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Preparation of new solid phase micro extraction fiber on the basis of atrazine-molecular imprinted polymer: Application for GC and GC/MS screening of triazine herbicides in water, rice and onion

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ABSTRACT

A simple polymerization strategy has been used to produce a monolithic solid phase micro extraction (SPME) fiber on the basis of molecularly imprinted polymer able to couple with GC and GC–MS for selective extraction and analysis of triazine herbicides. A fiber was produced by copolymerization of methacrylic acid–ethylene glycol dimethacrylate imprinted with atrazine.

The effective factors influencing the polymerization have been investigated and are detailed here. At the optimum conditions the prepared fiber is firm, inexpensive, durable and thermally stable up to 280 °C which has vital importance in SPME coupled with GC or GC/MS. In addition, the influences of pH, extraction time and temperature on the extraction efficiency of analytes were optimized. Selectivity of prepared fibers in relation to triazine herbicides and some of the other pesticide has been investigated. The high extraction efficiency was obtained for atrazine, simazine, propazine, cyanazine, ametryn, terbutryn and prometryn yielding the detection limits of 20, 70, 80, 81, 69, 88 and 68 ng mL^{-1}, respectively and the high quantities of recoveries. The reliability of prepared fiber to extraction of atrazine and other analogues in real samples has been investigated and proved by implementation of SPME in spiked samples such as tap water, onion and rice.

1. Introduction

Solid phase micro extraction (SPME), are widely used for sample preparation in analytical laboratories. SPME is a two-step process conducive to the simultaneous extraction and pre-concentration of analytes from sample matrixes. In the first step, target analytes partitions between sample matrix and fiber surface and in the second step the absorbed analytes desorbs directly into injection port for further analyses by chromatographic techniques [1,2]. SPME has also been successfully used as sampling device for variety of target compounds in environmental [3,4], pharmaceutical [5,6], biological [7,8], forensic [9], and food [10] samples.

In spite of cited advantages, the variety of commercially used fibers is limited and covers only the scale of polarity. Consequently, the selectivity of extraction process is low and determination of target analytes in trace levels in complex samples encounters a problem by chromatographic techniques coupled with common detectors. Thus, in the recent years the preparation of tailor-made fibers has been focused as one of the most important research fields in SPME [11–21].

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Molecular imprinting technology [22,23] gets increasingly interesting for the preparation of useful materials with predetermined selectivity for application in several areas of analytical chemistry [24]. Molecularly imprinted polymers (MIPs) are cross-linked synthetic polymers obtained by copolymerizing a monomer with a cross-linker in the presence of a template molecule (print molecule). The polymer, with its template being washed away, contains recognition sites that are complementary in size, shape and chemical functionality to the template molecules. The produced imprinted polymer is able to rebind selectively with the template (analyte) and its analogous structures. Interest in the molecular imprinting technique has increased considerably. This is also reflected in the number of excellent papers and reviews which have been published in recent years [25,26]. The highly selective recognition characteristics of molecular imprinted polymer are comparable to those of the natural biological species such as receptors and antibodies. However, MIPs possess several advantages over their biological counterparts including low cast, ease of preparation, and good physical and chemical stability over a wide range of experimental conditions and solvents. Many publications have dealt with use of MIPs for specific purpose, e.g. stationary phases for chromatography [27], capillary electrochromatography [28], electrochemical sensors [29], quartz crystal microbalance [30], biomimetic sensors [31], solid phase extraction [32,33], and membrane separation [34].

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. The first example of a MIP material use in SPME was reported by Mullet et al. [35]. In their study the MIP material was synthesized for use as an in-tube SPME adsorbent. An automated and on-line MIP SPME extraction method was developed for propranolol and related β-blockers determination in biological fluids. Koster et al. [36] reported the first work dealing with the use of MIP coatings on SPME fibers. The preparation of imprinted fibers was performed by silylation of silica fibers, which were subsequently immersed in the polymerization solution composed of clenbuterol as template and functional monomer, cross-linker and initiator in acetonitrile medium. Clenbuterol-imprinted fibers were then used in the selective extraction brombuterol from human urine. Monolithic SPME fiber based on MIPs, able to couple with GC and GC–MS was fabricated for the first time in our laboratory [37,38]. These fibers were used to selective extraction of diacetylmorphine and codeine from real samples followed by GC and GC/MS monitoring.

The aim of this work is the fabrication of a monolithic SPME fiber from atrazine imprinted polymers which were subsequently used for extraction of atrazine and its structural analogous for GC and GC–MS analyses.

2. Experimental

2.1. Chemicals

Methacrylic acid (MAA) and ethylene glycol dimethacrylate (EDMA), acetonitrile and 2,2′-azobis-isobutyronitrile (AIBN) were from Merck (Darmstadt, Germany); atrazine, amytrene, terbutryn, propazine, simazine, and cyanazine were from Sigma–Aldrich laborchemikalien Gmblt D-30918 Fig. 1. Isofenphos, chlorpyrifos, diazinon and profenophos with analytical grade were from Sigma–Aldrich.

Compound	R_1	R_2	X
Atrazine	Et	i-Pr	Cl
Simazine	Et	Et	Cl
Propazine	i-Pr	i-Pr	Cl
Cyanazine	Et	$C(CH_3)_2CN$	Cl
Ametryn	Et	i-Pr	$S\text{-}CH_3$
Prometryn	i-Pr	i-Pr	$S\text{-}CH_3$
Terbutryn	Et	t-Bu	$S\text{-}CH_3$
1,3,5-triazine	H	H	H

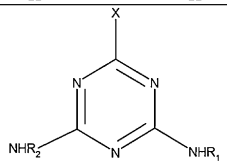

Fig. 1 – Molecules structures of triazine herbicides.

2.2. Equipments

Monitoring of the analytes was performed using a gas chromatograph (Shimadzu 2014, Kyoto, Japan), equipped with a FID and a hydrogen generator (model OPGU 1500S, Shimadzu). A chrompack capillary column of 50 m × 0.25 mm i.d. coated with a 0.12 μm film thickness (CP-Sil 8 CB, low bleed, Varian) was used.

Recognition of atrazine and other triazine herbicide was performed by Varian GC (model 3200, Palo Alto, USA) coupled to a mass spectrometer (model 2000, Varian). The chromatographic column used for GC–MS was CP-Sil5-CB, 30 m × 0.25 mm i.d. (Chrompack, Palo Alto, USA).

Pre-polymer solution was stirred in an ultrasonic bath (Grant, Cambridge, England) for 5 min, also polymerization was carried out in a water bath (Grant, England) at 65 °C. Thermal conditioning of the fibers was conducted in a carbolite furnace (Bemaford, Sheffield, England).

Extraction of analytes was performed in a 3 mL sample vials sealed with a silicone-rubber septum cap (Supelco) containing a magnetic stirring bar. Samples were agitated at 500 rpm during SPME by a magnetic stirrer (Gerhardt, Konigswinter, Germany).

2.3. Preparation of samples

The onion samples was weighted and crushed with juicer to produce a liquid including juice and scum. This liquid was spiked with two different amounts of atrazine, simazine, propazine, cyanazine, ametryn, terbutryn and prometryn as analogous with atrazine to reach a final concentration of 100 and 500 ng mL^{-1} of each compound. These spiked samples stirred in an ultrasonic bath for 10 min and centerfused. 3 mL of supernatant solution was used for SPME procedure.

The rice seeds were dried at room temperature. The polished rice was prepared by removing bran, which was also