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On-line and off-line solid-phase extraction with styrene–divinylbenzene-membrane extraction disks for determining pesticides in water by reversed-phase liquid chromatography–diode-array detection

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Abstract

The determination of a group of pesticides, two phenylureas, six triazines and four organophosphorous compounds was carried out using off-line and on-line solid-phase extraction–RPLC–diode-array detection using styrene–divinylbenzene-membrane extraction disks. Both systems are intercompared and their advantages and disadvantages are discussed. Lower limits of detection can be reached by the on-line method, which enables levels of 0.1 $\mu g\ l^{-1}$ of most pesticides to be determined in tap water, as is required by European Community (EC) rules, whereas the off-line mode gives higher limits of detection, but it is possible to determine the pesticides at levels recomended by EC rules for surface water (1–3 $\mu g\ l^{-1}$).

Keywords: Environmental analysis; Water analysis; Membrane extraction disks; Sample preparation; Pesticides

1. Introduction

Pesticides are widely used for agricultural purposes and it is important to monitor these compounds in environmental samples because of their toxicity. At present, European Community (EC) regulations limit the concentration of individual pesticides and toxic by-products in drinking water to 0.1 $\mu g\ l^{-1}$ and the total concentration to 0.5 $\mu g\ l^{-1}$ [1]; in surface water, these limits are about an order of magnitude higher (1–3 $\mu g\ l^{-1}$) [1].

Liquid chromatography and gas chromatography are the most used techniques for determining pesticides in water [2–4]. Depending on their polarity, volatility and thermodegradability, the use of one technique or another is preferred. The inherent advantage of GC is the high sensitivity of its detectors and its easy interfacing with mass spectrometry, but for medium and highly polar compounds, LC technique gives better results [5–8]. The use of diode-array detection (DAD) enables confirmation of the results through spectral comparison [9–11]. Obviously, this technique is much easier to handle than HPLC coupled to mass spectrometry with various interfaces such as thermospray [12,13], particle beam [10,14] and electrospray [15].

As HPLC–DAD does not give the detection limits required, it is necessary to introduce an enrichment step prior to the chromatographic analysis. Of the different techniques available at present, solid-phase extraction (SPE) is preferred because of its advantages over liquid–liquid extraction (LLE) [16–19]. In the SPE methods, cartridges and disks containing different sorbents can be used. The main advantages of the disks over the cartridges are the higher sampling flow-rate and the higher capacity for the

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same amount of sorbent because of a more homogeneously packed sorbent bed, the absence of channelling because the sorbent particles are immobilized and the possibility of using different types of sorbents in the same analysis [19–22]. Membrane extraction disks, mainly with C_{18} and styrene–divinylbenzene (S–DVB), have been used to determine a great deal of pesticides in the off-line mode [4,22–24] and they have already used in a few standard methods [2]; studies of pesticide stability in disks show they can be used to store the sample once it has been preconcentrated instead of storing high volumes of sample [19]. C_{18} membrane disks are widely used for pesticides [22,23] but S–DVB membrane disks have not been so studied although they have higher retention for some compounds, especially for medium and highly polar pesticides [23]. The on-line method has been increasingly used in recent years because the off-line method has several disadvantages, such as the loss of more volatile analytes, the use of organic solvents and sample handling [25–31]. In the on-line procedure, the most used technique is the precolumn containing the sorbent, but disks can also be coupled to the chromatographic system [21,28] with a special device.

The aim of this paper is to compare the results of an on-line SPE with the ones of an off-line SPE, using S–DVB membrane extraction disks in both systems, for the determination of a group of pesticides by RPLC–DAD. The pesticides included in this study are a group of six triazines, two phenylureas and four organophosphorous compounds. The optimization of different parameters affecting the chromatographic separation and the SPE procedures was carried out.

The performance of the methods was checked with tap and river water samples.

2. Experimental

2.1. Chemicals

All pesticides were of 98–99% purity and were obtained from Riedel-de Häen (Seelze, Germany). Stock solutions of 1000 μg ml^{-1} of each compound were prepared in HPLC-grade methanol (Scharlau, Barcelona, Spain) and were stored in the refrigerator at 4°C. Working solutions of all pesticides, at a concentration of 40 μg ml^{-1}, were prepared in methanol and used to spike water samples.

HPLC-grade acetonitrile and methanol were obtained from Scharlau. Ultra-pure water was prepared by ultrafiltration with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Phosphate buffer was prepared by dissolving an appropriate amount of disodium hydrogen phosphate and potassium dihydrogen phosphate, both of them supplied by Merck (Darmstadt, Germany).

