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Solid-phase extraction of polar compounds with a hydrophilic copolymeric sorbent

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Abstract

A new synthesized copolymer based on *N*-vinylimidazole–divinylbenzene (VIm–DVB) was tested as a sorbent for the solid-phase extraction (SPE) of polar analytes. In the on-line SPE, this synthesized sorbent enabled 100 ml of sample to be preconcentrated with recoveries as high as 80% for oxamyl, phenol (Ph) and derivates, bentazone and (4-chloro-2-methylphenoxy)acetic acid (MCPA). For the off-line SPE, 1000 ml of sample was extracted and recoveries were higher than 92% for all compounds with the exception of oxamyl (83%) and methomyl (78%). The VIm–DVB sorbent gives better recoveries than the previously synthesized 4-vinylpyridine–divinylbenzene (VP–DVB) resin and similar to such highly crosslinked commercial sorbents as LiChrolut EN or Oasis HLB. Real water samples were used to validate the on-line SPE method. Linearity was good and detection limits were between 0.1 and 0.2 $\mu g\,l^{-1}$.

Keywords: Solid-phase extraction; Sorbents; Vinylimidazole–divinylbenzene sorbent; Water analysis

1. Introduction

In recent years, solid-phase extraction (SPE) has become a well-established preconcentration technique in environmental analytical applications [1–3].

Extracting pollutants with a wide range of physical and chemical structures requires a variety of sorbents to be used in order to trap properly all the target compounds present in the samples. Polar compounds in particular have received most attention because they have several retention problems with the classical SPE sorbents (i.e. silica, graphitized carbon or polystyrene–divinylbenzene (PS–DVB) polymeric sorbents) [4,5].

Because of their larger specific surface area (800–1200 $m^2\,g^{-1}$) highly crosslinked polymeric sorbents retain considerably more polar compounds than conventional polymeric sorbents (350–500 $m^2\,g^{-1}$), which involve less π–π interactions. However, the hydrophobic character of their surface usually means that breakthrough volumes are low [6–8] when the most polar compounds are percolated.

To improve the retention of the polar analytes, some authors [9,10] have chemically modified the resin surface. The results with the chemically modified sorbents when extracting polar compounds were better than those obtained with the unmodified analogous sorbents, in spite of the low degree of modification, which the authors attributed to the restricted accessibility of the reactive sites.

An alternative to improving the reactivity is to copolymerize a suitable hydrophilic monomer mixed with a crosslinker, in order to obtain a sorbent which combines polarity with a high specific surface area. This synthetic option has been applied in the commercial resin Oasis HLB (Waters, Milford, MA, USA), which is based on *N*-vinylpyrrolidone (hydrophilic) crosslinked with divinylbenzene (PVP–DVB); and the resin previously synthesized by our group, 4-vinylpyridine–divinylbenzene (VP–DVB) [11].

In view of the satisfactory results obtained in SPE when polar compounds were extracted with these hydrophilic sorbents (Oasis HLB [6,12,13] and VP–DVB [14]), a monomer (*N*-vinylimidazole), which contains two nitrogen atoms, was selected to polymerize the sorbent, *N*-vinylimidazole–divinylbenzene (VIm–DVB) [15]. Thus, the increase in the polarity of the monomer used to synthesize the sorbent is expected to increase the polarity of the resin and, therefore, the ability to retain the most polar compounds.

The aim of this study is to test a synthesized polymer of VIm–DVB [15] on the retention of polar pollutants in on-line and off-line SPE. The VIm–DVB sorbent was compared with a polar VP–DVB resin and commercial highly crosslinked

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sorbents to evaluate how the VIm monomer affected the retention properties. The performance of the method was also tested with real water samples.

2. Experimental

2.1. Reagents and standards

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

Standard solutions of 2000 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. Hydrochloric acid was used to adjust the pH of the mobile phase and the sample before SPE to 3.0 and sodium sulphite was added to prevent the matrix influence. Both were supplied by Probus (Badalona, Spain).

The reagents used in the polymerization VIm–DVB (80%) and 2,2′-azobisisobutyronitrile (AIBN) were supplied by Aldrich. Toluene and methanol were supplied by Panreac (Barcelona, Spain), dibutylphthalate by Daesder (Barcelona, Spain) and poly(vinyl alcohol) (PVA) 23/88 (M_r 100 000, 88% hydrolyzed) by Erkol (Tarragona, Spain).

2.2. Chromatographic equipment

The chromatographic 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. The analytical column was a 250 mm × 4.6 mm i.d. stainless-steel column packed with Kromasil 100 C_{18}, 5 μm (Teknokroma, Barcelona, Spain).

