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Comparison of simplified methods for pesticide residue analysis Use of large-volume injection in capillary gas chromatography

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Abstract

The combination of manual and automated extraction procedures using low sample volumes (5–50 ml) with large-volume oncolumn injection (LVI) (200 μl) in capillary gas chromatography with flame photometric detection (GC–FPD) has allowed the determination of 16 organophosphorus pesticides in clean water samples at the low ng l^{-1} level with an important simplification in the sample preparation step. A simple and fast offline liquid–liquid microextraction procedure (2–5 ml water/1 ml methyl *tert*.-butyl ether) has been applied to spiked groundwater samples (containing 0.5 ng of each pesticide) with good recoveries (over 80%) and precision (better than 10%), giving detection limits between 5 and 100 ng l^{-1} using 200 μl injections in the GC–FPD system. The application of an inline automated liquid–liquid microextraction–LVI–GC procedure (2 ml water/2 ml methyl *tert*.-butyl ether: injection of 200 μl in GC–FPD) using the autosampler ASPEC XL led to lower recoveries (>50%) as a result of the low efficiency for mixing organic and aqueous phases, although with very satisfactory coefficients of variation (lower than 7%) and detection limits between 20 and 200 ng l^{-1}. Manual and automated solid-phase extraction procedures using the well known C_{18} cartridges and the new Oasis HLB have been applied to groundwater samples (5–50 ml) spiked with 1 ng of each pesticide. Results obtained for both the manual and the automated procedures were satisfactory (recoveries over 80%) and the limits of detection for 50 ml sample volume ranged from 1 to 6 ng l^{-1}.

Keywords: Extraction methods; Water analysis; Environmental analysis; Pesticides; Organophosphorus compounds; Large-volume injection; Injection methods

1. Introduction

Simplification and increasing automation of preliminary analytical operations, mainly as regards the extraction steps is one of the modern trends in analytical chemistry [1]. In environmental analysis, where concentration levels are in the edge of the parts per billion, it is necessary to increase sensitivity of the chromatographic determination in order to reduce sample size and to simplify sample preparation. In this sense, large-volume injection (LVI) is a powerful tool as it allows the introduction of up to several hundreds of microliters maintaining good chromatographic characteristics [2–4]. In addition, automated extraction procedures combined online with gas chromatography (GC) will require the transfer of large organic fractions to the chromatographic system, again feasible using LVI–GC techniques. As a result of the combination of microextraction procedures with LVI–GC, several advantages can be pointed out, including reduction in extraction time and solvent consumption, simplification of the extraction process (especially when considering liquid–liquid extraction), avoiding of solvent evaporation steps (loss of analytes), avoiding interference introduction due to large amounts of

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organic solvents and contribution to the ecological saving by diminishing of solvent wasting.

Determination of pesticides in aqueous environmental samples is one of the fields that can easily benefit from the indicated reduction of sample preparation steps, if sensitivity levels are maintained at the subparts per billion range. Some examples of the application of liquid–liquid microextraction (LLME) combined with LVI–GC to the determination of pesticide residues in water samples can be found in the literature. Thus, Tamilrasan et al. [4] obtained good recoveries for neutral chlorinated compounds using hexane as extraction solvent. Besides, automated LLME with methyl *tert.*-butyl ether (MTBE) combined on line with LVI–GC has been described for the determination of some organophosphorus pesticides in water samples [2]. In the same way, the application of solid-phase extraction (SPE) procedures combined with LVI–GC has been described in some papers using the offline [5] and the online approach [6–9]. These procedures have been applied, for example, to the determination of polar pesticides using PRLP-S precolumns coupled with the GC system via a loop-type interface with 500 μl injection loop [9].

In previous papers [10,11] we described the use and optimisation of LVI–GC via the injector of an Ultra Trace gas chromatograph (Fisons) for the some neutral pesticides (triazine herbicides) in water samples by LLME and SPE. The application of LVI–GC to different groups of compounds (as pesticides of different polarity) requires an accurate and careful optimisation of the variables involved in injection (injection speed, initial oven temperature, solvent vapour elimination, sample volume,...) as pointed out in many papers [10,12].

