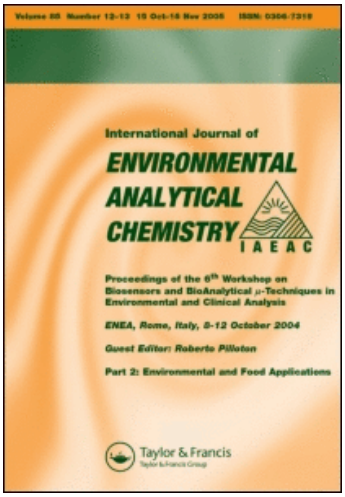

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of Naphthalenesul-Phonates in Water by On-Line Ion-Pair Solid-Phase Extraction and Ion-Pair Liquid Chromatography with Diode-Array UV Detection

R. El Harrak[a]; M. Calull[a]; R. M. Marcé[a]; F. Borrull[a]
[a] Departament de Química, Area de Química Analítica. Universitat Rovira i Virgili, Imperial Tarraco, Tarragona, Spain

To cite this Article Harrak, R. El , Calull, M. , Marcé, R. M. and Borrull, F.(1998) 'Determination of Naphthalenesul-Phonates in Water by On-Line Ion-Pair Solid-Phase Extraction and Ion-Pair Liquid Chromatography with Diode-Array UV Detection', International Journal of Environmental Analytical Chemistry, 69: 4, 295 — 305
To link to this Article: DOI: 10.1080/03067319808032595
URL: http://dx.doi.org/10.1080/03067319808032595

Intern. J. Environ. Anal. Chem., Vol. 69(4), pp. 295–305
Reprints available directly from the publisher
Photocopying permitted by license only

DETERMINATION OF NAPHTHALENESULPHONATES IN WATER BY ON-LINE ION-PAIR SOLID-PHASE EXTRACTION AND ION-PAIR LIQUID CHROMATOGRAPHY WITH DIODE-ARRAY UV DETECTION

R. El HARRAK, M. CALULL, R. M. MARCÉ and F. BORRULL*

Departament de Química. Area de Química Analítica. Universitat Rovira i Virgili. Imperial Tarraco. 43005 Tarragona. Spain

(Received 20 March 1997; In final form 20 May 1997)

Ion-pair solid-phase extraction was on-line coupled to a chromatographic system with a PLRP-s precolumn and the results were compared with those obtained when C_{18} sorbents are used. After optimization, the method was used to determine these compounds in two river waters. A sample of 20 ml of river water was preconcentrated with good recovery values for all the compounds studied and detected at 220 nm with detection limits between 0.25 and 0.1 $\mu g\ l^{-1}$. Some of the compounds were provisionally determined by diode-array UV detection.

Keywords: Naphthalenesulphonates; high-performance liquid chromatography; on-line solid phase extraction; river water

INTRODUCTION

Aromatic sulphonates with and without hydroxy, sulfo and amino substituents are widely used in the chemical industry as starting or intermediate material for many purposes, especially in the production of pharmaceuticals, dyes, pesticides and so on.

The low biodegradability of some sulphonic acids, especially the naphthalenesulphonates with nitro and amino groups means that these compounds are present in environmental waters. Moreover, since these waters are often used for drinking water and some sulphonates can only be removed by means of fre-

*Corresponding author. Fax: +34-77-559563. E-mail: borrull@quimica.urv.es

quently regenerated activated carbon,[1] the presence of these xenobiontic compounds should be controlled.[2]

Due to their high polarity and low vapor pressure, naphthalenesulphonates have to be derivatized before GC analysis,[3,4] and so the drawback of these methods is that they are time consuming because they need both concentration and derivatization steps. Capillary electrophoresis has also been applied to these compounds, and both capillary zone electrophoresis[5] and micellar electrokinetic chromatography[6] have been tested. However, liquid chromatographic methods are highly suitable for the separation of naphthalenesulphonates and have been described by several authors.[7–10] The most generally used approach is ion-pair chromatography[9–12] although ion exchange chromatography has also been used.[8,9] Fluorimetric detection[1,2,9,12] and DAD detection[9–11] are the most often used, but the mass spectrometric (MS) systems may also be used and particle beam-MS has been shown[8] to be suitable for determining these compounds, in particular for mono-sulphonic acids.

