants; Ethoxylates

1. Introduction

Surfactants are a group of chemicals which are widely used both industrially and domestically, hence they have become ubiquitous in the environment. Surfactants interact with other molecules to confer either hydrophilicity or hydrophobicity according to type of surfactant. Surfactant molecules may be divided into three individual main classes. These are anionic surfactants, e.g. alkylphenol sulphonates, cationic surfactants, e.g. quaternary ammonium salts, and non-ionic surfactants such as those produced by reacting alkylphenols with ethylene oxide.

The present world-wide surfactant consumption is approximately 15 million metric tonnes per year [1]. More than 50% of the estimated figure is accounted for by soaps. The most common anionic surfactants, the linear alkylbenzene sulphonates (LAS), have a total production estimated at 1.8 million tonnes per year. This can be regarded as 25% of the total consumption of synthetic surfactants. In the industrialised world, i.e., the US, W. Europe and Japan, the figure for the total LAS consumption is approximately 1 million tonnes per year. LAS consists of a long non-polar hydrocarbon side chain linked to a sulphonated benzene group which gives rise to the generic classification for this type of molecule as alkylbenzene sulphonates. Commonly, the alkyl chain varies in length from 11 to 14 carbon units.

*Corresponding author.

Non-ionic surfactants do not contain discrete charges; they do, however, contain highly polar, hydrophilic, hydroxyl groups. Most non-ionic surfactants are not single compounds but rather are the products of a reaction between ethylene oxide and organic compounds such as alkyl alcohols, alkylphenols and fatty acids. These reactions produce mixtures which have a range of ethoxymer chain lengths. The trivial nomenclature for these compounds is generally based on their average ethoxymer chain length with for example 'NP9' being used to describe a nonylphenol ethoxylate formulation with an average ethoxymer chain length of nine. The parent compound of this type of surfactant is described as the alkylphenol polyethoxylate (APEO). An estimated 350 000 tonnes per year of APEOs are currently used in the US, W. Europe and Japan [2].

Currently widespread interest in the determination of surface active agents in water has been generated by the work of Jobling and Sumpter [3], who have shown that alkylphenol polyethoxylates and their associated degradation products are weakly oestrogenic in nature. This work developed research originally carried out by Soto [4], who demonstrated a weakly oestrogenic response for nonylphenol. Sharpe and Skakkebaek [5] have linked these compounds, along with other environmental pollutants, to the apparent decrease in sperm production and increase in sexual reproductive problems observed throughout the Western Hemisphere.

The chemical complexity of surfactants, which are often mixtures of related compounds differentiated by variation in carbon chain length, has meant that analytical methodology has concentrated on determination by class. Simple, relatively fast and inexpensive quantitative or semi-quantitative methods based on titrimetric or spectrophotometric methods, have been commonly used. Generally however, methods which depend on a spectrophotometric reaction are no longer acceptable since they do not reliably reflect the concentration of either the individual surfactant types within the general classes of non-ionic, anionic or cationic, or the concentration of individual compounds (i.e. chain length distribution) within a class.

Major developments have been made in the identification and quantification of surfactants by gas chromatography–mass spectrometry (GC–MS) and high-performance liquid chromatography (HPLC). The GC–MS work is typified by the work of Stephanou et al. [6] where capillary GC–MS in conjunction with both electron impact and chemical ionisation was described. Many papers describing the use of HPLC for the analysis of surfactants have appeared [7–11]. Both normal- and reversed-phase separations have been used in conjunction with UV and fluorescence detection.

Marcomini and co-workers [12,13] have described the determination of alkylphenol ethoxylates and linear alkylbenzene sulphonates (LAS) in water. Isolation of surfactants from aqueous solution was achieved by solid-phase extraction [13,14]. Chromatographic analysis was by a combination of normal- and reversed-phase HPLC with either fluorescence or UV detection. The described methodology, whilst allowing determination of the homologue distribution for LAS, does not effect chain length separation for alkylphenol ethoxylates.

Castles et al. [15] have described a method for the determination of LAS. This method utilises a trimethylsilyl (TMS) column and an isocratic HPLC method using THF with added sodium perchlorate. Wang and Fingus [16] have described a method for the determination of alkylphenol ethoxylate using an isocratic HPLC method employing a TMS column with a methanol–ammonium acetate mobile phase. We have developed this method in order to allow the separation of two classifications of surfactants simultaneously including individual oligomer separation for the anionic alkylbenzene sulphonates and the non-ionic alkylphenol ethoxylates.

Growing attention is being paid to the analysis of the degradation products of commonly used surfactants. The biotransformation of LAS leads to the formation of mono- and dicarboxylic sulphophenyl acids (SPC). These are formed via the ω-oxidation of the molecules alkyl chain. β-Oxidation results in a shortening of this chain by two carbon units at a time [17]. APEOs are degraded to shorter-chain ethoxylates, alkylphenoxy acids and nonylphenol under aerobic conditions via ω-oxidation [18]. In this case, however, the biotransformation process is not fully understood. Data concerning the detection of surfactants and their degradation products have been published [18–21].

