Short communication

Solid-phase extraction disks for determining pesticides from soil leachates

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Abstract

Analytical techniques are essential for identifying and quantifying the chemicals present in environmental samples. A method for extracting pesticides from soil leachates was developed. The proposed method is based on solid-phase extraction and uses 47-mm disks of octyl-bonded silica. Analysis was carried out by gas chromatography with nitrogen–phosphorus and electron-capture detectors. Several factors that can provide better pesticide recoveries with this extraction method are discussed. These factors are: the kind and percentage of organic solvent used in the extraction procedure, the volume and the ionic strength (adding 15% of NaCl) of the aqueous phase which passes through the octyl-bonded silica sorbent. Finally, the proposed method was used to determine the pesticide concentration of leachates from soil samples taken from different plots of an important intensive agricultural area. © 1997 Elsevier Science B.V.

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1. Introduction

Environmental contamination caused by agricultural activities has increased constantly over the last few years. A wide variety of pesticides reach the soil in the agricultural area where they are applied, but they may be carried off soils and into surface waters by leaching as consequence of water displacement in soil environment [1,2].

Identifying the potential of pesticides for leaching to groundwater is important for assessing aquatic contamination. Therefore, finding an analytical method for determining the real concentration of chemicals present in samples as soil leachates, is of tremendous interest.

Solid-phase extraction (SPE) is widely used to determine pesticide residues in a large variety of environmental samples. It involves different solid phases packed in cartridges and disks [3–5]. Up till now, off-line SPE techniques have been more commonly used, but the use of on-line sample treatment in chromatographic determination is steadily increasing due its great versatility and also because it permits the injection of large volumes into the GC, thus increasing sensitivity [6,7]. The main difficulties encountered with any kind of bonded silica phase are caused by the presence of suspended particles in the sample, mainly when large volumes of sample are being processed. With respect to the performance of the SPE using the different types of phases, it has been reported that disks offer certain advantages over columns, because disks give higher extraction flow-

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rates than the traditional cartridges, which consequently leads to a decrease in processing time [3,4,8]. Octyl- and octadecyl-bonded silica sorbents are well suited for extraction of nonpolar or semipolar pesticides from water samples [9–13], sediments [14] or soil samples [15,16]. Membrane extraction disks with styrene–divinylbenzene have also been used to determine a large number of pesticides in water samples [17].

In this study we report the performance of an analytical method for determining pesticides in leachates by means of SPE with a C_8 membrane disk and capillary GC. Different experiments were carried out to optimize this method, modifying some of the factors which can provide better pesticide recoveries. The optimal aqueous solution volume, kind and percentage of organic solvent added just before the extraction to improve the contact between pesticide and bonded silica sorbent, and the influence of the ionic strength of the aqueous phase after adding 15% of sodium chloride, were all examined.

2. Experimental

2.1. Chemical and reagents

Triazines (atrazine, prometrine, propazine and simazine), carbamates (carbofuran, molinate, pirimicarb and thiobencarb), organophosphorus pesticides (chlorpyrifos, diazinon, malathion, methylchlorpyrifos and tetrachlorvinphos), the substituted anilide propanil and the organochlorine pesticide tetradifon were obtained from Promochem (Wesel, Germany). All of them with purity greater than 98%.

Ethyl acetate of pesticide grade was from Promochem, N,N-dimethylformamide (DMF) and tert.-butanol were from Merck (Darmstadt, Germany). Methanol was from Romyl (Leics., UK). Sodium chloride (NaCl) was from Panreac (Barcelona, Spain).

All pesticides stock solutions of 1000 μg/ml are prepared in ethyl acetate. Standard fortification solution is prepared in an adequate solvent at levels between 0.5 and 5 μg/ml.

2.2. Extraction apparatus

A standard Millipore 47-mm filtration apparatus equipped with 47-mm disks of octyl-bonded silica Empore (Varian, Harbor City, USA) was used.