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

A vacuum manifold was used to place the cartridges in the off-line solid-phase extraction process.

2.3. Polymerization

The polymer beads were obtained by an optimized suspension polymerization method [15] in a two-necked round bottomed flask reactor fitted with a mechanical stirrer and reflux condenser. At room temperature, the flask was charged with the aqueous phase (33 ml) containing 2% of PVA. The organic phase (66 ml) was divided into two portions, the first of which consisted of the monomer VIm (6.87 g, 0.07241 mol) mixed with half of the rest of the organic phase: toluene (20 ml) and dibutylphtalate (2.6 ml) as the diluents and the initiator (AIBN, 0.19 g). This portion was added to the aqueous phase at 80 °C and suspended by stirring. The second portion was added 30 min after the first portion and consisted of the monomer DVB (17.68 g, 0.1088 mol) mixed with the other half of the organic phase, as in the previous portion. Then, the reaction mixture was stirred for 48 h at 80 °C.

The sieved copolymer with fraction in the range 32–50 μm was selected for further studies.

The resin was characterized by measuring its surface area (627 m^2 g^{-1}) and the nitrogen content (6.26%, w/w, N) with elemental analysis.

2.4. Chromatographic conditions

The mobile phase consisted of Milli-Q water acidified to pH 3.0 with hydrochloric acid (solvent A) and acetonitrile (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, 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 at 240 nm (oxamyl, methomyl and bentazone), at 280 nm (all the phenolic compounds studied), at and at 230 nm (MCPA).

2.5. On-line solid-phase extraction

The laboratory-synthesized sorbent (in the fraction whose particle size was between 32 and 50 μm) and the commercial Oasis HLB were laboratory packed in a 10 mm × 3 mm i.d. stainless-steel precolumn used for the on-line trace enrichment in the solid-phase extraction process.

A Shimadzu LC-10AS pump with a switching valve was used to load the different volumes of both the solvent and the sample to be extracted. The protocol used was the same for both sorbents (VIm–DVB and Oasis HLB) and was the following: the SPE precolumn was conditioned by flushing 6 ml of acetonitrile and 2 ml of acidified Milli-Q water (pH 3.0) at 3 ml min^{-1}; different volumes (10–200 ml) of the sample acidified with hydrochloric acid at pH 3.0 at 3 ml min^{-1} were extracted; 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 [16].

Real samples from Ebre river and tap water were filtered through 0.45 μm nylon membranes (Supelco, Bellefont, PA, USA) before the preconcentration step to eliminate the particulate matter. The optimum addition of Na_2SO_3 (10%, w/v) was added prior to the preconcentration process in order to

decrease the initial band caused by humic and fulvic acids in the real water samples.

2.6. Off-line trace enrichment

A cartridge was packed with 200 mg of the synthesized sorbent 32–50 μm in a 6 ml polypropylene syringe and the sorbent was retained by two polyethylene frits (20 μm pore size). The retention capabilities of the VIm–DVB sorbent were compared with those of the commercial cartridge LiChrolut EN 200 mg/6 ml (Merck, Darmstadt, Germany). The procedure with both cartridges was the same: the cartridge was activated with 25 ml MeOH followed by 6 ml of Milli-Q water adjusted to pH 3.0 with hydrochloric acid at a flow rate of 10 ml min^{-1} using a vacuum manifold connected to the cartridge. Different sample volumes were passed through the cartridge. Compounds were eluted from the cartridge using 10 ml of MeOH.

3. Results and discussion

The response by direct injection was linear between 0.25 and 40 mg l^{-1} for all the compounds and regression coefficients (r^2) were higher than 0.9997.

3.1. On-line trace enrichment

Recoveries for the selected sorbent were determined in the on-line SPE by percolating different sample volumes (10–200 ml) in Milli-Q water acidified at pH 3.0 (with HCl) and spiked with the analytes. The concentration of the analytes depended on the preconcentrated volume with a constant mass of 0.2 μg. In the on-line system, the samples passed through the precolumn packed with ~40 mg of the synthesized VIm–DVB sorbent and Oasis HLB. The results for VIm–DVB sorbent are presented in Table 1. Recoveries were as high as 80% for all the compounds (except for methomyl for which recovery was 68%) when 100 ml of sample spiked at 2 μg l^{-1} were on-line preconcentrated. For the larger volumes (150 and 200 ml) the recoveries for oxamyl (59 and 55%, respectively) and methomyl (42 and 37%, respectively) decrease because of the high polarity of these compounds, but for phenol the results were still good, with recoveries of 71 and 62%, respectively, for 150 and 200 ml extracted volume.

