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Method development for trace determination of poly(naphthalenesulfonate)-type pollutants in water by liquid chromatography–electrospray mass spectrometry

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Abstract

A very sensitive analytical procedure based on LC–MS for determining trace amounts of the more relevant poly(naphthalenesulfonate) (PNS) contaminants present in environmental waters is presented. Extraction was performed on a styrene–divinylbenzene copolymer resin solid-phase extraction cartridge after addition of ammonium acetate to the sample. Small amounts of ammonium acetate in the mobile phase allowed the determination and characterisation of the four shorter oligomers by liquid chromatography–electrospray mass spectrometry. Under such conditions the electrospray process generates fully ionised molecules which greatly simplifies interpretation of spectra and quantitation. Additionally, confirmatory ions can be generated by the in-source collision-induced decomposition process. The effectiveness of the method was assessed in recovery experiments from drinking and river water samples spiked with commercial mixtures of PNS concrete plasticizers also referred as naphthalenesulfonate–formaldehyde condensates. Moreover, the performance of this method was compared to methods using ion-pair chromatography coupled with fluorimetric and mass spectrometric detection. Method detection limits were in the low picomolar range (1 ng/l for the monomer) for each isomer. In order to evaluate the environmental relevance of PNS type compounds waste, river and ground water grab samples were analysed. Concentrations of PNS oligomers detected in these samples ranged between 53 ng/l and 32 μg/l.

Keywords: Water analysis; Environmental analysis; Poly(naphthalenesulfonate); Naphthalenesulfonate–formaldehyde condensates

1. Introduction

Aromatic sulfonates are well-studied pollutants because of their wide spread occurrence in the environment and because of their potential hazard for human and wildlife health [1–4]. Despite this concern about monomeric aromatic sulfonates only few

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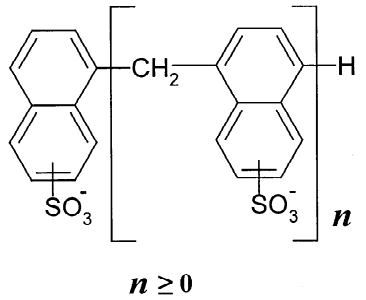

Fig. 1. Generic molecular structures of poly(naphthalenesulfonate) compounds.

researchers [5–7], investigated the environmental occurrence of polymeric naphthalenesulfonate (PNS) type compounds (schematically sketched in Fig. 1). The manufacturing of these products, by ''one pot reaction'' of naphthalene, sulfuric acid and formaldehyde was described in the BASF patent in 1913 [8]. Such chemicals are now included in the OECD list of high production chemicals and are widely used by industry as surfactants, dispersants, tanning agents or as plasticizers of concrete [9,10]. The estimated world-wide use of PNS as concrete admixture and as dye dispersant is about $300 \cdot 10^6$ kg/year. Compositions of technical mixtures vary in a high degree depending on the reaction used in the production process and the degree of polymerisation. Although these compounds have been in use for many years, relatively little is known about their constitution. Mechanisms of the reaction and characterization of single oligomers by NMR were studied by an Italian research group in 1990 [11,12]. Separation of PNS oligomers in commercial mixture has been achieved by size exclusion chromatography [17], salting-out [13,14], ion pair chromatography [15,16] and ultrafiltration [16].

Shorter PNS oligomers and monomers are usually considered as by-products of commercial PNS mixtures, but their concentration in commercial mixtures can be considerable (up to 15%) [17]. An extensive study indicates that β-naphthalenesulfonate and naphthalenedisulfonate are not adsorbed substantially on the cement particles, while the polymeric fraction is adsorbed to a different extent according to the molecular mass [17]. Other studies indicate that PNS can migrate into water which is in contact with the concrete [18]. On the basis of the wide spread use of PNS, the resistance to the biodegradability of naphthalenesulfonic acids [19,20], as well as their high mobility in aquatic systems [21], the concentration of short PNS in environmental waters is supposed to be relevant.