In this paper, a group of organophosphorus pesticides with a wide range of polarities has been investigated in order to evaluate the use of microextraction procedures coupled off- and inline to LVI–GC–flame photometric detection (FPD) for their determination in water samples. Extraction procedures included LLME, using solvents of different polarity, and SPE, comparing the performance of two types of sorbents as C_{18} and the recent Oasis HLB (Waters). The use of an autosampler ASPEC XL has also been tested for automated extraction of water samples, both using the SPE and the LLME approach. A discussion on the optimisation of the variables involved in the automated extraction process, as well as on the performance of the overall analytical procedure including extraction and LVI–GC–FPD is made.

2. Experimental

2.1. Chemicals

Organophosphorus standards (dimethoate, phorate, fonofos, chlorpyriphos-methyl, parathion-methyl, fenitrothion, malathion, chlorpyriphos, fenthion, chlorfenvinphos, methidathion, fenamiphos, ethion, phosmet, phosalone, azinphos-methyl) were purchased from Dr. Ehrenstorfer (Ausburg, Germany) and used without further purification. Stock standard solutions (ca. 500 $\mu g\ ml^{-1}$) were prepared in acetone and then diluted with hexane, dichloromethane, ethyl acetate or MTBE to prepare working solutions. Spiked samples were prepared from stock standard solutions in acetone, ensuring an acetone content of less than 1% in the final aqueous solution. Organic solvents (acetone, dichloromethane, ethyl acetate, hexane, methanol and MTBE) were of ultratrace grade (Scharlau, Barcelona, Spain). Sodium chloride (Scharlau) and anhydrous sodium sulphate (Baker, Deventer, The Netherlands) were pesticide-residue grade and were purified by heating at 300°C overnight.

Two hundred mg C_{18} cartridges (3 ml) (Varian, Harbor City, CA, USA), Empore C_{18} disks (Varian), 30 mg Oasis HLB cartridges (1 ml) (Waters, Milford, MA, USA) and 500 mg Carbon Black Supelclean ENVI-Carb cartridges (6 ml) (Supelco, Bellefonte, PA, USA) were used for solid-phase extraction of water samples.

Helium gas with a quality of 99.9995% and hydrogen and air with a quality of 99.995% were supplied by Carburos Metálicos (Barcelona, Spain).

2.2. Equipment

GC was performed with an Ultra Trace GC instrument (Fisons, Milan, Italy) based on the GC 8000 Series 2, equipped with oncolumn injector (with electronic control of carrier gas supply, DPFC

800), flame photometric detector (FPD-80 with the control module FPD-800), heated solvent vapour exit (SVE), autosampler AS 800 (90 vials and a 250 μl Hamilton syringe) which enabled injections of up to 240 μl at different rates between 1 and 100 μl s^{-1}, and PC-based data system (Chrom Card) to control data acquisition and instrument conditions. The pressure of the fuel and auxiliary gases, hydrogen and air, were set at 140 kPa and 60 kPa, respectively. A pressure of 60 kPa helium was used as make-up gas.

The SVE consisted of a three-way valve that switched between a high-flow outlet and a strongly restricting outlet consisting of a 30 cm fused-silica capillary tubing (25 μm I.D.) which left a small purge flow-rate (ca. 0.01 ml min^{-1}). The valve was maintained at 150°C to prevent solvent condensation.

Carrier gas (He) was controlled by regulating flow using flow programming.

The precolumn system consisted of 5 m×0.53 mm deactivated fused-silica tubing and 3 m×0.53 mm with 0.25 μm film thickness of DB-5 column connected using a press-fit connector. The analytical column was a 30 m×0.32 mm, with a 0.25 μm 5% phenyl methyl siloxane (Hewlett–Packard, Waldbronn, Germany).

An autosampler ASPEC XL Sampler Processor for Solid-phase Extraction (Gilson, Villiers-le-Bel, France) in combination with a low pressure pump Model 402 (Gilson) equipped with 1 and 10 ml syringes was used to perform automated water extractions.

In Fig. 1, a schematic diagram of the automated extraction system including ASPEC XL and Ultra trace GC is shown.

2.3. Chromatographic conditions for LVI

Conditions for LVI were initially selected according to previous data [10,11] and then optimised for the determination of organophosphorus pesticides using as solvents hexane, dichloromethane, ethyl acetate and MTBE. After optimisation of the injection variables in order to keep a small flooded zone (ca. 10–20 μl) and to ensure the elimination of the solvent through the SVE without analyte losses, the conditions used were as follows:

Flow program for carrier gas: Initial, 5 ml min^{-1} (147 kPa) (15 s); rate, infinite; final, 2 ml min^{-1} (75 kPa) (22 min).

