

Chemically modified polymeric resin used as sorbent in a solid-phase extraction process to determine phenolic compounds in water

N. Masqué^a, M. Galíà^b, R.M. Marcé^a, F. Borrull^{a,*}

^aDepartament de Química, Àrea de Química Analítica, Universitat Rovira i Virgili, 43005 Tarragona, Spain

^bDepartament de Química, Àrea de Química Orgànica, Universitat Rovira i Virgili, 43005 Tarragona, Spain

Received 3 October 1996; revised 23 January 1997; accepted 27 January 1997

Abstract

A chemically modified polymeric resin with an acetyl group is developed for use in a solid-phase extraction process. The breakthrough volumes and selectivity of several phenolic compounds were studied and compared with the ones obtained for several commercial sorbents such as PLRP-s, Amberchrom, Envi-Chrom P and LiChrolut EN. The study was carried out by coupling an on-line solid-phase extraction system to a modified liquid chromatograph where compounds were eluted only by the organic solvent of the mobile phase. The sorbent studied was used to establish a method for determining eleven Environmental Protection Agency priority phenolic compounds in water at low levels.

Keywords: Sorbents; Extraction methods; Water analysis; Phenolic compounds

1. Introduction

In the last few years, solid-phase extraction (SPE) has become a very important technique for preparing samples in different fields, and particularly in the environmental field. The advantages of this technique over the widely used liquid–liquid extraction technique are very well known [1]. Various types of sorbents have been developed, C₁₈ and C₈ bonded to silica, carbon black and polymeric resins being the most commonly used [2]. Whereas apolar compounds can be easily preconcentrated with a C₁₈ or C₈ sorbent, the most polar compounds, for which polymeric or carbon sorbent are recommended, can be a problem because of their low breakthrough volumes [3,4]. Different attempts have been made to

develop new materials for polar compounds mainly using highly crosslinking copolymers or by using chemically modified polymeric resins [5,6].

Of the polar compounds which are of environmental interest, phenolic compounds are a very significant group. While most of the eleven phenolic compounds controlled by Environmental Protection Agency (EPA) have high breakthrough volumes for commonly used polymeric sorbents and even for C₁₈ sorbents, phenol and some nitrophenols have low breakthrough volumes for both kinds of sorbents [7]. Some highly crosslinked styrene–divinylbenzene (Envi-Chrom P) and LiChrolut EN have higher breakthrough volumes for these compounds [8,9].

The phenolic compounds are usually determined by RPLC and UV or electrochemical detection [9–11]. Some phenolic compounds can also be detected by fluorescence [12]. However, even electrochemical detection, which is more sensitive for phenolic

*Corresponding author.

compounds, does not reach the levels required by legislation.

This is why SPE is applied. Both methods, the on-line and the off-line SPE, have been applied to determine pollutants in environmental waters [9,11,13,14]. The advantages of on-line SPE are the higher sensitivity, absence of organic solvents and less manipulation of the samples, which leads to greater precision, and makes it easier for it to be automated.

However, the use of sorbents with very different characteristics from the stationary phase of the column separation, such as a highly crosslinked sorbent in the precolumn and a C₁₈ analytical column, can lead to a significant broadening of peaks. Fortunately, this can be solved by modifying the instrument, so that the compounds retained in the precolumn are eluted only with the organic solvent of the mobile phase [15], and satisfactory results were obtained when a highly crosslinked styrene-divinylbenzene was coupled with a C₁₈ precolumn for the determination of phenolic compounds.

In the present paper, a chemically modified polymeric sorbent with an acetyl group was synthesized and tested for the on-line SPE of phenolic compounds. Results from the polymeric resin unmodified and the modified polymer are compared for a group of polar phenolic compounds. As far as breakthrough volumes, capacity and selectivity are concerned, the results of the new sorbent for the on-line SPE of the eleven EPA phenolic compounds are also compared with the results obtained with various commercial polymeric sorbents.

