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Journal of Chromatography A, 725 (1996) 85–92

JOURNAL OF CHROMATOGRAPHY A

Improvements in the determination of organophosphorus pesticides in ground- and wastewater samples from interlaboratory studies by automated on-line liquid–solid extraction followed by liquid chromatography–diode array detection

Silvia Lacorte, Damia Barceló*

Department of Environmental Chemistry, CID-CSIC, Jordi Girona 18–26, 08034 Barcelona, Catalonia, Spain

Abstract

On-line liquid–solid extraction coupled to liquid chromatography and diode array detection (LSE–LC–DAD) was validated by participating in interlaboratory calibration studies organized by Aquacheck (Medmenham, UK). The quantitation of 11 organophosphorus pesticides ground- and wastewater samples at levels varying from 30 to 600 ng/l respectively was carried out. The solution containing the organophosphorus pesticides and the water sample was provided by Aquacheck. Between 90 and 150 ml of wastewater and ground respectively were percolated through the Prospekt C_{18} precolumns (Spark Holland). The average error in comparison to the certified values from Aquacheck varied from 4 to 65%. The main problems encountered in the determination of these pesticides were the low UV absorbance of dichlorvos, mevinphos and malathion, the early breakthrough of dichlorvos and mevinphos and matrix interferences, specially abundant in the wastewater samples. In this type of water samples, the spiked level was one order of magnitude higher than in groundwater, but the error percentage was higher due to the matrix. One of the main advantages of this technique is that it permits the identification of two isomers of mevinphos, contrary to the rest of the participants who only reported *trans*-mevinphos. Moreover, by percolating 150 ml of water, limits of detection (LODs) below 0.1 μg/l are attained. The system behaved linearly over a concentration range of 0.4 to 5 ng/ml with 150 ml of water preconcentrated.

Keywords: Water analysis; Environmental analysis; Extraction methods; Interlaboratory validation; Pesticides

1. Introduction

Liquid–solid extraction methods coupled to liquid chromatography with diode array detection (LSE–LC–DAD) are gaining interest for the screening of pesticides in waters [1,2]. These methods are rapid, can be automated, confirmation is possible and they attain sensitivity below the EEC limits of 0.1 μg/l [3]. LSE methods include extraction using C_{18} cartridges [4,5], C_{18} discs both on-line [6] and off-line [7] or using more automated equipment such as the Prospekt (Spark Holland, Netherlands) [8] or the OSP-2 (Merck, Germany) [9]. In most cases, the analytical method is developed and directly aimed to detect the target pesticides in routine work, for instance in river water, such as Rhine basin program [10] or other European research programs [11]. At the same time that these on-line LSE methods are routinely used, there is a need to implement quality assurance parameters and the validation becomes a

*Corresponding author.

0021-9673/96/$15.00
SSDI 0021-9673(95)01207-9

key issue. The analytical method should provide statistical documentation of its capacity rendering quantitative parameters such as linearity, accuracy, precision and specificity. Interlaboratory validation studies are used to evaluate the performance of an analytical method by comparing the results of each laboratory with those of other researchers to reach a true value. To verify and validate the performance of the Prospekt–LC–DAD system, our group has been participating in several interlaboratory exercises organized by Aquacheck (WRC, Medmenham, UK) for the last two years. The present work was aimed to (i) validate the Prospekt–LC–DAD for determining 11 organophosphorus pesticides at levels of 0.1 μg/l level or lower in ground- and wastewaters and (ii) evaluate the quality of the results obtained by comparing them with the more standardized methods, i.e. gas chromatography (GC), used by most of the participating laboratories. This work complements preliminary studies on the validation of an automated precolumn exchange system coupled to LC–DAD for the determination of organophosphorus pesticides [11,12].

2. Experimental

2.1. Chemicals and reagents

Pesticides mevinphos, dichlorvos, azinphos-methyl and ethyl, parathion-methyl and ethyl, malathion, fenitrothion, chlorfenvinphos, fenthion, and diazinon were obtained from Promochem (Wesel, Germany). Pesticide-grade acetonitrile, methanol and Milli-Q water were purchased from J.T. Baker (Deventer, Netherlands).

