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Molecularly imprinted stir bar sorptive extraction coupled with high performance liquid chromatography for trace analysis of sulfa drugs in complex samples

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ABSTRACT

A novel sulfamethazine molecularly imprinted polymer (MIP)-coated stir bar for sorptive extraction of eight sulfa drugs from biological samples was prepared. The MIP-coating was about 20 μm thickness with the relative standard deviation (RSD) of 6.7% (n = 10). It was characterized by scanning electron microscope, infrared spectrum, thermogravimetric analysis, and solvent-resistant investigation, respectively. The non-imprinted polymer (NIP)-coating was used for comparison. The adsorptive capacity and selectivity of MIP-coating were evaluated in detail. The MIP-coating showed higher adsorption capability and selectivity than the NIP-coating. The saturated adsorption amount of the MIP-coating was 4.6 times over that of the NIP-coating in toluene. Sulfamethazine could be detected after the MIP-coated stir bar sorptive extraction even at a low concentration of 0.2 μg/L. The MIP-coating also exhibited selective adsorption ability to analogues of the template. A method for the determination of eight sulfa drugs in biological samples by MIP coated stir bar sorptive extraction coupled with high performance liquid chromatography (HPLC) was developed. The extraction conditions, including extraction solvent, extraction time, desorption solvent, desorption time and stirring speed, were optimized. The linear ranges were 1.0–100 μg/L and 2.0–100 μg/L for eight sulfonamides, respectively. The detection limits were within the range of 0.20–0.72 μg/L. The method was successfully applied to simultaneous multi-residue analysis of eight sulfonamides in spiked pork, liver and chicken samples with the satisfactory recoveries.

1. Introduction

Molecularly imprinted polymer (MIP) is a kind of synthetic material to generate the binding sites with a high affinity and selective recognition to the template molecule and its analogue compounds. Due to its advantages of high selectivity, easy preparation and low cost, it has been widely utilized as molecular recognition and separation materials in different fields, such as sensors [1], macromolecules and proteins recognition [2], chiral separation [3,4], drug delivery [5,6], sample pretreatment [7–9] and speciation analysis [10].

MIP is usually synthesized by covalent or non-covalent approaches. But the latter is the most common and flexible method since the template is easy to remove without chemical reaction [11,12]. In the application of MIP, it has been immobilized on different substrates for molecular recognition, such as magnetic beads [13,14], which can be separated easily by a magnet after extraction, and solid-phase microextraction (SPME) fiber [15–18], which could be coupled directly to high performance liquid chromatography (HPLC) for on-line analysis. But a method to further accelerate the adsorption equilibrium was necessary. Magnetic stirring is an efficient method to accelerate the adsorption equilibrium. But an additional stirrer may result in competitive adsorption. This problem can be solved by immobilizing the coating on a magneton. It was firstly proposed by Baltussen et al. to use a polydimethylsiloxane (PDMS) sorbent as the coating [19]. Some novel stir bars, such as "dumbbell-shaped" stir bar [20], rotating-disk [21] and stir rod [22] were developed. A MIP-coating coated on a commercial PDMS was also proposed for selective adsorption of monocrotophos [23]. To avoid the MIP-coating loss during stirring, improved extraction apparatus was also reported [24–26].

Sulfonamides, which belong to a group of antibacterial drugs, have been gained more and more concerns for the residues in food products and their potential carcinogenicity [27–29]. In some previous reports, molecularly imprinted polymers had been used as solid-phase extraction (SPE) for the selectively extraction of sulfonamides in various matrixes, such as milk [30,31], pork and chicken [32], pond water and fishes [33].

In this paper, a novel sulfamethazine molecularly imprinted polymer (MIP)-coated stir bar was prepared for the selective

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extraction of sulfonamides. The relationship between thickness and adsorption amounts was studied and the suitable thickness was selected. The MIP-coating was characterized and the extraction performance was investigated. The extraction conditions were optimized and a method for determination sulfonamides by MIP-coated stir bar sorptive extraction coupled with HPLC was developed. Spiked sample analysis was performed for the evaluation of MIP-coated stir bar sorptive extraction.

