



Development of selective and chemically stable coating for stir bar sorptive extraction by molecularly imprinted technique

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ARTICLE INFO

Article history:

Received 11 March 2010

Received in revised form 22 April 2010

Accepted 25 April 2010

Available online 26 May 2010

Keywords:

Stir bar sorptive extraction

Molecularly imprinted

Complex sample

Triazines

ABSTRACT

A novel stir bar coated with molecularly imprinted polymer (MIP) as selective extraction phase for sorptive extraction of triazine herbicides was developed. The stir bar was prepared by chemically bonding the MIP to the glass bar to improve its stability. A homogeneous and porous structure was observed on the stir bar surface. Extraction performance shows that the MIP-coated stir bar has stronger affinity to the template molecule terbuthylazine as compared with that of the reference stir bar without addition of template. Owing to the shape and structural compatibility, the obtained stir bar also demonstrated specific selectivity to the structural related-compounds of nine triazines, and thus can be applied to simultaneous determination of these compounds from complex samples coupled with high performance liquid chromatography. Four complex samples with different matrix, including rice, apple, lettuce and soil were used to evaluate this proposed method. The limits of detection obtained are in the range of 0.04–0.12 $\mu\text{g L}^{-1}$, and the recoveries for the spiked rice, apple, lettuce and soil samples were 80.8–107.7%, 80.6–107.8%, 72.0–109.8% and 89.0–114.8% with RSD from 1.2 to 7.9%, respectively. Moreover, this MIP-coated stir bar was firm, durable and can be prepared simply and reproducibly. The developed coating method would be useful to prepare a range of selective stir bars in order to extend the applicability of stir bar sorptive extraction (SBSE) in complex sample analysis.

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1. Introduction

In the past decades, the development of miniaturization in sample preparation techniques with reduced or eliminated solvent consumption has become a dominant trend in analytical chemistry. Among these techniques, a sorptive extraction technique using a stir bar coated with polydimethylsiloxane (PDMS) was first introduced in 1999 and called stir bar sorptive extraction (SBSE) [1]. SBSE is based on the same principles as those of solid-phase microextraction (SPME). However, the amount of PDMS typically coating the stir bars was 25–125 μL , which is 50–250 times higher than that on a SPME fiber, resulting in better recovery and sample capacity [2].

Since only the PDMS is available as extraction phase on commercial stir bars, the large majority of applications use this coating. Attempts have been made to apply other coatings in recent years. The crucial issues are associated with development of coating method to obtain stable and reproducible coating on the substrate with a magnetic core. Up to now, several coating methods have been reported for preparation of stir bars apart from the commercial PDMS tube jacketed on the glass. Lambert et al. [3] have prepared a stir bar by physically coating alkyl-diol-silica (ADS)

restricted access material (RAM) on the glass by an epoxy binding agent. However, lacking proper chemical bonding of the stationary phase with the glass surface may take responsibility for the low stability. The sol-gel approach provides direct chemical bond between the stationary phase and the silica substrate, resulting in higher thermal and solvent stability [4–6]. We have synthesized polydimethylsiloxane/ β -cyclodextrin coated stir bar for extraction of estrogens and bisphenol A by the sol-gel technique [6]. However, it was found that special skill for operator was required to prevent coating crack, since the sol-gel process is susceptible to humidity and temperature. Phase inversion method was applied by Zhu et al. to coat a molecularly imprinted polymer (MIP) film on the surface of the commercial PDMS stir bar, but the cost is a relatively high [7,8]. Another approach to prepare stir bars was reported by in situ co-polymerization method to form monolithic material on the glass surface [9,10]. The obtained coating has a thick film of a few millimeters, which contributes to its high extraction capacity, but has also some adverse effect on the adsorption and desorption kinetics.

In sorptive extraction, the properties of the extraction phase determine the extraction efficiency and selectivity. An ideal material for coating a stir bar should be capable of enriching the target molecules with high concentration factors, whilst leaving other interfering substances in the sample matrix. MIPs are tailor-made materials with high selectivity for a target molecule [11]. Their

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potential as sample pretreatment material especially in the solid-phase extraction (SPE) form has been extensively investigated [12–14]. MIPs have also been employed as molecular recognition media for use in solid-phase microextraction [15–21]. However, there are few literature concerning about SBSE with MIP coatings. The key problem is how to attach the MIP to the stir bar with robust connection. Zhu et al. [7,8] have applied the phase inversion imprinting technique to prepare the MIP-coated stir bar using nylon-6 polymer solution. The stir bars coated with MIP films were capable of extracting monocrotophos from environmental soil sample and separating enantiomers. In the phase inversion imprinting system, the MIPs were cast from the polymer solutions of the template molecule rather than polymerized from monomers. However, lack of suitable polymer species with high strength nature and desired functionality restricts wide application of this technique.

In this work, a stir bar coated with terbuthylazine imprinted films was prepared by chemical bonding the MIP to the stir bar through silylation of the substrate surface and then multiple co-polymerization reaction. Its sorption characteristics and applications as a high selective extraction material of triazines in complex samples were evaluated as compared with the reference stir bar without the addition of template molecule.

