



ELSEVIER

Journal of Chromatography A, 737 (1996) 47–58

JOURNAL OF
CHROMATOGRAPHY A

Automated sample preparation with extraction columns followed by liquid chromatography–ionspray mass spectrometry

Interferences, determination and degradation of polar organophosphorus pesticides in water samples

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Abstract

The determination of polar and/or thermally labile organophosphorus pesticides trichlorfon, dichlorvos, dimethoate, oxydemeton-methyl, mevinphos (*cis* and *trans*), demeton-S-methyl, fenamiphos, fenitrothion, fenthion and diazinon in water samples was investigated using solid-phase extraction followed by liquid chromatography–ionspray mass spectrometry (LC–ISP–MS). Pesticides were spiked at 0.2 $\mu\text{g}/\text{l}$ in ground water samples and 200 ml were preconcentrated by using an ASPEC XL system. To improve the recovery of the most volatile pesticides such as dichlorvos, a further drying step with a Baker Spe 12 G apparatus with the vacuum set at 15 p.s.i. was included. A further evaporation step was applied with a gentle stream of nitrogen. A variety of materials (Amberchrom, LiChrolut EN, cyclohexyl, SDB, C₁₈ and Isolute ENV) were used for the isolation of the target pesticides. The elution step took place at 1 ml/min, with a 5-min contact time between the eluent and the sorbent. LC–ISP–MS permitted the identification of diethyl and di-*n*-butyl phthalates present as impurities in the cartridge materials. The presence of transformation products of the pesticides, e.g., fenthion sulfoxide, was also observed. The influence of pH and the water matrix (distilled and ground water) on the extraction efficiency was examined. The use of LC–ISP–MS permitted *cis*- and *trans*-mevinphos to be distinguished in the water sample owing to the presence of a specific ion at m/z 99. The limits of detection of the overall method were in the range 0.01–0.20 $\mu\text{g}/\text{l}$ using LC–ISP–MS with selected-ion monitoring.

Keywords: Water analysis; Environmental analysis; Sample preparation; Pesticides; Organophosphorus compounds

1. Introduction

In a previous paper [1], a method for the determination of several organophosphorus pes-

ticides in distilled water samples involving solid-phase extraction (SPE) followed by liquid chromatography–ionspray mass spectrometry (LC–ISP–MS) was developed. Recoveries above 70% with limits of detection (LOD) between 0.01 and 0.2 $\mu\text{g}/\text{l}$ for several organophosphorus pesticides

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were obtained. However, poor recoveries were obtained for compounds such as trichlorfon and dichlorvos, probably because only C_{18} and styrene–divinylbenzene (SDB) Empore disks and monofunctional C_{18} cartridges were used. One way to solve the extraction problems is to extend the type of sorbents used and to improve the whole extraction method. As regards the use of LC–ISP–MS, it was demonstrated that it does not lead to any degradation of thermally labile compounds such as trichlorfon with considerable improved LODs (by ca. 100-fold) compared with conventional LC–thermospray MS using the selected-ion monitoring (SIM) mode [2].

Another aspect that also needs attention is the evaporation/drying of extracts from the cartridges. Compounds such as dichlorvos exhibit a very high vapour pressure (2100 mPa), so they may be lost during sample preparation steps. It is clear that the solvent evaporation step should be improved to avoid evaporation losses and hydrolysis of the target analyte. This is an added difficulty since automated sample preparation with extraction columns (ASPEC XL) involves a positive pressure. Other well established semi-automated systems such as the Zymark Auto-trace SPE workstation were used to develop the Baxter and Supelco procedures for phenols either using positive or negative (vacuum manifold) pressure [3]. The positive pressure involves the use of an HPLC pump for delivering the water through the cartridge and it only works when the cartridge is closed, leaving a small hole for the syringe, whereas negative pressure is the conventional system currently used in most laboratories and the water containing the pesticides is percolated through the cartridges using a vacuum manifold. In general, better recoveries were observed for samples involving a negative pressure, generally being 10–15% higher, e.g., the recoveries for phenol and 2,4,6-trichlorophenol were 62 and 73% (positive pressure) and 75 and 79% (negative pressure). Five methods of sample preparation were compared for pesticides used on golf courses, and it was concluded that centrifugation at 3500 rpm for 5 min after the samples had been loaded into the SPE cartridges was the best choice. After the centrifugation,

elution took place using methylene chloride and negative pressure for 15 min [4].

Another aspect that has not been sufficiently addressed when determining pesticides by LC–MS is the interferences from the matrix or the cartridges. In previous work, the interferences present in SPE material when using gas chromatographic–mass spectrometric (GC–MS) techniques were studied [5–7]. When LC techniques are applied in environmental analysis, to our knowledge no papers have reported the usual interferences, e.g., phthalates, from the SPE materials, except for the recommendations given by the US Environmental Protection Agency (EPA) using particle beam method [8]. In these recommendations, the method involves ions at m/z 75 and 313, which corresponded to $[(OH)Si(CH_3)_2]^+$ and $[(OH)(CH_3)SiC_{18}H_{37}]^+$, respectively, and are due to bleeding of demethyloctadecylsilanol from the C_{18} LC column.

