Bull. Environ. Contam. Toxicol. (2002) 69:123–128

DOI: 10.1007/s00128-002-0018-5

Bulletin of Environmental Contamination and Toxicology

Comparison of Liquid–Liquid Extraction (LLE), Solid-Phase Extraction (SPE), and Solid-Phase Microextraction (SPME) for Pyrethroid Pesticides Analysis from Enriched River Water

W. R. Barrionuevo, F. M. Lanças

University of São Paulo, Institute of Chemistry at São Carlos, 13560-970, São Carlos (SP), Brazil

Received: 30 May 2000/Accepted: 27 February 2002

In recent years, synthetic pyrethroid pesticides have become widely used as efficient pest control agents because of their advantageous environmental properties such as short field life, broad spectrum of insecticidal activity and relatively low mammalian toxicity (Zweig and Sherma 1986; Ling and Huang 1995). Nevertheless, pyrethroids residues still pose risks to human life and other species, manly aquatic organisms such as fish and crustaceans (Hoff et al. 1996) and non-target insects.

The low concentrations of pyrethroids usually found in water make necessary the use of very precise techniques for trace analysis. Conventional pesticide residue analysis of pyrethroids in environmental samples is often laborious since it involves manual samples extraction, and several concentration steps. The most difficult and time-consuming step is the extraction of the target analytes from the matrix. Several methods have been developed to accomplish this often-difficult task, including predominant analytical techniques such as liquid-liquid extraction (LLE) and solid-phase extraction (SPE). The most popular technique used by environmental agencies involves some LLE. The procedure itself is time-consuming, and often requires pre-concentration of the extract prior to analysis. The requirement of large quantities of expensive, toxic solvents that can be harmful to the environment is one of the biggest concerns with this method (Magdic et al. 1996). Solid-phase extraction is an attractive replacement for LLE since it is faster, extraction is more complete, and the amount of organic solvent used is a small fraction of that in LLE. Although regulations of the US Environmental Protection Agency (Aguilar et al. 1998) have specifications for drinking water, SPE has the disadvantage that it still requires toxic organic solvents for the elution step. Recently, a new extraction technique, solid-phase microextraction (SPME) has been introduced by Pawliszyn and workers (Pawliszyn 1992; Eisert and Pawliszyn 1997). It has some advantages over the more conventional extraction techniques, LLE and SPE, as it is a solvent-free sample preparation technique so it minimizes the cost of high-purity solvents, it is easy to use and fast, and very small sample volumes are necessary for the analysis.

Correspondence to: F. M. Lanças

Since pyrethroid analysis are usually carried out by LLE and SPE, the main subject of this work is to compare pyrethroid extractions from a river enriched water by using LLE, SPE and SPME techniques.

MATERIALS AND METHODS

The pyrethoids bifenthrin, permethrin, cypermethrin and deltamethrin were purchased from Supelco, Inc. Stock solutions were prepared by adding of 10 mg of each compound into 10 mL ethanol. A 1 mL aliquot of these stock solution was taken and diluted in river water to obtain 100 mL aqueous stock solution which were immediately used for the preparation of the desired concentration required for each respective extraction study (1 $\mu g.L^{-1}$). The river water was obtained from Espraiado Stream, a public water source, in São Carlos, São Paulo State, Brazil. Solid-phase micro extraction was performed with a SPME fiber assembler holding 1 cm long fused-silica fiber coated with a 100 μm thick layer of polydimethylsiloxane, all purchased from Supelco, Inc (USA). A Shimadzu GC-17A Gas Chromatograph with ^{63}Ni electron capture detection (ECD) system and a LM-5 (5% phenylmethylpolysiloxane), 30m x 0.25mm x 0.1μm (L&M Scientific, Brazil) fused-silica capillary column were used. General operating conditions was as follows: Injection port temperature, 250°C; detector temperature, 280°C; carrier gas (H_2) flow at 1.8 mL/min; makeup gas (N_2) at 20 mL/min; column temperature program: initially 150°C for 5 min, increase at 15°C/min to 250 for 5 min; increase at 3°C/min to 270, hold for 5 min.

For LLE extraction, 500 mL of river water sample enriched with pyrethroids (concentration: 1 μg L^{-1}) were extracted in a separatory funnel 6 times with dichloromethane (50 mL each), shaking for two minutes and allowing the phases separate for 10 minutes. The sample extracted on dichloromethane was dried over sodium sulfate and evaporated on a rotaevaporator apparatus. The residue was dissolved in 1 mL ethanol and then injected on GC-ECD.

