ELSEVIER

Journal of Chromatography A, 854 (1999) 187–195

JOURNAL OF CHROMATOGRAPHY A

On-line solid-phase extraction–ion-pair liquid chromatography–electrospray mass spectrometry for the trace determination of naphthalene monosulphonates in water

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Abstract

This paper presents an HPLC–MS method for the fully automated determination of a group of naphthalene monosulphonates in environmental water samples. The analytical procedure consisted of on-line ion-pair solid-phase extraction using a PLRP-S precolumn and ion-pair LC separation with triethylamine as ion-pair reagent in both cases. A mass spectrometric detector, coupled to LC through an electrospray interface and operated in negative ion mode, was used. Diagnostic ions usually corresponded to $[SO_3]^-$ and/or $[M-SO_2H]^-$ together with $[M-H]^-$ and/or $[M-2H+Na]^-$. The method was applied to the trace determination of several sulphonates present in tap water, seawater and water from the Ebro river. The analytes were determined at a concentration level between 0.05 and 1 $\mu g\ l^{-1}$ under selected ion monitoring acquisition by preconcentrating just 15 ml of sample. Naphthalene-1-sulphonate and naphthalene-2-sulphonate were identified and quantified in one of the samples of seawater.

Keywords: Water analysis; Environmental analysis; Naphthalene monosulfonates; Sulfonates

1. Introduction

Aromatic sulphonates and their hydroxy and amino derivatives are widely used in industrial processes, especially as intermediates in the manufacture of dyes and in tannery industries. These compounds, and mainly their nitro and amino derivatives, are not easily biodegraded, which suggests that they are not easily eliminated in water treatment plants. Because of this and because they occur in relatively high amounts in industrial waste waters, they are potentially hazardous for surface and groundwater and there have been concerns about the quality of drinking water [1].

Various chromatographic methods have been developed for determining aromatic sulphonates in environmental samples. Gas chromatography has not been widely used because in many instances volatile derivatives could not be produced [2]. There have been some applications of capillary electrophoresis [3–5], but the number of publications in this field is still limited. HPLC has been the preferred technique, with ion-pair chromatography the most generally used approach [6–10]. UV detectors have been used [9,10] to detect these compounds in HPLC although, due to their intense fluorescence, fluorimetric detectors are more sensitive and have been widely used [6–8]. Problems encountered with LC are related to the confirmation of these analytes that cannot be achieved either with UV or fluorescence detectors. Despite the well known identification capability of

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0021-9673/99/$ – see front matter
PII: S0021-9673(99)00664-0

the MS detector, HPLC–MS has rarely been used, because the non volatile ion-pair reagents commonly employed for the HPLC separation are incompatible with MS interfaces. Most HPLC–MS applications described in the literature are related to the determination of linear alkylbenzene sulphonates (LASs) [11] because ion-pair LC is not necessary for their separation. Zerbinati et al. [12] analysed river water polluted with aromatic sulphonates by FAB (fast atom bombardment) MS–MS, but in that case quantitation was almost impossible because previous separation of the analytes did not occur. However, these techniques have been applied simply to confirm the presence of the compounds studied in the real samples, while LC–IR has been applied to quantify or identify. Kim et al. [13] determined some aromatic sulphonates together with other contaminants by HPLC–PB (particle beam)-MS, but they used anion-exchange LC and the limits of detection have not been as good as those with conventional detectors like fluorimetric ones. To our knowledge, electrospray (ES) interface has not been widely applied for the determination of aromatic sulphonates [14].

The low concentration levels of aromatic sulphonates in most environmental waters require the use of an enrichment step. Ion-pair solid-phase extraction (SPE) has been the approach most used in both modes of operation, off-line [4,6,10] and on-line [7–9,15]. Furthermore, this technique has also been used to eliminate interfering chemicals to enhance chromatographic separation and column life time.

This paper describes the determination of a group of naphthalene-monosulphonates at low $\mu g\ l^{-1}$–$ng\ l^{-1}$ levels in environmental waters by an on-line SPE–HPLC–ES-MS method. Both the extraction and separation processes are carried out by using an ion-pairing reagent, indicating that an electrospray interface can be coupled with ion-pair chromatography. This method is suitable for routine analysis because it is fully automated and the total analysis time is adequate. To our knowledge, no previous work involving the one of automated on-line SPE followed by LC–ES-MS has been reported for most of these compounds. The analytes that have been selected are either representative water contaminants or are suspected contaminants in the zone under study.