2. Experimental

2.1. Chemicals

Sulfamethazine, sulfachloropyridazine, sulfamethizole, sulfathiazole, sulfameter and sulfamethoxazole were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Sulfamerazine and sulfadiazine were purchased from Alfa Aesar (Lancaster, UK). Triazolone was obtained from Factory of Limin (Yancheng, China). Pyridine and N,N-dimethylaniline were obtained from Guanghua Chemical Plant (Shantou, China). Acetonitrile (HPLC grade) was obtained from LAB-SCAN (Bangkok, Thailand). Other chemicals were analytical pure. Glass capillary (1 mm diameter, 15 mm length) was purchased from West China University of Medical Sciences Instrument Plant. Water used for HPLC was doubly distilled and filtered through a 0.45 μm nylon filter.

2.2. Stir bar preparation

MIP-coated stir bar was prepared based on the method of our previous work [24,25]. The substrate should be silanized before polymerization. Subsequently, 185.0 mg sulfamethazine and 0.22 mL methacrylic acid (MAA) were dissolved in 10 mL methanol. The solution was mixed thoroughly and kept for 12 h at room temperature. Then 1.26 mL ethylene glycol dimethacrylate (EGDMA) and 75.0 mg azoisobutyronitrile (AIBN) were added. The mixture solution was degassed in an ultrasonic bath for 5 min. Then 1.5 mL solution was transferred into a test tube. Then a silylated glass capillary was inserted into the test tube and the polymerization was performed at 60 °C. The capillary was pulled out 2 h later. A suitable thickness can be got by repeating the procedure. A NIP-coated stir bar was prepared following the same procedures but without sulfamethazine in the synthesis. New coated stir bars were eluted by methanol–acetic acid (9:1, v/v) to remove the template until it could not be monitored by HPLC.

2.3. Coating characterization

The scanning electron micrography was obtained with an S-4300 scanning electron microscope (HITACHI, Japan). An AVATAR 330 Fourier transform infrared (FT-IR) spectrometer (Thermo Nicolet, USA) was used for the coating composition investigation. A thermal gravity (TG) analyzer (Netzsch-209, Bavaria, Germany) was used to evaluate the thermal stability of coatings. The solvent-resistant ability was also examined by immersing the MIP-coating in different polar solvents.

2.4. Stir bar sorptive extraction procedure

Extraction experiment was performed in a round bottom flask. The stirring speed was 500 rpm at room temperature. The extraction solution was 5 mL. After extraction, the stir bar was taken out and inserted in a 200 μL glass vial, desorbed with 150 μL methanol by ultrasonic bath for 10 min. Then 20 μL desorption liquid was injected for HPLC analysis.

2.5. Chromatographic conditions

Sulfonamides were determined by a LC-20AB (Shimadzu, Japan) with a UV detector at 270 nm and a C_{18} column (250 mm × 4.6 mm i.d., 5 μm packing, Dikma). The mobile phase was acetonitrile/1% (v/v) acetic acid (2:8, v/v) at the flow rate of 1.0 mL/min. The mixture of sulfonamides was separated by gradient elution at the flow rate of 1.2 mL/min. Acetonitrile phase was increased from 10 to 23% during 5 min, and held for 20 min.

2.6. Sample preparation

Pork, liver and chicken were selected for spiking sample analysis. 5 g of thinly sliced tissue of each sample was mixed with sulfonamides mixed standard solution. It was mixed thoroughly and kept for 0.5 h at room temperature. The spiking concentrations for each sulfonamide were set with three levels of 5.0, 10 and 25 μg/kg. The spiked sample was extracted by 10 mL dichloromethane in an ultrasonic bath for 10 min. The operation was repeated for another two times and the extraction solution was dried with the reduced pressure distillation. Then it was dissolved with 5 mL toluene for MIP-coated stir bar sorptive extraction. The NIP-coated stir bar sorptive extraction was used for comparison. The extracted solutions after reduced pressure distillation were also dissolved in 2 mL methanol by direct injection for comparison.