With regard to the problems encountered with the SPE of organophosphorus pesticides from water samples, some of these compounds, e.g., demeton-S-methyl, dichlorvos and trichlorfon, do not exhibit a good chromophore in conventional LC–UV detection [9]. In addition, a few reports have indicated the difficulties encountered in determining certain organophosphorus pesticides, such as fenthion and dimethoate [10,11], fenamiphos [12] and dichlorvos [1,13], in water.

The development of extraction methods for priority organophosphorus pesticides within the European Community (EC) is of importance [1,14]. The Water Research Centre (Medmenham, UK) currently organizes interlaboratory exercises (Aquachek) through various European laboratories using other priority organophosphorus pesticides (e.g., mevinphos, fenthion and diazinon) spiked at 0.02–0.2 $\mu\text{g/l}$ in ground water samples [15]. When participating in these interlaboratory exercises, generally automated SPE followed by LC–diode array detection (DAD) is used. Problems occur such as the degradation of fenthion, mainly due to photolysis and hydrolysis in water, partly attributed to the presence of the SCH_3 group [13], and the fact that mevinphos has two isomers, *cis* and *trans*, that are always present in water samples [15].

This was surprising for us because in the inter-laboratory results only mevinphos is indicated and not the two separate isomers. The degradation and half-lives of several organophosphorus pesticides in water samples showed that in many cases the transformation products, e.g., fenthion sulfoxide and disulfuton sulfoxide, are more stable than the parent compounds [16].

The aims of this work were pursued by (i) optimizing the different SPE parameters using various sorbent materials with the ASPEC XL system combined with a controlled solvent evaporation/drying step with the Baker Spe 12G apparatus, (ii) paying special attention to different operations related to the preconcentration of pesticides from water such as the formation of transformation products during the water analysis and interferences present in the cartridges or the matrix and (iii) carrying out specific investigations to distinguish *cis*- and *trans*-mevinphos, which is difficult under current LC-DAD conditions owing to the poor chromophore of *cis*-mevinphos.

2. Experimental

2.1. Chemicals

HPLC-grade water and methanol were obtained from J.T. Baker (Deventer, Netherlands) and were passed through a 0.45- μm membrane filter before use. The organophosphorus pesti-

cides were purchased from Promochem (Wesel, Germany). The major physico-chemical properties of some of the pesticides studied are shown in Table 1.

2.2. Liquid chromatography–mass spectrometry

The eluent was delivered by a gradient system from Waters Model 616 pumps controlled by a Waters Model 600S Controller (Waters–Millipore, Milford, MA, USA). A methanol–water gradient was applied from 28% methanol (10 min under isocratic conditions) to 72% methanol in 20 min at a flow-rate of 0.3 ml/min. A 15 mm \times 2.1 mm I.D. column, packed with 5- μm particles of Zorbax (Rockland Technologies, Nuenen, Netherlands) coated with a cyanopropyl stationary phase.

This gradient LC system was connected to a VG Platform Electropray (ESP) system (Fisons Instruments, Manchester, UK) equipped with a Megaflow ESP probe (here called ISP). The design of this ISP and the optimization of the different conditions of ISP-MS operation were reported in a previous paper [1]. The ISP using a VG Platform instrument was operated at a flow-rate of 0.3 ml/min and a source temperature of 150°C. This parameter was not changed, although few experiments (not reported here) showed a substantial decrease in sensitivity when the flow-rate was increased to 0.5–0.6 ml/min; 0.3 ml/min was an acceptable flow-rate for our experiments

Table 1
Physico-chemical properties of organophosphorus pesticides which offer problems in conventional SPE procedures

Compound	Water solubility (g/l)	Vapour pressure (mPa)	K_{oc} (ml/g)
Trichlorfon	120	0.21	29
Dichlorvos	8	2100	38
Mevinphos	600	17	44
Demeton-S-methyl	22	40	66
Dimethoate	25	1.1	29
Oxydemeton-methyl	100	3.8	75
Fenamiphos	0.7	0.12	267
Fenthion	0.004	0.37	1500

From Ref. [31].

since it permits the use of 2.1 mm I.D. LC columns and conventional LC pumps without any specific restriction. At 0.2 ml/min, although a higher sensitivity was achieved, the performance of the system was poor owing to increased band broadening. Experiments were performed using either methanol–water and acetonitrile–water mixtures. The drying gas flow-rate was kept at 350 l/hr and the nebulizing gas at 10 l/hr, the ISP voltage was 3.1 kV, the HV lens voltage was 0.3 kV and the source temperature was maintained at 150°C. The extraction or cone voltage was varied between 20 and 100 V to study the fragmentations of the different pesticides. Generally, a cone voltage of 20 V was used in all the analyses owing to the enhanced sensitivity compared with higher cone voltages.

2.3. Sample preparation

Ground water samples (pH 8.0, 75 mg/l nitrate, 387 mg/l sulfate, 254 mg/l Ca, 88 mg/l Mg, conductivity 2020 $\mu\text{S}/\text{cm}$) were used. The pesticides were spiked in 200 ml of water to give a final concentration of 0.2 $\mu\text{g}/\text{l}$ and subsequently the water was acidified at lower pH, depending on the experiments. Immediately after this operation, the water samples were extracted with the ASPEC XL system in order to avoid degradation.

