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Comparison of different sorbents for on-line solid-phase extraction of pesticides and phenolic compounds from natural water followed by liquid chromatography

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Abstract

Three different sorbents, Carbopack B, a carbon black, Bond Elut PPL, a functionalized polymeric resin, and HYSphere-1, a higher cross-linking polymeric resin, in a steel precolumn of 10×3 mm I.D., were compared for solid-phase extraction (SPE) of a group of pesticides and phenolic compounds in water which was on-line coupled to reversed-phase liquid chromatography and UV detection. HYSphere-1 gave a higher breakthrough volume for phenol, one of the most polar compounds studied and enabled 100 ml of water to be concentrated with no significant losses of the compounds studied (73% for phenol). Recoveries in tap water were between 67% for phenol and 86% for eight polar analytes, and detection limits were between 0.03 and 0.17 μg l^{-1}. © 1998 Elsevier Science B.V.

Keywords: Pesticides; Phenolic compounds

1. Introduction

Phenolic compounds and pesticides are important water pollutants which are subject to legislation because of their toxicity, even at low concentrations. A European Community (EC) Directive specifies a legal tolerance level of 0.1 μg l^{-1} for each phenolic compound or pesticide and 0.5 μg l^{-1} for the sum of all compounds in water intended for human consumption [1,2].

Pesticides are usually determined by gas chromatography (GC) or reversed-phase liquid chromatography (RPLC) with a variety of detection systems [3–8]. Phenolic compounds are usually determined by RPLC with different detection systems such as UV and DAD [7–13], electrochemical [10,12] or fluorescence [8,14]. Chromatographic techniques cannot reach the low levels allowed in natural waters and so samples need to be preconcentrated.

Nowadays, solid-phase extraction (SPE) is the most important technique for sample enrichment, because it overcomes many of the disadvantages of liquid–liquid extraction (LLE) [15]. Several sorbents have been tested for determining pesticides and phenolic compounds. The most widely used sorbents for these analytes are C_8 and C_{18} chemically bonded to silica [11,16–20], carbon black [21,22] and polymeric resins (such as PLRP-S) [3,4,10–12,20]. The most polar compounds have low breakthrough volumes with these sorbents [3,11] except for carbon

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material [23] and for some highly cross-linked styrene–divinylbenzenes (Envi-chrom P) [10,11].

In recent years, chemically modified polymeric resins with a polar functional group have been developed and used in the SPE of these compounds, and the breakthrough volumes were higher than those obtained with their unmodified analogues [7,8,13,24,25].

Recently, new highly cross-linked styrene–divinylbenzene packing materials, such as LIChrolut EN [6–9,26,27], Styrosorb and Macronet Hypersol [28], Isolute ENV [9] and HYSphere-1 [29] have become available. These sorbents have a higher degree of cross-linking, and so have an open structure (high-porosity materials), which increases their specific surface area [30] and allows greater $\pi-\pi$ interactions between analytes and sorbent. This means that the breakthrough volumes will be higher than the ones obtained when less cross-linked sorbents are used.

In this work, three different sorbents, a carbon black (Carbopack B), a functionalized polymeric resin (Bond Elut PPL) and a highly cross-linked polymeric resin (HYSphere-1), are compared for the SPE of some polar pesticides and phenolic compounds from surface and drinking waters.

These sorbents have been chosen because Bond Elut PPL has been recommended for the extraction of highly polar species such as phenolic compounds from large volumes of water samples, HYSphere-1 provides high recoveries for the 11 EPA priority phenols as has been previously reported [29], and the carbon black sorbents have given high recovery values for the off-line SPE of pesticides and phenolic compounds [21–23], although they do have some problems with the on-line SPE because of the peak broadening caused by the analytes being strongly retained by carbon. But, in this work, the analytes were desorbed in the backflush mode only by the organic solvent of the mobile phase to prevent the peaks from broadening.