2. Experimental

2.1. Equipment

Chromatographic experiments were performed using two Shimadzu (Tokyo, Japan) LC-10AD pumps with a Shimadzu SPD-10A UV spectrophotometric detector. To determine phenol at low detection limits and without matrix interference, an HP 1046A (Hewlett-Packard, Palo Alto, CA, USA) programmable fluorescence detector was connected

in series with the other one. The temperature of the column was controlled by a Shimadzu CTO-10A oven and the chromatographic data were collected and recorded using an HP-3365 Series II Chemstation which was controlled by Windows 3.1 (Microsoft). The separation was performed using a 250×4 mm I.D. Spherisorb ODS-2 column steel cartridge with a particle size of 5 µm purchased from Teknokroma (Barcelona, Spain).

To check the response of the instrument, standard solutions were injected through a Rheodyne valve with a 20-µl loop, but an automatic Must column-switching device (Spark Holland, Emmen, Netherlands) was used for the on-line SPE. The trace enrichment experiments were performed using steel columns of 10×3 mm I.D. laboratory-packed with the different sorbents studied. A Waters (Milford, MA, USA) M45 pump was used to deliver the sample.

2.2. Reagents and standards

The phenolic compounds studied were: hydroquinone (Hy), resorcinol (Re), catechol (Ca), orcinol (Or), guaiacol (Gu), phenol (Ph), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), 2-chlorophenol (2-CP), 2-nitrophenol (2-NP), 2,4-dimethylphenol (2,4-DMP), 2-methyl-4,6-dinitrophenol (2-M,4,6-DNP), 4-chloro,3-methylphenol (4-C-3-MP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP). They are all supplied by Aldrich (Steinheim, Germany) except PCP, which was obtained from Janssen (Geel, Belgium). Standard solutions of 2000 mg l⁻¹ of each compound were prepared in methanol. A mixture of the phenolic compounds used in the different studies was prepared weekly by diluting the standard solutions with Milli-Q water (Millipore, Bedford, MA, USA), and more diluted working solutions were prepared daily by diluting this solution with purified Milli-Q or river water.

HPLC-grade methanol (Scharlau, Barcelona, Spain) and Milli-Q quality water were used in the preparation of the eluent and in the SPE system. The pH of the eluent was adjusted with sulphuric acid (Panreac, Barcelona, Spain).

Acetyl chloride, nitrobenzene, aluminium chloride,

hydrochloric acid and acetone, supplied by Scharlau, were used in the synthetic procedure.

2.3. Synthetic procedures

The chemically modified resin was obtained from porous crosslinked poly(styrene–divinylbenzene) (PS–DVB) beads. Amberchrome GC-161 (TosoHaas, Montgomeryville, PA, USA) is a spherical resin with an average particle size of 50–100 μm and an average pore size of 110–175 \AA .

The acetyl derivative was prepared using the following procedure: 3.4 g of aluminium chloride were added slowly and under mechanical stirring to 2 g of resin and 50 ml of nitrobenzene. The reaction mixture was cooled to 0°C and 2.2 g of acetyl chloride was added dropwise. The reaction was stirred for 3 h and then syringed into methanol with 1% hydrochloric acid. The filtered polymer was washed twice with methanol and acetone and dried under vacuum at 60°C. The polymer was characterized by IR and ^1H NMR spectroscopy. The extent of the modification (30%) was established from elemental analyses.

2.4. Chromatographic conditions

Two chromatographic methods were used in this study, one of them for the analysis of more polar phenolic compounds (Hy, Re, Ca, Or, Ph, 4-NP, Gu and 2,4-DNP) and the other one for the eleven EPA priority phenolic compounds. In both cases, water adjusted to pH 2.5 with acetic acid was used as solvent A and methanol as solvent B. The gradient used in the first method was 10 min in isocratic elution at 10% of solvent B, a gradient elution from 10% B to 20% in 15 min and then an isocratic elution at 20% of B for 5 min. The other gradient used in the second method to determine eleven EPA priority phenolic compounds was a linear gradient elution from 25% of B to 60% in 25 min, a linear gradient up to 100% of B in 5 min and an isocratic elution to 100% for 2 min. Flow-rate was set at 1 ml min^{-1} .