In environmental waters an enrichment step is required to determine real-life concentrations of some naphthalenesulphonates which are normally at low levels. At present, off-line ion-pair solid-phase extraction has been reported for selected aromatic sulfonates using a wide variety of sorbents such as ion-exchange,[12] C_8 and C_{18}[9,12] or graphitized carbon black.[11] On-line solid-phase extraction has also been described for determining naphthalenesulphonates, mainly using C_{18} sorbent[1,2] and PLRP-S has also been used for aromatic sulfonic acids although only one of these was a naphthalenesulphonic acid.[10]

The aim of the present paper is to compare the use of PLRP-s and C_{18} in on-line solid-phase extraction coupled to ion-pair chromatography and a diode array detector for determining naphthalenesulphonates in water. After studying different variables that affect the separation and the preconcentration step, the method was used to determine these compounds in all water types.

EXPERIMENTAL

Apparatus

Chromatographic experiments were performed using a Hewlett-Packard (Waldbronn, Germany) Model 1090 ternary gradient liquid chromatograph with an HP 1040M diode-array detector. The system was controlled by an HP 7999A workstation which also acquired data from DAD. Separation was carried out using a Spherisorb ODS-2 column (250 × 4.6 mm I.D.) with a particle size of 5-μm. A loop of 100 μl was used to directly inject the sample.

Reagents

The naphthalenesulfonate compounds studied were the following: (1) 6-amino-4-hydroxynaphthalene-2-sulphonate, (2) 6-amino-1-hydroxynaphthalene-3-sulphonate, (3) 5-aminonaphthalene-2-sulphonate, (4) 8-amino-1-hydroxynaphthalene-3,6-disulphonate, (5) naphthalene-2,6-disulphonate, (6) naphthalene-1,5-disulphonate, (7) 1-hydroxynaphthalene-3,6-disulphonate, (8) 2-hydroxynaphthalene-3,6-disulphonate, (9) 2-aminonaphthalene-1-sulphonate, (10) naphthalene-1-sulphonate and (11) naphthalene-2-sulphonate. They were all obtained from Aldrich Chemie (Beerse, Belgium) or Fluka (Buchs, Switzerland). A standard solution of 1000 mg l^{-1} of each compound was prepared in Milli-Q water and stored in a refrigerator. In some cases, several drops of 1M sodium hydroxide were added to enhance the solubility. More diluted solutions were prepared daily.

Acetonitrile (Scharlau, Barcelona, Spain) and Milli-Q quality water were used as the mobile phase solvent. Disodium hydrogen phosphate and sodium dihydrogen phosphate (Merck, Germany) were used to adjust the pH of the mobile phase and tetrabutylammonium bromide was used as the ion pair reagent, (Aldrich Chemie, Beerse, Belgium).

Chromatographic Conditions

The chromatographic separation was carried out using a gradient with three solvents: a 15 mM solution of TBA as solvent A, a buffer solution of disodium hydrogen phosphate and sodium dihydrogen phosphate adjusted to pH 6.5 as solvent B and acetonitrile as solvent C. The percentatge of solvent A was kept constant at 20% so that the concentration of ion-pair reagent during the chromatographic separation stayed the same. Initial conditions were 80% of B, then a linear gradient until 5% of C at minute 5 and finally another linear gradient until minute 50 to finish with 20% of C. Separation was carried out at 40°C and detection at 220 nm, but the spectrum of each compound was recorded between 200 and 400 nm.

