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Application of hollow fiber liquid phase microextraction for the determination of insecticides in water

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Abstract

In the present work, a novel sample pre-treatment technique for the determination of trace concentrations of some insecticide compounds in aqueous samples has been developed and applied to the determination of the selected analytes in environmental water samples. The extraction procedure is based on coupling polypropylene hollow fiber liquid phase microextraction (HF-LPME) with gas chromatography by flame thermionic detection (GC-FTD). For the development of the method, seven organophosphorous insecticides (dichlorvos, mevinphos-cis, ethoprophos, chlorpyrifos methyl, phenthoate, methidathion and carbofenothion) and one carbamate (carbofuran) were considered as target analytes. Several factors that influence the efficiency of HF-LPME were investigated and optimized including agitation, organic solvent, sample volume, exposure time, salt additives and pH. The optimized methodology exhibited good linearity with correlation coefficient = 0.990. The analytical precision for the target analytes ranged from 4.3 to 11.1 for within-day variation and 4.6 to 12.0% for between-day variation. The detection limits for all analytes were found in the range from 0.001 to 0.072 μg/L, well below the limits established by the EC Drinking Water Directive (EEC 80/778). Relative recoveries obtained by the proposed method from drinking and river water samples ranged from 80 to 104% with coefficient of variations ranging from 4.5 to 10.7%. The present methodology is easy, rapid, sensitive and requires small sample volumes to screen environmental water samples for insecticide residues.

Keywords: Hollow fiber liquid phase microextraction (HF-LPME); Water analysis; Organophosphates; Carbamates

1. Introduction

Organophosphates and *N*-methylcarbamates are two classes of insecticides extensively used as alternatives to the high persistent, bioaccumulate organochlorine compounds for crop protection and tree treatment [1]. However, many of these compounds display high acute toxicity (potent cholinesterase inhibitors) [2,3] and are suspected for mutagenic [4,5], carcinogenic and endocrine disruptor effects [5–9]. Hence, methods that allow for the accurate measurement of organophospates and *N*-methylcarbamates residues in drinking and surface waters are needed for risk assessment analysis.

Current methods for the screening of pesticides in environmental matrices typically require a sample preparation step prior to analysis by either high performance liquid chromatography (HPLC) or gas chromatography (GC). In the present era of "green chemistry", sample preparation methods such as liquid–liquid extraction (LLE) suffer from the disadvantage of being time-consuming, expensive, and requiring large volumes of toxic organic solvents. In contrast, solid-phase extraction (SPE) techniques typically require reduced amounts of organic solvents relative to LLE, but SPE can be tedious, time-consuming, and suffer analyte breakthrough when large sample volumes are analyzed. Thus, sample preparation methods that alleviate these disadvantages while simultaneously providing a simplified and miniaturized procedure are desirable [10].

Recently, liquid-phase microextraction (LPME) has emerged as an attractive alternative for sample preparation. LPME can be performed by using a single drop of solvent or a small length of porous hollow fiber-protected solvent. This novel technique, which is fast and simple, eliminates the disadvantages of conventional extraction methods, such as time consuming operation and using specialized apparatus.

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It is inexpensive and there is considerable freedom in selecting appropriate solvents for extraction of different analytes. Since very little solvent is used, there is minimal exposure to toxic organic solvent for the operator. At the same time, LPME combines extraction, concentration and sample introduction in one step. The important feature of the LPME is that almost all of the organic solvent into which the analytes are extracted can be injected into the GC, while only part of the concentrated organic solvent is injected using LLE or SPE. Similar to SPME, there are two modes of LPME sampling: direct-immersion LPME and headspace LPME (HS-LPME). Today, both modes have been successfully used for the extraction of organic pollutants from a variety of matrices [10–19]. It has been demonstrated that LPME shows comparable extraction efficiency and reproducibility as the widely used solid-phase microextraction technique.

The objective of this study is to investigate the suitability of HF-LPME procedure for extraction of seven organophosphate and one carbamate pesticides from drinking and surface water samples in compliance with the European Union directives on water quality.