Because of legal implications, it is highly recommended that analytical results indicating the presence of environmental contaminants are confirmed by mass spectrometric methods [22]. No LC–MS methods for trace analysis of these analytes have been so far proposed. Two main impediments probably explain this lack. The low compatibility of non-volatile ion pair reagents (commonly used for LC analysis of sulfonated compounds) with LC–MS interfaces, and the lack of reference compounds. The object of this work has been that of developing a method for the determination and characterisation, at trace level, of PNS compounds and screening the presence of the relevant PNS type pollutants in environmental and waste waters.

2. Experimental

2.1. Reagents and chemicals

Naphthalene-1-sulfonate (1-NS) and naphthalene-2-sulfonate (2-NS) were obtained from Fluka (Buchs, Switzerland). Commercial mixtures of naphthalenesulfonate–formaldehyde condensates (NSFCs) were kindly supplied by BMG Eng. (Schlieren, Switzerland). 8,8′-Methylenebis-2-naphthalenesulfonate (a single PNS dimer isomer) was kindly supplied by DVGW-Technologiezentrum Wasser (Karlsruhe, Germany). Linear alkylbenzenesulfonate (*n*-C_8-LAS) was obtained from Aldrich (Milwaukee, WI, USA). Ammonium acetate ($AcNH_4$, >99% pure), Tetrabutylammonium fluoride (TBAF, >99% pure), both of analytical grade, were from Fluka. HPLC-grade solvents and reagents were from Carlo Erba (Milan, Italy). For LC analysis, distilled water was further purified by passing it through a Milli-Q Plus apparatus (Millipore, Bedford, MA, USA).

2.2. Sample treatment and recovery of PNS commercial mixtures

Solid-phase extraction (SPE) was performed with syringe-like polypropylene tubes (1.3 cm I.D.) packed with 0.5 g of styrene–divinylbenzene copolymer resin, Envichrom-P, supplied by Supelco (Bellefonte, PA, USA). Polypropylene frits (Supelco), were placed on top and below the sorbent bed.

Before extraction of the aqueous samples, the SPE cartridges were washed with 10 ml of CH_3OH and 20 ml of water containing 1 mol/l $AcNH_4$. Grab samples of two Italian rivers (Tiber and Piave), wastewater and ground water samples from concrete manufactory plants were collected in brown glass bottles and stored at 4°C until analysed. Unless they contained suspended materials able to plug the SPE cartridge, such as algae and debris, samples were extracted unfiltered (although at lower flow-rates). For the recovery study, river water samples were spiked with a suitable volume of working standard solution. Solid $AcNH_4$ up to 1 mol/l was added to the water samples, which were agitated for 2 min in order to disperse homogeneously suspended solid particles, and, immediately thereafter, aliquots of waste (10 ml), river (100 ml) and ground (1000 ml) water were extracted. The cartridge was fitted to a side arm filtration flask that was connected with a vacuum water pump. The sample was extracted directly from the bottle by a Teflon tube connected to the cartridge at a flow-rate of approximately 50 ml/min. Reservoirs used for subsampling were washed with 2×10 ml of an aqueous solution of $AcNH_4$ 1 mol/l, and this solution was also passed through the extraction cartridge. Both the operation of drawing an aliquot of the sample, while the solid material is still uniformly dispersed, and washing of the reservoir with the $AcNH_4$ solution ensured quantitative recoveries of PNS. Short-chain PNS oligomers are partially adsorbed on particles present in the aqueous sample. This particulate matter can stick to the wall of the reservoir containing the aqueous sample with the ultimate consequence that a fraction of analytes can be lost. The cartridge was finally washed with 10 ml of water containing 1 mol/l $AcNH_4$, followed by 5 ml of distilled water and then dried by applying vacuum for 1 min. Adsorbed analytes were finally recovered with 7 ml of methanol. Extracts were collected in a 1.4-cm I.D. round-bottom glass vial and dried in a water bath at 60°C by allowing a gentle nitrogen stream to flow into the tubes. Residues were reconstituted in 200 μl of a mixture of water–CH_3OH (80:20, v/v) containing *n*-C8-LAS as internal standard (I.S.) and 30 μl of these reconstituted extracts were analysed by HPLC–MS.