2. Experimental

2.1. Reagents and standards

The compounds used in this study were purchased from Aldrich (Beerse, Belgium) or Fluka (Buchs, Switzerland) and were: naphthalene-1-sulphonate (1-NS), naphthalene-2-sulphonate (2-NS), 2-amino-naphthalene-1-sulphonate (2-NH_2-1-NS), 8-amino-naphthalene-2-sulphonate (8-NH_2-2-NS), 5-amino-naphthalene-2-sulphonate (5-NH_2-2-NS), 1-hydroxy-naphthalene-4-sulphonate (1-OH-4-NS), 7-amino-4-hydroxynaphthalene-3-sulphonate (7-NH_2-4-OH-2-NS) and 6-amino-4-hydroxynaphthalene-2-sulphonate (6-NH_2-4-OH-2-NS). Stock solutions (1000 $mg\ l^{-1}$) were prepared by weighing and dissolving each compound in water or water with several drops of 1 *M* sodium hydroxide to enhance the solubility, and storing them in a refrigerator. These solutions were used to prepare diluted standard solutions and to spike water samples to the required concentrations.

HPLC-grade methanol and water were obtained from Scharlau (Barcelona, Spain). Acetic acid and sodium hydroxide for regulating the pH of the mobile phase and the samples were from Probus (Badalona, Spain). Triethylamine (TEA) with a purity higher than 98% was used as the ion-pairing reagent and was purchased from Fluka.

Both helium for degassing the LC solvents and nitrogen for the ES interface were 99.998% pure and supplied by Air Liquide (Barcelona, Spain).

2.2. LC–ES-MS conditions

A Hewlett-Packard (Palo Alto, CA, USA) 1090 liquid chromatograph equipped with a six-port rotary valve with a 20-μl loop and an autosampler was used. Separation was performed on a 25×0.46 cm stainless steel analytical column packed with 5 μm Kromasil 100 C_{18} (Tecknokroma, Barcelona, Spain). Elution was accomplished at room temperature using a binary gradient composed of methanol (A) and 5 m*M* TEA (acidified to pH 6.5 with acetic acid) (B), at a flow-rate of 1 $ml\ min^{-1}$, with the following gradient: 10% (A) held for 15 min, then changed linearly to 25% at 28 min, then to 40% at 34 min and to 90% at 38 min. After 2 min at 90%, the mobile

phase returned to the initial conditions in 3 min. It took less than 15 min to reequilibrate the column; most of this time was used to perform the preconcentration step.

For the mass spectrometric analysis an HP 1100 MSD was used. The system was equipped with an ES interface. The mass spectrometer was operated in negative ion mode by applying a voltage of 3500 V to the capillary. The fragmentor parameter was set at 150 V. Nitrogen was used as drying gas with a flow-rate of 12 l min^{-1} and as nebulizer gas with a pressure of 413 685 Pa (60 p.s.i). Mass spectra in full-scan mode were collected by scanning over the range 70–400 m/z in 3.77 s. In selected ion monitoring (SIM) acquisition, two of the most abundant ions of each compound were monitored. Table 1 shows the main ions obtained for each compound. The first two ions mentioned for each compound correspond to the selected ions to be quantified under SIM mode. The ions selected to be quantified under full scan mode are indicated in the same table.

Table 1
Main ions, corresponding fragments and their relative abundance (R.A.)

Compound	M_r	m/z selected and tentative ions[a]	R.A. (%)
6-NH_2-4-OH-2-NS	238	*238* $[M-H]^-$	100
		260 $[M-2H+Na]^-$	35
		80 $[SO_3]^-$	5
7-NH_2-4-OH-2-NS	238	*238* $[M-H]^-$	100
		260 $[M-2H+Na]^-$	40
		80 $[SO_3]^-$	7
5-NH_2-2-NS	222	*222* $[M-H]^-$	100
		158 $[M-SO_2H]^-$	25
		80 $[SO_3]^-$	7
1-OH-4-NS	223	*223* $[M-H]^-$	100
		245 $[M-2H+Na]^-$	65
		80 $[SO_3]^-$	27
2-NH_2-1-NS	222	*222* $[M-H]^-$	100
		158 $[M-SO_2H]^-$	10
		80 $[SO_3]^-$	8
8-NH_2-2-NS	222	*222* $[M-H]^-$	100
		158 $[M-SO_2H]^-$	15
		80 $[SO_3]^-$	4
1-NS	207	*207* $[M-H]^-$	100
		143 $[M-SO_2H]^-$	50
		80 $[SO_3]^-$	18
2-NS	207	*207* $[M-H]^-$	100
		143 $[M-SO_2H]^-$	25
		80 $[SO_3]^-$	5

[a] Ions in the quantification for scan acquisition are shown in italics.

