

# Physically incorporated extraction phase of solid-phase microextraction by sol–gel technology

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## Abstract

A sol–gel method for the preparation of solid-phase microextraction (SPME) fiber was described and evaluated. The extraction phase of poly(dimethylsiloxane) (PDMS) containing 3% vinyl group was physically incorporated into the sol–gel network without chemical bonding. The extraction phase itself is then partly crosslinked at 320 °C, forming an independent polymer network and can withstand desorption temperature of 290 °C. The headspace extraction of BTX by the fiber SPME was evaluated and the detection limit of *o*-xylene was down to 0.26 ng/l. Extraction and determination of organophosphorus pesticides (OPPs) in water, orange juice and red wine by the SPME-GC thermionic specified detector (TSD) was validated. Limits of detection of the method for OPPs were below 10 ng/l except methidathion. Relative standard deviations (RSDs) were in the range of 1–20% for pesticides being tested.

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## 1. Introduction

The use of pesticides in agricultural and plant protection practices causes extensive pollution of the environment and constitutes a potential risk for human health. As a result, both Environmental Protection Agency (EPA) regulations and EU legislation established a maximum pesticide residue level in agricultural commodity. Organophosphorus pesticides (OPPs) are among the most widely applied pesticides worldwide, especially in developing countries, causing residues of these substances in agricultural products and in derivate food commodities, such as wine, fruit juices and so on.

The analytical procedures used to determine the type and amount of pesticides present in agricultural samples have to be robust, precise and sensitive if they are to be used in regulatory situations.

Solid-phase microextraction (SPME) has been used in the analysis of volatile and semi-volatile chemicals as its superiority over conventional extraction methods has been recognized

[1–3]. A significant drawback of commercial SPME is that their recommended operating temperatures are relatively low, because the extraction phases of commercial SPME are prepared by physical deposition of the polymer coating rather than bonding and cross-linking. The lack of proper chemical bonding between the stationary phase and fused silica fiber surface and cross-linking among the stationary phase itself may be responsible for the low thermal and chemical stability of commercial SPME.

Sol–gel column technology combines a capillary surface treatment, deactivation, coating, and stationary phase immobilization into a single step [4–6]. It provides an efficient incorporation of organic components into the inorganic polymeric structures in solution under extraordinarily mild thermal conditions. Reports on application of sol–gel technology to SPME coating is increasing in recent years [7–11]. Generally, inorganic materials have high thermal stability while organic ones have flexibility and processability, which may enhance the dynamic characters and thermal stability of the materials. One of the many advantages of sol–gel technique is the strong adhesion of the coating to the fiber.

The sol–gel reactions are catalyzed by acid or base, which lead to the formation of polymeric network. There are two

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styles of formation of the composite coating, i.e. the precursor is hydrolyzed in organic solutions, and then the organic material is wrapped in the sol–gel network; or the precursor hydrolyzed and then poly-condensed with sol–gel active organic material (–OH-terminated) obtaining the porous polymeric network. As reported previously, OH-PDMS, poly(ethyleneglycol)s (PEG) and some novel sorbents have been used as the extraction phase in the preparation of microextraction fiber by sol–gel method because they are sol–gel active [5,12–14]. In fact, when the molecular weight of extraction phase used in SPME, such as PDMS, PEG, was larger than 100 000 with very long molecular chains, the spatial blockage will prohibit reaction of –OH groups with the sol–gel network, leading to physical incorporation of most of the extraction phase in the sol–gel network rather than chemical bonding, as was reported in the preparation of stir bar for sorptive extraction (SBSE) by sol–gel method [15].

In this study, we demonstrated a new coating technology for the preparation of SPME coating by sol–gel method. The extraction phase of PDMS containing 3% vinyl group without –OH (having no sol–gel activity) group was thoroughly incorporated into the sol–gel network, and then, the vinyl group of PDMS cross-linked among PDMS chains during aging process, forming two inter-embed network. Applications of headspace SPME for the determination of BTX and direct immersion extraction of pesticides in real sample were demonstrated.