2.2. Procedures

The experimental set up was as follows: a certified standard solution containing an unknown concentration of pesticides and a 2-l bottle with ground- or wastewater with 0.5% HNO_3 was provided by Aquacheck. The aim was to spike the water sample with the solution provided in order to determine the levels of these pesticides in water using on-line LSE–LC–DAD. The water samples were filtered through 0.45 μm filters (Millipore, MA, USA) to remove suspended particles before the addition of the standard supplied by Aquacheck.

LSE–LC–DAD was performed with the automated preconcentration system (Prospekt, Spark Holland, Netherlands). Volumes of 90–150 ml of the spiked water sample (depending on the intercalibration exercise) were preconcentrated on 10×2 mm I.D. disposable precolumns prepacked with 40 μm octadecylsilica (Spark Holland) at a flow-rate of 3 ml/min. Before extraction, the precolumns were conditioned via a solvent-delivery unit (SDU) from Spark Holland with 10 ml acetonitrile, 10 ml of methanol and 10 ml of water at a flow-rate of 2 ml/min. After preconcentrating the water sample, the precolumns were rinsed with 3 ml of HPLC water. The elution step was done by coupling the precolumn 'on-line' with the analytical column and starting the gradient. Quantification was carried out by external standard calibration at the wavelengths indicated in Table 1.

2.3. Chromatographic analysis

The LC analysis were performed with a Waters 600-MS solvent delivery unit with a 20-μl injection loop and equipped with a Waters 996 photodiode array detector. For groundwater samples, a Superspher 60 RP-8 endcapped cartridge column of 250×4 mm I.D. packed with 4 μm C_8 (Merck, Germany) was used. The gradient elution was:

Table 1
Breakthrough volumes (ml) of the studied pesticides (amount of each pesticide injected=100 ng)

Compound	Identification No.	Wavelength (nm)	V_b (ml)
Azinphos-methyl	1	220	>300
Dichlorvos	2	220	51
Fenitrothion	3	254	>300
Malathion	4	220	>300
Mevinphos-*cis*	5	220	58
Mevinphos-*trans*	5'	220	94
Chlorfenvinphos	6	254	>300
Diazinon	7	n.r.[a]	n.r.
Azinphos-ethyl	8	254	>300
Fenthion	9	n.r.	n.r.
Parathion-ethyl	10	280	>300
Parathion-methyl	11	280	>300

[a]n.r.=Not reported.

Solvent A=80% acetonitrile and 20% methanol; solvent B=HPLC water. From 10% A and 90% B to 40% A and 60% B in 10 min, isocratic for 5 min and to 90% A and 10% B in 33 min. Back to initial conditions in 5 min with the flow-rate set at 1 ml/min. For wastewater analysis, a Supelcosil column of 250×4.6 mm I.D. packed with 5 μm C_{18} (Supelco, USA) was used. The gradient elution was from 10% acetonitrile and 90% water to 35% acetonitrile and 65% of water in 5 min, then to 55% acetonitrile and 45% water in 6 min, and isocratic for 9 min, to 80% acetonitrile and 20% water in 8 min, and isocratic for 5 min, and then to 100% acetonitrile in 7 min, with a total run time of 40 min Back to initial conditions in 5 min with a flow-rate of 1 ml/min. Exercises corresponding to July and November 1993 were performed as described in Ref. [12].

2.4. Breakthrough volumes

The breakthrough volumes of all the studied pesticides was carried out by percolating 20, 40, 60, 100, 150, 200 and 300 ml of spiked groundwater through C_{18} precolumns in such a way that the amount injected was always 100 ng.

2.5. Instrument calibration

Calibration plots were constructed by percolating 150 ml of HPLC-grade water spiked at levels of 0.4, 0.7, 1, 2, 3, 4 and 5 ng/ml using on-line LSE–LC–DAD, following the methodology described in the Experimental section, in such a way that the amount of each pesticide injected varied from 60 ng to 750 ng.