2. Experimental

2.1. Instrumentation

A RET basic C magnetic stirrer was obtained from IKA (IKA, Germany) for SBSE and SPME procedure. An ultrasonicator model BG-06C (Bangjie, Guangzhou, China) was used for liquid desorption. HGC-12A nitrogen evaporator (Quandao, Shanghai, China) was used to heat the polymerized solution. An XL-30FEG scanning electron microscope (Philips, Holland) was used to investigate the coating surface. An AVATAR 330 Fourier transform infrared (FT-IR) spectrometer (Thermo Nicolet Company, USA) was used for the investigation of the coating composition.

2.2. Reagents

Cyanazine, simazine, simetryne, atrazine, ametryn, propazine, terbuthylazine, prometryn, terbutyrn standards were obtained from Bingzhou Pesticide Plant (Shandong, China). The individual stock solutions of triazines were prepared at a concentration of 200 mg L^{-1} in methanol, and the standard solutions of lower concentration were prepared by the serial dilution of the stock solutions. Methacrylic acid (MAA) and azo(bis)-isobutyronitrile (AIBN) were purchased from Damao Reagent Plant (Tianjin, China). Trimethylolpropane trimethacrylate (TRIM) were purchased from Corel Chemical Plant (Shanghai, China). 3-(Methacryloxy)propyltrimethoxysilane was obtained from Shengda Fine Chemical Industry Corporation (Beijing, China). Acetonitrile and methanol of HPLC grade were purchased from Merck (Darmstadt, Germany). Water was doubly distilled. All solutions used for HPLC were filtered through a nylon $0.45\text{ }\mu\text{m}$ filter before use. Glass capillary was obtained from West China University of Medical Sciences Instrument Plant (Chengdu, China).

2.3. Preparation of MIP-coated stir bar

A glass capillary (1 mm diameter, 15 mm length) was used as the support of MIP coating. One end of the glass capillary was closed using a propane torch. Before coating, the glass capillary was first etched in a steam bath of HF:H₂O (1:3, v/v) solution heated at $60\text{ }^{\circ}\text{C}$ to enhance its surface area. Subsequently it was dipped in 1 mol L^{-1} NaOH solution for 8 h to expose the maximum number of silanol groups on the surface, cleaned with water, and then placed

in 0.1 mol L^{-1} HCl solutions for 1 h to neutralize the excess NaOH, cleaned again and dried at $150\text{ }^{\circ}\text{C}$.

Prior to the coating procedure, the glass capillaries were silylated for 1 h by immersing them into a 25% (v/v) 3-(methacryloxy)propyltrimethoxysilane solution in acetone at room temperature. Then the glass capillaries were washed with methanol and dried with a stream of nitrogen. The pre-polymer solution for molecularly imprinted polymer was prepared by dissolving 0.5 mmol of terbuthylazine and 2.0 mmol of MAA in 5 mL of toluene. The mixture was vortexed thoroughly and incubated overnight at room temperature. After this, 0.02 mmol AIBN and 2.0 mmol of TRIM were added. Subsequently 1.5 mL of the mixture was transferred into a small glass tube and deoxygenized with a stream of nitrogen for 5 min. Subsequently, the silylated glass capillary was dipped vertically into the solution and the polymerization was allowed to react at $60\text{ }^{\circ}\text{C}$ for about 90 min. After being pulled out, a MIP coating was formed on the surface of the glass and aged at $60\text{ }^{\circ}\text{C}$ subsequently. The coating procedure was repeated for four times. After accomplishment of the coating process, a magnet was inserted into the glass capillary and the open side was then sealed with the propane torch. A dumbbell shaped stir bar was obtained by sintering the two ends of the glass capillary into globules. The unwanted coatings on the two ends were scraped using a penknife to prevent abrasion during stirring. The template molecules were removed from the coating by soaking it in 5 mL of 10% (v/v) acetic acid solution in methanol. The non-imprinted polymer (NIP) coated stir bar was prepared following the same procedure except for the addition of terbuthylazine.

2.4. SBSE procedure

In a typical assay, 5 mL of $10\text{ }\mu\text{g L}^{-1}$ of triazines dissolved in toluene was introduced into a 50 mL round-bottom glass flask. The MIP-coated stir bar was immersed and stirred at 500 rpm for 60 min. After extraction, the stir bar was removed from the sample solution, and gently dried with a lint-free tissue. Then it was placed into a $150\text{ }\mu\text{L}$ glass vial filled with $150\text{ }\mu\text{L}$ of methanol, ensuring its total immersion, and liquid desorption for 5 min was carried out at ultrasonic treatment. A portion of $20\text{ }\mu\text{L}$ solution were injected in HPLC system and analyzed. Control experiments were conducted with the NIP-coated stir bar instead of the MIP-coated stir bar.

