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Development of relatively selective, chemically and mechanically robust solid-phase microextraction fibers based on methacrylic acid–trimethylolpropanetrimethacrylate co-polymers

Jingbin Zeng[a], Jinmei Chen[a], Yiru Wang[a], Wenfeng Chen[a], Xi Chen[a,b,*], Xiaoru Wang[a]

[a] *Department of Chemistry and the Key Laboratory of Analytical Sciences of the Ministry of Education, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China*
[b] *State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China*

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ABSTRACT

A versatile, relatively selective, chemically and mechanically robust solid-phase microextraction (SPME) fiber based on methacrylic acid–trimethylolpropanetrimethacrylate (MAA/TRIM) co-polymers was developed in a simple way and directly coupled with gas chromatography. Thus, using a glass capillary as a “mold”, MAA/TRIM co-polymers were immobilized on a stainless steel wire base as a novel coating for SPME. The extraction performance of the MAA/TRIM-coated fiber was evaluated in detail using four triazines as model compounds, and several typical and important species of chemical compounds including opioids, xanthic alkaloids and phenoxyacetic acid herbicides were selected as additional examples to further illustrate the extraction mechanism and applicability of the fiber. The fiber showed high extraction efficiency for highly functionalized molecules (typically containing multiple amino, hydroxy, carbonyl and carboxy groups) via a hydrogen-bonding extraction mechanism. The maximum extraction ability and selectivity of the fiber could be obtained only in non-polar (aprotic) organic solvents, which are effective for the hydrogen-bonding interaction. The inherent chemical stability of MAA/TRIM co-polymers and the mechanical strength of the stainless steel wire as the fiber support made the MAA/TRIM-coated fiber highly durable in practical use.

1. Introduction

In recent years, solid-phase microextraction (SPME), which was introduced by Arthur and Pawliszyn [1], has proved to be an effective and powerful tool for the analysis of volatile and semi-volatile organic compounds in environmental samples, when coupled with gas chromatography (GC) [2,3] or high-performance liquid chromatography (HPLC) [4]. Basically, the fiber coating is the key factor of the SPME technique because the extraction performance primarily depends on the coating characteristics. Currently, several SPME coating materials, including non-polar polydimethylsiloxane (PDMS), Carboxen/PDMS, semi-polar PDMS/divinylbenzene (DVB) and polar polyacrylate, Carbowax/DVB and Carbowax/templated resin, are commercially available [5]. Although these commercial fibers are widely favored for routine SPME analysis, several natural drawbacks such as lack of extraction selectivity, non-resistance to high temperature, swelling in organic solvents, high cost and short life have undoubtedly restricted the possible fields of SPME application. Consequently, much research effort has been devoted lately to the development of tailor-made fibers to overcome some of the drawbacks related to commercial fibers. Several fiber coating approaches, including sol–gel technology [6–8], physical deposition [9], electrochemical procedure [10–12], vapor deposition [13] and on fiber derivatization [14], have been developed. These approaches provide a wide range of laboratory-made fiber coatings with enhanced selectivity, high thermal, mechanical and chemical stability, which have doubtlessly extended SPME application to a broader analytical field. Unfortunately, limited cases have been reported in the direct application of these fibers in real samples with complex matrixes, and this makes it difficult to identify the actual selectivity of these fibers.

Recently, molecular imprinting polymers (MIPs) have been applied as useful materials for SPME [15–22], as well as in other fields of analytical chemistry, such as solid-phase extraction [23], electrochemical sensors [24] and capillary electrochromatography [25]. The application of MIPs in the preparation of coating materials provides high selectivity for SPME technology, and thus all of the MIP-coated fibers were successfully applied for the

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[*] Corresponding author at: Department of Chemistry and the Key Laboratory of Analytical Sciences of the Ministry of Education, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. Tel.: +86 592 2184530.
E-mail address: xichen@xmu.edu.cn (X. Chen).

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analysis of real samples with complex matrixes, such as vegetables, soil and urine. Generally, the first and most critical step to prepare the MIPs is the pre-organization of imprinted molecules using functional monomers, which can strongly interact with imprinted molecules via intermolecular interaction (such as hydrogen bonding, dipole–dipole or ionic interaction) [26,27]. After a co-polymerization reaction with a cross-linker, the monomers will be fixed in the polymer network in the presence of the imprinted molecules. Finally, after the removal of the imprinted molecules, the functional monomer groups at defined position in a spatial arrangement will selectively interact with the imprinted molecules. From the process of preparation of MIPs, we can find that the functional monomer groups play an important role in the selective recognition of MIPs for the imprinted molecules. Theoretically, the amount of functional monomer groups in MIPs and the corresponding non-imprinted polymers (NIPs) should be equal, since their only difference is the addition of the imprinted molecule for MIP preparation. Accordingly, NIPs are likely to show high affinity (although not highly selective) for those compounds which are always favored as imprinted molecules for preparing MIPs. Generally, highly functionalized molecules, which typically contain multiple amino, hydroxy, carbonyl or carboxy groups, are known to provide sufficiently strong interactions with functional monomers, and thus are popularly selected as imprinting molecules [28]. In this sense, NIPs are also supposed to show high affinity for these highly functionalized molecules via the interaction between analytes and functional monomer groups in the fiber coating. It is no doubt that NIPs will not be as highly selective as MIPs for one specific species of analytes, but they are supposed to be relatively selective for those highly functionalized molecules, which indicates that they are able to extract a wider range of analytes without the restriction of MIP fiber only capable to extract imprinted molecule or related compounds.