Injection conditions: Volume, 50–200 μl; injection rate, between 2 and 5 μl s^{-1}.

SVE time: Around 15 s.

Temperature program: Initial temperature (2

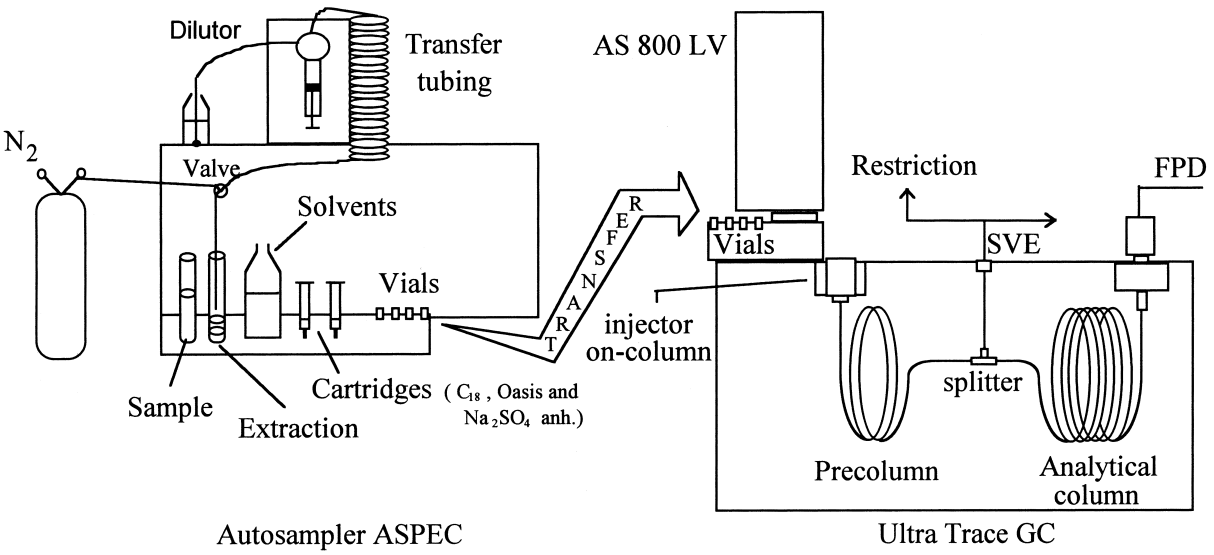

Fig. 1. Schematic diagram of the equipment used for automated LLME and SPE including ASPEC XL and Ultra Trace GC system.

min), 80°C (hexane), 65°C (MTBE), 60°C (dichloromethane), 87°C (ethyl acetate); rate, 30 C° min^{-1} up to 180°C; rate, 10 C° min^{-1} up to 270°C (hold time 7 min).

2.4. Extraction procedures

Different manual and automated LLME and SPE procedures were applied for the determination of organophosphorus pesticides in water samples:

LLME: A 2–5 ml water sample (containing 10% NaCl) was shaken mechanically (Vortex) with 1 ml of MTBE during 1 min in a centrifuge tube. Then, the organic layer was separated, dried over anhydrous sodium sulphate and transferred to a GC vial for injection.

Automated LLME: A 2 ml water sample was extracted with 2 ml of MTBE using the autosampler ASPEC XL. The extraction was carried out by dispensing 20 fractions of 100 μl of MTBE over sample at a flow-rate of 95 ml min^{-1}, thus forcing the organic solvent into the water phase. After a small waiting time, 1.5 ml of organic extract were removed and passed through an anhydrous sodium sulphate cartridge. The final dry extract was directly collected in a GC vial for injection.

SPE: A 5 to 50 ml water sample was passed through a 200 mg C_{18} or 30 mg Oasis HLB cartridge which had been conditioned by passing MTBE, methanol and water (two cartridge volumes each). Sample flow-rate was controlled to be around 6–8 ml min^{-1} for C_{18} cartridges and lower than 1 ml min^{-1} for Oasis. The cartridges were dried by passing air using vacuum for 20 min and then they were eluted with 2 ml of MTBE. The extract was dried over anhydrous sodium sulphate prior to injection in GC.

Automated SPE: This was performed by using the autosampler ASPEC XL. The procedure was similar to that indicated above, with the difference that the drying of cartridges was carried out by passing nitrogen for 20 min (2 bar). After elution of cartridges, extracts were aspired again and passed through another set of cartridges containing anhydrous sodium sulfate, collecting the final extract directly into glass vials. All the steps of the SPE procedure were performed automatically (conditioning, loading of sample, drying and elution).