The instruments, including both the liquid chromatograph and the mass spectrometer, were controlled and the data were processed through an HP LC/MSD A.05.04 [273] CHEMSTATION.

2.3. On-line sample preparation

A six-port valve from an automated SPE device, OSP-2 (Merck, Darmstadt, Germany), which was connected on-line with the LC pumps, was used for sample enrichment. A LichroGraph Model L-6200A intelligent pump (Merck-Hitachi) was used to deliver the solvents and the samples to the precolumn. The OSP-2 connections were modified to use a 10×3.0 mm precolumn (Free University, Amsterdam, The Netherlands), laboratory-packed with PLRP-S (15–25 μm particle size) (Spark Holland, Emmen, The Netherlands). Only valve 1 of the OSP-2 system was used in the SPE process and elution. The precolumn was conditioned by flushing 2 ml of methanol and then 2 ml of water with 5 m*M* TEA at pH 6.5 adjusted with acetic acid. Before the preconcentration step, the pH of the sample was adjusted to 6.5 with acetic acid and TEA was added at a concentration of 5 m*M*; 15 ml of the sample were then preconcentrated. Finally, the analytes were desorbed by backflushing with the mobile phase and on-line transferred to the analytical column. The flow-rate was 2 ml min^{-1} throughout the extraction process. The precolumn could be used at least for 30 analysis of real samples.

Real samples were filtered through a 0.45-μm filter (Teknokroma) before preconcentration. When tap water was analysed, 300 μl of a 10% Na_2SO_3 solution was added for each 100 ml of water before standard addition to eliminate free chlorine, which could disturb the method performance.

3. Results and discussion

3.1. Ion-pair LC–ES-MS

The aromatic monosulphonates were separated by

ion-pair chromatography because this is the best way to separate them in a reasonable time. Although TBA (tetrabuthylammonium) is one of the most often used ion-pairing reagents [8,14], it could not be used in our study because its volatility is not compatible with the ES interface. TEA was selected as ion-pairing reagent because there were no problems with condensation in the MS interface and it separated the eight aromatic sulphonates well. The concentration of TEA and the pH of the mobile phase were selected according to previous work [16]. The gradient profile was optimised and the compounds were separated in under 40 min. The optimal LC conditions are reported in Section 2.2.

The operational conditions of the ES-MS operating in the negative ion mode were optimised in a previous work [16]. The mass spectrum of each analyte was obtained under full-scan conditions with a fragmentor value of 150 V by directly injecting each compound at a concentration of 50 mg l^{-1} into a carrier stream of methanol–5 m*M* TEA (pH 6.5 with acetic acid) (30:70, v/v). The main ions of each compound are listed in Table 1. The spectra obtained show $[M-H]^-$ as the major ion. Fragmentation is small in most of them. The amino derivatives and 1-NS and 2-NS show $[M-SO_2H]^-$ as the second major ion, while the hydroxy derivative and the aminohydroxy derivatives show $[M-2H+Na]^-$. This can be attributed to the fact that hydroxy derivatives have a second polar group (the hydroxy group) in the molecule. The hydroxy group can lose a proton, leaving the sulphonate group with either a proton or a sodium cation attached to it. All the compounds studied show the $[SO_3]^-$ corresponding to the ion m/z 80 with a relative abundance varying between 4 and 27. As example, Fig. 1 shows the spectra obtained for 7-NH_2-4-OH-2-NS and 8-NH_2-2-NS. The abundances obtained for each compound at the same concentration level were quite different.

3.2. On-line trace enrichment

Preconcentration was performed by on-line ion-pair SPE on styrene–divinylbenzene copolymer. This sorbent was selected according to previous results [9] when this sorbent and C_{18} were compared. The polymeric sorbent gave better recoveries than C_{18} for most aromatic sulphonates studied.

In the previous study [9], TBA was used as the ion-pair reagent. In this study, TEA was used instead of TBA because the latter caused a change in retention times and some peaks were distorted. The concentration of TEA and sample pH were optimized in order to obtain the best recoveries in the preconcentration step and the optimal values were 5 m*M* and 6.5, respectively.

The breakthrough volumes of the aromatic sulphonates were determined by preconcentrating different sample volumes, between 10 and 20 ml, of Milli-Q water under full-scan acquisition. These samples were spiked at different concentrations to obtain the same theoretical final amount. A sample volume of 15 ml was selected to carry out further studies. The recoveries obtained by preconcentrating 15 ml were 95% for 2-NH_2-1-NS, 8-NH_2-2-NS, 1-NS and 2-NS, 80% for the 5-NH_2-2-NS, 42% for the 1-OH-4-NS and 25% for the hydroxyamino derivatives (6-NH_2-4-OH-2-NS and 7-NH_2-4-OH-2-NS). Sample volumes of 20 ml gave very low recoveries (10–15%) for the first three compounds, 37% for the 5-NH_2-2-NS and 76–85% for the rest of the analytes. Sample volumes lower than 15 ml did not significantly increase the recoveries of the first three aromatic sulphonates.