2.3. HPLC–MS analysis

Chromatographic separation was carried out with a Varian (Walnut Creek, CA, USA) Model 9010 HPLC equipped with a Rheodyne Model 7125 injector having a 50-μl loop. The analytes were separated on an ''Alltima'' analytical column (5 μm C_{18}, 25 cm ×4.6 mm I.D.) supplied by Alltech (Sedriano, Italy). Mobile phases were acetonitrile (A) and water (B), both containing 0.2 mmol/l $AcNH_4$. The initial mobile phase composition was 10% A, that was first increased to 20% in 13 min and then to 80% in 17 min. The flow of the mobile phase was 1 ml/min.

The mass-spectrometer was a Fisons VG Platform LC–MS detector (Fisons Instruments/VG BioTech, Milan, Italy) equipped with an electrospray ionisation (ESI) interface and a single quadrupole. The ESI-MS detector was operated in negative ionization mode and selected ion monitoring (SIM) acquisition mode (see Table 1). The source temperature was 70°C and the skimmer cone voltage was set at 25 V. The ion current profile for the selected PNS oligomers is shown in Fig. 2. Quantitation of each oligomer was performed by extracting its ion chromatographic profile from the total ion current chromatogram, measuring the peak areas of all isomers as a total, and relating this area to that of the I.S. The obtained ratio was corrected by a response factor which was different for each oligomer and calculated by injecting the standard working mixture. Calibration curves were generated by randomly injecting different amounts of the standard working mixture.

2.4. HPLC with fluorescence (FL) and UV detection

In order to compare the sensitivity of this method with one using the ion-pair chromatography (IPC)

Table 1
Mass charge ratio (m/z) of fully and partially deprotonated PNS oligomers

PNS oligomer	Mass/charge ratio (m/z)			
n	$[M_n]^{(n+1)-}$	$[M_n+H]^{(n)-}$	$[M_n+2H]^{(n-1)-}$	$[M_n+3H]^{(n-2)-}$
0	207.0[a]	–	–	–
1	213.0[a]	427.0 (n.d.)	–	–
2	215.0[a]	323.0 (n.d.)	647.1 (n.d.)	–
3	216.0[a]	288.4 (n.d.)	433.0 (n.d.)	867.1 (n.d.)

n.d., not detected
[a] m/z selected of SIM acquisition.