Detection was at 280 nm for all compounds except for PCP which was detected at 302 nm. When a fluorometric detector was used to determine phenol,

275 nm and 305 nm were chosen as excitation and emission wavelengths, respectively.

2.5. On-line trace enrichment

In this study, several polymeric sorbents were compared with the new synthesized sorbent. The sorbents chosen were PLRP-s of 100 \AA and 20 μm (Polymer Labs., Amherst, MA, USA), Amberchrom [poly(styrene–divinylbenzene)] of 50–100 μm (TosoHaas), Envi-Chrom P (highly crosslinked styrene–divinylbenzene) (Supelco, Bellefonte, PA, USA) and LiChrolut EN (highly crosslinked ethylbenzene–divinylbenzene) of 40–120 μm (Merck, Darmstadt, Germany) and they have all been applied to determine phenolic compounds.

Prior to the preconcentration step, the pH of the sample was adjusted to pH 2.5 with sulphuric acid. To desorb the phenolic compounds from the sorbents, a modification of the common elution design was used [15]. A Must column-switching device with two switching valves was used to clean up the tubes, activate the precolumn and measure the sample volume in the preconcentration step more accurately. First, the preconcentration system was washed with methanol for 5 min at 2 ml min^{-1} to remove all the solvents between the delivery system and the pump delivering the sample. Then, the cartridge was cleaned up and conditioned with methanol for 1 min. The next step, to prepare cartridge previous sample preconcentration and to remove methanol, was cleaning up the tubes and the cartridge with water at pH 2.5 (sulphuric acid) for 5 and 1 min, respectively, and then the preconcentration step started after cleaning up the tubes for 5 min with the sample. The length of this step can be changed depending on the sample. In the next step, the analytes trapped on the precolumn were desorbed in the backflush mode and transferred on-line to the analytical column. Real samples were filtered through a 0.45 μm filter before preconcentration.

3. Results and discussion

The derivatization of polymeric resins with some functional groups is known to enable the retention capacity of polar compounds to be increased. Some

authors [16] have used these sorbents in the chromatographic separation of several polar compounds, and, the retention time was shown to increase compared to PS–DVB. In particular, the acetyl group was shown to increase the retention time of the phenolic compounds studied. So, in the present study a sorbent based on the modification of polymeric resin by an acetyl group, is checked for the solid-phase extraction of phenolic compounds.

The PS–DVB beads were chemically modified by aromatic electrophilic substitution with acetyl chloride. The polymer was characterized by IR spectroscopy and the presence of the modified unity was proved by the appearance of a band assignable to the carbonyl group (1690 cm^{-1}) and $^1\text{H NMR}$ spectroscopy showed signals at δ_{H} (ppm, 300 Mhz, C_6H_6): 1.2–1.6 ($\text{CH}_2\text{--CH}$), 1.8–2.1 ($\text{CH}_3\text{--CO}$), 7.0–7.8 (C_6H_5 and C_6H_4) with the signal (1.8–2.1 ppm) attributable to the CH_3 protons of the acetyl moiety. Several reaction times (3, 5, 7 and 24 h) were tested in order to study the progress of the Friedel–Crafts reaction, and from the results it can be concluded that the reaction time does not influence the modification degree. The low degree of substitution obtained (30%) can be attributed to the restricted accessibility of reactive sites. The reaction was carried out at 0°C , since higher reaction temperatures lead to untractable products.

After the derivatization and characterization of the sorbent, it was tested for the on-line SPE of phenol which is a polar compound with a low breakthrough volume for most of the sorbents.

To carry out this study a standard solution of 10 mg l^{-1} of phenol dissolved in Milli-Q water pH 2.5 (with sulphuric acid) was introduced directly into the detector bypassing the Rheodyne with the precolumn; when a stable response was obtained in the recorder, by moving the Rheodyne valve the sample was passed through the precolumn at 1 ml min^{-1} . The signal was measured with a UV detector at 280 nm. Fig. 1 shows the curves obtained when PLRP-s, Amberchrom, Envi-Chrom P, LiChrolut EN and the new acetyl sorbent were used.

