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Determination of naphthalenesulfonates in water by on-line ion-pair solid-phase extraction and ion-pair liquid chromatography with fast-scanning fluorescence detection

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Abstract

A fast analytical method for quantifying a mixture of 12 naphthalenesulfonates and naphthalenedisulfonates has been developed. This method consists of on-line ion-pair solid-phase extraction with PLRP-s sorbent and ion-pair liquid-chromatography using fast-scanning fluorescence spectrometer as a detection system and multivariate calibration. As complete separation is unnecessary, the compounds were analysed in isocratic conditions and the chromatographic analysis took only 25 min. Three-way partial least-squares (PLS) was used to carry out multivariate calibration for spiked tap water. In these conditions, quantification limits were between 0.01 and 3 $\mu g\ l^{-1}$. Repeatability was also evaluated and relative standard deviations ($n=3$) were between 0.5 and 4, depending on the compound. Finally, spiked tap and Ebro river waters were analysed to evaluate prediction capability of the method.

Keywords: Water analysis; Solid-phase extraction; Partial least squares calibration; Fast scanning fluorescence detection; Detection, LC; Naphthalenesulfonates

1. Introduction

Naphthalenesulfonates and their amino- and hydroxy-derivatives are widely used in the pharmaceutical and textile industries [1]. But these compounds are not easily eliminated from water by conventional methods and can occur in water that may be used as drinking water [2,3]. Their low biodegradability [4,5] makes them potentially hazardous and an efficient analytical system is therefore required to control their presence in water.

Gas chromatography analysis with a process of derivatization to increase the volatility of analytes may be used [1,4], but liquid chromatography [2–4] or capillary electrophoresis [6–10] are preferred. The limitation of capillary electrophoresis is the low sensitivity [9,10] although for naphthalenesulfonates good results have been obtained using a ultraviolet laser-induced fluorescence detection [7,8]. But, at present, liquid chromatography is still the preferred technique. Due to the high polarity of naphthalenesulfonates with amino- and hydroxy-functional groups, the most frequently used technique is ion-pair liquid chromatography [2–4,11–13], although analysis with ion-exchange liquid chromatography is also described [1,14].

UV or DAD is used as the detection system [12,13], although recently mass-spectrometry detec-

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tion has also been applied with interesting results [15,16]. However, the fluorescence detector is still preferred for aromatic sulfonates because of the higher sensitivity than UV detection and simpler instrumentation than mass spectrometry [2–4,11]. Recently, the fast-scanning fluorescence spectrometer (FSFS) has been developed, which records spectra of the effluent from the chromatographic system at a fixed excitation wavelength by scanning emission wavelength at a high rate [17,18]. In this case, coeluted analytes can be quantified by different emission wavelengths, deconvolution methods or multivariate calibration. Complete separation of chromatographic peaks is therefore not necessary and analysis time considerably decreases.

Since low concentrations of naphthalenesulfonates had to be detected and quantified, a preliminary enrichment step is required. The most frequently used preconcentration technique for determining aromatic sulfonates in water is ion-pair solid-phase extraction (SPE) using C_{18} or polymeric sorbents [11–13,15,16].

The aim of this paper is to develop a fast method for determining 12 naphthalenesulfonates and naphthalenedisulfonates with amino- and hydroxy-functional groups in tap and river waters. For this purpose, an on-line ion-pair solid-phase extraction and ion-pair liquid chromatography were used and, in order to quantify overlapped peaks and decrease the analysis time, a fast-scanning fluorescence spectrometer was used and a three-way PLS was chosen for multivariate calibration.

2. Experimental

2.1. Reagents and standards

All the compounds studied were obtained as free acids or sodium salts from Fluka (Buchs, Switzerland), Aldrich Chemie (Beerse, Belgium) or Across (Geel, Belgium). Standard solutions of each compound in a concentration of 1000 mg l^{-1} were prepared in Milli-Q quality water. To increase solubility of some compounds, several drops of sodium hydroxide 0.1 N were added, except for naphthalene-2-sulfonate, which was solubilized in Milli-Q water–methanol (Merck, Germany; 85:15, v/v). From these solutions, mixtures of compounds in different concentrations were prepared to perform the calibration.

Disodium hydrogen phosphate (Panreac, Barcelona, Spain), sodium dihydrogen phosphate (Probus, Badalona, Spain), phosphoric acid 85% (Probus, Badalona, Spain), tetrabutylammonium bromide (Fluka, Buchs, Switzerland) and methanol (Merck, Germany) were used to prepare mobile phase and samples.

