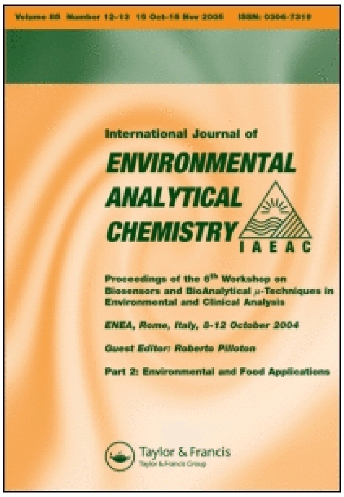

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Determination and Stability of Phenmediphan, Ethofumesate and Fenamiphos in Ground Water Samples Using Automated Solid Phase Extraction Cartridges Followed by Liquid Chromatography High Flow Pneumatically Assisted Electrospray Mass Spectrometry

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DETERMINATION AND STABILITY OF PHENMEDIPHAN, ETHOFUMESATE AND FENAMIPHOS IN GROUND WATER SAMPLES USING AUTOMATED SOLID PHASE EXTRACTION CARTRIDGES FOLLOWED BY LIQUID CHROMATOGRAPHY HIGH FLOW PNEUMATICALLY ASSISTED ELECTROSPRAY MASS SPECTROMETRY

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The determination and stability of polar pesticides phenmediphan, ethofumesate and fenamiphos in ground water samples was subjected to analysis with solid phase extraction (SPE) followed by liquid chromatography-high flow pneumatically assisted electrospray mass spectrometry (LC-ESP-MS). Pesticides were spiked at 6 μg/L in ground water samples and 80 mL were preconcentrated by using an Automated Sample Preparation with Extraction Columns (ASPEC XL) system.

After preconcentration, several different storage conditions were tested, which included storage at 4°C, at –20°C and at room temperature using styrene divinylbenzene (SDB) cartridges. The percentage of degradation varied from 20 to 80% for all the studied pesticides after 20 days of storage at room temperature. Phenmediphan and ethofumesate were stable at 4°C and –20°C during all the studied period whereas fenamiphos was recovered only 32 and 50% at 4 °C and –20°C, respectively, after 80 days of storage.

The L.O.D under LC-ESP-MS and SIM conditions were between 10–20 pg, 5–60 times lower as compared to LC-thermospray-MS with no thermal degradation of phenmediphan.This higher sensitivity of LC-ESP-MS permitted the determination of fenamiphos sulphoxide formed during the extraction and storage and the identification of the interferences present in the cartridges e. g., diethyl and di-n-butyl phthalates.

KEY WORDS: Polar pesticides, solid phase extraction, stability studies, ground water, electrospray mass spectrometry

INTRODUCTION

In a previous paper[1] a method for the determination of several priority organophosphorus pesticides in distilled water samples involving solid phase extraction (SPE) followed by liquid chromatography-high flow pneumatically assisted electrospray-mass spectrometry (LC-ESP-MS) was developed. The technique was proved to be useful for the analysis of

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pesticides in water since no degradation for thermally labile compounds such as trichlorfon was noticed. The L.O.D were also considerable improved (by a ~ 100) as compared to conventional LC-thermospray MS. Combined with automated SPE the trace level determination of chlorinated phenoxy acids and their metabolites in water samples was feasible[2]. A conventional ESP with flow rate of 30 μL/min was used for the determination of acidic herbicides in combination with SPE using graphitised carbon black[3]. For all these reasons, the use of LC-ESP-MS with SPE is a good method for the trace level determination of pesticides in water samples and it can be used to solve the problems of their determination, specially for those not easily detected by other methods, either GC or LC-thermosprayMS.

The European Commission published a report on pesticides in Ground and Drinking Water that indicated the need to study better analytical procedures for certain priority pesticides with a leaching potential to ground water widely used in Europe (over 50 or 500 tones per year)[4]. Many of them are also of importance in USA[5]. This list included phenmediphan, ethofumesate[5] and fenamiphos[4]. A recent library report indicated that still many problems arise with these three pesticides and although various analytical methods were tested for these three priority pesticides, no report has indicated the use of LC-ESP/MS[6]. Recently[7] recoveries of 15 and 56% were reported for phenmediphan and fenamiphos after extraction from surface water samples spiked at 2 μg/L level and analyzed by LC UV. Detection limits of the three target pesticides using the best analytical method up till now involving LC-thermospray (TSP)-MS varied from 70–90 pg to 600 pg (phenmediphan)[7]. Thermally assisted hydrolysis in the TSP vaporiser has been reported for phenmediphan with a strong dependence of S/N ratio on the ion source and vaporizer temperatures and consequently with poor detection limits[8]. In previous interfacing systems in LC-MS, such as direct liquid introduction, a similar behavior was observed for this compound with decomposition at source temperatures above 200°C[9].

Another aspect that has not been sufficiently addressed when analyzing pesticides by LC-MS are the interferences from the matrix or the cartridges. In this respect we should indicate that in previous works[10–12] the interferences present in SPE material when using gas chromatography-mass spectrometric (GC-MS) techniques were shown. When LC techniques were applied to environmental analysis, to our knowledge no papers reported the usual interferences, e.g., phthalates, from the SPE materials, except the recommendations given by the US EPA using particle beam LC-MS method[13]. In these recommendations, the method pays attention to m/z ions at 75 and 313 which corresponded to the bleeding of dimethyloctadecylsylanol from the C_{18} LC column.