2. Experimental

2.1. Chemicals

All solvents (pesticide-grade) were supplied from Labscan (Dublin, Ireland) and sodium chloride from Merck (Darmstadt, Germany). Distilled water was prepared on a water purification system (Model 2108) supplied by GFL (Germany). Individual standards of insecticides (Table 1) were obtained from Riedel de Haën (Seelze, Germany). A toluene solution (1 mg/L) of diazinon was prepared and used as the internal standard (IS). Stock standard solutions (1000 μg/L) were prepared in methanol and were stored in a freezer at about −20 °C. Working solutions were prepared by dilution of stock standards solutions with distilled water and were stored at 4 °C.

2.2. HF-LPME procedure

The Accurel Q 3/2 polypropylene hollow fiber membrane used for liquid phase microextraction was purchased from Membrana GmbH (Wuppertal, Germany). The inner diameter was 600 μm, the thickness of the wall was 200 μm, and the pore size was 0.2 μm. A 10 μl Hamilton gastight syringe (Hamilton, Bonaduz, Bonaduz, Switzerland) model 1701 RNR (length: 5.1 cm, o.d.: 0.071 cm, and i.d.: 0.015 cm), with a bevel needle tip was used to introduce the acceptor phase, support the hollow fibre and act as the injection syringe. Before use the hollow fiber was ultrasonically cleaned in acetone for several minutes in order to remove any contaminants. After being dried, the hollow fiber was cut manually into 1.3 cm lengths prior to use. The length and consequently the volume capacity of the hollow fibres were adjusted to the size of the vials used in the present studies. Due to the low cost, a new fibre was used for each extraction.

Extractions were performed according to the following scheme [13]. A 5 mL aliquot of sample solution was placed in the reagent vial a 0.8 cm × 0.2 cm width magnetic stirring bar. A 3.0 μL aliquot of organic solvent (typically toluene) was withdrawn into the syringe followed by an equal volume of water. The needle tip was inserted into the hollow fiber, and the assembly was immersed in the organic solvent for ∼10 s in order for the solvent to impregnate the pores of the fiber wall. Since the hollow fiber was hydrophobic, the fiber channel could be filled with organic solvent. After solvent impregnation, the water in the syringe was injected carefully to flush the hollow fiber in order to remove the excess organic solvent from the inside (this procedure was performed while the fiber remained immersed in the organic solvent). The prepared fiber was removed from the solvent and subsequently immersed in the aqueous sample. Finally, the organic solvent in the syringe was injected carefully and completely into the hollow fiber. The experimental results indicated that the residue water inside the hollow fiber had no effect on extraction efficiency and precision. The sample was continuously stirred at room temperature (25 °C) with a magnetic stirrer to facilitate the mass transfer process and to decrease the time required for the equilibrium to be established. The stirring speed was fixed at 800 rpm After 20 min extraction, the analyte-enriched solvent (1.5 μl) was withdrawn into the syringe, the fiber segment was removed and the organic phase was then injected into the heated injection port of the GC-FTD for further analysis. The experimental setup of HF-LPME procedure is illustrated in Fig. 1.

2.3. Equipment

Analyses of insecticides were performed using a Shimadzu 14A capillary gas chromatograph equipped with flame thermionic detector (FTD) at 250 °C. The DB-5 column, 30 m × 0.32 mm i.d., used contained 5% phenyl–methyl–polysiloxane (J&W Scientific, Folsom, CA). The column was programmed from 150 °C (2 min) to 200 °C

