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Determination of organochlorine pesticides in textiles using solid-phase microextraction with gas chromatography–mass spectrometry

Jin'an Cai [a,b,c], Fang Zhu [a,b,*], Wenhong Ruan [a,b], Liqin Liu [d], Rong Lai [a,b], Feng Zeng [a,b], Gangfeng Ouyang [a,b,*]

[a] Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China
[b] MOE Key Laboratory of Aquatic Product Safety of Ministry of Education, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China
[c] Guangzhou Quality Supervision and Testing Institute, Guangzhou 510110, China
[d] Guangzhou Institute of Textiles Fibres Analysis, Guangzhou 510220, China

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ABSTRACT

A method based on solid-phase microextraction (SPME) and gas chromatography with mass spectrometry (GC/MS) for the determination of 10 organochlorine pesticides (OCPs) in ecological textiles was described. Commercially available SPME fibers, 100 μm PDMS, 85 μm PA, 65 μm PDMS–DVB, 75 μm CAR/PDMS and 30 μm PDMS were compared and 100 μm PDMS exhibited the best performance to the OCPs. Various parameters affecting the extraction efficiency of SPME were optimized, including extraction time, desorption time, extraction temperature, salinity and pH. The optimized conditions were 40 min extraction at room temperature, 2% NaCl content, pH 6.0, and 4.0 min desorption in GC injector port at 250 °C. Under the optimized conditions, the limits of detections ranged from 0.04 μg L^{-1} (dieldrin) to 0.41 μg L^{-1} (aldrin) and the RSDs were between 3.2% and 11.3%. The optimized method was then used to analyze 10 OCPs in textile samples, and good relative recoveries were obtained (from 70.0 to 112.6%). This study illustrated the potential applicability of SPME for routine analysis of OCPs in textiles.

1. Introduction

Organochlorine pesticides (OCPs) are known to be one of the most persistent organic pollutants in environment. They are persistent, estrogenic, carcinogenic [1,2], and able to bioaccumulate and biomagnify through the biological chain [3]. Because of the industrial and agricultural benefits, OCPs were ever widely used in the planting of inartificial textiles such as cotton and hemp. OCP residue in the textile may take a risk or threat to human health by skin contact and sweat secreting. Thus, developing a simple, rapid and sensitive method on OCP collection, pre-preparation and continuous monitoring in textiles is of great importance.

Chromatographic techniques are usually used to determine pesticides. Before determination, many preliminary steps, such as sampling, extraction, and clean-up for interference removal, need to be done. Typically, the sample pre-treatment methods of OCPs include liquid–liquid extraction (LLE) [4], solid phase extraction (SPE) [5], automated pressurized liquid extraction (PLE) [6] and so on. Solid-phase microextraction (SPME) is a solvent-free extraction technique that represents an easily automated alternative to conventional extraction methods [7]. SPME can avoid the toxic solvents or plugging of cartridges [8], so it is obviously more beneficial than the traditional sample pre-treatment methods [9,10].

Gradually SPME has been used to determine OCP residue in many matrices. Different methods based on SPME have been developed to assess environmental samples such as surface water [11–15], distilled water [16], soil [17], and sediments [18,19]. SPME methods for the determination of OCPs in human serum [20], mussels and cockles [21], butter [22], honey [23], milk [24], herbal infusions [25], fruits and vegetables [13,26,27] have also been reported. In textile samples, SPME has been used to determine the VOCs [28] and OPPs [29], but the determination of OCPs in textiles by SPME is not reported.

Herein, a simple and rapid SPME method for the determination of OCPs in textile samples was studied. Different parameters affecting the extraction performance of OCPs were investigated. Afterwards, the optimized method was applied to the determination of OCPs in real textile samples.

2. Experimental

2.1. Materials

The individual OCP standards were made up by hexachlorobenzene (HCB), heptachlor, aldrin, *cis*-chlordane, *trans*-chlordane, dieldrin,

* Corresponding authors. Tel./fax: +86 20 84110953.
E-mail addresses: ceszhuf@mail.sysu.edu.cn (F. Zhu), cesoygf@mail.sysu.edu.cn (G. Ouyang).

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endrin, *o,p*-DDT, *p,p*-DDT and mirex (purity > 98%), obtained from Dr. Ehrenstorfer GmbH (Freiburg, Germany). Acetone and sodium chloride (analytical grade) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Stock acetonic solution was 100 μg mL^{-1} for most OCPs, besides *cis*-chlordane and *trans*-chlordane were 40 μg mL^{-1}. The stock solution was stored at 4 °C in the dark before use.

The SPME fiber holder and fibers were obtained from Supelco (Mississauga, Canada). Five commercial fiber coatings were used in the experiment, including 30 μm and 100 μm polydimethylsiloxane (PDMS), 85 μm polyacrylate (PA), 65 μm PDMS/DVB, and 75 μm carboxen/polydimethylsiloxane (CAR/PDMS), respectively. All of the fibers were pre-conditioned according to the instruction of the manufacturer before initial use.

2.2. Instrument

A magnetic stirrer (MSH-20D, DAIHAN Scientific Co., Ltd, Seoul, Korea) was utilized to stir the sample and maintain the water bath with a fixed temperature.

