Short communication

New hydrophilic polymeric resin based on 4-vinylpyridine–divinylbenzene for solid-phase extraction of polar compounds from water

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Abstract

A 4-vinylpyridine–divinylbenzene (VP–DVB) resin was synthesized to be used for on-line solid-phase extraction process and it was tested for a group of polar compounds. The high specific surface area and the nitrogen content of the VP–DVB sorbent increased the interactions with the polar analytes in the preconcentration process. The sorbent enabled 100 ml of water to be concentrated with recoveries higher than 70% for several polar compounds (including phenol) except for oxamyl (55%) and methomyl (43%). The method was used to analyse water samples by liquid chromatography and UV detection. Linearity was good and detection limits were 0.1–0.2 μg l^{-1} for all compounds. Several tap and river water and waste water treatment plant samples were analyzed; phenol and (4-chloro-2-methyl-phenoxy)acetic acid (MCPA) were tentatively determined in some samples.
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1. Introduction

In recent years, solid-phase extraction (SPE) has been the most widely used technique for sample enrichment in the environmental field [1–3], because of the low concentration of the organic pollutants which must be determined in real samples.

The choice of the SPE sorbent is important because it determines the kind of interactions with the compounds during the percolation. The sorbents used for extracting polar compounds are from carbon-based [4] to polymeric resins (styrene-divinylbenzene (St-DVB)) and, particularly, highly crosslinked resins such as ENVI-ChromP, Hysphere-1, Lichrolut EN or Isolute ENV+ [5–7], since their high specific surface area (800–1200 m^2 g^{-1}) contains numerous active aromatic sites that allow, among other things, greater π–π interactions between the sorbent and the analytes.

On the other hand, their hydrophobic character means that recoveries in the retention of most polar com-

pounds are low. Modifying existing polymers is one possible way of obtaining more polar sorbents. Sun and Fritz [8] modified polymeric resins by introducing acetyl, hydroxymethyl or cyanomethyl groups. Masqué et al. [9] modified a commercial St-DVB resin with such chemical groups as benzoyl, *o*-carboxybenzoil, 2-carboxy-3/4-nitrobenzoyl, and 2,4-dicarboxybenzoyl, and tested for the on-line SPE of some organic pollutants. In comparison with the unmodified polymer the results were clearly better, particularly for the most polar compounds.

Another alternative is copolymerizing appropriate monomers that contain suitable functional groups. Although there are many studies on this sort of polymerization, they mainly focus on batch experiments for one group of slightly polar compounds and there is no application to SPE [10,11]. Oasis HLB, which is a commercially available macroporous copolymer [poly(divinylbenzene-co-*N*-vinylpyrrolidone)], has been tested in some SPE studies for the extraction of pollutants [6,12] and results were better than with hydrophobic sorbents. Bagheri and Saraji [13] synthesized polymeric materials based on polyaniline and used them as sorbents for SPE to preconcentrate chlorophenols before

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GC-ECD analysis. They did not, however, determine polar phenols in this study.

Several resins based on 4-vinylpyridine–divinylbenzene (VP–DVB) were synthesized in our laboratory and various polymerization parameters were tested to improve the morphological properties and the nitrogen content of the copolymer [14]. In the present paper, a VP–DVB resin, which combines a greater specific surface area and a proportion of nitrogen, is evaluated as a sorbent for on-line solid-phase extraction of a group of polar compounds. The synthesized sorbent was compared to other chemically modified resins and also to hydrophobic highly crosslinked commercial ones. The performance of the method was investigated with real water samples and various analytical parameters were determined.

2. Experimental

2.1. Reagents and standards

The compounds selected to check the sorbent were: phenol (Ph), 4-nitrophenol (4-NP), and 2,4-dinitrophenol (2,4-DNP) obtained from Aldrich (Steinheim, Germany) and pesticides such as carbamates (methomyl and oxamyl), (4-chloro-2-methyl-phenoxy)acetic acid (MCPA), and bentazone, all from Riedel-de-Haën (Seelze, Germany).

Standard solutions of $2000 \, \text{mg} \, l^{-1}$ of each compound were prepared in methanol. The mixture of all the compounds was prepared by diluting the standard solution with Milli-Q water (Millipore, Bedford, MA, USA).

HPLC-grade acetonitrile (SDS, Peypin, France) and Milli-Q water were used to prepare the mobile phase. HCl was used to adjust the pH of the mobile phase and the sample before SPE to 3, and sodium sulfite to prevent the humic band, both from Probus (Badalona, Spain).