The advent of suitable interface technology has also led ourselves and other groups to investigate liquid chromatography–mass spectrometry for the determination of surfactants. Particle-beam liquid

chromatography–mass spectrometry (PB-LC–MS) has been used in the determination of surfactants in drinking water. Clark et al. [22] determined alkylphenol ethoxylates in drinking water after continuous liquid–liquid extraction of $500 \, l^{-3}$ of finished water. The resulting extract was analysed by PB-LC–MS and low detection limits of parts per trillion (10^{-12}) were obtained. Although this method produces excellent sensitivity the initial $500 \, l^{-3}$ sample size taken would appear to make it impractical for routine use. A second limitation of the described methodology arises from the use of a chromatographic system which does not achieve individual oligomer separation.

Papers describing the use of thermospray LC–MS in the analysis of surfactants have appeared from Evans et al. [23] and Schroder [24]. Evans et al. showed that the thermospray mass spectra of linear primary alcohol ethoxylates are characterised by intense $[M+NH_4]^+$ ions, with little or no structural information. They established limits of detection in the low nanogram region for each species analysed. The thermospray method was applied to the analysis of surface water and sewage effluent samples by using solid-phase extraction as a method of sample preparation. The method was validated for concentrations of individual alcohol ethoxylates in the range 0.06 to 2.17 $\mu g \, l^{-1}$ by spiking 1-l samples.

Schroder [24] examined the concentrations of a range of surfactants in sewage treatment plants by thermospray LC–MS using flow injection as a means of sample introduction. The resulting mass spectrum can be regarded as a 'survey' of components present. Using this technique it was possible to identify both anionic and non-ionic surfactants in waste water plant influent. Liquid chromatography–electrospray mass spectrometry of surfactants has been investigated by Crescenzi et al. [25] after their extraction from raw sewage, treated water, river water and drinking water. The analysis of municipal water revealed the presence of analytes at $ng \, l^{-1}$ levels. Pattanaargson et al. [26] have used APCI-MS as a means of determination of oligomer distribution, but have not applied this technique to environmental samples.

In all of this previous work, with the exception of the experiments carried out by Crescenzi et al. [25], some compromise in either practical sample volumes or chromatographic integrity or both has been re-

quired in order to use mass spectrometry for detection. In the particle beam work large initial sample volumes were required to achieve the desired sensitivity. In the thermospray work optimum HPLC conditions for the separation of individual oligomers were not used as they were not compatible with this type of interface. The APCI work used only direct introduction of non-ionic surfactant samples. No chromatographic separation of oligomers was attempted before introduction.

We now report a method for the determination of linear alkyl benzene sulphonates and alkylphenol ethoxylates in water using a simple solid-phase extraction procedure followed by isocratic HPLC separation on a C_1 column. Data from a preliminary investigation of the compatibility of the mobile phases used with the C1 column and liquid chromatography–mass spectrometry with an atmospheric pressure chemical ionisation (APCI) interface is reported. The analysis of the degradation products of anionic and non-ionic surfactants has not been addressed using this method.

2. Experimental

2.1. Samples

Standard solutions of Triton X100 (an octylphenol ethoxylate) (Sigma Chemicals, Poole, Dorset, UK), Synperonic 9 (a nonylphenol ethoxylate) (a gift from ICI Materials Research Centre, Wilton, Middlesborough, UK) and Nansa SS (a commercial dodecyl alkylbenzene sulphonate formulation, Albright and Wilson, Castleford, UK) were prepared by weighing and dissolution in HPLC mobile phase (details below)

Grab samples of surface water (2 l) were taken from the River Rother in South Yorkshire, UK (map reference OSS 111 435 877). The samples were stored in amber glass bottles at 4°C prior to analysis. At the time of sampling water pH was found to be 6.9

2.2. Extraction and clean-up of samples

Water samples were extracted using either a Shandon (Warrington, Cheshire, UK) Hypersep C_{18} solid-phase extraction cartridge (500 mg packing

material) alone or placed in series with a SAX solid-phase extraction cartridge (Whatman, NJ, USA). The cartridges were first conditioned with 7 ml of methanol and then 7 ml of reagent water. Samples were then taken through under vacuum and the cartridges air-dried. The cartridges were washed with 12 ml of water–methanol (70:30). Elution of surfactants was achieved using 3 cm³ of methanol. Finally, the sample extract was blown down to dryness using a steady flow of nitrogen. The samples were dissolved in the appropriate HPLC mobile phase prior to analysis.

2.3. High-performance liquid chromatography

All HPLC analyses were performed on a Gilson 302 gradient pumping system. The column employed was a Hichrom (Reading, UK) 15 cm×4.6 mm I.D. TMS HPLC column. Fluorescence detection was carried out using a Hewlett-Packard 1046A (Palo Alto, CA, USA) fluorescence detector, $\lambda_{ex}=220$ nm and $\lambda_{em}=302$ nm for alkylphenol ethoxylates and $\lambda_{ex}=220$ nm and $\lambda_{em}=290$ nm for the linear alkyl benzene sulphonates. Data were output to a Shimazdu integrator. Injections (50 μl) were made using a Waters Wisp 712 autosampler.