On-line Solid-phase Extraction Process

The trace-enrichment process was performed using a six-port injection valve (Rheodyne) with a stainless-steel precolumn (10 × 2 mm I.D.) (Free University, Amsterdam, The Netherlands) packed with 10 μm Spherisorb ODS-2 or with 15–25 μm PLRP-s both of which were purchased from Teknokroma (Barcelona,

Spain). A M45 Waters pump (Mildford, MA, USA) was used to deliver the aqueous sample (2 ml min^{-1}).

The method used in the on-line solid-phase extraction process was the following: the precolumn was washed with methanol (2.5 minutes) and the mobile phase in the initial conditions (2.5 minutes), and then, while the mobile phase was conditioning the column in the initial conditions, the sample was preconcentrated in the precolumn after the ion-pair reagent had been added and the pH value adjusted. Afterwards, the compounds were eluted and analysed.

RESULTS AND DISCUSSION

In the first step, the different variables which affect the resolution of the chromatographic separation of the eleven compounds studied were optimized. These variables were pH, TBA concentration and temperature. The pH was optimized because different values have been reported in literature. To carry out this study, a standard solution of 10 mg l^{-1} of each compound, with different pH values of the mobile phase, was injected. When the pH was increased (4 to 7) the retention time for all compounds decreased slightly, but no important changes in resolution were observed. There was only one change in the elution order between 2-aminonaphthalene-1-sulphonate and naphthalene-1-sulphonate peaks. In this study, 6.5 was chosen as the optimum value because the resolution was similar to the resolution at pH 5 but had a shorter analysis time.

The concentration of TBA as ion-pair reagent was the other variable studied. The same standard solution was analyzed at several TBA concentrations between 5 and 20 mM. There was an increase in the retention time and a change in the elution order for one of compounds when the concentration was increased. The best conditions were at 15 mM with good resolution between peaks and reasonable analysis time.

Temperature was the last variable studied. There was a slight decrease in the retention time for all the compounds studied between 35 and 50°C. The temperature chosen was 40°C because at 50°C several peaks were seen to overlap.

At optimum conditions (pH values of 6.5, 15 mM of TBA and 40°C) the eleven naphthalene sulphonate compounds were analysed with the above mentioned gradient elution. Figure 1 shows the chromatogram obtained when 100 μl of a standard solution of 10 mg l^{-1} of each compound was injected. Good resolution was obtained for all compounds in an analysis time of less than 50 minutes. Good linearity was obtained for all compounds between 0.5 and 10 mg l^{-1} and the correlation coefficients (r^2) were higher than the 0.994 obtained