GC–MS analysis was performed by an Agilent 6890N gas chromatography (Agilent Technologies, CA, USA) coupled to a MS5975 mass spectrometer and equipped with a split/splitless injector port. The samples were separated by a HP-5MS capillary column (5% phenyl–95% methyl siloxane, 30 m × 250 μm × 0.25 μm).

Helium was used as carrier gas at a constant flow of 1.2 mL min^{-1}; splitless injection; injection temperature was 250 °C; the oven temperature was initially maintained at 70 °C (held for 1 min), then increased to 180 °C at a rate of 10 °C min^{-1} (held for 1 min), and finally reached 270 °C at 3 °C min^{-1} (held for 3 min). The total run time was about 35 min. The GC transfer line was set at 280 °C. The mass spectrometer was maintained in the electron impact (EI) ionization mode with a source temperature of 230 °C. The electron energy was 70 eV and the filament current was 200 μA. Chromatograms were acquired in "scan" mode scanning the quadrupole from m/z 35 to m/z 450.

2.3. Sample preparation

2.3.1. Preparation of the standard solutions

The harmful chemical substances in textiles were probably absorbed into the human being's body by the sweat on the skin as touching each other. The 0.5% sodium chloride (w/v) (NaCl) solution is similar to the human sweat, thus it was prepared to extract OCPs from the textiles.

The OCP standard solutions at different levels were prepared by spiking the stock acetonic solution into 10 mL of the above NaCl solution contained in a 15 mL clean amber glass vial.

2.3.2. Pretreatment of the textile samples

The pretreatment of textile samples was similar to the reported method [29]. Briefly, 4 g of cotton textile, being cut into pieces of 5 mm × 5 mm, was put into a cone-shaped flask, and then a quantitative stock solution of OCPs was dropped onto the surface of the sample. After 20 min, 80 mL of the NaCl solution was added. The mixture solution in the flask was agitated quickly and thoroughly with the water bath of 37.4 °C for 1 h and then was adjusted into 100 mL with the NaCl solution.

2.4. SPME procedures

The direct-immersing SPME mode was chosen due to the low volatility of OCPs. Working solution of OCPs was contained in a vial of 15 mL. Stirring bar was put into the vial and then sealed with a septum cap. The solution was magnetically stirred at 1000 rpm. The outside needle of the SPME device was used to penetrate the septum and then the fiber was pushed out and exposed directly into the sample solution for a certain time. After extraction, the fiber was retracted and immediately transferred to the GC injector for analysis. The desorption time in the injector was 4.0 min and then the fiber was conditioned in another GC injector for 10 min at 250 °C to avoid any carryover of OCPs.

3. Results and discussion

3.1. Optimization of SPME method

To obtain high extraction efficiency, the parameters affecting the extraction performance were optimized. Besides the fiber coating, extraction and desorption time, extraction temperature of the SPME method, as well as the salinity and pH of the sample solution were investigated.

3.1.1. Fiber coating

Five types of commercial SPME fiber coatings, 100 μm PDMS, 85 μm PA, 65 μm PDMS–DVB, 75 μm CAR/PDMS and 30 μm PDMS, were used for the extraction of the 100 μg L^{-1} OCPs in NaCl solution

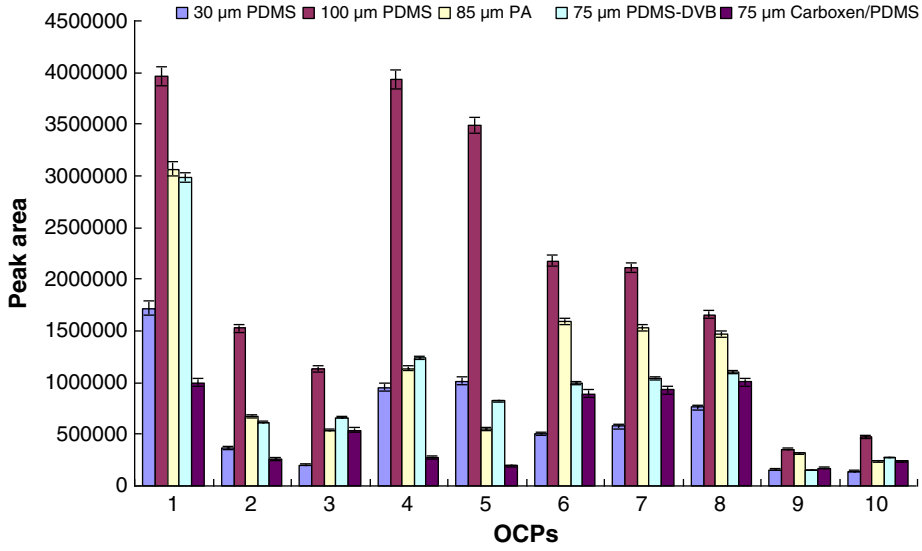

Fig. 1. Comparison of five kinds of SPME fibers for the extraction of the OCPs in NaCl solution. Concentration, 100 μg/L (except for *cis*-chlordane and *trans*-chlordane, 40 μg/L); extraction time, 10 min; extraction temperature, 25 °C. Peaks: (1) HCB, (2) heptachlor, (3) aldrin, (4) *cis*-chlordane, (5) *trans*-chlordane, (6) dieldrin, (7) endrin, (8) *o,p′*-DDT, (9) *p,p′*-DDT, and (10) mirex.