2. Experimental

2.1. Equipment

The chromatographic experiments were performed using two Shimadzu (Tokyo, Japan) LC-10AD pumps with a Shimadzu SPD-10A UV spectrophotometric detector. The column oven was a Shimadzu CTO-10A and the standard solutions were injected through a Rheodyne (Cotati, CA, USA) valve with a 20-μl loop. The nine analytes were completely separated using a 250×4.6 mm I.D. stainless-steel column packed with Spherisorb ODS2, 5 μm (Teknokroma, Barcelona, Spain). The chromatographic data were collected and recorded using an HP-3365 Series II Chemstation which was controlled by Windows 3.11 (Microsoft).

An automatic Must column-switching device (Spark Holland, Emmen, The Netherlands) was used in on-line SPE. The on-line trace enrichment process was carried out using steel precolumns of 10×3 mm I.D. purchased from the Free University (Amsterdam, The Netherlands) and laboratory-packed with the above-mentioned sorbents. An Applied Biosystems (Ramsey, MN, USA) 400 pump was used to deliver the sample.

2.2. Chemicals

The compounds studied were: the phenolic compounds phenol (Ph), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP), and the pesticides simazine and atrazine (triazines), methomyl and oxamyl (carbamates), MCPA (chlorphenoxy acid) and bentazone (diazine). The phenolic compounds were purchased from Aldrich-Chemie (Steinheim, Germany), and the pesticides, except bentazone which was obtained from Dr. Ehrenstorfer (Augsburg, Germany), were from Riedel-de Haën (Seelze, Germany).

HPLC-gradient-grade acetonitrile (Scharlau, Barcelona, Spain) and Milli-Q quality water, adjusted to pH 3 with sulphuric acid (Probus, Badalona, Spain), were used to prepare the mobile phase.

A stock standard solution of 2000 mg l^{-1} of each compound was prepared in methanol. Working standard solutions were prepared daily by diluting the stock standard solutions with Milli-Q purified (Millipore), tap or river water. All solutions were stored at 4°C in the refrigerator. Hydrochloric acid (Probus, Badalona, Spain) was added to adjust the pH of the sample to 2.5 before the SPE. Different volumes of 10% solution of Na_2SO_3 (Panreac, Barcelona, Spain)

were added to real samples in order to eliminate the free chlorine in tap water, which may react with phenols and produce chlorophenols, and to reduce the peak that appears at the beginning of the chromatogram because of the presence of humic and fulvic acids [13]. Tap and river water samples were filtered through a 0.45-μm nylon membrane (MSI, Westboro, MA, USA) before the preconcentration step to eliminate particulate matter.

2.3. Chromatographic conditions

The gradient elution was carried out with Milli-Q water at pH 3 (solvent A) and acetonitrile as organic modifier (solvent B). The flow-rate was 1 ml min^{-1} and the temperature of the column oven was set at 65°C. The solvent program was a linear gradient from 20% B to 40% B in 20 min, 100% B at 25 min, isocratic for 2 min, and the mobile phase returned to initial conditions in 2 min for subsequent analysis runs.

The detection was performed at 280 nm for phenolic compounds and at 240 nm for pesticides, except for MCPA which was quantified at 230 nm. The wavelength program used allows each compound to be detected at its maximum absorbance.

2.4. On-line trace enrichment

On-line trace enrichment was carried out using three different sorbents: a carbon black Carbopack B 120/400 (Supelco, Bellefonte, PA, USA), a highly cross-linked styrene–divinylbenzene copolymer, HYSphere-1 (5 μm) (Spark Holland, Emmen, The Netherlands) and Bond Elut PPL (125 μm) (Varian, Harbor City, CA, USA). The last of these sorbents is a functionalized polymeric resin.

As a pretreatment step, the water samples were acidified with hydrochloric acid to pH 2.5 in order to prevent the analytes from taking their ionic form.

The Must automatic column-switching device was used in the SPE process, which enabled the sample preconcentration program shown in Table 1 to be automated. The Applied Biosystems 400 pump was used to deliver the sample and the conditioning solutions.

The analyte was desorbed in the backflush mode, only by the organic solvent (acetonitrile) of the mobile phase, so as to prevent the peaks from broadening due to the different nature of the analytical column and the precolumn sorbent. So the sample band in the precolumn was compressed into a narrow band before entering the analytical column and the band broadening effect reduced [11].

