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Stability of pesticides stored on polymeric solid-phase extraction cartridges

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Abstract

The stability of four pesticides (desethylatrazine, fenamiphos, fenitrothion and fonofos) was examined under different storage conditions after preconcentration in disposable solid-phase extraction (SPE) cartridges containing new polymer sorbent materials (Hysphere-1, IST EnviroLut and LiChrolut). Complete recovery for all the compounds was observed in precolumns kept at -20°C for 1 month when preconcentrating 26 ml of ground water sample spiked at $10\ \mu\text{g/l}$. Degradation of fenamiphos and fenitrothion occurred in precolumns stored at 4°C and at room temperature after 1 month. Fonofos was stable when compared to their storage in C_{18} precolumns. Problems in the quantification of the analytes after storage at 4°C and at room temperature were encountered due to the presence of many interfering peaks in the chromatograms. Analysis of blanks with C_{18} precolumns was carried out, to determine the interferences. The stability of the pesticides was also examined in acidified and non-acidified ground water in order to compare it to the stability of pesticides stored on SPE cartridges. Significant losses of fenamiphos and fenitrothion were achieved and were related to the pH of the water sample and their chemical structure. Finally, the new polymeric sorbent Hysphere-1 was evaluated in terms of breakthroughs and compared with those of C_{18} , obtaining higher recoveries for desethylatrazine. © 1997 Elsevier Science B.V.

Keywords: Stability studies; Polymeric extraction analysis; Sample handling; Pesticides; Organophosphorous compounds

1. Introduction

The stability of the different pesticides in water during transport and storage is an important quality assurance issue to take into account in monitoring programs. A number of physical, chemical and biological processes may take place in a water sample in the time between sampling and analysis [1]. These processes involve a change in the real concentration including degradation, so it is important to carry out studies regarding the stability of pesticides during transport and storage of the water samples. Some degradation studies have been performed under controlled climate conditions: es-

tuarine, natural or artificial water, sunlight and high temperatures (20 – 40°C), at low spiking levels [2,3]. These studies indicated, in most of the cases, degradation of pesticides in water.

The use of a solid-phase extraction (SPE) cartridge is an alternative to storage of the original matrix [4]. The sample handling, transport and storage of the samples are also improved because of the small volume of such cartridges as compared with the more common large water volumes collected in environmental programs. It allows easy transport from the sampling site to the laboratory and storage at cool temperatures such as -20°C which it is not possible for water samples due to the increment in their volume and consequent breakdown of the glass bottles. Recent studies using Empore disks

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indicated that various corn herbicides had equivalent or greater stability in SPE disks as compared to their storage in water at 4°C [5,6]. Other ways of stabilization were also studied, e.g., freeze-drying [7] but poor recoveries were obtained after 1.5 months of storage for the most polar compounds such as fenamiphos [8].

Also, several studies of different type of cartridges, including disposable precolumns, were carried out indicating good stability for many compounds at cool temperatures [9–11]. Automated precolumn technology involving disposable solid-phase extraction precolumns has been proved to be an useful tool for the monitoring of pesticides in water, obtaining accurate results [12]. In a previous study on disposable SPE cartridges only C₁₈ cartridges were evaluated and they showed poor recoveries for unstable organophosphorus pesticides [10]. So, it is of interest to examine the stability of unstable organophosphorus pesticides, under different storage conditions, after preconcentration in disposable SPE cartridges containing new polymer sorbent materials (Hysphere-1, IST EnviroLut and LiChrolut). Compound selection was based on the problems with various unstable organophosphorus pesticides (fenamiphos and fonofos) encountered in a previous work using disposable C₁₈ precolumns [10]. Fenitrothion was selected for comparison with the previous work.

The specific objectives of this work were: (i) to study the storage stability of four priority pesticides (desethylatrazine, fenamiphos, fenitrothion and fonofos), spiked at 10 µg/l in ground water, after preconcentration to 26 ml; (ii) to compare the different disposable polymeric precolumns of Prospekt in terms of breakthroughs and recovery of samples with the conventional C₁₈ columns. It is important to know the retention of the analytes in the new sorbent materials as it is related to the polarity and thus to the stability in water media. In this respect desethylatrazine is a polar compound that can be used to evaluate the breakthrough volume; and (iii) to carry out the stability study during a period of 1 week up to 1 month at three different temperatures (–20°C, 4°C and room temperature) for the different cartridges and at two temperatures (4°C and room temperature) for the same pesticides spiked in ground water. To our knowledge this is the first

article that considers the use of disposable polymeric material for stability study of unstable organophosphorus pesticides in water.

