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Journal of Chromatography A, 1029 (2004) 267–273
JOURNAL OF CHROMATOGRAPHY A
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Short communication

Continuous solid-phase extraction and gas chromatographic determination of organophosphorus pesticides in natural and drinking waters

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Received 20 June 2003; received in revised form 1 December 2003; accepted 3 December 2003

Abstract

A simple, rapid continuous-flow solid-phase extraction method with gas chromatographic detection for the determination of organophosphorus pesticides is proposed. The continuous system consists of an adsorbent column where pesticides are preconcentrated and subsequently eluted with ethyl acetate. Various sorbent materials were assayed of which RP-C_{18} was found to provide the best results, with a sorption efficiency close to 100%. A comparative study of the determination of pesticides in aqueous samples was conducted using gas chromatography with nitrogen-phosphorus (NPD) and flame ionization (FID) detection. The detection limits of the method for 10 ml of sample were between 50–130 ng/l and 4.5–11.7 μg/l with NPD and FID detection, respectively. The method was used to determine organophosphorus pesticides in river, pond, well and tap waters, all with good precision (2.9–4.3%) and recoveries ranging from 93.8 to 104.5%.

Keywords: Water analysis; Solid-phase extraction; Pesticides; Organophosphorus compounds

1. Introduction

Various types of pesticides have been used over the past decades to fight the enormous number of crop-eating insects that have caused infective and parasitic diseases to humans, and losses to harvests. However, these compounds, and their residues, contaminate ground and surface waters, and food. In most cases, these substances are organochlorines, organonophosphates or carbamates that exhibit a high environmental persistence; this causes various health and safety problems. The analytical interest aroused by organophosphorus pesticides (OPPs) in recent years can be ascribed to the gradual replacement of the highly persistent, bioaccumulative organochlorine pesticides with organophosphates [1].

Environmental waters and water resources for the preparation of drinking water, can only be evaluated with sensitive methods for the determination of OPPs in surface, ground and drinking water. EEC Directive 80/778/EEC [2,3] has established a maximum allowed concentration of 0.1 μg/l for individual pesticides and related products, and of 0.5 μg/l for total pesticides in drinking water [2] and 1–3 μg/l in surface water [3].

In general, environmental water samples cannot be analysed without some preliminary sample preparation; this step is frequently a major source of error. Thus, water samples are still widely processed by liquid–liquid extraction (LLE) with dichloromethane as solvent as this is sufficiently polar enough to efficiently extract most organophosphorus pesticides [4–6]. Other less polar solvents such as *n*-hexane [7], *n*-heptane [8] and cyclohexane [9] provide quantitative extraction of a small number of OPPs. However, liquid–liquid extraction is being gradually superseded by solid-phase extraction (SPE) for the separation of OPPs from water in many methods as a result of the wide availability of selective sorbent materials and also to avoid the need to dispose of organic solvents. Macroreticular Amberlite XAD resins [7,10–12], C_8- [13] or C_{18}-modified silica [14–16] and graphitized carbon black [17] are among the sorbents used for this purpose. Solid-phase microextraction (SPME) is a relatively new extraction technique for the analysis of both gaseous, liquid and solid samples. Thus, SPME has been used to determine organophosphorus pesticides in water samples [18,19].

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doi:10.1016/j.chroma.2003.12.009

The analysis of OPPs in real samples is usually carried out by gas chromatography (GC) or high-performance liquid chromatography (HPLC). The GC detectors most commonly used for this purpose are of the flame ionization (FID) [4,18], nitrogen-phosphorus (NPD) [11,17,20], flame photometric (FPD) [21] or mass spectrometric (MS) type [22,23]. On other hand, UV absorption detectors have been the most widely used to develop HPLC methods for the determination of OPPs [8,24,25]. Other detection methods used in the HPLC determination of these types of pesticide are diode array UV (DAD) [13] and MS [26].

An on-line LC trace enrichment-GC system was used for the determination of OPPs in aqueous samples that consisted of a laboratory-made membrane extraction disk holder and four valves [27]. Also, immunosorbent columns coupled on-line with liquid chromatography/MS were used for the determination of pesticides in natural waters [28]. Finally, a continuous liquid-solid extraction system coupled to a gas chromatograph equipped with an FID was used for the preconcentration of *N*-methylcarbamate pesticides and their metabolites [29].