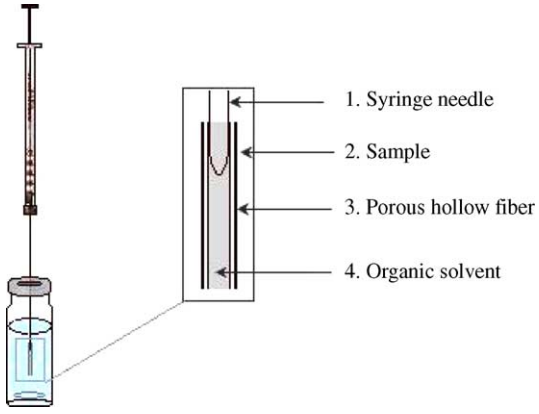
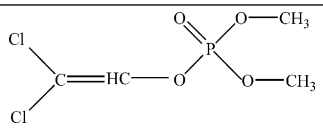
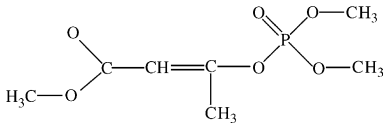
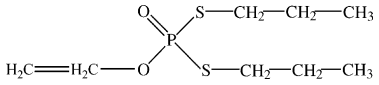
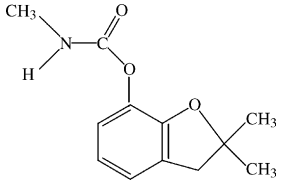
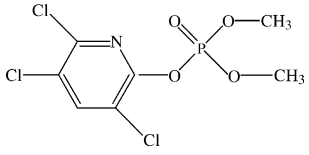
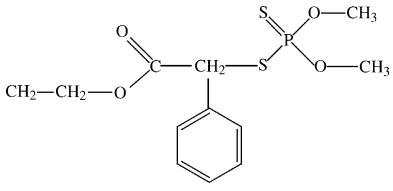
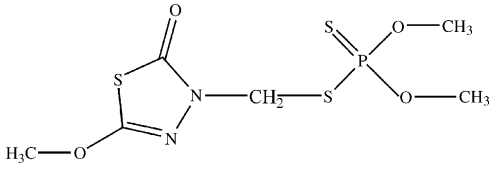
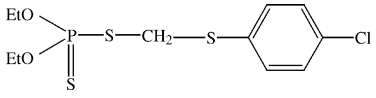


Fig. 1. Schematic representation of HF-LPME system.

Table 1
Physicochemical properties of the target insecticides

Insecticides	Chemical structure	Molecular mass	Water solubility (mg/L)	log K_{ow} [a]	Soil sorption, K_{oc} [b]
Dichlorvos		220.98	10.000	1.47	30
Mevinphos-cis		224.15	600.000	0.13	44
Ethoprophos		242.30	750	3.59[c]	70
Carbofuran		221.25	351	1.63	22
Chlorpyrifos methyl		322.55	4	4.3	3000
Phenthoate		320.37	11	3.96	1000
Methidathion		302.33	220	2.42	400
Carbofenothion		342.96	0.34	5.12	50000

[a] log K_{ow}, water–octanol partition coefficients [20].
[b] K_{oc}, sorption coefficient normalized to organic carbon content from Wauchop et al. [21].

(8 min) at 5 °C/min, to 200–210 °C (2 min) at 1 °C/min and to 210–270 °C (4 min) at 10 °C/min. The injection temperature was 240 °C. Helium was used as the carrier at 1.5 ml/min and make-up gas (40 ml/min). The detector gases were air and hydrogen, and their flow rates were regulated at 120 and 4.0 ml/min, respectively. The ion source of FTD was an alkali metallic salt (Rb_2SO_4) bonded to a 0.2 mm spiral of platinum wire.

2.4. Validation of the HF-LPME procedure

The calibration study was performed using distilled water samples spiked with the solution containing the eight insecticides. The samples were spiked at five different concentrations (Table 2) and three replicates were prepared at each level. To each sample diazinon was added as internal standard to obtain a final concentration of 1 mg/L.

Table 2
Validation data of the HF-LPME method and relative recoveries of the tested compounds in drinking and river water samples