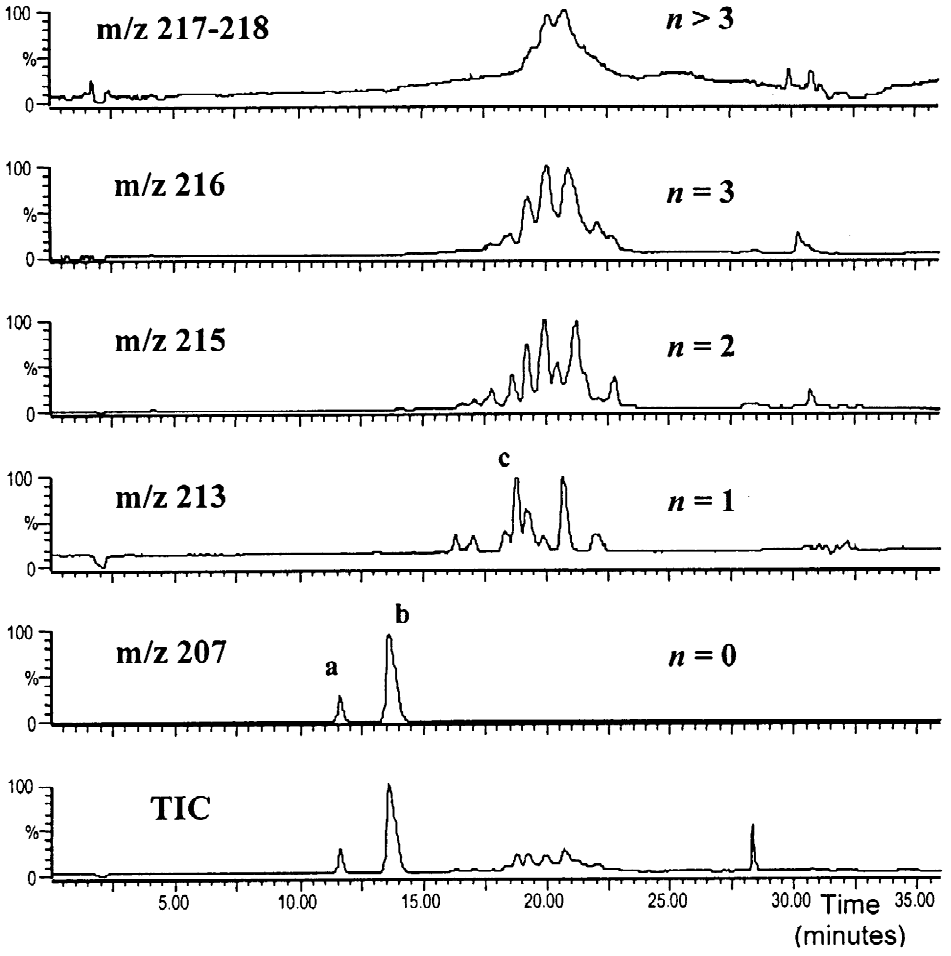

Fig. 2. Total ion current chromatogram (TIC, lower) and extracted ion current profiles obtained injecting 10 μg of the working mixture. (a) 1-naphthalenesulfonate; (b) 2-naphthalenesulfonate; (c) 8,8′-methylenebis-2-naphthalenesulfonate.

mode, and for the purpose of standardizing the working solution, IPC was used with both FL and UV detection. The mobile phase was consisting of acetonitrile (A) and water (B), both containing 5 mmol/l of TBAF. The initial mobile phase composition was 30% A, which was linearly increased to 99% in 120 min. The flow-rate of the mobile phase was 1 ml/min and the LC column was a Phenomenex Luna C_{18}-2 (5 μm C_{18}, 25 cm×4.6 mm I.D.) supplied by Phenomenex (Torrance, CA, USA). The chromatographic apparatus consisted of a 1050 series liquid chromatograph (Hewlett-Packard, Avondale, PA, USA) equipped with a HP model 1046A fluorescence detector (Hewlett-Packard) having a flow cell volume of 5 μl and operating at 228-nm (excitation) and at 360-nm (emission) wavelengths. The UV detector was a HP model 1050 (Hewlett-Packard) with a flow cell volume of 8 μl, operating at 228-nm wavelength. The samples were injected by a manual 7725 injector (Rheodyne, Rohnert Park, CA, USA) equipped with a 100-μl loop.

Standards of single PNS isomers were available only for first two oligomers; so the concentrations of oligomers $n=2$ and $n=3$ were estimated attributing to them the same UV response factors of the dimer ($n=1$). Because molar absorbances of the analytes vary with the number of chromophore groups this arbitrary assumption will cause an overvaluation of the concentrations of oligomers with $n=2$ and $n=3$ in the real samples. Recovery studies, attribution of response factors and linearity assessment were performed by using a working solution prepared from a commercial mixture of NSFCs. Because of the low concentration of oligomer $n=1$ in the commercial product, a suitable amount of 8,8′-methylenebis-2-naphthalenesulfonate was added to the working mixture. The composition of the working mixture (with exact concentrations for $n=0$–1 and estimated for $n=2$–3) is reported in Table 2.

3. Results and discussion

3.1. Extraction procedure

In previous works, graphitized carbon black [23,24] and silica derivatized [25–28] sorbents have been used for the extraction of naphthalenesulfonate. Polystyrene–divinylbenzene (PS–DVB) resins, especially those with a high surface area, also proved to be a valuable sorbent in extracting these analyte from environmental waters [29–32]. In this study the extraction step was performed after adding ammonium acetate to the sample and using a PS–DVB resin (particle size range 80–160 μm, pore 20–300 Å, surface area 900 m^2). The use of ammonium acetate instead of alkylammonium ion pair agents resulted to be more compatible with the LC–MS determination of sulfonated compounds [33,34]. This procedure quantitatively recovered the considered PNS oligomers ($n<4$) from spiked drinking water samples (Table 2). Quantitative recoveries for these analytes were also obtained in recovery experiments from spiked surface water samples (Table 3).

