

SOLID-PHASE EXTRACTION OF PHENOLS AND PESTICIDES IN WATER WITH A MODIFIED POLYMERIC RESIN

ABSTRACT

A comparative study of a chemically modified polymeric resin which has a benzoyl group and several commercial sorbents such as PLRP-S, Envi-Chrom P and LiChrolut EN, for the solid-phase extraction of various phenolic compounds and pesticides was carried out. Selectivity and breakthrough volumes for these compounds with different sorbents were studied by coupling an on-line solid phase extraction system with a modified liquid chromatograph equipped with a UV detector. After determining the chromatographic conditions, linear range and detection limits, the method was applied to the determination of these compounds in drinking and surface water. For 25 ml of sample, the recovery was >70% for all compounds, except for 4-nitrophenol (62%), and detection limits were between 0.2 and 0.8 $\mu\text{g l}^{-1}$.

Keywords: Modified polymeric resin; Solid-phase extraction; Phenols; Pesticides; Water.

INTRODUCTION

Phenolic compounds and pesticides are two very important groups of compounds which are of interest for the environment and their determination is receiving increasing attention because of their toxicity. Phenolic compounds are usually determined by reversed-phase liquid chromatography (RPLC) using different detection systems such as UV (diode-array detection) [1-4], electrochemical [5,6] or fluorescence [7,8]. On the other hand, pesticides are usually determined by GC or RPLC, with a variety of detection systems [9-13].

Unfortunately, the use of these detectors usually does not enable the detection limits required by legislation to be reached and hence it is necessary for the sample to be enriched prior to the chromatographic analysis. In recent years, solid-phase extraction (SPE) has become a very important technique for sample preparation in the environmental field, because of its advantages over liquid-liquid extraction [14,15]. Two methods, the on-line and the off-line SPE, have been applied to determine phenolic compounds and pesticides in environmental waters [12,16]. The advantages of on-line trace enrichment procedures are better sensitivity, lower consumption of organic solvents, higher automation potential and simplicity of the analysis compared with off-line procedures [17,18].

Several types of sorbents have been developed, such as C₁₈ and C₈ bonded to silica for apolar compounds, and carbon black and polymeric resins for more polar compounds [19]. While most of the 11 phenolic compounds controlled by the EPA and some pesticides have high breakthrough volumes for commonly used sorbents, phenol, some nitrophenols, oxamyl and methomyl have low breakthrough volumes [9,20], except for some highly crosslinked styrene-divinylbenzenes (Envi-Chrom P and LiChrolut EN) [21,22] or carbon material [23].

Different sorbents, mainly based on the use of highly cross-linked copolymers or chemically modified polymeric resins, have been developed [7,24,25]. However,

using sorbents in the precolumn which have very different characteristics from the stationary phase in the analytical column (such as a highly cross-linked sorbent and a C₁₈ column, respectively) may lead to significant peak broadening. This can be solved by eluting the compounds retained in the precolumn with only the organic solvent of the mobile phase [18,23].

In this paper, a chemically modified polymeric sorbent with a benzoyl group was synthesized and tested for the on-line SPE of some pesticides and phenolic compounds in order to obtain better breakthrough volumes for the determination of polar compounds in environmental waters. The results obtained with the synthesized sorbent, viz., breakthrough volumes, capacity and selectivity, were compared with those obtained for different commercial polymeric sorbents.

EXPERIMENTAL

Equipment

The chromatographic experiments were performed with two Shimadzu (Tokyo, Japan) LC-10AD pumps, with a Shimadzu SPD-10A UV spectrophotometric detector. The temperature of the column was controlled by a Shimadzu CTO-10A oven and the chromatographic data were collected and recorded using a Hewlett-Packard (Avondale, PA, USA) HP-3365 Series II Chemstation which was controlled by Windows 3.1 (Microsoft). The analytical column was a 250x4 mm id stainless-steel column packed with Spherisorb ODS 2, 5 μm (Teknokroma, Barcelona, Spain).

To check the response of the instrument, standard solutions were injected through a Rheodyne (Cotati, CA, USA) valve with a 20 μl loop, and an automatic Must column-switching device (Spark Holland, Emmen, The Netherlands) was used with

on-line SPE. The on-line trace enrichment process was carried out using steel precolumns of 10x3 mm I.D. laboratory-packed with the different sorbents studied. A Waters (Milford, MA, USA) M45 pump was used to deliver the sample.

