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

Jingbin Zeng*, Jinmei Chen, Yiru Wang, Wenfeng Chen, Xi Chen†, Xiaoru Wang

Departments 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

State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China

A V I L E R


Contents lists available at ScienceDirect
Journal of Chromatography A

ARTICLE INFO

Article history:
Received 15 July 2008
Received in revised form 19 August 2008
Accepted 19 August 2008
Available online 22 August 2008

Keywords:
Extraction mechanism
Hydrogen bonding
Solid-phase microextraction
Methacrylic acid–trimethylolpropanetrimethacrylate co-polymers

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.

© 2008 Elsevier B.V. All rights reserved.

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 matrices, 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 electrophoresis [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...
analysis of real samples with complex matrices, 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, acetylcocine, 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 Shimadzu 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, N2 (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 (FID), H2 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, H2 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
stainless steel wire were placed in an oven and heated at 60 °C for 12 h. Finally, the fiber was moved from the glass mold by dipping it in a 40% hydrofluoric acid solution for 10 min to remove the glass mold. A schematic diagram of fiber preparation is given in Fig. 1. The prepared fiber was soaked in methanol for 20 min to remove any residue reactants. Before use, the MAA/TRIM-coated fiber was conditioned at 260 °C for 30 min to remove any possible contaminants. SEM images obtained (Fig. 2) show that the coating possessed a porous, rigid and homogeneous structure and its average thickness was 100 μm.

2.4. SPME

The MAA/TRIM-coated fiber was assembled in a laboratory-made SPME holder modified from a 5 μL micro-injector, the modification details of which were described in our previous report [29]. A 15 mL glass vial was used as a sample container, and 10 mL of standard solution or sample extract was placed into the sample vial with a 1 cm spin bar. All SPME extraction was performed by direct immersion of the fiber in the sample under stirring at 500 rpm for 20 min. Subsequently, the fiber was pulled out and immersed in n-hexane for 5 min to eliminate any adsorbed interfering substances if needed (only in the case of real sample analysis). Finally, the fiber was air-dried for 3 min, and introduced into the GC inlet and desorbed at 240 °C for 6 min.

2.5. Sample preparation

An aliquot of 40 mL of acetonitrile was added to 10 g of the grain samples (black rice and ormosia), and the mixture was sonicated for 30 min. After extraction, 10 mL of the supernatant solution was transferred to the sample vial and then vaporized to dryness using a gentle stream of nitrogen. 10 μL of 0.1 mg/mL acetonitrile standard solution containing each triazine was added to the sample vial and
also vaporized to dryness using a gentle stream of nitrogen. Finally, 10 mL of hexane was added to the sample vial for SPME. The blank sample solution for SPME was prepared using identical procedures, but without the addition of the triazine mixed standard solution.