2. Experimental

2.1. Chemicals

HPLC-grade solvents acetonitrile and water were purchased from Merck (Darmstadt, Germany). Pesticide standards: desethylatrazine, fenamiphos, fenitrothion and fonofos were obtained from Promochem (Wesel, Germany). Hydrochloric acid was also purchased from Merck. The C₁₈ cartridges and the polymeric sorbent materials, Hysphere-1, IST EnviroLut and LiChrolut, were obtained from Spark Holland. Their physical characteristics such as their particle size and surface area are summarized in Table 1.

2.2. Sample preparation

Stock standard solutions of 1000 µg/ml were prepared by weighing each of the solutes and dissolving them in acetonitrile. For the stability study in cartridges, a stock solution of 20 µg/ml containing the four pesticides was used to spike non-acidified ground water at the 10 µg/l level for the preconcentration and storage of the cartridges. The characteristics of the ground water were as follows: pH=7.4; conductivity 2.020 µΩ/cm; alkalinity 315 mg CaCO₃/l; chlorine 369 mg Cl/l; sulfates 387 mg SO₄²⁻/l; nitrates 75 mg NO₃⁻/l; and hardness 100 mg CaCO₃/l. A total of 26 ml of the spiked water sample was preconcentrated on 10×2 mm I.D. disposable precolumns with different packing materials at a flow-rate of 2 ml/min. A blank cartridge containing only 26 ml of ground water without pesticides was preconcentrated in order to study the

Table 1
Properties of the new polymeric sorbent materials

Sorbent	Particle size (µm)	Surface area (m ² /g)
Hysphere-1	5–20	>1000
IST EnviroLut	40–120	1100
LiChrolut	40–120	1200

interferences. Before extraction, the precolumns were preconditioned via a solvent delivery unit (SDU) from Spark Holland with 20 ml of acetonitrile and 10 ml of HPLC water at a flow-rate of 2 ml/min. After the preconcentration step of all the cartridges with the same spiked water, three precolumns were eluted (time 0). The other precolumns were wrapped in aluminium foil and stored without performing any drying treatment at three different temperatures: at room temperature, at 4°C and at -20°C for 1 week and 1 month. After this period of time desorption was carried out by placing the precolumns in the precolumn holder of the Prospekt and starting the gradient to the analytical column in the backflush mode. The cartridges stored at -20°C were brought to room temperature over 6–8 h prior to analysis in order to remove the frozen water matrix involving the stationary phase. Three replicate analyses were performed for each storage condition and period.

Eight cartridges were preconcentrated with non-acidified ground water without pesticides and were kept at 4°C as blanks because it was at this temperature the greatest number of interferences were observed, in a previous work [10] and as is shown in Fig. 1. This experiment was performed with four C₁₈ cartridges and four Hysphere-1 cartridges, kept at 4°C for 1 week and 1 month, in order to see whether the interferences were also observed with the conventional C₁₈ cartridges or arose from the new polymeric phase. Furthermore, the same experiment was carried out preconcentrating only HPLC water through C₁₈ cartridges to confirm that the interferences arose from the interaction of any kind of water with the solid-phase at this temperature and not from the ground water. Two blank cartridges of C₁₈ preconcentrated with ground water sample were analyzed on-line by liquid chromatography–atmospheric pressure chemical ionization–mass spectrometry (LC–APCI–MS) to find out the molecular mass and the major fragment ions of the various interferences encountered in the chromatograms.