3. Results and discussion

3.1. Preparation of MIP-coated stir bar

The molecularly imprinted polymer was synthesized by co-polymerization. A suitable thickness of 20.1 μm with the relative standard deviations (RSDs) of 6.7% (n = 10) was obtained by reproducible method. Then a 1.7 cm magnetic core was inserted in a 2.3 cm glass capillary, which was coated with 2.0 cm coating. It was sealed by flame to generate a stir bar. The precision of stir bars was investigated to extract 20 μg/L sulfamethazine standard solution. The RSD was 3.3% (n = 4) in batch and 12.0% (n = 4) for inter-batch, respectively. The MIP-coating was eluted with methanol to remove absorbents. Both the MIP- and NIP-coatings could be used at least 40 times. It could be kept at least 6 months in a dryer.

3.2. Coating characterization

The morphological structure of sulfamethazine MIP-coating was investigated with the scanning electron micrographics. Fig. 1 shows the surface structure and pore structure of MIP- and NIP-coatings under the magnification of 2500 and 10,000. It was obvious that the MIP-coating surface was homogeneous and porous (Fig. 1(a) and (c)), whereas the NIP-coating appeared to consist of larger cluster units and less pores (Fig. 1(b) and (d)). The porous structure of MIP was beneficial to adsorb analytes.

The infrared spectra indicated that the NIP-coating (Fig. S1(a)) and MIP-coating (Fig. S1(b)) almost had the same absorption peaks. Fig. S1(b) and (c) shows the infrared spectra of MIP-coating after and before eluting template. There were no obvious differences except the absorption peak at 1597 cm^{-1}, which could be found in the infrared spectra of template (Fig. S1(d)) and corresponded to C=C stretching vibration in the benzene ring of sulfamethazine molecular. The results indicated that both MIP- and NIP-coatings had the same chemical constitution, and the template molecule only interacted with the functional monomer by hydrogen bond but did not take part in the polymerization.

The thermal stabilities of MIP- and NIP-coatings were investigated with the thermogravimetric analysis. The results indicated

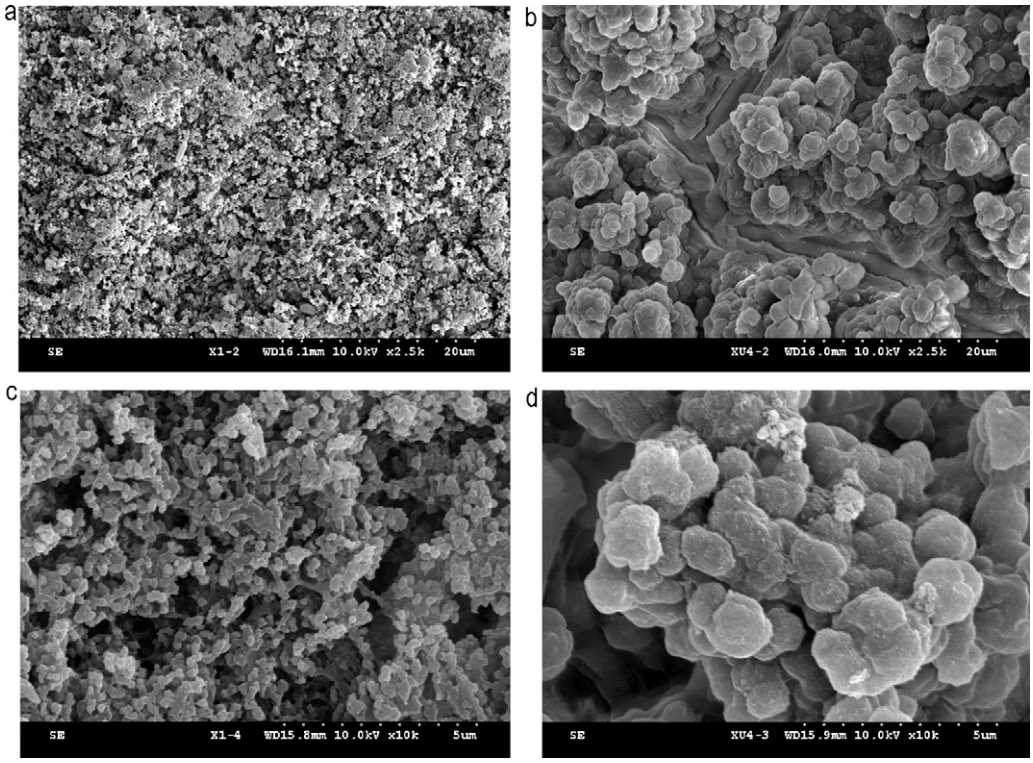


Fig. 1. Scanning electron micrographs of sulfamethazine MIP- and NIP-coatings. (a) 2500× for MIP-coating, (b) 2500× for NIP-coating, (c) 10,000× for MIP-coating, and (d) 10,000× for NIP-coating.

that the weight loss curve and corresponding 1st derivatives of MIP-coating were similar with that of NIP-coating (Fig. S2). The obvious mass loss occurred at about 220 °C for both coatings, and the fastest mass loss for MIP- and NIP-coatings occurred at 423.4 and 414.0 °C, respectively.