The styrene–divinylbenzene membrane-extraction disks were Empore disks manufactured by 3M (St. Paul, MN, USA) and supplied by J.T. Baker (Deventeer, Netherlands). They were 0.5 mm thick and 47 mm in diameter and each contained 500 mg of S–DVB.

Helium for the mobile phase degasification system was 99.995% pure and was supplied by Carburos Metálicos (Tarragona, Spain).

2.2. Chromatographic conditions

Chromatographic analyses were performed with an HP 1090 Series II liquid chromatograph (Hewlett-Packard, Palo Alto, CA, USA), equipped with a ternary solvent-delivery system, an injection valve with a 25 μl loop and an HP 1040M diode-array detector. The separation was carried out using a Spherisorb ODS-2 column (25×0.46 cm I.D., 5 μm particle size) (Hewlett-Packard). For multi-wavelength monitoring, the DAD was set at 220, 254 and 280 nm with a bandwidth of 4 nm. Absorbance spectra were recorded from 200 to 400 nm. Chromatographic data were collected and recorded using the HP 79994A Workstation.

The chromatographic separation was carried out using a gradient profile of a phosphate buffer (pH 7) containing 5% acetonitrile (solvent A) and acetonitrile (solvent B), going from 15% of solvent B to 30% in 15 min and 100% of solvent B at 35 min and then back to the initial conditions in 5 min. All solvents were degassed with helium. The flow-rate of the mobile phase was 1 ml min^{-1} and the column temperature was kept at 40°C.

2.3. Off-line solid-phase extraction procedure

A standard Millipore 47 mm filtration apparatus was used. The extraction procedure was as follows: the disks, placed in the conventional Millipore apparatus connected to a vacuum system, were conditioned with 10 ml of methanol, then with 10 ml of acetonitrile and finally with 10 ml of Milli-Q purified water. The spiked samples with a previous addition of 10 g l^{-1} of NaCl were passed through the S–DVB disks, under an adjusted vacuum at a flow-rate of about 20 ml min^{-1}. The disk was not allowed to dry completely during the extraction process. The pesticides trapped on the disk were collected with 10 ml of acetonitrile and this was then transferred to a concentration tube and the solution was concentrated to 1 ml. An aliquot of 25 μl was injected into the LC system.

2.4. On-line solid-phase extraction procedure

In the on-line SPE mode, the precolumn consists of a stainless-steel membrane disk holder constructed in the workshop of the Free University of Amsterdam, in which nine 4.6 mm I.D. S–DVB Empore extraction disks were placed [28]. A cutting device was used to cut small membrane disks from the original 47mm disks and arrange them in the holder. For trace enrichment, an LC-9A Shimadzu pump was used to deliver the sample to the precolumn.

The membrane disk holder was connected to the analytical column by a switching valve. The disks were flushed with 15 ml of methanol at 5 ml min^{-1}, and 5 ml of the chromatographic separation's solvent at initial conditions, at 1 ml min^{-1}. Subsequently, a 100-ml sample was preconcentrated at a flow-rate of 5 ml min^{-1}. After switching the valve, the analytes trapped on the membrane extraction disks were eluted in the backflush mode with the initial chromatographic conditions and were transferred to the analytical column.

2.5. Sample pretreatment

Water samples from the Ebro river were filtered through a 0.45-μm PTFE filter (Millipore) before the preconcentration step, to eliminate particulate matter. Samples were spiked with the different pesticides and 10 g l^{-1} of NaCl was added to all of them prior to the extraction process.

3. Results and discussion

3.1. Analytical LC separation

Acetonitrile was chosen as the organic modifier because of its lower absorbance at low wavelengths. As regards the aqueous solvent, three different solvents of different pH values were tested for linear gradient separation.

An aqueous solution, adjusted to pH 3 with perchloric acid, was the first mobile phase tested. This acid is recommended because of its low absorbance at low wavelengths [32], but some compounds were not present in the chromatogram. Another mobile phase tested was KH_2PO_4 adjusted to pH 5 with perchloric acid, but there was a significant baseline distortion although the three triazines were eluted in a reasonable time. Finally, the third aqueous solution tested was of pH 7 and it was prepared with 0.01 *M* Na_2HPO_4 and 0.01 *M* KH_2PO_4. The elution profile used is included in Section 2.

Quantification of the different compounds was carried out at its maximum absorbance value. Thus, all the compounds were measured at 220 nm, with the exception of isoproturon (254 nm) and fenitrothion (280 nm).