3. Results and discussion

3.1. LLME

Preliminary experiments were carried out in order to study the effect of shaking time, NaCl content and organic phase:aqueous phase ratio using three different solvents (hexane, dichloromethane, MTBE).

Results obtained (extracting 1 ml of water sample spiked at 10 μg l^{-1} level with 1 ml of organic solvent) showed that there were no significant differences when shaking for 1 or 20 min, whereas the use of a 10% NaCl improved slightly the recoveries of some pesticides (those with higher water solubility). The phase ratio was then increased by shaking 1 ml of organic solvent with either 1, 2 or 5 ml of water sample (phase ratios 1:1, 1:2 and 1:5, respectively), the recoveries being similar for almost all pesticides (except phorate, dimethoate and fenitrothion, whose recoveries decreased when the water sample volume increased). Regarding the type of solvent, hexane was rejected since it led to worse recoveries for the more polar pesticides due to its lower polarity. Both dichloromethane and MTBE showed similar results as regards recoveries and precision, but the use of dichloromethane produced faster degradation in the precolumn GC system, possibly due to its higher polarity which results in more water dissolved in the organic phase during extraction. The degradation of the retention gap on introduction of water-containing solvents has been reported in several papers [8,13,14]. So, MTBE was chosen as the best option.

The LLME procedure (2 or 5 ml of water sample containing 10% NaCl with 1 ml of MTBE shaking for 1 min) was applied to groundwater samples containing 0.5 ng of each pesticide except for dimethoate, chlorfenvinphos and fenamiphos (1 ng) and ethion (0.25 ng). Extracts obtained were dried over anhydrous sodium sulphate and 200 μl were injected in the GC system. Results obtained are shown in Table 1. Recoveries were found to be satisfactory (over 80%) when using a 1:2 phase ratio for all pesticides except for chlorpyriphos (43%). Recoveries of chlorpyriphos have been low throughout all the work carried out, LLME and SPE, although it is not feasible to obtain an explanation based on its physico–chemical properties. When the

Table 1
Mean recoveries (R.S.D., $n=5$) obtained after manual and automated LLME of a groundwater sample spiked with 0.5 and 1 ng of each pesticide, respectively

	Recovery% (R.S.D.%)			LOD[a,b] (ng l^{-1})
	Manual LLME		Automated LLME	
	Phase ratio 1:2	Phase ratio 1:5	Phase ratio 1:1	
Phorate	98 (5)	60 (5)	49 (7)	60[c]
Dimethoate	81 (8)	38 (7)	57 (2)	100[c]
Fonofos	103 (5)	77 (3)	68 (7)	9
Chlorpyriphos-methyl	76 (5)	105 (4)	57 (6)	8
Parathion-methyl	114 (5)	98 (7)	57 (6)	11
Fenitrothion	90 (6)	43 (7)	68 (5)	10[c]
Malathion	103 (3)	117 (7)	73 (6)	10
Chlorpyriphos	43 (3)	62 (3)	52 (4)	7
Fenthion	104 (3)	87 (4)	72 (4)	7
Chlorfenvinphos	102 (4)	80 (5)	16 (9)	17
Methidathion	101 (3)	83 (3)	103 (7)	13
Fenamiphos	102 (13)	97 (5)	51 (12)	20
Ethion	88 (4)	112 (8)	15 (7)	5
Phosalone	93 (4)	88 (9)	46 (5)	50
Azinphos-methyl	94 (9)	91 (13)	46 (5)	50

[a] LOD, limit ot detection.
[b] Detection limits corresponding to the LLME procedure using a phase ratio 1:5.
[c] Detection limits corresponding to the LLME procedure using a phase ratio 1:2.

phase ratio was increased up to 1:5, recoveries for phorate, dimethoate and fenitrothion decreased below 60%. Precision was good in all cases, with coefficients of variation lower than 10% for five replicates. Only fenamiphos and azinphos-methyl showed coefficients of variation higher than 10%. Detection limits calculated as three times background noise over chromatograms obtained for 5 ml water sample at the 0.1 μg l^{-1} level were found to be lower than 0.05 μg l^{-1} (Table 1). Detection limits for fenitrothion, phorate and dimethoate were calculated from the chromatograms corresponding to 2 ml of water sample (0.1 μg l^{-1}) and they were 0.01, 0.06 and 0.1 μg l^{-1}, respectively. Fig. 2 shows a chromatogram obtained after LLME of 5 ml of groundwater sample spiked at 0.1 μg l^{-1} level.