3. Results and discussion

3.1. Breakthrough volumes

The study of the breakthrough volumes of the organophosphorus pesticides onto the C_{18} precolumns of the Prospekt was carried out in order to determine the maximum water volume that can be percolated through the precolumn without undergoing losses of the analytes. According to Hennion [2], the study of the breakthrough volumes renders equivalent information as the recovery of the pesticides, therefore it is possible to determine the water volumes which render 100% recovery of the analytes through the figures of the breakthrough volumes. In this sense, the breakthrough information is essential for selecting a water volume where 100% recovery of all analytes is achieved. However, in order to decrease the LOD, it is often necessary to work with a volume of water higher than the breakthrough volume. Despite the fact that breakthrough of some of the analytes occurs, the total amount of pesticide preconcentrated in the precolumn are increased, and therefore, it is possible to reach lower levels of detection. In conclusion, in many cases a compromise between breakthrough volumes and LOD should be reached. In addition, the fact to work with automated methods avoids manipulation and allows a better accuracy.

A linear regression analysis was carried out to calculate the breakthrough values. Table 1 shows the breakthrough values for all the studied pesticides. No breakthrough was observed for the most apolar analytes by percolating 300 ml of water. When breakthrough occurred, as for dichlorvos and mevinphos, the breakthrough value shown in Table 1 was calculated by a linear regression plot at 20% loss of the initial concentration. This value indicates the volume of water that can be percolated through the precolumn which yields 20% loss of the analyte. It is advantageous to calculate the breakthrough values using this method since it is possible to extrapolate the recoveries of each analyte at each spiking concentration. In this case, the breakthrough volumes were calculated at spiking levels from 5 to 0.33 μg/l. Breakthrough at 20% of the initial concentration was chosen since it follows EPA requirements [13] in which accepted recoveries can vary from 70 to 130%. The value of 80% is an intermediate at which the extreme limit of allowance is not reached.

Breakthrough was observed for mevinphos and dichlorvos. Mevinphos-*cis* and *trans* exhibited breakthrough at 58 and 94 ml, respectively. The breakthrough values of these two isomers has not been cited before in the literature. This pesticide is miscible in water, and therefore, it is a quick eluting compound under LC. Mevinphos-*cis* is a more polar compound than its isomer, noticed from the retention

time values (Fig. 1). Therefore, a lower breakthrough value is expected, as found in this study. For these two isomers, the regression analysis from 20 to 300 ml range gave correlation coefficients of 0.977 and 0.965 respectively, which are acceptable values if we take into consideration that the error percentage of the method is below 10%.

The breakthrough of diazinon and fenthion were not determined due to the fact that these two compounds coeluted and quantification was not possible at different wavelengths since they have very similar spectra.