Reagents and Standards

Various phenolic compounds and pesticides were studied. The phenolic compounds were: phenol (Ph), 4-nitrophenol (4-NP), 2,4- dinitrophenol (2,4-DNP) and 2-chlorophenol (2-CP); they were obtained from Aldrich-Chemie (Steinheim, Germany). The pesticides studied included triazines (simazine and atrazine), carbamates (methomyl and oxamyl), (4-chloro-2-methyl-phenoxy) acetic acid (MCPA) and bentazone. Except for bentazone, which was obtained from Dr. Ehrenstorfer (Augsburg, Germany), the remainder of the compounds were from Riedel-de Haën (Seelze, Germany).

Standard solutions of 2000 mg l⁻¹ of each compound were prepared in methanol. A mixture of all compounds used 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 with Milli-Q or river water. All solutions were stored at 4°C in a refrigerator.

HPLC-gradient-grade methanol (Scharlau, Barcelona, Spain) and Milli-Q water were used to prepare the mobile phase. Hydrochloric acid (Probus, Badalona, Spain) was used to adjust the pH of the mobile phase and the sample before SPE to 3 and 2.5, respectively.

Synthetic Procedure

The chemically modified resin was obtained from porous cross-linked polystyrene-divinylbenzene (PS-DVB beads. Amberchrom 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 benzoyl derivative was prepared as follows: a portion (2.5 g) of Amberchrom GC-161 was stirred in 15 ml of nitrobenzene at room temperature for 12 h. Aluminium chloride (4.3 g) was added slowly and under mechanical stirring and the reaction mixture was cooled to 0°C. Then 4.9 g of benzoyl chloride were added dropwise and the reaction mixture was stirred for 3 h. The reaction mixture was quenched by adding acetone with 1% hydrochloric acid, and excess liquid was decanted. The polymer was washed twice with methanol and dried under vacuum at 60°C. The recovery of the beads was essentially quantitative. The polymer was characterized by IR spectrometry and the extent of the modification (60%) was established from the elemental analyses.

Chromatographic Conditions

The eluents for the chromatographic separation were Milli-Q water adjusted to pH 3 with sulphuric acid (solvent A) and methanol (solvent B). The flow-rate was 1 ml min^{-1} and the temperature of the column oven was set at 65°C. The gradient profile was 20% B initially, 50% solvent B after 25 min, and 100% solvent B after 28 min (held for 2 min), after which the mobile phase returned to the initial conditions in 2 min.

The detection was carried out at different wavelengths (at 240 nm for oxamyl, methomyl, bentazone, simazine and atrazine; at 280 nm for Ph, 4-NP, 2,4-DNP and 2-CP; and at 230 nm for MCPA) with a programme of wavelengths: first at 240

nm, at 280 nm after 7 min, at 240 nm again at 13.5 min, then at 230 nm after 21.2 min and finally at 240 nm at 23 min.

On-line Trace Enrichment

On-line trace enrichment was carried out with several polymeric sorbents so as to compare them with the sorbent synthesized here. The sorbents chosen were PLRP-S of 100 Å and 20 µm (Polymer Laboratories, Amherst, MA, USA), Envi-Chrom P (Supelco, Bellefonte, PA, USA) and LiChrolut EN of 40-120 µm (Merck, Darmstadt, Germany).

Prior to the preconcentration step, the pH of the samples was adjusted to pH 2.5 with hydrochloric acid. A modification of the common elution design was used to desorb the analytes from the sorbents [18]. A Must column-switching device with two switching valves was used to clean the tubes, activate the precolumn and control the sample volume to be preconcentrated. Before use, all precolumns were conditioned by flushing with methanol for 1 min at 2 ml min⁻¹ and activated with 2 ml of Milli-Q water adjusted to pH 2.5 with hydrochloric acid. Then, different sample volumes were preconcentrated at 4 ml min⁻¹. In the next step, the analytes trapped on the pre-column were desorbed in the backflush mode only by the organic solvent (methanol) of the mobile phase so as to prevent broadening of peaks due to the different nature of the sorbent on the precolum and the analytical column. This enables sorbents with high retention for the compounds to be used.

Real samples were filtered through 0.45 µm nylon membranes (Supelco) before preconcentration.

RESULTS AND DISCUSSION

This study discusses a sorbent obtained by chemically modifying a PS-DVB resin, which can be used in the SPE of some phenolic compounds and pesticides.

The electrophilic substitution of the PS-DVB resin with benzoyl chloride was carried out by the Friedel-Crafts reaction. Nitrobenzene was used as solvent in the presence of aluminium chloride as catalyst at low temperatures. In order to prevent the beads from degrading, suitable stirring conditions were established. The polymer was characterized by IR spectrometry and the presence of the modified material was proved by the appearance of a band assignable to the carbonyl group (1670 cm^{-1}). Several reaction times (3, 5, 7 and 24 h) were tested in order to study the length of the reaction, and similar degrees of substitution (60%) were obtained. Hence, it was concluded that the reaction time does not affect the degree of modification.