The development of an automated LLME procedure with MTBE as solvent and using the autosampler ASPEC XL was also studied. Several experiments were performed in order to optimise the mixing between the organic (2 ml) and the aqueous phase (2 ml). One option, used by other authors [2], was the dispensing of solvent over the sample and, then, to aspirate and dispense repeatedly the organic phase. In our case, this option was not suitable because losses of solvent were observed after the first aspiration. The dispensation of 2 ml of solvent in 20 fractions of 100 μl at a flow-rate of 95 ml min^{-1} (maximum value allowed by the pumping system) was found to be the best option to ensure a good contact between the phases. After separation of the phases, 1.5 ml of upper organic layer were removed and passed through a cartridge containing anhydrous sodium sulphate, collecting the extract in a vial for injection in GC (200 μl). Due to the problems related to the mixing of the phases, it was not feasible to increase the sample volume as recoveries obtained decreased considerably.

The automated LLME procedure using 2 ml of water sample was applied to groundwater samples fortified at the 0.5 μg l^{-1} level (1 μg l^{-1} for dimethoate, chlorfenvinphos and fenamiphos and 0.25 μg l^{-1} for ethion). Results obtained (Table 1) showed low recoveries (especially for chlorfenvinphos and ethion), possibly due to a not suitable contact between the organic phase and the water sample during the extraction. So, the efficiency of the mixing of both phases was not good enough to

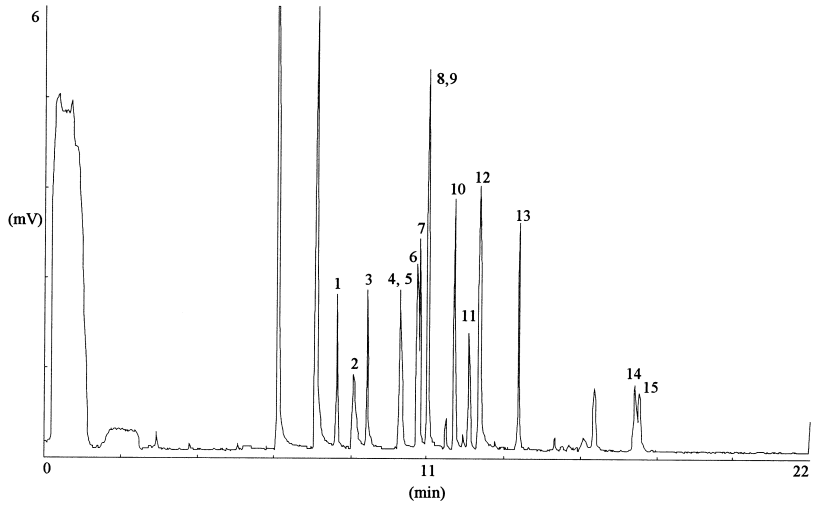

Fig. 2. Chromatogram obtained after manual LLME with 1 ml of MTBE of 5 ml of groundwater sample fortified at 0.1 μg l^{-1} level and injection of 200 μl of sample extract in GC–FPD. (1) Phorate, (2) dimethoate, (3) fonofos, (4) chlorpyriphos-methyl, (5) parathion-methyl, (6) fenitrothion, (7) malathion, (8) chlorpyriphos, (9) fenthion, (10) chlorfenvinphos, (11) methidathion, (12) fenamiphos, (13) ethion, (14) phosalone, (15) azinphos-methyl.

ensure the quantitative extraction of pesticides. However, for the majority of the compounds recoveries were higher than 50% and R.S.D.s (n=5) were very satisfactory ranging between 2 and 7%. Experimental detection limits obtained when applying this automated procedure ranged between 0.02 and 0.2 μg l^{-1}. However, the good repeatabilities and the low detection limits obtained could allow the use of this automated LLME procedure for organophosphorus pesticide residue analysis. Obviously, the application of this procedure to pesticide monitoring in routine studies would require the simultaneous extraction of fortified water samples (n=2), as efficiency assessment.