The use of an automated off-line sample preparation system (ASPEC) with conventional 6 mL cartridges together with an improved and controlled solvent evaporation and drying step followed by LC-ESP-MS should facilitate the determination of selected priority pesticides at low μg/L level in water. The incorporation of the drying step will also be an improvement for the stability studies, since water will be removed avoiding hydrolysis of the pesticides during storage.

Knowledge about the stability of the different contaminants in water during transport and storage is a key issue. Recently[14] we have reported about the stability of 19 organophosphorus pesticides in ground water samples using disposable SPE precolumns of C 18 material. Although most of the pesticides were stable at –20°C, fenamiphos suffered a complete degradation when the precolumns were stored at room temperature (RT) and 4°C after 45 days. The disposable SPE precolumns were of 10 × 2 mm i.d., thus allowing 20–30 mg of C 18 material in it. In this work conventional cartridges of 200 mg will be used containing styrene-divinylbenzene material instead of C 18. The introduction of the drying step - in contrast to the previous work[14]- it should also facilitate stability since hydrolysis is prevented. Apart from the physicochemical properties of each pesticide: vapor pressure (VP) and the soil organic partition coefficient (K_{OC}), other parameters to take into account in stability studies are: type and grams of sorbent material.

The aim of the present paper will be achieved by: (i) the optimization of the different SPE parameters and styrene-divinylbenzene material (SDB and Lichrolut EN) using the ASPEC XL combined with a controlled solvent evaporation/drying step with the Baker spe 12G (ii) the use of LC-ESP-MS as an analytical method for the determination of ethofumesate, phenmediphan and fenamiphos in water samples at low µg/L level (iii) carrying out a stability study during 80 days at three different temperatures (–20°C, 4°C and RT) in order to assess the ideal storage conditions for pesticide stability and (iv) determining possible transformation products formed during the storage conditions. The paper, which follows prior research from our group on the analysis, degradation and storage of pesticides in water samples[1,2,14–16] can be of help for improving quality assurance parameters in relation to sample handling, analysis, transport and storage of pesticides in water samples.

EXPERIMENTAL

Chemicals. HPLC-grade water and methanol were obtained from J.T. Baker (Deventer, The Netherlands) and were passed through a 0.45-µm membrane filter before use. The pesticides were purchased from Promochem (Wesel, Germany).The major physicochemical properties of these pesticides are shown in Table 1.

Liquid chromatography-mass spectrometry. The eluent was delivered by a gradient system from Waters 616 pumps controlled by Waters 600S Controller from Waters-Millipore (Milford, Massachusetts). The LC eluent conditions varied form 28:72 (10 min isocratic conditions) to 72:28 methanol-water in 20 min at 0.3 mL/min.15 mm × 2.1 mm i.d. column, packed with 5-µm particles from Zorbax, Rockland Technologies Inc., (Nuenen, The Netherlands) coated with a cyanopropyl stationary phase.

This gradient LC system was connected to a VG Platform ESP from Fisons Instruments (Manchester, U.K.) equipped with a Megaflow ESP probe. The design of this ESP and the optimization of the different conditions of ESP-MS operation have been reported in a previous paper[1]. The high-flow pneumatically assisted ESP using a VG Platform instrument has been used at a flow rate of 0.3 mL/min and at a source temperature of 150°C. This parameter was not changed, although we have performed few experiments (not reported here) that showed a substantial decrease in sensitivity when the flow rate increased up to 0.5–0.6 mL/min. 0.3 mL/min was an acceptable flow rate for our experiments since it permits to use 2.1 mm i.d. LC columns and conventional LC

Table 1 Physicochemial properties of organophosphorus pesticides which offer problems under conventional SPE procedures

Compound	*Water solubility mg/L*	*Vapor pressure mPa*	*Half-life days*	*Koc cc/g*
Ethofumesate	50	0.65	25 (soil)	340
Phenmediphan	4.7	0.0000013	30 (soil)	2400
Fenamiphos	700	0.12	1.8 (water)	267

pumps without any specific restriction. At 0.2 ml/min, although somewhat higher sensitivity was achieved the performance of the system was poor due to increased band broadenning.

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 μmhos/cm) were used . The pesticides were spiked in 80 mL of water to give a final concentration of 6 μg/L and afterwards the water was acidified at pH 4. Immediately after spiking, the samples were preconcentrated by the ASPEC XL.

An Automatic Sample Preparation with Extraction Columns (ASPEC) XL fitted with an external 306 LC pump for the dispensing of samples through the SPE cartridges and with a 817 switching valve for the selection of samples, was a gift from Gilson (Villiers le-Bel, France). Disposable 6 mL cartridge columns from Merck (Darmstadt, Germany) packed with 200 mg Lichrolut-EN, and from J.T. Baker (Deventer, Holland) packed with 200 mg styrene divinylbenzene (SDB) were used. An optimum flow rate of 10–15 mL/min was used (at 40 mL//min we have noticed losses in certain compounds) as indicated in our previous work[1]. A further step was introduced in order to achieve a better drying step of the SPE cartridges avoiding also losses by evaporation.