3.3. Analysis of real water samples

The performance of the method was checked with real samples such as tap water, water from the Ebro river and seawater.

First of all, a blank of tap water and water from the Ebro river were analysed. None of the peaks eluted at the same retention time as the analytes being studied. Recoveries were then calculated by preconcentrating 15 ml of tap water or Ebro river water spiked at a concentration level of 50 μg l^{-1} under full-scan acquisition. The recoveries for both types of samples were similar to those specified above for Milli-Q water. When tap or Ebro river water spiked with different levels of analytes were analysed under full-scan acquisition, linearity was good between 0.5 and 70 μg l^{-1}, although the lower limit was higher for the first four compounds. The correlation values were between 0.991 and

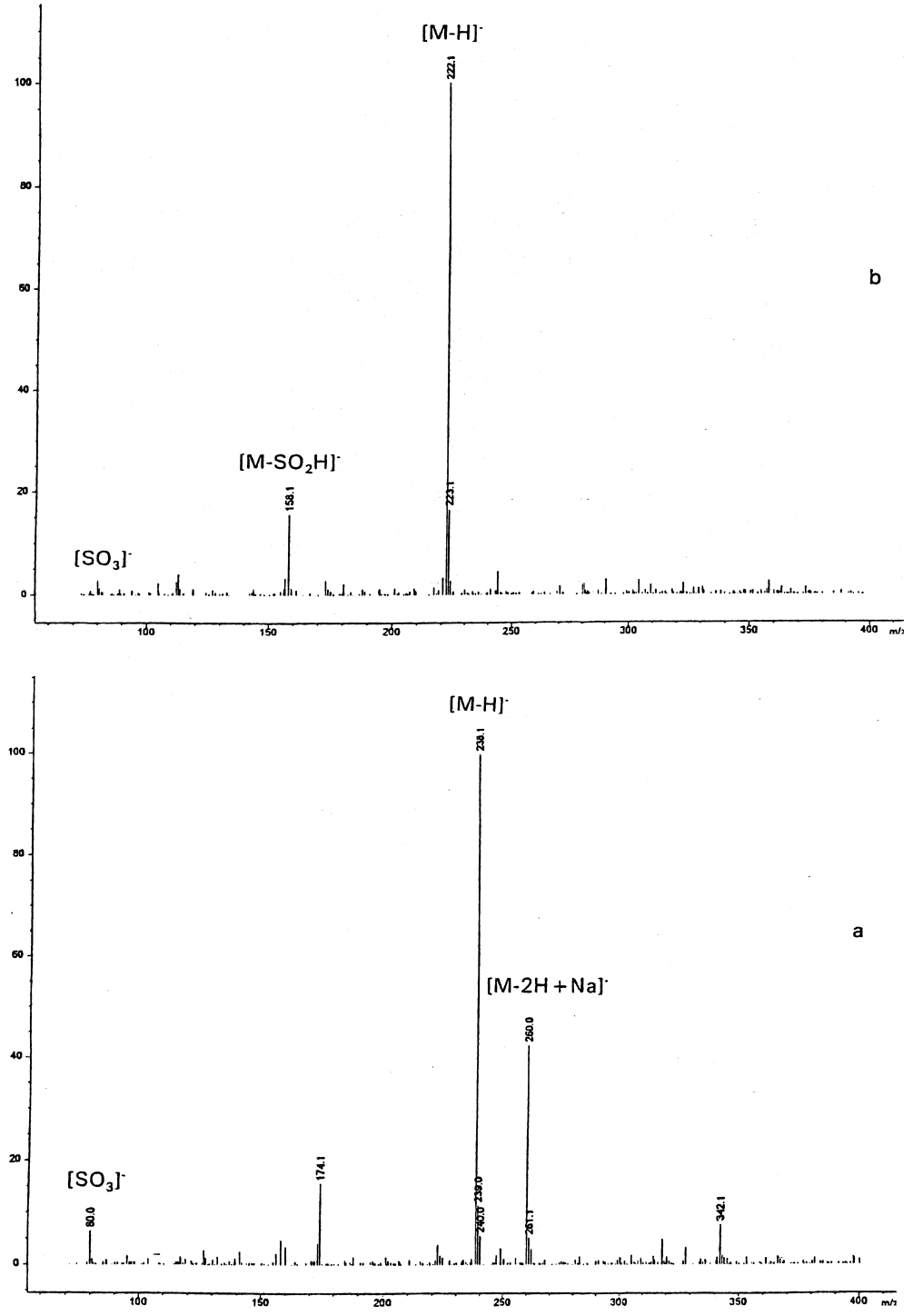

Fig. 1. Spectra of (a) 7-NH_2-4-OH-2-NS and (b) 8-NH_2-2-NS obtained by FIA analysis. For flow injection analysis (FIA) conditions see ion-pair LC–ES-MS in the Results and Discussion section.

Table 2