Table 1
Recoveries obtained in on-line SPE with the VIm–DVB synthesized sorbent for different sample volumes spiked with the analyte mixture with a constant mass of 0.2 μg in Milli-Q water

Compound	Recovery (%)				
	10 ml	50 ml	100 ml	150 ml	200 ml
Oxamyl	87	87	80	59	55
Methomyl	88	84	68	42	37
Ph	85	92	88	71	62
4-NP	83	84	84	83	83
2,4-DNP	80	83	82	79	78
Bentazone	82	86	84	84	83
MCPA	81	83	81	85	84

RSDs ($n = 3$) were lower than 6%. For all the conditions see text.

The recovery values obtained with the commercial Oasis HLB sorbent with the same conditions were quite similar. For instance, the values for 100 ml of sample with Oasis HLB for oxamyl, methomyl and phenol were 75, 63 and 82%, respectively.

On the other hand, the recoveries provided by the VIm–DVB sorbent are better than those obtained with a previously synthesized sorbent based on VP–DVB [14]. For example, the recoveries when 100 ml of sample spiked at 2 μg l^{-1} was on-line preconcentrated with VP–DVB sorbent for the most polar compounds (oxamyl, methomyl and phenol) were 55, 43 and 70%, respectively; whereas these values increased considerably (80, 68 and 88%, respectively) with the VIm–DVB resin.

The *N*-vinylimidazole monomer has two nitrogen atoms in its structure and the synthesized copolymer (VIm–DVB) contains $N_{wt.\%} = 6.26$. The VP–DVB resin, on the other hand, has only one nitrogen atom in the 4-vinylpyridine monomer and a nitrogen content of $N_{wt.\%} = 2.18$. Both monomers (VIm and VP) have an aromatic ring in their structure. The higher recoveries with the VIm–DVB resin may be due to the additional nitrogen, which favors the polar interactions between the polar analytes and the sorbent, and the π–π interactions are remained because of the aromatic rings present in either the hydrophobic (DVB) or hydrophilic monomer (VIm or VP), even though the specific surface area of the VP–DVB resin is slightly higher (710 m^2 g^{-1}) than that of the VIm–DVB resin (627 m^2 g^{-1}).

When the synthesized VIm–DVB sorbent is compared, in the same conditions, to commercial highly crosslinked sorbents, which are based on PS–DVB (hydrophobic character) and have high specific surface areas, such as Hysphere (<1000 m^2 g^{-1}) [17] or LiChrolut EN (1200 m^2 g^{-1}) [18,19], the results are better for the VIm–DVB resin. Therefore, although both the nitrogen content and the specific surface area affect the sorption capabilities of the VIm–DVB sorbent, the quantity of nitrogen had a considerable influence on its capacity to absorb the most polar analytes.

3.2. Off-line trace enrichment

The off-line approach was also tested for the synthesized sorbent. The home-made cartridge packed with the Vlm-DVB sorbent (200 mg) in the particle size between 32 and 50 μm was loaded with the sample volumes (500–2000 ml) in Milli-Q water (pH 3.0) spiked with the analyte mixture between 40 and 10 μg l^{-1}. In the elution step, 10 ml of methanol was required for the complete elution of all the compounds. The eluted solution (2 mg l^{-1}) was directly injected into the chromatographic system. For

Table 2
Recoveries obtained with the synthesized VIm–DVB sorbent and commercial LiChrolut EN in off-line SPE for different sample volumes spiked with the analyte mixture in Milli-Q water

Compound	Recovery (%)							
	VIm–DVB synthesized sorbent				LiChrolut EN			
	500 ml	1000 ml	1500 ml	2000 ml	500 ml	1000 ml	1500 ml	2000 ml
Oxamyl	89	83	55	52	80	81	78	81
Methomyl	98	78	39	39	97	97	97	99
Ph	101	97	68	62	97	89	61	56
4-NP	94	95	95	93	94	95	95	96
2,4-DNP	91	92	85	83	91	91	90	90
Bentazone	97	99	97	96	95	95	93	92
MCPA	96	97	95	96	92	91	90	90

RSDs ($n = 3$) were lower than 2%. For all the conditions see text.

purposes of comparison the same kind of experiments were performed with the commercial highly crosslinked sorbent LiChrolut EN 200 mg/6 ml (1200 $m^2\,g^{-1}$), which is based on PS–DVB according to the information provided by the supplier.