Two isocratic mobile-phase systems were employed. System A: 65% water–35% acetonitrile with an overall buffer concentration of 0.065 M ammonium acetate; flow-rate, 0.7 ml min^{-1}. System B: 58% methanol–42% 0.008 M ammonium acetate (aq); flow-rate, 0.7 ml min^{-1}.

2.4. Liquid chromatography–mass spectrometry

All analyses were performed on a VG Organic (Altrincham, Cheshire, UK) Quattro triple quadrupole mass spectrometer, equipped with a VG Organic atmospheric pressure chemical ionisation (APCI) liquid chromatography–mass spectrometry interface. A Hewlett-Packard 1050 (Palo Alto, CA, USA) HPLC system was used in this case (see above for HPLC conditions). Data were acquired in full scan mode, range 50–1000 at 3 s/scan. Alternate positive ion/negative ion switching was used to acquire spectra of both positive and negative ion modes.

The APCI source conditions were as follows: corona discharge voltage, 3.5 kV; high voltage lens,

500 V; source temperature, 120°C; APCI probe temperature, 500°C.

3. Results and discussion

Fig. 1 shows a typical HPLC–fluorescence chromatogram from a standard mixture of commercial surfactants, Nansa SS and Triton X100. These data were obtained using mobile-phase system A. Via this simple isocratic experiment it was possible to separate the anionic and non-ionic surfactants and each of their individual homologues (LAS) and ethoxymers (OPEO). Peaks from the Nansa SS eluting at t_R 3.1–15.7 min and those for Triton at t_R 22.6 min onwards. Of interest are the side peaks on the alkylbenzene sulphonate homologue peaks. These may be observed at t_R 2.6, 9.4 and 12.9 min and we attribute them to positional isomers of each LAS homologue.

Fig. 2 displays a typical HPLC-fluorescence chromatogram from the same mixture of standards obtained using HPLC mobile-phase system B. Using this mobile-phase system it was also possible separate the anionic and non-ionic surfactants so that each individual homologue (LAS) and ethoxymer (OPEO) was observed. Peaks from the LAS eluting at t_R 4.5–10 min and those for OPEO at t_R 12 min onwards. However, this method does not show the
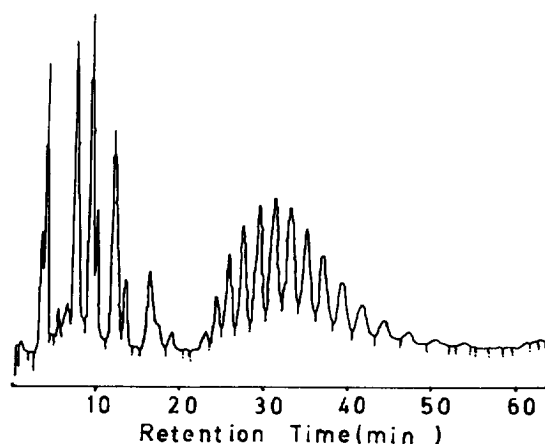

Fig. 1. HPLC chromatogram for the separation of linear alkylbenzene sulphonate and octylphenol ethoxylate surfactant standards on a C₁ (TMS) column using mobile-phase system A (see text for further details).
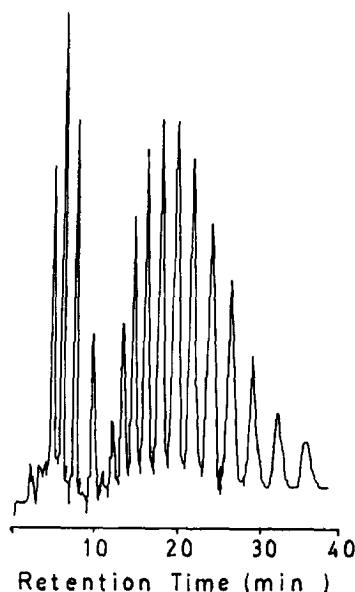
Fig. 2. HPLC chromatogram for the separation of linear alkyl-benzene sulphonate and octylphenol ethoxylate surfactant standards on a C_1 (TMS) column using mobile-phase system B (see text for further details).

Fig. 3. HPLC chromatogram for the separation of linear alkyl-benzene sulphonate and nonylphenol ethoxylate surfactant standards on a C_1 (TMS) column using mobile-phase system B (see text for further details).

positional isomers of the individual LAS homo-logues, but does allow more rapid analyses. Increasing chain length, be it alkyl in the case of LAS and ethoxylate in the case of OPEO, results in an increased retention time with respect to each component of the mixture. This statement is valid in both HPLC methods reported.