The drying step was carried out using a Baker spe 12 g apparatus connected to a vacuum system with 15 psi (negative pressure).The time used for drying was 20 min. Although the recovery study was carried out using Lichrolut EN and SDB cartridges, finally the storage study to test the stability of the trapped pesticides was carried only with SDB. This was due to the fact that both types of cartridges offered the same recovery to the compounds of study and that the sorbent material, SDB, was also similar between both cartridges. After drying, 30 cartridges of SDB were wrapped with aluminum foil and stored at 4°C, –20°C and RT during a period of 80 days. After each period of storage, the cartridges were defrozen for a period varying from 1–2 h up to 6–8 h depending if the storage was carried out at 4°C or –20°C, respectively. The elution step took place with two aliquots of 4.5 mL × 2 of methanol. The elution of the cartridges took place with a waiting time of 5 min between the two aliquots in order to keep a good contact time between the solvent and the trapped compound. The final evaporation step of the extra solvent was performed with a gentle stream of nitrogen in a way that the extracts were dried till a final volume of 200 μL but never to dryness to prevent losses of the more volatile compounds. All the analyses were carried out in triplicate at each storage period. Before LC-ESP-MS, the extract was diluted with 200 μL of water, to improve the performance under LC-ESP-MS, as reported[1]. All these precautions: loading into the cartridges, drying and evaporation step are very important for these three polar pesticides (see Table 1, for physicochemical properties).

Quantitation. External calibration was used with the quantitation of the extract after SPE with an standard. The system was linear in most of the cases using 7–9 points from 0.1 to 80 ng (0.012, 0.025, 0.060, 0.12, 0.61, 1.23, 2.0 to 8.0 μg/L). The calibration equations (R^2 = 0.998) for the different pesticides analyzed were constructed as previously reported[1] and were linear over the studied range. The quantitation of the water extracts was achieved usually by using time-scheduled-selected-ion-monitoring using $[M + Na]^+$ ion for each pesticide (see Table 2). The L.O.D's were calculated by using a signal-to-noise ratio of 3–6 (the ratio between the peak intensity with SIM conditions and intensity of the noise was used). For the pesticides L.O.D's of 10–20 pg, were obtained. These LODs are considerable lower (between 5–60 times) as compared to TSP-MS (with L.O.D of 70–90 pg for ethofumesate and fenamiphos and 600 pg for phenmediphan).

Table 2 Mean recoveries (%) and standard deviation (n = 6) with the different SPE sorbents using 80 mL of ground water sample spiked at 6 µg/L. Sorbents:(SDB) and Lichrolut EN

No	*Compounds*	*[M + Na]⁺ m/z ion*	*Sorbents*	
			SDB	*LICHROLUT EN*
1	Fenamiphos sulfoxide	342	95 ± 0.7	90 ± 1
2	Phenmepdiphan	323	83 ± 0.7	70 ± 4
3	Ethofumesate	309	82 ± 0.2	93 ± 3
4	Fenamiphos	326	70 ± 0.6	72 ± 0.8

Statistical evaluation. All results were converted to a percentage of the initial concentration. The precision and variability of the ASPEC XL procedure for each pesticide was calculated through the relative standard deviation. The sources of variation (storage conditions, time, compound) were measured with the analysis of variance using the Fischer test (α = 0.05). Variability for each time period within a storage condition was examined.

RESULTS AND DISCUSSION

General considerations about mass spectra

All pesticides followed the general ESP ionization patterns indicated in our previous publication[1]. $[M + Na]^+$ and $[M + H]^+$ ions were the base peak and the second most abundant peak, respectively, at 20 V of extraction voltage. Fenamiphos and fenamiphos sulfoxide were already reported in a previous paper from us, whereas the LC-ESP-MS spectra of ethofumesate and phenmediphan are here reported for the first time (see Figure 1). Both give as base peak the $[M + Na]^+$ ions, which is a typical feature of such interfacing system. $[M + H]^+$ ion is also formed in much minor degree (10% relative abundance). Another advantage of LC-ESP-MS as regards to previous techniques such as LC-TSP-MS is the enhanced structural information obtained. The ion formed by phenmediphan at m/z 168 match with that reported by LC-TSP-MS. The abundance in LC-TSP-MS was dependent on the source temperature, varying from 13 to 38% at 200 and 300°C of ion source temperature, respectively[8]. The base peak under LC-TSP-MS corresponded always to m/z 185 (168 + 17).[8,17]. Both ions, at m/z 168 and 185 indicate that phenmediphan suffered degradation by thermally assisted hydrolysis in the LC-TSP-MS vaporizer. The m/z ion at 168 was already observed under direct liquid introduction LC-MS being also an indication of sample decomposition[9]. This ion was used for monitoring of phenmediphan in water samples with LOD of 600 pg[7], around 60 times higher than using the present system involving LC-ESP-MS using SIM of the ion at m/z 323.

The gas-phase thermal degradation of phenmediphan and other carbamates[8] and organophosphates as trichlorfon is common under LC-TSP-MS. Due to this thermal degradation in the interface, the fragment ions should be used as quantitative ions in SIM, as reported[17]. The formation of $[M + H]^+$ and $[M + NH_4]^+$ ions account for less than