The ASPEC XL system fitted with an external Model 306 LC pump for dispensing samples through the SPE cartridges and with a Model 817 switching valve for the selection of samples was a gift from Gilson (Villiers-le-Bel, France). Disposable 6-ml cartridge columns from Isolute International Sorbent Technology (Hengoed, UK) packed with 1 g of monofunctional C_{18} -bonded silica or cyclohexyl, or 200 mg of ENV (Merck, Darmstadt, Germany) packed with 200 mg of LiChrolut-EN (Supelco, Bellefonte, PA, USA) packed with 1 g of Amberchrom 161c resin and from J.T. Baker (Deventer, Netherlands) packed with 200 mg of styrene–divinylbenzene copolymer were used. An optimum flow-rate of 10–15 ml/min was used (at 40 ml/min we observed losses in certain compounds), as indicated previously [1].

The drying step was carried out using a Baker Spe 12G apparatus connected to a vacuum system with 15 p.s.i. (negative pressure). The time used for drying was dependent on the sorbent used and varied from 10 min for LiChrolut to ca. 60 min for Amberchrom. The elution step took place with two aliquots of 4.5 ml of the same solvent as used for conditioning step, acetonitrile or methanol, depending on the technique used subsequently. Most of the experiments were performed with methanol, but a few were carried out with acetonitrile when using diode-array detection (DAD) owing to the better background signal caused by the wavelength cut-off. This protocol was adapted for the cartridges containing 1 g of sorbent, whereas for the cartridges containing 200 mg the amount of solvent used for the conditioning and elution step was halved. Elution of the cartridges took place with a waiting time of 5 min between the two aliquots. The final evaporation of the surplus solvent was performed with a gentle stream of nitrogen in such a way that the extracts were dried to a final volume of 200 μl but never to dryness in order to prevent losses of the more volatile compounds. At this point, samples were stored at 4°C before analysis (maximum 1 day) in order to avoid degradation of the most polar analytes. Before LC–ISP–MS, the extract was diluted with 200 μl of water. To improve the performance of LC–ISP–MS, avoiding band broadening due to the fact that the LC gradient starts at high water percentages, the sample extracts were injected in a similar solution as the eluent [methanol–water (50:50)] instead in 100% methanol.

2.4. Quantification

External calibration was used with quantification of the extract after SPE with an standard. The system was linear in most cases using 7–9 points from 0.1 to 60 ng (0.012, 0.025, 0.060, 0.12, 0.61, 1.23 to 6 $\mu\text{g}/\text{l}$). From 400 μl of the sample extract, 10 μl were injected into the LC–ISP–MS system. The calibration equations for the different pesticides were constructed as reported previously [1] and were linear ($r^2 = 0.998$) over the range studied. The quantification of the water

extracts was achieved usually by using time-scheduled SIM using the $[M + Na]^+$ ion for each organophosphorus pesticide (see Table 2). The limits of detection (LODs) were calculated by using a signal-to-noise ratio of 3–6 (the ratio between the peak intensity under SIM conditions and the intensity of the noise was used). For the organophosphorus pesticides studied the LODs varied from 10 to 200 pg under SIM conditions, whereas under full-scan conditions they were 10 times higher than those reported in Table 2.

3. Results and discussion

3.1. General considerations on $[M + Na]^+$ ion

In LC–ISP–MS, different points arise concerning the formation of the $[M + Na]^+$ ion. In earlier work by Ikonomou et al. [17], it was reported that the sodium ions present originate as an impurity in the methanol solution. Since in ISP–MS the vaporization takes place from the solution, it was reported that 90% of the observed ions are due to ions present in the solution. The second point arises from the use of methanol or acetonitrile in the mobile phase. Acetonitrile certainly decreases the abundance of the sodium-cationized ions vs. methanol, as reported for various organophosphorus pesticides [18], monuron and carbofuran [19]. Indeed, this can be observed in Fig. 1, which shows the

higher total ion current of the $[M + Na]^+$ and $[M + H]^+$ ions when using methanol as compared with acetonitrile. In the case of acetonitrile, the abundances of these two ions were similar whereas when using methanol the $[M + Na]^+$ ion was much more abundant (see Fig. 1).

It was also noticed that sodium ion addition is thermodynamically favoured and occurs preferentially in dilute solution, but in more concentrated solution the sodium ions are depleted and protonation becomes dominant, as reported for sulfonylurea herbicides [20].

The formation of abundant sodium-cationized ions has been reported in the determination of a variety of pesticides, including sulfonylureas [20,21], alachlor and metolachlor [21,22] and phenylurea herbicides [22]. In general, we can conclude that the formation of abundant adduct ions with sodium (i) is related to the use of methanol in the mobile phase, (ii) it is compound dependent, as observed in previous work [22] that showed very low abundances of the sodium adduct ion for triazine herbicides whereas for phenylurea the sodium adduct ion was the base peak, and (iii) it is dependent on the concentration of the compound and on the cone voltage used. In this respect, it was observed that the $[M + Na]^+$ ions can exhibit high or low abundances with increasing cone voltage. This is again dependent on the compound, as shown for aldicarb and propoxur [23]. Similar behaviour is shown in Figs. 2 and 3, where the abundances of

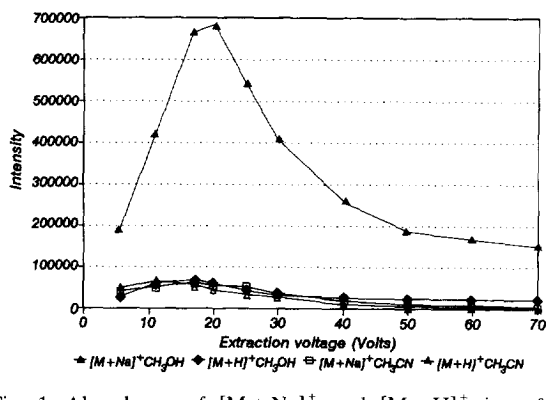


Fig. 1. Abundance of $[M + Na]^+$ and $[M + H]^+$ ions for dimethoate using methanol–water and acetonitrile–water eluents at various extraction voltages from 5 to 70 V.