For SPE, a cartridge containing 1 g of florisil was conditioned with 10 mL of hexane and loaded with 2 liters of river water enriched with pyrethroids (concentration 1 μg L^{-1}). The aqueous phase was discharged and the analyte was eluted with 20 mL of acetonitrile and dried on a rotaevaporator apparatus. The residue was dissolved in 1 mL ethanol and then injected on GC-ECD.

For SPME, pyrethroid samples (concentration 1 μg L^{-1}) were introduced into 5 mL screw-cap glass vials with teflon coated septa. The triangular bottom of the vials was fitted with a triangular stirring bar for sample mixing. Heating was performed by introducing the sample vial into a copper spiral, placed on a magnetic stirring equipment and connected to a water bath. Magnetic stirring was used to reduce the extraction time. After 10 minutes of extraction, the SPME fiber device was removed from the sample vial and immediately inserted into the GC injector for thermal desorption.

Table 1. Sample volume, solvent volume and extraction time for a river water solution enriched with pyrethroids (concentration 1 μL mL^{-1}) and extracted by Liquid-Liquid Extraction (LLE), Solid-Phase Extraction (SPE) and Solid-Phase Microextraction (SPME).

	LLE	SPE	SPME
Sample volume (mL)	500	500	5
Solvent volume (mL)	301	30	0
Extraction time (h)	2:27 ± 0:32	2:18 ± 0:12	0:10

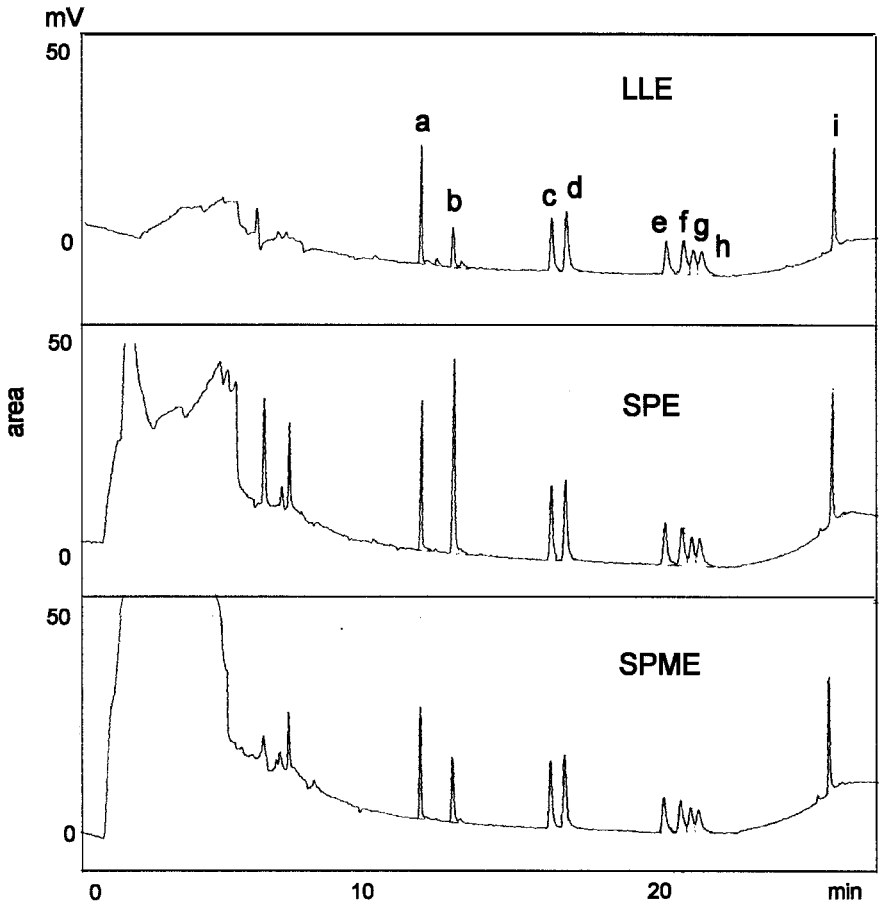

Figure 1. Chromatogram of pyrethroids extracted by liquid-liquid extraction-LLE, solid-phase extraction-SPE and solid-phase microextraction-SPME, according to conditions on Table 1. Sample concentration: 1 μg L^{-1}.
a,b: bifenthrin; *c, d*: permethrin; *e, f, g, h*: cypermethrin; *i*: deltamethrin