Table 2 shows the recoveries with the VIm–DVB and LiChrolut EN. The recovery for phenol, which usually has early breakthrough volumes and, therefore, the lowest recoveries when larger sample volumes are extracted [8,12,20], was comparable with the synthesized sorbent. When 500 or 1000 ml of the sample were loaded, the recoveries for oxamyl and methomyl with VIm–DVB were similar to those obtained with the highly crosslinked sorbent, or even a little higher in the case of oxamyl. The recovery values decreased as the sample volume increased (1500 and 2000 ml) with the VIm–DVB resin. However, the recoveries remained constant with the highly crosslinked resin. The highly crosslinked network structure has a high specific surface area and a very low packing density of polymer chains, which makes it accessible to smaller molecules [21], such as oxamyl and methomyl. Therefore, they are not eluted when high sample volumes are percolated.

In spite of the good recoveries obtained in the off-line approach, an evaporation step is necessary if the detection limits are to be lower than those obtained in on-line SPE. However, after the evaporation step, the recoveries of some volatile compounds, such as phenol [20], decreased. This may be due to a partial evaporation of these compounds during the evaporation step. Because of this and other drawbacks (greater sample manipulation, much slower sample throughput, less automation, etc. [3]) we chose the on-line approach for further experiments.

3.3. Performance of the method

The method was applied to the on-line preconcentration of 100 ml of river and tap water.

When a sample of 100 ml of river water spiked at 1 $\mu g\,l^{-1}$ with the analyte mixture was on-line preconcentrated, the presence of humic substances in real water samples, which were eluted early, made it difficult to identify the most polar compounds (Fig. 1a). In order to prevent the emergence of this humic band an amount of Na_2SO_3 was added [22]. The addition of 1000 μl of 10% (w/v) of sulphite per 100 ml of sample makes it possible to quantify oxamyl and methomyl in 100 ml of the preconcentrated river water sample spiked at 1 $\mu g\,l^{-1}$; however, the 2,4-DNP and bentazone compounds were slightly eluted (Fig. 1b), presumably because of the variability in the octanol–water distribution coefficient of these compounds [1]. And, it was 400 μl of 10% Na_2SO_3 per 100 ml of sample the most suitable quantity of sulphite for all the compounds to be quantified (Fig. 1c).

The same quantity of sulphite (400 μl) was also necessary to add for the preconcentration of tap water samples.

Table 3
Recoveries and RSD ($n = 5$) of the on-line SPE with the VIm–DVB sorbent for 100 ml of standard solution spiked with 0.5 $\mu g\,l^{-1}$ of each compound in Milli-Q, tap and Ebre river water

Compound	Milli-Q water		Tap water[a]		River water[a]	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Oxamyl	80	4	68	3	57	11
Methomyl	69	5	59	13	58	10
Ph	86	6	70	7	80	2
4-NP	84	1	85	4	83	3
2,4-DNP	83	2	80	3	74	5
Bentazone	80	2	80	2	79	5
MCPA	80	2	85	4	83	7

[a] With the addition of 400 μl 10% Na_2SO_3 solution.

Table 4
Linear range and detection limits with on-line trace enrichment of 100 ml of Ebre river water at pH 3.0 and addition of 400 μl 10% Na_2SO_3

Compound	Linear range ($\mu g\,l^{-1}$)	r^2	Detection limit ($\mu g\,l^{-1}$)
Oxamyl	0.5–25	0.9996	0.2
Methomyl	0.5–25	0.9998	0.2
Ph	0.4–25	0.9988	0.2
4-NP	0.2–25	0.9995	0.1
2,4-DNP	0.5–25	0.9998	0.2
Bentazone	0.2–15	0.9996	0.1
MCPA	0.5–25	0.9989	0.2