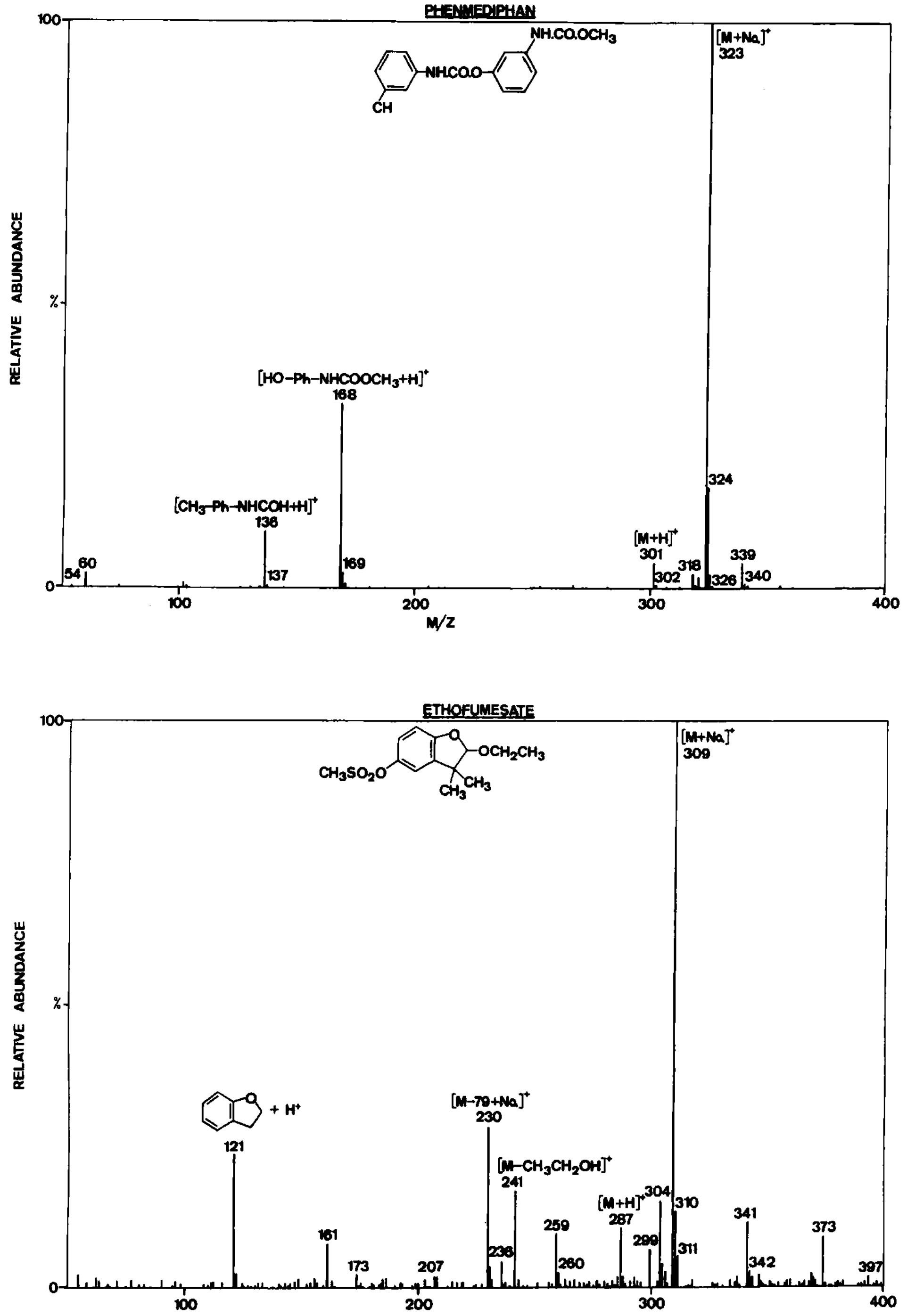


Figure 1 LC-high flow pneumatically assisted ESP MS spectra of phenmediphan and ethofumesate. Amount injected: 40 ng. Extraction voltage: 20 V.

4%, which is not a common behavior under LC-TSP-MS and it is only caused because phenmediphan degrades. The high interface jet temperature of ca. 235°C needed under LC-TSP-MS induce this chemical dissociation of phenmediphan in the vaporizer probe and makes fragmentation unavoidable. Similarly this was observed for trichlorfon but the use of LC-ESP-MS has solved this problem[1]. Under LC-ESP-MS there is no heat in the interface and only the ESP voltage and the nebulizing gas helps the vaporization of the compound, so thermal degradation is avoided. The poor detection limits observed for this compound under LC-TSP-MS are due to this fact and indicates that LC-TSP-MS method is not suitable for trace level determination of phenmediphan in water. The LOD were 600 pg[7] as compared to 10 pg under LC-ESP-MS.

As regards to ethofumesate, the base peak formed under LC-TSP-MS corresponds to $[M + NH_4]^+$, which is a common feature and it corresponds to m/z ion at 304 with a LOD under SIM of 70 pg[7]. The fragmentation pattern of ethofumesate gives much more information under LC-ESP-MS as compared to LC-TSP-MS with different diagnostic ions at m/z 121, 230 ,and 241, corresponding to $[M - CH_3SO_2O - CH_3\text{-}CH_3\text{-}OCH_2CH_3 + H]^+$, $[M - CH_3SO_3 + Na]^+$ and $[M - CH_3CH_2OH]$, respectively, whereas the base peak corresponds, as usual to $[M + Na]^+$ ion. The increased fragmentation observed under LC-ESP-MS is a common feature of this technique and it has been compared in a way to tandem MS methods[1,2].

Recoveries. The introduction of drying step, after the application of the positive pressure by the ASPEC XL, and the use of an appropriate material, SDB, has enhanced the recoveries of the compounds previously reported, usually in the range of 15–65%,[7,18]. The improved recovery is attributed to the fact that: (i) the extract is not submitted to total dryness so losses by evaporation are minimized and (ii) to the improved drying step of the cartridge so less hydrolysis is expected. Another aspect to be considered is the high conductivity of the water used for recovery experiments, around 5–10 times higher than common ground waters[5,19]. The high conductivity will help that the compounds are ionizable and consequently their recoveries will be lowered. For this reason, all the experiments have been performed acidifying the water matrix.