In this work, we assessed the performance of a continuous solid-phase extraction method for the preconcentration of OPPs in natural and drinking waters. Various sorbents and eluents were tested in order to adopt the best possible analytical conditions for the determination of pesticides at low levels. For this purpose, two gas chromatographic detectors (FID and NPD) were used to determine pesticides at concentrations below the maximum allowed level for individual pesticides [2,3].

2. Experimental

2.1. Materials

The chemicals used as analyte standards and reagents were all reagent-grade or better. Organophosphorus pesticides and bromophos-methyl were obtained from Riedel-de-Haën (Seelze, Germany). All solvents (ethyl acetate, methanol, ethanol, *n*-hexane, dichloromethane and acetone) were supplied by Merck (Darmstadt, Germany). Polymer sorbents such as XAD-7 and XAD-16, and octadecyl derivatized silica gel for reversed phase chromatography (RP-C_{18}), 40–3 μm, were purchased from Sigma (Madrid, Spain). The XAD-2 sorbent and triphenylphosphate were supplied by Supelco (Madrid, Spain) and Fluka, respectively. Finally, the XAD-4 sorbent was obtained from Fluka (Madrid, Spain).

Standard stock solutions containing 10 g/l of each OPP pesticide (dimethoate, diazinon, fenthion, fenthion sulfoxide, malathion, methidathion, parathion ethyl and parathion methyl) were prepared in 99.9% acetone and stored in glass-stopped bottles at 4 °C in the dark. Appropriate volumes of these stock solutions were diluted with Milli-Q water to prepare working-strength solutions containing the organophosphorus pesticides at nanogram-per-litre or microgram-per-litre levels. Ethyl acetate containing 200 μg/l (NPD) or 70 mg/l triphenylphosphate (FID) as internal standard was used as eluent.

2.2. Apparatus

Analyses were performed on an Agilent 6890 Series gas chromatograph and controlled by a computer running Agilent ChemStation software (Agilent Technologies, Madrid, Spain). The GC instrument was equipped with two types of detector (NPD and FID) and a 30 mm × 0.25 mm i.d., 0.25 μm HP-5 (crosslinked 5% phenylmethylpolysiloxane) fused-silica column. Helium, at a flow-rate of 1.0 ml/min, was used as carrier gas. The injector port and detector temperatures were kept at 250 and 300 °C, respectively. The oven temperature program was as follows: 150 °C, ramp to 180 °C at 3 °C/min, held for 16 min; ramp to 240 °C at 10 °C/min, held for 8 min. Sample injection was done in the splitless mode, using an injection volume of 1 μl. Nitrogen was used as make-up gas. The purity of all gases used was greater than 99.999%.

The proposed continuous extraction system consisted of a Gilson Minipuls-3 peristaltic pump fitted with poly(vinyl chloride) pumping tubes; and two Rheodyne 5041 injection valves. PTFE tubing (0.5 mm i.d.) and commercially available connectors were also employed. A custom-made adsorption column packed with RP-C_{18}, silica gel, Florisil, activated charcoal, XAD-2, XAD-4, XAD-7 or XAD-16 was also used.

The sorbent column for SPE was made from poly(tetrafluoroethylene) capillaries (3 mm i.d.). The end-caps were formed by fitting 30 mm × 0.5 mm i.d. PTFE tubing into a 10 mm × 1 mm i.d. PTFE tube, which facilitated insertion into the continuous system, both ends being sealed with small swabs of cotton wool to prevent material losses. The sorbent column was conditioned by passing 200 μl of ethyl acetate, 4 ml of air (sorbent drying step) and 2 ml of Milli-Q water.