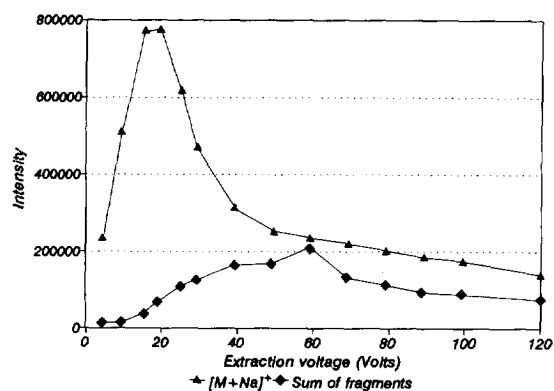


Fig. 2. Variation of $[M + Na]^+$ and the sum of fragment ions for dimethoate at various extraction voltages up to 120 V.

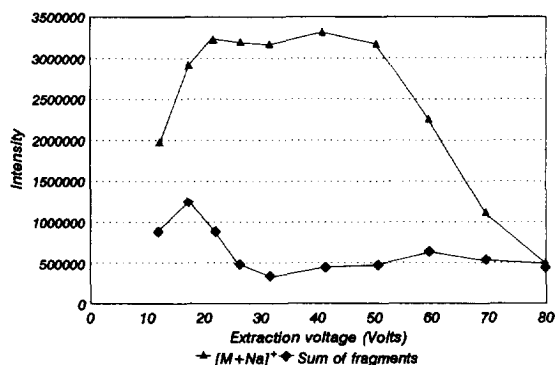


Fig. 3. Variation of $[M + Na]^+$ and the sum of fragment ions for fenamiphos at various extraction voltages up to 80 V.

the $[M + Na]^+$ ions and the various fragment ions are plotted against cone voltage for dimethoate and fenamiphos. For most of the compounds, on increasing the cone voltage the sum of fragments increases whereas the $[M + Na]^+$ ion decreases, as observed for dimethoate (Fig. 2), whereas for certain compounds, in our case only fenamiphos, the $[M + Na]^+$ ion remains constant when the cone voltage increases (see Fig. 3).

For comparison, we found previously [22] that the $[M + Na]^+$ ion was stable for phenylurea herbicides, it being impossible to obtain any fragmentation even at a cone voltage of 100 V. This behaviour was totally different to that of triazine herbicides and it was attributed to the greater stability of the aromatic structure of the phenylurea herbicides with the sodium adduct ion compared with triazines. Again, the fact that the $[M + Na]^+$ ion is stable at different extraction voltages is compound dependent. In addition, if additives such as NH_4^+ and H^+ are added to the eluent, then the signal intensity of the sodium adduct ions diminishes sharply.

3.2. Mass spectra of organophosphorus pesticides

All organophosphorus pesticides followed the general ESP ionization patterns indicated previously [1]. $[M + Na]^+$ and $[M + H]^+$ ions were the base peak and the second most abundant peak, respectively, at a cone voltage of 20 V. On

increasing the cone voltage to 100 V, an enhanced fragmentation was observed and in many cases also the base peak either remained the same or changed (see Figs. 2 and 3). The new base peak at higher cone voltages was in many instances a typical fragment of organophosphorus pesticides originating from the $[M + H]^+$ ion, e.g., for diazinon at 40 V the base peak and the second most abundant ion corresponded to m/z 169 and 153 (66%), respectively, and were attributed to $[(C_2H_5O)_2POS]^+$ and $[M - 169 + OH + H]^+$, as also reported using electrospray MS-MS [18]. This fragmentation also matches that observed with LC-atmospheric pressure chemical ionization (APCI) MS, although in this particular case the $[M + H]^+$ ion was the base peak [24]. Of the compounds studied, diazinon showed the most dramatic change in the relative abundances of the various ions on changing the extraction voltage from 20 to 40 V, as found previously for fenitrooxon and demeton-S-methyl [1].

The characterization of *cis*- and *trans*-mevinphos (Fig. 4) was of interest. When using UV DAD, the *trans* isomer elutes at longer retention times under conventional reversed-phase conditions [15]. However, the *cis* isomer has a very poor chromophore, giving quantification problems after SPE from water samples. We carried

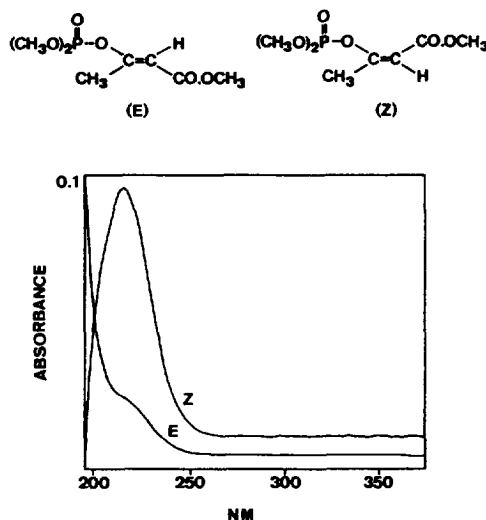


Fig. 4. Structures and UV DAD spectra of mevinphos isomers [*cis* (E) and *trans* (Z) (with respect to carbon chain)].