2.3. Gas chromatographic analysis

Identification and quantification of chemical analytes were conduced using GC techniques. GC is performed with a Hewlett-Packard 5890-Series II (Waldbronn, Germany), equipped with a nitrogen–phosphorus detector (NPD) and electron-capture detector (ECD), an automatic injector Model H-P 7673 and an H-P 3365 integrator. The injector and detector temperatures were 285 and 300°C, respectively. Two capillary columns were assayed, a 30 m DB-17 capillary column, film thickness 0.25 μm provided by J&W Scientific (Folsom, CA, USA), and a 25 m RSL 400 capillary column with 0.2 μm film thickness provided by Alltech (Kromxpex Analitica S.A., Barcelona, Spain)

Splitless injection was performed at oven temperature of 50°C. This temperature was programmed (50°C to 140°C at a rate of 30°C min^{-1}, held 2 min, then at 1°C min^{-1} to 152°C, and then at 10°C min^{-1} to 240°C). Helium is used as carrier gas, at 1.6 ml min^{-1}. Detector gases: air 70.9 ml min^{-1}, hydrogen 2.7 ml min^{-1} and helium 18.3 ml min^{-1}.

2.4. Preparation of leachates from soil samples

The leaching procedure was carried out according to official methods (84/449/EEC) [18]. The leachates were prepared by means of a 24-h extraction with Milli-Q water. After filtration through a membrane filter with a pore size of 0.45 μm, which uses a pressure filter apparatus under nitrogen gas pressure (HWSF Millipore filtration system), the aqueous extracts were stored at 4°C until analysis.

2.5. Extraction procedure

Once the leachate is obtained, the extraction procedure is carried out by decanting 100 ml of this aqueous solution into a reservoir, and adding 2.5 ml

of DMF. These are the optimal conditions to obtain the best pesticide recoveries. Then, the sample was passed through a conditioned 47-mm disk of octyl-bonded silica sorbent, previously activated with methanol and distilled water. The adsorbed residues are eluted with 10 ml of ethyl acetate. The extract is concentrated at 45°C to 1 ml, and 2-μl samples are injected into the GC system.

3. Results and discussion

3.1. Gas chromatography

The RSL-400 capillary column provides better resolution of all pesticides than the DB-17 column, so the RSL-400 was selected to perform the GC analyses.

Fig. 1 shows the chromatograms, with the RSL-400 column, of an extract obtained by the SPE procedure described, from a non-fortified leachate and a leachate spiked with 1 ml of the fortification solution. The SPE technique provides clean blank extracts without interferences during GC, and therefore, clean-up of the leachate from soil is not required.

3.2. Extraction method

Recovery studies were performed by spiking the leachates with 1 ml of the standard fortification solution. The best recoveries were obtained using 100 ml of leachate adding with 2.5 ml of DMF as organic solvent, as is shown in Table 1.

Limits of detection (LODs) of the proposed method were calculated by extrapolation and represent amounts that produce a chromatographic peak with a height equal to three times the standard deviation of the baseline noise [19]. Detection limits (μg/l in soil leachate) were 0.2 for prometrine, 0.3 for atrazine, pirimicarb and thiobencarb, 0.4 for malathion, simazine and tetradifon, 0.6 for methylchlorpyrifos, 0.7 for chlorpyrifos and molinate, 1.0 for diazinon, 1.2 for tetrachlorvinphos, 1.3 for propanil, 1.4 for carbofuran and 1.8 for propazine.

3.3. Factors affecting solid-phase extraction

3.3.1. Effect of aqueous solution volume on octyl-bonded silica disks

Since pesticide structures vary greatly, the aqueous solution volume is an important parameter to optimize in the extraction procedure.

Different volumes of the leachate are examined: 100, 250, 500 and 1000 ml. When the aqueous solution volume increase, pesticides highly soluble in water like carbofuran, pirimicarb and propanil, show sharp decreases in their recoveries. These results are in agreement with those reported by Chiron and Barceló [10]. Also, triazine herbicides show a significant decrease in their recoveries. However, for the carbamate molinate, recoveries increase slightly when the aqueous solution volume increases, thus coinciding with the results reported by Jiménez et al. [20].