In order to verify the influence of the concentration of the ammonium acetate, recovery experi-

Table 2
Recovery (%) and relative standard deviation of short-chain ($n<4$) PNS oligomers in 1 litre of drinking water spiked with 10 μg of standard working mixture and after addition of $AcNH_4$ giving final concentration of 0.25, 0.5 and 1 mol/l[a]

PNS n	Spike (ng)	$AcNH_4$ concentration (mol/l)			
		0.25 x (%)	0.5 x (%)	1	
				x (%)[b]	$s-1$[c]
0	288	92±8	116±19	103	15
1	58	89±4	106±12	101	14
2	37[b]	75±9	92±10	102	8
3	10[b]	65±12	61±7	104	3

[a] Mean of three determinations.
[b] Estimated concentrations.
[c] Value calculated on six recoveries.

Table 3
Recovery of short chain ($n<4$) PNS oligomers in 100 ml of river water spiked with 30 μg of the standard working mixture and addition of $AcNH_4$ (1 mol/l)

PNS oligomer	Spike (ng)	Recovery (%)[a]	$s-1$ (%)
1	865	90	12.2
2	174	89	13.4
3	110[b]	85	12.1
4	30[b]	88	17.0

[a] Mean recovery and precision values calculated from six determinations.
[b] Estimated concentration.

ments were performed for a sample at different concentrations. As shown in Table 2, the extraction efficiency is strongly influenced by this parameter.

Moreover, IPC–FL analysis of the drinking water samples indicated that no loss of long-chain PNS oligomers (not detectable by MS detection) occurred.

3.2. IPC and MS detection of PNS compounds

IPC is the common approach in the analysis of aromatic sulfonates [1]. Unfortunately, the relatively high concentration of tetralkylammonium salts, used to achieve a reproducible chromatography, caused a dramatic weakening of the signal of the ESI-MS detector due to competition effects [35,36]. This precluded quantitation of PNS compounds also at relatively high concentrations (depending on the oligomer, this ranged between 0.4 and 1.4 μg/l). In preliminary experiments much effort has been spend to reach an acceptable compromise between the ion pairing and the ion suppression effect of alkyammonium salts. In spite of this, it was not possible to obtain reproducible chromatography for longer oligomers ($n>4$) when using low concentrations (<5 mmol/l) of ion-pairing salts as TBAF. The best compromise was found using acetonitrile (A) and water (B), both containing 0.5 mmol/l TBAF). The initial mobile phase composition was 30% A, which was linearly increased to 99% in 60 min. Under these conditions, after the electrospray process, the sulfonic groups of PNS appear to be completely deprotonated and partially neutralised by a variable number of TBA counterions (Fig. 3). In Table 4 the ions observed by analysing a commercial mixture of PNS are shown. The relative abundances of these ions varied from one chromatographic run to another, and were depending on the injected amount. From a practical point of view, it was necessary to select two or three ions for each oligomer to obtain an acceptable accuracy over a wide range of concentrations. Moreover the presence of adducts of PNS with a large number (up to 10) alkylammonium molecules made the assignation of ions with very similar mass/charge ratios very difficult. Reproducibility and repeatability were not excellent (repeatabilities ranged between 5 and 20%, depending on the oligomer). Insufficient chromatographic separation and the large number of ions formed by each single oligomer preclude the possibility of using SIM detection, thus decreasing further the method sensitivity. Furthermore the absence of any buffer in the mobile phase shortened the lifetime of the LC column. The use of triethylamine and acetic acid instead of tetralkylammonium salts did not give any improvement, since, acceptable chromatography for longer oligomers was not possible even at high concentrations (0.1 mol/l).

The most important factor limiting trace analysis of longer PNS oligomers by LC–MS is the absence of an acceptable compromise between the need of relatively high concentrations of ion pair salts, in order to obtain a chromatographic retention, and the signal weakening of the LC–MS detector when such salts are used.