In this study, we aimed to develop a versatile, relatively selective, chemically and physically robust fiber, in a simple way and at low cost, based on methacrylate NIPs for SPME and then to directly couple it to GC. With this goal in mind, methacrylic acid (MAA)–trimethylolpropanetrimethacrylate (TRIM) co-polymers, which are typically employed for preparing MIPs and have proved to possess high thermal stability up to 260 °C [17], were used to prepare the SPME coating through a thermal radical co-polymerization procedure. As discussed above, the MAA/TRIM-coated fiber is supposed to show high extraction efficiency for the highly functionalized molecules via the interaction between analytes and functional carboxy groups in the fiber coating. To verify the hypothesis, triazine possessing multiple amino groups was selected as a typical example to evaluate in detail the extraction performance of an MAA/TRIM-coated fiber. In addition, several typical and important species of compounds including xanthic alkaloids, opioids, and phenoxyacetic acid herbicides were selected to investigate further the extraction mechanism and to serve as additional evidence concerning the applicability of this MAA/TRIM-coated fiber. So the goal of this study was not to develop a validated analytical method for the selected analytes but to develop a novel SPME fiber, and try to find the applicability in the analytical application based on its extraction mechanism study.

2. Experimental

2.1. Reagents and solutions

The triazines (ametryn, simetryn, propazine, cyanazine) used in this study were obtained from the Binnong Technology Corporation (Shandong, China). 2,4-Dichlorophenoxyacetic acid (2,4-D), 4-chlorophenoxyacetic acid (CPOAc), and phenoxyacetic acid (POAc) were purchased from Acros (Geel, Belgium). Organophosphorus pesticides (ethion and iprobenphos) were purchased from the China Standard Technology Development Corporation (Beijing, China). Theophylline, caffeine, acetylcodein, and diacetylmorphine were obtained from the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). All the standard solutions or sample extracts used for SPME extraction were prepared in *n*-hexane unless otherwise mentioned. The MAA and TRIM were purchased from Aldrich (Milwaukee, WI, USA). 2,2′-Azobis(isobutyronitrile) (AIBN) was obtained from the National Medicines Corporation (Shanghai, China) and recrystallized using methanol prior to use. The acetone and *n*-hexane used in this study were of pesticide residue grade and purchased from Tedia (Fairfield, OH, USA). Acetonitrile and methanol were of HPLC grade (Tedia), and all the other solvents were of analytical reagent grade. Stainless steel wires (O.D., 0.15 mm), and the 5 μL and 100 μL micro-injectors were purchased from the AnTing Micro-Injector factory (Shanghai, China). Glass capillaries (I.D., 0.5 mm) were obtained from the XinPeng Glassware Corporation (Shanghai, China).

2.2. Instrumentation

For data comparison, commercial manual sampling SPME devices with 65 μm PDMS/DVB fiber were obtained from Supelco (Bellefonte, PA, USA), and the ceramic/carbon-coated fiber (60 μm) were prepared based on our previous report [29]. SPME–GC experiments were carried out on a Shimadazu GC-2010 GC system equipped with a flame thermionic detection (FTD) system and a flame ionization detection (FID) system. The extracted analytes were analyzed using a 30 m × 0.25 mm I.D., 0.25 μm DB-1 column (J&W Scientific, Folsom, CA, USA). The instrumental parameters for the analysis of selected triazines, organophosphorus pesticides (OPPs) and xanthic alkaloids were as follows: injector temperature (240 °C), splitless mode (6 min); column flow, N_2 (1.89 mL min^{-1}); column temperature program: held at 100 °C for 2 min, then the temperature increased by 10 °C min^{-1} to 190 °C and held for 2 min, and finally the temperature increased by 30 °C min^{-1} to 280 °C and held for 2 min; detector (FTD), H_2 flow (1.5 mL min^{-1}), air flow (150 mL min^{-1}), temperature (300 °C). The parameters used in the analysis of selected opioids and phenoxyacetic acids were the same as the other analytes except for the detector parameters: FID, H_2 flow (40 mL min^{-1}), air flow (400 mL min^{-1}), temperature (300 °C). An LEO 1530 (LEO, Oberkochen, Germany) was used to obtain the scanning electron microscopy (SEM) images.

2.3. Preparation of MAA/TRIM-coated SPME fibers

Based on the laboratory-assembled SPME device and the position of the "hot spot" in the GC injector, the length of the stainless steel wires was kept constant at 17 cm in this study. Prior to coating, the stainless steel wire was cleaned with acetone and methanol in an ultrasonicator for 5 min, then washed using distilled water, and finally air dried. After this process, the stainless steel wire was covered with a piece of rubber at one end leaving a 1.5 cm length for coating. The MAA/TRIM polymerization solution was prepared as follows based on previous reports [17,30]: 30 μL functional monomer (MAA), 290 μL cross-linker (TRIM), 16.2 mg initiator (AIBN) and 445 μL toluene were added in a centrifuge tube and mixed ultrasonically for 3 min to ensure uniform mixing, and then the mixture was degassed with a gentle nitrogen stream for 10 min. Subsequently, the polymerization mixture was introduced into a glass capillary using a 100 μL micro-injector. The stainless steel wire with the piece of rubber on one end was placed in the middle of the glass capillary, both ends of which were then closed by pieces of rubber. After that, the filled glass capillary and the