Insecticides	Linear dynamic range		LODs (ng/L)	Precision (R.S.D. %)		Spiked amount (μg/L)	Drinking water		River water	
	(μg/L)	R^2		Repeatability	Reproducibility		Relative recovery (%)	R.S.D. (%)	Relative recovery (%)	R.S.D. (%)
Dichlorvos	0.100–100	0.994	32	5.2	6.1	0.150	99	5.7	93	6.6
Mevinphos cis	0.120–100	0.993	40	6.2	6.8	0.150	95	6.5	89	7.1
Ethoprophos	0.010–50	0.995	4	8.8	8.9	0.050	101	8.8	91	9.0
Carbofuran	0.300–100	0.990	72	10.2	12.0	0.300	89	10.6	88	10.9
Chlorpyrifos methyl	0.010–50	0.997	1	4.3	4.6	0.050	105	4.5	98	4.6
Phenthoate	0.010–50	0.993	2	9.4	10.3	0.050	101	9.4	94	9.5
Methidathion	0.010–50	0.994	3	11.1	12.0	0.050	97	11.3	102	11.3
Carbofenothion	0.010–50	0.994	5	10.5	12.0	0.050	84	10.5	80	10.7

The limits of detection (LODs) were calculated as the minimum concentrations providing chromatographic signals three times higher than background noise.

The repeatability and reproducibility of the experimental procedure was evaluated by carried out six replicates of a sample during 1 day ($n = 6$, intra-day precision), spiked at a level of 0.50 μg/L of the target compounds and two replicates at three different days (inter-day precision), over of period of 1 week.

3. Results and discussion

3.1. Agitation

As with other microextraction techniques, the extraction in HF-LPME can be enhanced by agitation of the sample solution, thereby reducing the "time" required to attain thermodynamic equilibrium especially for the higher molecular mass analytes [12,13]. For single drop DI-LPME, stirring speeds above 600 rpm resulted in dislodgement of the acceptor phase and difficulties in analyte quantification, especially with prolonged exposure time [11,22–24]. In HF-LPME the organic solvent is sealed and protected by the hydrophobic hollow fiber membrane, so it is easier to handle and can tolerate higher stirring speed. In our experiments, partitioning of the analytes into the organic solvent was enhanced with the increase of the stirring speed from 400 to 800 rpm (data not shown). However, higher rpms were not evaluated since it would cause excessive air bubbles on the surface of the hollow fiber, which could lead to poorer precision and possible experimental failure. Therefore, we choose 800 rpm as a suitable stirring speed for LPME on the basis of the above consideration.

3.2. Extraction solvent

The type of organic solvent immobilized in the pores of the hollow fiber is a critical factor in HF-LPME. Ideally, the organic solvent should be compatible with the fiber, immiscible in water, and stable enough over the extraction time. Based on preliminary experiments (data not shown), three water-immiscible solvents including, hexane, isooctane, and toluene were evaluated. Five millilitres of water samples were spiked with all insecticides at 20 μg/L, and the extraction time and stirring rate were 20 min and 800 rpm, respectively. Extraction efficiency decreased in the order of toluene, isooctane and hexane (data not shown). Moreover, toluene demonstrated good selectivity for all analytes, exhibited low solvent loss, and was immobilized in the fiber pores within seconds. Consequently, subsequent experiments were conducted with toluene.

3.3. Sample volume

The influence of sample volume on the peak area was studied in the range of 2.5–15 ml. The results shown in Fig. 2 indicates that for the most of the target analytes the analytical signal virtually increases with sample volume in the range of 2.5–5 ml and after 5 ml the rate of increase slows down or even decreases. Hence, a sample volume of 5 ml was applied to subsequent experiments.

3.4. Exposure time

The effect of exposure time on extraction efficiency was evaluated by spiking 5 mL water samples at 20 μg/L. Extractions were conducted for 5, 10, 20, 30, and 40 min at a

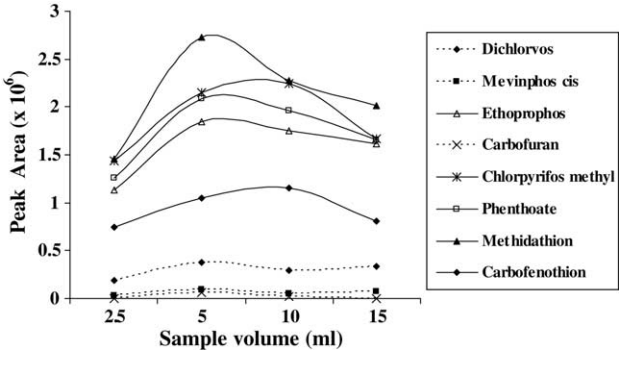


Fig. 2. Effect of sample volume on HF-LPME.