Formation of fenamiphos sulfoxide. In Figure 2 the traces of the extract at time 0 showed already the formation of fenamiphos sulfoxide. Although all the precautions were taken during the preconcentration of the three pesticides, this compound was formed (it can be noticed by the SIM chromatogram of the ion at m/z 342). Although the water sample was acidified at pH 4, the compound is already formed. The formation of this metabolite accounts 30% and that is the main reason of the recovery of 70% observed for fenamiphos at time 0 (see Table 2). Previous results[12] using on-line SPE followed by LC-DAD showed recoveries of 100%. There is an explanation to that, first in the present system 80 mL of water at 10 mL/min are preconcentrated with a drying step of 20 min, which makes a total period of time of 28 min. In the case of on-line SPE[12], 26 mL of water are preconcentrated at a flow rate of 2 mL/min, which makes a total period of 13 min to introduce fenamiphos into the analytical column. In addition to that, in the on-line SPE analysis, there are no manipulation of the samples and no losses during the drying step are produced because there is no drying step. The formation of fenamiphos sulfoxide- which is caused by the easy hydrolysis and instability of fenamiphos in water (with half life of 1.8 day, see Table 1 and ref. 16) is attributed mainly to the much higher contact time- in the case of SPE cartridge, as compared to the on-line system. The high solubility of fenamiphos in water has favored the formation of fenamiphos sulfoxide, although the ground water sample was acidified.

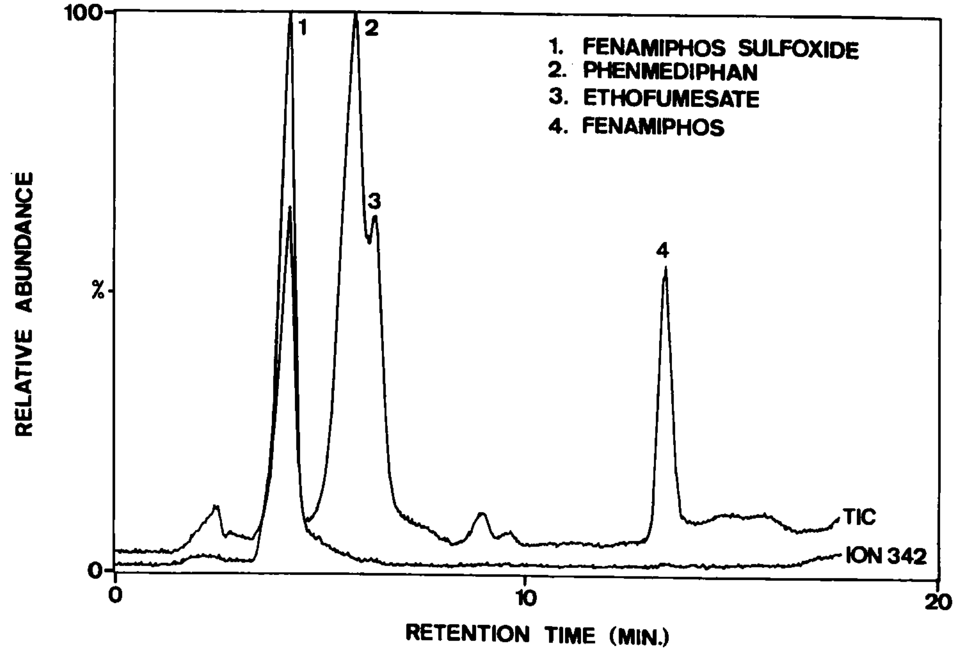


Figure 2 LC-ESP-MS SIM chromatograms obtained after preconcentration of 80 mL of ground water spiked at 6 μg/L level at time 0 of storage into the SPE columns. The m/z 342 ion corresponds to fenamiphos sulfoxide.

Another reason of the fast degradation of fenamiphos can also be explained by the type of water used. In previous paper using distilled water the recovery of fenamiphos was between 70–94%, depending on the sorbent used[1]. The water used in the present study had a very high conductivity, as reported in the Experimental section. So, compounds may not be easily extracted from solution. The high conductivity of the water, around 5–10 times as compared to US[5] and European ground waters[19] makes that fenamiphos is in its ionizable form. In addition, it has been reported that high concentrations of nitrates can be a source of oxidation of compounds in water and consequently photo degradation can also be enhanced[20]. In this respect it should be added that fenamiphos is a compound very sensitive to photolysis, as reported in ref. 16.

Storage conditions. The degradation of the different pesticides during the extraction procedure is a key issue. At RT, 20% of degradation was observed for phenmediphan and ethofumesate whereas for fenamiphos was 80% after 20 days of storage. So the study did not continue at RT, since indicated unstability of the pesticides although for ethofuemsate and phenmediphan the loss of 20% could still be acceptable, if there is no other way to keep the SPE cartridges under cooler conditions.

Figure 3 shows the % recovery of the three priority pesticides stored in the SPE at 4° and –20°C. First of all, we can notice that phenmedipham and ethofumesate are stable during all the storage period, which may be expected from their physicochemical properties and quite a high half-life (more that 25–30 days).