Another batch of eight cartridges were preconcentrated with 26 ml of acidified (pH=3.5) ground water sample spiked with the mixture of the four pesticides at 10 µg/l. They were kept at 4°C and at room temperature for 1 week and 1 month. This experiment was performed to see whether the interferences could be minimized by acidifying the

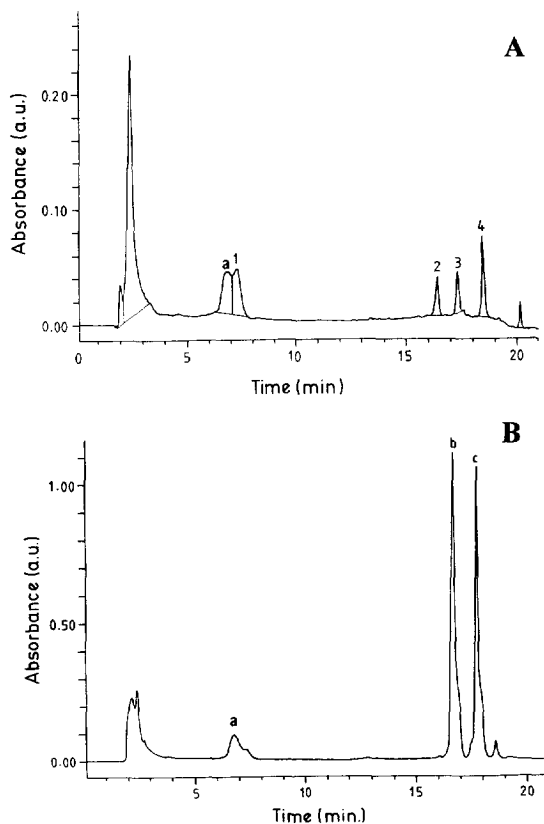


Fig. 1. (a) LC–DAD chromatogram corresponding to the elution of one Hysphere-1 cartridge, preconcentrated with spiked ground water, after the storage at -20°C for 1 month. Peak numbers: 1=desethylatrazine; 2=fenamiphos; 3=fenitrothion; 4=fonofos; a=interfering peak. (b) LC–DAD chromatogram corresponding to the elution of one Hysphere-1 cartridge, preconcentrated with ground water, after the storage at 4°C for 1 month. Peaks: a, b and c=interferents. Chromatographic conditions as described in Section 2.3.1. Detection at $\lambda=220$ nm.

ground water samples and to see if the pesticides, especially desethylatrazine, were affected by acidification.

After preconcentration of ground water sample spiked with the pesticides, two cartridges were frozen and then lyophilized in order to eliminate the remaining water that always is present in the cartridge.

For the stability study in ground water samples, four bottles were filled with 1 l of ground water and spiked with the mixture (10 µg/l) of the four pesticides. Glass bottles were used in order to study

the stability of the pesticides in water media and to compare it to the stability of pesticides stored on SPE cartridges. Two of the bottles were acidified at pH=3.5 with HCl and kept at 4°C and at room temperature, respectively. The other two bottles were not acidified and also kept at these two temperatures. The bottles stored at room temperature were not wrapped with aluminium foil but they all were capped. A water sample of 26 ml from every bottle was analyzed after 1 week and 1 month of storage in order to assess the stability of every compound in water media and then compare it to their stability in cartridges.

For the obtention of the breakthrough curves, 20, 40, 60, 100, 150, 200 and 300 ml of ground water sample were percolated through the cartridges. A stock solution of 1 µg/ml was used to spike ground water sample, at different concentrations, in such a way that the total amount injected was always 100 ng after the percolation of the different volumes. For this study only C₁₈ and Hysphere-1 cartridges were evaluated in order to compare the conventional C₁₈ sorbent phase with the polymeric one.

2.3. Apparatus

2.3.1. Prospekt–LC–DAD

LC analyses were performed with a Waters 600-MS solvent delivery unit with a 20 µl injection loop and a Waters 996 photodiode array detector (Waters, Millipore, Milford, MA, USA). The analytical column used was a 25 cm×4.6 mm I.D. packed with 5 µm octylsilica gel (Shandon). Trace enrichment was performed on an automated solid-phase extraction (SPE) system (Prospekt). It consists of a cartridge exchange module, a solvent delivery unit (SDU) (Spark Holland) and a low-pressure six-port valve, which is connected to the gradient pumps. Water samples were preconcentrated on 10 mm×2 mm I.D. disposable precolumns of Prospekt (Spark, Emmen, Netherlands) prepacked with 40 µm C₁₈ (Baker, Deventer, Netherlands), Hysphere-1, IST EnviroLut and LiChrolut. For more details see Ref. [13,14].