The MIP-coating showed a broad solvent-resistant ability. Methanol, acetonitrile, dimethylsulfoxide, acetone, chloroform, benzene, toluene, and acetic acid in methanol (9:1, v/v) were used for solvent-resistant study. After immersing for 30 min in each solvent, there was no cracking on the MIP-coating surface. Therefore, it was suitable for adsorption and desorption in the above solvents.

3.3. Extraction performance investigation

3.3.1. Extraction capability of MIP-coated stir bar

The extraction amounts of MIP-coated stir bar were investigated with sulfamethazine standard solutions. The NIP-coated stir bar was used for comparison. The extraction time and desorption time were 60 and 10 min, respectively. As Fig. 2 shows, the adsorption amount of MIP-coating was much higher than that of NIP-coating. The saturated adsorption amounts were 149.1 and 32.2 ng for the MIP- and NIP-coatings, respectively. It was 4.6 times of the MIP-coating over the NIP-coating. The MIP-coating exhibited higher capacity to the template molecule than the NIP-coating based on specific adsorption, which was due to the imprinting effect of sulfamethazine template.

In order to further investigate the recognition ability of MIP- and NIP-coatings to the template, 0.2 μg/L sulfamethazine was also used for adsorption test for both coatings. Fig. S3 indicates that the low concentration of 0.2 μg/L sulfamethazine could be detected by the MIP-coated stir bar sorptive extraction following with HPLC analysis. It was much lower than the other reported sulfamethazine MIP materials [31,33]. It was a sensitive method for sulfamethazine analysis by coupling the MIP-coated stir bar sorptive extraction with HPLC.

3.3.2. Selectivity of MIP-coated stir bar

Eight sulfonamides, including sulfamerazine, sulfamether, sulfamethazine, sulfadiazine, sulfachloropyridazine, sulfamethoxazole, sulfamethizole and sulfathiazole, were applied for selectivity studies. Three reference compounds, pyridine, N,N-dimethylaniline and triazolone, were used for comparison. To avoid the competitive adsorption, all the analytes were prepared individually at the concentration of 20 μg/L in toluene. The results are shown in Table 1. Three reference compounds could not be adsorbed by both coatings since the molecular structure and character were much different from the template. The selected sulfa drugs, which had similar molecular structure and character to the

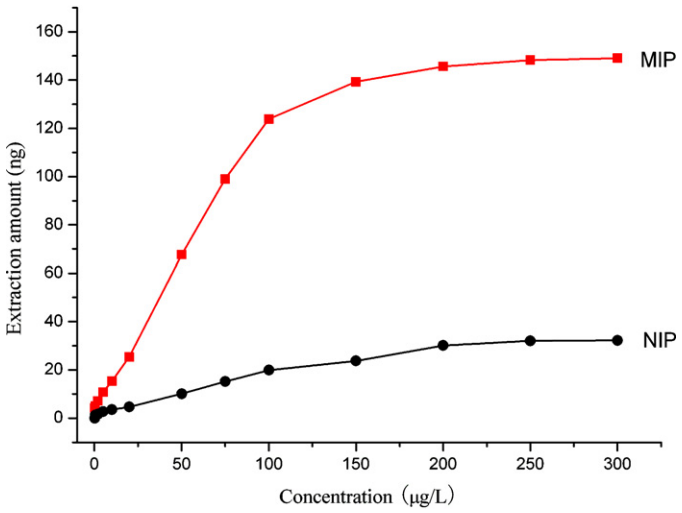
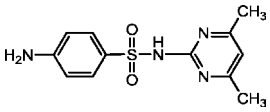
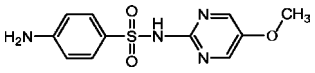
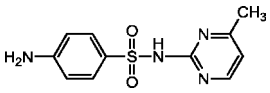
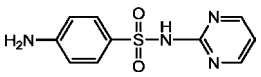
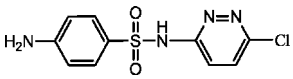
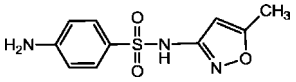
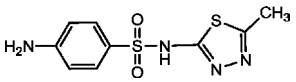
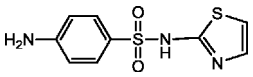
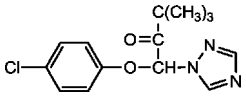
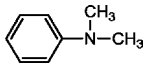