After the sorbent had been synthesized and characterized, it was initially tested for the on-line SPE of Ph, which is a polar compound with a low breakthrough volume for most of the commercial sorbents [6,9,12].

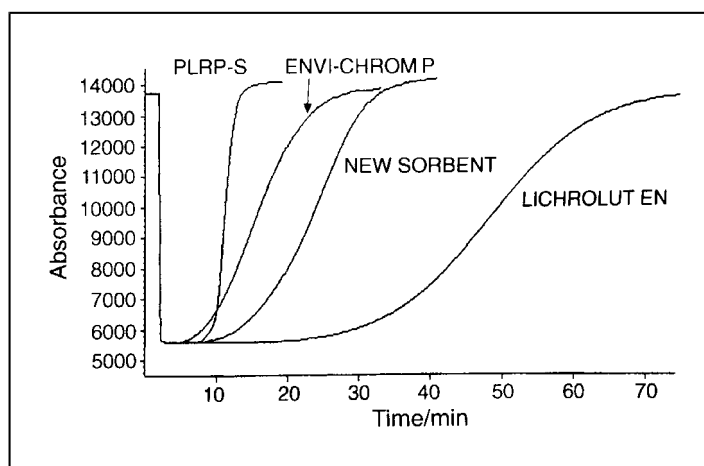


Fig. 1. Breakthrough curves for a standard solution of 10 mg l^{-1} of Ph, adjusted to pH 2.5, obtained for the different sorbents used.

The different breakthrough curves for Ph obtained for the synthesized sorbent and the commercial sorbents (PLRP-S, Envi-Chrom P and LiChrolut EN) are shown in Fig. 1. To obtain these curves, a standard solution of 10 mg l^{-1} of Ph dissolved in Milli-Q water at pH 2.5 (with hydrochloric acid) was directly introduced into the detector, by-passing the Rheodyne valve with the precolumn; when a stable response was obtained, the Rheodyne valve was moved so that the sample was passed through the precolumn at 1 ml min^{-1} . The signal was measured with a UV detector at 280 nm. If the breakthrough volume is considered as the volume at which the detector signal reaches 10% of the total signal, the breakthrough volumes obtained for PLRP-S, Envi-Chrom P, the synthesized sorbent and LiChrolut EN were 4, 7, 13 and 30 ml, respectively. Fig. 1 confirms that the synthesized sorbent is better than the PLRP-S and Envi-Chrom P but no better than LiChrolut EN for Ph recovery.

A gradient separation was optimized to separate the ten compounds studied. The chromatogram obtained under optimum conditions is shown in Fig. 2. A programme of wavelengths in the UV spectrophotometric detector enabled each compound to be detected at its maximum absorbance.

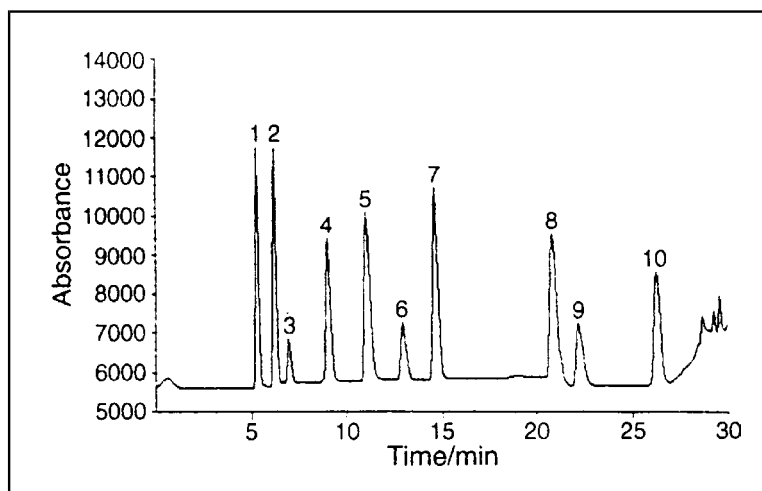


Fig. 2. Chromatogram corresponding to a standard solution of 10 mg l⁻¹ of each compound studied under optimum conditions. 1, Oxamyl; 2, methomyl, 3, Ph; 4, 4-NP; 5, 2,4-DNP; 6, 2-CP; 7, bentazone; 8, simazine; 9, MCPA; and 10, atrazine.

