STUDIA UBB CHEMIA, LIX, 3, 2014 (p. 43 - 48)
(RECOMMENDED CITATION)

DETERMINATION OF CHLORPYRIFOS IN SURFACE WATER USING SPE-DI-SPME/GC-ECD

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ABSTRACT. In this study a combined extraction method was performed for analysis of chlorpyrifos in surface water samples (Somes and Aries rivers and Tarnita Lake) collected in Cluj County, Romania, namely: solid phase extraction (SPE) and solid-phase microextraction (SPME) with direct immersion of the fiber, followed by gas chromatography – electron capture detection (GC-ECD). The target compound was detected in water samples collected from Somes and Aries rivers in concentrations exceeding the maximum admitted concentration (MAC) set by Romanian legislation, but lower than the MAC set by USEPA water quality criteria. The used method represents a very sensitive, simple and fast technique, easy to use, allowing the simultaneous sample extraction and analyte enrichment.

Keywords: *chlorpyrifos, SPE, SPME, GC-ECD, surface water*

INTRODUCTION

High levels of pesticides are used every year in the production and post-production treatments of agricultural commodities. Chlorpyrifos (CPF) is one of the most frequently used organophosphorus pesticides (OPPs) in agriculture and in households. OPPs are mostly sprayed over crops or applied to soils, leading to their direct transfer from drainage of agricultural lands to other parts of surrounding environments, including ground and surface waters. Therefore, there is an increasing concern with regard to the determination of these compound [1, 2].

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Chlorpyrifos is moderately toxic and classified in Toxicity Category II for all exposure routes. According to the United States Environmental Protection Agency, exposure to CPF could result in neurotoxicity in animals and humans, decreased birth weight of babies and increased risk of lung cancer. The maximum permissible level for CPF in fresh water is 0.041 μg/L, according to the USEPA water quality criteria [3].

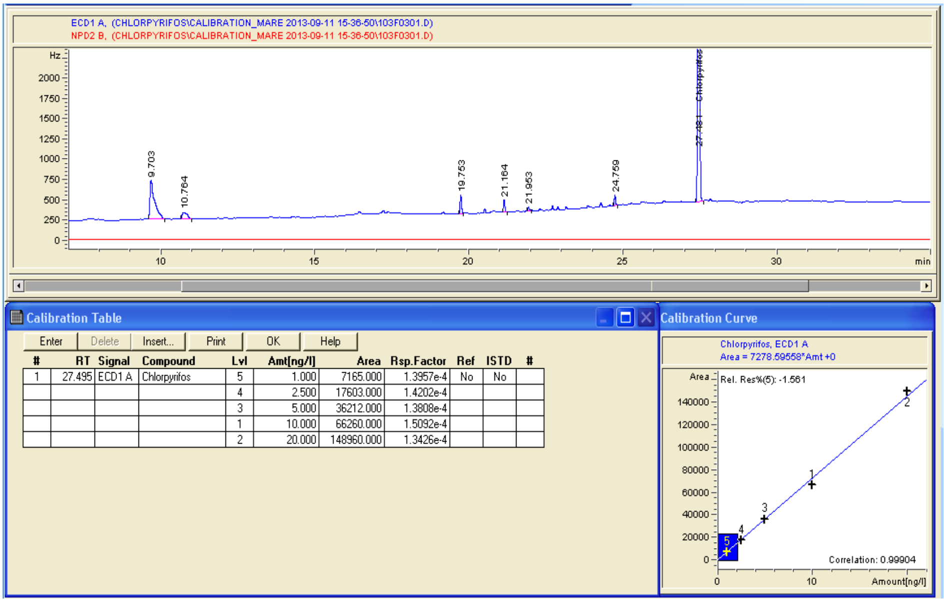
Due to the low concentration of chlorpyrifos in the aquatic environment, sensitive and reliable methods are required for determination. Sample preparation remains one of the main bottlenecks in chromatographic analysis [4]. Previously reported extraction / preconcentration methods included: liquid-liquid extraction [5, 6], solid-phase extraction (SPE), solid-phase microextraction (SPME), cloud point extraction (CPE), single drop microextraction (SDME), ultrasound-assisted emulsification microextraction (USAEME), vortex-assisted liquid–liquid microextraction (VALLME), dispersive liquid-liquid microextraction (DLLME) and SPE-DLLME, followed by gas chromatography-nitrogen phosphorus detection (GC-NPD), gas chromatography-mass spectrometry (GC-MS), gas chromatography-flame photometric detection (GC-FPD) and high-performance liquid chromatography (HPLC) [7]. Bonansea reported a combined extraction method: SPE with SPME, followed by GC-MS [6].