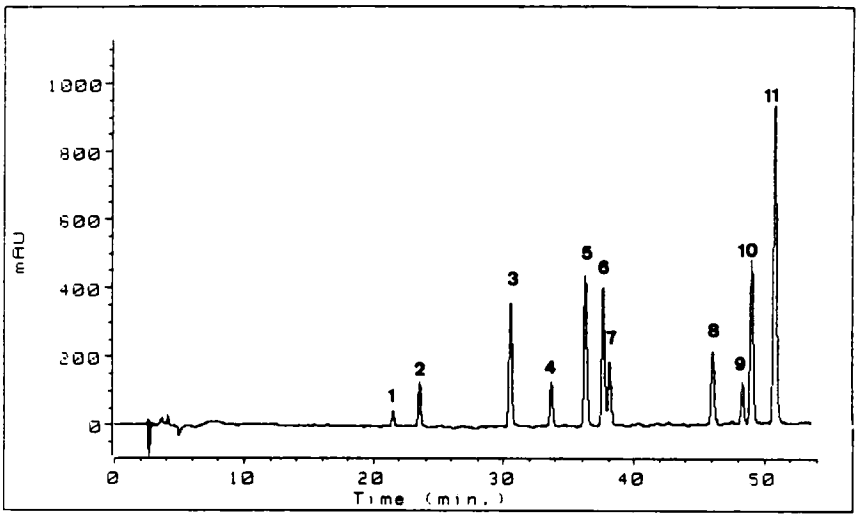

FIGURE 1 Chromatogram of the standard solution of 10 mg l^{-1} in optimum conditions. (1) 6-amino-4-hydroxynaphthalene-2-sulphonate, (2) 6-amino-1-hydroxynaphthalene-3-sulphonate, (3) 5-aminonaphthalene-2-sulphonate, (4) 8-amino-1-hydroxynaphthalene-3,6-disulphonate, (5) naphthalene-2,6-disulphonate, (6) naphthalene-1,5-disulphonate, (7) 1-hydroxynaphthalene-3,6-disulphonate, (8) 2-hydroxynaphthalene-3,6-disulphonate, (9) 2-aminonaphthalene-1-sulphonate, (10) naphthalene-1-sulphonate and (11) naphthalene-2-sulphonate. For other conditions see text.

for 2-hydroxynaphthalene-3,6-disulphonate. The limits of detection of the direct method using a signal to noise ratio of 3 were between 50 and 100 $\mu g\ l^{-1}$.

To decrease the detection limits of the method, the solid-phase extraction process was coupled on-line with the chromatographic system. C_{18} is the sorbent which is most often used to concentrate naphthalene sulphonate compounds in water, but low recoveries (low breakthrough volumes) were obtained for some of the more polar compounds, such as amino-hydroxyderivatives.[1] In this work, the PLRP-s sorbent was tested and compared with C_{18} in order to increase the volume of the concentrate sample and decrease the detection limits of the method.

Firstly, the pH and the TBA concentration of the sample were optimized to obtain the best results in the concentration step. Ranges between 5.5 and 7 for the C_{18} precolumn and 6 and 9 for the polymeric sorbent PLRP-s precolumn were tested. Figures 2a and 2b show the recovery values for 10 ml of standard solution of 50 $\mu g\ l^{-1}$ with 3 mM of TBA and adjusted to the different pH values for C_{18} and PLRP-s respectively. The best results were obtained at pH 7 using PLRP-s as the sorbent, with recovery values higher than 85% for all compounds. On the other hand, no big differences were obtained for any of the compounds when C_{18} was used as the sorbent at pH values between 5.5 and 7,