2.5. Chromatographic separation

HPLC-UV detection was performed on a Shimadzu LC-2010 system consists of a low pressure gradient solvent pump, an auto-sampler and a UV-vis detector. The analytical column was a C₁₈ column $250\text{ mm} \times 4.6\text{ mm}$ I.D., $5\text{ }\mu\text{m}$ (Dikma) with an attached 7.5-mm C₁₈ security guard column (Phenomenex, USA). The mobile phase was acetonitrile/water (30:70, v/v) and then acetonitrile/water (68:32, v/v) within 28 min at a flow rate of 1.0 mL min^{-1} . The detection wavelength was 225 nm for triazines.

2.6. Sample applications

Rice, apple, lettuce and soil were selected for the spiked sample analysis. These samples were chopped and triturated in a blender, sifted and a portion of 5 g was mixed with 0.5 mL of $100.0\text{ }\mu\text{g L}^{-1}$ triazine standard solutions and homogenized. Then 30 mL of acetonitrile was added. Subsequently, the spiked samples were extracted by ultrasonic assisted extraction at room temperature for 10 min. This procedure was performed twice, and the extraction solutions were merged and dried. Then the analytes were re-dissolved with 5 mL of toluene and subjected to SBSE extraction.

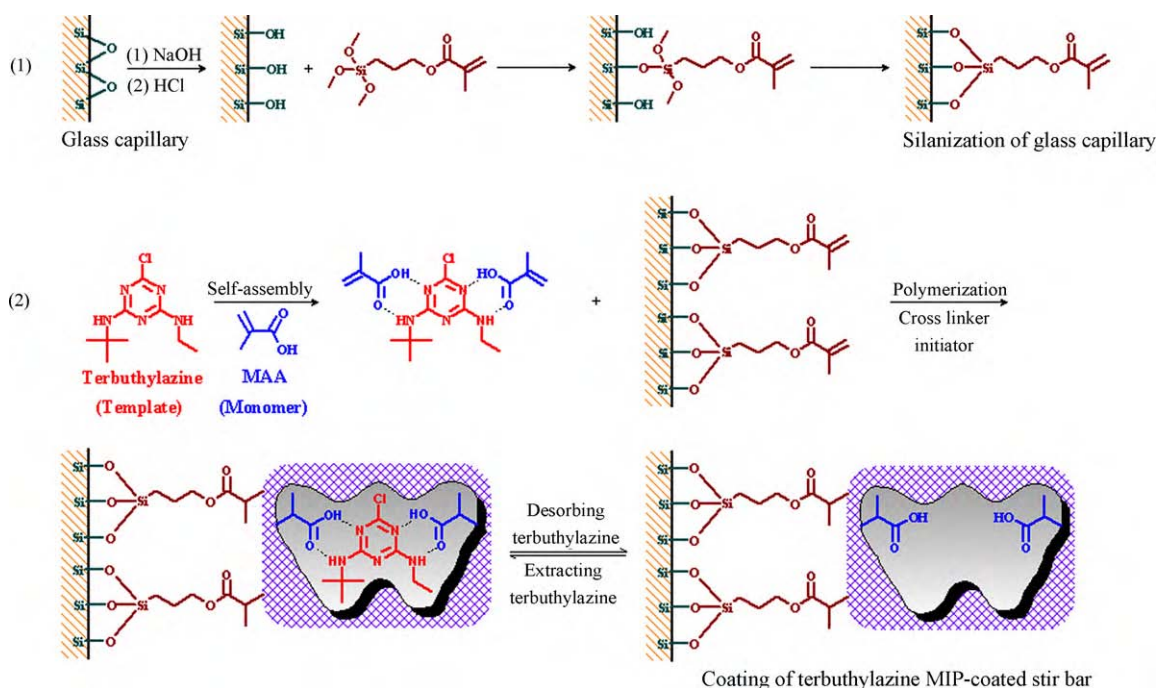


Fig. 1. Schematic diagrams of the preparation of MIP-SBSE coating using terbuthylazine as template molecule.

3. Results and discussions

3.1. Preparation of the MIP-coated stir bar

In order to immobilize organic polymers on the glass bar and thus to obtain extraction phase with low bleeding, good repeatability and long lifetime, chemical bonding of the polymer coating to the glass surface is essential. Our previous work adopted sol-gel method to strengthen the connection between the coating and substrate. However, the main obstacle in the creation of film by sol-gel method is cracking of the coating. In the current study, the surface of the glass tube was first silylated with 3-(methacryloxy)propyltrimethoxysilane, which acts as a bridge for the coating layer and the glass substrate. One end of the coupling agent could react with hydroxyl group exposed on the glass surface through open-ring bonded reaction. The double bond ends of the agent could participate in the co-polymerization of the MIP bulk, and thus form robust coatings on the glass tube. The preparation scheme is illustrated in Fig. 1.

For MIP coating preparation, the experimental parameters such as functional monomer, polymerization solvent, time and temperature were optimized. The results show that polymerization in toluene provided a homogeneous surface with the highest thickness for a single coating procedure. In order to enhance the extraction capacity, the coating procedure was repeated to obtain a film thickness of 21 μm . MAA was used as the monomer, because MIP could possess better extraction performance for triazines with this monomer [22,23]. TRIM and EGDMA, the most frequently used cross linkers in the MIP preparation, were fine tuned with serial molar ratio of monomer and cross linker from 1:4 to 2:3. The results indicated that the coating prepared with MAA and TRIM with the molar ratio of 1:1 had better uniformity.