The more hydrophobic compounds like chlorpyrifos, malathion, methylchlorpyrifos, tetrachlorvinphos and tetradifon were extracted with large volumes of aqueous phase without losses, but passing large volumes through the extraction disk extends analysis time unnecessarily.

In conclusion, 100 ml of aqueous solution volume was chosen as the optimum volume, because this volume passes through the 47-mm Empore disk quite rapidly, and, moreover, it is the volume which provides the highest pesticide recoveries.

3.3.2. Proportion and kind of organic solvent

Three different organic solvents, ethyl acetate, DMF and tert.-butanol were added at different volumes (1, 2.5 and 5 ml) to 100 ml of leachate in order to establish how affect the solid membrane capacity for retaining pesticides.

The results demonstrated that the best recoveries, for all the pesticides tested, are obtained with 2.5 ml of DMF in the aqueous solution with recovery rates higher than 80% for eight of the studied pesticides. Use of a large amount of DMF (>2.5 ml) does not result in improved pesticide recoveries, except in the case of chlorpyrifos. Data of 2.5-ml additions for the other two solvents indicate that both ethyl acetate and tert.-butanol give worse overall recoveries. R.S.D. (n=5) values were between 4 and 14 for all kinds and percentages of organic solvent tested.
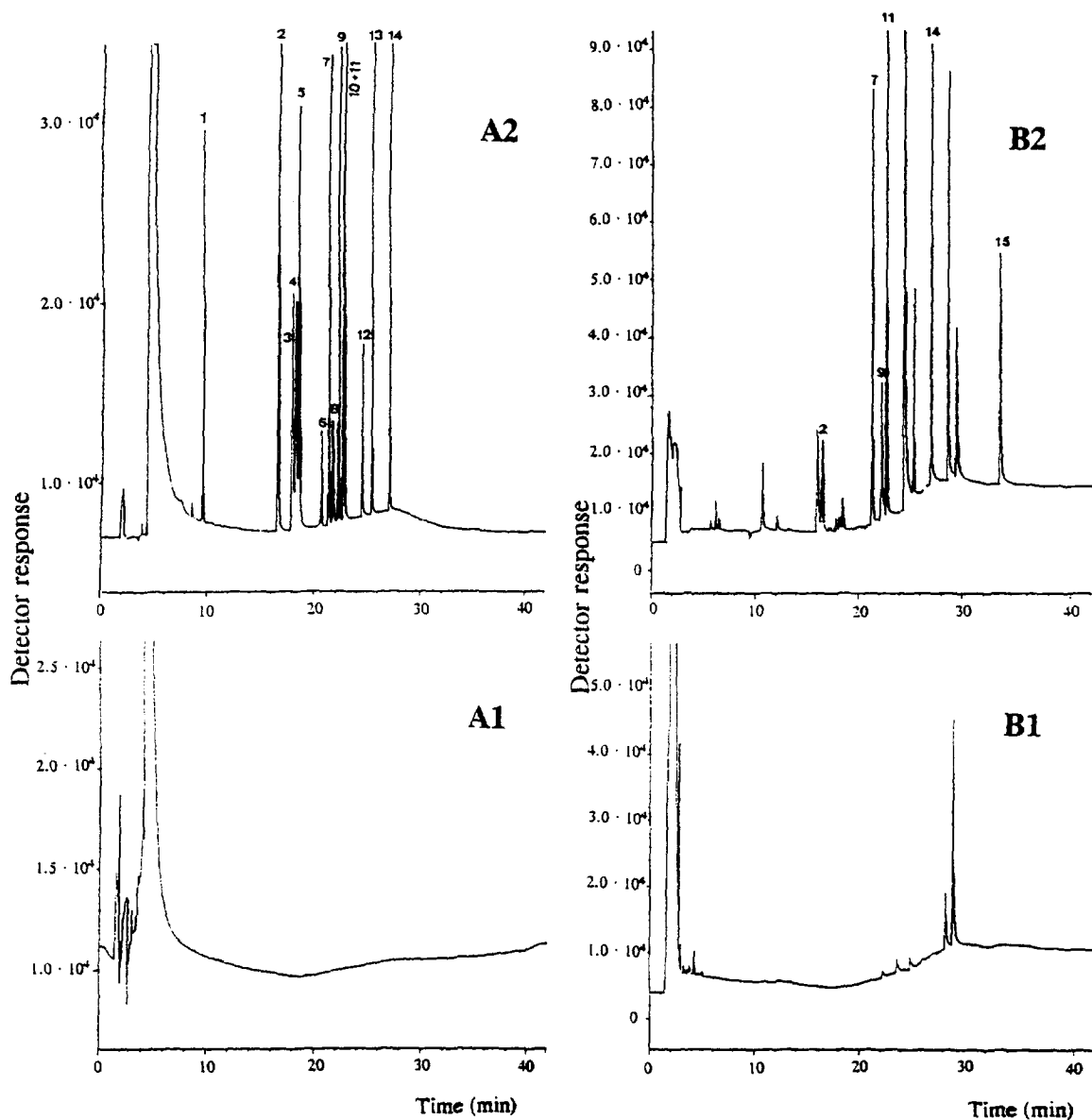
Fig. 1. Gas chromatograms showing the separation of pesticides after SPE with the proposed method. (A) NPD detection: (A1) extract of non-fortified leachate; (A2) extract of leachate spiked with fortification solution. (B) ECD detection: (B1) extract of non-fortified leachate; (B2) extract of leachate spiked with fortification solution. Peaks: 1=molinate, 2=diazinon, 3=propazine, 4=atrazine, 5=simazine, 6=carbofuran, 7=methylchlorpyrifos, 8=prometrine, 9=thiobencarb, 10=pirimicarb, 11=chlorpyrifos, 12=propanil, 13=malathion, 14= tetrachlorvinphos, and 15=tetradifon.