Good linearity of response by direct injection of between 0.25-0.1 and 40 mg l⁻¹ was obtained for all compounds with good regression coefficients (r^2) ranging from 0.9993 for atrazine to 0.9999 for simazine. Detection limits [26] attained ranged from 10 µg l⁻¹ for oxamyl, methomyl, 2,4-DNP and simazine to 50 µg l⁻¹ for Ph, 2-CP and MCPA.

Table 1

Recoveries obtained with the synthesized sorbent using different volumes of 20 µg l⁻¹ standard solution. Values are the means of three determinations and are expressed as a percentage. For conditions, see text.

Compound	Recovery (%) [*]			
	10 ml	25 ml	50 ml	100 ml
Oxamyl	84	80	77	77
Methomyl	82	76	73	70
Ph	91	70	58	40
4-NP	81	78	78	78
2,4-DNP	81	81	80	85
2-CP	80	72	75	79
Bentazone	85	85	82	88
Simazine	80	80	79	83
MCPA	80	73	73	78
Atrazine	86	76	75	79

^{*}% RSDs are lower than 9% in all instances

In order to calculate the recoveries for each compound, different sample volumes (10, 25, 50 and 100 ml) of the analyte mixtures studied were preconcentrated on the synthesized sorbent. In Table 1 the recoveries of these compounds are shown. Good recoveries were obtained for all compounds when 100 ml of a standard solution at the $20 \mu\text{g l}^{-1}$ level were analysed with the synthesized sorbent. Only Ph has a recovery value near 40%; the remainder of the compounds have values higher than 70% with RSDs lower than 3% for three replicate analyses. In this study, to obtain a good recovery of Ph, 25 ml of sample were selected for further studies.

Table 2

Recoveries obtained with PLRP-S, Envi-chrom P, the synthesized sorbent and LiChrolut EN using 25 ml of standard solution spiked at the $8 \mu\text{g l}^{-1}$ level. Values are the mean of three determinations and are expressed as a percentage. For all conditions, see text.

Compound	Recovery (%) [*]			
	PLRP-S	Envi-Chrom P	Synthesized sorbent	LiChrolut EN
Oxamyl	75	65	74	70
Methomyl	68	64	72	74
Ph	33	47	71	78
4-NP	73	71	62	81
2,4-DNP	77	73	72	77
2-CP	75	71	80	83
Bentazone	86	78	79	83
Simazine	73	77	76	84
MCPA	81	79	74	83
Atrazine	77	75	77	83

^{*}%RSDs are lower than 10% in all instances.

A comparative study of the different sorbents, preconcentrating 25 ml of a standard solution spiked at $8 \mu\text{g l}^{-1}$ adjusted to pH 2.5 with HCl, was carried out. Table 2 shows the recoveries found. The values obtained for Ph with the synthesized sorbent are better than those obtained using commercial sorbents such as PLRP-S or Envi-Chrom P, and similar to those obtained with LiChrolut EN. For the other compounds similar results were obtained for all sorbents when this volume of sample was analysed.

Table 3

Mean recoveries and RSDs ($n=3$) of the SPE with the synthesized sorbent and PLRP-S for 100 ml of standard solution spiked with $2 \mu\text{g l}^{-1}$ of each compound in Milli-Q and Ebro river water. All values in %.

Compound	Synthetized sorbent (Milli-Q water)		PLRP-S (Milli-Q water)		PLRP-S (River water)	
	Recovery	RSD	Recovery	RSD	Recovery	RSD
Oxamyl	77	2	23	3	21	5
Methomyl	69	2	15	1	16	2
Ph	40	3	---	---	---	---
4-NP	78	2	32	4	40	8
2,4-DNP	85	2	79	4	81	3
2-CP	79	3	71	1	69	1
Bentazone	88	1	86	6	80	1
Simazine	83	3	65	4	57	8
MCPA	78	1	75	1	89	2
Atrazine	78	3	75	3	80	1

When 100 ml of sample spiked at the $2 \mu\text{g l}^{-1}$ level were preconcentrated on PLRP-S, the recoveries of oxamyl and methomyl were lower (23% and 15%, respectively)

and Ph was eluted; however, when the same volume was preconcentrated on the synthesized sorbent, the recoveries of oxamyl and methomyl were 77% and 70%, respectively, and Ph had a recovery of nearly 40%. Table 3 shows that the synthesized sorbent is suitable for determining these compounds. When Ebro river water was analysed, similar recoveries were obtained. The results obtained for oxamyl and methomyl are higher than those obtained for carbon sorbents which are recommended for polar compounds [23].