The linearity of the response of the chromatographic method was checked by injecting 25 μl of a solution of pesticides at levels between 0.2 and 40 mg l^{-1}. The linearity was good for all compounds $r^2>0.998$) but for organophosphorous compounds linearity was between 1.0–40 mg l^{-1} (chlorpyriphos-methyl and fenitrothion) and 4.0–40 mg l^{-1} (fenchlorophos and parathion-ethyl).

Low sensitivity of the technique for the organophosphorous compounds in this study can be seen, much as was expected. It is known that higher sensitivity can be obtained with some of the common detectors of gas chromatography, but here the possibility of including some of these compounds in the same RPLC analysis together with other pesticides, such as triazines and phenylureas, will be studied.

3.2. Off-line solid phase extraction system

To determine the optimum conditions of the extraction process, several variables were optimized. The first parameter studied was the extraction solvent for the elution of the compounds retained in the S–DVB disk. A 100-ml volume of Milli-Q water, spiked with a standard solution of pesticides at a level of 1 mg l^{-1}, was passed through the disk. The disks were eluted with different volumes of acetonitrile or methanol. The best recoveries were obtained with the first solvent and the recovery did not improve for any of the volumes tested that were higher than 10 ml. So the eluting solvent was 10 ml of acetonitrile.

A blank of the membrane extraction disks was checked in order to observe the presence of any peak that could elute at the same retention time as one of the pesticides, but none was found. In fact, some studies have already shown the high chemical stability of S–DVB disks [19].

In order to study the effect of pH on the pesticides' recovery, two different conditions were tested: a pH of 3 (acidified with HCl) and a pH of about 7, with no pH adjustment. No significant differences were found, so further analysis were carried out with no pH adjustment.

The next parameter was the addition of sodium chloride, because it has been shown that for some compounds higher ionic strength increases the retention [4]. In a previous paper [4], 10 g l^{-1} of NaCl was added although other authors [33] used concentrations as high as 100 g l^{-1}. We tried adding 10, 20 and 100 g l^{-1} of NaCl and although the addition of 10 g l^{-1} increased the recoveries for some compounds compared with the results without NaCl addition, especially terbutryn and the organophosphorous compounds, no improvement was observed with the addition of higher amounts.

Finally, the sample volume preconcentrated onto the disk was examined to test differences in recoveries. The extraction process was carried out with 100, 250, 500 and 1000 ml of Milli-Q water spiked with pesticides at different levels, involving the same amount of pesticides, which were passed through the disk. The results of recovery against sample volume are given in Table 1. When 1000 ml of sample were preconcentrated there was a significant decrease in the recovery of organophosphorous pesticides, so from these results, a 500-ml volume was chosen as the optimum volume. However, for triazine and phenylurea pesticides, higher sample volumes can be used, which enables the detection of lower concentrations of pesticides.

The performance of the method for real samples was tested in tap and Ebro river water. On the first instance, 500 ml of tap water containing 10 g l^{-1} of NaCl was analysed and since no peaks corresponding

Table 1
Recoveries and R.S.D. ($n=3$) for the off-line preconcentration with S–DVB disks of different Milli-Q water volumes. Study of sample volume

Pesticide	Sample volume (ml)							
	100		250		500		1000	
	Recovery (%)	R.S.D.	Recovery (%)	R.S.D	Recovery (%)	R.S.D	Recovery (%)	R.S.D
Simazine	91	5.3	92	5.8	92	6.3	80	7.2
Cyanazine	92	4.6	90	6.4	92	5.6	76	7.8
Chlortoluron	69	5.1	67	8.1	67	6.4	63	9.9
Atrazine	80	6.3	79	7.6	77	5.9	78	4.6
Isoproturon	101	3.8	101	7.4	103	4.3	94	6.7
Ametryn	87	4.2	83	5.9	80	6.8	79	6.2
Prometryn	78	6.9	80	6.2	76	7.2	73	9.8
Terbutryn	75	7.8	70	9.4	71	5.3	69	8.3
Chlorpyriphos-methyl	78	5.9	73	7.9	69	6.2	38	6.8
Fenitrothion	70	6.6	67	8.3	68	4.0	23	8.1
Fenchlorphos	88	8.2	83	7.7	85	5.4	30	7.3
Parathion-ethyl	79	5.4	80	6.2	76	4.9	43	5.9

Table 2
Recoveries and R.S.D. ($n=3$) for the preconcentration with S–DVB disks of 500 ml of sample spiked at a level of 4 $\mu g\ l^{-1}$