2.3. Solid-phase extraction procedure

The flow system used to extract the organophosphorus pesticides from water samples is depicted in Fig. 1. In the preconcentration step, 10 ml of sample or standard solution containing 150–40,000 ng/l (NPD) or 20–8000 μg/l (FID) was passed through the sorbent column (located in the loop of injection valve IV_1) at 4.0 ml/min; retention of pesticides was instantaneous and the sample matrix was sent to waste. In the drying step, IV_1 was switched and the sorbent column dried for 5 min with an air stream at 2.0 ml/min inserted via the carrier line of the second valve (IV_2); simultaneously, the loop of IV_2 (100 μl) was filled with ethyl acetate (eluent) containing the internal standard (200 μg/l or 70 mg/l triphenylphosphate for NPD and FID, respectively) by means of a syringe. In the elution step, IV_2 was switched and the loop

contents (100 μl of eluent) were injected into the same air stream used in the drying step, and passed through the column to elute the pesticides. The whole organic extract was collected in a glass vial containing 25 mg anhydrous sodium sulphate and a 1 μl aliquot was injected into the gas chromatograph for analysis. Triplicate analyses were performed in all tests except the study of precision, where 11 extractions were carried out. Between samples, the sample aspiration channel was flushed with 1 ml of water (containing 2% acetone) and the sorbent column was washed with 200 μl of ethyl acetate and 2 ml of Milli-Q water. Under these conditions, the sorbent column remained active for 4 months.

3. Results and discussion

3.1. Selection of the sorbent and eluent

The selection of the sorbent and eluent was made by using a continuous system similar to that depicted in Fig. 1. Organic extracts were analyzed by GC with FID.

Seven typical sorbent materials for conventional SPE of organic compounds (viz. RP-C_{18}, XAD-2, XAD-4, XAD-7 and XAD-16) were assayed for the preconcentration of organophosphorus pesticides. Sorption tests were carried out by using a column packed with 100 mg of the sorbent tested in each case. Aqueous standard solutions (sample) containing 50 mg/l of each OPP (eight compounds) were passed through the sorbent column at 2.0 ml/min. Fractions of 1 ml of sample were collected before and after the sorbent column in glass vials. Both fractions were extracted with 1 ml of ethyl acetate and the extracts dried over anhydrous sodium sulphate. Finally, 1 μl aliquots of the extracts were injected into the chromatograph for analysis. After each sample was processed, the column was rinsed with 400 μl of ethyl acetate and 2 ml of water to remove adsorbed analytes. The sorption efficiency was assessed by comparing the amount of each compound recovered from the extract (unsorbed) with its concentration in the sample (taken to be 100%). As can be seen from Table 1, the best results were

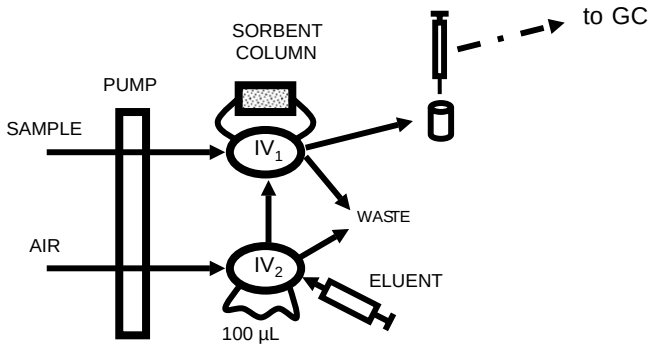

Fig. 1. Schematic diagram of the proposed continuous system for the preconcentration of organophosphorus pesticides in water. IV, injection valve; GC, gas chromatograph (NPD or FID).

Table 1
Sorption efficiency (%) of various materials for organophosphorus pesticides

Pesticide	RP-C_{18}	XAD-2	XAD-4	XAD-7	XAD-16
Dimethoate	99.1	44.6	25.0	34.1	57.1
Diazinon	98.8	59.8	32.5	62.6	77.9
Parathion methyl	99.5	97.7	52.0	80.3	71.1
Malathion	98.7	66.7	34.1	68.3	85.4
Fenthion	96.8	70.4	46.1	59.1	90.8
Parathion ethyl	99.0	94.6	54.1	80.4	73.6
Methidathion	99.2	68.1	40.6	66.7	84.1
Fenthion sulfoxide	98.6	33.3	15.3	28.2	49.0

obtained with RP-C_{18} (sorption efficiency close to 100%). The average sorption efficiencies on porous polymer sorbents (XAD-16, XAD-7, XAD-2 and XAD-4) were 75, 70, 60 and 40%, respectively. RP-C_{18} was thus selected as it exhibited the best adsorption properties.