out the characterization of both compounds by LC–ISP–MS using extraction voltages of 20 and 40 V. The spectra are shown in Fig. 5 and the major ions at m/z 127, 193, 225 and 247, corresponding to $[(\text{CH}_3\text{O})_2\text{P}(\text{OH})_2]^+$, $[\text{M} - \text{CH}_3\text{O}]^+$, $[\text{M} + \text{H}]^+$ and $[\text{M} + \text{Na}]^+$, respectively, were characterized. the *trans* isomer contains the m/z 99 ion, which is not formed with the *cis* isomer. The structures of the two isomers (see Fig. 4) indicate that the *trans* isomer can easily form this m/z 99 ion, similarly to the *ortho* effect observed for certain organophosphorus pesticides [25]. The m/z ions at 127 and 225 were also noticed with LC–APCI–MS–MS [26]. Fig. 6 shows the LC–ISP–MS traces for a water extract containing

8 $\mu\text{g}/\text{l}$ of *cis*- and *trans*-mevinphos after pre-concentration of 200 ml of ground water using SPE (Amberchrom), the amount injected being 24 ng (40 ng would be the theoretical amount but the recovery is only 60%). The m/z 99 ion can be used to differentiate the mevinphos isomers at 40 V.

3.3. Recoveries

A poor recovery for dichlorvos was obtained previously [1] and was attributed to its high vapour pressure with losses during the sample preparation step. The fact that the Gilson ASPEC system uses a positive instead of a

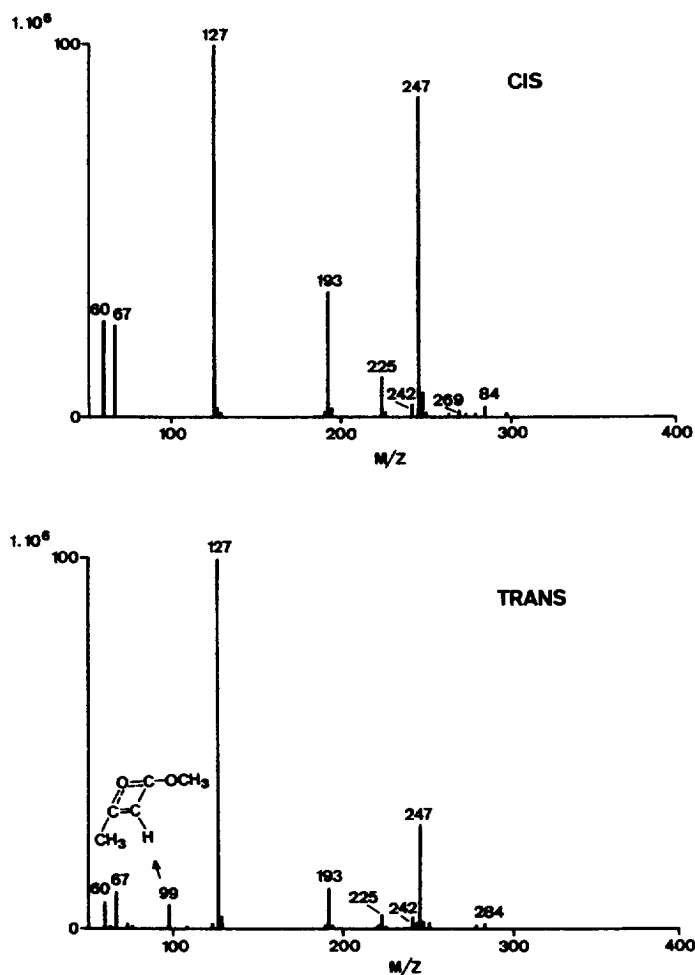


Fig. 5. LC–ISP mass spectra of *cis*- and *trans*-mevinphos. Amount injected, 40 ng; extraction voltage, 40 V.

