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Determination of organophosphorus pesticides in ecological textiles by solid-phase microextraction with a siloxane-modified polyurethane acrylic resin fiber

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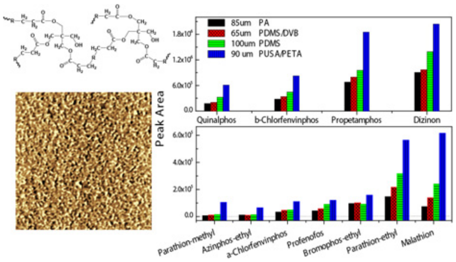
HIGHLIGHTS

- A PUSA/PETA SPME fiber coating was prepared by photo-cured technology.
- The ratio of two monomers was optimized for better extraction performance.
- The fiber showed very good performance for OPPs analysis in textiles.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel solid-phase microextraction (SPME) fiber coating was prepared with siloxane-modified polyurethane acrylic resin by photo-cured technology. The ratio of two monomers was investigated to obtain good microphase separation structure and better extraction performance. The self-made fiber was then applied to organophosphorus pesticides (OPPs) analysis and several factors, such as extraction/desorption time, extraction temperature, salinity, and pH, were studied. The optimized conditions were: 15 min extraction at 25 °C, 5% Na_2SO_4 content, pH 7.0 and 4 min desorption in GC inlet. The self-made fiber coating exhibited better extraction efficiency for OPPs, compared with three commercial fiber coatings. Under the optimized conditions, the detection limits of 11 OPPs were from 0.03 $\mu g\,L^{-1}$ to 0.5 $\mu g\,L^{-1}$. Good recoveries and repeatabilities were obtained when the method was used to determine OPPs in ecological textile.

1. Introduction

Natural fabrics are considered as one of the most potential ecological textiles in the 21st century. But lots of pesticides were used to control the various pests and diseases throughout the cotton or hemp growth cycle. Organophosphorus (OPs) are the most commonly used insecticides because of its high toxicity and rapid degradation after use [1–3], which makes them as an attractive alternative of persistent organochloride pesticides. Since the organophosphorus pesticide (OPP) residues in ecological textiles may also cause some damage to human health, some of relevant laws and regulations such as Oeko-Tex100 (2012) were drawn to restrict the limits of pesticide residues (0.5 $mg\,kg^{-1}$ for product class I, and 1 $mg\,kg^{-1}$ for class II, III, and IV) in the ecological textile recently. The pretreatment of textile samples is usually in a conventional liquid–liquid extraction way, which consumes lots of organic solvent as well as labor force. Therefore, developing green and convenient sample pretreatment method is very important [4].

Solid-phase microextraction (SPME) is a solvent-free sample preparation technology. Due to its undoubted advantages, such

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as simplicity of operation, short of extraction time, possibility of automation and relatively good results of the isolation of trace amounts of analytes [5], SPME has been widely used in different fields including the environment, food, natural products, pharmaceuticals, biology, toxicology, and forensics [6–10]. SPME is based on the partition of analyte between the fiber coating and the sample matrix. Owing to the limitation of existing commercial available fiber coatings, it is believed that the development and further extension of the technique depend on the new breakthroughs in coating materials and coating technology [11]. More and more extensive researches are also being pursued on SPME coating preparation and fiber fabrication [5,12–16].

Polyurethane is an incredibly resilient, flexible, and durable material by changing different diisocyanate and a diol (or tow hydroxyl monomers) through a chemical reaction under anhydrous condition. It might be hard like fiberglass, squishy like upholstery foam, protective like varnish, bouncy like rubber wheels, or sticky like glue depending on the composition of diisocyanate and diols [17,18]. Polyurethane has been used as air sampling medium and extraction phase, due to its good extraction ability for various compounds [19,20]. Since the structure of polyurethane can be adjusted during the preparation, it may offer an effective way to fabricate a new SPME coating containing both polar and nonpolar parts.

In our previous study, commercial polydimethylsiloxane (PDMS) and polyacrylate (PA) fibers were used for the determination of OPPs in ecological textiles [21]. In this paper, toluene diisocyanate was chosen to couple alkylhydroxyl-terminated siloxane and hydroxyethyl methacrylate to prepare a prepolymer and then the double bond of hydroxyethyl methacrylate was used for further crosslinking reaction with pentaerythritol triacrylate under UV curing processing. This siloxane-modified polyurethane acrylic resin integrating the siloxane with polyacrylate was used as SPME fiber coating. A series of experiments were carried out to evaluate the performance of the self-made fiber through the determination of OPPs in ecological textiles, and several commercial SPME fibers including PDMS, PA, and PDMS/DVB were utilized for comparison study.