3.2. Morphology characterization

Fig. 2 shows the SEM image of the surface structure of the MIP-coated stir bar, as well as that of the NIP-coated stir bar which was used for comparison. It was obvious that both MIP and NIP coating

had a homogeneous surface. However, the MIP coating exhibited a more porous structure than the NIP coating. This may be ascribed to the reason that partition of the template molecule in the polymerization procedure would change the structure of the polymer network.

3.3. Binding properties of the template molecule to the MIP-coated stir bar

To study the recognition characteristics of the terbuthylazine imprinted stir bar, the binding experiments were performed with various terbuthylazine concentrations in the range of 1–180 $\mu\text{g L}^{-1}$, and the results are illustrated in Fig. 3. As the extraction amounts of terbuthylazine increased with time and became flat at longer time than 60 min, the binding experiment was performed with the extraction time of 60 min. For bulk imprinted polymer, slow dynamic adsorption of the template molecule usually leads to extremely long equilibrium time, such as 10–24 h. The decreased equilibrium time for the MIP-coated stir bar was benefit from its loose and porous structure, as well as the thinner coating layer compared to conventional stir bar.

As shown in Fig. 3, the saturation behavior of the terbuthylazine binding indicated that the extraction capacity of the MIP was approximately 302 pmol (curve a). Whilst the imprinted stir bar could highly bind terbuthylazine, the stir bar coated with the NIP showed little binding of the terbuthylazine with much lower extraction capacity of 36 pmol (curve b). This capacity difference was probably caused by different extraction mechanism. For the MIP-coated stir bar, specific adsorption of terbuthylazine on the created imprinted sites contributes to the higher extraction capacity, whilst for the NIP-coated stir bar, the non-specific adsorption is dominant, but is inhibited in the non-polar solvent. The binding behavior of the terbuthylazine imprinted SPME fiber prepared in the same way was also investigated for comparison (curve c). It is obvious that the MIP-coated stir bar exhibited much higher extraction capability than that of the MIP-coated SPME fiber. The maximum extraction amounts of the stir bar were 54.5 folds of that for the SPME fiber, which ascribed to the much higher

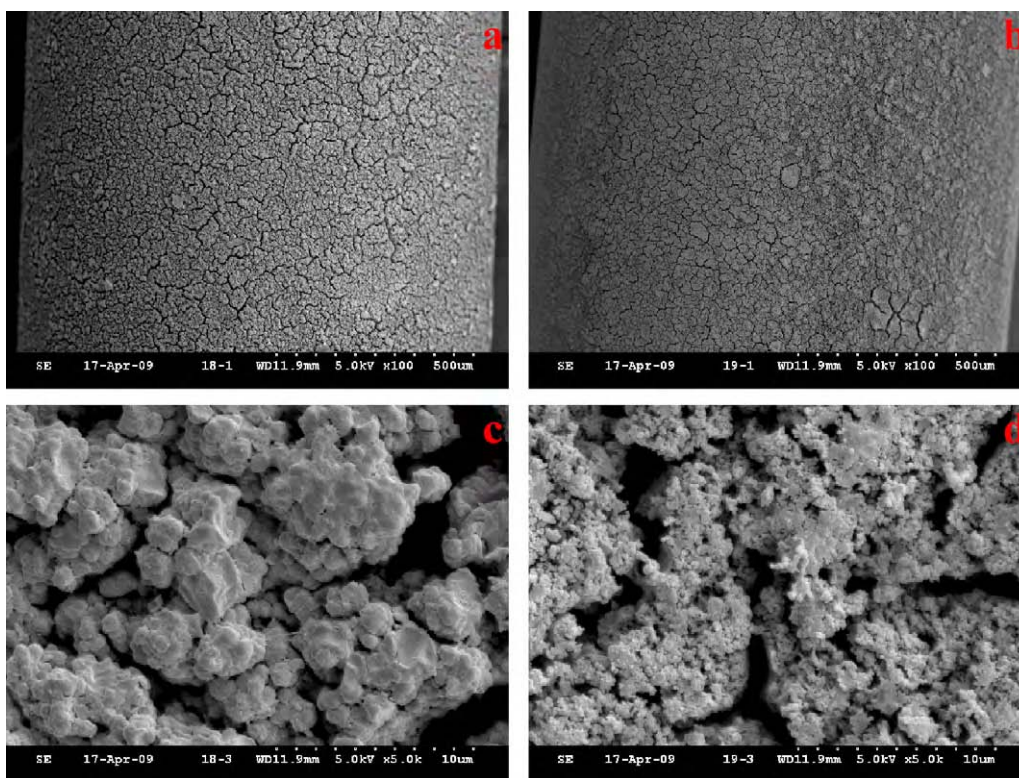


Fig. 2. Scanning electron micrographs of the surface structure of the MIP- and NIP-coated stir bar; (a) and (c) are the NIP coating for magnitude of 100 and 5000, respectively, (b) and (d) are the MIP coating for magnitude of 100 and 5000, respectively.

extraction phase volume of the stir bar than that of the SPME fiber.