2.2. Apparatus

The chromatographic system consisted of a System 525 pump (Bio-Tek Kontron Instruments) and a 25-μl injection loop. The chromatographic column was a 15.0×0.4-cm Kromasil 100 C_{18} with a 5-μm particle size (Teknokroma, Barcelona, Spain).

The detection system was an Aminco Bowman Series 2 spectrofluorimeter (SLM-Aminco, Rochester, NY, USA), equipped with a 25-μl flow cell (Hellma 176.752, Baden, Germany).

Extraction was carried out with a 10×3-mm precolumn packed with 20 μm PLRP-s (Polymer Laboratories, Shropshire, UK). This precolumn was on-line coupled to the chromatographic system by a Reodyne 7010 valve.

An Applied Biosystems (Ramsey, USA) pump was used to preconcentrate samples through the extraction precolumn.

2.3. Experimental conditions

2.3.1. Chromatographic separation

Chromatographic separation was performed in isocratic conditions. The mobile phase was 35% methanol and 65% aqueous phase, which contained 6.9 m*M* of a disodium hydrogen phosphate–sodium dihydrogen phosphate buffer and 4.6 m*M* of tetrabutylammonium bromide. The pH of the aqueous phase was adjusted to 6.5 with phosphoric acid and filtered through a 0.45-μm membrane filter. The mobile phase was degassed with a stream of helium. Analysis was performed at room temperature. The mobile phase flow-rate was 1 ml min^{-1}.

2.3.2. Detection

With fast-scanning fluorescence detection, two different excitation wavelengths were used: 293 nm

for compounds 1–8 and 308 nm for compounds 9–12. The emission wavelengths were scanned from 350 to 450 nm at 50 nm s^{-1} and readings were taken every 1 nm. In this way, one spectrum was recorded every 2.7 s (the time required by the monochromator to return to the initial position is included).

Data were obtained in a flow cell, so every spectral point corresponds to a different composition of chromatographic eluent. Moreover, a fluorescent blank (due to the mobile phase and the flow cell) and a background noise caused by the low integration time in the fast-scanning system are added to the fluorescence of the analytes. Our data therefore had to be corrected [17]. The rectification process was as follows: blank was first subtracted from the initial chromatogram; the fluorescent intensities were then corrected by spline interpolation to obtain the spectra at a fixed time; finally, the resulting spectra were smoothed out to minimise background noise [17]. This process was carried out using a computer program written in MATLAB language (Mathworks, Natick, MA, USA).

2.3.3. Solid-phase extraction

Tetrabutylammonium bromide was added to samples at a concentration of 3 m*M* as the ion-pairing reagent. Disodium hydrogen phosphate–sodium dihydrogen phosphate buffer was also added at a concentration of 2.5 m*M* to ensure that the pH of the samples were appropriate for ion-pair formation [12].

The process of on-line solid-phase extraction was as follows: the precolumn was washed with 8 ml of methanol at 4 ml min^{-1}; the position of the valve was then changed and the precolumn was conditioned by mobile phase; the position of valve was then changed again and 20 ml of sample was preconcentrated at 4 ml min^{-1}; finally, the retained analytes were eluted in backflush mode and injected into the chromatographic column by mobile phase.

3. Results and discussion

Because the characteristics of the compounds are very similar, the gradient for acceptable separation of the naphthalenesulfonates has to have a gentle slope and the analysis usually took 1 h [12]. A fast-scanning fluorescence spectrometer was used as a detection system because this can measure coeluted analytes and complete separation is therefore not necessary. An isocratic analysis was selected because of the simpler instrumentation and blank subtraction. For this purpose, a partial separation of the compounds was optimised, taking into account that at least 10 spectra had to be acquired for every chromatographic peak [17], and 35% methanol was selected. In this way, the analysis took less than 25 min, although the 10 first eluted peaks were eluted in only 10 min (see Fig. 1).

Different mixtures of the compounds were injected to determine linear range. The lower limit of this range was obtained from quantification limit, calculated as 10 times the standard deviation of the noise of a blank chromatogram, and the upper limit was taken from the maximum quantity of analyte that can be read before the detector is saturated.