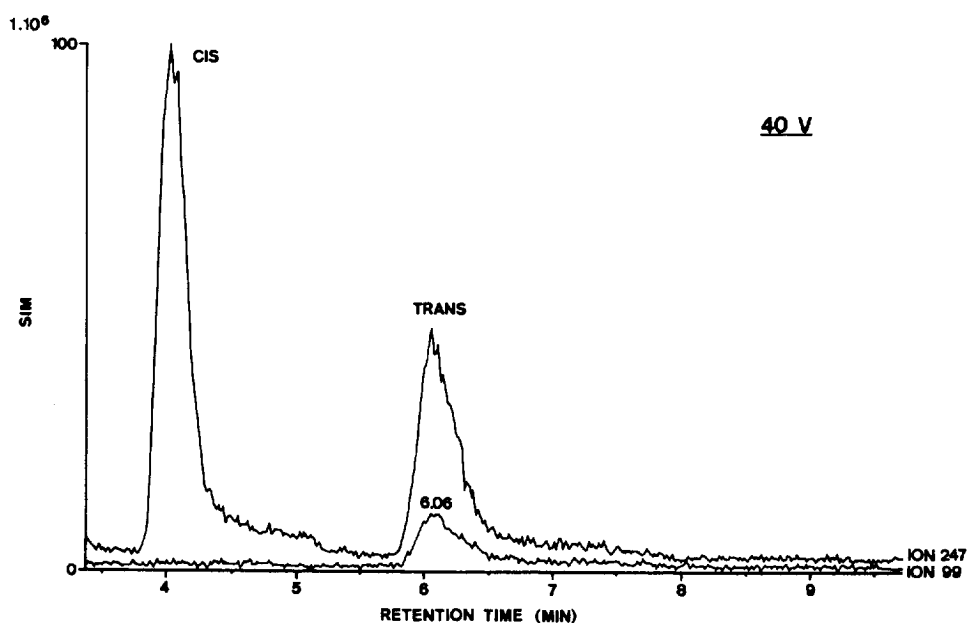


Fig. 6. LC-ISP-MS SIM results obtained after preconcentration of 200 ml of ground water spiked at $8 \mu\text{l/l}$. The ion at m/z 247 corresponds to *cis*- and *trans*-mevinphos, whereas the ion at m/z 99 corresponds only to *trans*-mevinphos.

negative pressure as compared with a vacuum manifold makes the drying of the cartridges difficult. As reported in a previous paper [2], better recoveries (7–17% for phenols) were obtained using negative than positive pressure.

The improved recovery (Table 2) compared with previous work [1] is attributed (i) to the fact that in the present work the extract was not evaporated to total dryness (see Experimental) and (ii) to the improved drying of the cartridge, so that less hydrolysis is expected. Another aspect to be considered is the high conductivity of the water used for the recovery experiments, around 5–10 times higher than that of common ground waters in Europe [27,28] and the USA [29]. The high conductivity of the water will favour ionization of the compounds and consequently will decrease their recoveries. For this reason, experiments were performed acidifying or not the water matrix.

Fig. 7 shows examples of the different traces for the extracts obtained using LC-ISP-MS. It can be seen that all the compounds studied can be easily quantified by LC-ISP-MS at levels

below $0.2 \mu\text{g/l}$. Several aspects deserve special attention, as follows.

3.3.1. Effect of water type

When using distilled water in the present system (results not reported), the recoveries were always improved, especially for compounds that still do not show very good recoveries using ground water, e.g., using Lichrolut EN at pH 4.7 trichlorfon and dichlorvos had recoveries of 114 and 80%, respectively. When using cyclohexyl, the extraction recovery of dichlorvos from distilled water was 93% compared with 46% for ground water (see Table 2). Fenamiphos and demeton-S-methyl were also affected. The high concentrations of nitrates in the water can be a source of oxidation of compounds via photo-degradation [30].

3.3.2. Effect of pH

On lowering the pH from 7 to 4, the recoveries of mevinphos, dichlorvos and trichlorfon were improved. Only acidic pH values are reported in Table 2 when using LiChrolut EN and C_{18} . In

Table 2

Mean recoveries (%) with the different SPE sorbents using 200 ml of ground water sample spiked at 0.2 $\mu\text{g/l}$ and LODs (under SIM conditions)

No.	Compound	[M + Na] ⁺ (m/z)	Sorbent ^a						LOD (pg) ^b
			1	2	3	4	5	6	
1	Oxydemeton-methyl	269	96	105	88	130	89	96	10
2	Triclorfon	279	65	47	47	39	41	5	100
3	<i>cis</i> -Mevinphos	247	79	86	52	87	60	84	20
4	Dimethoate	252	89	67	59	97	62	95	30
5	<i>trans</i> -Mevinphos	247	81	65	65	78	63	85	30
6	Dichlorvos	243	67	69	56	46	57	67	60
7	Demeton-S-methyl	253	70	17	17	14	10	47	20
8	Fenamiphos sulfoxide	342	95	103	90	124	130	129	100
9	Fenitrooxon	284	90	74	65	91	95	133	200
10	Fenamiphos sulfone	358	87	80	67	94	89	132	100
11	Fenamiphos	326	71	25	16	8	10	120	10
12	Diazinon	327	65	86	31	64	75	126	10
13	Fenthion	301	57	52	50	50	51	57	200

The R.S.D. ($n = 6$) varied between 10 and 15% for recoveries higher than 70%, but varied up to 30% for low recoveries values (8–50%).

^a Sorbents: 1 = LiChrolut (water pH = 4); 2 = SDB; 3 = Amberchrom; 4 = cyclohexyl; 5 = C₁₈ (water pH = 3); 6 = IST-ENV. Sorbents 2, 3 and 4: water pH = 6.

^b LODs under full-scan conditions are 10 times higher.