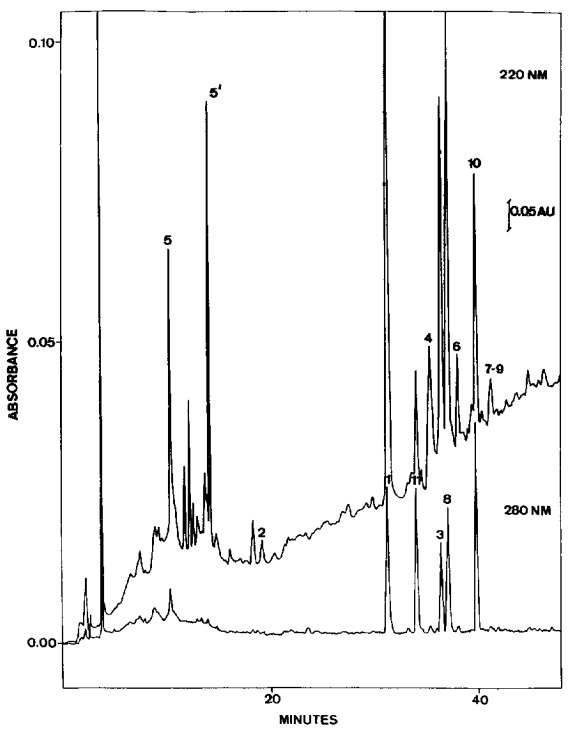

Fig. 1. LSE–LC–DAD of a groundwater sample. Column: Superspher 60 RP-8 endcapped cartridge column of 250×4 mm I.D. packed with 4 μm C_8. Gradient: Solvent A=80% acetonitrile and 20% methanol; solvent B=HPLC water. From 10% A and 90% B to 40% A and 60% B in 10 min, isocratic for 5 min and then to 90% A and 10% B in 33 min. Back to initial conditions in 5 min. Flow-rate set at 1 ml/min. Peak identification number and peak retention times (in min): 5=mevinphos-*cis* (10.677); 5'=mevinphos-*trans* (14.112); 2=dichlorvos (19.112); 1=azinphos-methyl (31.245); 11=parathion-methyl (34.012); 4=malathion (35.345); 3=fenitrothion (36.412); 8=azinphos-ethyl (37.045); 6=chlorfenvinphos (38.043); 10=parathion-ethyl (39.812); 7–9=fenthion and diazinon (39.812).

3.2. Calibration plots

Table 2 shows the calibration equations of the studied pesticides. All compounds have a linear behaviour between 0.4 and 5 ng/ml, having correlation coefficients in the order of 0.99. The calibration plots agree with previous works from our group [12] which report calibration graphs for polar pesticides such as vamidothion and its transformation products and others [14]. The LODs obtained by preconcentrating 150 ml of HPLC water are indicated in Table 2. These values were calculated using $S/N=3$. In such conditions, LODs below 0.1 μg/l were obtained, except for malathion and mevinphos due to poor UV absorbance. It is expected that for environmental water samples these LODs will be increased, especially for the first eluting compounds such as mevinphos and dichlorvos, due to the presence of dissolved organic matter in the water sample which is reflected as a hump in the beginning of the chromatogram.

3.3. Validation of the system

The LSE–LC–DAD method was validated by participating in five interlaboratory exercises organized by Aquacheck. The interlaboratory study consisted of the analysis of identical material by different laboratories. Each laboratory used its own developed method to determine organophosphorus pesticides. In order to provide a reliable statistical report on the results obtained by all participants, a minimum of 8 laboratories participating in interlaboratory exercises is mandatory [15]. In this exercise this criterium was followed and the number of participants varied from 8 to 14 (Table 3). The rest of the participants used gas chromatography (GC) with selective detectors such as nitrogen–phosphorus (NPD) or flame photometric detector (FPD) or thermionic detector (TSD). GC techniques are well-known and have been widely used for the determination of organophosphorus pesticides in various matrices [16]. However, limitations arise due to the fact that GC is unable to analyze non-volatile and polar compounds, and thus time-consuming derivatization is necessary prior to the final chromatographic step. Our work involves the use of automated on-line LSE–LC–DAD for the analysis of

Table 2
Calibration data for organophosphorus pesticides after preconcentration of 150 ml of HPLC water spiked at 0.4–5 ng/ml level through C_{18} precolumns and analyzed by LC–DAD

Compound	Calibration equation	R^2	LOD (ng/l)
Azinphos-methyl	$Y=-62700+305216X$	0.997	59
Dichlorvos	$Y=-2638+11345X$	0.997	99
Fenitrothion	$Y=210+17395X$	0.995	40
Malathion	$Y=-3607+16838X$	0.998	190
Mevinphos-*cis*	$Y=-5859+24608X$	0.991	111
Mevinphos-*trans*	$Y=-5534+75448X$	0.996	39
Chlorfenvinphos	$Y=-23528+118961X$	0.998	90
Diazinon	n.r.[a]	n.r.	n.r.
Azinphos-ethyl	$Y=-3865+107216X$	0.988	50
Fenthion	$Y=-13733+136200X$	0.991	65
Parathion-ethyl	$Y=-18210+137864X$	0.996	48
Parathion-methyl	$Y=-8178+90086X$	0.996	48

[a]n.r=Not reported.

organophosphorus pesticides in the Aquacheck samples. This technique had not been used previously in interlaboratory studies, and its validation becomes necessary before implementing the methodology in routine analysis.