The gradient elution was performed as follows: from 25% A (acetonitrile) and 75% B (HPLC water) to 41% A and 59% B in 8 min, to 100% A in 8 min more and then kept isocratic for 5 min at a flow-rate of 1 ml/min.

Quantification was carried out with UV detection at 215 nm for desethylatrazine, at 254 nm for fenamiphos and fonofos and at 270 nm for fenitrothion.

2.3.2. LC–APCI–MS

LC–APCI–MS with positive and negative mode of operation was used for the determination of the interference peaks. The eluent was delivered by a gradient system from Waters 616 pumps coupled to a model Waters 600S controller (Waters). A VG Platform from Fisons Instruments (Manchester, UK) equipped with an APCI interface was used. The Platform APCI interface consists of a heated nebuliser probe and the standard atmospheric pressure source configured with a corona discharge needle. The LC eluents enter the probe at 1 ml/min where it is pneumatically converted into an aerosol and rapidly heated into the vapor/gas phase at the probe tip [15]. The different operating parameters included a drying gas flow-rate of 250–300 l/h and a nebulizing gas flow-rate of 10 l/h. The cone voltage was set at 20 V and the corona voltage at 3.5 kV. The ion source was set at 180°C and the probe temperature was of 400°C. A disposable holder connected to a switching valve was used for the on-line analysis of the cartridges stored at 4°C.

3. Results and discussion

3.1. General remarks

The US Environmental Protection Agency methods recommend acidification of the water samples after collection in order to avoid the degradation of pesticides during storage. Nevertheless, some problems can arise from those compounds that have an acid hydrolysis. The addition of HgCl₂ is also recommended as a biological inhibitor to preserve some pesticides from bacterial attack or from other unknown mechanisms of degradation. This is the case for carbamate pesticides like carbaryl, ethiofen-carb and methomyl. However, up to a 100% loss 100% for 21 days at 4°C has been observed for some compounds (fenitrothion, dimethoate, parathion, chlorpyrifos) stored in the presence of HgCl₂ while

they suffer less than a 40% loss when stored in bottled water [9].

Previous stability studies carried out following an on-line SPE methodology using only C₁₈ sorbent phases [10]. This work showed interfering peaks in the middle of the chromatogram when cartridges were stored at 4°C for a period of 2 weeks in a similar way as shown in Fig. 1.

Polymeric phases have been tested using off-line methodologies [11,16] indicating good recoveries for LiChrolut and Isolut sorbents for polar organophosphorus pesticides as fenamiphos and several phenols. Three new materials were specially packed in disposable precolumns by Spark Holland for this work. These polymeric materials with high surface area (see Table 1) were considered to be useful for performing the stability study of pesticides in water.

The pesticides were selected regarding different aspects encountered in previous works and concerning to their physicochemical properties [17,18] (see Table 2). Relatively high soil half-lives for all pesticides except for fenitrothion are reported [18]. Fonofos exhibits a high vapour pressure whereas fenamiphos exhibits high water solubility. Compounds like fenamiphos and fonofos were selected as long as they had a poor recovery in C₁₈ precolumns after a period of 1.5 months at 4°C [10]. Conversely, we selected desethylatrazine, a metabolite of atrazine with higher solubility, in order to study the breakthrough volumes obtained with the new polymeric material such as Hysphere-1 for their use in current monitoring of pesticides. Desethylatrazine is a compound that offers a good stability in C₁₈ solid-phase extraction disks after a period of 3 months at -20°C and at 4°C [6].

3.2. Breakthroughs

As can be seen in Fig. 2 the breakthrough volumes

are comparable for the two kind of sorbent materials with the exception of desethylatrazine. The breakthrough volume obtained with Hysphere-1 cartridges for desethylatrazine is higher than 300 ml while in C₁₈ cartridges the breakthrough is around 20 ml. As expected, the polymeric phase retains polar analytes in a larger extension than the conventional C₁₈ ones. Other studies from our own group in off-line [11] and on-line [19] for organophosphorus and phenolic compounds indicated that LiChrolut and Isolut offer high recoveries due to a large surface area and the type of interaction with polar analytes.