Fig. 2. Extraction amounts of MIP- and NIP-coatings to sulfamethazine standard solution of 0.2–300 μg/L.

Table 1
Extraction amounts of eight sulfonamides and three reference compounds with MIP- and NIP-coated stir bar.

Compounds	Structure	Q^{MIP} (pmol)	Q^{NIP} (pmol)	Q^{MIP}/Q^{NIP}
Sulfamethazine		91.3	16.9	5.4
Sulfamether		76.3	19.3	4.0
Sulfamerazine		76.8	19.7	3.9
Sulfadiazine		119.1	32.4	3.7
Sulfachloropyridazine		153.5	37.9	4.1
Sulfamethoxazole		170.2	47.8	3.6
Sulfamethizole		127.6	81.4	1.6
Sulfathiazole		134.4	110.1	1.2
Triazolone		0	0	–
N,N-Dimethylaniline		0	0	–
Pyridine		0	0	–

Q^{MIP}: extraction amount for MIP-coated stir bar, Q^{NIP}: extraction amount for NIP-coated stir bar.

template, exhibited higher affinity to the MIP-coating than to the NIP-coating.

It could be found from Table 1 that the MIP-coating had the best selectivity to the template. The quotients of MIP adsorption amount to corresponding NIP adsorption amount for sulfamerazine, sulfamether, sulfamethazine, sulfadiazine, sulfachloropyridazine, sulfamethoxazole, sulfamethizole and sulfathiazole were 3.9, 4.0, 5.4, 3.7, 4.1, 3.6, 1.6 and 1.2, respectively. Though the MIP-coating had higher adsorption amounts to sulfamethoxazole, sulfamethizole and sulfathiazole than that to the template, the NIP-coating also had high adsorption amounts to sulfamethoxazole, sulfamethizole and sulfathiazole. It indicated that the adsorption of MIP-coating to sulfamethoxazole, sulfamethizole and sulfathiazole was affected by the non-specific adsorption. The reference also revealed that the sulfamethoxazole MIP material almost had the same adsorptive capacity to the NIP material [34]. Therefore, the MIP-coating in this study had less non-specific adsorption and achieved excellently imprinted effect to the template.

Table 2
The linear range, detection limit (DL) and RSD of MIP-SBSE coupled with HPLC for the detection of 8 sulfonamides.

Compound	Linearity			DL[a] (μg/L)	RSD[b] (%) ($n = 5$)
	Range (μg/L)	Equation	r		
Sulfadiazine	1.0–100	$Y = -158 + 534X$	0.9995	0.30	5.2
Sulfathiazole	2.0–100	$Y = 115 + 638X$	0.9998	0.57	4.9
Sulfamerazine	1.0–100	$Y = -5.47 + 499X$	0.9990	0.41	5.5
Sulfamethazine	1.0–100	$Y = -0.477 + 379X$	0.9993	0.20	3.7
Sulfamethizole	2.0–100	$Y = 260 + 526X$	0.9993	0.61	6.7
Sulfamether	1.0–100	$Y = -157 + 421X$	0.9992	0.37	5.8
Sulfachloropyridazine	2.0–100	$Y = 193 + 483X$	0.9998	0.72	5.0
Sulfamethoxazole	2.0–100	$Y = -37.3 + 417X$	0.9998	0.66	6.0

[a] Detection limits were estimated on the basis of 3:1 signal to noise ratios.
[b] RSD was monitored with 10.0 μg/L sulfonamides mixed solution.