The optimum amount of RP-C_{18} sorbent was determined by using various columns containing between 5 and 200 mg that were prepared as described in Section 2.2. A series of calibration graphs was run for each OPP and column by passing 10 ml of aqueous standard solutions containing between 100 and 1000 μg/l and eluting with 100 μl of ethyl acetate. The amount of sorbent used was influential; thus, the sensitivity (slope of the calibration graph) was five times higher with 80 mg than with 20 mg. Columns containing more than 125 mg of RP-C_{18}, required increased volumes of eluent for complete elution of the pesticides. This was confirmed by a second injection (100 μl) of eluent subjected to no preconcentration, which resulted in carry-over that increased with increasing amount of sorbent above 125 mg. A working column packed with 100 mg RP-C_{18} was adopted for further testing. Finally, different volumes of aqueous standard solution containing 1000 μg/l of each OPP were passed through the sorbent column. A sorption efficiency close to 100% was obtained with volumes of up to 50 ml of the aqueous solution (breakthrough volume).

Several organic solvents of variable polarity were assayed as eluents for the organophosphorus pesticides adsorbed on RP-C_{18} sorbent, namely—ethyl acetate, methanol, ethanol, acetone, *n*-hexane and dichloromethane. In these tests, 10 ml of aqueous standard solutions containing pesticides at a concentration of 200 μg/l was passed through the sorbent column at 2.0 ml/min. The column was then dried with an air stream and a volume of 100 μl of the different eluents was injected into the same air stream via IV_2 (see Fig. 1). Ethyl acetate, methanol and ethanol proved the most effective eluents for these pesticides. *N*-hexane, acetone and dichloromethane were less efficient (ca. 1.5 times) than the previously commented. Therefore, ethyl acetate was selected as eluent for OPPs, because it is less water-soluble than ethanol and methanol, and any water traces in it can be easily removed with anhydrous sodium sulphate.

In order to confirm the previous results for the sorbents and eluents, 10 ml of aqueous standard solutions containing

0.5 μg/l of each pesticide were passed through the RP-C_{18} sorbent column (100 mg) and the adsorbed pesticides were eluted with 100 μl of ethyl acetate. The organic extracts were analysed by GC with NPD. The results were similar to those obtained with FID in terms of sorption and elution efficiencies.

3.2. Optimization of experimental variables

One of the most important reactions of the OPPs is water hydrolysis. This reaction can take place via the P atom or the alkyl chain and, in general, reduces pesticide action, which is favoured by an alkaline pH (1). Therefore, the retention of organophosphorus pesticides can be dependent on the sample pH. The effect of pH on the sorption of the eight pesticides was studied over the range 1.0–11.5, the desired values being adjusted with dilute HNO_3 or NaOH. The chromatographic areas obtained from 10 ml of aqueous samples spiked with OPPs at a 200 μg/l concentration (FID) remained constant over the pH range 2–8.5. In aqueous solutions at pH values outside this range, hydrolysis was favoured and retention on RP-C_{18} decreased. Therefore, a sample pH of 5.5–7.5 (viz. the usual values for natural and drinking waters) was selected. The ionic strength of the water samples, adjusted with potassium nitrate, had no effect on the signal up to 1.5 M.

The flow-rate of the sample (10 ml solution) through the column during the preconcentration step had very little effect on the adsorption efficiency over the studied range (0.5–4.0 ml/min). The effect of the elution process was studied by changing the air flow-rate between 0.5 and 3.0 ml/min. Sorbed pesticides were eluted throughout this range with no carry-over (i.e., elution was complete) with an eluent volume of 100 μl. A sample flow-rate of 4.0 ml/min and an air flow-rate (eluent carrier) of 2.0 ml/min were thus chosen in order to boost sample throughput. The same air flow-rate was used to dry the sorbent column before elution.

The effect of the eluent volume was studied between 50 and 450 μl by using loops of variable length in the injection valve (IV_2 in Fig. 1). Obviously, as the eluent volume was increased, desorption was more efficient (but analytes were also diluted). Because of the these two opposing effects, the only way to correctly determine the most suitable eluent volume was to dilute extracts to a constant volume with the same solvent (ethyl acetate). Thus, the column eluent (between 50 and 450 μl) was always diluted to 600 μl with ethyl acetate. Desorption efficiency increased with increasing injected volume up to 90 μl, above which the analytical signals for all pesticides remained constant. The same experiment was repeated with different eluent volumes (between 50 and 450 μl) without dilution to a constant final volume, however, the chromatographic signals increased with increasing volume up to 100 μl and decreased at higher volumes through increasing dilution of desorbed pesticides. An injected volume of 100 μl ethyl acetate was selected as optimal. A second injection with the same eluent volume revealed the absence of carry-over; thus, complete elution of analytes was obtained with one injection of 100 μl of ethyl acetate.