The binding properties of the MIP stir bar for template molecules have a close relationship with the extraction solvent media. For estimation of the specific binding properties of the MIP-coated stir bar in different media, the stir bar was equilibrated with $10 \mu\text{g L}^{-1}$ terbuthylazine in toluene, tetrahydrofuran, ethyl acetate, chloroform, acetone, acetonitrile, methanol and dimethyl sulfoxide respectively for 60 min (Fig. 4). The results revealed that the extraction amounts of terbuthylazine in toluene were much higher than that in other organic solvents. According to some reports, the extraction performance of MIP material would be better with the polymerization solvent [24]. Toluene was used in the stir bar preparation in the current study, and thus has the best compatibility for

the specific interaction between the template molecule and the MIP cavity.

3.4. Cross-selectivity of the MIP-coated stir bar

In order to investigate the cross-selectivity of the terbuthylazine imprinted stir bar over the structural analogues, extraction for nine triazine herbicides was performed in toluene solution for 60 min. The solutions were prepared at concentration of $10 \mu\text{g L}^{-1}$ either individually or with the mixed standard solution in order to investigate the competitive adsorption among these structural analogues. Table 1 illustrated the extraction amounts of triazines on the MIP- and NIP-coated stir bar, as well as the corresponding ratio between them. The results proved that the prepared MIP-coated stir bar exhibited much higher extraction ability to triazines both in the

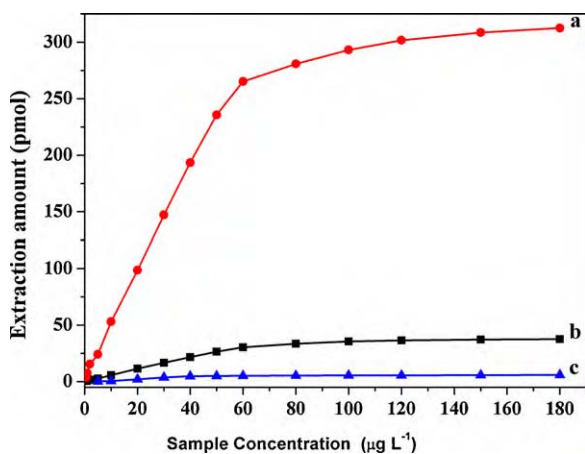


Fig. 3. The binding behavior of the MIP-coated stir bar (a), NIP-coated stir bar (b) and the MIP-coated SPME fiber (c) with various terbuthylazine concentrations.

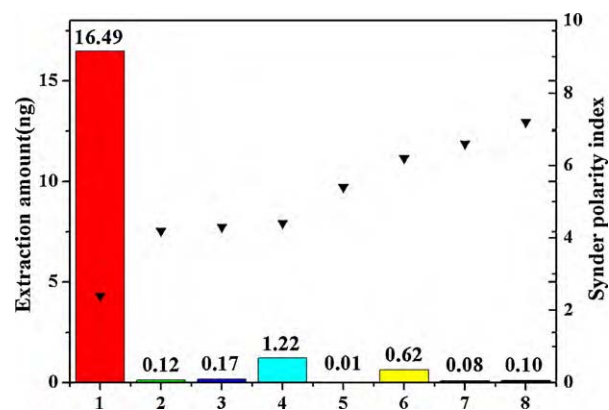


Fig. 4. The extraction amounts of 5 mL of $10 \mu\text{g L}^{-1}$ terbuthylazine in different solvents. (1) Toluene, (2) tetrahydrofuran, (3) ethyl acetate, (4) chloroform, (5) acetone, (6) acetonitrile, (7) methanol, and (8) dimethyl sulfoxide.

Table 1
The extraction amounts of triazines on the MIP- and NIP-coated stir bar and the respective imprinting efficiency either in the individual standard solution or the mixed standard solution.

Compounds	Extraction amounts on MIP stir bar (pmol)		Extraction amounts on NIP stir bar (pmol)		Ratio of extraction amounts (MIP/NIP)	
	Individual solution	Mixed solution	Individual solution	Mixed solution	Individual solution	Mixed solution
Prometryn	18.7	11.3	8.63	1.30	2.17	8.70
Terbutyrn	21.7	9.74	3.92	1.57	5.54	6.20
Ametryn	27.8	17.2	4.32	2.54	6.43	6.77
Simetryne	34.9	23.5	6.36	3.38	5.49	6.94
Propazine	55.2	31.2	5.86	2.36	9.42	13.2
Cyanazine	71.5	37.8	13.5	5.26	5.30	7.19
Terbutylazine	71.8	44.9	3.79	3.77	18.9	11.9
Atrazine	82.0	46.7	8.72	4.91	9.40	9.51
Simazine	92.0	62.3	11.5	6.87	8.03	9.06