For the SPE process, the preconcentration volume was checked for tap and river water using PLRP-s as a sorbent. From previous work [12] and additional experiments, 20 ml of sample was preconcentrated. Results are shown in Table 1. Recoveries for the first eluted compounds are lower because of the polarity, but they are slightly greater than with other sorbents like C_{18} for most compounds [2,11]. This table also shows the linear ranges obtained for each compound,

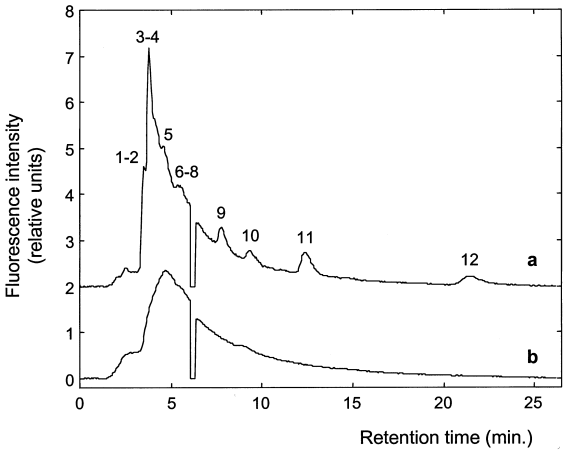

Fig. 1. (a) Profile plot of spiked Ebro river water obtained with fast-scanning fluorescence spectrometer. Concentration (μg l^{-1}): 0.1 (compounds 3, 4, 7, 9), 0.3 (compounds 1, 5, 6, 10), 0.8 (compound 8), 3 (compounds 2, 11) and 6 (compound 12). For peak identification, see Table 1. (b) Profile plot of unspiked Ebro river water.

Table 1
Recoveries (%) and %RSD when 20 ml of tap and Ebro river waters are preconcentrated ($n=3$) and linear ranges in tap water

No.	Compound	Tap water			River water	
		Linear range ($\mu g\ l^{-1}$)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
1	6-Amino-4-hydroxy-2-naphthalenesulfonate	0.07–1.50	54	7	62	6
2	5-Amino-1-naphthalenesulfonate	0.3–15.0	56	1	54	3
3	7-Amino-4-hydroxy-2-naphthalenesulfonate	0.01–0.30	54	3	66	7
4	4-Amino-1-naphthalenesulfonate	0.01–0.50	58	1	66	2
5	Naphthalene-2,6-disulfonate	0.2–0.5	84	1	74	16
6	5-Amino-2-naphthalenesulfonate	0.07–1.50	76	2	50	4
7	Naphthalene-1,5-disulfonate	0.07–0.50	85	1	69	6
8	Naphthalene-2,7-disulfonate	0.3–4.0	88	2	87	4
9	4-Hydroxy-1-naphthalenesulfonate	0.07–0.10	86	1	82	14
10	8-Amino-2-naphthalenesulfonate	0.07–1.50	92	7	76	4
11	2-Amino-1-naphthalenesulfonate	0.3–15.0	90	3	83	3
12	2-Naphthalenesulfonate	3–15	88	1	102	17

which were determined by preconcentrating different samples containing non-overlapped peaks. We can see that the quantification limits were low and a few ng l^{-1} in some cases could be quantified. These limits are lower than those obtained by UV detection [12] and quite similar to those obtained by mass spectrometry [15] at the same extraction conditions.

For calibration, eight tap water samples spiked at different concentrations of compounds were analysed. These concentrations were chosen in such a manner that all the linear range for each compound was included and different ratios of concentration were used. The three-way PLS was chosen as the multivariate calibration method [19]. The optimum model was built with the minimum number of factors that give an error of prediction which is not significantly different from the minimum. This error was calculated by a leave-one-out cross-validation procedure. The number of factors for every compound and the relative error in each case are shown in Table 2. For most compounds, this error is small enough, if we take into account that the concentrations are low.

Three tap water samples were analysed to evaluate repeatability and the results, expressed in %RSD, were between 0.5 and 4, depending on the compound.

For checking the prediction capability of the method, three tap water samples spiked with naphthalenesulfonates were analysed. The comparison of real and predicted concentrations is included in Table 3. The values are very similar and errors are accept-

Table 2
Parameters of three-way PLS calibration

No.	Compound	No. of factors	Relative error of calibration (%)
1	6-Amino-4-hydroxy-2-naphthalenesulfonate	3	9
2	5-Amino-1-naphthalenesulfonate	6	10
3	7-Amino-4-hydroxy-2-naphthalenesulfonate	3	55
4	4-Amino-1-naphthalenesulfonate	5	27
5	Naphthalene-2,6-disulfonate	4	15
6	5-Amino-2-naphthalenesulfonate	5	15
7	Naphthalene-1,5-disulfonate	6	32
8	Naphthalene-2,7-disulfonate	3	10
9	4-Hydroxy-1-naphthalenesulfonate	3	3
10	8-Amino-2-naphthalenesulfonate	2	9
11	2-Amino-1-naphthalenesulfonate	2	10
12	2-Naphthalenesulfonate	2	19