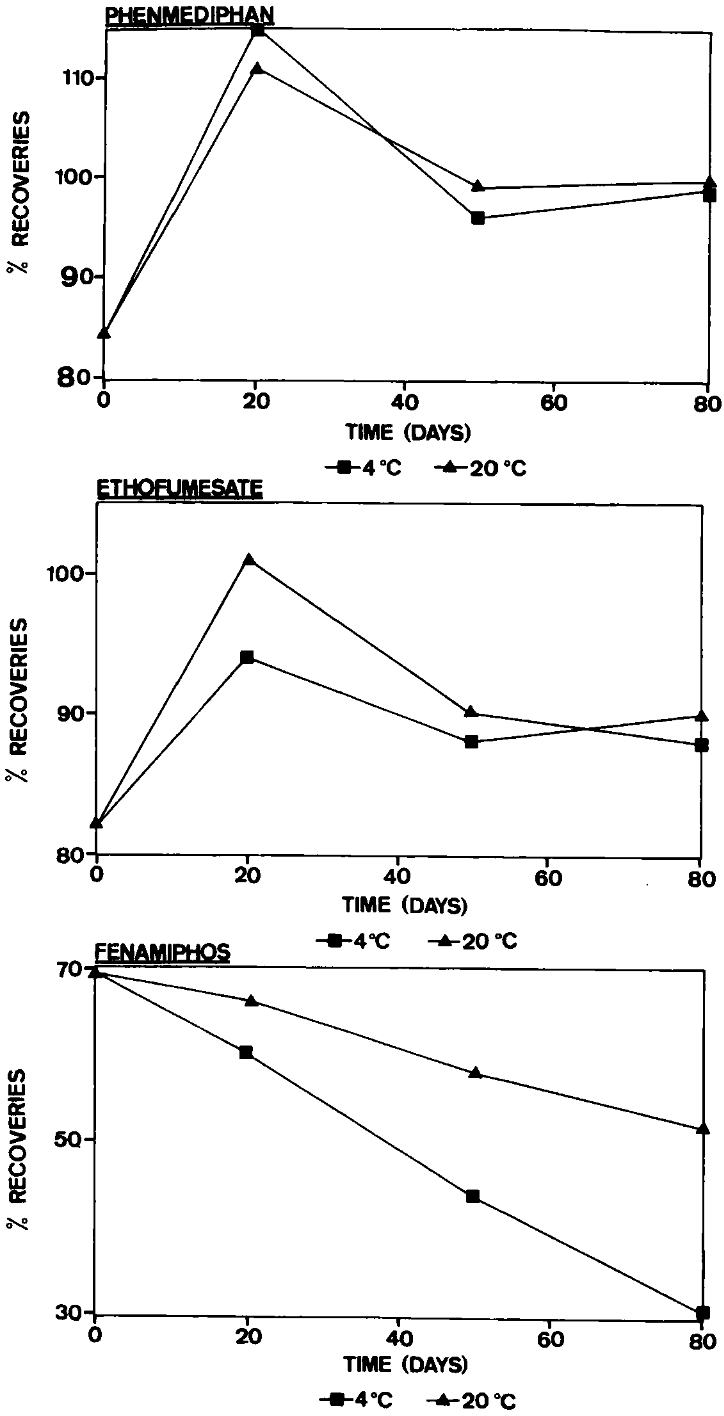
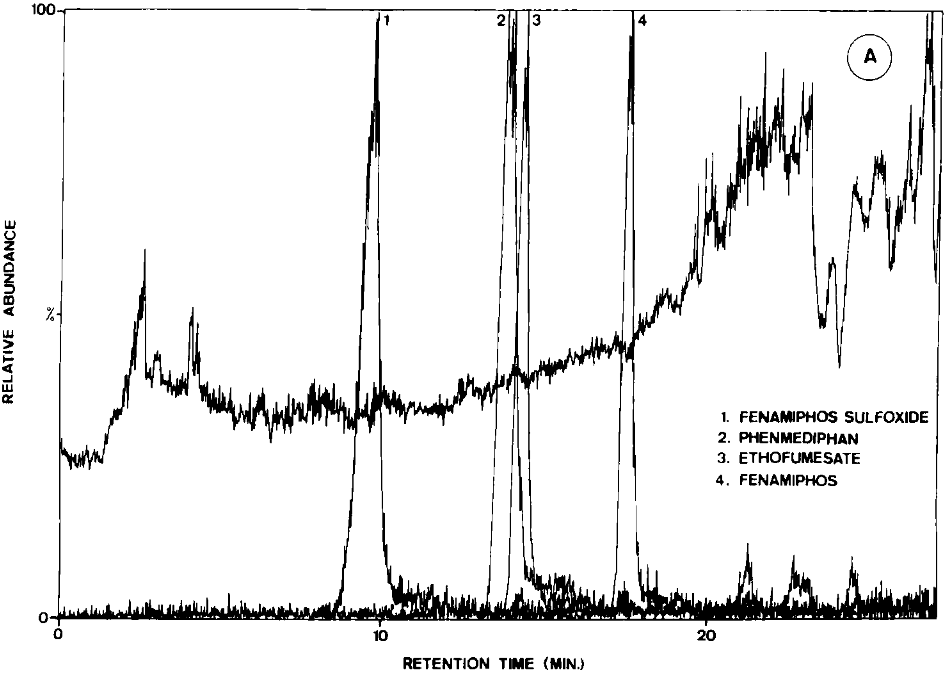


Figure 3 Mean recovery (three replicates) of phenmediphan, ethofumesate and fenamiphos from SPE columns stored at 4 °C and -20°C up to a period of 80 days.

Fenamiphos is the compound with more problems. We can notice that even at -20°C it is unstable (after 80 days only 50% of the compound is recovered), whereas at 4°C only 30% of the parent compound is obtained after the same storage period. These results are, again, in contrast with prior results from us using disposable SPE precolumns. Previously we have noticed that at -20°C, fenamiphos was stable during a period up to 8 months without any degradation but at 4°C fenamiphos was one of the few compounds unstable, and complete degradation occurred after 1.5 months of storage[14]. The reasons for this discrepancy are: at -20°C we noticed some degradation that was not observed previously using disposable SPE precolumns. The question is that here we are using more water volume (80 mL versus 26 mL) and the amount of packing material here is also higher (200 mg versus (20–30 mg)[14]. The higher water volume and more packing material may favor that water still can be trapped in the sorbent pores and hydrolysis occurred as more packing material is present (approximately 10 times more in this study).