individual and the mixed compounds solution, as compared with that of the NIP-coated stir bar. For the individual extraction mode, the highest selectivity was obtained for the template molecule terbuthylazine and the cross-selectivity of analogues was relative to their structural similarity with the template molecule. This specific selectivity is mainly caused by the imprinted cavity in the MIP network and the hydrogen bonding interaction between secondary amino groups possessed by triazines and carboxylic groups in the MIP coating. When extraction was performed in solution of mixed triazine compounds, the extraction behavior exhibited minor difference. Similar to the individual extraction mode, higher extraction amounts of chloro-triazines than methylthio-triazines were obtained with the MIP-coated stir bar, however, the extraction amounts decreased for each of the compounds. From the total extraction amounts calculated for nine triazines (285 pmol), it could be concluded that the imprinted sites were saturated under this condition. In addition, competitive adsorption of the analogues was observed in the mixed triazines solution. The degree of competitive adsorption has close relationship with the structure similarity. The property of cross-selectivity can be exploited for extraction of series of compounds rather than trapping only one analyte. This is very important in environmental analysis, since in many cases pesticides are present as mixtures of several compounds [24].

3.5. Durability investigation and batch-to-batch reproducibility

Stability investigation showed the coating was stable in conventional organic solvents, such as n-hexane, toluene, tetrahydrofuran, ethanol, methanol, ethyl acetate, chloroform and acetonitrile. No decomposition has been found during stirring. In addition, a modified extraction setting was applied in this study. The stir bar was fabricated in a dumbbell form as described in Yu's article [25], and additionally the extraction was performed in a round-bottom flask instead of the flat-bottom bottle. Consequently, friction between the stir bar and the glass vessel during stirring has been dramatically reduced. Fig. 5 shows the extraction amounts of nine triazines by the MIP-coated stir bar after 10, 20, 30, 40, 50 times extraction. The results indicate that there was no obvious difference in extraction efficiency among the different extraction times (RSD from 1.7 to 5.0%).

The batch-to-batch reproducibility of the MIP-coated stir bar was also studied and illustrated in Fig. 6. The RSD ($n=5$) of extraction amounts for nine triazines were in the range of 2.6 and 8.8%, respectively.

3.6. Application of the MIP-coated stir bar to extract triazines in complex samples

The obtained MIP-coated stir bar was coupled with HPLC and UV detection to establish a method for simultaneous determination of cyanazine, simazine, simetryne, atrazine, ametryn, propazine,

terbuthylazine, prometryn and terbutyrn in complex samples. To validate the analytical methodology, the linearity, precision and detection limits were investigated (Table 2). The MIP-SBSE-HPLC procedure showed linear ranges of 0.5–20.0 $\mu\text{g L}^{-1}$ for prometryn and terbutyrn, 0.2–20.0 $\mu\text{g L}^{-1}$ for other seven triazines. Compared with the prometryn imprinted SPME fiber in our previous study, the current method has wider linear ranges owing to the larger extraction capacity of the stir bar than SPME fiber. The limits of detection (LODs, signal-to-noise equal to 3) obtained for the stud-

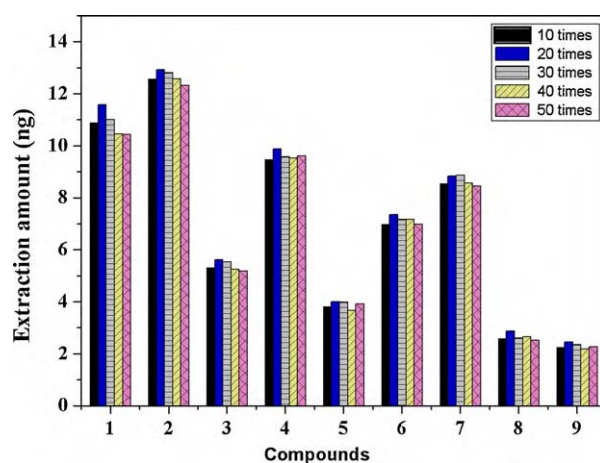


Fig. 5. Extraction amounts of triazines after the MIP-coated stir bar was used for 10, 20, 30, 40, 50 times. (1) Cyanazine, (2) simazine, (3) simetryne, (4) atrazine, (5) ametryn, (6) propazine, (7) terbuthylazine, (8) prometryn, and (9) terbutyrn.

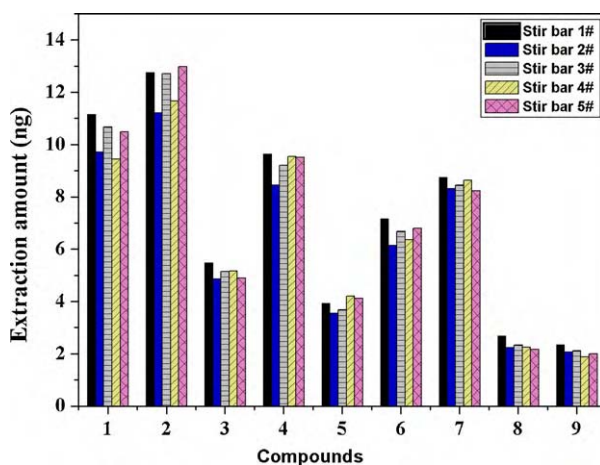


Fig. 6. Extraction amounts of triazines among five batches. (1) Cyanazine, (2) simazine, (3) simetryne, (4) atrazine, (5) ametryn, (6) propazine, (7) terbuthylazine, (8) prometryn, and (9) terbutyrn.