3. Results and discussion

3.1. Extraction performance of the MAA/TRIM-coated fiber

3.1.1. Extraction ability

Functional carboxy groups in the MAA/TRIM-coated fiber were supposed to enable the fiber to selectively extract species containing multiple amino, hydroxy, carbonyl and carboxy groups via hydrogen bonding. In this study, four triazines containing multiple amino groups (the structures are shown in Fig. 3) were selected as model compounds to investigate the extraction performance of the novel coating. The extraction ability of the MAA/TRIM-coated fiber was initially evaluated by comparison of direct injection of 1 μL of each of the four triazines at 10 μg/mL and the MAA/TRIM SPME of the same sample. As shown in Fig. 4, obvious enhancement of the peak areas was found in the SPME chromatogram, indicating the remarkable extraction efficiency of the MAA/TRIM-coated fiber for the selected triazines. The enrichment factors and extraction yields for four triazines were in the range 61.3–96.3% and 0.61–0.96%, respectively. These low values of extraction yields are typical for SPME, because it is generally not based on an exhaustive extraction mode [15,31,32], especially when the volume of extraction phase in this study is much smaller (about 1.18 μL) than the sample volume (10 mL). Taking into account the possible adsorption of the triazines on bare stainless steel wire, we used it as the blank fiber to test for the extraction of the triazines selected. Based on the experimental results, no analytes could be detected after the extraction of 10 μg/mL triazines using three blank fibers, which demonstrated that the extraction ability of the MAA/TRIM-coated fiber was irrelevant to adsorption by blank fibers. To further investigate the extraction ability of the MAA/TRIM-coated fiber for the triazines selected, the ceramic/carbon-coated fiber previously developed by our group [29] and a commercial PDMS/DVB fiber were selected as the representatives of traditional fibers based on “like dissolves like” principle and used for comparison. The results (Fig. 5) illustrate that the extraction efficiency for selected triazines by the MAA/TRIM-coated fiber was much higher than that of the ceramic/carbon-coated fiber and PDMS/DVB fiber. The higher extraction efficiency was attributed mainly to the strong interaction between fiber coating and analytes via hydrogen bonding in an apolar organic solvent. It could be observed from Fig. 5 that the ceramic/carbon-coated fiber could hardly extract the analytes from hexane solution, since the extraction of ceramic/carbon-coated...
fiber was generally based on its hydrophobicity and lack of extraction ability in non-polar organic solvents. Although PDMS/DVB fiber proved to show good affinity towards triazines in aqueous solution [33,34], the extraction efficiencies for selected triazines in hexane were 3.3–5.8-folds lower than those of MAA/TRIM-coated fiber since the large volume of organic solvents showed better affinity towards the analytes than that of PDMS/DVB coating. It should be noted that most of the commercial fibers are not recommended for use in non-polar organic solvents, especially in the chlorinated solvents [35].

3.1.2. Selectivity

Two OPPs, ethion and iprobenphos (with structures as shown in Fig. 3), were selected as the reference compounds to investigate the selectivity of the MAA/TRIM-coated fiber in hexane solution. To make the response signals for OPPs and triazines comparable in the direct injection, the concentrations for OPPs were two magnitudes lower than that of triazines, since the responses for phosphorous compounds are generally two magnitudes higher than that for nitrogen compounds in a FTD system. As can be seen in Fig. 6, the peak area for each of the four triazines and each of the two OPPs in the direct injection was comparable. However, after extraction by the MAA/TRIM-coated fiber, peak areas of ethion (peak 6) and iprobenphos (peak 3) were much lower than those of triazines. The extraction yields were 1.01%, 0.58%, 0.62%, 0.72% for four triazines, and were 0.11% and 0.025% for two OPPs, respectively. The result indicated that the MAA/TRIM-coated fiber revealed higher selectivity to the triazines, and this is attributed mainly to the strong hydrogen-bonding interaction between amino groups in triazines and carboxy groups in the MAA/TRIM coating. It should be noted that, for the two reference compounds, the MAA/TRIM-coated fiber exhibited better extraction efficiency for iprobenphos since the P=O in iprobenphos was reactive to form hydrogen bonding [36] with the MAA/TRIM-coated fiber, and hence led to higher extraction efficiency. This result further proved that hydrogen bonding was the main interaction between the analytes and the coating in MAA/TRIM-coated fibers.

To investigate the selectivity of the MAA/TRIM-coated fiber in aqueous samples, the fiber was used to extract the same concentration level of organophosphorous and triazine mixed standard solution as mentioned above in an aqueous sample. The results (Fig. 6c) revealed that the overall extraction efficiencies for the triazines in aqueous samples were comparable to those in hexane standard solution. However, no selectivity was obtained since the extraction efficiencies for the two reference compounds, ethion and iprobenphos, were comparable to or even higher than those of the triazines. This result also indicated that the MAA/TRIM-coated fiber could also be used for the extraction of target analytes in aqueous samples primarily via “like dissolves like” interaction as the traditional SPME fibers.