3. Results and discussion

Before the on-line solid-phase extraction study, gradient elution and wavelength were optimized in order to separate the nine compounds in a short analysis time. Fig. 1 shows the chromatogram obtained in the analysis of a standard solution of 10 mg l^{-1} of analytes under optimum conditions. These optimum conditions are described in Section 2. Good linearity was found, for all compounds, between 0.05 or 0.1 and 40 mg l^{-1} and regression coefficients (r^2) were higher than 0.9995. Detection limits were calculated by the statistical program ULC (Univariate Linear Calibration) with k equal to 6 [31] and the values found were between 10 μg l^{-1} for oxamyl and 32 μg l^{-1} for phenol.

3.1. Comparison of sorbents

To compare the three sorbents used, the break-

Table 1
Sample preconcentration program in the on-line SPE process

Step	Time (min)	Flow rate (ml min−1)	Event
1	0	2	Washing tubes with acetonitrile
2	5	2	Conditioning precolumn with acetonitrile
3	6	2	Washing tubes with Milli-Q water at pH 2.5
4	11	2	Activating precolumn with Milli-Q water at pH 2.5
5	12	2	Washing tubes with sample
6	17	4	Sample preconcentration

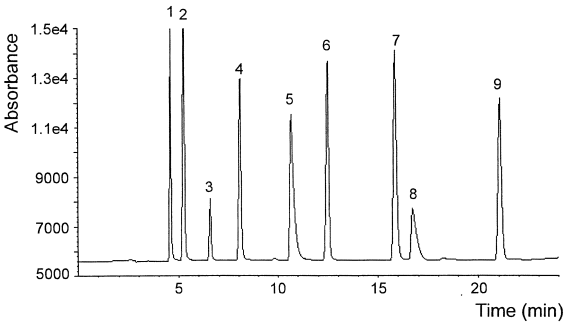

Fig. 1. Chromatogram of standard solution of 10 mg l^{-1} of compounds. For conditions, see text. Peaks: (1) oxamyl, (2) methomyl, (3) phenol, (4) 4-nitrophenol, (5) 2,4-dinitrophenol, (6) bentazone, (7) simazine, (8) MCPA and (9) atrazine.

through curves of phenol for each sorbent were obtained introducing a standard solution of 10 mg l^{-1} of phenol in Milli-Q water at pH 2.5 (with HCl) directly into the UV detector at 280 nm bypassing the Rheodyne with the precolumn, and when a stable response was obtained, the Rheodyne valve was moved so that the sample passed through the sorbent at 1 ml min^{-1}. If the breakthrough is the volume at which the detector reaches 10% of its 100% value, the breakthrough volumes for phenol obtained with these sorbents were 2 ml with Carbopack B 120/400, 14 ml with Bond Elut PPL and 22 ml with HYSphere-1. The breakthrough volumes for Ph with Bond Elut PPL and HYSphere-1 were higher than the ones obtained with other commercial sorbents such as C_{18}, PLRP-S, Envi-chrom P and Amberchrom [7,8,29]. The chemically modified polymeric resin, Bond Elut PPL, gave breakthrough volumes for Ph which were similar to the ones obtained with new chemically modified polymeric sorbents synthesized in our laboratory in previous works [7,8,13]. HYSphere-1 had a greater capacity than Bond Elut PPL because of its higher degree of cross-linking, which increases the specific surface area [30], and its smaller particle size (HYSphere-1, 5 μm, and Bond Elut PPL, 125 μm) which increases the surface area between the water sample and the sorbent and allows more interactions between the analytes and the resin surface. The use of an SPE sorbent with a smaller particle size has a positive effect on capacity and efficiency [29].