The aim of this study was to determine the content of chlorpyrifos in surface water samples (two rivers and one lake) in Cluj County, Romania using GC-ECD, subsequent to SPE/SPME combined extraction method.

RESULTS AND DISCUSSION

The standard solutions were prepared by successive dilutions of chlorpyrifos, in methanol. External calibration was performed using 5 different concentration levels of CPF, using the same method presented before in the SPE-SPME combined extraction procedure, for the extraction of standard solutions. The linearity of calibration curve was assessed in the range of 1.0 - 20 ng/L, with 0.99904 correlation coefficient. The calibration curve is presented in Figure 1.

The detection (LOD) and quantification (LOQ) limits were evaluated according to the signal-to-noise ratio of 3 and 10 respectively, and were 0.32 ng/L and 0.95 ng/L, respectively. It is worth mentioning that the limit of quantification reported for water was 50 ng/L for water, after liquid-liquid extraction, followed by Gas Chromatography with Nitrogen-Phosphorous Detector [8], more than 50 times higher than in the method used in the present study.


ECD1 A, (CHLORPYRIFOS\CALIBRATION_MARE 2013-09-11 15-36-50\103F0301.D)
NPD2 B, (CHLORPYRIFOS\CALIBRATION_MARE 2013-09-11 15-36-50\103F0301.D)

#	RT	Signal	Compound	Lvl	Amt[ng/l]	Area	Rsp.Factor	Ref	ISTD	#
1	27.495	ECD1 A	Chlorpyrifos	5	1.000	7165.000	1.3957e-4	No	No	
				4	2.500	17603.000	1.4202e-4			
				3	5.000	36212.000	1.3808e-4			
				1	10.000	66260.000	1.5092e-4			
				2	20.000	148960.000	1.3426e-4			

Chlorpyrifos, ECD1 A
Area = 7278.59558*Amt +0

Rel. Res%(5): -1.561

Correlation: 0.99904

Figure 1. Calibration curve for CPF in water

The collected water samples were analysed using the above mentioned method and the obtained results are shown in Table 1. The SPE-DI-SPME/GC-ECD chromatogram of Somes river water sample is presented in Figure 2.

The presence of CPF was detected in both river water samples, with a higher value in Somes than in Aries river, possibly reflecting a combined sources of pollution for Somes water: urban and agricultural, in accordance with the findings reported by Bonansea et al. (2013) in Suquía River (Argentina), collecting the wastewater of Córdoba city [6].

Table 1. Concentration of chlorpyrifos in surface water samples

Sampling point	**Chlorpyrifos**
Somes River	7.2 ng/L
Aries River	4.5 ng/L
Tarnita Lake	<LOQ

The obtained concentrations of CPF exceeded the MAC value set by Romanian legislation (0.46 ng/L) [9] and also the Canadian Water Quality Guidelines established for the protection of the aquatic biota in freshwaters (3.5 ng/L) [6], for the both river water samples. These obtained concentrations of CPF in river water samples were lower than the MAC set by USEPA water quality criteria (41 ng/L) [3] and were comparable with those reported by Bonansea et al. (2013) in Suquía River (Argentina) [6]. The concentration of CPF was lower than quantification limit in the lake water sample, indicating no use of CPF in the adjacent area.

CONCLUSIONS

This study report the concentrations of chlorpyrifos in surface water samples: Somes River, Aries River and Tarnita Lake, collected in Cluj County, Romania. In river samples, the target compound was detected in concentrations exceeding the MAC set by Romanian legislation, but lower than the MAC set by USEPA water quality criteria. In the lake water sample, chlorpyrifos was not detected.

For the analysis of chlorpyrifos, a combined extraction method was used: SPE followed by SPME, and then GC-ECD quantitative analysis. Because the analyte is concentrated on the cartridge and then on the fiber and is rapidly delivered to the column, minimum detection limits were achieved. SPME technique is an advanced methodology for rapid determination of aroma compounds and is "environmentally friendly" due to the absence of any organic solvents involved in the analysis. The method represents a very sensitive, simple and fast technique, easy to use and permit simultaneous sample extraction and analyte enrichment.