3.1.3. Solvent effects

In order to further investigate the nature of interaction between target analytes and fiber coating, solvents stretching across a wide range of polarities including hexane, toluene, dichloromethane, chloroform, methanol and acetone were employed. The experiments were originally designed by preparing the triazine mixed standard solution in the above-mentioned solvents for SPME. The experimental results (Fig. 7A) indicated that the extraction efficiency decrease directly corresponding to the increase of the solvent polarity (Snyder polarity index [37]), except in the case of acetone and methanol. There is no detectable peak of analytes could be found in acetone and methanol standard solution, since the presence of a large volume of the polar solvent strongly interrupted the

Fig. 6. Comparison of chromatograms between (a) the direct injection of 1.0 μL of each of four triazines at 10 μg/mL and each of two organophosphorus pesticides at 100 ng/mL and (b) the MAA/TRIM SPME of the same samples. (c) The MAA/TRIM SPME of the aqueous samples containing the same concentration level of triazines and OPPs in (a). (Peaks: (1) simetryn; (2) propazine; (3) iprobenphos; (4) ametryn; (5) cyanazine; (6) ethion.)

Fig. 7. (A) The extraction amounts on the MAA/TRIM-coated fiber in different extraction solvents (column) and the corresponding polarity of extraction solvents (solid square); (B) the remaining extraction amounts on the MAA/TRIM-coated fiber after being eluted by different solvents for 30 s (column) and the corresponding polarity of elution solvents (solid square). (Solvents: (1) hexane; (2) toluene; (3) dichloromethane; (4) chloroform; (5) acetone; (6) methanol.)
interaction between analytes and fiber coating. Accordingly, a redesigned experiment was performed using the solvents to elute the adsorbed analytes on the fiber after extraction for a short period of time (30 s) and comparing the remaining amounts of analytes. Fig. 7B indicates that the elution efficacy increased corresponding to the increase of the solvent polarity, except in the case of methanol and acetone. Besides the polarity effect, it can be taken into account that the carbonyl group in acetone is more active than the hydroxyl in methanol to disturb the hydrogen-bonding formation between analytes (secondary amino) and the fiber coating (carboxyl). The above results illustrate that the main interaction between analytes and fiber coating can be considered as hydrogen bonding, and the maximum extraction ability and selectivity could only be achieved in non-polar (aprotic) solvents.

### 3.2. Chemical and mechanical stability of the MAA/TRIM-coated fiber

To investigate its chemical stability, the MAA/TRIM-coated fiber was immersed into distilled water, methanol, acetonitrile, hexane, dichloromethane, tetrahydrofuran, hydrochloric acid and sodium hydroxide (both 5 mol/L) for 2 h, together with a solvent free control. After the MAA/TRIM-coated fiber was immersed into all the above solvents, the extraction efficiency of the fiber for the selected triazines was compared to that of the solvent free control. Based on the results obtained, no measurable degradation of extraction ability was observed after the fiber was immersed into each of the solvents. The resistance of the prepared MAA/TRIM-coated fiber to the organic solvents, strong acid and base indicates the high chemical stability of the fiber. This remarkable chemical stability makes the MAA/TRIM-coated fiber a suitable alternative for SPME coupled to HPLC, since the desorption of analytes from the fiber in HPLC generally involves various liquid solvents.

In the previous reports on preparing a MIP-coated fiber (using MAA/TRIM co-polymers), a silylated silica fused fiber was selected as a support for the fiber coating since the Si-OH on the silica fiber surface led to bonding with the coating and thus resulted in the coating becoming firmly attached [17,18]. In this study, it is feasible and reasonable to prepare this MAA/TRIM-coated fiber using a silylated silica fused fiber as a support. As expected, the coating deposited on the silylated fused silica fibers was not found to bleed. However, during the process of extraction and injection, fiber breakage frequently occurred due to the fragility of the fiber itself. To enhance the mechanical strength of the fiber and to make the fiber more robust in practical use, stainless steel wire was applied as a fiber support. Generally, due to the lack of possible bonding between stainless steel substrate and fiber coatings, stainless steel wire was selected as a fiber coating support only in the case of using the adhesives (epoxy or similar) to attach the adsorbents or depositing the coatings electrochemically [38–40]. Although these fibers are more robust and thus have longer life-time, the thermal instability of the epoxy causes ghost peaks in chromatograms, and the coatings are prone to bleed due to the lack of bonding. Accordingly, in this study, the stainless steel wire was early considered to be unsuitable to deposit the coating, since there is no possible bonding between the stainless steel substrate and the coatings. However, SEM images (Fig. 2) revealed that the MAA/TRIM coating was firmly immobilized on the surface of the stainless steel wire due to the solidification of the polymer solution. Based on the experimental results, the fiber with the coating deposited on stainless steel wire proved to be more durable in practical use, and the majority of the experiments in this study were completed using one single MAA/TRIM-coated fiber more than 150 times without obvious decrease in extraction ability.