One point that should be taken into consideration for the evaluation of the results is the repeatability and precision of each method. Repeatability was studied by preconcentrating 5 times HPLC water spiked with the solution containing all the pesticides at 0.3 ng/ml, and using the method described in the Experimental section. Relative standard deviations were in the range of 2–5%, similar to the work of Hennion [14]. The precision was evaluated by comparing the results obtained by our group with those of the organization and of the other laboratories.

Groundwater samples

Table 4 shows the results of 3 interlaboratory studies obtained by our laboratory using groundwater samples, and the % of error in comparison to the certified value from Aquacheck. Fig. 1 shows the chromatogram of the intercalibration of March 1994 obtained after spiking groundwater analyzed with Prospekt–LC–DAD of the solution provided by the organization. The results are evaluated according to

Table 3
Number of laboratories producing acceptable, flagged (17% error) and double flagged (34% error) results from intercalibration studies of March 1994 and September 1994.

Compound	March 1994				September 1994			
	T[a]	A	S	D	T	A	S	D
Azinfos-methyl	12	7	1	4	12	6	2	4
Diclorvos	11	7	2	2	11	3	3	5
Fenitrothion	12	8	1	3	13	7	2	4
Malathion	11	3	5	3	13	6	4	3
Mevinfos-*trans*	8	4	2	2	8	5	1	2
Chlorfenvinfos	12	9	2	1	14	6	1	7
Diazinon	12	2	6	4	14	1	4	9
Azinphos-ethyl	11	7	0	4	10	5	2	3
Fenthion	11	3	4	4	10	1	5	4
Parathion-ethyl	11	4	3	4	13	8	3	2
Parathion-methyl	10	4	3	3	10	5	2	3

[a]T=Total number of participating laboratories; A=laboratories giving acceptable results; S=laboratories giving single flagged results; D=laboratories giving double flagged results.

Table 4
Mean concentration (ng/l) and mean difference (%) ($n=4$) in relation to reference values of organophosphorus pesticides from 3 intercalibration studies (results are obtained from spiking groundwater with the certified material from Aquacheck)

Compound	July 1993		Nov. 1993		March 1994	
	ng/l	Error (%)	ng/l	Error (%)	ng/l	Error (%)
Azinfos-methyl	98.3	23	24.4	32	97.8	6
Diclorvos	46.0	36	63.9	21	54.9	69
Fenitrothion	34.0	17	23.4	9	47.3	14
Malathion	154	89	24.9	55	94.2	24
Mevinfos-*trans*	n.r.[a]	n.r.	64.6	0.9	74.3	4
Chlorfenvinfos	47.7	36	37.0	11	31.4	22
Diazinon	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
Azinphos-ethyl	95.2	12	41.9	24	100	12
Fenthion	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
Parathion-ethyl	n.r.	n.r.	111	3.7[b]	78.0	6
Parathion-methyl	26.0	22	97.4	15	69.7	24

[a]n.r.=Not reported or unable to quantify.
[b]The percentage of error was calculated by summing the concentration of parathion-ethyl and diazinon.

the limits imposed by the organization: results below 17% are acceptable. Flagged and double flagged results are results exceeding the maximum acceptable error or twice the maximum acceptable error. If we consider the AOAC limits, the maximum error between laboratories is of 22% [15]. In the present paper, 22% is considered to be the maximum allowable error. The reason is that Aquacheck interlaboratory exercises have the objective to improve and control the quality of water analysis. The target for bias and for precision set at 17% by Aquacheck is unrealistic as this limit cannot be established for the analysis of water samples spiked with pesticides. The target values for bias and precision can only be established after a sufficient period of expertise of the participating laboratories. Owing to the difficulties of analyzing polar pesticides in water, the coefficient of variation and target values should be higher. As an example, the EEC-BCR certificate exercises for PCBs, an easier interlaboratory exercise, has established a precision of 12% in standard solutions and 25% in spiked samples [17]. Among these values with the different participating laboratories analyzing PCBs in spiked samples, the coefficient of variation ranged from 17.6 to 37%. This is a more realistic approach than the 17% set by Aquacheck.