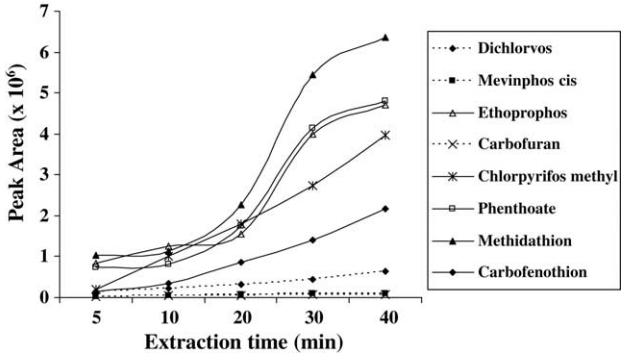


Fig. 3. Plots of peak area vs. extraction time for selected insecticides obtained with HF-LPME.

stirring rate of 800 rpm. For all compounds, extraction efficiency increased with exposure time, and equilibrium was >40 min (Fig. 3). HF-LPME is not an exhaustive extraction technique, and is similar to LLE and SPME in that it is based on the analyte's partitioning between the aqueous sample and the organic solvent. Consequently, when using HF-LPME it is not practical to match extraction time with extraction equilibrium in that the potential for solvent loss due to dissolution increases with time. Moreover, equilibrium exposure times are not necessary for analytical methods when extraction time, mixing rate, and sample volumes remain constant [25]. Thus, the extraction time for all subsequent experiments was standardized at 20 min.

3.5. Salting out effect

The effect of salt on extraction efficiency was determined by adding sodium chloride to 5 mL water samples at 0, 2.5, 5, 10, and 15% (w/v). For compounds with a low or moderate water solubility including ethoprophos, chlorpyrifos methyl, phenthoate, carbofenothion, and carbofuran, extraction efficiency reached a maximum at 5% (w/v) (Fig. 4). In contrast, the extraction efficiency of relatively polar compounds with a high water solubility including dichlorvos and mevinphos-cis increased up to 15% (w/v). Since the extraction efficiency for most of the compounds decreased beyond 5% (w/v),

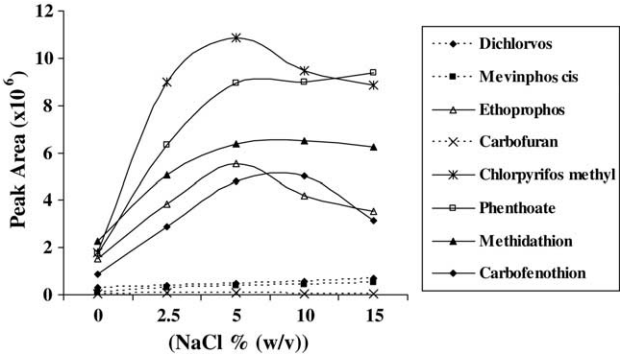


Fig. 4. Salting out effect on the extraction efficiency of HF-LPME for selected insecticides.

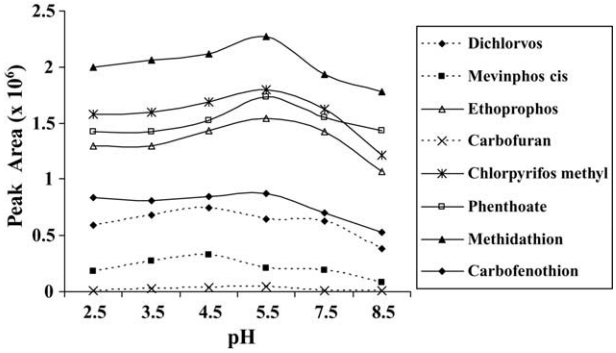


Fig. 5. Effect of pH of sample solution on HF-LPME.

all subsequent experiments were conducted at this concentration.