Similar results were obtained using NPD with 10 ml of aqueous standard solutions containing 0.5 μg/l of each pesticide.

Using an internal standard corrected the chromatographic signals obtained by injection of 1 μl because it allowed a relative area (the ratio of analyte peak area to internal standard peak area) to be used; in addition, it improved the precision substantially. Two organic compounds (viz. triphenylphosphate and bromophos-methyl) were evaluated as internal standards for addition to the eluent (ethyl acetate). Because bromophos-methyl was partially retained on the sorbent and triphenylphosphate was not retained at all, the latter was selected.

3.3. Analytical performance

Analytical curves for aqueous samples containing different amounts of organophosphorus pesticides prepared according to the procedure described in Section 2.3 were obtained by plotting the analyte-to-internal standard peak-area ratio against the analyte concentration. The sensitivity (slope of the calibration graph) and the linear ranges for the

Table 2
Analytical figures of merit of the determination of organophosphorus pesticides using the proposed solid-phase extraction system

Pesticide	NPD detection				
	Sensitivity[a] (10^4)	Linear range (ng/l)	Limit of detection (ng/l)	RSD[b] (%)	Prec. factor[c]
Dimethoate	7.3	200–40,000	110	3.5	96.3
Diazinon	8.0	200–40,000	80	3.6	98.6
Parathion methyl	7.2	200–40,000	100	3.1	95.4
Malathion	5.8	200–40,000	120	3.3	98.2
Fenthion	6.4	200–40,000	110	4.3	95.0
Parathion ethyl	5.2	200–40,000	130	4.0	96.8
Methidathion	6.0	150–40,000	50	2.9	97.5
Fenthion sulfoxide	5.6	150–40,000	60	3.0	97.3

[a] Relative area (analyte/internal standard peak area ratio) (ng/l).
[b] Relative standard deviation ($n = 11$) for 300 ng/l.
[c] Preconcentration factor for a sample volume of 10 ml.