Analytical data obtained for fortified Ebro river water under full-scan and SIM acquisition

Compound	Full-scan			SIM		
	Linearity range ($\mu g\ l^{-1}$)	LOD ($\mu g\ l^{-1}$)	r^2	Linearity range ($\mu g\ l^{-1}$)	LOD ($\mu g\ l^{-1}$)	r^2
6-NH_2-4-OH-2-NS	20–70	7	0.9913	1–10	0.3	0.9994
7-NH_2-4-OH-2-NS	30–70	10	0.9992	1–10	0.3	0.9995
5-NH_2-2-NS	5–70	1.5	0.9986	0.05–10	0.02	0.9994
1-OH-4-NS	30–70	10	0.9962	0.1–10	0.02	0.9989
2-NH_2-1-NS	0.5–70	0.2	0.9920	0.05–10	0.007	0.9998
8-NH_2-2-NS	0.5–70	0.2	0.9978	0.05–10	0.01	0.9998
1-NS	0.5–70	0.1	0.9914	0.05–10	0.004	0.9997
2-NS	0.5–70	0.1	0.9943	0.05–10	0.003	0.9999

0.999; the limits of detection, calculated for a signal-to-noise ratio of 3, were between 0.1 and 10 $\mu g\ l^{-1}$. The repeatability and reproducibility between days was also checked by analysing six samples spiked with 30 $\mu g\ l^{-1}$ of 7-NH_2-4-OH-2-NS and 1-OH-4-NS, 20 $\mu g\ l^{-1}$ of 6-NH_2-4-OH-2-NS, 5 $\mu g\ l^{-1}$ of 5-NH_2-2-NS and 1 $\mu g\ l^{-1}$ of the rest of analytes. The results, expressed as relative standard deviation (RSD), varied between 10 and 22% for repeatability and between 15 and 28% for