3.3. Cartridge storage

(a) At 4°C. Two broad co-eluting peaks with almost the same retention time that fenamiphos and fenitrothion were observed in all the chromatograms obtained after the elution of the cartridges stored at 4°C, so that the quantification of these two compounds was in many cases difficult at this temperature. The two coeluting peaks seem to be due to the interaction of the organic aqueous matrix of the ground water with the stationary phase of the cartridges. Nevertheless, in the case of cartridges stored for 1 week, recoveries between 75 and 96% were achieved for fenitrothion and fonofos, respectively, indicating that degradation did not occur during this period of time (see Table 3). Lower recoveries for fonofos were obtained during a period of 1 month (see Table 4). Fenamiphos was not determined due to the first coeluting peak as mentioned before. Desethylatrazine was not quantified also in all instances due to the fact of a double peak obtained in all cases. This double peak appeared also in all the blanks and when the sample was acidified. It may be related with the two other coeluting peaks obtained at higher percent of organic mobile phase.

Table 2
Physicochemical properties of the pesticides studied

Compound	Vapour pressure (MPa)	Water solubility (mg/l)	Soil half-life (days)
Deethylatrazine	n.a.	3200	n.a.
Fenamiphos	0.12	400	50
Fenitrothion	18	30	4
Fonofos	28	17	40

n.a. = not available.