The results obtained in the intercalibration study of March 1994 show that out of 11 determinations, 6 have errors below 22%, 2 have errors of 24% and 2 are exceeding 44% or are not calculated.

For dichlorvos, the cause of high error percentage is its poor UV absorbance and the fact that this compound is very polar and therefore elutes at the beginning of the chromatogram, where matrix interferences are more abundant. The poor UV absorbance accounts for the quantification error of malathion. The quantification error of diazinon was originated by its coelution with fenthion. Therefore, the results of these two compounds have not been included in Table 4 and Table 5. A second derivative permitted to see the presence of the two compounds in a single peak. Furthermore, peak purity analysis confirmed the non-homogeneity of the peak. Due to the high similarity between the two spectra it was impossible to discern both compounds through wavelength selection. The deconvolution and quantification of such compounds can be accomplished by a chemometric approach [18].

As reported previously, mevinphos is a compound that gave problems due to the presence of two isomers [19]. Both of them could be identified in 2 of the 3 interlaboratory exercises using groundwater samples, in contrast to GC techniques. The error encountered for mevinphos-*trans* in the exercises of November 1993 and March 1994 was of only 0.9 and 4%, using groundwater samples, which lead us to the conclusion that the isomer quantified and

Table 5
Mean concentration (ng/L) and % of mean difference in relation to reference values of organophosphorus pesticides from 2 intercalibration studies. Results are obtained from spiking wastewater with the certified material from Aquacheck.

Compound	Sept'94		Feb'95	
	ng/l	% Error	ng/l	% Error
Azinfos-methyl	594	4	707	11
Diclorvos	n.r.	n.r.	n.r.	n.r.
Fenitrothion	638	16	n.r.	n.r.
Malathion	391	21	n.r.	n.r.
Mevinfos-cis	n.r.	n.r.	n.r.	n.r.
Mevinfos-trans	n.r.	n.r.	n.r.	n.r.
Chlorfenvinfos	717	6	151	47
Diazinon	n.r.	n.r.	n.r.	n.r.
Azinphos-ethyl	446	55	n.r.	n.r.
Fenthion	n.r.	n.r.	n.r.	n.r.
Parathion-ethyl	342	40	426	44
Parathion-methyl	437	19	774	51

n.r.=not reported.
*=The percentage of error was calculated by summing the concentration of azinphos-ethyl and fenitrothion.

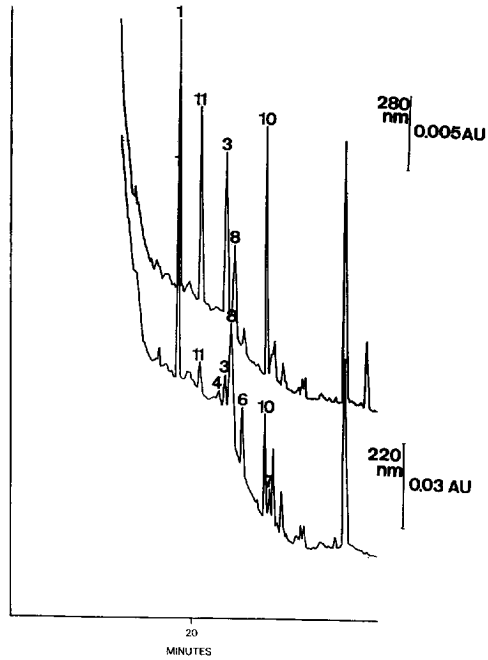

Fig. 2. LSE–LC–DAD of a wastewater sample. A Supelcosil column of 250×4.6 mm I.D. packed with 5 μm C_{18} (from Supelco) was used. Gradient: from 10% acetonitrile and 90% water to 35% acetonitrile and 65% of water in 5 min, to 55% acetonitrile and 45% water in 6 min, isocratic for 9 min, then to 80% acetonitrile and 20% water in 8 min, and isocratic for 5 min, and to 100% acetonitrile in 7 min, with a total run time of 40 min. Back to initial conditions in 5 min. Flow-rate of 1 ml/min. Peak identification number and peak retention times (min): 1=azinphos-methyl (18.633); 11=parathion-methyl (21.067); 4=malathion (23.067); 3=fenitrothion (23.867); 8=azinphos-ethyl (24.533); 6=chlorfenvinphos (25.767); 10=parathion-ethyl (28.203); 7=diazinon (28.703).