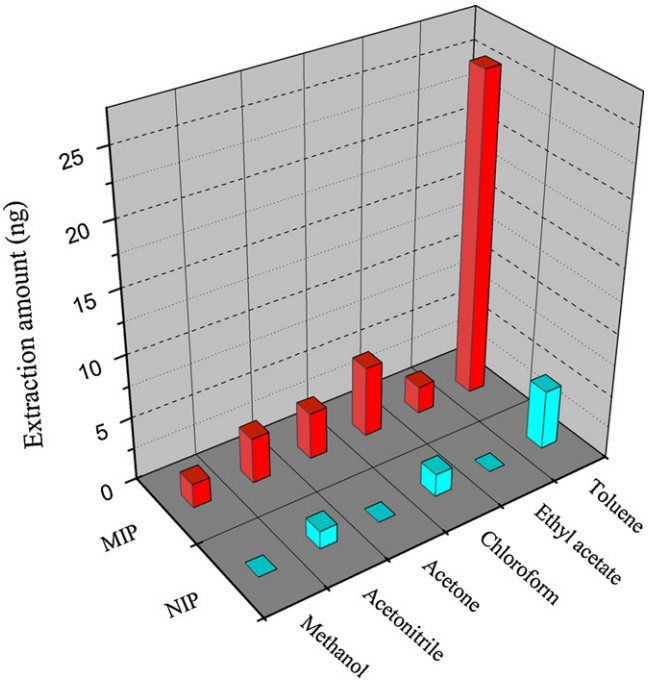


Fig. 3. Extraction amounts of MIP- and NIP-coatings in different extraction solvents: methanol, acetonitrile, acetone, chloroform, ethyl acetate, and toluene.

On the other hand, the selectivity of MIP-coating correlated with the shape and size of the cavity in addition to the strength of interaction between the target molecule and binding sites [35]. The quotients of MIP adsorption amount to corresponding NIP adsorption amount also illuminated this point. The analogues of sulfadiazine, sulfamerazine and sulfamether had much similar molecular shape and size to template, so the better molecular recognition results were obtained. But the analogues of sulfamethoxazole, sulfamethizole and sulfathiazole had some difference in the molecular structure and functional groups. Hence the imprinted effect was not significant. The three reference compounds had less similarity to the template and it could not be extracted by both coatings.

3.4. Optimization and application of MIP-coated stir bar sorptive extraction

3.4.1. Optimization of extraction conditions

A series of solvents, including methanol, acetonitrile, acetone, chloroform, ethylacetate and toluene, were selected to investigate the effect of solvent on the extraction amount (Fig. 3). The concentration of sulfamethazine in each solvent was 20 μg/L. It could be found that the MIP-coating had better adsorption amounts than that of the NIP-coating in each solvent. The highest adsorption amounts could be obtained in the solvent of toluene.

The effect of desorption solvent on the MIP-coated stir bar sorptive extraction for 20 μg/L sulfamethazine in toluene was also investigated. Methanol, acetonitrile, methanol–acetic acid (9:1, v/v) and acetonitrile–acetic acid (9:1, v/v) were selected for study. The desorbed amounts were 25.4, 7.3, 20.5 and 15.5 ng, respectively. So methanol was chosen as the best desorption solvent.

The extraction time and desorption time were optimized. The extraction time was varied from 5 min to 150 min. Results indicated that the extraction equilibrium reached at 60 min (Fig. S4). It was much sooner than the monolithic material stir bar sorptive extraction equilibrium time of 150 min [36]. Desorption time was also studied from 1 min to 20 min. The results indicated that the desorption equilibrium reached at 10 min (Fig. S5). So 60 min

Table 3
Recoveries of sulfonamides for spiked pork, liver and chicken samples ($n = 5$).