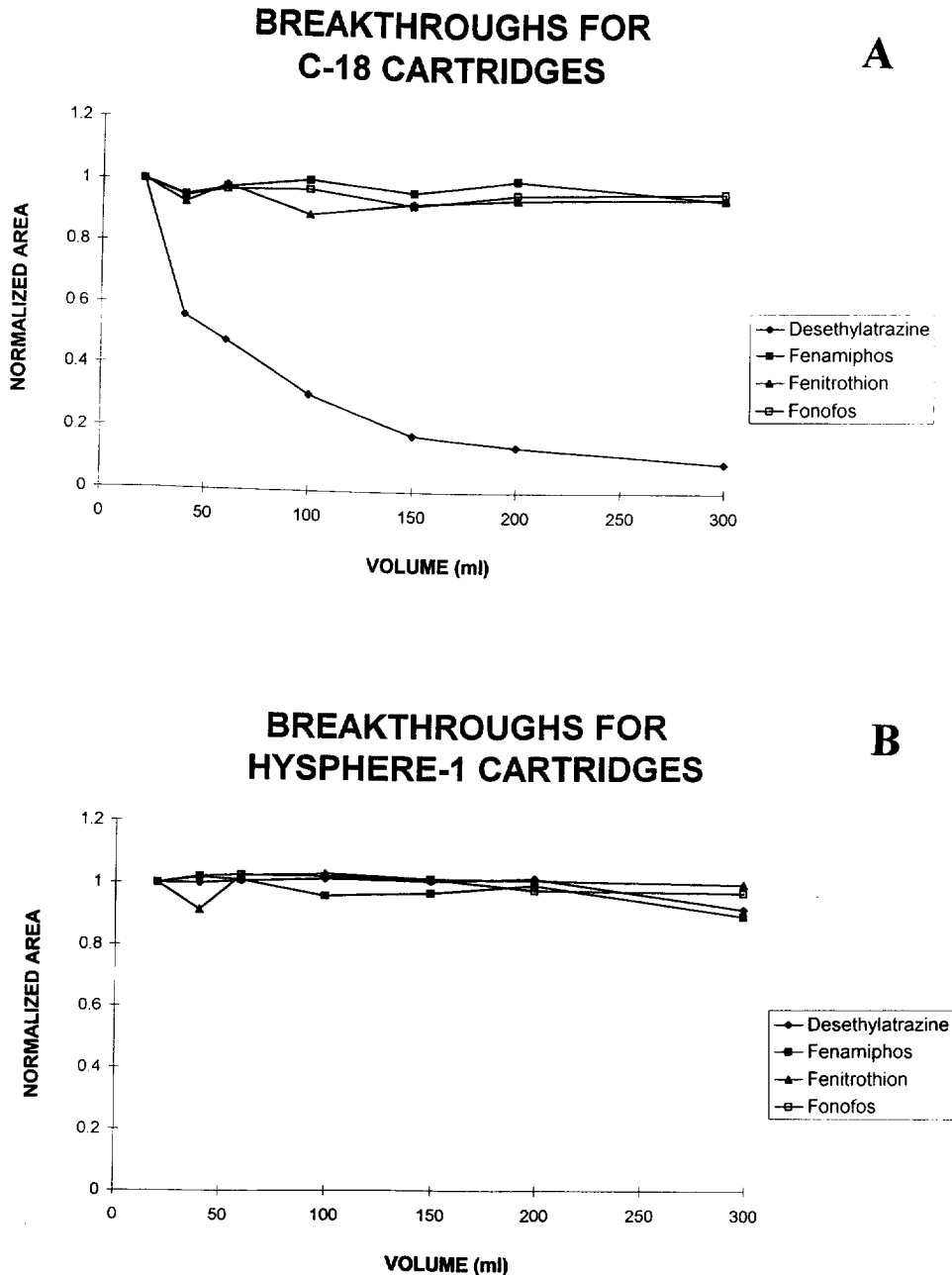


Fig. 2. Breakthrough curves obtained after the preconcentration of different volumes of spiked ground water upon: (a) C₁₈ cartridges and (b) Hysphere-1 cartridges. Total amount injected: 100 ng of each pesticide.

In general, no difference in storage stability between any of the cartridges types was observed.

(b) At -20°C . Recoveries between 85% and 99% were obtained for all compounds and for every

different cartridge indicating a good stability of such compounds at this low temperature. In the case of desethylatrazine no quantification was performed due to the double peak observed as reported before. The

Table 3

Mean % recovery ($n=3$) of pesticides stored in Hysphere-1, IST EnviroLut and LiChrolut cartridges at room temperature (RT), at 4°C and at -20°C for 1 week using on-line SPE-LC-DAD

Compound	ID No.	λ (nm)	Hysphere-1			IST EnviroLut			LiChrolut		
			RT	4°C	-20°C	RT	4°C	-20°C	RT	4°C	-20°C
Fenamiphos	2	254	74	nq ^a	92	68	nq	89	65	nq	90
Fenitrothion	3	270	nf ^b	81	94	75	85	85	97	75	96
Fonofos	4	254	92	93	97	91	96	98	101	87	94

Concentration of pesticides in spiked water: 10 $\mu\text{g/l}$. Volume percolated: 26 ml.

^a nq, unable to quantify.

^b nf, not found.

Desethylatrazine was not quantified due to the interferences of the water matrix.

Relative standard deviation: 2–10%.

Table 4

Mean % recovery ($n=3$) of pesticides stored in Hysphere-1, IST EnviroLut and LiChrolut cartridges at room temperature (RT), at 4°C and at -20°C for 1 month using on-line SPE-LC-DAD

Compound	ID No.	λ (nm)	Hysphere-1			IST EnviroLut			LiChrolut		
			RT	4°C	-20°C	RT	4°C	-20°C	RT	4°C	-20°C
Fenamiphos	2	254	nf ^b	nq ^a	90	nf	nq	89	nf	17	99
Fenitrothion	3	270	nf	nf	98	nf	nf	86	nf	106	89
Fonofos	4	254	nf	51	98	nf	86	97	75	86	97

Concentration of pesticides in spiked water: 10 $\mu\text{g/l}$. Volume percolated: 26 ml.

^a nq, unable to quantify.

^b nf, not found.

Desethylatrazine was not quantified due to the interferences of the water matrix.

Relative standard deviation: 2–10%.

other two interferences were not encountered at this temperature.

(c) At room temperature. The recoveries obtained for 1 week of storage range from 65 to 101% indicating that all compounds are stable at this temperature. However in all cases the integration of the compounds was difficult due to the bad peak shape. No compound was found in cartridges stored at room temperature for 1 month with the exception

of fonofos in LiChrolut cartridges which had a recovery of 75%.