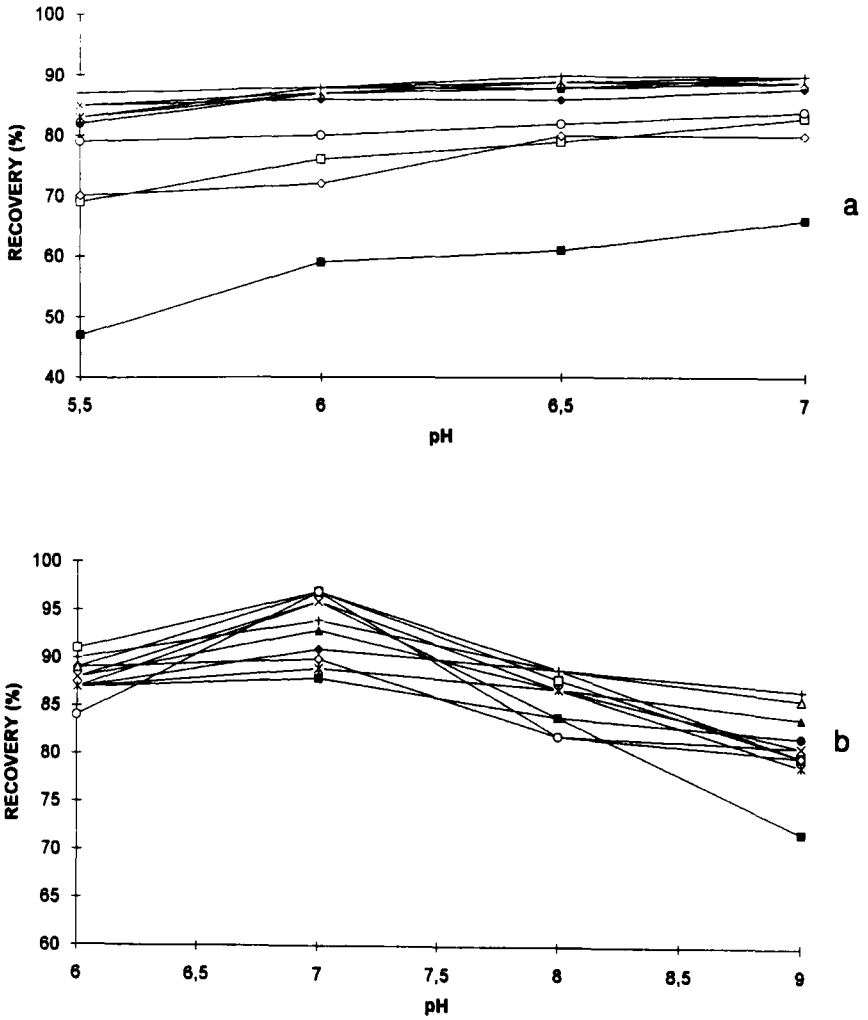

FIGURE 2 Determination of the recovery value versus pH value in the solid-phase extraction process of standard solution of 50 $\mu g\ l^{-1}$ with 3 mM TBA concentration. Peak assignation (□) 6-amino-4-hydroxynaphthalene-2-sulphonate, (■) 6-amino-1-hydroxynaphthalene-3-sulphonate, (♦) 5-aminonaphthalene-2-sulphonate, (◇) 8-amino-1-hydroxy-naphthalene-3,6-disulphonate, (▲) naphthalene-2,6-disulphonate, (△) naphthalene-1,5-disulphonate, (●) 1-hydroxynaphthalene-3,6-disulphonate, (○) 2-hydroxynaphthalene-3,6-disulphonate, (×) 2-aminonaphthalene-1-sulphonate, (*) naphthalene-1-sulphonate and (+) naphthalene-2-sulphonate.

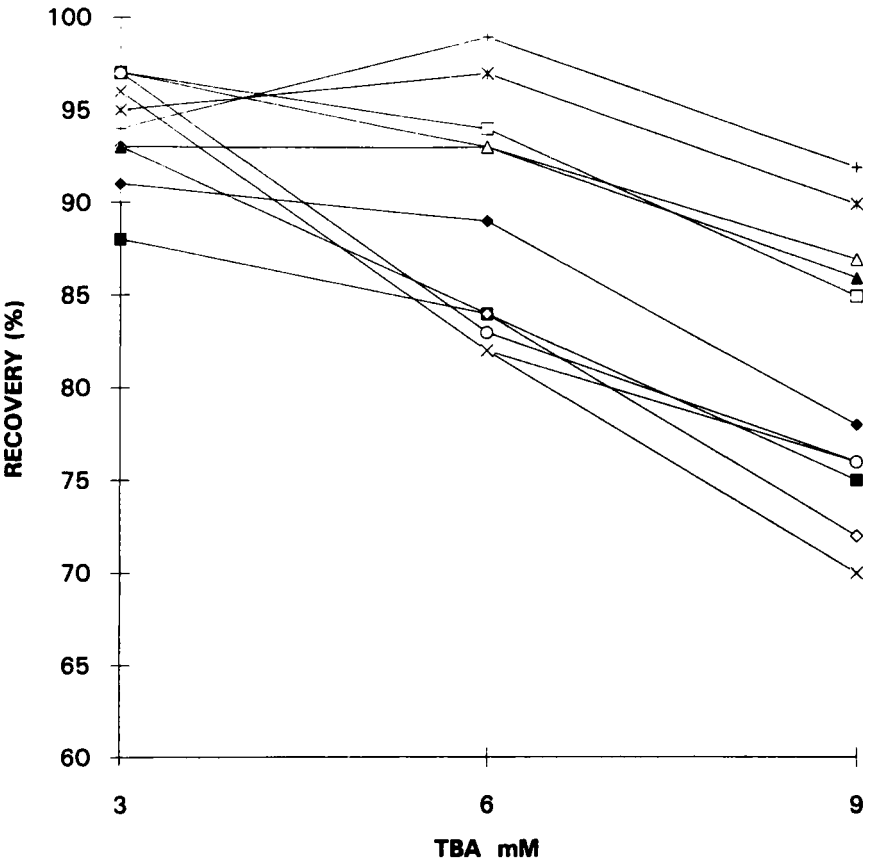

FIGURE 3 Study of the variation in recovery value versus TBA concentration in the solid-phase extraction process. For conditions and peak assignation see Figure 2.