3.3.3. Addition of 15% sodium chloride

The effect of salt addition on bonded silica sorbent has been investigated previously, but the results are highly variable. Some authors have observed a positive effect on adsorption of some herbicides and some organochlorinate and organophosphorus pesticides on octyl or octadecyl-silica [20–22]. However, the addition of 10 g/l NaCl to the aqueous

Table 1

Mean recoveries (%) of pesticides in 100 ml of liquid phase after SPE using different kind and percentage of organic solvent in the extraction

Pesticide	Recoveries (%)				
	DMF			Ethyl acetate	*tert.*-Butanol
	1 ml	2.5 ml[a]	5 ml	2.5 ml	2.5 ml
Atrazine	69	90	57	79	62
Carbofuran	87	67	43	28	31
Chlorpyrifos	54	55	70	38	65
Diazinon	81	90	67	65	82
Malathion	72	86	69	66	68
Methylchlorpyrifos	52	56	69	51	62
Molinate	45	53	69	61	68
Pirimicarb	67	86	72	49	48
Prometrine	64	92	83	63	74
Propanil	78	92	80	80	79
Propazine	75	75	74	53	67
Simazine	76	70	54	49	49
Tetrachlorvinphos	63	92	92	83	77
Tetradifon	64	70	73	50	78
Thiobencarb	73	85	69	56	74

[a] DMF volume used in the proposed extraction method.

phase has no significant effect on the extraction of triazines and organophosphorus pesticides with styrene–divinylbenzene disks [17].

Recoveries with and without addition of 15% NaCl to 100 ml of leachate volume with 2.5 ml DMF are shown in Fig. 2. On the whole, the increase of ionic strength has a slightly negative effect on pesticide recoveries. This effect is greater for the more polar compounds of the pesticides studied, like carbofuran, pirimicarb and molinate, and coincides with the results obtained by Albanis and Hela [13].