### 3.3. Sample analysis

To evaluate the repeatability (one single fiber), seven triplicates of analyses of blank spiked rice samples (100 ng/g) were constructed, and the relative standard deviation (RSD) was in the range 5.1–9.0%. Fiber-to-fiber reproducibility was assessed by using three fibers prepared in one batch, and the RSD were lower than 10.6% for all four triazines. This satisfactory result of fiber-to-fiber reproducibility was attributed to the homogeneous polymer solutions and the glass mold with fixed dimension used for the preparation of fiber coating.

To test its applicability for the analysis of real samples with complex matrixes, the MAA/TRIM-coated fiber was used for the analysis of triazines in samples of the grains, black rice and ormosia. Generally, extracts of real samples with complex matrixes are not allowed to be directly injected into GC or HPLC since the interfering substances caused by the matrixes can contaminate the column and cause difficulty for the quantitative determination of analytes. Accordingly, a cleanup step is always necessary for real sample analysis prior to the GC or HPLC analysis. In this study, after the solvent extraction of the analytes from the grain samples, the co-extracted interfering substances such as lipids, amylum and pigments make the extracts opaque and even turbid. When the MAA/TRIM-coated fiber was removed from the sample solution after SPME, it was visibly covered with co-extracted interfering sub-

---

Fig. 8. Chromatograms obtained for (a) the direct injection of 1 μL of ormosia or 1 μL of black rice sample extract spiked with four triazines at 100 ng/mL; (b) the MAA/TRIM SPME of the same sample solution with [a]; (c) the MAA/TRIM SPME of the 100 ng/mL triazine standard solution. (Peak marks as in Fig. 4.)
stances which would increase the difficulty for the determination of target analytes. In this study, an apolar organic solvent hexane was used to eliminate the physically adsorbed substances while not to weaken the hydrogen bonding formed between the fiber coating and target analytes. By this simple approach, a convenient and effective cleanup was obtained. As shown in Fig. 8, no analytes were detected in the 100 ng/mL spiked samples by direct injection due to the low concentration of analytes or the interfering substances caused by the matrix effect. After the extraction with the MAA/TRIM-coated fiber, all four triazine peaks appear in the chromatograms and the recoveries for selected triazines in black rice and ormosia were 79.5–102.2% and 79.8–98.7%, respectively. This result indicated that substances co-existing in the sample matrix did not hinder the binding sites of the fiber and interrupt the interaction between target analytes and the fiber coating.

3.4. Additional information concerning the applicability of the MAA/TRIM-coated fiber

To extend the application fields of the MAA/TRIM-coated fiber and to verify further the hypothesis that the MAA/TRIM-coated fiber would show high extraction efficiency for compounds containing multiple amino, hydroxy, carbonyl and carboxy groups via hydrogen bonding, several typical and important chemical compounds including xanthic alkaloids (caffeine and theophylline), opioids (diacetylmorphine and acetylcodeine) and phenoxyacetic acid herbicides (2,4-D, POAC and CPOAC) were selected (structures shown in Table 1). Comparison of the results for the compounds in Table 1:

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Enrichment factor</th>
<th>Extraction yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caffeine</td>
<td><img src="image1" alt="Structure" /></td>
<td>609</td>
<td>3.04</td>
</tr>
<tr>
<td>Theophylline</td>
<td><img src="image2" alt="Structure" /></td>
<td>1341</td>
<td>6.71</td>
</tr>
<tr>
<td>Diacetylmorphine</td>
<td><img src="image3" alt="Structure" /></td>
<td>34</td>
<td>0.34</td>
</tr>
<tr>
<td>Acetylcodeine</td>
<td><img src="image4" alt="Structure" /></td>
<td>73</td>
<td>0.73</td>
</tr>
<tr>
<td>POAC</td>
<td><img src="image5" alt="Structure" /></td>
<td>761</td>
<td>7.61</td>
</tr>
<tr>
<td>CPOAC</td>
<td><img src="image6" alt="Structure" /></td>
<td>526</td>
<td>5.26</td>
</tr>
<tr>
<td>2,4-D</td>
<td><img src="image7" alt="Structure" /></td>
<td>182</td>
<td>1.82</td>
</tr>
</tbody>
</table>

a The enrichment factor was calculated as the mass of analyte extracted over that obtained by direct injection.
b The extraction yield was calculated by dividing the mass of analyte extracted by the total mass of analyte in the sample.