Pesticide	Tap water		River water	
	Recovery (%)	R.S.D.	Recovery (%)	R.S.D.
Simazine	94	8.3	76	7.2
Cyanazine	96	7.2	92	6.4
Chlortoluron	58	12.3	61	15.1
Atrazine	78	9.3	74	11.2
Isoproturon	103	6.9	100	7.4
Ametryn	81	6.4	80	9.3
Prometryn	76	6.3	74	8.0
Terbutryn	75	8.2	71	9.1
Chlorpyriphos-methyl	70	5.5	67	9.2
Fenitrothion	60	4.2	64	6.3
Fenchlorphos	84	8.0	88	6.8
Parathion-ethyl	79	7.1	71	10.3

to any pesticide studied were present, this water was used as the blank for measuring the recoveries. Recoveries obtained for a tap water sample spiked at a level of 4 $\mu g\ l^{-1}$ are shown in Table 2. The linearity for the total method was also tested and the results obtained are included in Table 3. The same analysis was carried out with Ebro river water and the recovery values and the R.S.D. ($n=3$) obtained for a 500-ml sample, spiked at a level of 4 $\mu g\ l^{-1}$, are shown in Table 2. As can be seen, similar recoveries were obtained for tap and river water. The linearity values were also similar to those obtained for tap water. This means that, although there was a greater amount of organic matter present in river water, the capacity of the disks was sufficient. The chromatogram corresponding to a 500-ml sample of Ebro river water and the sample spiked at the 1 $\mu g\ l^{-1}$ level are included in Fig. 1. A peak at the same retention time as terbutryn appeared in the chromatogram, but from the spectra comparison it could not be confirmed as such.

The repeatability of the method was determined by analyzing 500 ml of spiked tap water and river water. R.S.D. ($n=3$) values were between four and twelve, and six and fifteen respectively. The limit of detection ($S/N=3$) of the method was between 0.05 $\mu g\ l^{-1}$ and 1.0 $\mu g\ l^{-1}$ for tap water and similar values were obtained for river water.

It should be pointed out that the method is suitable for determining pesticides in river water, but it does

Table 3
Range of linearity, r^2 and detection limit (L.O.D.) for the on-line method

Pesticide	Off-line method			On-line method		
	Range of linearity ($\mu g\ l^{-1}$)	r^2	L.O.D. ($\mu g\ l^{-1}$)	Range of linearity ($\mu g\ l^{-1}$)	r^2	L.O.D. ($\mu g\ l^{-1}$)
Simazine	0.5–50	0.9985	0.1	0.1–8	0.9990	0.03
Cyanazine	0.5–50	0.9973	0.1	0.1–8	0.9987	0.03
Chlortoluron	0.5–50	0.9960	0.1	0.2–8	0.9956	0.05
Atrazine	0.5–50	0.9980	0.1	0.1–8	0.9999	0.03
Isoproturon	1.0–50	0.9990	0.1	0.2–8	0.9993	0.05
Ametryn	0.5–50	0.9985	0.05	0.1–8	0.9993	0.03
Prometryn	0.5–50	0.9989	0.05	0.1–8	0.9995	0.03
Terbutryn	0.5–50	0.9980	0.05	0.1–8	0.9985	0.03
Chlorpyriphos-methyl	2.0–50	0.9962	0.5	0.5–8	0.9980	0.20
Fenitrothion	2.0–50	0.9983	0.5	0.5–8	0.9993	0.20
Fenchlorphos	5.0–50	0.9950	1.0	1.0–8	0.9927	0.30
Parathion-ethyl	5.0–50	0.9944	1.0	1.0–8	0.9995	0.30

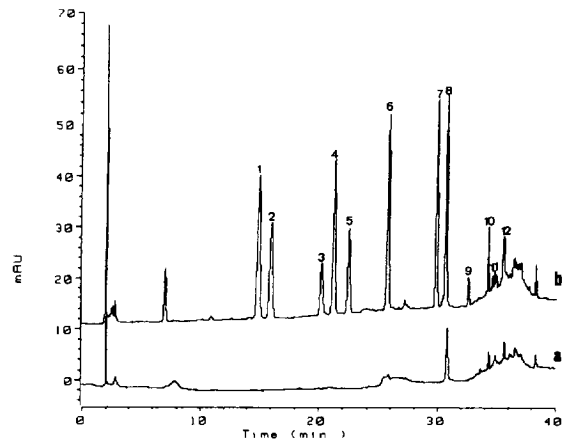

Fig. 1. Chromatogram at 220 nm after the S–DVB disk extraction of: (a) a 500-ml sample of river water, (b) a 500-ml sample of river water spiked with pesticides at 1 $\mu g\ l^{-1}$. 1, simazine; 2, cyanazine; 3, chlortoluron; 4, atrazine; 5, isoproturon; 6, ametryn; 7, prometryn; 8, terbtutryn; 9, chlorpyriphos-methyl; 10, fenitrothion; 11, fenchlorphos; 12, parathion-ethyl.

not reach the levels required by the EC for drinking water.