but all recovery values were lower than the ones obtained using the other sorbent. Low recovery values were also obtained for the more polar compounds such as 6-amino-4-hydroxynaphthalene-2-sulphonate.

The modification of the TBA concentration between 3 and 9 mM was also studied. An increase in this concentration did not give better recovery values for any of the compounds which were to be obtained, and so a concentration of 3 mM was chosen to carry out the experiments. The results obtained can be see in Figure 3.

In these conditions, the breakthrough volumes of both sorbents were determined using a standard solution of 10 $\mu g\ l^{-1}$. Table I shows the recovery values obtained and it can be seen that the best results were obtained for PLRP-s. With

TABLE I Determination of the recovery value versus volume of sample preconcentrated using C18 and PLRP-s with a standard solution of 10 μg l^{-1}. RSD values are the mean of four determinations.

	10 ml				*20 ml*				*50 ml*				*100 ml*			
	C_{18}		*PLRP-s*		C_{18}		*PLRP-s*		C_{18}		*PLRP-s*		C_{18}		*PLRP-s*	
Comp.	*R(%)*	*RSD (%)*	*R(%)*	*RSD (%)*	*R(%)*	*RSD (%)*	*R(%)*	*RSD (%)*	*R(%)*	*RSD (%)*	*R(%)*	*RSD (%)*	*R(%)*	*RSD (%)*	*R(%)*	*RSD (%)*
1	68	5.4	92	1.5	52	8.7	88	3.4	14	12.8	75	4.2	n.d.	–	60	5.5
2	65	4.8	90	1.3	54	8.3	85	2.2	16	10.4	70	3.7	n.d.	–	62	4.3
3	75	5.2	95	2.7	60	6.2	88	2.5	22	9.2	80	3.2	n.d.	–	74	3.8
4	80	3.6	91	3.2	74	2.3	82	2.1	39	7.2	75	2.3	15	7.9	69	4.4
5	88	2.8	91	2.8	79	2.8	86	2.8	57	5.8	83	3.5	23	8.5	75	4.7
6	86	1.5	90	1.8	77	2.5	87	3.5	49	4.2	82	2.4	33	9.3	78	3.8
7	93	3.4	89	2.5	80	3.5	86	2.6	68	5.7	82	2.6	23	10.5	75	3.2
8	82	2.6	90	3.3	75	4.1	87	3.5	50	6.3	83	4.2	13	6.3	79	3.5
9	94	2.5	89	3.7	83	3.9	87	2.5	45	4.7	82	3.7	32	8.4	75	2.8
10	90	3.8	97	2.6	82	4.5	92	3.8	48	3.6	85	2.8	30	5.2	77	3.6
11	92	4.1	98	3.8	84	4.8	95	3.7	50	5.2	87	3.8	33	8.0	80	4.5

n.d. Not detected.

TABLE II Determination of the recovery value with Francolí river water using a standard solution of 50 $\mu g\ l^{-1}$ of the studied compounds. RSD values are the mean of four determinations.