3.6. Effect of pH

It is a common practice to acidify natural samples shortly after collection in order to limit both abiotic and biotic degradation of organic contaminants. However, changing pH will change the ionization form of certain analytes and thereby it will affect their water-solubility and extractability. In the present study, the effect of pH upon insecticide extractability with HF-LPME was also investigated by varying the pH values from 2.5 to 8.5 (Fig. 5). Better extraction efficiency for the most of the insecticides was observed at pH 5.5, with the exception of dichlorvos and mevinphos-cis the extraction of which is improved by lowering the neutral pH values to acidic ones with better results at pH 4.5 [26–29]. At pH higher than 5.5, and especially at alkaline conditions (pH 8.5), the signal for all insecticides was significantly decreased due to the effect of hydrolysis [26,30,31]. As a result of these data, the pH 5.5 value (the usual value for distilled water sample) was selected for the subsequent analysis (Fig. 6).

3.7. Performance of the HF-LPME procedure

After analyzing all experimental results, the following conditions have been selected to evaluate the performance

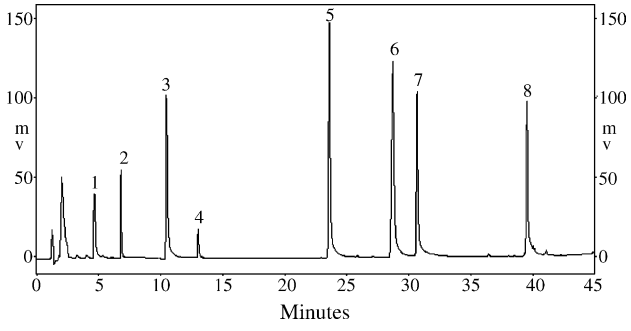


Fig. 6. Chromatogram of target compounds obtained by HF-LPME in river water sample at concentration level of 20 μg/L. Peaks: (1) dichlorvos, (2) mevinphos-cis, (3) ethoprophos, (4) carbofuran, (5) chlorpyrifos methyl, (6) phenthoate, (7) methidathion, (8) carbofenothion.

Table 3
Analytical performance of hollow fiber LPME technique in river water samples

Insecticides	Spiked amount (μg/L)	Detected amount (μg/L)	Relative recovery (%)	Linear dynamic range	R^2	LODs (ng/L)
Dichlorvos	0.150	0.140	93	0.100–100	0.992	34
Mevinphos-cis	0.150	0.134	89	0.130–100	0.990	43
Ethoprophos	0.050	0.046	91	0.015–50	0.993	5
Carbofuran	0.300	0.264	88	0.300–100	0.989	74
Chlorpyrifos methyl	0.050	0.049	98	0.010–50	0.995	1
Phenthoate	0.050	0.047	94	0.010–50	0.992	2
Methidathion	0.050	0.051	102	0.015–50	0.990	5
Carbofenothion	0.050	0.040	80	0.020–50	0.988	7

of the method: toluene as organic solvent, 5 ml water samples, 800 rpm stirring rate, 5% NaCl content, pH 5.5, and 20 min sampling time.

Linearity, precision and detection limits have been evaluated in order to asses the performance of the microextraction method. Results are shown in Table 1.

The calibration curves were linear in the range studied for each compound, with correlation coefficients *R* between 0.990 and 0.9995, so a directly proportional relationship between the extracted amount of compounds and the initial concentration of the sample was demonstrated.

LODs were below 40 ng/L for all analytes except from carbofuran (72 ng/L) underlining the good sensitivity of the method. The latest analyte (carbofuran) with higher LODs are the compound with the lower response in the GC system and the lower sensitivity can be also attributed to lower enrichment factor which was achieved in the organic solvent than the other compounds. Nevertheless, the analytical method for all target compounds meets the EU regulatory levels for drinking water of 0.1 μg/L.

Overall, the detection limits which were achieved by the proposed method are better or comparable to other mentioned to others published extraction techniques for organophosphate and carbamate compounds [23,26–32].