3.3. Identification and limit of detection

The use of small amounts of ammonium acetate in the chromatographic phase allowed the determination and characterisation by LC–ESI-MS of the more relevant members of the PNS environmental contaminants class. Under these conditions, ESI negative ionisation generates, for the selected analytes, fully dissociated $[M_n-(n+1)H]^{(n+1)-}$ ions. Absence of partially protonated ions or other adducts ion simplifies identification and quantitation. Compared to ion pair chromatography conditions, the limit of detection of the LC–MS decreased by a factor of ca. 10^3. It is remarkable that in the SIM acquisition mode the limit of detection (LOD) for a single isomer of the dimer ($n=1$) was about 0.5 ng (1.2 pmol). The linearity was good ($r^2>0.98$) between 1 ng and 10 μg.

A single quadrupole mass spectrometer equipped with an ESI interface can generate fragment ions by inducing in-source collision-induced decomposition (CID) process that are useful for structure elucidation. Confirmatory ions by CID have been obtained by setting the skimmer lens voltage to 55 V and setting the full scan acquisition range from m/z 70 to m/z 400. Fragmentation of sulfonated naphthalene compounds mainly generated a characteristic m/z 80 ion corresponding to the $[SO_3]^-$ group.

3.4. Real samples

Liquid chromatography with fluorescence detection [5,37], and LC–MS [7] have been used to detect