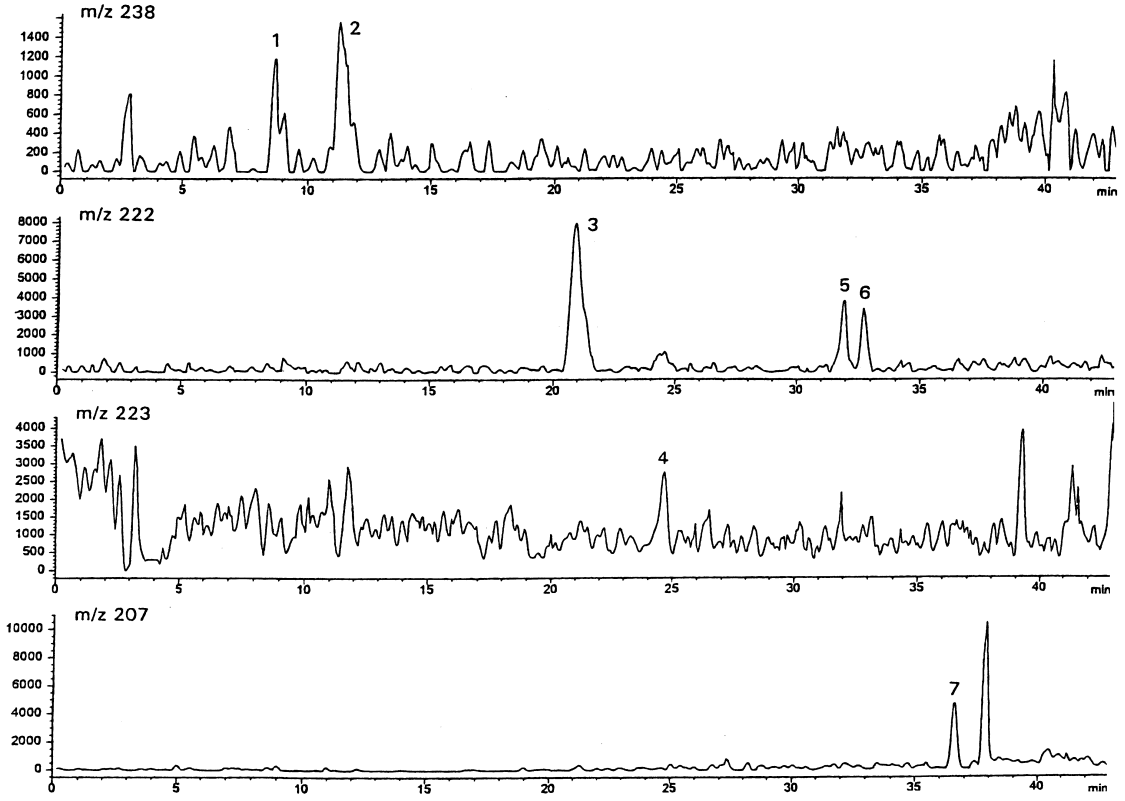

Fig. 2. Extracted ion chromatogram obtained by preconcentrating 15 ml of Ebro river water. For more details see text. (1) 6-NH_2-4-OH-2-NS, (2) 7-NH_2-4-OH-2-NS, (3) 5-NH_2-2-NS, (4) 1-OH-4-NS, (5) 2-NH_2-1-NS, (6) 8-NH_2-2-NS, (7) 1-NS, 8) 2-NS.

reproducibility. The results obtained for Ebro river water under full-scan acquisition are shown in Table 2. Fig. 2 shows the extracted ion chromatograms obtained when Ebro river water was spiked at 30 μg l^{-1} of 7-NH_2-4-OH-2-NS and 1-OH-4-NS, 20 μg l^{-1} of 6-NH_2-4-OH-2-NS, 5 μg l^{-1} of 5-NH_2-2-NS and 1 μg l^{-1} of the rest of analytes, and analysed by SPE–HPLC–ES-MS under full-scan acquisition. No peaks appeared in the chromatogram for the blank at the same retention times as the analytes studied. Peaks for the compounds studied were well-defined except for the first two eluted compounds due to the high noise observed.

When SIM acquisition was used, the linearity of the response was good in the range from 0.05 to 10 μg l^{-1} for most of the compounds, with correlation coefficients between 0.998 and 0.999. The limits of detection varied between 0.003 and 0.3 μg l^{-1} and were calculated from the same criterion as before. The repeatability and reproducibility between days were similar to those obtained under full-scan acquisition. These data were calculated by analysing six samples spiked with 1 μg l^{-1} of 6-NH_2-4-OH-2-NS and 7-NH_2-4-OH-2-NS, 0.1 μg l^{-1} of 1-OH-4-NS and 5-NH_2-2-NS and 0.05 μg l^{-1} of the rest of aromatic sulphonates. The results obtained for Ebro river water under SIM acquisition are also included in Table 2. Fig. 3 shows the chromatogram obtained from the analysis of Ebro river water and the same sample spiked at 1 μg l^{-1} of 6-NH_2-4-OH-2-NS and 7-NH_2-4-OH-2-NS, 0.1 μg l^{-1} of 1-OH-4-NS and 5-NH_2-2-NS and 0.05 μg l^{-1} of the rest of aromatic sulphonates studied in the SIM acquisition.

The method was also tested by analysing sea water from samples taken from along the Tarragona coast. In one of these samples, none of the analytes were