The reagents used in the polymerization, 4-vinylpyridine, divinylbenzene (80%), and 2,2′-azobisisobutyronitrile (AIBN) were supplied by Aldrich. Toluene was from Panreac (Barcelona, Spain) and poly(vinylalcohol) (PVA) 23/88 (MW 100.000, 88% hydrolyzed) from ERKOL (Tarragona, Spain).

2.2. Polymerization

The polymer beads were obtained by the usual suspension polymerization method [14] in a two-necked round-bottomed flask reactor fitted with a mechanical stirrer and reflux condenser. The organic phase (50 ml) containing the monomers 4-vinylpyridine (3.1 g) and divinylbenzene (15.4 g), toluene (33 ml) as diluent and AIBN (0.35 g) as initiator, was added to the aqueous phase (50 ml), containing 2% of PVA, and suspended by stirring at 80 °C for 24 h. The sieving copolymer with fraction in the range 32–50 μm was selected for further studies.

The resulting polymer has a specific surface area of $710 \, \text{m}^2 \, \text{g}^{-1}$ and 2.14 wt.% N.

2.3. LC equipment and conditions

The experiments were performed with two LC-10AD$_{VP}$ pumps, an on-line connected degasser DGU-14A and CTO-6AS column oven (all from Shimadzu (Tokyo, Japan)), an injection valve with a 20-μl loop and a Hewlett Packard (Avondale, PA, USA) Series 1100 UV spectrophotometric detector. A 250 mm × 4.6 mm i.d. stainless-steel column packed with Kromasil 100 C$_{18}$, 5 μm (Teknokroma, Barcelona, Spain) was used.

The eluents were Milli-Q water adjusted to pH 3 with HCl (solvent A) and acetonitrile (solvent B). The flow-rate was 1 ml min^{-1} and the temperature of the column oven was 65 °C. The gradient profile was 20% B initially, 55% B after 20 min, and 100% B at 25 min (held for 2 min), after which the mobile phase was returned to the initial conditions in 3 min.

The wavelengths used to detect the compounds were 240 nm (oxamyl, methomyl, and bentazone), 280 nm (all phenolic compounds), and 230 min (MCPA).

2.4. On-line trace enrichment

The SPE system was on-line connected to the LC system by means of a six-port switching valve (Rheodyne, Cotati, CA, USA). A LC-10AS pump (Shimadzu) was used to preconcentrate samples on a stainless-steel precolumn of 10 mm × 3 mm i.d. purchased from Free University (Amsterdam, The Netherlands) and laboratory-packed with the 32–50 μm sorbent.

Prior to the extraction, the pH of all samples was adjusted to 3 with HCl and for real samples 1 ml of 10% sodium sulfite solution was added for every 100 ml of water in order to decrease the signal from the humic and fulvic acids [15].

Before use, the precolumn was conditioned by flushing with acetonitrile for 3 min at 3 ml min^{-1} and with 2 ml of Milli-Q water adjusted to pH 3 with HCl. Sample volumes were preconcentrated at 3 ml min^{-1} and, the analytes trapped on the precolumn were desorbed in the backflush mode by the organic solvent of the mobile phase instead of the mobile phase in the initial conditions [5].

Real samples from Ebre river and a waste water treatment plant were filtered through 0.45 μm nylon membranes (Supelco Bellefonte, PA, USA) before preconcentration to eliminate the particulate matter.

3. Results and discussion

Before using the new sorbent for SPE, the LC separation was optimized. The linearity of the method was determined by directly injecting, 20 μl of the standard solutions (1–40 mg l^{-1} of analytes). The regression coefficients (r^2) were good and ranged from 0.9985 for methomyl to 0.9999 for phenol and MCPA.

Table 1
Recoveries obtained with the VP–DVB synthesized sorbent using different volumes of a standard solution of Milli-Q water spiked with the analyte mixture with a constant mass of $0.2\,\mu g$

Compound	Recovery (%)			
	10 ml	50 ml	100 ml	200 ml
Oxamyl	83	70	55	34
Methomyl	83	64	43	22
Ph	89	83	70	42
4-NP	83	86	85	82
2,4-DNP	78	80	78	78
Bentazone	80	84	83	81
MCPA	79	84	87	106

For all the conditions, see text. % Relative standard deviations (R.S.D.) ($n = 3$) were lower than 6.