The chromatographic methodology developed is also applicable to mixtures of LAS and nonylphenol ethoxylates (Fig. 3). Peaks for Nansa SS elute from 5.5 min to 10 min and those for NP9 from 11.5 min onwards. The chromatographic resolution of the nonylphenol ethoxylates is not as good as that for the octylphenol ethoxylates but is still adequate for sample analyses. This phenomenon has also been observed by Wang and Fingus [27]. During our research it was noticed that some C_1 columns were able to resolve NPEO oligomers to a greater degree than others. This led to the selection of the column manufactured by Hichrom (Reading, UK). It was also noted during this work that a particular column's ability to resolve NPEO oligomers degrades more quickly that its ability to resolve OPEO oligomers. In situations where LAS, NPEO and OPEO were all present in the sample, the OPEO and
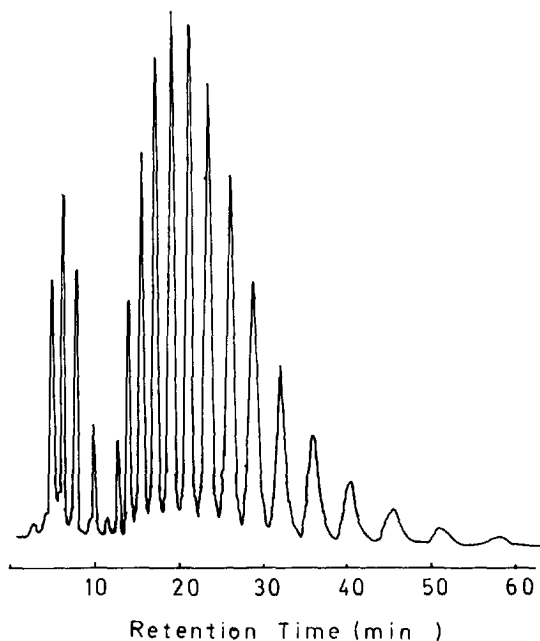
NPEO would co-elute. It is in this situation that the specificity introduced by liquid chromatography–mass spectrometry would be useful and some preliminary data from analysis by this method are reported below.

During recovery experiments adsorption of analyte onto the surface of the glassware used was a recurrent theme. In order to minimise this problem acid washes were carried out followed by silanization; however, this was shown to be unsuccessful. Subsequently, use of PTFE volumetric flasks for the storage of standard and extracted samples improved calibration curve linearity. Soto [4] has described the leakage of nonylphenol from plastic vessels. Obviously environmental analysis looking at non-ionic surfactants and their degradation products (which include alkylphenols) could be affected by this problem. However, no such occurrence has been observed during this work. This may be due to the use of mobile phase for the preparation of solutions or to the type of plastic vessel used.

Table 1 shows the recoveries achieved using the

Table 1
Recovery data for a NP9 alkylphenol exthoxylate from reagent water using C_{18} solid-phase extraction (for experimental conditions see text)

	Ethoxymer number									
	3	4	5	6	7	8	9	10	11	12
Extract 1	81	66	86	106	110	118	118	114	87	71
Extract 2	94	69	88	107	108	127	127	115	103	81
Extract 4	76	55	88	107	113	123	123	116	90	70

single stage C_{18} solid-phase extraction method from samples of reagent water. Samples were spiked at 11.2 μg l^{-1} with nonylphenol ethoxylate and recoveries calculated from calibration data generated from peak areas in the HPLC chromatograms of standards. The recoveries of each individual ethoxymer from 3–12 chain length of ethylene oxide units are shown in Table 1. The recoveries for each oligomer ranged from 63 to 122%. Using these data the limit of detection using fluorescence detection based on 2× signal-to-noise ratio definition for the most intense peak in the oligomer distribution is estimated to be equivalent to 0.05 μg l^{-1} for alkylphenol ethoxylates and 0.005 μg l^{-1} for alkyl-benzene sulphonate in the original sample with a concentration factor of 500 generated by the extraction procedure. Table 2 shows results obtained from the simultaneous extraction of both LAS and NP9. Reagent water samples (500 cm^{-3}) were spiked with 14 μg l^{-1} of nonylphenol ethoxylate and 2 μl^{-1} of Nansa SS. The recoveries for each oligomer of NP9 ranged from 54 to 95%. The recoveries for each individual homologue of Nansa SS ranged from 69 to 149%.

This methodology was applied to the analysis of samples of surface water taken from the River Rother in South Yorkshire, UK. In chromatograms obtained after extraction of this high-sediment-con-taining sample using a C_{18} SPE cartridge only (Fig. 4a) several large interfering peaks eluted early in the chromatogram. It was assumed that these might be acidic components originating from the sediment. Hence it was decided to remove all anionic components from the sample extract by employing a SAX solid-phase extraction cartridge in series with the C_{18} cartridge. This methodology results in the cleaner chromatogram shown in Fig. 4c where the characteristic distribution pattern for alkylphenol ethoxylate oligomers can be clearly seen and compared with the chromatogram obtained from a standard sample (Fig. 4b). Any LAS present in the sample is now obviously retained by the SAX cartridge and not observed. Further work is required to investigate the possibility of selectively fractionating the anionic components trapped onto the SAX cartridge such that simultaneous analysis of LAS and APEOs would still be possible in such a situation. Using external calibration the level of alkylphenol ethoxylate found in these samples was calculated at 5.6 μg l^{-1} taking an average of the individual oligomers.