Table 3
Real and predicted concentrations in tap and Ebro river waters for $n=3$

No.	Compound	Real concentration ($\mu g\ l^{-1}$)	Predicted concentration ($\mu g\ l^{-1}$)	
			Tap water	Ebro river water
1	6-Amino-4-hydroxy-2-naphthalenesulfonate	0.3	0.24±0.04	0.36±0.05
2	5-Amino-1-naphthalenesulfonate	3	2.9±0.1	4.5±0.5
3	7-Amino-4-hydroxy-2-naphthalenesulfonate	0.1	0.14±0.04	0.21±0.06
4	4-Amino-1-naphthalenesulfonate	0.1	0.08±0.01	0.17±0.02
5	Naphthalene-2,6-disulfonate	0.3	0.23±0.01	0.09±0.02
6	5-Amino-2-naphthalenesulfonate	0.3	0.23±0.04	0.45±0.03
7	Naphthalene-1,5-disulfonate	0.1	0.16±0.11	0.13±0.01
8	Naphthalene-2,7-disulfonate	0.75	0.70±0.04	1.32±0.05
9	4-Hydroxy-1-naphthalenesulfonate	0.1	0.08±0.01	0.16±0.01
10	8-Amino-2-naphthalenesulfonate	0.3	0.31±0.07	0.58±0.01
11	2-Amino-1-naphthalenesulfonate	3	1.5±0.5	2.3±0.1
12	2-Naphthalenesulfonate	6	5.2±1.6	7.7±0.1

able taking into account the low levels of concentration. So, the method enabled low levels of naphthalenesulfonates to be quantified in a short time and with an isocratic elution.

The calibration model was also tested for river water sample in order to check if it can be applied to this kind of samples. Three spiked river water samples were analysed at the same levels than in tap water and results are shown in Table 3. Results are not so good as for tap water which may be due to the differences in sample matrix and the possible interference of humic and fulvic acids,

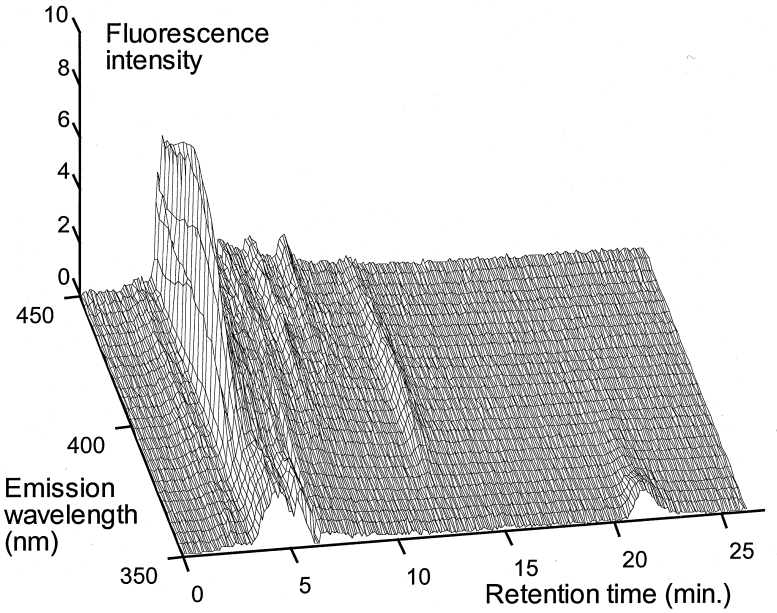

Fig. 2. Chromatogram of spiked Ebro river water obtained with fast-scanning fluorescence spectrometer. For concentration of compounds, see Fig. 1.

which may be significant when river water is analysed. However, for a fast control of the presence of these compounds the method may also be suitable. As an example of spiked Ebro river water analysis, a profile plot including the blank signal is shown in Fig. 1, where the partial separation of the compounds can be seen and a three-dimensional chromatogram obtained using the fast-scanning fluorescence spectrometer for a spiked Ebro river water is shown in Fig. 2.

4. Conclusions

An analytical method consisting of on-line ion-pair solid-phase extraction with PLRP-s sorbent and ion-pair liquid-chromatography with a fast-scanning fluorescence spectrometer has been developed for quantifying a mixture of 12 naphthalenesulfonates and naphthalenedisulfonates using a three-way PLS to perform multivariate calibration. The method is simple because an isocratic elution is used and fast since a reduction in analysis time from 1 h to about 25 min has been achieved, since complete separation of analytes is not needed. In these conditions, a concentration of 0.01–3 $\mu g\ l^{-1}$, depending on the compound, can be quantified in tap water with good repeatability.

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