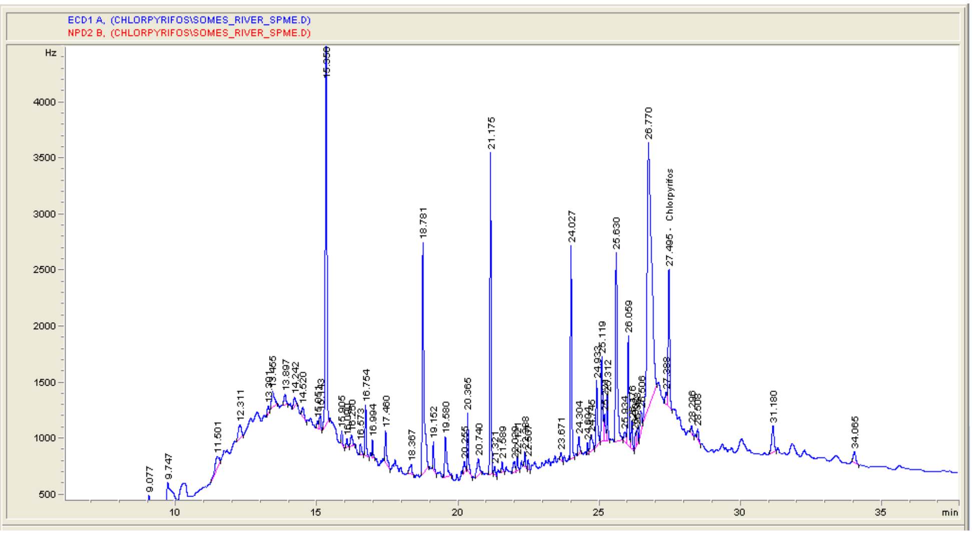


Figure 2. The SPE-DI-SPME/GC-ECD chromatogram of Somes river water sample

EXPERIMENTAL SECTION

Study area and sampling

In September 2013, water samples were collected from Somes River (sampling point 1), Aries River (sampling point 2) and Tarnita Lake (sampling point 3) in Cluj-County, Romania. The sample 1 was collected about 4 km downstream the municipal sewage treatment plant, which collect and filter the urban residues of Cluj-Napoca, a city with approximate 400000 inhabitants. The sample 2 was collected near Turda town and sample 3, about 30 km away of Cluj-Napoca city. The geographic coordinates of sampling points are shown in Table 2. Water samples were collected manually, by immersing the bucket under the surface of water and then by filling the precleaned amber-glass bottles. Samples were stored at 4°C until filtration and extraction.

Table 2. Geographic coordinates of sampling points

Sampling point	Latitude, N	Longitude, E
1	46°45'54.01"N	23°32'59.81"E
2	46°33'58.98"N	23°47'7.02"E
3	46°43'7.27"N	23°16'51.34"E

Materials and reagents

All chemicals were analytical reagent grade. Chlorpyrifos (98.0%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Methanol HPLC-grade, acetone, dichloromethane and sodium chloride (NaCl, 99%) were purchased from Merck (Darmstad, Germany). Sodium chloride was used to decrease the solubility of CFP and increase the adsorption of analyte by SPME technique. Ultrapure water (18.2 MΩ cm) was prepared by a Direct Q UV 3 Millipore system (Bedford, MA, USA).

For solid phase extraction, SPE Lichrolut RP-18 (40-63 μm) cartridges were used and were purchased from Merck (Darmstad, Germany). SPE extractions were performed with the Visiprep DL Vacuum Manifold for 12 samples from Supelco Inc. (Bellefonte, PA, USA). For the SPME extraction, a manual fiber holder Supelco Inc. (Bellefonte, PA, USA) with an 85 μm polyacrylate (PA) fiber from Supelco Inc. (Bellefonte, PA, USA) were used. Before use, the fiber was conditioned in the gas chromatograph inlet for 2 h at 300°C, according to the instructions of supplier.

Instrumentation

The samples were analyzed by GC (Agilent 6890, USA) equipped with electron capture detector (ECD). The column was HP-5 (0.25 mm film thickness, 30 m length, 0.25 mm i.d., J&W Scientific, USA) for chlorpyrifos determination. Helium was used as carrier gas.

SPE and SPME combined extraction procedure

SPE and SPME combined extraction was performed according to the extraction reported by Bonansea et al. (2013). In short, prior to SPE extractions, the cartridges were treated with 10 mL dichloromethane, followed by 10 mL methanol and 10 mL water. Aqueous samples (1 L) were passed through cartridges, after that the cartridges were dried by vacuum, and the elution was carried out with 5 mL methanol. The eluent was evaporated to dryness under nitrogen in 10 mL SPME glass vials.

After SPE extraction, SPME extraction was carried out using the SPE extract dissolved in 7 mL water and 0.1 mL acetone and sealed with a PTFE/Silicone septum and then, it was placed in a water bath. An amount of 3 g NaCl and a magnetic stirrer bar for samples were put in a vial sealed. The extractions were performed with the immersion of the PA (Supelco) fiber in the sample for 30 min at 70°C, under constant stirrer (100 rpm). After extraction, the fiber was removed from the sample and introduced in the GC injector for 5 min at 250°C for thermal desorption.

ACKNOWLEDGMENTS

This work was supported by Romanian financing authority CNCS – UEFISCDI, Capacities, Romania-China bilateral cooperation project, project number 630/01.01.2013.

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