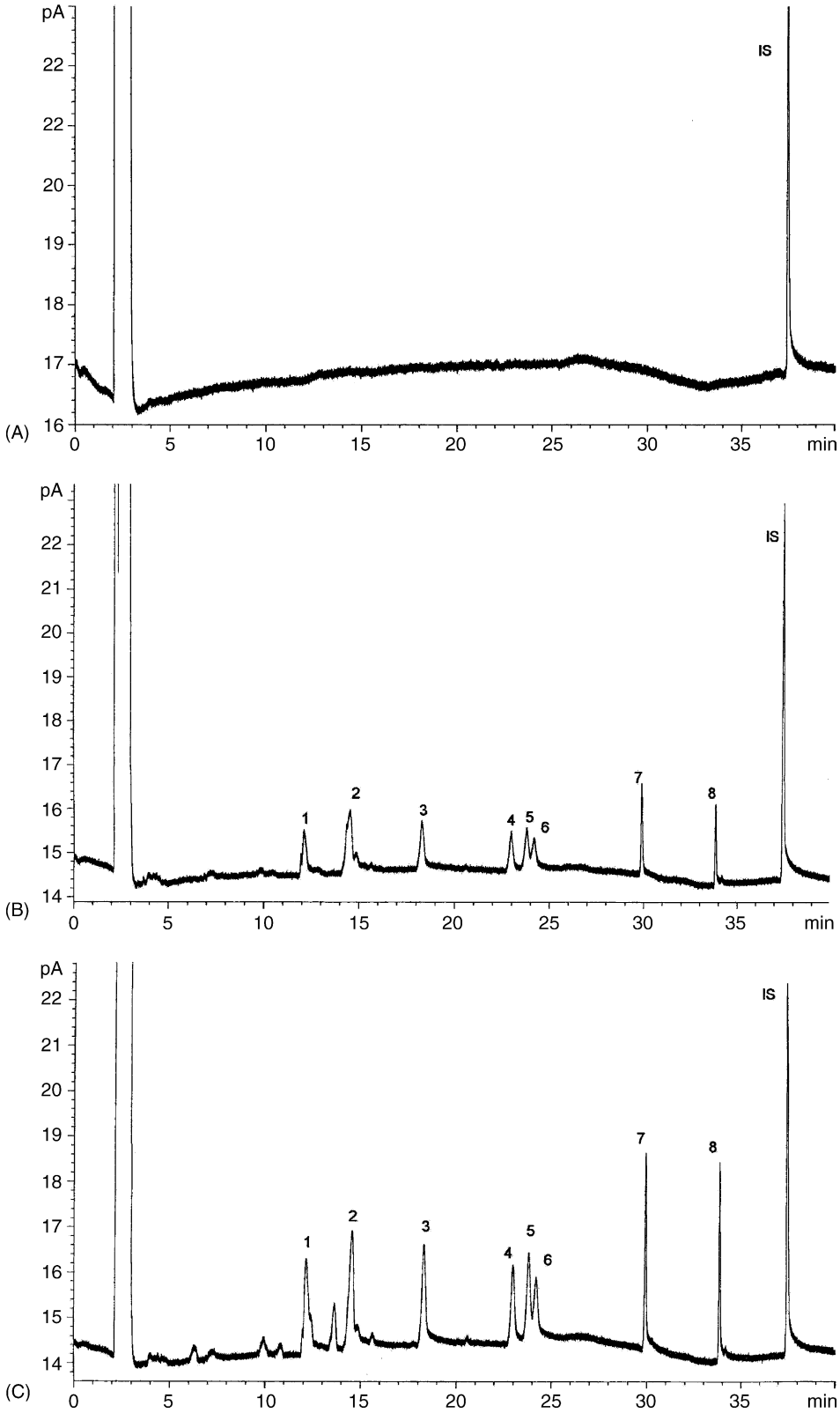

Fig. 2. Gas chromatograms obtained following the preconcentration of 10 ml of tap water (A), tap water spiked with 0.5 μg/l organophosphorus pesticides (B), and pond water spiked with 1.0 μg/l organophosphorus pesticides (C). 1, Dimethoate; 2, diazinon; 3, parathion methyl; 4, malathion; 5, fenthion; 6, parathion ethyl; 7, methidathion; 8, fenthion sulfoxide; IS, internal standard.

Table 3
Percent recoveries of organophosphorus pesticides spiked to water samples[a]

Pesticide	River water (μg/l)		Pond water (μg/l)		Well water (μg/l)		Tap water (μg/l)	
	0.5[b]	1.0[b]	0.5[b]	1.0[b]	0.5[b]	1.0[b]	0.5[b]	1.0[b]
Dimethoate	99.2 ± 3.2	101.0 ± 3.1	98.4 ± 3.2	103.8 ± 3.6	95.2 ± 3.2	101.3 ± 3.0	102.3 ± 3.2	99.9 ± 3.1
Diazinon	97.8 ± 2.9	103.3 ± 3.0	101.7 ± 3.1	96.6 ± 2.9	94.0 ± 3.3	98.6 ± 2.9	98.2 ± 3.0	102.9 ± 3.4
Parathion methyl	103.6 ± 3.2	99.1 ± 3.6	93.8 ± 2.9	102.5 ± 3.5	104.1 ± 3.7	97.5 ± 3.7	95.6 ± 2.9	100.2 ± 3.0
Malathion	103.5 ± 3.1	94.5 ± 4.1	101.3 ± 4.1	103.3 ± 3.0	102.3 ± 4.2	101.3 ± 3.3	97.6 ± 3.4	104.5 ± 3.5
Fenthion	101.8 ± 4.0	98.1 ± 3.2	98.1 ± 3.3	96.4 ± 3.0	104.0 ± 3.5	103.2 ± 3.6	95.9 ± 4.2	101.3 ± 3.8
Parathion ethyl	98.3 ± 4.3	100.8 ± 3.5	95.2 ± 4.0	100.9 ± 2.9	101.9 ± 3.3	95.3 ± 3.8	102.8 ± 3.5	94.6 ± 3.6
Methidathion	103.4 ± 3.0	103.0 ± 3.2	100.5 ± 3.1	99.3 ± 3.0	100.1 ± 2.9	99.1 ± 3.3	98.5 ± 3.4	97.3 ± 3.0
Fenthion sulfoxide	97.8 ± 3.1	100.1 ± 2.9	101.9 ± 3.0	98.1 ± 3.2	97.3 ± 2.9	99.3 ± 3.4	103.2 ± 2.8	99.5 ± 2.9