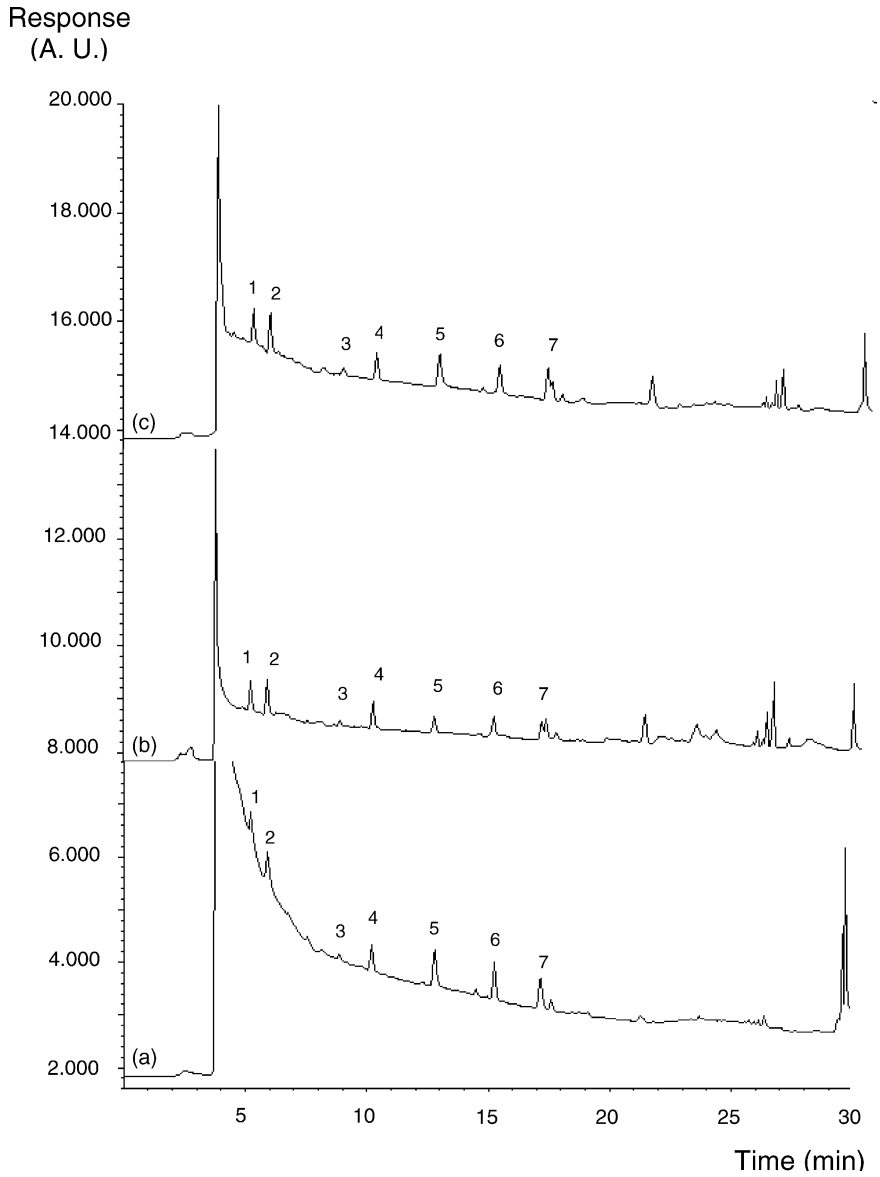

Fig. 1. Chromatograms obtained by on-line trace enrichment of 100 ml of Ebre river water spiked at 1 $\mu g\,l^{-1}$ level of the analytes without (a) and with the addition of 1000 μl (b) and 400 μl (c) 10% Na_2SO_3 solution for every 100 ml of sample. Peak designation: (1) oxamyl, (2) methomyl, (3) phenol, (4) 4-NP, (5) 2,4-DNP, (6) bentazone, (7) MCPA.

Table 3 summarizes the recoveries obtained by percolating 100 ml of tap and Ebre river water sample spiked with the analyte mixture at 0.5 $\mu g\,l^{-1}$ with the addition of 400 μl of 10% Na_2SO_3. The results with real water samples are similar to those obtained with Milli-Q water samples.

The linear range, detection limits (LODs) (calculated as the response for which the signal-to-noise ratio was 3), repeatability and reproducibility (between days) were determined for the total analytical system including the preconcentration step for 100 ml of spiked Ebre river water with the addition of 400 μl of 10% Na_2SO_3. Table 4 shows the linear range and LODs. The method's repeatability and reproducibility, expressed as the relative standard deviation (RSD) of five analyses of 100 ml of Ebre river water spiked at 0.5 $\mu g\,l^{-1}$ were lower than 11% for all the compounds.

Subsequent analyses of samples taken from different points of the Ebre river revealed that one of the samples had a compound at the same retention time as phenol but this could not be quantified because it concentration it was between the detection limit and the quantification limit.

4. Conclusions

It has been shown that the VIm–DVB polymeric sorbent gives good recoveries in the extraction of polar compounds. The recoveries values are comparable to other hydrophilic polymeric sorbents, such as the VP–DVB resin or commercial highly crosslinked sorbents both in on- and off-line mode.

Polar compounds at low $\mu g\,l^{-1}$ levels were efficiently extracted from 100 ml of real water samples with the addition of 400 μl of 10% Na_2SO_3 by on-line SPE and quantitative recoveries were obtained.

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