Data from a preliminary investigation of the compatibility of the mobile-phase system employed with liquid chromatography–atmospheric pressure chemical ionisation mass spectrometry (LC–APCI-MS) is shown in Figs. 5, 6 and 7. Fig. 5 shows the

Table 2
Recovery data for a NP9 alkylphenol exthoxylate and Nansa SS linear alkylbenzene sulphonate from reagent water using C_{18} solid-phase extraction (for experimental conditions see text)

	Ethoxymer number								Homologue number			
	3	4	5	6	7	8	9	10	1	2	3	4
Extract 1	54	46	96	67	66	76	90	116	82	78	69	110
Extract 2	54	67	76	71	91	90	88	89	77	71	86	143
Extract 3	68	92	95	91	90	89	91	92	110	97	99	149
Extract 4	66	80	85	81	85	86	84	82	78	87	84	96
Extract 5	54	74	76	78	81	77	76	73	77	75	63	69

213

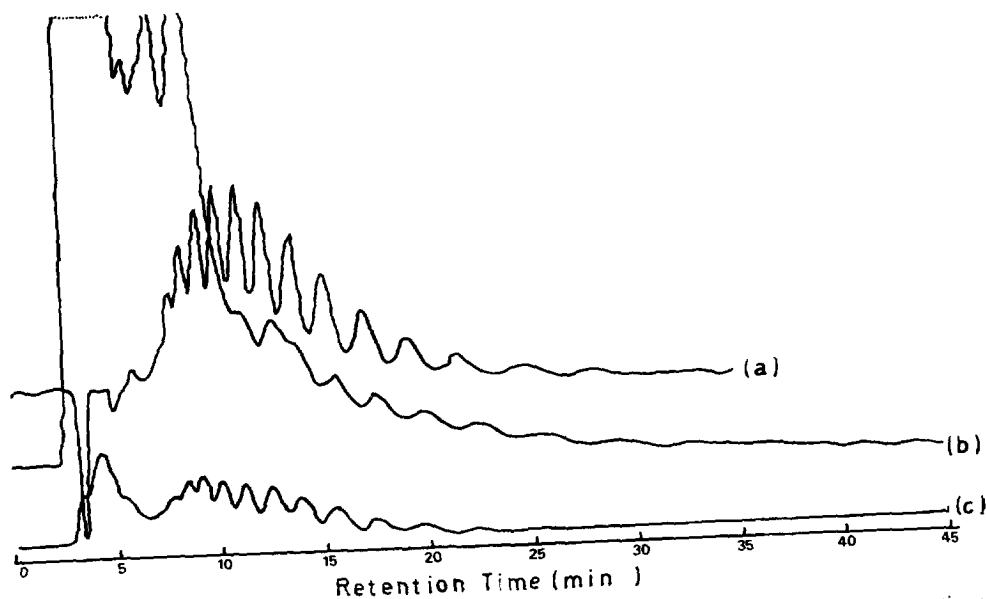S.D. Scullion et al. / J. Chromatogr. A 733 (1996) 207–216

Fig. 4. HPLC chromatograms for the analysis of extracts from the River Rother (South Yorkshire, UK). Trace (a), extraction using C_{18} SPE cartridge only. Trace (b), standard NP9. Trace (c), extraction using C_{18} and SAX SPE extraction cartridges. Mobile-phase conditions A used throughout.
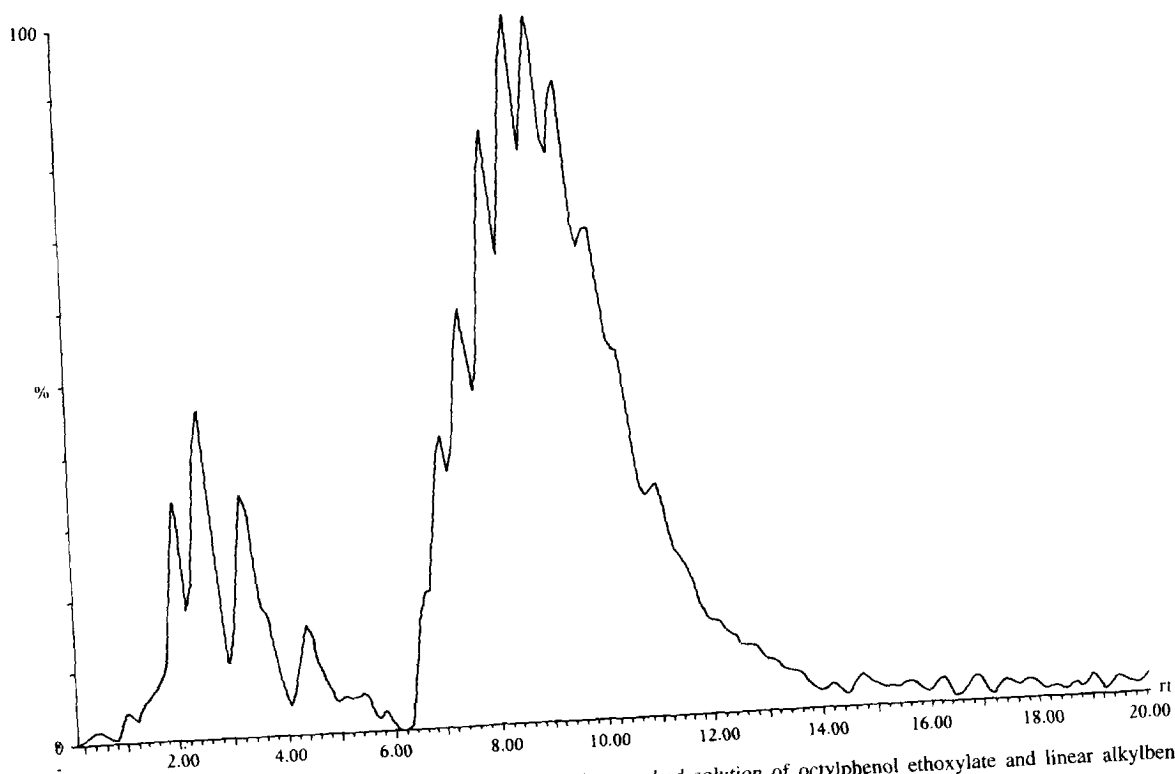