Linearity of the response for the total analytical system, including the preconcentration step, was checked for a sample volume of 25 ml of Ebro river water spiked at different concentrations. Good linearity was obtained from 0.8-4 to 50 $\mu\text{g l}^{-1}$. R^2 values were between 0.9996 and 0.9999 and the detection limits [26] were between 0.2 and 0.8 $\mu\text{g l}^{-1}$. The results obtained are shown in Table 4.

Table 4
Study of the linear range and detection limits of the method

Compound	Linear range ($\mu\text{g l}^{-1}$)	Detection limit ($\mu\text{g l}^{-1}$)
Oxamyl	0.8-50	0.2
Methomyl	1-50	0.4
Ph	4-50	0.8
4-NP	1-50	0.4
2,4-DNP	0.8-50	0.2
2-CP	4-50	0.8
Bentazone	0.8-50	0.2
Simazine	0.8-50	0.2
MCPA	1-50	0.4
Atrazine	0.8-50	0.2

In order to compare the selectivity of the synthesized sorbent with that of the other commercially available sorbents which are highly recommended for the determination of selected compounds, 25 ml of Ebro river water spiked with $8 \mu\text{g l}^{-1}$ of each compound were analysed with the different sorbents chosen. With LiChrolut EN, additional peaks appeared and the peak at 14 min was larger with this sorbent than with the synthesized sorbent.

Fig. 3 shows the chromatograms of 25 ml of sample and the same sample spiked with a standard solution of $4 \mu\text{g l}^{-1}$ of each compound in tap and Ebro river water (3c and 3d, and 3a and 3b, respectively). In the river water chromatograms, four peaks with the same retention time as oxamyl, methomyl, Ph and bentazone appear; however, for the first three compounds, the signal was near the detection limits, whereas for bentazone, a concentration of $1.5 \mu\text{g l}^{-1}$ was found. This pesticide has already been found in samples of the same origin in our laboratory using MS as the detection technique in the chromatographic system.

CONCLUSIONS

It has been shown that the synthesized sorbent has higher recoveries for the determination of some phenolic compounds and pesticides in surface and tap water than other commercially available sorbents such as PLRP-S or Envi-Chrom P. Compared with these commercial sorbents, the synthesized sorbent gives better results for oxamyl, methomyl and Ph, and similar results for the less polar compounds. The matrix effect was similar to that obtained when Envi-Chrom P or LiChrolut EN was used.

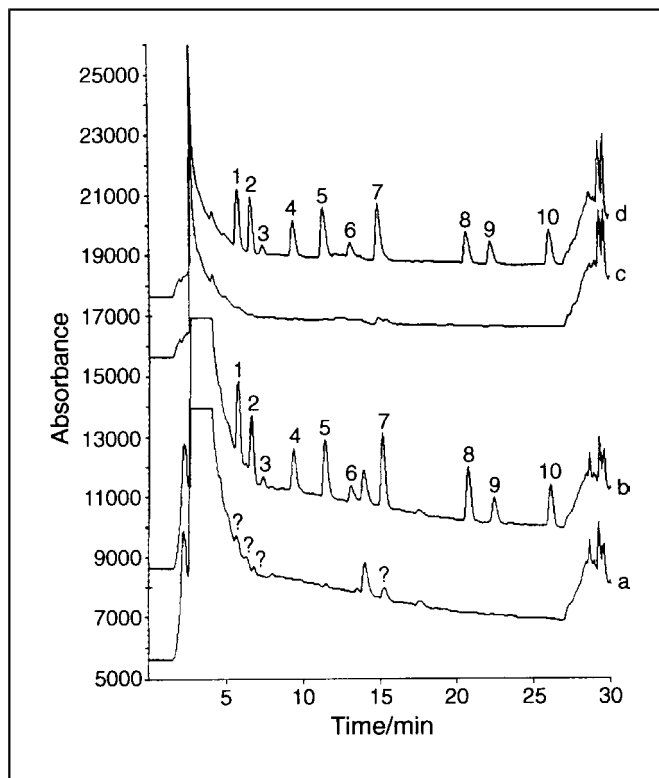


Fig. 3. Chromatograms obtained by on-line trace enrichment with the synthesized sorbent of a 25 ml sample. (a) Ebro river water, (b) Ebro river water spiked with $4 \mu\text{g l}^{-1}$ of each compound, (c) tap water and (d) tap water spiked with $4 \mu\text{g l}^{-1}$ of each compound. For peak designation, see Fig. 2.

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