Table 2

The linear range, detection limit (DL) and RSD of MIP-SBSE-HPLC method for the detection of triazines.

Compounds	Linearity			DL ^a ($\mu\text{g L}^{-1}$)	RSD (%) ($n=5$)
	Equation	Range ($\mu\text{g L}^{-1}$)	r		
Cyanazine	$Y=1181.86X+44.06$	0.20–20	0.9985	0.06	4.4
Simazine	$Y=1860.33X+115.46$	0.20–20	0.9966	0.05	8.4
Simetryne	$Y=697.80X+41.67$	0.20–20	0.9970	0.08	7.5
Atrazine	$Y=1367.07X+68.05$	0.20–20	0.9972	0.04	7.6
Ametryn	$Y=514.83X+20.30$	0.20–20	0.9955	0.09	8.8
Propazine	$Y=999.73X+35.72$	0.20–20	0.9980	0.05	4.3
Terbutylazine	$Y=1283.95X+141.87$	0.20–20	0.9940	0.05	3.1
Prometryn	$Y=370.02X+22.26$	0.50–20	0.9980	0.10	8.6
Terbutyrn	$Y=250.92X+48.61$	0.50–20	0.9961	0.12	8.8

^a Detection limits were estimated on the basis of 3:1 signal-to-noise ratios.

ied triazine compounds are in the range of $0.04\text{--}0.12\ \mu\text{g L}^{-1}$. The precision of method for six replicate analyses of model solutions is also presented in Table 2 for a solution containing $10\ \mu\text{g L}^{-1}$ of each compound. The RSD varied from 3.1 to 8.8% for different analytes. Basically, The RSD of the methylthio-triazines is relatively higher than chloro-triazines, for example, RSD higher than 8.6% was found for ametryn, prometryn and terbutyrn. This could be ascribed to the lower extraction efficiency of these compounds, resulting in smaller peak and thus higher deviation. In contrast, as the template molecule, terbutylazine has the lowest RSD of 3.1% owing to its high extraction efficiency and detection response. Rice, apple, lettuce and soil spiked with $10\ \mu\text{g kg}^{-1}$ triazines were ana-

lyzed to validate the selectivity of the prepared stir bar in complex sample matrix. 5 g of samples were firstly extracted by microwave-assisted extraction technique. Fig. 7 shows chromatograms of the standard triazines solution at concentration of $50\ \mu\text{g L}^{-1}$ (curve d), the samples by direct injection analysis of microwave extract (curve a) and following the stir bar sorptive extraction with MIP coating (curve c) and NIP coating (curve b). The results revealed that the chromatogram was very complex before extracted by the stir bar, but was significantly cleaner after the MIP-SBSE cleanup protocol. Moreover, the sensitivities of nine triazines in the spiked samples were greatly enhanced with the MIP-SBSE-HPLC analysis. The NIP-coated stir bar possessed extraction capability much