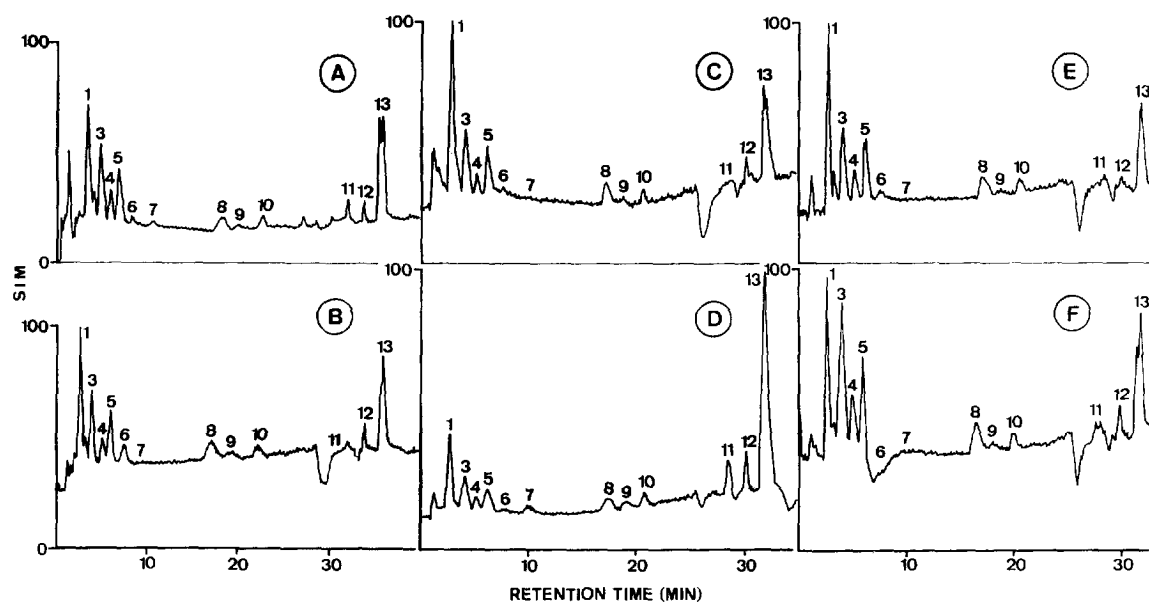


Fig. 7. LC-ISP-MS SIM results obtained after preconcentration of 200 ml of ground water spiked at 0.2 $\mu\text{g/l}$. Sorbents (A) LiChrolut EN; (B) SDB; (C) C₁₈; (D) IST ENV; (E) Amberchrom; (F) cyclohexyl. For peak identification, See Table 2.

both cases using LiChrolut EN, the recoveries of *cis*-mevinphos, dichlorvos and trichlorfon at pH 7 varied from 26, 34 and 34%, respectively, of the values shown in Table 2.

Trichlorfon has been the subject of some controversy in the literature. The Pesticide Manual [31] indicates that it is not stable at $\text{pH} < 5.5$, whereas a report from WHO [32] shows just the contrary, that it is stable for 46 days at pH 2. We observed that on lowering the pH better results were achieved as compared with pH 7. For LiChrolut the two pH values were compared and the recoveries varied from 35 to 65% on acidifying the water (see Table 2). The recovery of trichlorfon using ENV is very low (5%) (see Table 2), which is strange since both sorbents have similar structures, both being cross-linked polymeric materials with a surface area of 1100–1200 m^2/g . For this reason, experiments were performed by extracting the water samples at pH 4 and comparing the two types of extraction. It was found that the recovery of trichlorfon could only be improved up to 15%

using ENV, but was still much lower as compared with 65% obtained when using LiChrolut EN (Table 2). This indicates that there are still some differences between the two sorbents, which might be expected as they correspond to different manufacturers.

3.4. Degradation

The degradation of the different pesticides after spiking into water and during the extraction procedure is a key issue. First, from the data in Table 2 it can be seen that fenthion always had lower recoveries of $< 60\%$. Previous experiments [15,16] using on-line SPE followed by LC-DAD indicated that this compound degraded in water and during extraction from water samples after ca. 30 min and various transformation products could be identified from the spectra. Fig. 8 shows different experiments performed for this compound with the investigation of fenthion sulfoxide as the major transformation product by monitoring the ion at m/z 317, which is specific

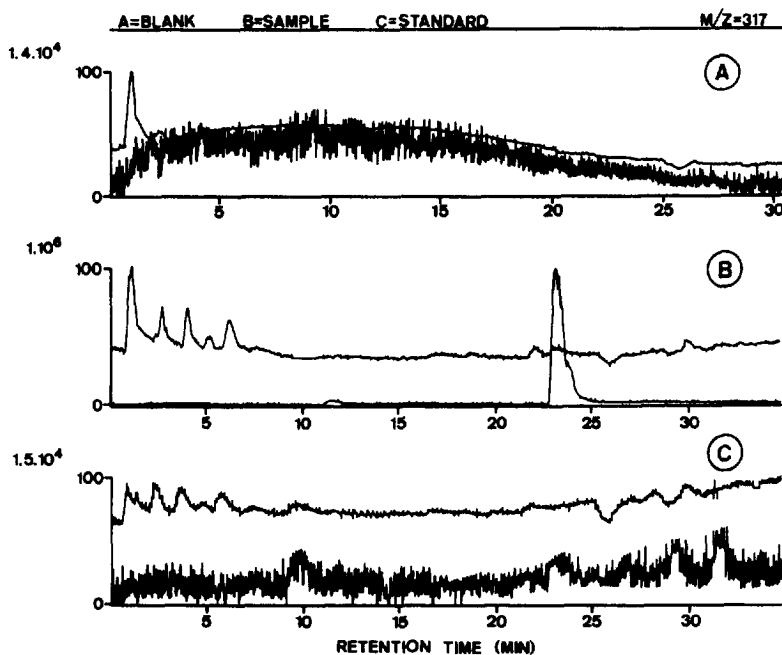


Fig. 8. LC-ESP-MS SIM results for the ion at m/z 317 (fenthion sulfoxide) obtained after (A) preconcentration of 200 ml of ground water sample, (B) 200 ml of ground water sample spiked with fenthion at 0.2 $\mu\text{g}/\text{l}$ and (C) fenthion standard (35-ng injection).