3.4. Ground water storage

(a) Non-acidified sample. As can be seen in Table 5 the recoveries obtained after 1 week and 1 month of storage ranged from 88 to 118 for all the compounds studied with the exemption of fenitro-

Table 5

Mean % recovery ($n=3$) of pesticides in non acidified water (pH=7.4) stored at room temperature (RT) and at 4°C for 1 week and 1 month using on-line SPE-LC-DAD and C₁₈ cartridges

Compound	ID No.	λ (nm)	1 week		1 month	
			RT	4°C	RT	4°C
Desethylatrazine	1	215	115	118	101	112
Fenamiphos	2	254	98	102	88	95
Fenitrothion	3	270	96	102	57	80
Fonofos	4	254	98	101	97	97

Concentration of pesticides in spiked water: 10 $\mu\text{g/l}$. Volume percolated: 26 ml.

Relative standard deviation: 1–10%.

thion which suffered a 43% and 20% loss at room temperature and 4°C, respectively. Fenitrothion is rapidly degraded under neutral and basic conditions as shown in previous works [20,21] where half-lives of 72 h under laboratory conditions and 11 h under environmental conditions are reported. Therefore, to preserve the degradation of fenitrothion we need to acidify the water samples as recommended by the EPA. Moreover, losses by volatilization due to the high vapour pressure of this compound are achieved in the environment. The results obtained for 1 week of storage at room temperature are in agreement with those of Crescenzi et al. [9].

(b) Acidified sample. After 1 week of storage the recoveries for all the compounds are near 100% except for fenamiphos when stored at room temperature (see Table 6). This fact may indicate a degradation due to the hydrolysis of this compound in acidic media. Fenamiphos is a slightly basic compound that has a tendency to become protonated in acidic media and consequently be degraded. The main degradation path of fenamiphos is by sunlight, as occurs with many organophosphorus compounds containing the S-methyl group and the aromatic ring in their chemical structure. Organophosphorus compounds with sulfur groups are particularly sensitive to photolysis, as shown previously [2,3]. This is the reason for what in this study the half-life of fenamiphos is larger (1 month) than reported before (2 days) [3] where the climate conditions were more similar to environmental ones (sunlight). After one month of storage at 4°C all the compounds remain stable except fenamiphos for the same reason as mentioned before. At room temperature we can observe a slightly degradation for fonofos as compared with the non acidified sample. The reason for

such degradation in acidic media is the same than for fenamiphos. Fonofos suffers an acidic hydrolysis at this low pH [22].

3.5. Analysis of blanks

The analysis of the blank cartridges preconcentrated with a ground water sample without any pesticide showed the same interferences in the chromatogram as those encountered in the previous analysis of the cartridges. This fact indicates some interaction between the cartridge phase and the water remaining in the cartridge after the percolation step as any drying treatment is applied to the cartridge before the storage. The interference peak coeluting with the desethylatrazine peak appears at every storage temperature and with each different cartridge type used, but it is not present when analyzing ground water samples directly without taking out the cartridge from the Prospekt, thus indicating an interaction between the water sample and the sorbent phase during a minimum 1 week. The two other coeluting interference peaks with fenamiphos and fonofos only appear during the storage in the fridge, at 4°C. The percolation of acidified ground water did not minimize the problem of the interfering peaks as they still appeared after the storage period at 4°C. When the percolation of only HPLC water was carried out through the cartridges, the three interfering peaks were present in the chromatogram after 1 month of storage, so that, some reaction or interaction occurs between the water and the solid-phase during a certain period of time and temperature. The intention of eliminating the remainder water in the cartridge through freeze-drying was not successful

Table 6

Mean % recovery ($n=3$) of pesticides in acidified water (pH=3.5) stored at room temperature (RT) and at 4°C for 1 week and 1 month using on-line SPE-LC-DAD and C_{18} cartridges

Compound	ID No.	λ (nm)	1 week		1 month	
			RT	4°C	RT	4°C
Desethylatrazine	1	215	101	104	98	111
Fenamiphos	2	254	79	90	51	73
Fenitrothion	3	270	95	99	82	96
Fonofos	4	254	91	97	81	95

Concentration of pesticides in spiked water: 10 $\mu\text{g/l}$. Volume percolated: 26 ml.

Relative standard deviation: 1–10%.

since the same interfering peaks showed up in the chromatogram after the analysis.