3.2. SPE

Different types of sorbents (C_{18}, Oasis HLB and Carbon Black cartridges and C_{18} disks) were initially tested by applying an SPE procedure combined with LVI–GC optimised in a previous work [11]. Carbon Black cartridges and C_{18} disks were found to be not suitable. Carbon Black cartridges showed low recoveries for all organophosphorus pesticides studied, also requiring a large elution volume. The use of C_{18} was not considered because of the problem of removing water present in the lower part of the holder after the drying step. Then, C_{18} cartridges, extensively used in several works for the SPE of pesticides [15,16], and Oasis HLB cartridges were chosen for carrying out this study. Oasis HLB is a new polymeric reserved-phase sorbent for SPE designed to have a hydrophilic–lipophilic balance (HLB) that should retain both polar and nonpolar compounds [17].

The SPE procedure was optimised in relation to the type and volume of eluent (MTBE and ethyl acetate), salting out effect, mass sorbent and sample volume. Both MTBE and ethyl acetate presented good performance in eluting the adsorbed compounds, giving complete elution with a maximum volume of 2 ml. As in LLME and according to the results obtained, MTBE was selected because of its lower polarity which makes it more suitable for LVI–GC. The effect of addition of 10 and 20% NaCl to the water samples and the use of 500 mg C_{18} cartridges was not significant over recoveries. Sample volume was increased from 5 to 50 and 100 ml, obtaining similar recoveries for 5 and 50 ml, while when extracting 100 ml, some losses for several compounds were observed (phorate, dimethoate and fenamiphos) due to the fact that the breakthrough volume was exceeded.

Once the optimum conditions for retention and

elution of organophosphorus pesticides in the SPE procedure were established (5 to 50 ml of water passed through 200 mg C_{18} or 30 mg Oasis HLB cartridges, and elution with 2 ml MTBE), an automated SPE procedure was developed using the autosampler ASPEC XL. The most critical aspect was the drying step of the cartridges after loading water samples. Passing air using the ASPEC low pressure pump was not suitable for this purpose; however, better results were obtained by passing nitrogen through the cartridges at a pressure of 2 bar during 20 min. Although higher pressures would be desirable in order to obtain more efficient drying, the ASPEC valve has a limit pressure of 2 bar, which makes necessary the application of an additional drying step with anhydrous sodium sulphate to ensure the absence of water.

In order to compare the performance of the SPE procedures (manual and automated), they were applied to 5 and 50 ml of spiked groundwater samples (containing 1 ng of each pesticide) using both the C_{18} and the Oasis HLB cartridges. Results obtained for manual SPE were, generally, satisfactory with recoveries over 80%, with no significant differences between the two sorbents used. In relation to the automated SPE, better results were obtained when using the C_{18} cartridges, mainly in relation to the repeatability of the procedure (Table 2). The use of Oasis HLB cartridges in the automated mode led to higher coefficients of variation, probably due to the fact that drying of cartridges was not efficient enough in the selected conditions (20 min at 2 bar), which could have led to less efficient pesticide elution. Higher nitrogen pressures should be preferable but they were not feasible because of restrictions of the valve system.

Table 2 also gives the limits of detection for the SPE procedure based on the chromatograms obtained after extraction of 50 ml of sample (0.01 μg l^{-1} pesticide level), elution with 2 ml of MTBE and final injection of 200 μl of extract in the GC–FPD system. Values obtained were in the range of 1 to 6 ng l^{-1}. These values are considerably lower than those obtained with the LLME procedure due to the possibility of extracting higher sample volumes (up to 50 ml). Fig. 3 shows a chromatogram obtained after automated SPE (200 mg C_{18}) of 50 ml of spiked groundwater sample (0.02 μg l^{-1} level) and

Table 2
Mean recoveries (R.S.D., $n=5$) obtained after manual and automated SPE with C_{18} or Oasis HLB cartridges of 50 ml of a groundwater sample spiked with 1 ng of each pesticide