3.1. Evaluation of the sorbent

To determine the recovery of the compounds, 10–200 ml sample volumes of Milli-Q water at pH 3 (with HCl) were spiked with the analytes in concentrations of $1–20\,\mu g\,l^{-1}$, depending on the volume, and then on-line preconcentrated. Table 1 shows that recoveries were acceptable when 100 ml of $2\,\mu g\,l^{-1}$ was analyzed. The recoveries for 200 ml were low for the most polar compounds but they were better than those obtained with PLRP-S 10 (a commercial St-DVB resin, $500\,m^2\,g^{-1}$) in the same conditions [16].

The recoveries obtained for phenol with the VP–DVB synthesized sorbent were higher than those obtained with the highly crosslinked materials, such as Amberchrom GC-161m ($900\,m^2\,g^{-1}$), Envi-Chrom ($800–950\,m^2\,g^{-1}$) or Lichrolut EN ($1200\,m^2\,g^{-1}$) [17], in which larger $\pi–\pi$ interactions can be expected. The VP–DVB resin is hydrophilic (due to the presence of the 4-vinylpyridine monomer) and has a specific surface area of $710\,m^2\,g^{-1}$. This enabled two types of interactions with the analytes (polar and $\pi–\pi$), which explains the increase in the phenol recoveries. Moreover, the recoveries for this compound were lower when a functional group such as acetyl [17], 2,4-dicarboxybenzoyl or 2-carboxy-3/4-nitrobenzoyl [18] was introduced to a commercial crosslinked sorbent (Amberchrom GC-161m), in order to increase the polarity of the surface. This indicates that the sorbent obtained by introducing a polar monomer in the polymerization process, gives better results than the styrene-divinylbenzene chemically modified sorbent.

In order to obtain acceptable recoveries for phenol (and also the earlier eluting oxamyl and methomyl), and to improve the detection limits, 100 ml volumes were selected for further studies.

3.2. Performance of the method

When 100 ml of river water spiked at $1\,\mu g\,l^{-1}$ of each compound were on-line preconcentrated, the most polar compounds, eluted at the beginning of the chromatogram (Fig. 1a), were masked by a band corresponding to ful-
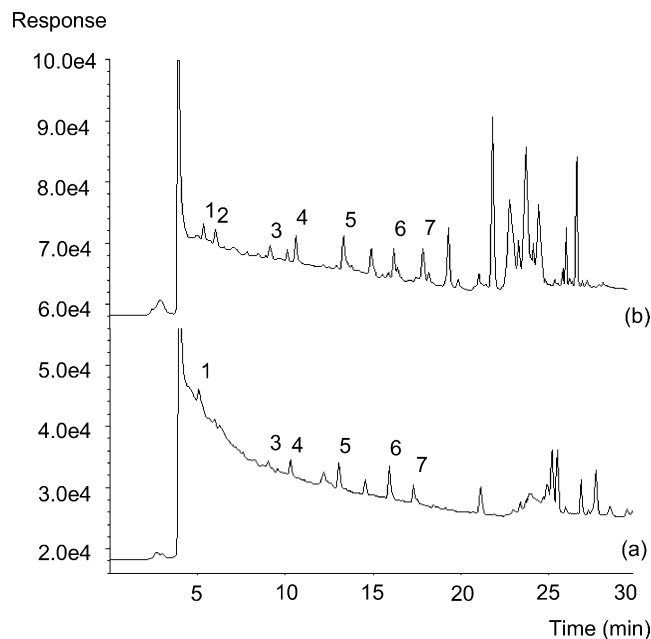

Fig. 1. Chromatograms obtained by on-line trace enrichment of 100 ml of Ebre river water spiked with $1\,\mu g\,l^{-1}$ of the analytes without (a) and with (b) the addition of 1 ml of 10% Na_2SO_3 solution for every 100 ml of sample. Peak designation: (1) oxamyl, (2) methomyl, (3) phenol, (4) 4-NP, (5) 2,4-DNP, (6) bentazone, (7) MCPA.

vic and humic acids. In order to reduce the influence of matrix, several options have been proposed, such as using a dual column set-up [19,20] or adding a chemical [15]. We tested this latter option because it is less tedious and it presented good results [15], and therefore, we added 1 ml of 10% (w/v) Na_2SO_3 for every 100 ml of sample. With this approach some additional peaks may appear at the end of the chromatogram, but they did not interfere in the quantification and the initial peak was narrower (Fig. 1b).

The recovery values obtained with river samples were similar to those obtained with Milli-Q water (Table 2).

The linearity and the detection limits (signal-to-noise = 3) for the whole analytical system were determined and results are shown in Table 2.