The R.S.D. values obtained were satisfactory and ranged between 4.3 and 12.0% for all analytes indicating that HF-LPME precision is at least at the same level and in some cases slightly better than with other conventional extraction methods [30–33].

3.8. Application of HF-LPME in spiked real water samples

In order to investigate the applicability of the proposed trace enrichment microextraction method, two water samples of different origin were studied. Performance of the overall method for a drinking and river water sample (Aliakmonas River, Macedonia, Greece) was compared with that for distilled water. All water samples were used without treatment or filtration and measured from pH (range for the analyzed water samples 6.5–7.5); a volume of 10 ml water was analyzed using the solid phase microextraction method (SPME) [30]. However, none of the selected compounds were detected. Therefore, the water samples were spiked with pesticides and analyzed in triplicate by the proposed method by adjusting the pH of the samples at 5.5. The recoveries were calculated from $n = 3$ samples (Table 2). HF-LPME is a non-exhaustive extraction procedure and as such the relative recovery (determined as the ratio of the concentrations found in natural and distilled water samples, spiked with the same amount of analytes), instead of the absolute recovery (used in exhaustive extraction procedures), was employed. The relative recoveries of the spiked real samples were ranged between 80 and 102%.

The precision obtained with river water samples (Table 3) was comparable with that of distilled and drinking water samples (Table 2), indicating that is only a minor influence of sample matrix, since matrix compounds did not hamper peak integration. This result was also supported by the similar relative recoveries obtained with river and drinking water samples. Minor matrix effect on the LPME extraction is probably attributed to the selectivity of the hollow fiber because of the pores in its wall. It is apparent that porous hollow fiber functions as a filter in "dirty" samples, since large molecules, which can also be soluble in the organic solvent, will not be extracted. In this way, this newly developed microextraction technique can be potentially used to extract complex matrixes, while preventing coextraction of extraneous materials.

Linearity and detection limits were also evaluated in river water samples in FTD system at the same concentration levels as for distilled water (Table 3). Correlation coefficients (*R*) were between 0.988 and 0.995 and LOD provided results (1–74 ng/L) were similar to those for distilled water (Table 2).

Fig. 3 shows the chromatogram obtained from spiked river water sample at concentration level of 20 μg/L.

3.9. Comparison of HF-LPME performance with SPME

A comparison between HF-LPME and SPME (data taken from the literature) [33–36], which are non-exhaustive extraction methods, showed that both extraction methods exhibited comparable extraction performance in terms of linearity, precision and relative recoveries. In addition, both methods share the advantages of being fast, simple and (minimal solvent consumption in the case of HF-LPME) solvent-free meth-

ods. However, LODs with HF-LPME (Table 2) were better (carbofuran was the only exception) than those obtained with SPME and especially for dichlorvos (SPME: 1.50 μg/L) [36], mevinphos-cis (SPME: 22.50 μg/L) [36], methidathion (SPME: 0.5–0.12 μg/L) [35] and carbofenothion (SPME: 0.302 μg/L) [34], reflecting the fact that HF-LPME provides high enrichment of analytes and consequently high sensitivity. Also, the disposable nature of the hollow fiber eliminated the main problems common encountered with SPME such as carry over effects between analyses, limited lifetime and fragility of the fiber.

Future work should be focused on extraction of more insecticides to further support that HF-LPME is an alternative for a broad range of applications, and that validation data is comparable with existing microextraction techniques.

4. Conclusions

A novel, simple and sensitive mode of LPME referred as HF-LPME has been successfully employed to determine residues of insecticides in water samples. After optimization of the extraction conditions for the target analytes, detection limits of 1–40 ng/L were achieved, using 5 ml of aqueous sample, 3 μL of toluene in hollow fiber and an injection volume of 1.5 μg/L. Only carbofuran could not be detected below 72 ng/L. The relative recoveries obtained in drinking and river water samples were between 80 and 104% and the R.S.D. values were found to in the range of 4.3–12.0%.

Overall, the resulting procedure was shown to be a good alternative methodology for the determination of selected organophosphates and carbamates residues in environmental samples, being a simple, fast, reproducible, and effective and also an environmental friendly analytical method.

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