Fig. 9. Chromatograms obtained for (top) selected xanthic alkaloids with (a) the direct injection of 1 μL of mixed standard solution containing theophylline and caffeine at 100 μg/mL and 10 μg/mL, respectively, and (b) the MAA/TRIM SPME of the mixed standard solutions containing theophylline and caffeine each at 2 μg/mL; (middle) opioids with (a) the direct injection of 1 μL of diacetylmorphine and acetylcodeine at 10 μg/mL, and (b) the MAA/TRIM SPME of the same sample; and (bottom) phenoxyacetic acids with (a) the direct injection of 1 μL of phenoxyacid herbicides at 100 μg/mL, and (b) the MAA/TRIM SPME of phenoxyacid herbicides at 10 μg/mL.
selected between SPME and direct injection were consistent with the hypothesis. As shown in Fig. 9, a distinct enhancement of peak areas was found in all the SPME–GC chromatograms, indicating the high extraction efficiency of the MAA/TRIM-coated fiber for the selected analytes.

As outlined in Table 1, the extraction yield for theophylline was approximately twice as high as that for caffeine, which was mainly based on the fact that theophylline allowed for the formation of stronger cyclic double hydrogen bonding (Fig. 10) [41,42]. The same phenomenon could be observed in the case of diacetyl morphine and acetylcodine. The only difference of the structure in diacet ylmorphine and acetylcodine was the alkyl and carbonyl group joining to oxygen. Consequently, a possible explanation was that the electron-donating alkyl group released electrons towards the oxygen better than did the electron-withdrawing carbonyl group, which made the alkyl oxygen more active to form hydrogen bonding and hence it gave a twice higher extraction yield. The high extraction efficiency of the MAA/TRIM-coated fiber for phenoxacycetic acids was further convincing evidence that the interaction between fiber coating and analytes was hydrogen bonding (Fig. 10). It should be emphasized that the data for phenoxacycetic acids are not recommended for use in quantitative analysis, since they are known to be easily adsorbed in the GC injector and cause problems such as tailing and irreproducible results.

4. Conclusion

In this study, we developed a versatile, relatively selective, chemically and mechanically robust MAA/TRIM-coated fiber for SPME. The proposed fiber exhibited high extraction efficiency towards highly functionalized molecules containing multiple amino, hydroxyl, carboxyl and carboxy groups via hydrogen bonding in apolar solvents. In addition, the fiber could also be used for the extraction of target analytes in aqueous samples, primarily via hydrophobic interaction. The versatility, selectivity, chemical and mechanical robustness of the proposed MAA/TRIM-coated fiber makes it an excellent alternative for the practical application of SPME. Using a glass capillary as a mold, the coating was homogeneously deposited on the fused silica fiber or stainless steel wires at a desired thickness. By this approach, several fibers could be prepared simultaneously with good fiber-to-fiber reproducibility. Since monomers with various chemical structures are able to be polymerized, different NIPs with different functionalities as SPME fibers can be specially designed for each specific analysis using the simple approach proposed, and this would potentially provide a great many novel polymeric materials for SPME coatings. From another point of view, SPME may provide a convenient and effective tool for studying the characteristics of other NIPs.

Acknowledgements

This research was financially supported by the Program for New Century Excellent Talents in Chinese Universities (NCET), the National Natural Scientific Foundation of China (Nos. 20775064, 20775002), the Science and Technology Projects of Fujian Province (2007Y0032) and NFFTBS (No. J0630429), which are gratefully acknowledged. Furthermore, we would like to extend our thanks to Professor John Hodgkiss of The University of Hong Kong for his assistance with English.

References