Fig. 1 shows a higher breakthrough volume of phenol in the new sorbent compared with Amberchrom, the polymer which was chemically modified. Among the other sorbents compared, the breakthrough volume of phenol in the acetyl sorbent was

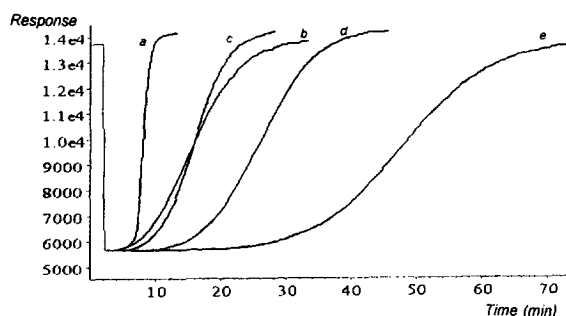


Fig. 1. Breakthrough curves of phenol with PLRP-s (a), Envi-Chrom P (b), Amberchrom (c), the new sorbent (d) and LiChrolut EN (e).

higher than in PLRP-s, a styrene–divinylbenzene polymer, and in Envi-Chrom P, although a higher breakthrough volume was obtained with LiChrolut. If the breakthrough volume is considered as the volume at which the detector signal reaches 10% of the total signal, breakthrough volumes of 4.5, 6.8, 7.5 and 14 and 30 ml were obtained for PLRP-s, Envi-Chrom P, Amberchrom, the acetyl sorbent and LiChrolut, respectively.

From the results obtained for phenol, the study of the suitability of this sorbent for polar compounds was extended to a group of polar compounds and the recoveries of these compounds in the new sorbent were determined and compared with the recoveries of the unmodified polymeric resins.

Since the analytical column was a C_{18} and there would probably be peak broadening due to the different nature of the sorbents in the precolumn and in the analytical column, a modification of the common design was used [15] consisting of the elution of the retained compounds by only the organic solvent of the mobile phase instead of the mobile phase at initial conditions, as in the most common design. This enables sorbents with high retention for the compounds to be used.

The recoveries of eight high polar compounds were determined by analyzing 100 ml of a standard solution of $2\text{ }\mu\text{g l}^{-1}$ of (hydroquinone, resorcinol, catechol, orcinol, phenol, 4-nitrophenol, guaiacol and 2,4-dinitrophenol). Previously, the linearity range for direct injection was established between 0.5 and 20 mg l^{-1} . Table 1 shows the recovery values of these compounds. Hydroquinone was not retained for any

Table 1

Recovery values (R, %) and relative standard deviation (R.S.D., %) ($n=3$) of polar phenolic compound after preconcentration of 100 ml of a standard solution of $2 \mu\text{g l}^{-1}$ with a cartridge of $10 \times 3 \text{ mm I.D.}$ using different sorbents

Compound	PLRP-s		Amberchrom		Envi-Chrom P		New		LiChrolut EN	
	R	R.S.D.	R	R.S.D.	R	R.S.D.	R	R.S.D.	R	R.S.D.
Hydroquinone	<0.1	–	<0.1	–	<0.1	–	<0.1	–	<0.1	–
Resorcinol	<0.1	–	0.7	20	1	21	4	15	16	13
Catechol	<0.1	–	3.5	15	3	16	4	18	17	15
Orcinol	<0.1	–	11	15	8	18	30	10	60	9
Phenol	5	18	18	14	16	15	50	11	60	11
4-NP	41	12	83	10	70	9	73	9	81	8
Guaiacol	75	7	103	5	90	9	86	8	108	7
2,4-DNP	75	8	84	7	77	8	76	10	78	9

of the sorbents studied and for less polar compounds, such as 2,4-dinitrophenol or guaiacol, similar results were obtained for all sorbents. However, for the rest of compounds there was a significant increase in recovery when the new sorbent was applied, compared with PLRP-s, Amberchrom and the other two commercial sorbents (Envi-Chrom P and LiChrolut EN) recommended for determining phenolic compounds in water. If the recovery of the new sorbent is compared with the values obtained for the polymer previously to the derivatization (Amberchrom) the higher recovery obtained for the acetyl may be explained by the increase of polarity of the sorbent which increase the retention with polar compounds. The higher results for LiChrolut EN compared with other sorbents are due to its high specific area

because of is a higher crosslinked and porous copolymer [9].