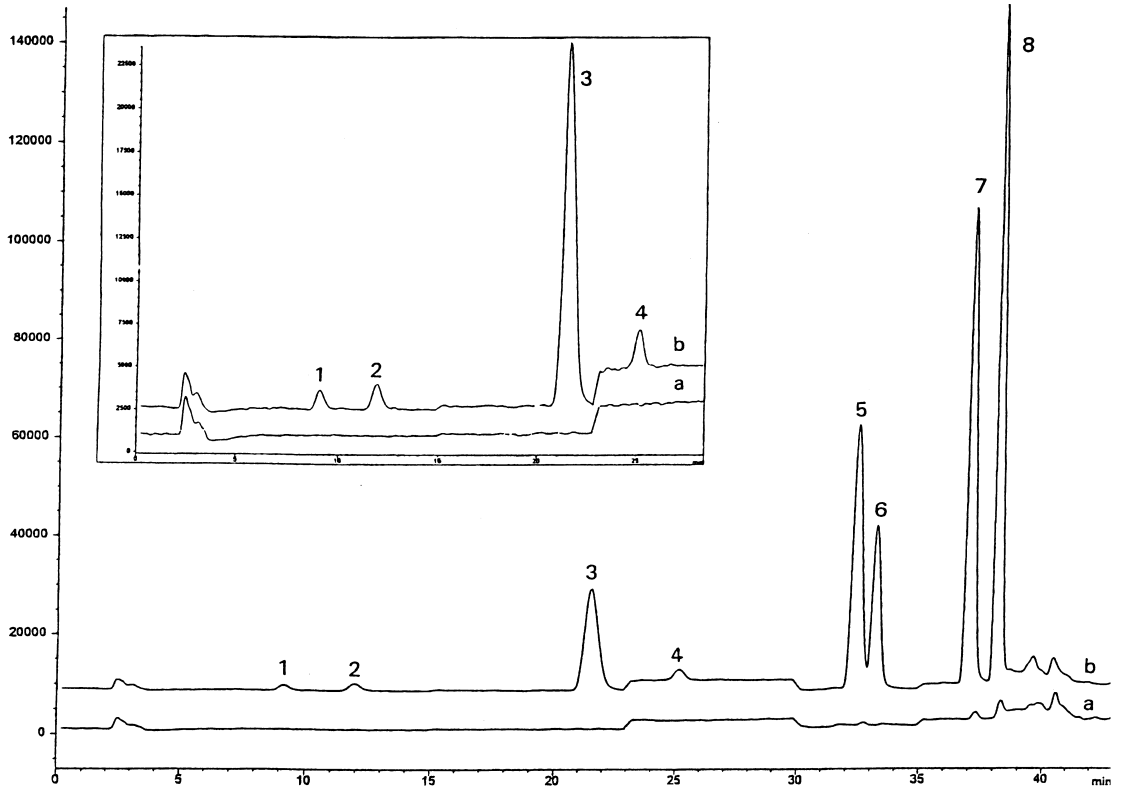

Fig. 3. Chromatograms obtained by SPE–LC–ES-MS(SIM) by analysing (a) 15 ml of Ebro river water and (b) 15 ml of Ebro river water spiked at 1 μg l^{-1} of 6-NH_2-4-OH-2-NS and 7-NH_2-4-OH-2-NS, 0.1 μg l^{-1} of 1-OH-4-NS and 5-NH_2-2-NS and 0.05 μg l^{-1} of the rest of aromatic sulphonates. The insert shows an amplification of both chromatograms from time zero to 28.5 min. For peak assignation, see Fig. 2.

detected in the blank chromatogram. The recoveries calculated by preconcentrating 15 ml of a sample of sea water spiked at a concentration level of 50 $\mu g\ l^{-1}$ under full-scan acquisition, decreased for 10% for all the compounds studied except for 5-NH_2-2-NS whose recovery was 60%, for 1-OH-4-NS whose recovery was 15%, and for 6-NH_2-4-OH-2-NS and 7-NH_2-4-OH-2-NS, whose recovery was 10%. These results agree with those already reported [14] which show the negative effects of inorganic species such as chloride on the recoveries. Despite this decrease in recoveries, four of the eight analytes studied still had a recovery higher than 85%. Compounds with recoveries lower than 20% were omitted from the next studies. The linearity of the response was checked for a sample of sea water under full-scan acquisition in the same range as for tap water and Ebro river water and the results were similar, except for the 5-NH_2-2-NS whose linearity range was between 10 and 70 $\mu g\ l^{-1}$, with a correlation coefficients higher than 0.995. The limits of detection were between 0.1 and 0.2 $\mu g\ l^{-1}$ except for the amino derivative mentioned whose limit of detection (LOD) was 3 $\mu g\ l^{-1}$. For SIM acquisition, the linearity range, correlation coefficients and limits of detection were also similar to those values obtained for tap water and Ebro river water except for the 5-NH_2-2-NS. For this compound, the linearity range varied between 0.1 and 10 $\mu g\ l^{-1}$ with a correlation coefficient higher than 0.994 and a detection limit of 0.02 $\mu g\ l^{-1}$. The precision of the method, expressed in terms of repeatability and reproducibility, was calculated for sea water in the same way as for tap water and Ebro river water and the values obtained were similar.