However the results obtained at 4°C are better in this work than in the previous study since approximately 50% of the compound is recovered after 45 days, whereas in the previous study all the compound was degraded. This can be attributed to the drying step incorporated in the present work. No drying step was introduced in the disposable cartridges before storing[14] whereas here the drying step was implemented. Without any drying step, and although the cartridge contained less packing material, some water may be introduced in the cartridge and at 4°C hydrolysis and microbial degradation can still take place and enhance degradation of fenamiphos, as observed[14]. Another factor to take into consideration is that in the present case we are using SDB material, and not a silica based sorbent, so in this work hydrolytic process with the support are less favored as compared to a C 18 material. In general we should say that probably the best solution will be to use on-line SPE with polymeric material and incorporating a drying step. Examples on the LC-ESP-MS trace analysis of the samples analyzed are shown in Figure 4 corresponding to the storage after 80 days at 4°C and -20°C . The traces are obtained under full scan conditions and selected ions are also plotted. To have an idea of the sensitivity and for comparison with other works the traces of this figure correspond to 10–12 ng of compound under full scan conditions, which is a signal 3–5 times higher as compared to the traces of 30 ng obtained for ethofumesate under LC-TSP-MS[7]. This proves once more that LC-ESP-MS is an appropriate method for trace analysis.

Blanks. Blanks were another aspect that has not been sufficiently addressed when analyzing pesticides by LC-MS and interferences are related to the matrix or the cartridges. In this respect we should indicate that in previous works[10–12] the interferences present in SPE material when using gas chromatography-mass spectrometric (GC-MS) techniques were shown. When LC techniques are applied to environmental analysis, to our knowledge no papers reported the usual interferences, e.g., phthalates, from the SPE materials, except the recommendations given by the US EPA using particle beam method[7]. In these recommendations, the method pays attention to m/z ions at 75 and 313 which corresponded to the bleeding of dimethyloctadecylsylanol from the C_{18} LC column. An exploration of this subject is of interest, if we consider that the current cartridge materials contain different plasticisers. Compounds identified were diethyl phthalate (at m/z 245 corresponding to $[M + Na]^+$), di-n-butyl phthalate (at m/z301 corresponding also to $[M + Na]^+$) (see Figure 5). The retention time and fragments of these compounds matched with those of authentic standards. No traces due to the bleeding of the LC column were detected.



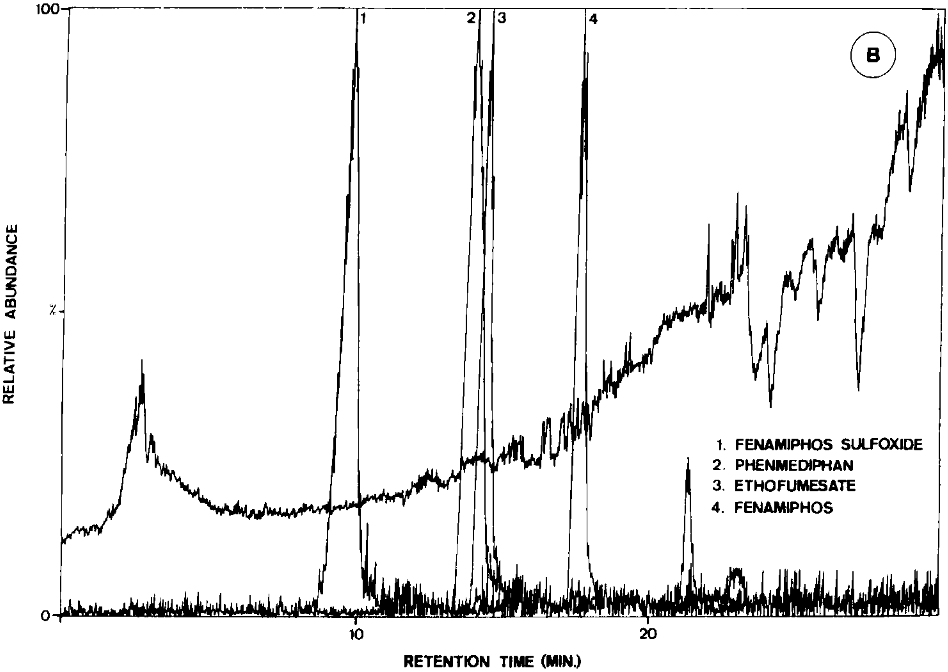


Figure 4 LC-ESP-MS SIM chromatograms obtained after preconcentration of 80 mL of ground water spiked at 6 µg/L level after storage during 80 days at (A) 4°C and (B) -20°C in SPE columns. Compound No. see Table 2.