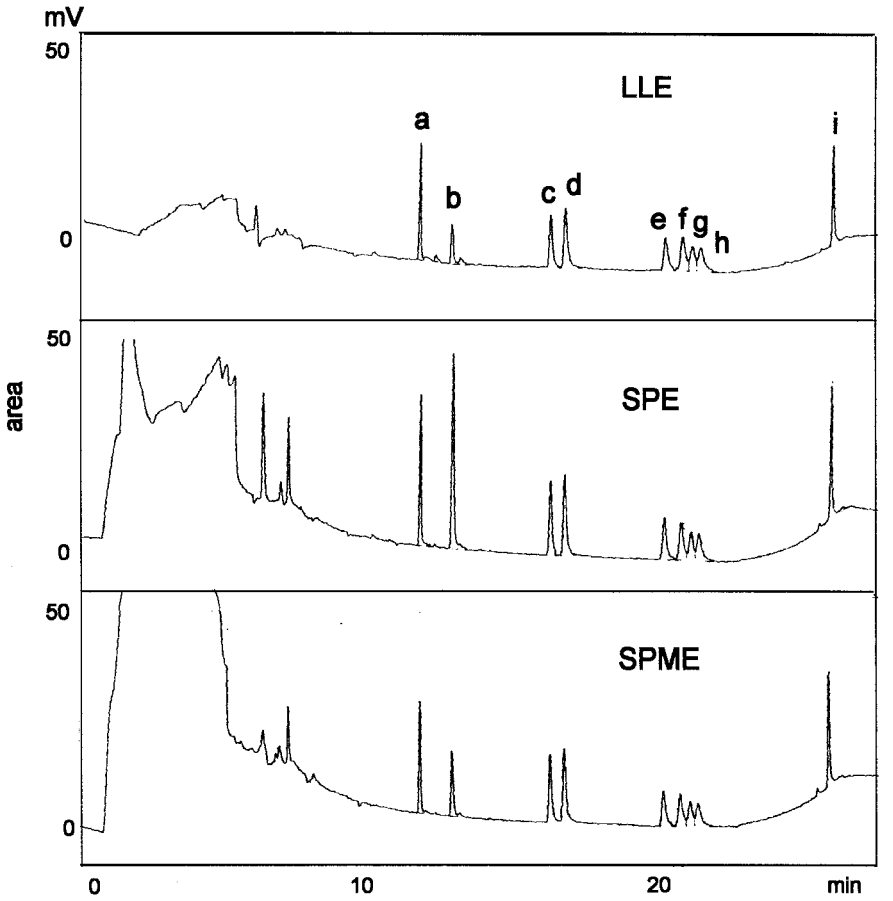

Figure 1. Chromatogram of pyrethroids extracted by liquid-liquid extraction-LLE, solid-phase extraction-SPE and solid-phase microextraction-SPME, according to conditions on Table 1. Sample concentration: 1 μg L^{-1}.
a,b: bifenthrin; *c, d*: permethrin; *e, f, g, h*: cypermethrin; *i*: deltamethrin

Table 1. Sample volume, solvent volume and extraction time for a river water solution enriched with pyrethroids (concentration 1 μL mL^{-1}) and extracted by Liquid-Liquid Extraction (LLE), Solid-Phase Extraction (SPE) and Solid-Phase Microextraction (SPME).

	LLE	SPE	SPME
Sample volume (mL)	500	500	5
Solvent volume (mL)	301	30	0
Extraction time (h)	2:27 ± 0:32	2:18 ± 0:12	0:10