To study the breakthrough volumes for all compounds, different sample volumes (50, 100 and 200 ml) of a standard solution of the analyte mixtures were preconcentrated in the three sorbents. The results of this study are shown in Table 2, where it can be seen that better recoveries were obtained for all compounds with HYSphere-1. When 100 ml of 2 μg l^{-1} was analyzed, the recovery value for phenol was 43% with Bond Elut PPL, whereas with HYSphere-1 it was 73%. For the rest of the compounds both sorbents gave similar recoveries, between 77–78% for methomyl and 87–88% for simazine. When Carbopack B was used, recoveries lower than 68% were obtained for all compounds (3% for phenol), except for simazine, MCPA and atrazine, the values of which were similar to the ones for HYSphere-1 and Bond Elut PPL. The recoveries for oxamyl and methomyl (35 and 68%, respectively) with Carbopack B were similar to the recoveries when another graphitized carbon black (Envi-Carb)

Table 2
Recovery values obtained preconcentrating different sample volumes with the three sorbents (n=6)

Compound	Carbopack B		Bond Elut PPL			Hysphere-1		
	50 ml	100 ml	50 ml	100 ml	200 ml	50 ml	100 ml	200 ml
Oxamyl	68	35	82	82	81	82	82	82
Methomyl	80	68	79	77	74	78	78	80
Ph	7	3	68	43	23	77	73	50
4-NP	57	38	86	86	86	84	83	83
2,4-DNP	24	27	85	87	89	84	86	86
Bentazone	64	54	82	82	83	86	82	83
Simazine	86	88	85	88	89	86	87	89
MCPA	82	102	83	86	86	79	87	86
Atrazine	82	83	81	82	82	83	83	84

For all conditions, see text.

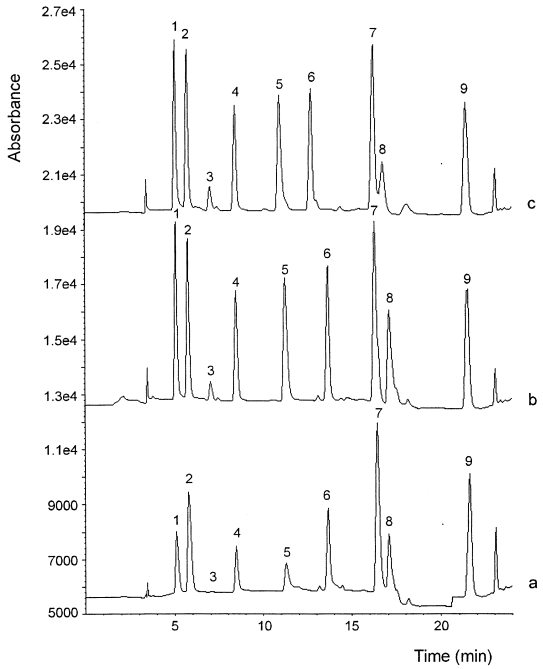

Fig. 2. Chromatograms obtained by on-line trace enrichment of 100 ml of standard solution of 2 μg l^{-1} using as a precolumn (a) Carbopack, (b) Bond Elut PPL and (c) Hysphere-1. For peak assignation, see Fig. 1.

was used by other authors [23]. When 200 ml of a standard solution at a level of 1 μg l^{-1} was analyzed with Bond Elut PPL and HYSphere-1 the recoveries did not decrease, except for phenol which had values of 23% with Bond Elut PPL and 50% with HYSphere-1. For these reasons, 100 ml of sample and HYSphere-1 sorbent were selected for further analysis. The typical relative standard deviations (R.S.D.) were 2–3%, and they were invariably lower than 8% (n=6). Fig. 2 shows the chromatograms obtained when analysing 100 ml of a standard solution of 2 μg l^{-1} and it can be seen that there was no peak broadening in the chromatogram when precolumns with sorbents such as carbon black or highly cross-linked polymeric resin were coupled to a C_{18} analytical column.

3.2. Application

The performance of the method was tested on real samples using HYSphere-1 as sorbent. When real samples were analysed, we added 0.5 and 1 ml of 10% Na_2SO_3 solution for every 100 ml of tap and Ebro river water, respectively [13], in order to decrease the initial band due to humic and fulvic acids, and also to prevent the formation of chlorinated compounds when a standard solution of phenolic compounds are added to a real sample with residual chloride. The recoveries for real samples, including the Na_2SO_3 treatment, were similar to the ones obtained when Milli-Q water was used. Recovery values of 67–85 and 64–80% were obtained for tap water and Ebro river water, respectively.

The linearity of the response for the total analytical system, including the preconcentration step with the HYSphere-1 sorbent, was checked for a volume of 100 ml of tap water spiked at different concentrations. The results obtained for the linearity range and the detection limits (with k equal to 6) [31] are shown in Table 3.