Compound	Pork						Liver						Chicken					
	5.0 μg/kg		10 μg/kg		25 μg/kg		5.0 μg/kg		10 μg/kg		25 μg/kg		5.0 μg/kg		10 μg/kg		25 μg/kg	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Sulfadiazine	81.9	5.9	82.0	5.2	89.9	4.2	89.5	9.4	93.6	4.9	96.7	4.8	85.5	10.6	91.4	6.6	102.2	6.3
Sulfathiazole	62.8	9.3	70.0	8.4	73.1	5.6	60.3	11.8	55.6	7.8	65.2	6.9	69.9	9.3	66.6	4.3	70.4	4.8
Sulfamerazine	82.8	10.7	77.5	8.7	84.3	4.0	93.8	5.8	99.7	4.1	100.8	3.3	94.9	8.0	101.9	3.7	101.4	3.2
Sulfamethazine	97.1	8.0	105.8	3.5	110.9	3.3	104.6	6.2	108.4	4.7	106.3	3.2	81.2	4.9	85.1	4.7	81.8	3.9
Sulfamethizole	77.8	8.4	73.8	7.7	83.0	4.4	69.5	7.0	57.0	6.8	76.3	6.0	88.6	7.2	78.5	3.9	79.6	3.8
Sulfamether	82.3	10.2	83.6	5.2	98.1	5.5	94.1	7.5	102.1	5.5	103.5	4.7	69.6	6.1	85.8	6.2	89.5	6.3
Sulfachloropyridazine	78.7	9.4	90.5	6.0	93.4	6.9	67.1	9.6	87.1	4.8	90.5	4.0	83.5	4.2	86.7	4.2	88.0	4.0
Sulfamethoxazole	75.6	8.3	82.7	3.5	91.3	3.5	72.7	8.0	93.4	5.0	94.4	4.6	86.7	6.1	87.8	4.8	90.0	4.5