Fig. 5. APCI positive total ion chromatogram for the analysis of a standard solution of octylphenol ethoxylate and linear alkylbenzene standards (using HPLC conditions A).
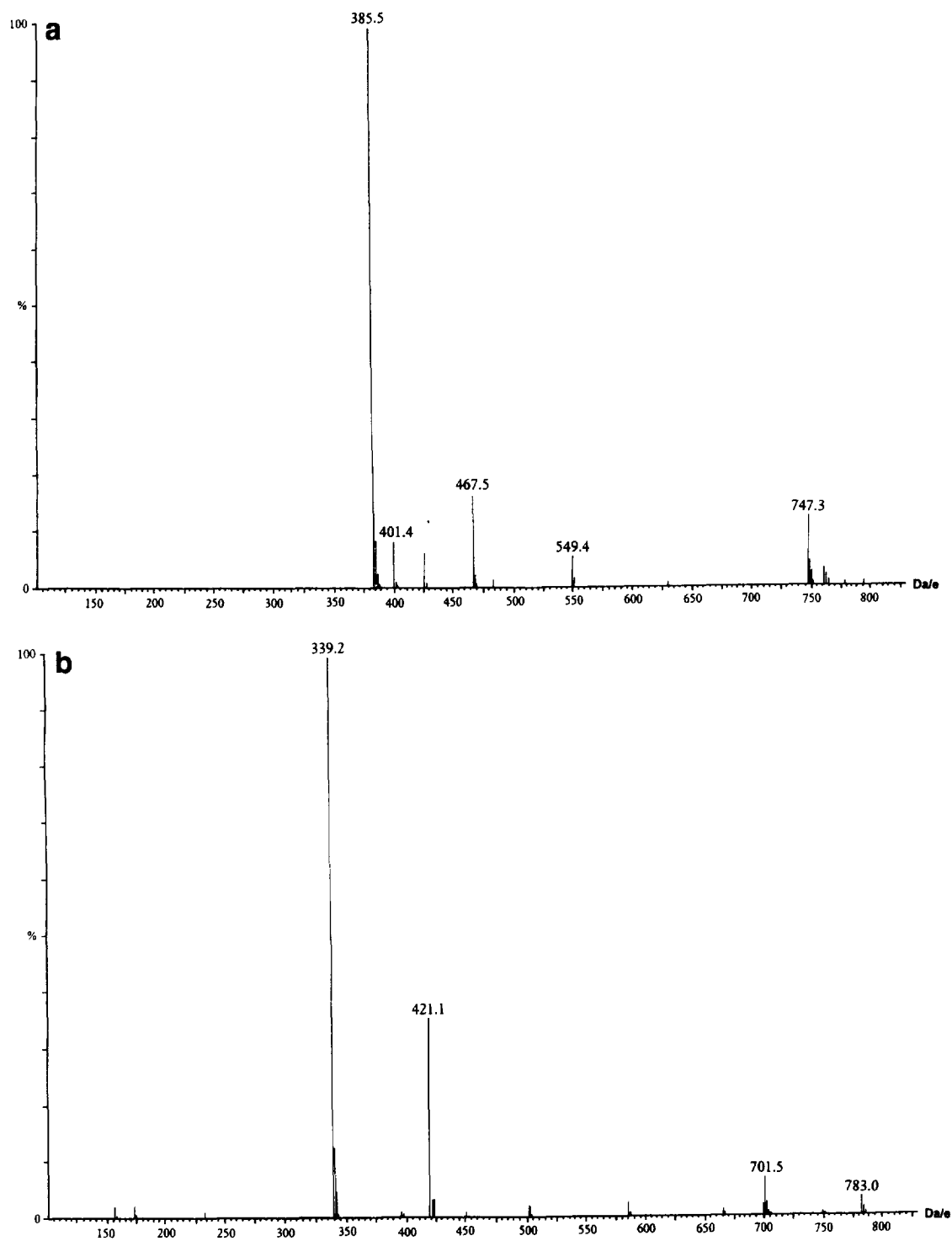
Fig. 6. (a) Positive ion APCI mass spectrum for the peak eluting at $t_R = 3.2$ min in Fig. 5. (b) Negative ion APCI mass spectrum for the peak eluting at $t_R = 3.2$ min in Fig. 5. Taken together these data can be assigned as arising from the LAS homologue with a side chain of thirteen –CH$_2$– units.

