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Evaluation of a new method for chemical coating of aluminum wire with molecularly imprinted polymer layer. Application for the fabrication of triazines selective solid-phase microextraction fiber

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ABSTRACT

A new solid-phase microextraction (SPME) fiber is fabricated through ultra violet irradiation polymerization of ametryn-molecularly imprinted polymer on the surface of anodized–silylated aluminum wire. The prepared fiber is durable with very good chemical and thermal stability which can be coupled to GC and GC/MS. The effective parameters on the fabrication and application procedures such as spraying mode, ultra violet irradiation (polymerization) time, number of sprayings and polymerizations, pH and ionic strength of sample and extraction time were optimized. This fiber shows high selectivity with great extraction capacity toward triazines. SPME and GC analysis of ametryn, prometryn, terbutryn, atrazine, simazine, propazine and cyanazine using the fabricated fiber result in the detection limits of 9, 32, 27, 43, 51, 74 and 85 ng mL^{-1}, respectively. The reliability of the prepared fiber in real samples has been investigated and proved by using spiked tap water, rice, maize and onion samples.

1. Introduction

In recent years, SPME has widely been used in different fields including the analysis of environmental, food, natural products, pharmaceuticals, toxic and forensic samples [1]. This method is based on the distribution of analytes between sample solution and a fiber coated with a stationary phase. Commercially available SPME fibers have a number of drawbacks including relatively low operating temperature (generally in the range of 240–280 °C), mechanical fragility, low stability in acidic or alkaline samples [2,3], less selectivity and swelling in organic solvents [3]. Consequently, in recent years the preparation of tailor made fibers has been the focus of interest [4–10].

The use of metal wires as fiber supports with high mechanical stability makes this technique more robust for routine analysis. Several studies have been developed using different material coatings over the traditional fused silica support, such as platinum [11,12], anodized aluminum [5], gold [13,14], stainless steel [11,15,16], copper [17], titanium [18] and NiTi alloy [9,19] wires.

Molecular imprinting is a technology to produce polymers programmed to recognize a target or a class of target molecules which have been applied as useful materials in many fields such as liquid chromatography [20], solid-phase extraction [21], simulated enzyme catalysis [22], chemical sensor [23], and membrane separation [24]. Molecularly imprinted polymer (MIP) is very suitable as the material for SPME fiber coatings because of high selectivity, chemical stability, and easy preparation characteristics. The combination of molecular imprinting and SPME methods would perfectly provide a powerful analytical tool which includes simplicity, flexibility and selectivity characteristics of both methods.

Monolithic MIP-SPME fibers which are able to be coupled with GC and GC/MS were fabricated for the first time in our laboratory [25–28]. These fibers were used for selective extraction of diacetylmorphine, codeine and triazine herbicides from real samples followed by GC and GC/MS monitoring.

The aim of this study is the fabrication of a SPME fiber obtained through photo-polymerization (under UV irradiation) of pre-polymer solution on the surface of silylated anodized aluminum wire to achieve a chemically bonded coating with ametryn imprinted polymer. This fiber was evaluated and subsequently used for extraction of ametryn and its structural analogous for GC and GC/MS analyses.

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2. Experimental

2.1. Apparatus

Monitoring of the analytes was performed using a gas chromatograph (Shimadzu 2014, Kyoto, Japan) equipped with flame ionization detector and a hydrogen generator (model OPGU 1500S, Shimadzu). Gas chromatographic separations were carried out with a chrompack capillary column of 50 m × 0.25 mm i.d. coated with a 0.12 μm film thickness (SPB-50, Varian, Palo Alto, CA, USA).

Recognition of studied triazine herbicides in spiked and real samples was performed by Varian GC (model 3200, Palo Alto, CA, USA) coupled with a Varian mass spectrometer (model 2000, Palo Alto, CA, USA). The chromatographic column used for GC/MS was CP-Sil 5-CB, 30 m × 0.25 mm i.d. (Chrompack, Palo Alto, CA, USA).

Pre-polymer solution containing template molecule, functional monomer, cross-linking agent and porogen was stirred in an ultrasonic bath (Grant, Cambridge, UK). Pre-polymer solution was sprayed on the surface of modified aluminum wires with home made pneumatic spray device. Photo-polymerization was carried out with UV-lamp (Osram, 300 W).

SPME of analytes was performed in a 3 mL sample vials sealed with a silicone-rubber septum cap (Supelco, PA, USA) containing a magnetic stirring bar. Samples were agitated at 600 rpm during SPME by a magnetic stirrer (Gerhardt, Konigswinter, Germany).

2.2. Reagents and chemicals

Methacrylic acid (MAA), ethylene glycol dimethacrylate (EDMA), acetonitrile and 2,2′-azobis-isobutyronitrile (AIBN) were purchased from Merck (Darmstadt, Germany). Atrazine, ametryn, terbutryn, prometryn, propazine, simazine and cyanazine were from Sigma–Aldrich laborchemikalien Gmblt D-30918. Isofenphos, chlorpyrifos, diazinon and Profenophos with analytical grade, 3-(trimethoxysilyl) propylmethacrylate (TMPM) were purchased from Sigma–Aldrich. A roll of aluminum wire of 0.3 mm diameter with high purity was obtained from the Sim-Kat factory (Tabriz, Iran).