Different seawater samples collected randomly were analysed under full-scan acquisition and, in one of them, two peaks appeared at the same retention

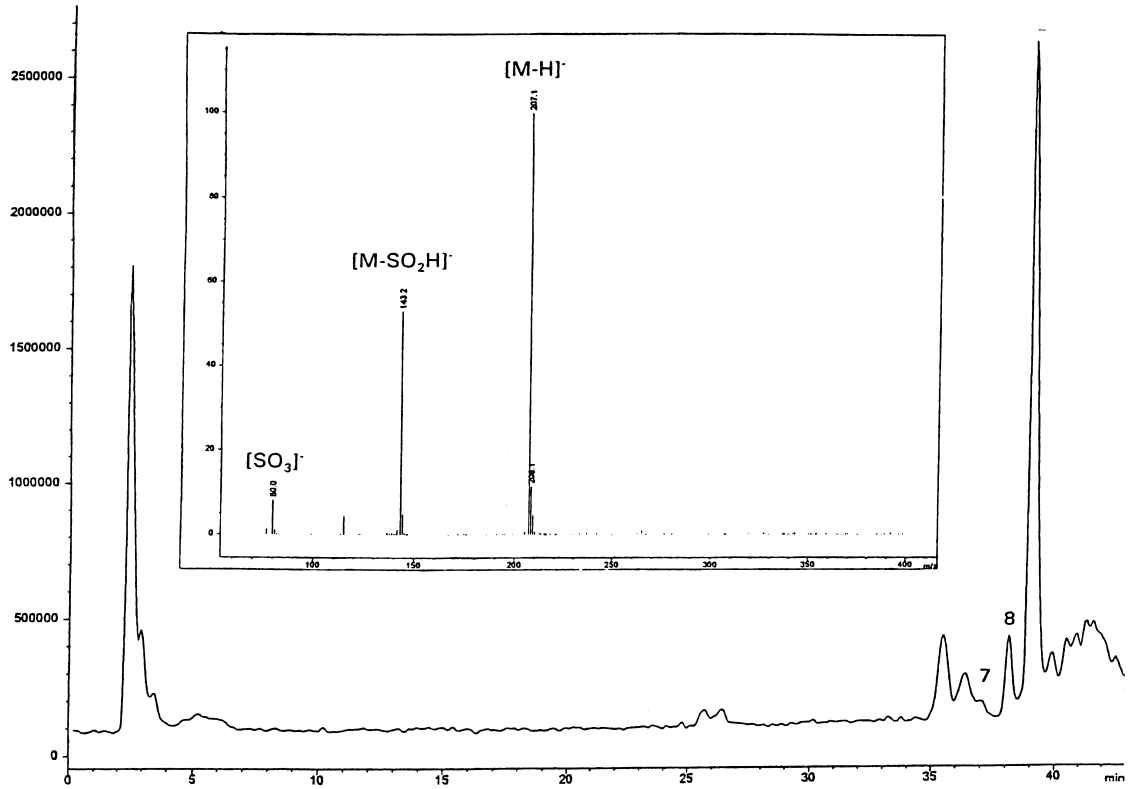

Fig. 4. Total ion chromatogram obtained by preconcentration of a 15-ml sea water sample. The insert shows the spectrum of 1-NS. For peak assignation, see Fig. 2.

time as 1-NS and 2-NS. Fig. 4 shows the total ion chromatogram obtained under full-scan acquisition for a seawater sample taken from near the coast of Tarragona. The inserts show the spectra of the 1-NS with diagnostics ions corresponding to $[SO_3]^-$ (m/z 80), $[M-SO_2H]^-$ (m/z 143) and $[M-H]^-$ (m/z 207). These two peaks were identified as the aromatic sulphonates indicated from the comparison between the spectra and that of the standard. Quantitation was also possible in full-scan acquisition and from an average value of three different determinations, the concentration was 0.8 μg l^{-1} for 1-NS and 0.5 μg l^{-1} for 2-NS with a standard deviation value of 12 and 14%, respectively. The other peaks which appeared in the chromatogram could not be identified. 1-NS and 2-NS in seawater samples have not been determined, to our knowledge, although they were found in some river waters [15].

4. Conclusions

An on-line SPE–HPLC–ES-MS method was developed for determining a group of eight hydroxy and amino monosulphonates in environmental waters. The method is fully automated and enables the sample to be preconcentrated and LC separated in less than 1 h. Moreover, a mass spectrometric detector has been successfully coupled to ion-pair LC through an ES interface, which enhances the identification capability of the method.

The method allows most of these compounds to be determined at levels of 0.1 μg l^{-1} or less by preconcentrating small sample volumes of 15 ml using a PLRP-S sorbent and a SIM acquisition mode.

The method was applied for the determination of these compounds in tap water, water from the Ebro river and seawater from the Tarragona area. 1-NS and 2-NS were identified in a sample of seawater by comparing the MS spectra and quantified under full-scan acquisition.

Acknowledgements

This work was supported by the Spanish Interministerial Commision for Science and Technology (CICYT) (AMB98-0913) and by the European Union, Environment and Climate Program (OWWA) (ENV4-CT97-0608).

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