Table 2
Recoveries, linear range, and detection limits with on-line trace enrichment of 100 ml of spiked Ebre river water and addition of 1 ml of 10% Na_2SO_3

Compound	Recovery (%)[a]	Linear range ($\mu g\,l^{-1}$)	r^2	Detection limit ($\mu g\,l^{-1}$)
Oxamyl	39	0.4–20	0.9948	0.2
Methomyl	35	0.4–20	0.9943	0.2
Ph	63	0.5–20	0.9866	0.2
4-NP	89	0.2–20	0.9994	0.1
2,4-DNP	72	0.2–20	0.9979	0.1
Bentazone	88	0.2–20	0.9994	0.1
MCPA	79	0.2–20	0.9990	0.1

% R.S.D. ($n = 4$) were lower than 9 in all instances.
[a] Recoveries of the samples spiked at $1\,\mu g\,l^{-1}$ of each compound.
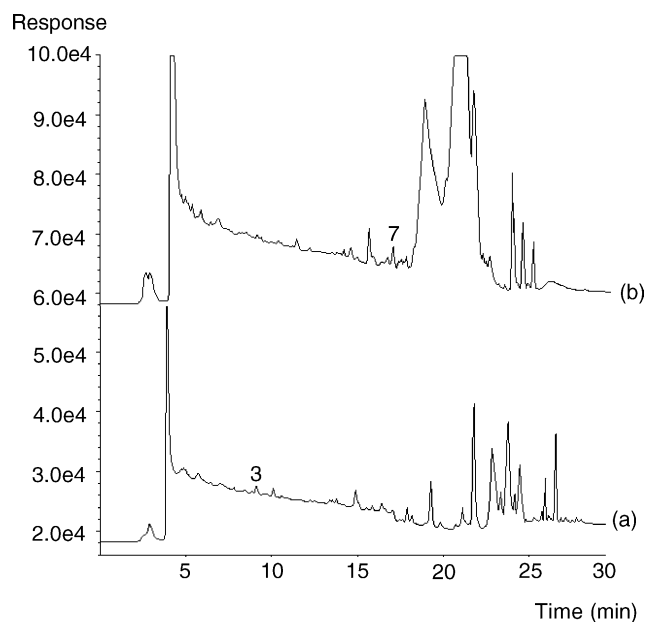
Fig. 2. Chromatograms obtained by on-line trace enrichment of 100 ml of water sample from the Ebre river (a) and from the waste water treatment plant (b). For peak designation, see Fig. 1.

The method's repeatability and reproducibility between days, expressed as the R.S.D.s ($n = 4$) of 100 ml of Ebre river water spiked at $1 \, \mu g \, l^{-1}$ were lower than 9% in all instances.

The method was used to analyze several water samples from tap, river and a waste water treatment plant. In tap water, no compound was found. Fig. 2a shows a chromatogram obtained for a Ebre river sample. A peak at the same retention time as phenol was found. Afterwards, a standard addition was made to this sample, and the peak corresponding to phenol increased. So it was tentatively identified as phenol although it was not confirmed by mass spectrometry. The phenol was found at a level of $1.2 \, \mu g \, l^{-1}$ in this river water sample. Phenol had already been found in Ebre river at $3 \, \mu g \, l^{-1}$ [21].

Water samples from the outlet of the waste water treatment plant in Tarragona were also analyzed. In the chromatogram of one sample (Fig. 2b), a lot of unknown peaks appeared, one of which was at the same retention time as MCPA. This peak increased after the standard addition of $1 \, \mu g \, l^{-1}$ of the analyte to the sample. It was tentatively identified as MCPA and quantified at $0.8 \, \mu g \, l^{-1}$. MCPA may be present in this waste water treatment plant because it is widely used as a herbicide and, in particular, to control weeds in roadside verges [22].

Although this method does not involve the confirmation of the compounds, for instance by mass spectrometry or electrochemical detection at several voltages, it involves simple instrumentation and can be used for preliminary screening for the possible presence of these compounds at low $\mu g \, l^{-1}$ levels; when "positive" is found, it should be confirmed by MS.

4. Conclusions

This study demonstrates that introducing a hydrophilic monomer into the resin led to more polar interaction between the sorbent and the analytes. The recoveries of the compounds studied were higher than when most commercial hydrophobic or chemically modified sorbents were used.

Pesticides and phenolic compounds were determined at low $\mu g \, l^{-1}$ levels and acceptable recoveries were obtained from 100 ml of real water samples, after the problems of a high matrix influence had been solved by adding Na_2SO_3.

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