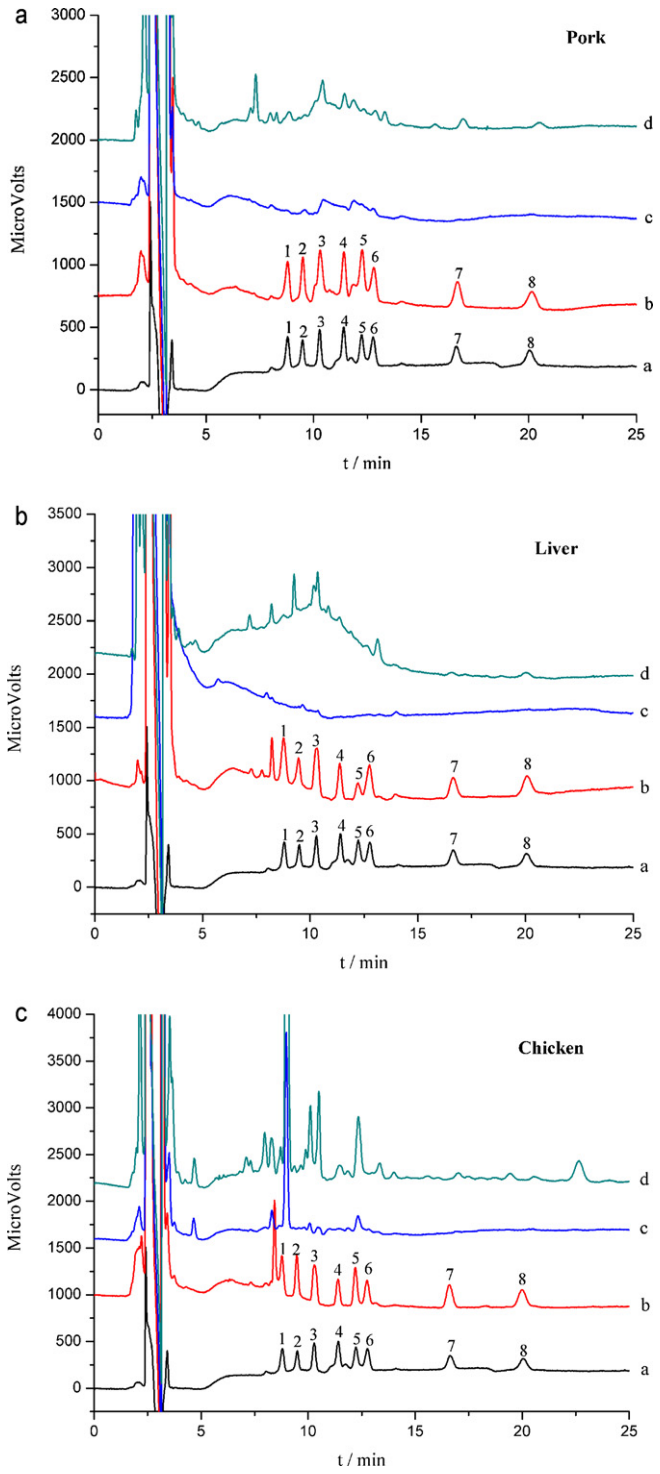


Fig. 4. HPLC chromatograms of spiked pork, liver and chicken samples with eight sulfonamides. (a) 50 μg/L sulfonamides mixed standard solution. (b) MIP-coated stir bar sorptive extraction of 10 μg/kg spiked sample. (c) NIP-coated stir bar sorptive extraction of 10 μg/kg spiked sample. (d) Direct injection of the extract solution of 10 μg/kg spiked sample. (1) Sulfadiazine, (2) sulfathiazole, (3) sulfamerazine, (4) sulfamethazine, (5) sulfamethizole, (6) sulfamether, (7) sulfachloropyridazine, (8) sulfamethoxazole.

and 10 min were adopted for extraction and desorption procedures.

Stirring speed was also studied. The increasing of stirring speed could enhance the extraction amounts. But when the stirring speed was too fast, the stir bar could not thoroughly immerse in 5 mL extraction solution. On the other hand, much higher speed may lead to cracking of the glass capillary. So, 500 rpm was adopted in the following research.

3.4.2. Linearity, limit of detection and precision

A method for the analysis of eight sulfonamides by sulfamethazine MIP-coated stir bar sorptive extraction coupled with HPLC was developed (Table 2). The linear ranges were 1.0–100 μg/L and 2.0–100 μg/L for eight sulfonamides, respectively. The detection limits were within the range of 0.20–0.72 μg/L. The method precision was monitored with 20 μg/L mixed standard solution and the RSDs of extraction amounts of eight sulfonamides were within 3.7–6.7%.

3.4.3. Sample analysis

To validate the established method in real samples with complex matrix, pork, liver and chicken were selected for the spiking analysis at three levels of 5, 10 and 25 μg/kg with eight sulfonamides of sulfamerazine, sulfamether, sulfamethazine, sulfadiazine, sulfachloropyridazine, sulfamethoxazole, sulfamethizole and sulfathiazole. Solvent extraction and NIP-coated stir bar sorptive extraction were used for comparison. The spiked sample analysis of 10 μg/kg is shown in Fig. 4. Sulfonamides could not be quantitatively analyzed in curve c and d. But in curve b, the eight sulfonamides could be accurately analyzed after MIP-coated stir bar sorptive extraction. The MIP-coated stir bar could eliminate the matrix interferences to extract the template and its analogues. The recoveries for eight sulfonamides in pork, liver and chicken samples were 62.8–110.9%, 55.6–108.4%, and 66.6–102.2%, respectively, as shown in Table 3. The results indicated that this method could be applied to extract trace sulfonamides in complex biological samples.

4. Conclusions

In this work, a novel sulfamethazine molecularly imprinted polymer (MIP)-coated stir bar was prepared for the selective extraction of eight sulfonamides. Rapid extraction equilibrium could be established by the stirring strategy with a simple and easy method. The saturated adsorption amount of the MIP-coating was 4.6 times over that of the NIP-coating. The MIP-coating could selective extract sulfamethazine for HPLC analysis even at the low concentration of 0.2 μg/L. It was much lower than the strict maximum residue level (MRL) in milk of 10 μg/L in USA. The MIP-coating also exhibited an excellent selectivity to analogues of the template. A method for the determination of eight sulfonamides by MIP-coated stir bar sorptive extraction coupled with HPLC was developed. It was successfully applied to simultaneous multi-residue analysis of eight sulfonamides in spiked pork, liver and chicken samples with satisfactory recoveries. The results indicated that the sulfamethazine MIP-coated stir bar sorptive extraction could be used for selective enrichment of trace sulfonamides in complex samples.

The MIP-coated stir bar sorptive extraction has the advantages of easy to prepare, with high extraction capability and good selectivity in complex matrix. But the reported MIP coatings are still very limited. Novel MIP coatings for stir bar sorptive extraction are expected, especially the MIP coatings suitable for extraction in water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.03.041.

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