reported by the organizers was mevinphos-*trans*, which could be quantified effectively with LC–DAD. Comparing our values with the other laboratories, we found that of 8 participants, only 4 gave errors below 17%, thus indicating that the use of LC–DAD is a good choice to detect both isomers. In the GC results reported by all the Aquacheck studies, and also by the organizers, only one isomer was indicated.

Wastewater samples

Table 5 shows the mean concentration (n=3) and mean difference (%) in comparison to reference values of organophosphorus pesticides after analysis of wastewater sample spiked with the certified solution from Aquacheck. Fig. 2 shows a chromatogram corresponding to the exercise of February 1995. One of the main problems in analyzing wastewater with on-line LSE–LC–DAD is the appearance of an industrial effluent peak which interfered with the determination of many compounds. Even though the precolumn was rinsed with 3 ml of water before elution, this treatment was inadequate to remove all the interferences. The importance of the water matrix is thus apparent for the detection and quantification of the analytes. Comparing Table 4 and Table 5 it is remarkable that the levels of pesticides in wastewater samples were one order of magnitude higher than in groundwater samples, and in spite of that, the indeterminations and errors encountered were more significant when analyzing wastewaters. In none of the exercises was it possible to determine mevinphos nor dichlorvos, since they are camouflaged by the water matrix. Looking at the results of September 1994, it can be seen that 5 out of 8 determinations are correct. However, in general, the errors obtained in the analysis of wastewaters by on-line LSE–LC–DAD are higher than those obtained by the other participants, where the water matrix is not a problem when using GC–NPD and off-line extraction (Table 3). Compounds appearing

at the end of the chromatogram, such as diazinon, fenthion and parathion-ethyl also gave quantification problems due to the fact that they elute at a high percentage or organic solvent where matrix and precolumn impurities also elute, interfering with the analyte of interest. In view of this, it is possible to conclude that on-line LSE–LC–DAD is not an appropriate method for the analysis of organophosphorus pesticides in wastewater samples.

Moreover, in the exercise of February 1995, coelution occurred for fenitrothion and azinphos-ethyl. The results are not reported.

4. Conclusions

The determination of 11 organophosphorus pesticides in ground- and wastewaters was achieved using on-line LSE–LC–DAD. In groundwater samples, levels varying from 0.02 to 0.2 μg/l were encountered for each individual pesticide. The error of the mean values varied from 4 to 36% for 20 of the 26 determinations performed. The presence of interferences, coelution of compounds and poor chromophoric behaviour were the main causes of error. In wastewater samples, levels varied from 0.15 to 0.8 μg/l, with an error from 4 to 65%. The method was found to be not suitable for detecting organophosphorus pesticides at such low levels, due to matrix interferences and to an industrial effluent peak that appears at the beginning of the chromatogram.

The results reported in the interlaboratory exercise suggested that LSE coupled on-line to LC–DAD is a robust method for the analysis of organophosphorus pesticides, and it is equivalent to conventional GC techniques in many aspects, as shown by flagged and double flagged results given by many laboratories. Furthermore, it allows the detection of the two isomers of mevinphos. Future work will include the use of on-line LSE–LC–MS techniques for the application of interlaboratory studies.

Acknowledgments

This work has been supported by the Environment R and D Program (Commission of the European Communities, CEE) contract EV5V-CT92-105, by PLANICYT (AMB95-0075-C03-1). Research agreement 7978/CF from the International Atomic Energy Agency (IAEA) is also acknowledged. S.L thanks financial support from CICYT (Grant AMB92-0218).

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