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HEADSPACE SOLID PHASE MICROEXTRACTION COUPLED WITH GAS CHROMATOGRAPHY - ELECTRON CAPTURE DETECTOR FOR DETERMINATION OF CHLORPYRIFOS IN SEDIMENTS

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ABSTRACT. A rapid, sensitive and accurate method for quantification of chlorpyrifos pesticide in sediment by Headspace solid phase microextraction (HS-SPME) coupled with gas chromatography - electron capture detection (GC-ECD) was developed, validated and applied to sediment sample collected from Somes River, Romania. The SPME fiber used was coated with polyacrylate (PA, 85µm) and the extraction conditions optimized. The average recovery was 81% and the limit of detection 0.2 µg/kg. The concentration of chlorpiryfos in sediment sample collected from Somes River was 6.5 µg/kg. The method is fast, cheap and environment-friendly because it employs a simple sample preparation procedure with minimal organic solvent consumption.

Key words: *chlorpyrifos, HS-SPME/GC-ECD, sediment*

INTRODUCTION

Chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl)-phosphorothioate] is one of the most widely used organophosphate pesticides. Chlorpyrifos is a non-systemic insecticide, which is effective against a wide range of insect pests of economically important crops (Fang et al., 2006). Its residues have been detected in various ecological systems. A considerable amount of the pesticide either accumulates in the soil or enters into water bodies after application. Unfortunately, less than 0.1% of the total applied pesticide reaches the target and the rest remains in the environment (Chishti et al., 2013). Its massive application has led to the contamination of water and soil, and disruption of biogeochemical cycles, resulting in a risk to the ecological balance (Kulshrestha and Kumari, 2011). Moreover, serious damage to non-target species, such as endocrine disruption, birth defects, low birth weights, nervous system disorders and immune system abnormalities, has also been reported (Rauh et al., 2011). In addition, it is found to be associated with bladder cancer and chromosomal damage (Lee et al., 2004).

In the last years, the analytical methods tended towards simplification, miniaturization, and improvement of sample extraction and cleanup methods with universal micro extraction procedures. Among these extraction and cleanup methods, solid phase micro extraction (SPME) has become a popular technique. It is an inexpensive, environment-friendly and solvent-free technique with reliable and excellent sensitivity, as well as good selectivity. This sample preparation prior to the GC analysis can be carried out by direct immersion of the fiber into the sample (DI-SPME) or via the exposure of the fiber in the headspace above a liquid or solid sample (HS-SPME) (Chai and Tan, 2009).

The aim of this study was to develop a method for chlorpyrifos determination in sediments using HS-SPME extraction technique, to perform the validation of the method and to apply the method on real samples, collected from Somes River, near Cluj-Napoca, Romania.

MATERIALS AND METHODS

Reagents and instrumentation

Methanol, HPLC grade, purchased from Merck (Darmstadt, Germany) was used for successive dilution of chlorpyrifos standard, 99.9% purity Ultra Scientific (LGC Standards, Germany). Sodium chloride was obtained from Merck (Darmstadt, Germany).

The instrumentation used consists in an Agilent Technologies 6890N gas chromatograph (GC) with electron-capture detector (μ-ECD). The used capillary column was a 30 m L×0.32 mm ID×0.50 μm, DB-608 (Agilent J&W). High purity Helium was used as carrier gas.

For the SPME extraction a manual fiber holder Supelco Inc. (Bellefonte, PA, USA) with an 85 μm polyacrylate (PA) fiber Supelco Inc. (Bellefonte, PA, USA) were used. Prior to analysis, the fiber was conditioned in the GC inlet for 1 h at 280°C.

Ultrasonic bath (Bandelin, Sonorex, Germany) was used for samples ultrasonication.

HS-SPME procedure

The extraction was performed in 20 ml glass vials, capped with PTFE/ Aluminum caps. An amount of 5 g previously homogenized sediment sample was weighed in the glass vial, then 1 g NaCl and 5 ml distilled water were added. The mixture was shaken ultrasonically for 10 min (Abdulra'uf and Tan, 2013). The PA fiber was exposed to the sample headspace for 30 min at 60°C. After the extraction, the fiber was desorbed in the GC injector at 280°C for 5 min.

GC- μECD analysis

The GC-μECD was operated in split less mode and the oven temperature was: initial temperature 80°C, held for 5 min, then ramped to 280°C at 10°C/min and held for 15 min. Detector temperature was set at 300°C.