From the results obtained, the new sorbent seems to be suitable for determining phenolic compounds. So it was tested for the eleven EPA priority phenolic compounds. Good recovery was obtained for all phenolic compounds when 100 ml of a standard solution of the eleven phenols at $2 \mu\text{g l}^{-1}$ levels was analyzed with the new sorbent. Only phenol had a recovery value near 60%, and the rest of the compounds had values higher than 75% with a R.S.D. lower than 10% for 5 replicated analyses. These values are better than those obtained using commercial sorbents such as PLRP-s or Envi-Chrom P, and minor than when LiChrolut EN was used. Table 2 shows recovery values obtained in the analysis of

Table 2

Recovery values (R, %) and relative standard deviation (R.S.D., %) ($n=3$) of eleven EPA priority phenolic compounds

Compound	Envi-Chrom P ^a		New sorbent ^a		LiChrolut EN ^a		New sorbent ^b	
	R	R.S.D.	R	R.S.D.	R	R.S.D.	R	R.S.D.
Ph	50	4	66	9	80	5	58	3
4-NP	79	8	84	6	81	5	79	4
2,4-DNP	76	4	88	3	92	4	80	3
2-CP	76	3	88	2	84	5	84	4
2-NP	74	5	87	4	85	2	99	3
2,4-DMP	84	2	90	2	92	3	82	4
2-M-4,6-DNP	83	4	88	3	87	5	78	4
4-C-3-MP	78	3	84	4	95	3	88	4
2,4-DCP	76	5	88	3	95	4	78	3
2,4,6-TCP	75	8	85	7	89	6	79	3
PCP	40	6	44	4	42	6	96	5

^a Analysis of 25 ml of Ebro river water spiked with $4 \mu\text{g l}^{-1}$ of phenolic compounds.

^b Analysis of 100 ml of standard solution of $2 \mu\text{g l}^{-1}$ of phenolic compounds.

100 ml of standard solution of $2 \mu\text{g l}^{-1}$ of eleven EPA priority phenolic compounds using the new sorbent.

To check the selectivity of the sorbent, water from the Francoli, a river near to Tarragona with an important industrial zone, was analyzed using the on-line solid-phase extraction method with the new sorbent and compared with the other commercially available ones. First, a volume of sample was chosen; 100, 50 and 25 ml of river water spiked with the eleven compounds studied were pre-concentrated and analyzed according to the specified method using the new sorbent. Fig. 2 shows the chromatogram obtained by concentrating 25 and 100 ml of Francoli river water spiked with a standard solution of $4 \mu\text{g l}^{-1}$. Obviously, the higher the volume, the wider the peak at the beginning of the chromatogram, and from the results, a volume of 25 ml was selected for further studies. A decrease in the recovery value of phenol was observed when 100 ml of river water was analyzed, and so the, volume of sample was established at 25 ml, for which good recoveries were obtained for all phenolic compounds (see Table 2).

In order to study the capacity of the sorbent, the recoveries of each compound with river water spiked at levels of $1 \mu\text{g l}^{-1}$ and $100 \mu\text{g l}^{-1}$ were de-