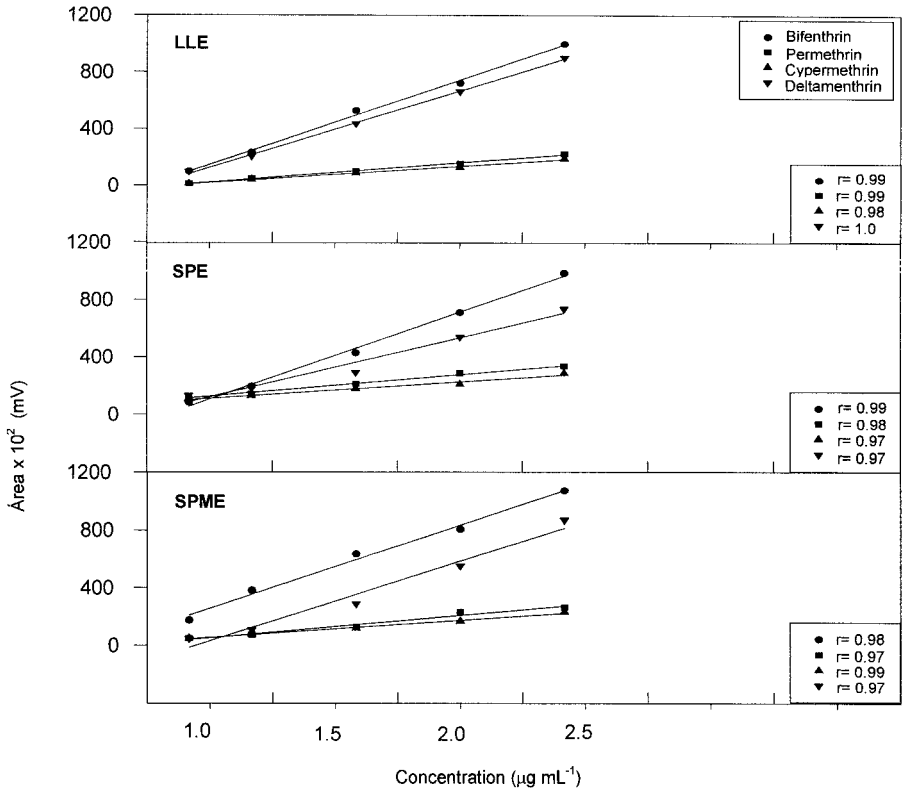

Figure 2. Calibration curves for pyrethroids extracted by LLE, SPE, and SPME

The procedure above was optimized after several experiments. For comparison, sample volumes which gave about the same area peak on GC-chromatogram for LLE, SPE and SPME techniques were chosen (Figure 1). The peak areas were compared by using the Kruskal-Wallis Analysis of Variance test. The calibration curve linear regressions (Figure 2) were performed by using the Sigma Plot for Windows Computer Program (Jandel Corporation, USA).

RESULTS AND DISCUSSION

The results obtained from river water enriched analysis are on Table 1 and Figure 1. For pyrethroid extraction, SPE showed to be better than LLE since it spends 10 times less volume of toxic solvents; the time-consuming of both techniques has not been considered significantly different (Kruskal-Wallis test). Among the three techniques SPME, was faster and did not require solvents at all.

Figure 2 shows the calibration curves for the pyrethroids extracted by LLE, SPE, and SPME which presents a linear response for all used techniques, since the correlation coefficient *r* for each curve is higher than 0.97 %.

Although the data showed that the three extraction methods were able to isolate the pesticide residues from water samples, the best results were obtained by using SPME which is more sensitive, faster, cheaper, being a more useful technique for the analysis of pyrethroids in drinking water.

Acknowledgment. We thank FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) for financial support (Proc. 96/9269-5 and 98/04017-3).

REFERENCES

Aguilar C, Peñalver S, Pocurull E, Borrul F, Marcé RM (1998) Solid-phase microextraction and gas chromatography with mass spectrometric detection for the determination of pesticides in aqueous samples. J Chromatog A, 695: 75-82

Eisert R, and Pauliszyn J (1997) Design of automated solid-phase microextraction for trace analysis of organic compounds in aqueous samples. J Chromatog 776:293-303

Hoff GR Van der, Pelusio F, Brinkman U A Th, Baumann RA, Zoonen P (1996) Automated solid-phase extraction coupled to gas chromatography with eletron-capture detection: a combination of extraction and clean-up of pyrethroids in the analysis of surface water. J Chromatog A 719:59-67

Ling YC, Huang IP (1995) Multi-residue matrix solid-phase dispersion method for the determination of six synthetic pyrethroids in vegetables followed by gas chromatography with electron capture detection. J Chromatog A 795:105-115

Magdic S, Boyd-Boland A, Jinno K, Pawlizzyn JB (1996) Analysis of organophosphorous insecticides from environmental samples using solid-phase microextraction. J Chromatog A 736:219-228

Pawliszyn J. (1992) *In*: Instrumentation and trace organic monitoring. Clement R, Siu KWM, Hill H.H, Lewis Jr (editors) Cheksea, MI, p.253.

Zweig G, Sherma L (1986) Analytical methods for pesticides and plant regulators, vol XIV. Academic Press, New York