total ion chromatogram for the analysis of a 0.001% standard solution of LAS and octylphenol ethoxylates by LC–APCI-MS in positive ion mode. As can be seen, peaks arising from both the anionic alkylbenzene sulphonate and non-ionic octylphenol ethoxylate can be seen in this ionisation mode. However, in negative ionisation mode only the anionic surfactants are observed. The relative sensitivity for detection of anionic surfactant is approximately 5:1 in favour of the positive ion mode (based on a comparison of peak areas). It is therefore desirable to use this ionisation mode for quantitative work.

A comparison of mass spectra from one dodecyl benzene sulphonate component of this standard mixture is shown in Fig. 6. In Fig. 6a the APCI positive ion spectrum from the peak eluting at t_R 3.2 min is shown. The major ion in this spectrum at m/z 385 can be assigned to a $[M+2Na]^+$ ion. The corresponding negative ion spectrum is shown in Fig. 6b. In this spectrum as might be expected, the $[M-H]^-$ peak at m/z 339 dominates. These two spectra together allow an assignment of this peak as arising from the LAS homologue with a side chain of thirteen $-CH_2-$ units.

Fig. 7 shows the APCI positive ion mass spectrum from the peak eluting at $t_R=8.92$. This mass spectrum exhibits a small $[M+H]^+$ ion at m/z 559. However, the dominant pseudo-molecular species are sodium adduct ions. These can be observed and assigned to $[M+Na]^+$ at m/z 581 $[M+2Na]^+$ at m/z 604 and $[M+3Na]^+$ at m/z 626. This multiple adduction can be explained if it is assumed that each ethylene oxide unit has the potential to gain a sodium atom from this obviously sodium-rich sample. Taken together these data can be used to identify this peak as the eight ethylene oxide unit containing oligomer of Triton X100. This non-ionic surfactant did not yield any negative ion APCI mass spectra. Also observable in this non background subtracted data
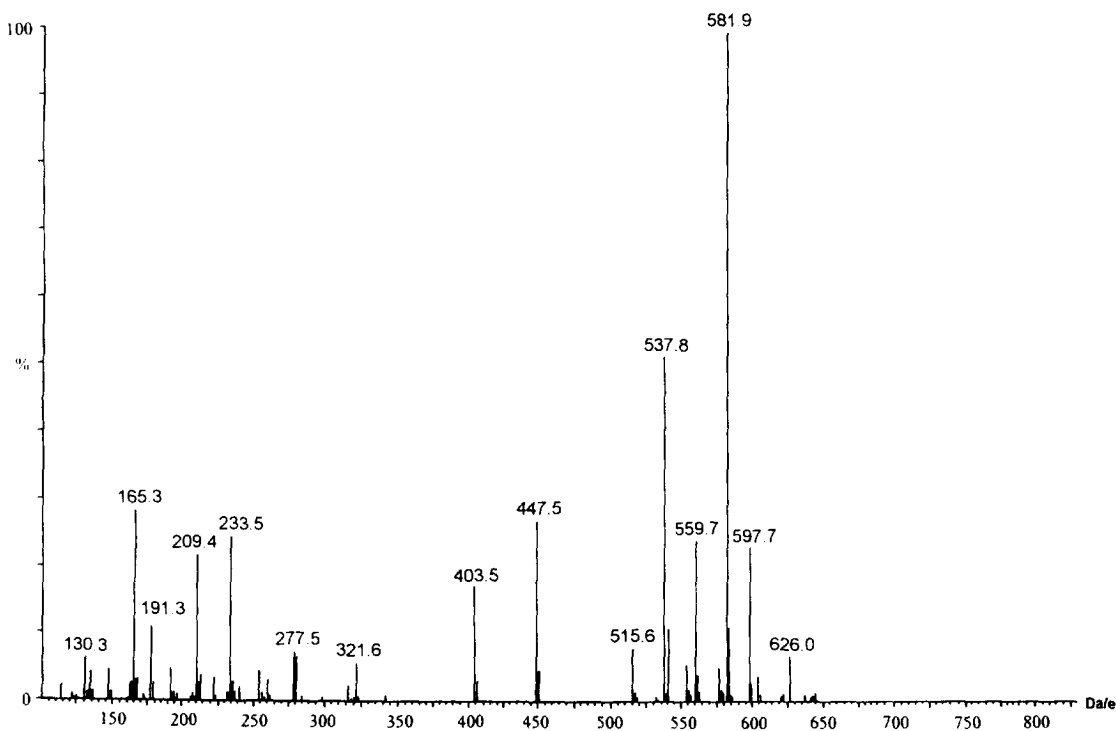