2. Experimental

2.1. Materials and reagents

The individual OPPs standards including diazinon, propetamphos, quinalphos, profenofos, chlorfenvinphos, parathion-ethyl, azinphos-ethyl, parathion-methyl, malathion, and bromophos-ethyl were purchased from Sigma–Aldrich (purity >98%, St. Louis, USA). The standard mix solution was diluted to the concentration of 100 mg mL^{-1} with acetone (HPLC grade, Sigma–Aldrich, USA). This stock solution was stored in refrigerator at 4 °C until use. Working solutions of OPPs were diluted using acid simulative sweat. The fused silica fiber was obtained from Feilihua Quartz Glass Co., Ltd. (Hubei, China).

Alkylhydroxyl-terminated siloxane was obtained for Taige Polymer Co., Ltd. (Chemically pure, China). Pentaerythritol triacrylate (PETA) was obtained from Zhenlin Trade Co., Ltd. (Chemically pure, China). Toluene diisocyanate (TDI) was purchased from BASF Company (Chemically pure, Germany), and photo initiator 4265 was obtained from Ciba Company (Chemically pure, Switzerland).

2.2. Preparation of SPME fiber

2.2.1. Synthesis of polysiloxane urethane acrylate resin (PUSA) prepolymer

The prepolymer was prepared as follows: first adding appropriate TDI into the four necked flask equipped with the thermometer, blender, and condenser. Then 5 drops of catalyst and appropriate amount of alkylhydroxyl siloxane (according to the mole ratio NCO:OH = 1.25:1, 1.50:1, and 2.00:1) were added. The solution was reacted for 2 h at room temperature (Reaction 1 in Fig. 1), and then hydroxyethyl methacrylate (HEA) was fed to react with the remaining NCO group (Reaction 2 in Fig. 1). The conversion rate of NCO was monitored by titrating during the reaction. When the conversion rate reached 95%, the reaction temperature was increased to 70 °C and the reaction was stopped until the NCO content was below 0.5% [22].

2.2.2. Fabrication of SPME fiber

Before preparing the fiber coating, 4 cm of O.D. 90 μm quartz fiber was fixed in a 8.5 cm length, 150 μm I.D. stainless tubing with epoxy glue. The exposed 2 cm of quartz fiber was then dipped into the prepared solution, which contained 2.0 g prepolymer, 6% (wt) photoinitiator and 20% (wt) PETA. After that, the fiber was immediately transferred into a UV-curing oven (Interlay 400, USA) for solidification of about 5 s (Reaction 3 in Fig. 1). This procedure was repeated until the needed thickness was obtained. This fiber was abbreviated to PUSA/PETA in the following section. Prior to use, the exposed fiber was cut into 1 cm and fixed into the screw cap of a used commercial SPME fiber assembly together with the stainless tubing by using epoxy glue.

2.2.3. Aging of the fiber

The self-made fibers were aged under the following procedures: conditioned at 80 °C for 30 min, then increased to 200 °C and kept for 30 min finally the temperature was increased to 250 °C and kept for 1 h.

2.3. Instrument

GC–MS experiments were carried out on a Trace GC/DSQ (Thermo, USA) equipped with a DB-35 capillary column (30 m × 0.25 mm × 0.25 μm) and a MS detector in SIM model. The inlet temperature was set at 240 °C. The interface temperature was 280 °C. The oven temperature was set at 55 °C at the beginning and held for 1 min, then increased to 190 °C at a rate of 25 °C min^{-1}, held for 3 min, and finally the temperature was increased to 300 °C at a rate of 10 °C min^{-1} and held for 3 min. Helium was used as carry gas and the flow rate was set at 1.0 mL min^{-1} in splitless model.

2.4. Sample preparation

The OPPs in textiles could be absorbed through sweat or saliva by human skin in the following experiments, simulative sweat was used to marinate the spiked textile samples before extraction with SPME fiber. The simulative human sweat was prepared as previous study [21].

For textile sample preparation, four grams of textile, being cut into piece of 5 mm × 5 mm, was put into the cone-shaped flask marinated in 80 mL simulative sweat at 37.4 °C for 1 h. After that all the marinating solution was transferred to a 100 mL volumetric flask and make up to volume with simulative sweat. Ten milliliters of the mixture was then transferred into a glass vial for SPME extraction. The spiked textile sample was prepared by adding a certain amount of the standard stock solution (Section 2.1) to 4.0 g Standard Adjacent Fabrics and then pretreated as mentioned above before SPME extraction.

Preparation of the OPPs standard solution was described as follows: a quantitative stock OPPs acetone solution (100 mg L^{-1}) was diluted with 10 mL of the simulative sweat solution in a 15 mL amber glass vial. To study the salt addition influence of the extraction efficiency, different amount of Na_2SO_4 was added into the same