## 2. Experimental

### 2.1. Instrument

SPME-GC analysis of benzene, toluene and xylene (BTX) was carried out on a Trace GC 2000 (ThermoQuest CE Instruments, USA) equipped with a flame ionization detector (FID) and split/splitless injector, SPME-GC analysis of OPPs was performed on a CP 3800 GC (Varian, USA) system equipped with a thermionic specified detector (TSD) and split/splitless injector. A 30 m × 0.53 mm, 1 μm OV-1 crosslinked fused-silica capillary column was used to analyze BTX, and a 30 m × 0.25 mm, 0.3 μm SE-54 crosslinked fused-silica capillary column (Columns were provided by Dalian Scien-Tech Instrument Inc., Dalian, China) was used to analyze OPPs.

The holder of SPME fibers was a modified 5 μl GC syringe (Shanghai Medical Laser Instrument Company, China). Optical fiber (140 μm O.D.) with protective polyimide coating was obtained from Yongnian Optical Factory (Hebei, China). GX FTIR spectrometer (Perkin-Elmer, USA) was used to measure infrared absorption spectrum of the coating material. A JSM-6360 scanning electron microscope (JEOL, Tokyo, Japan) was used to examine the sol–gel PDMS coatings (including the surface and thickness of the sol–gel coating). A SK-1 quick blend machine (Jiangsu, China) was used for thorough mixing of various ingredients in the sol solution.

### 2.2. Reagents and materials

The PDMS containing 3% vinyl group was obtained from Jilin Chemical Engineering Research Institute (Jilin Province,

China). Methyltrimethoxysilane (MTMOS) was purchased from Danyang organic silane company (Jiangsu Province, China). Poly(methylhydrosiloxane) (PMHS) was obtained from the Chemical Plant of Wuhan University (Wuhan, China). Trifluoroacetic acid (TFA) was purchased from Shanghai Chemical Plant (Chinese Medicine Group, China). HPLC grade methylene chloride was purchased from Tedia (Tedia, USA). BTX were purchased from Beijing Chemical Plant (Beijing, China), OPPs were purchased from J&K Acros Organics (Beijing, China). The water used in this experiment was Wahaha purified water (Hangzhou, China). Orange juice and red wine (ethanol volume ratio 11%) were purchased from a local market. All glassware used was purchased from Schott Duran (Schott, Germany).

### 2.3. Preparation of standard solutions

BTX and OPPs were dissolved in methanol and acetone to prepare 100 and 1 μg/ml stock solutions, respectively. Aqueous test samples containing 10 ng/ml BTX were diluted from methanolic stock solution, and the working solutions of OPPs with concentration of 0.10, 0.20, 0.40, 0.50, 1.00 and 10.00 ng/ml of each pesticide were prepared in purified water by diluting the OPPs stock solution.

### 2.4. Fiber preparation

Prior to sol–gel coating, the protective polyimide layer was removed as follows: one end of optical fiber was dipped into concentrated sulfuric acid (1 cm deep) and soaked for 40 min at 70 °C to remove the original polymeric layer and to expose the fused silica core. The fused silica fibers were then rinsed with distilled water and dipped into 1 mol/l NaOH solution for 1 h to expose the maximum number of silanol groups on the silica surface of the fibers, and then into 0.1 mol/l HCl for 30 min. The activated fibers were rinsed with distilled water, dried at 120 °C for 12 h in a GC oven before use.

The sol solution was prepared as follows: 200 mg of PDMS was thoroughly dissolved in 300 μl methylene chloride; then 100 μl MTMOS and 50 mg PMHS were added, after the PDMS completely dissolved, 80 μl TFA (containing 5% water, v/v) was added, and vortexed quickly until the mix to be a clear solution which was used for fibers coating. After 30 min of stay, the treated fiber was dipped into the sol for 1 h. Repeated coating can increase the coating thickness. The coated fiber was then placed in a desiccator at room temperature for 12 h coating gelation. After that, the fiber was soaked by methylene chloride for 6 h followed by another 12 h gelation in the GC oven at 40 °C. Conditioning of the fiber was as follows: the fiber was put into the GC injector under nitrogen flow of 1 ml/min, at 120 °C for 1 h, then 240 °C for 1 h, and finally 320 °C for 3 h. The final temperature and aging time insures cross-linking of the PDMS phase and formation of independent polymer network from the sol–gel network. After the conditioning process the fiber was ready for SPME experiments. The thickness of the fiber coating was 50 μm.

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