3.4. Application to real soil leachates

Soil samples were collected from three different plots in Mediterranean agricultural areas, on the basis of their economic significance. The crops raised in these areas were rice, citrus fruits and orchard crops. After collection the samples were passed through a 2-mm sieve and stored at 4°C until analysis. Leachates were obtained as above by the official method, and analyzed according to the proposed method. The characteristics of the leachates

are shown in Table 2 and were also determined according to the official methods.

Because of the widespread and heavy use of pesticides in agriculture in Valencia, detection of pesticides in leachates might have been expected. In spite of this, none of the pesticide searched for were identified by GC techniques after SPE in the leachates.

The study complemented the toxicity data of the leachates provided by the bacteria luminescent *Photobacterium phosphoreum* assay (Microtox), an ecotoxicity test greatly employed to evaluate the acute toxic effects of chemicals on aquatic organisms [23,24]. At 5-min exposure acute toxicity values ranging from 1.2 to 1.8 toxicity units were obtained while after a 15-min exposure toxicity values were between 1.2 and 4.4, implying that leachate samples contain compounds capable of causing a toxicological response, although these values indicate low toxicity [25].

Data from the leachate toxicity bioassay can be explained by the fact that contaminants may exist in concentrations that are below analytical detection
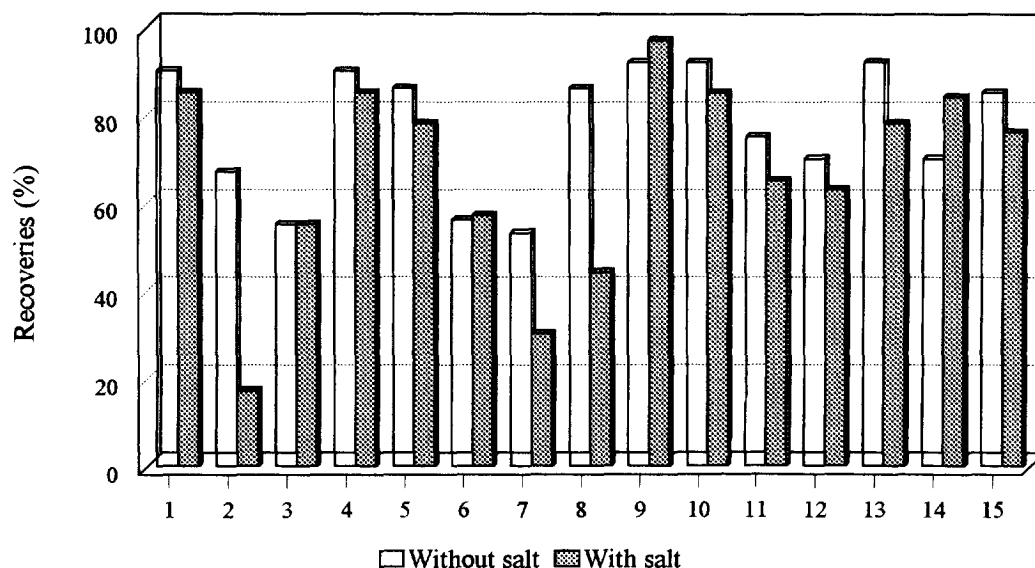
Fig. 2. Pesticide recoveries with and without 15% sodium chloride in the leachate. Peaks: 1=atrazine, 2=carbofuran, 3=chlorpyrifos, 4=diazinon, 5=malathion, 6=methylchlorpyrifos, 7=molinate, 8=pirimicarb, 9=prometrine, 10=propanil, 11=propazine, 12=simazine, 13=tetrachlorvinphos, 14=tetradifon, 15=thiobencarb.

levels but are still able to cause toxicological effect. An alternative explanation is that many pesticide metabolites could be more toxic than the parent compounds, but that because of their different chemical properties it is not possible to analyze them with the same analytical method.

Acknowledgments

Table 2
Characteristics of leachates from soil samples.

Property	Soil A	Soil B	Soil C
pH	4.93	5.75	5.90
Conductivity (mS/cm^2)	2.81	6.96	7.42
Temperature (°C)	29.6	26.1	27.5

A: Citrus soil, B: orchard soil, C: rice soil.

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