Fig. 3 shows the chromatograms for 100 ml of tap and Ebro river water with and without standard

Table 3
Study of the linearity range and detection limits in the preconcentration of 100 ml of tap water at pH 2.5 and with 0.5 ml of 10% Na_2SO_3 solution added

Compound	Linearity range (μg l^{-1})	r^2	Detection limit (μg l^{-1})
Oxamyl	0.2–50	0.9998	0.06
Methomyl	0.2–50	0.9997	0.06
Ph	0.5–50	0.9987	0.17
4-NP	0.1–50	0.9997	0.03
2,4-DNP	0.2–50	0.9997	0.07
Bentazone	0.2–50	0.9998	0.07
Simazine	0.2–50	0.9994	0.06
MCPA	0.2–50	0.9992	0.07
Atrazine	0.2–50	0.9996	0.07

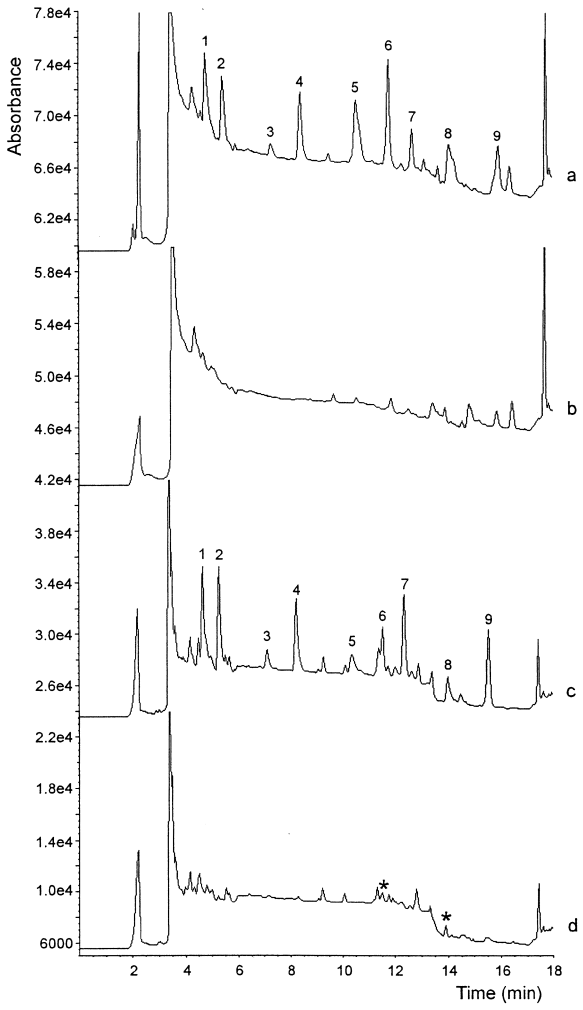

Fig. 3. Chromatograms obtained by on-line trace enrichment of 100 ml of tap water with and without standard addition of 2 μg l^{-1} of compounds (a,b) and 100 ml of Ebro river water with and without standard adition of 2 μg l^{-1} of compounds (c,d). For peak assignation, see Fig. 1.

addition of 2 μg l^{-1} of compounds. It should be pointed out that the retention times of some analytes in this figure are slightly different to those in Figs. 1 and 2 because the analytical column had been replaced by another one. In the Ebro river water sample two peaks at the same retention time as bentazone and MCPA appeared in the chromatogram, which would correspond to concentrations of 0.24 and 0.52 μg l^{-1}, respectively. Because of their low concentrations, the presence of the herbicides could not be confirmed by LC–PB-MS available in our laboratory [32].

4. Conclusions

This study demonstrated that HYSphere-1 has higher recoveries for some pesticides and phenolic compounds in surface and tap water than other commercially available sorbents such as Bond Elut PPL and Carbopack B.

Pesticides and phenolic compounds at low μg l^{-1} levels could be efficiently concentrated from 100 ml of water sample volume by on-line SPE with HYSphere-1 and quantitative recoveries were obtained.

Problems arising from high contents of fulvic and humic acids were solved by adding 10% Na_2SO_3 solution to the samples.

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