Compound	*Sample volume (ml)*					
	20 ml		*50 ml*		*100 ml*	
	Recovery (%)	*RSD (%)*	*Recovery (%)*	*RSD (%)*	*Recovery (%)*	*RSD (%)*
1	64	4.5	55	4.7	20	6.5
2	60	4.4	54	4.8	26	5.8
3	92	4.4	68	3.8	25	4.9
4	62	3.9	54	3.5	22	5.2
5	97	4.1	73	4.5	20	6.7
6	98	4.1	81	5.1	25	5.1
7	95	3.5	80	3.9	22	5.5
8	98	4.7	85	5.1	35	4.9
9	85	3.8	84	4.8	65	4.5
10	96	4.2	88	4.5	75	5.1
11	110	4.5	102	4.9	90	5.8

100 ml of sample recovery values were higher than 70%, except for the first two compounds. An RSD (n = 4) lower than 10% was obtained except when the recovery value was low. In these conditions, the linearity was studied between 0.5 and 10 $\mu g\ l^{-1}$ with a correlation factor (r^2) higher than 0.994. Detection limits were established according to a signal-noise ratio of 3 with values between 0.25 and 0.1 $\mu g\ l^{-1}$.

The matrix has a considerable influence on the recovery of the solid-phase extraction procedure when river water is analyzed. For this reason the breakthrough volume was determined in Francolí river water. Table II shows the recovery values obtained when Francolí river water spiked with a standard solution of 10 $\mu g\ l^{-1}$ of each compound was analysed. It can be seen that only 20 ml of sample can be analyzed with recovery values higher than 90%, except compounds 1, 2 and 4, for which the recovery value was nearly 60%. In all cases, the RSD (n = 4) was lower than 7%. In these conditions, good correlation coefficients between 2.5 and 50 $\mu g\ l^{-1}$ were obtained in the study of the linearity with detection limits between 2 and 0.5 $\mu g\ l^{-1}$.

The method was used to determine these compounds in two surface water, Francolí and Ebro river water. River water taken from the Francolí near an industrial zone was analysed first. Figures 4a and 4b show chromatograms of 20 ml of sample (4a) and the same sample spiked with a standard solution of 50 $\mu g\ l^{-1}$ of the compounds studied (4b). They were both filtered through a 0.45 μm filter after adding TBA to a final concentration of 3 mM and adjusting the pH to 7. In this case, several peaks appeared in the chromatogram and two of them had the same retention time as the compounds studied. The spectra were compared with the ones obtained from the standard solutions but naphthalene-