to fenthion sulfoxide and corresponds to the $[M + Na]^+$ ion. The specific mass fragments corresponded to $[M + Na]^+$, $[M + H]^+$ and $[M - CH_3 + H]^+$ ions (see Fig. 9). It should be noted that the formation of the $[M - CH_3 + H]^+$ ion only occurs for fenthion sulfoxide and not for fenthion itself and it has similarities with conventional GC-MS fragmentation [33]. This was the main reason for the observed low recovery. Further unequivocal confirmation of this compound was achieved by LC-ISP-MS with injection of a standard giving the same fragmentation pattern as shown in Fig. 9.

Recoveries $>100\%$ were obtained for fenamiphos sulfoxide whereas fenamiphos usually showed poor recoveries. In order to investigate if fenamiphos sulfoxide was also formed, several water samples containing fenamiphos were analysed. Fenamiphos sulfoxide appeared in the chromatographic traces and this was attributed not only to the water type (ground water) used in this work, but also to the compound itself, since this degradation has also been observed using estuarine water [16].

The degradation of fenamiphos and fenthion can be explained partly also by their structures. Both contain $-C_6H_3SCH_3$ with an *ortho*- CH_3

group. It was shown that compounds with this sulfomethyl group (SCH_3) substituent degraded faster in water than compounds with a nitro group in the same position, e.g., fenitrohion or fenitrooxon, mainly owing to the faster photolysis rate and adsorption on particulates [13].

Finally, the second transformation product of fenamiphos, fenamiphos sulfone, did not show any change in recovery (Table 2). Although the oxidation of fenamiphos to fenamiphos sulfoxide was a relatively easy process, further oxidation to sulfone usually requires photosensitizers, e.g., acetone, or further oxidizing conditions. Under the experimental conditions in this work and with the type of water used, such oxidation it not expected to occur.

4. Conclusions

By applying the proposed automated off-line SPE (ASPEC XL) method followed by LC-ISP-MS, it was feasible to determine a variety of organophosphorus pesticides which generally offer problems in extraction from water samples. The improvement in the sample preparation system was achieved, apart from the use of an

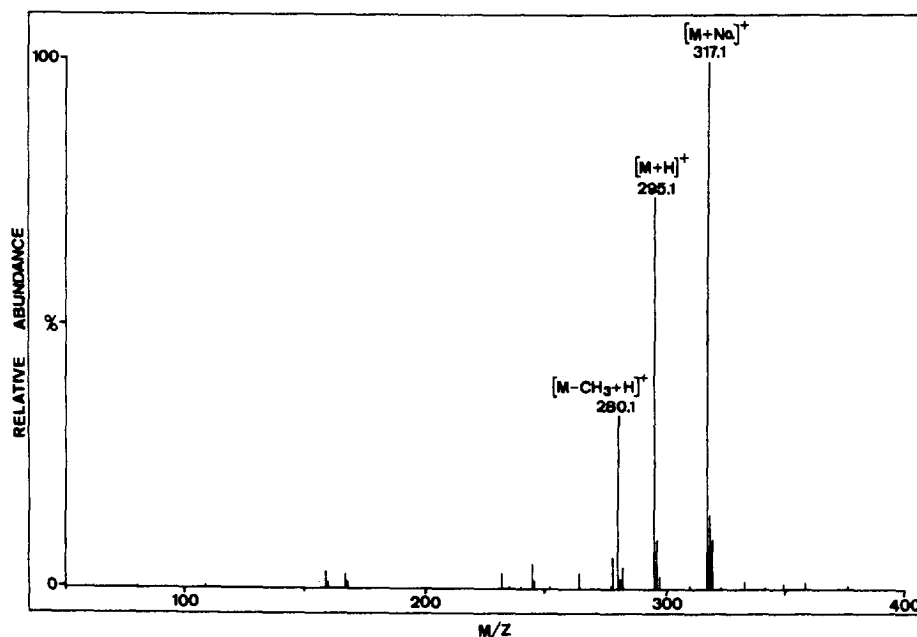


Fig. 9. LC-ISP mass spectrum of fenthion sulfoxide from Fig. 8.

automated method using conventional 6-ml cartridges that reduce the relative standard deviation, by the introduction of a drying step. This permitted careful evaporation of the extract, which was never continued until dryness, so losses of the more volatile pesticides were avoided. Of the various sorbent materials tested in the SPE procedure LiChrolut EN and IST ENV (with the exception of application to trichlorfon) offered the best results and can be recommended for the determination of polar pesticides in water samples. The water type was investigated and the importance of the water matrix and pH in the extraction procedure was shown. The best results were always obtained at lower pH values (ca. 4). The use of LC-ISP-MS demonstrated the problems encountered with the cartridge blanks and the presence of phthalates was detected.

Acknowledgements

This work was supported by the Environment R & D Program 1991–1994 (Commission of the European Communities) (Contract EV5V-CT92-0061). C. Molina received a grant from CICYT (AMB94-0950-CE). We thank Merck and IST for supplying the SPE cartridges. Gilson (Villers-le-Bel, France) and its Spanish representative (Pacisa) are thanked for the kind loan of the Gilson Aspec equipment.

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