3.3. On-line solid-phase extraction system

The different parameters that affect the response for the on-line solid-phase extraction preocedure were optimized and thus, the effects of pH and the addition of sodium chloride were studied.

Different pH values were tested, pH 4 and a pH of about 7 and, as in the off-line mode, no significant differences were found and thus, analysis were also carried out with no pH adjustment.

The effect of the addition of sodium chloride to water samples was also confirmed by the on-line procedure and a significant improvement was observed mainly for organophosphorous compounds when 10 $g\ l^{-1}$ of NaCl were added.

Different Milli-Q water volumes were preconcentrated in order to select the maximum volume that rendered good recoveries. The volumes were 10, 50, 100 and 150 ml and were spiked at different concentrations in order to reach the same amount of pesticides. From the results obtained, a sample volume of 100 ml was chosen because an important decrease was observed for parathion-ethyl with higher volumes, although for the rest of compounds only a slight decrease was observed.

The performance of the method was tested with tap and Ebro river water. The recovery values in both cases were similar to those obtained with Milli-Q water. The linearity of the response for the complete method was tested by preconcentrating 100 ml volumes of tap water spiked at different levels of pesticides. The linearity range, correlation coefficient and limits of detection ($S/N=3$) are shown in Table 3. From these results, it can be deduced that the method enables the determination of low levels of pesticides in tap water, except for organo-phosphorous compounds, because of its lower sensitivity to these compounds.

The same analysis was carried out for river water samples and good linearity was also obtained for the same range. Fig. 2 shows the chromatogram obtained for the analysis of 100 ml of river water sample and the same sample spiked at 1 $\mu g\ l^{-1}$.

The repeatability of the method was checked with a 100-ml volume of tap water spiked at a level of 4 $\mu g\ l^{-1}$ with an addition of 10 $g\ l^{-1}$ of sodium chloride. R.S.D. values were between 0.4 and 11% ($n=3$). Reproducibility between days was also

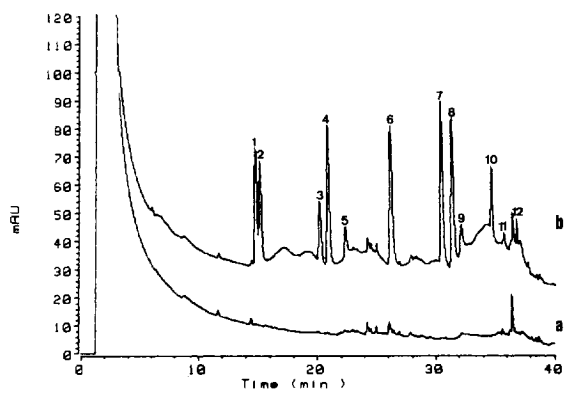

Fig. 2. On-line trace enrichment RPLC–DAD chromatogram at 220 nm of 100 ml of Ebro river water (a) and 100 ml of Ebro river water spiked with pesticides at 1 $\mu g\ l^{-1}$ (b). Peak numbers are as in Fig. 1.

checked for the same level of pesticides in tap water and R.S.D. values were lower by up to 10%.

It should be pointed out that the peak that appeared at the beginning of the chromatogram is usually much higher with S–DVB than with C_{18} disks, but even this does not interfere with the determination of these pesticides. However, in the off-line procedure, no significant peak appeared at the beginning of the chromatogram.

3.4. Comparison between off-line and on-line procedures

Comparing the application range for both procedures, the on-line procedure enables lower concentrations of pesticides to be determined and for most compounds the EC regulations can be achieved. On the other hand, for river water, both procedures can get the levels required, although on-line procedure enables the determination of lower concentrations of pesticides compared with the off-line procedure. Moreover, the on-line procedure requires lower volumes of samples and involves an automation of the analysis and thus, a shorter time of analysis.

4. Conclusions

A selection of pesticides, including the organophosphorous compounds, were determined in one run in tap and river water by SPE–RPLC and DAD. The best conditions for the SPE procedures involve a sample volume of 500 ml for the off-line mode and a 100-ml volume for the on-line mode. NaCl was added in order to increase the recovery of some pesticides. Good linearity was obtained for both procedures. With the on-line procedure, most pesticides are determined at a level of 0.1 $\mu g\ l^{-1}$, the maximum concentration allowed in drinking water by the EC. For river water, both procedures reach the levels required for most compounds. Repeatability and reproducibility are good in both cases. The on-line procedure involves a shorter time of analysis, less manipulation of sample, lower volumes of organic solvents and lower limits of detection.

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