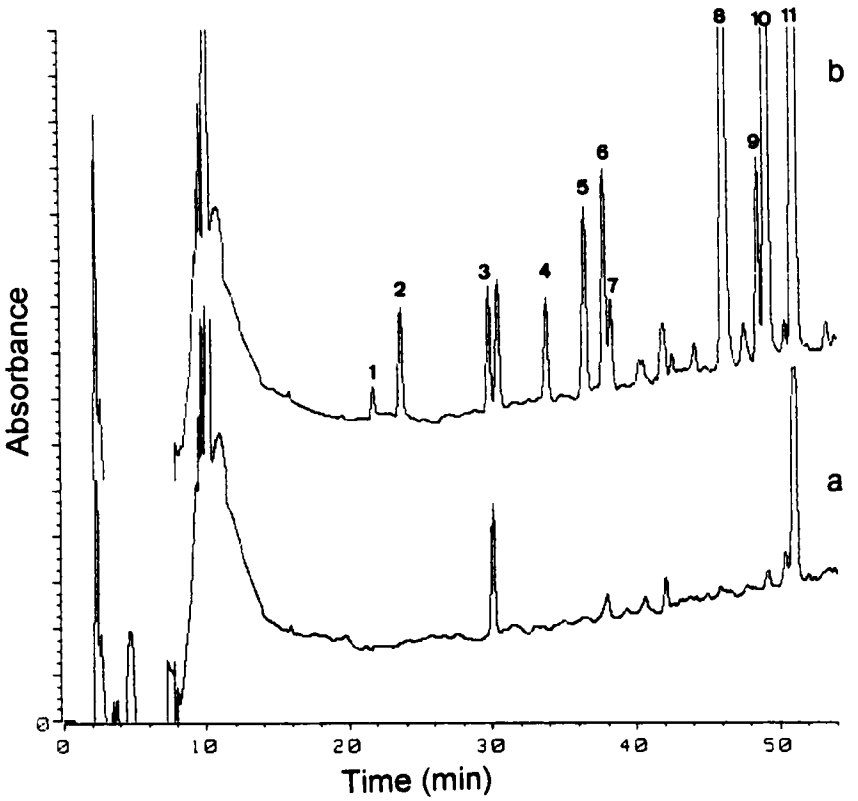

FIGURE 4 Analysis of Francolí river water. A) Chromatogram of 20 ml of Francolí river water. B) Chromatogram of the same sample spiked with a standard solution of 50 $\mu g\ l^{-1}$. For peak assignation see Figure 1.

1-sulphonate and naphthalene-2-sulphonate could not be positively identified. The match factors were 886 and 936 respectively. The Ebro river water was treated in the same way as above. In this case, a peak with the same retention time as naphthalene-2-sulfonate can be observed. It was positively identified by comparing its spectrum to the library spectrum which had been obtained from standard solutions. The match factor was 993 and the concentration was 4 $\mu g\ l^{-1}$.

CONCLUSIONS

This comparative study of PLRP-s and C_{18}, which are both used in the on-line solid-phase extraction for determining naphthalenesulphonates in surface water, confirms that polymeric sorbents give better results. In optimum conditions, the

method enables 100 ml of standard solution to be preconcentrated with Milli-Q water without considerable compounds losses. There was a considerable decrease in the breakthrough volume when surface water was preconcentrated and in this case only 20 ml of sample could be concentrated with no compounds loss.

In these conditions the method enables the compounds to be detected at low $\mu g\ l^{-1}$ levels. The method has been used to detect these compounds in two rivers in the Tarragona region, and in one of them, naphthalene-2-sulfonate was positively identified by comparing the DAD spectra.

Acknowledgements

The authors would like to thank the "Direcció General de Recerca de la Generalitat de Catalunya" for supporting this study.

References

[1] F. Th. Lange, M. Wenz and H. J. Brauch, *J. High Resol. Chromatogr.*, **18**, 243–252 (1995).
[2] S. Fichtner, F. Th. Lange, W. Schmidt and H. J. Brauch, *Fresenius J. Anal. Chem.*, **353**, 57–63 (1995).
[3] H. Kataoka, T. Okazaki and M. Makita, *J. Chromatogr.*, **473**, 276–283 (1989).
[4] M. L. Trehy, W. E. Gledhill and R. G. Orth, *Anal. Chem.*, **62**, 2581–2585 (1990).
[5] S. J. Kok, E. H. M. Koster, C. Gooijer, N. H. Velhorst, U. A. Th. Brinkman and O. Zerbinati, *J. High Resol. Chromatogr.*, **19**, 99–104 (1996).
[6] H. Harino, M. Tanaka, T. Araki, Y. Yasaka, A. Masuyama, Y. Nakatsuji, I. Ikeda, K. Fuzano and S. Terabe, *J. Chromatogr. A*, **715**, 135–141 (1995).
[7] B. Bastian, T. P. Knepper, P. Hoffman and H. M. Ortener, *Fresenius. J. Anal. Chem.*, **348**, 674–679 (1994).
[8] I. S. Kim, F. I. Sasinos, D. K. Rishi, R. D. Stephens and M. A. Brown, *J. Chromatogr.*, **589**, 177–183 (1992).
[9] S. Schullerer and F. H. Frimmel, *Anal. Chim. Acta*, **283**, 251–257 (1993).
[10] E. R. Brouwer, J. Slobodnik, H. Lingeman and U. A. Th. Brinkman, *Analusis*, **20**, 121–126 (1992).
[11] B. Altenbach and W. Giger, *Anal.Chem.*, **67**, 2325–2333 (1995).
[12] O. Zerbinati, G. Ostacoli, D. Gastaldi and V. Zelano, *J. Chromatogr.*, **640**, 231–240 (1993).