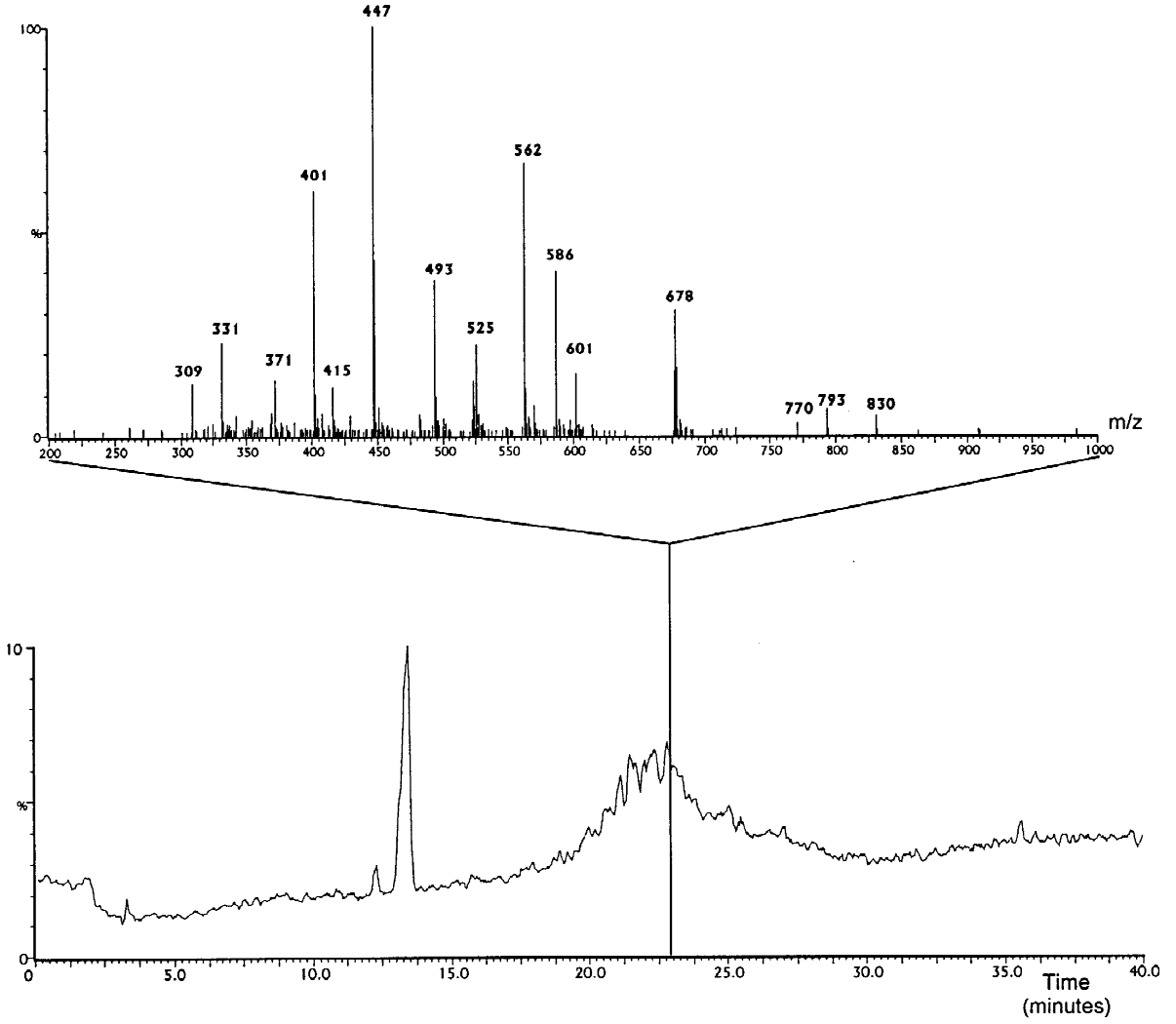

Fig. 3. Complexity of LC–ES-MS spectra using mobile phases containing 0.5 mmol/l of alkylammonium salts. Chromatogram obtained injecting 100 μg of working solution.

relatively high concentrations the PNS in river and wastewaters. Actual relevance of PNS as water pollutants and the effectiveness of the present method in environmental impact assessment was explored in a small monitoring survey at a concrete factory site and on grab samples of two large Italian rivers (Tiber and Piave). Exemplary results are reported in Table 5. The relative abundance of PNS oligomers in the wastewater sample reflects the composition of the technical PNS mixture adopted in the monitored concrete factory. Only the shorter oligomers were detected in all the analysed environmental water samples. Furthermore the IPC–FL analysis was used to detect the eventual presence of longer PNS.

It is interesting to note that in the river samples considered the concentration of oligomer $n=1$ (dimer) is in the same range as naphthalenesulphonic acid. The presence of dimeric compounds in ground water, sampled from a 110-m deep well close to a concrete factory, demonstrated the high mobility of shorter oligomers and confirm the risk of contamination of water intended for human consumption [38].

Table 4
The relevant adducts (m/z) of PNS detected by analysing a PNS commercial mixture by IPC and MS[a]

n	No. TBA^+ Molecules									
	$T=0$	$T=1$	$T=2$	$T=3$	$T=4$	$T=5$	$T=6$	$T=7$	$T=8$	$T=9$
0	207.0									
1	213.0	668.0								
2	(215.0)	444.0								
3		368.7	(674.0)							
4		331.3	522.5							
5		(308.9)	446.7	676.3						
6			401.1	562.0	(830.1)					
7			(370.8)	493.4	677.3					
8				447.7	585.6	(792.6)				
9				(415.0)	524.5	677.9				
10					(480.9)	601.4	770.2			
11						546.8	678.3	862.4		
12						(505.8)	612.7	755.2		
13							563.5	678.6	832.1	
14								621.1	744.1	908.9
15								576.5	678.8	810.4

[a] T is the number of TBA molecules in the adducts, n identifies the oligomers. Ions having a relative abundance between 5 and 10% are reported between brackets.

The effects of these compounds on the environment are still unknown but there is concern of the authorities due to the persistence of naphthalene-sulfonate compounds [39].

4. Conclusion

The presented method provides good support for a structural characterisation of short PNS oligomers in an aquatic environment. A high mobility in the aquatic environment was demonstrated for shorter PNS oligomers, while longer PNS oligomers are mainly adsorbed on particulate matter and on sediments. These results can be useful for a reliable assessment of the impact of this class of compounds on the environment. Another significant advantage of this analytical procedure is the good separation of isomers. This opportunity was further exploited in a study on biodegradability of PNS [40].

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Table 5
Concentration (ng/l) of short chain ($n<4$) PNS oligomers in the environmental samples analysed

PNS oligomer	Tiber River	Piave River	Waste water from concrete factory	Groundwater, below concrete factory
0	240	20	20	50
1	180	10	3200	73
2	60[a]	nd	4300[a]	nd
3	11[a]	nd	300[a]	nd

nd, not detected.
[a] Estimated concentration.

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