[a] Percent recovery ± standard deviation ($n = 3$).
[b] Concentration added.

preconcentration of sample volumes of 10 ml and determination by GC with NPD are listed in Table 2. All the pesticides analyzed had correlation coefficients, r^2, from 0.992 to 0.998. The limits of detection (LOD) were calculated as the minimum concentrations providing chromatographic signals three times higher than background noise. Tests on real samples aimed at determining the LOD provided results similar to those for distilled water except for a few additional peaks which had no effect on the detection of OPPs. The preconcentration factor was calculated as the ratio between the slopes of the calibration graphs obtained by using the manifold depicted in Fig. 1 and the slopes obtained by manual injection of standards containing 50–1000 μg/l (NPD) or 50–500 mg/l (FID) in ethyl acetate (containing 200 μg/l or 70 mg/l internal standard for NPD and FID, respectively). Preconcentration factors were close to 100 in all instances. The precision of the method (expressed as repeatability, $n = 11$) was checked on standards containing 300 ng/l (NPD) or 100 μg/l (FID). The relative standard deviation was 2.9–4.3% for NPD and 3.7–4.7% for FID.

3.4. Application to water samples

The proposed trace enrichment method was applied to the determination of the eight organophosphorus pesticides in four different types of water: tap (Linares, Spain), well (Andújar, Spain), river (Guadalquivir, Spain) and pond (Guadalén, Spain). For this purpose, NPD was used because it provided higher sensitivity than FID as shown in the previous Section.

All water samples were passed through 0.45 μm filters (Micro Separations Inc, 4 mm diameter, Westboro, MA, USA) to remove particulates, and measured for pH (range for the analyzed water samples 6.5–7.5); a volume of 10 ml of filtered water was analysed using the proposed continuous method. However, no OPPs were detected. Therefore, the water samples were fortified with 0.5 and 1.0 μg/l of pesticides and analysed in triplicate by inserting 10 ml of sample into the preconcentration system. Fig. 2 shows the chromatograms obtained for tap water, and spiked tap and pond water samples. As can be seen in Fig. 2C, some peaks corresponding to other organic products present in water are observed, which, however, do not disturb the detection of the spiked pesticides. Table 3 lists the average recoveries obtained under the optimum working conditions for river, pond, well and tap spiked water. Recoveries ranged from 93.8 to 104.5%.

4. Conclusions

The proposed method provides a simple means for preconcentration and determination of organophosphorus pesticides in contaminated natural waters. Manual injection of extracts into the GC with a syringe can be readily replaced with the use of an injection valve, that enables the on-line coupling of a gas chromatograph to an SPE system, similarly as in the determination of *N*-methylcarbamate pesticides in waters [29]. Other authors have used an on-line trace level enrichment gas chromatographic system for the determination of organophosphorus and other pesticides in drinking and surface waters consisting of two pump, a valve-switching unit, a laboratory-made precolumn packed with PLRP-S styrene–divinylbenzene copolymer, and a drying cartridge [30]. In this system, the organic extract was introduced into a retention gap mounted in the on-column injector of the gas chromatograph.

Of the two gas chromatographic detectors tested (FID and NPD), NPD was selected because it allowed the pesticides to be determined at concentrations of a few nanograms-per-litre with a high precision (2.9–4.3%), thus fulfilling the requirements for drinking and surface water analysis as per EU Directives [2,3]. However, the detection limits obtained (50–130 ng/l for 10 ml of sample) can be reduced by preconcentrating 50 ml of sample with some loss of throughput. This is therefore a competitive, simple, fast, inexpensive method, and as such an effective alternative to conventional methods for the determination of pesticides.

Acknowledgements

The authors wish to thank the University of Jaén (Spain) for financial support (Plan de Ayuda para el Fomento de la Investigación, UJA 2002). Drs. M. Valcárcel and M. Gallego (Department of Analytical Chemistry, University of Córdoba, Spain) are thanked for stimulating discussions. The authors would also like to thank Servicios Técnicos de Investigación of University of Jaén for providing access to the gas chromatograph.

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