RESULTS AND DISCUSSION

Method validation

For the validation of the proposed method, the following figures of merit were determined: linearity, limit of detection, recovery and linearity.

Calibration was performed using external standard calibration curve with 5 concentration levels of chlorpyrifos, prepared in the sample matrix using the same procedure for extraction and chromatographic determination. The standard solutions were prepared by diluting accurate volumes of chlorpyrifos in methanol. The method linearity ranged from 0.5 to 50 μg/kg, with correlation coefficient of 0.9968.

The limits of quantification and detection values were estimated experimentally using a signal-to-noise ratio of 3 and 10, respectively. The limits of detection and quantifications were 0.35 μg/kg and 1.0 μg/kg, respectively. Because the analyte is concentrated on the fiber, and is rapidly delivered to the column, minimum detection limits are achieved.

The accuracy of the method was determined in terms of recovery experiments by extracting the chlorpyrifos from spiked sediment samples, prepared by adding adequate volumes of working solution to 5 g of blank matrix. The precision, expressed as the repeatability (% RSD) was determined by three consecutive extractions of chlorpyrifos from spiked sediment samples. The values obtained for recovery and for RSD were 84.2% and 12.6%, respectively.

Determination of chlorpyrifos in sediment samples

In September 2013, three sediment samples were collected from Somes River, near Cluj-Napoca city, Romania, using a grab sampler. The samples were subjected to the HS-SPME extractions and then to the GC analyses, respecting the conditions described above. Fiber blanks were measured before each sample in order to check the carry-over effect.

In sediments, chlorpyrifos was not detected in two samples and registered a level of 0.85 μg/kg in one sample. In Fig. 1 is shown the chromatogram of sediment sample with detectable concentration of chlorpyrifos.

In scientific literature, limited data on chlorpyrifos residues in sediments were reported and, generally, it was not detected in different sediments (ATSDR).

Chlorpyrifos exhibited affinity for aquatic soils and sediments, to differing degrees. Adsorption tends to reduce chlorpyrifos mobility, but adsorption to dissolved organic matter enhances its mobility. Adsorption to suspended sediments constitutes a major off-site migration route for chlorpyrifos to surface waters, leading to a potential danger to aquatic organisms (Gebremariam et al., 2012).

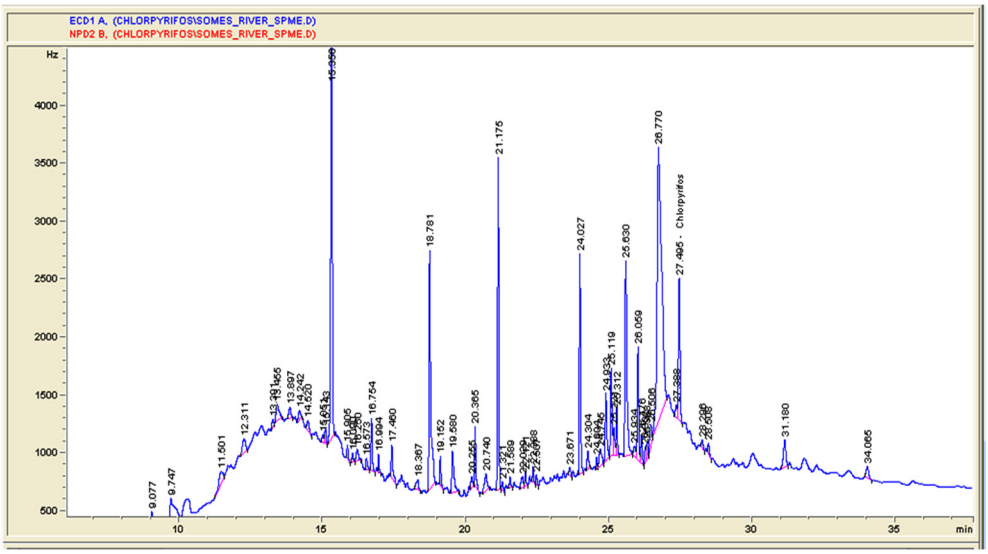

Fig. 1. *GC-ECD chromatogram of sediment sample.*

CONCLUSIONS

The proposed method for determination of chlorpyrifos in sediments, HS-SPME/GC-ECD is simple, rapid and highly sensitive. In the three sediment samples investigated, collected from Somes River near Cluj-Napoca, Romania, chlorpyrifos was not detected in 2 samples and registered a value of 0.85 µg/kg in one sample.

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