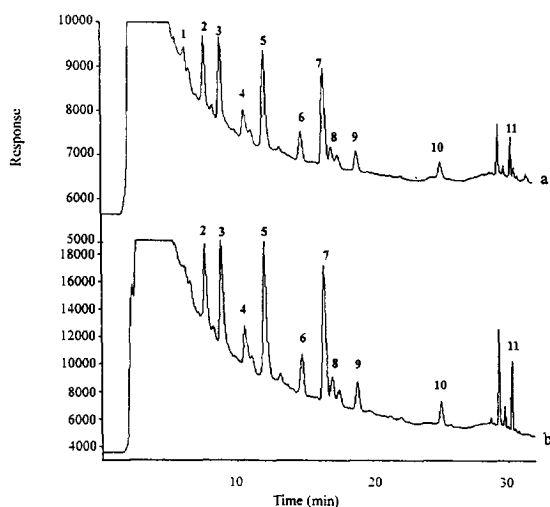


Fig. 2. Analysis of (a) 25 ml and (b) 100 ml of Francoli river water spiked with a standard solution of $4 \mu\text{g l}^{-1}$ of phenolic compounds. (1) Phenol, (2) 4-NP, (3) 2,4-DNP, (4) 2-CP, (5) 2-NP, (6) 2,4-DMP, (7) 2-M,4,6-DNP, (8) 4-C,3-MP, (9) 2,4-DCP, (10) 2,4,6-TCP and (11) PCP.

termined and no significant differences were obtained, which showed that its capacity is enough for it to be applied to real samples at the levels usually present in the samples.

When the sample volume was established, linearity and detection limits of the method were determined with real samples. The linearity of the method was studied between 1.5 and $100 \mu\text{g l}^{-1}$, and good correlation coefficients were obtained, with values between 0.9985 for PCP and 0.9999 for 2,4-DNP. The limits of detection of the method were established according to the signal-to-noise relation rule equal to 3 and were between $0.6 \mu\text{g l}^{-1}$ for phenol to $0.2 \mu\text{g l}^{-1}$ for 2-M-4,6-DNP and 2-NP. These values, however, are not enough to reach the levels required for tap water, but they are suitable for surface water.

In order to decrease the detection limit of phenol, a fluorescence detector was connected in series with a UV detector. The use of a fluorescence detector also involved the disappearance of the peak at the beginning of the chromatogram which enabled phenol to be quantified more accurately. Fig. 3 shows the chromatogram obtained for river water spiked with a standard solution of $4 \mu\text{g l}^{-1}$ of phenolic compounds with both detectors. It can be seen that phenol can be better determined with a fluorescence detector because it involves a better integration.

In order to compare the selectivity of the new sorbent with that of other commercially available sorbents which are highly recommended for the determination of phenols, an Ebro river water sample

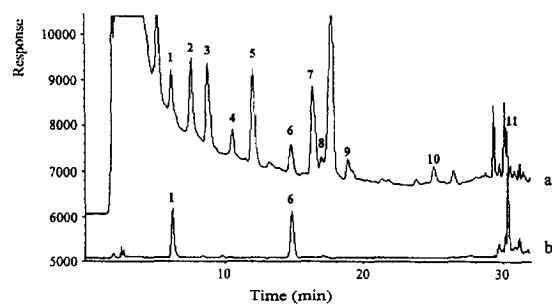


Fig. 3. Chromatogram of 25 ml of Ebro river water spiked with a standard solution of $4 \mu\text{g l}^{-1}$ of phenolic compounds with (a) UV detection and (b) fluorescence detection. For peak designation, see Fig. 2.

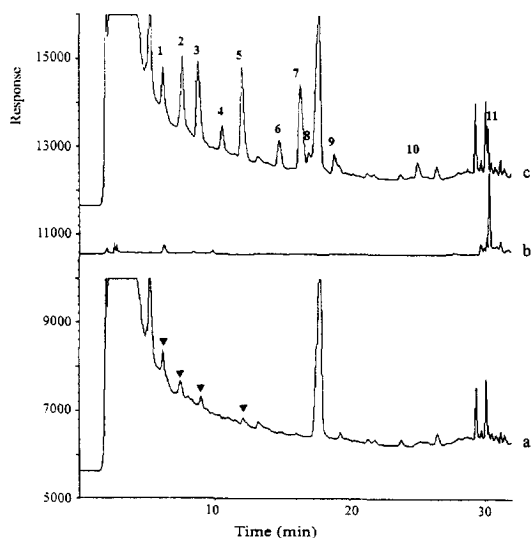


Fig. 4. Chromatogram of an analysis of 25 ml of Ebro river water using the new sorbent. (a) Ebro river water with UV detection; (b) with fluorescence detection and (c) sample spiked with $4 \mu\text{g l}^{-1}$ of phenolic compounds with UV detection. For peak designation, see Fig. 2.