	Recovery% (R.S.D.%)				LOD[a] (ng l^{-1})
	Manual SPE		Automated SPE		
	C_{18}	Oasis	C_{18}	Oasis	
Phorate	89 (8)	81 (9)	95 (5)	84 (11)	1
Dimethoate	83 (10)	98 (4)	93 (8)	82 (6)	1
Fonofos	110 (5)	96 (6)	[b]	[b]	1
Chlorpyriphos-methyl	108 (5)	110 (3)	105 (3)	90 (6)	1
Parathion-methyl	98 (5)	86 (3)	98 (4)	108 (7)	1
Fenitrothion	108 (5)	89 (4)	116 (7)	92 (10)	1
Malathion	110 (8)	94 (4)	118 (6)	102 (10)	1
Chlorpyriphos	39 (8)	33 (9)			1
Fenthion	67 (8)	75 (9)	77 (6)	81 (12)	2
Chlorfenvinphos	88 (4)	80 (4)	71 (2)	52 (13)	1
Methidathion	106 (8)	89 (6)	127 (2)	87 (7)	1
Fenamiphos	[b]	67 (9)	88 (5)	70 (12)	5
Ethion	80 (12)	52 (9)	43 (6)	42 (13)	1
Phosmet	129 (8)	82 (9)	109 (14)	84 (19)	4
Phosalone	116 (10)	91 (3)	78 (9)	58 (16)	4
Azinphos-methyl	100 (10)	67 (3)	67 (9)	43 (16)	6

[a] LOD, limit of detection.
[b] Recoveries higher than 140% due to interferences in the sample extract.

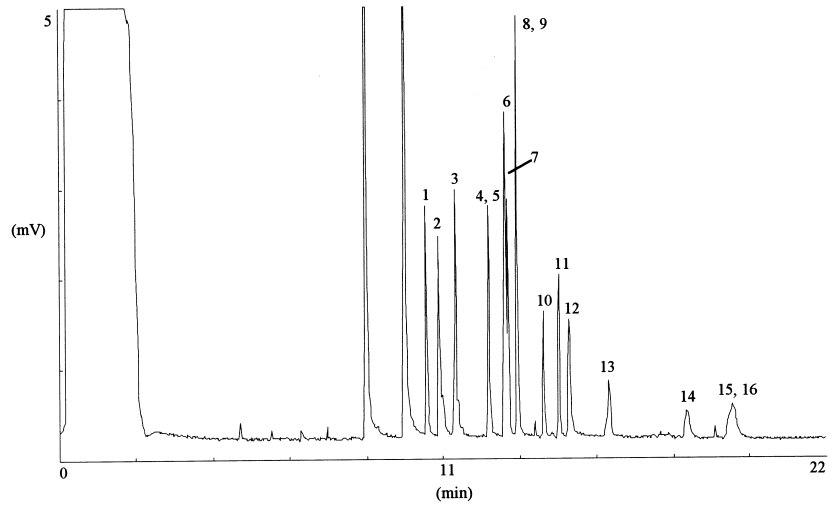

Fig. 3. Chromatogram obtained after automated SPE (200 mg C_{18}) of 50 ml of groundwater sample fortified at 0.02 μg l^{-1} level and injection of 200 μl of sample extract in GC–FPD. (1) Phorate, (2) dimethoate, (3) fonofos, (4) chlorpyriphos-methyl, (5) parathion-methyl, (6) fenitrothion, (7) malathion, (8) chlorpyriphos, (9) fenthion, (10) chlorfenvinphos, (11) methidathion, (12) fenamiphos, (13) ethion, (14) phosmet, (15) phosalone, (16) azinphos-methyl.

injection of MTBE extract (initial isothermal time of the oven programme was increased in 2 min, thus ensuring a constant temperature during solvent peak).

4. Conclusions

In this paper the feasibility of application of LVI–GC has been evaluated for the determination of organophosphorus pesticide residues in water samples. The combination of extraction procedures using low sample volumes (5–50 ml) with LVI–GC allows the determination of up to 16 pesticides in clean water samples at the low ng l^{-1} level. The simplification in the extraction step, which results in less solvent consumption and waste, and in time reduction specially in LLME, is only feasible thanks to the use of the LVI–GC technique.

Although the performance of the manual LLME procedure has been better than that for the automated LLME, possibly due to the low efficiency of the later for mixing the organic and the aqueous phases, this seems to be an interesting approach due to the low coefficients of variation obtained, and it can be useful in routine monitoring programs as it can be carried out in nonattended mode.

The utility of SPE has been demonstrated comparing the well known C_{18} cartridges with the new Oasis HLB. The good results obtained, both in manual and automated SPE, confirm the vast applicability of this technique. The Oasis HLB cartridges did not show better performance than the C_{18} cartridges and no additional advantages have been found for their use in the SPE procedures applied to organophosphorus pesticide analysis.

The development of automated extraction procedures will achieve its maximum interest with the online coupling to the LVI–GC, obtaining in this way a completely automated procedure for pesticide residue analysis in water.

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