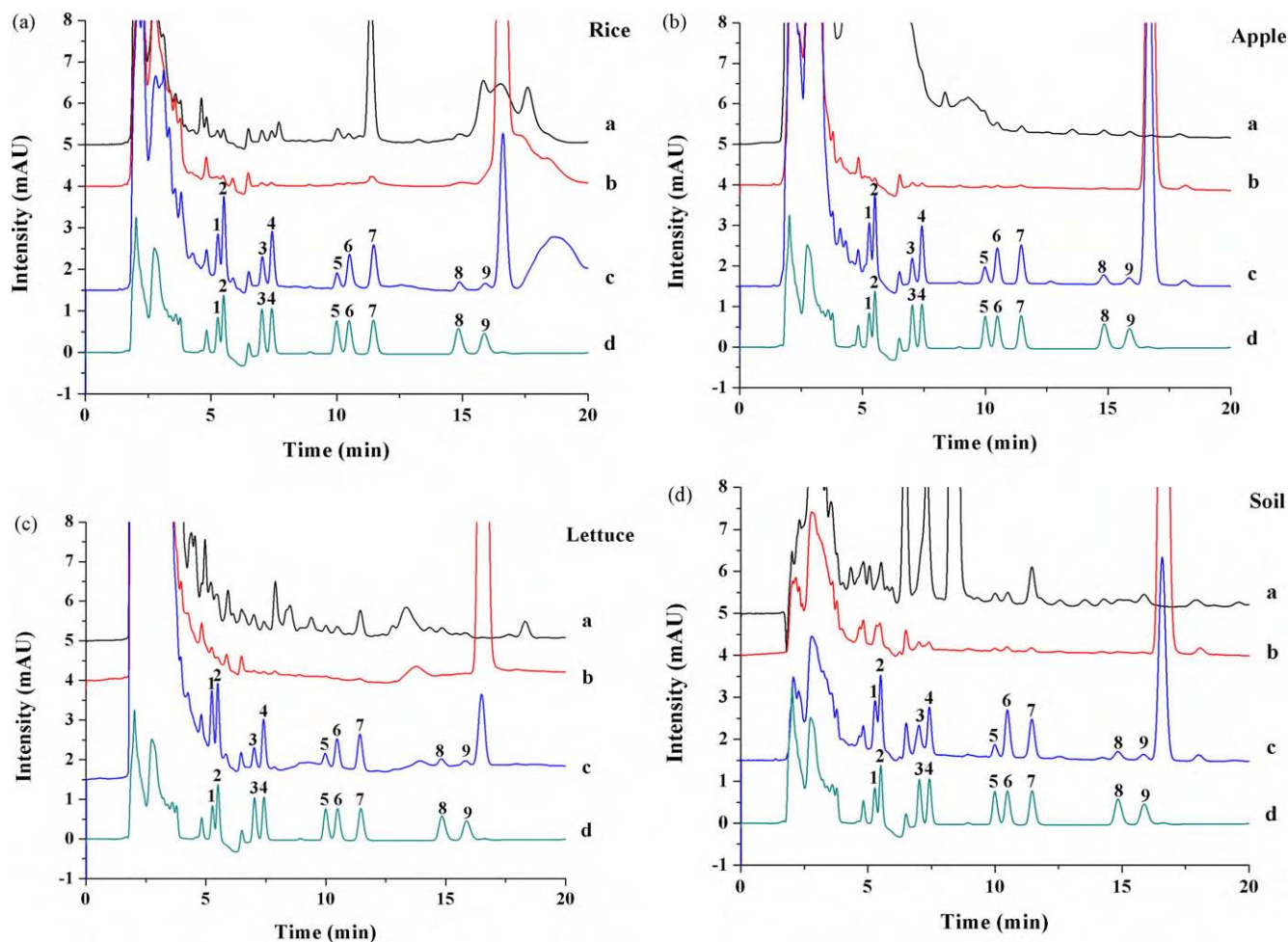


Fig. 7. Chromatograms of the spiked rice, apple, lettuce and soil samples with $10\ \mu\text{g kg}^{-1}$ triazines by direct injection of microwave extract (curve a) and following the stir bar sorptive extraction with MIP coating (curve c) and NIP coating (curve b), as well as the chromatograms of the standard triazines solution at concentration of $50\ \mu\text{g L}^{-1}$ (curve d). Peaks: (1) cyanazine, (2) simazine, (3) simetryne, (4) atrazine, (5) ametryn, (6) propazine, (7) terbutylazine, (8) prometryn, and (9) terbutyrn.

Table 3The recoveries of triazines for the spiked rice, apple, lettuce and soil samples ($n = 3$).

Compounds	Rice		Apple		Lettuce		Soil	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Cyanazine	80.8	1.2	89.7	2.4	109.8	3.2	95.4	4.6
Simazine	96.7	1.5	89.0	1.0	86.1	5.3	106.0	5.3
Simetryne	101.9	1.4	80.6	5.7	72.0	6.7	111.6	3.3
Atrazine	101.5	5.4	96.3	5.4	98.5	6.8	94.2	4.6
Ametryn	93.9	3.1	92.8	4.2	76.5	6.1	89.0	7.9
Propazine	107.4	1.5	107.8	4.3	101.5	7.5	114.8	2.1
Terbutylazine	107.7	1.4	102.0	5.2	106.5	4.4	112.7	2.3
Prometryn	100.2	4.2	106.1	5.1	106.0	2.4	103.3	2.1
Terbutyrn	105.7	2.7	90.0	5.8	85.0	6.3	104.8	7.3

lower than that of the MIP-coated stir bar, leading to lower sensitivity. Owing to the specific recognition of the MIP-coated stir bar to the structure-related triazines, the method could be applied to selective and sensitive monitoring of trace triazine herbicides in complex samples. As shown in Table 3, the recoveries for the spiked rice, apple, lettuce and soil samples were 80.8–107.7%, 80.6–107.8%, 72.0–109.8% and 89.0–114.8% with RSD from 1.2 to 7.9%, respectively.

4. Conclusions

A novel stir bar for SBSE of triazine herbicides was prepared based on MIP material. The MIP coating on the glass bar was homogeneous and porous and showed good mechanical and chemical stability. High selectivity and good enrichment capability to the structural related triazines were obtained as compared with that of the NIP coating. Both preparation and extraction performance are reproducible as several homemade MIP-coated stir bar were used throughout the study yielding similar results. The MIP-coated stir bar was successfully used for selective extraction of triazines spiked in rice, apple, lettuce and soil samples with recoveries from 80.8 to 107.7%, 80.6 to 107.8%, 72.0 to 109.8% and 89.0 to 114.8%, respectively. As MIPs can be synthesized for many analytes by selecting appropriate template molecule, this can be a valid method to prepare a range of selective stir bars in order to extend the applicability of SBSE in complex sample analysis.

Acknowledgements

The authors would like to thank the National Natural Science Foundation of China for financially supporting this research under grant numbers 20775095, 20705042 and 90817012, and by the key Program of Guangdong Provincial Natural Science Foundation of China under grant number of 9251027501000004, respectively.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.04.057.

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