spiked with $4 \mu\text{g l}^{-1}$ of each phenolic compound was analyzed with the different sorbents: Envi-Chrom P, LiChrolut EN and the new sorbent. No very significant differences were observed among the three sorbents. In LiChrolut EN, an additional peak appeared in the chromatogram (at about 13 min) and the interfering peak at 18 min was bigger in this sorbent.

The new sorbent was used to determine phenolic compounds in Ebro river water. Fig. 4 shows the chromatogram of an Ebro river water sample and the same sample spiked with a standard solution of $4 \mu\text{g l}^{-1}$. A peak with the same retention time as phenol appears in the chromatogram but no positive identification could be made because the relation between the fluorescence signals and the UV detector was not correct. Three other peaks with the same retention time as 4-NP, 2,4-DNP and 2-NP also appear in chromatogram, but no positive identification could be carried out.

4. Conclusions

The new sorbent is more suitable for the de-

termination of phenolic compounds in water than other commercially available sorbents such as PLRP-s, Amberchrom or Envi-Chrom P, but obtains lower results than those of the LiChrolut EN sorbent. More polar compounds such as phenols are retained more strongly by the resins with a hydrophilic group such as acetyl. In the analysis of eleven EPA priority phenolic compounds the new sorbent gives better results for phenol and similar ones for the less polar compounds. The matrix effect was similar to the one obtained when Envi-Chrom P or LiChrolut EN was used in the analysis. Moreover, using both the UV and the fluorescence detectors in series provides more information for the phenols to be identified in water.

References

- [1] M.C. Hennion, *Trends Anal. Chem.*, 10 (1991) 317.
- [2] I. Liska, A. Kuthan and J. Krupik, *J. Chromatogr.*, 509 (1990) 123.
- [3] J. Schülein, D. Martens, P. Spitzauer and A. Ketrup, *Fresenius J. Anal. Chem.*, 352 (1995) 565.
- [4] P. Mussmann, K. Levsen and W. Radeck, *Fresenius J. Anal. Chem.*, 348 (1994) 654.
- [5] J.J. Sun and J.S. Fritz, *J. Chromatogr.*, 590 (1992) 197.
- [6] M.P. Tsyurupa, M.M. Ilyin, A.I. Andreeva and V.A. Davankov, *Fresenius J. Anal. Chem.*, 352 (1995) 672.
- [7] E. Pocurull, M. Calull, R.M. Marcé and F. Borrull, *Chromatographia*, 38 (1994) 579.
- [8] E. Pocurull, M. Calull, R.M. Marcé and F. Borrull, *J. Chromatogr. A*, 719 (1996) 105.
- [9] D. Puig and D. Barceló, *J. Chromatogr. A*, 733 (1996) 371.
- [10] M.T. Galcerán and O. Jáuregui, *Anal. Chim. Acta*, 304 (1995) 75.
- [11] E. Pocurull, G. Sánchez, F. Borrull and R.M. Marcé, *J. Chromatogr. A*, 696 (1995) 31.
- [12] G. Lamprecht and J.F.K. Huber, *J. Chromatogr. A*, 667 (1994) 47.
- [13] U.A.Th. Brinkman, *J. Chromatogr. A*, 665 (1994) 217.
- [14] C. Aguilar, F. Borrull and R.M. Marcé, *J. Chromatogr. A*, 754 (1996) 77.
- [15] E. Pocurull, R.M. Marcé and F. Borrull, *Chromatographia*, 41 (1995) 521.
- [16] J.J. Sun and J.S. Fritz, *J. Chromatogr.*, 522 (1990) 95.