2.3. Real samples

54 g portions of crushed onion and maize were separately spiked with the determined amounts of ametryn, terbutryn, prometryn, atrazine, propazine, simazine and cyanazine. The mixtures were diluted up to 50 mL with ultra pure water to reach a final concentration of 100 and 500 ng mL^{-1} or 0.09 and 0.47 mg kg^{-1} of each compound. These spiked samples were stirred in an ultrasonic bath for 10 min and centerfused. 3 mL of supernatant solution was filtered through 0.2 μm filters (ACRODISC 13 CR PTFE) and was used for SPME procedure.

10 g portions of dried (at room temperature) and powdered rice seeds including rice and bran were spiked with the determined amounts of ametryn, terbutryn, prometryn, atrazine, propazine, simazine and cyanazine. These samples were introduced into 25 mL flasks containing 12.5 mL of methanol diluted up to 25 mL with ultra pure water to reach the final concentrations of 100 and 500 ng mL^{-1} or 0.25 and 1.25 mg kg^{-1} of each compound. The prepared mixtures were placed in ultrasonic water bath at room temperature for 8 min. They were filtered through 0.2 μm filters (ACRODISC 13 CR PTFE). 3 mL of this solution was used for SPME procedure.

2.4. Fabrication of MIP-coated SPME fiber

2.4.1. Anodizing of aluminum wire

Aluminum wire was anodized as described in the literature [5]. Aluminum wire (0.3 mm diameter) was cut into lengths of 30 cm and formed into spring (circular) shape. The pieces were washed in dilute detergent solution and distilled water several times. It was then thermally activated in a furnace from 100 to 500 °C at a rate of 40 °C min^{-1} and held at 500 °C for 30 min. Aluminum wires were boiled in the detergent and distilled water for 15 min to have a fully clean wires. The aluminum wires were anodized in 16% (w/v) sulfuric acid solution at a controlled potential of 15 V, using an aluminum plate as the cathode, for 60 min. The anodized aluminum wires were then cut into lengths of 2.5 cm.

2.4.2. Silylation of anodized aluminum wires

Anodized aluminum wires were soaked in boiling detergent solution and cleaned with ethanol. It was then immersed in 0.1 mol L^{-1} sodium hydroxide for 1 h to create hydroxyl groups in their surface. Afterwards, the wire pieces were again washed in water and dried preliminarily with a stream of helium. In order to remove all water from the aluminum surface, the wires were dried continuously in furnace at 400 °C for 15 min.

The wires were silylated for 2 h by immersing into a 10% (v/v) 3-(trimethoxysilyl) propylmethacrylate solution in acetone at room temperature. Then they were washed in methanol and dried with a stream of helium.

2.4.3. Coating of silylated wires with MIP and non-imprinted polymer (NIP)

Ametryn imprinted pre-polymer solution was prepared as our previous papers [28]. 2.2 mmol template molecules (ametryn) were dissolved in 30 mL of acetonitrile and placed in a sealed glass tube. 30 mmol functional monomer (MAA), 120 mmol cross-linking monomer (EDMA) and 280 mg initiator (AIBN) were then added to the above solution. The mixture was degassed with helium for 10 min.

For the coating of wires with MIP, the pre-polymer MIP solution was sprayed by laboratory-made pneumatic sprayer on the surface of anodized–silylated aluminum wires from a distance of 20 cm for 10 s. Photochemical polymerization was performed under UV irradiation for 10 min. To obtain the optimum thickness of MIP layer, spraying and polymerization procedures were repeated for four times. These wires were used as SPME fibers. The procedures of modification and coating are shown in Fig. 1 schematically.

The NIPs fibers were also prepared according to the above procedures except in the absence of ametryn during polymerization.

2.5. Fiber conditioning

Removing of templates and any contaminations from prepared fibers is very essential. Therefore, the prepared aluminum-MIP-coated and aluminum-NIP were washed with excessive amount of mixture of methanol, acetic acid and double-distilled water (4:1:1, v/v/v) until template and non-reacted compounds were removed as much as possible. The fibers were then modified by heating at 220 °C in the presence of water vapor in a carbolite furnace for 15 min. All modified fibers were conditioned at 270 °C for 20 min in GC injection port under helium flow.

2.6. SPME procedure

Desired fibers were mounted on the laboratory-made SPME device and used for the extraction and sampling of triazine herbicides from model standard solutions and real samples. 3 mL of aqueous samples with a pH of 7 adjusted by phosphate buffer (0.06 M) were introduced into 3 mL sealed sample vial containing magnetic stirrer bar. SPME was accomplished by direct immersion of 20 mm of fiber in the sample for 12 min at the room temperature. Samples were agitated during SPME by a magnetic stirrer at 600 rpm. The fiber was removed from the vial and washed with