Fig. 7. Positive ion APCI mass spectrum for the peak eluting at $t_R=8.2$ min in Fig. 5. This can be assigned to the eight ethoxylates containing oligomer of the octylphenol ethoxylate standard. (For discussion see text.)

are the equivalent $[M+H]^+$ ion at m/z 515 $[M+Na]^+$ at m/z 537 $[M+2Na]^+$ at m/z 560 and $[M+3Na]^+$ at m/z 583 for the seven ethylene oxide units containing oligomer.

4. Conclusions

A method allowing the determination of common anionic and non-ionic surfactants has been developed. The method allows both total surfactant and individual homologue (LAS) or oligomer (APEO) distribution to be determined. Simultaneous extraction of LAS and alkylphenol ethoxylates is possible using a C_{18} solid-phase extraction cartridge only, and simultaneous analysis, i.e. extraction and chromatographic separation has been demonstrated for these analytes in reagent water. However, for the surface water samples analysed which contained a high level of sediment, it was found necessary to add a further SPE clean-up stage which removed all anionic components, including the LAS. Further work is required to investigate the possibility of selectively fractionating the anionic components trapped on the SAX cartridge such that simultaneous analysis would still be possible in this situation.

Fluorescence detection provides a sensitive and specific method of detection. Where additional confirmation of peak assignments is required, a preliminary investigation has indicated that LC–APCI-MS is compatible both with the mobile-phase systems used for chromatographic analysis and offers adequate sensitivity.

In future work we will investigate methods for the selective elution of LAS from the SAX cartridge and the application of the developed methodology to the determination of surfactants in the marine environment.

References

[1] P. Berth and P. Jeschke, Tenside Surfact. Deterg., 26 (1989) 275.
[2] B.F. Greek and P.L. Layman, Chem. Eng. News, 63 (1989) 29.
[3] S. Jobling and J.P. Sumpter, Aquatic Toxicol., 27 (1993) 361.
[4] A. Soto, Environ. Health Perspect., 92 (1991) 167.
[5] R. Sharpe and N.E. Skakkebaek, Lancet, 341 (1993) 1392.
[6] E. Stephanou, M. Reinhard and H.A. Ball, Biomed. Environ. Mass Spectrom., 15 (1988) 275.
[7] J.A. Pilc and P. Sermon, J. Chromatogr., 398 (1987) 375.
[8] M. Ahel and W. Giger, Anal. Chem., 57 (1985) 375.
[9] M.S. Holt, J. Chromatogr., 362 (1986) 419.
[10] Y. Yokoyama and S. Hisakuni, J. Chromatogr., 555 (1991) 155.
[11] A Nakae and K. Kunihiro, J. Chromatogr., 152 (1978) 137.
[12] A. Marcomini and W. Giger, Anal. Chem., 59 (1987) 243.
[13] A. Marcomini, S. Capri and W. Giger, J. Chromatogr., 403 (1987) 243.
[14] A. Marcomini, B. Pavoni, A. Sfriso and A.A. Orio, Mar. Chem., 29 (1990) 307.
[15] M.A. Castles, B.L. Moore and S.R. Ward, Anal Chem., 61 (1989) 2534.
[16] Z. Wang and M. Fingas, J. Chromatogr., 673 (1993) 145.
[17] P. Schoberl, Tenside Surfact. Deterg., 26 (1989) 2 86.
[18] M. Ahel, W. Giger and M. Koch, Water Res., 28 (1994) 5 1131.
[19] A. Marcomini, A. Di Corca and R. Samperi, J. Chromatogr., 644 (1993) 59.
[20] A. Di Corca, R. Samperi and A. Marcomini, Environ. Sci. Technol., 28 (1994) 850.
[21] M. Ahel, W. Giger and C. Schaffner, Water Res., 28 (1994) 5 1143.
[22] J.B. Clarke, R.T. Rosen, T.G. Hartman, J.B. Louis and J.D. Rosen, Int. J. Environ. Anal. Chem., 45 (1991) 169.
[23] K.A. Evans, S.T. Dubey, L. Kravetz, T. Dzidic, R. Mueller and J.R. Stork, Anal Chem., 68 (1994) 699.
[24] H.Fr. Schroder, J. Chromatogr., 647 (1993) 219.
[25] C. Crescenzi, A. Di and R. Samperi, Anal. Chem., 67 (1995) 1797.
[26] S. Pattanaargson, P. Sangvanich, A. Petsom and S. Roengsumran, Analyst, 20 (1995) 1573.
[27] Z. Wang and M. Fingas, J. Chromatogr. Sci., 31 (1993) 509–518.