3.6. LC-APCI-MS

The confirmation of all the compounds studied was carried out by coupling a cartridge on-line with

Table 7

Typical fragment ions and relative abundances (RA) of desethylatrazine, fenamiphos, fenitrothion, fonofos and interfering peaks present in cartridges stored at 4°C during a one week period, in LC-APCI-MS in PI mode of operation

Compound	M_n	m/z and tentative ions	RA
Desethylatrazine	187	188 $[M+H]^+$	100
		146 $[M-C_3H_6+H]^+$	10
Fenamiphos	303	304 $[M+H]^+$	100
		276 $[M-C_2H_3+H]^+$	15
		262 $[M-C_3H_6+H]^+$	10
Fenitrothion	277	97 $[PS(OH)_2]^+$	100
		248 $[M-NO+H]^+$	100
		262 $[M-CH_3]^+$	15
Fonofos	246	247 $[M+H]^+$	20
		137 $[PSO(CH_2CH_2)_2]^+$	100
		109 $[M-PSO(CH_2CH_2)_2]^+$	10
Peak a		91	80
		111	100
		115	35
		149	20
		167	15
Peak b		110	100
		111	15
Peak c		61	40
		74	35
		111	100
		215	30
		241	20
		297	25
Peak d		64	15
		69	15
		71	15
		97	10
		111	100
		112	10

Cone set at 20 V and corona at 3.5 kV. Carrier stream: acetonitrile-water containing 1% acetic acid at a flow-rate of 1 ml/min. M_n =Nominal mass.

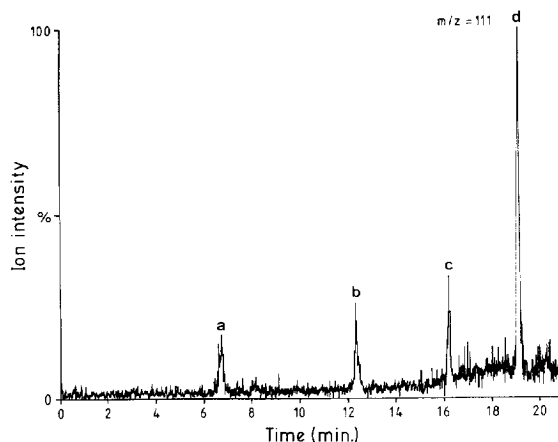


Fig. 3. LC-APCI-MS chromatogram, using $m/z=111$, obtained after the elution of a Hysphere-1 cartridge, pre-concentrated with ground water, after the storage at 4°C for 1 month. Peaks: a, b, c and d=interferents.

the LC-APCI-MS system in the positive mode of operation and under Scan conditions. The main ions and typical fragments corresponding to each pesticide are shown in Table 7. By analyzing the blank cartridges stored at 4°C with the LC-APCI-MS system, four interfering peaks were detected with a m/z of 111 (see Fig. 3). These peaks were unknown compounds and appeared at the same retention time than the two first peaks obtained after the LC-diode array detection (DAD) analysis. When analyzing cartridges, pre-concentrated with ground water, directly (without storing them at 4°C) on-line by LC-APCI-MS these interfering peaks did not appear in the chromatogram obtained.

4. Conclusions

The present study has demonstrated an improvement on the stability of fenamiphos and fonofos with regard to previous work since fenamiphos is stable for 1 week at room temperature and fonofos is stable for 1 month at 4°C and at room temperature when using disposable polymeric cartridges. In addition to this, LiChrolut cartridges are the best sorbents because high recoveries are obtained after storage for 1 month. In water media, many organophosphorus pesticides containing the S-methyl group in their structure are degraded by sunlight as glass bottles

were not protected against it. The acidification and the addition of biological inhibitors have a negative effect in many cases as regards the stability of pesticides in water since many of them become hydrolyzed or totally degraded. There is not a common rule concerning the storage of pesticides in water bottles since acidification may damage some pesticides such as fenamiphos while other compounds like fenitrothion need an acidic media for keeping their stability. So that, solid-phase extraction with new polymeric sorbent materials is a better alternative than C_{18} or storage in water. Nevertheless, the problem of the interfering peaks encountered in all the chromatograms after the storage at 4°C remains. An attempt was made to identify the interfering peaks by means of APCI-MS. The best storage conditions for all the pesticides on polymeric precolumns were those corresponding to storage at -20°C, since no losses and no interfering peaks were achieved after 1 month of storage.

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