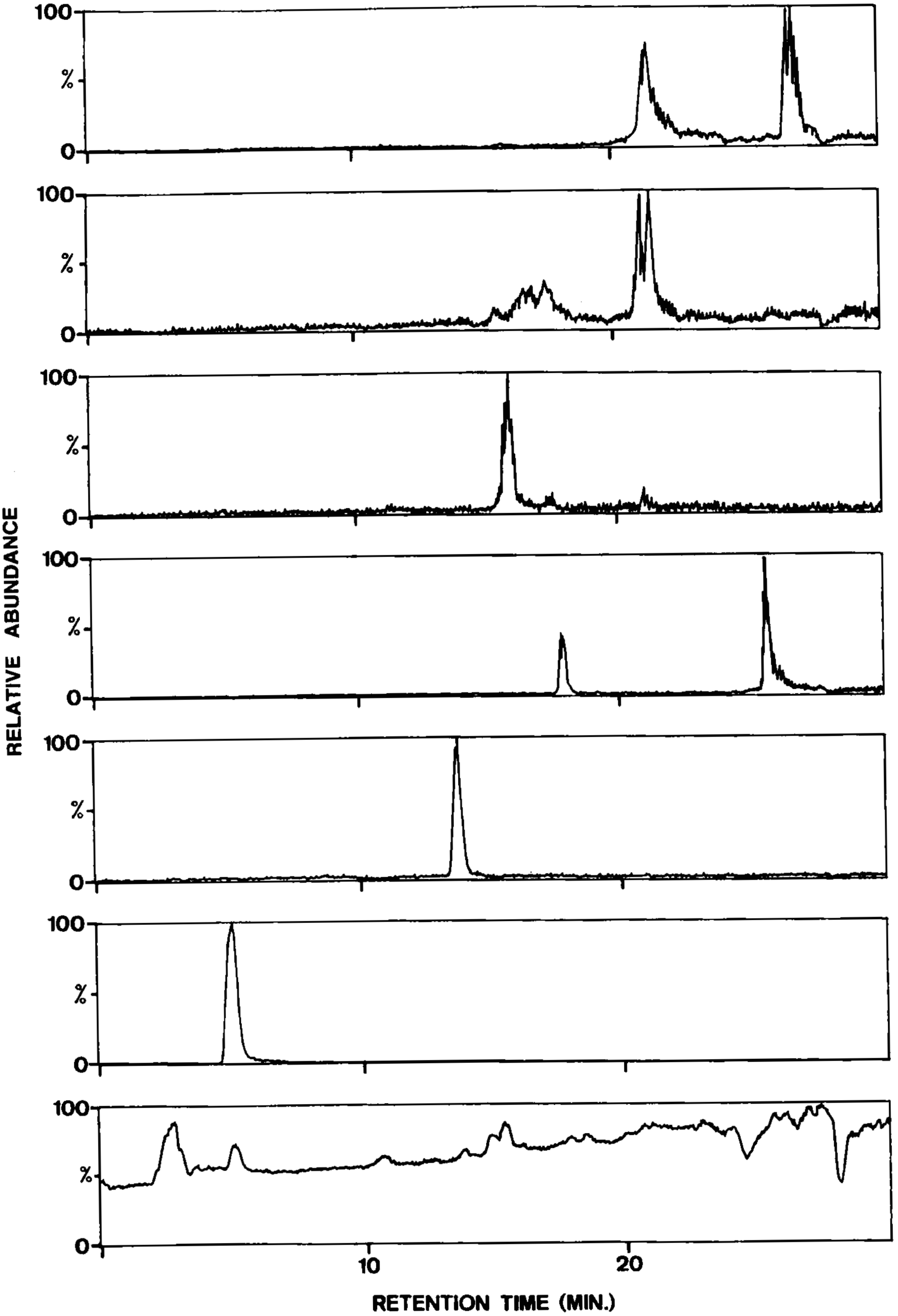


Figure 5 LC-ESP-MS SIM chromatograms of interferences present in the cartridges with m/z ions at 363, 301 (di-n-butyl phthalate), 282, 337, 245 (diethyl phthalate) 136 and the TIC after preconcentration of 80 mL of ground water without any spiking.

CONCLUSIONS

An analytical method for the analysis and stability of three priority pesticides in water at low level of detection was established from the three compounds, phenmediphan was the compound that offered more problems when analyzed under other LC-MS techniques and suffered thermal degradation. With the use of LC-ESP-MS these problems were solved and no thermal degradation and higher sensitivity were achieved.

Fenamiphos was a compound that suffered degradation during the extraction protocol and 30% of the compound was dissipated. This degradation continued during the storage period, and only 30 and 50% of the compound could be recovered, respectively after 80 days of storage at 4°C and –20°C, respectively. The formation of fenamiphos sulfoxide was monitored by LC-ESP-MS during all the storage study. Still improvements are needed as regards to the storage of this compound since degradation occurs with SPE cartridges during the period of study and even with storage at –20°C. The transformation product, fenamiphos sulfoxide, was stable during all the study and its concentration increased as the concentration of fenamiphos decreased. This indicates that the stability of pesticide transformation products in solid phase extraction cartridges is of importance and it needs further attention. Fenamiphos sulfoxide and other transformation products are included in pesticide priority lists, e.g., the National Pesticide Survey.

The use of a drying step after loading the cartridges and prior to storing, indicates that an increased stability was noticed for fenamiphos as compared to previous work when storing at 4°C. The use of a drying step permitted to recover 45% of the compound after 45 days of storage as compared to a complete loss without such drying step.

Finally the use of LC-ESP-MS has permitted the determination of the impurities present in the cartridge material, mainly coming from phathalates. This technique, with levels of sensitivity that can be compared to GC-MS techniques, and with a sensitivity around 100 times better than LC-TSP-MS makes it possible to study the interferences present in the cartridge material in a similar way as GC-MS.

The combination of SPE analysis with LC-ESP-MS is a powerful method that will be of help for carrying out monitoring studies and improving the quality assurance parameters in monitoring programs.

Acknowledgements

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