

Extraction and preconcentration of sulfonamides in honey samples by cetyltrimethylammonium bromide coated silica gel and their determination by HPLC

Setiltrimetilamonyum bromür kaplı silika jel kullanılarak bal örneklerindeki sülfonamitlerin özütlenmesi, önderiştirilmesi ve HPLC ile tayini

Research Article

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ABSTRACT

A simple, rapid, sensitive, and inexpensive solid phase extraction method using cetyltrimethylammonium bromide-silica gel for preconcentration of sulfadiazine, sulfamethazine, sulfamerazine and sulphamethoxazole antibiotics prior to the determination by high performance liquid chromatography was developed. The effects of parameters such as type of surfactant, pH, amount of surfactant, flow rate, type and volume of eluting agent were examined. The detection limits of sulfonamides were in the range of 3-13 $\mu\text{g L}^{-1}$. The calibration curves were linear in the range of 0.010-2.0 $\mu\text{g/mL}$. The proposed method was successfully applied to determine sulfonamides in different honey samples.

Key Words

Sulfonamides, surfactant, solid phase extraction, honey

ÖZET

Sunulan çalışmada, antibiyotiklerin yüksek performans sıvı kromatografisi tayininden önce setiltrimetilamonyum bromür-silika jel kullanılarak sülfadiazin, sulfametazin, sülfametazin ve sülfometoksazol antibiyotiklerinin ön deriştirilmesi için basit, hızlı, hassas ve ucuz katı faz özütleme yöntemi geliştirildi. Sürfaktan türü, pH, sürfaktan miktarı, akış hızı, elüsyon maddesinin tipi ve hacmi gibi parametrelerin etkisi incelendi. Sülfonamitlerin tayin limiti 3-13 $\mu\text{g L}^{-1}$ aralığındadır. Kalibrasyon eğrileri 0.010-2.0 $\mu\text{g/mL}$ aralığında doğrusaldır. Önerilen yöntem başarılı bir şekilde farklı bal örneklerindeki sülfonamitleri belirlemek için uygulanmıştır.

Anahtar Kelimeler

Sülfonamitler, yüzey aktif maddeler, katı faz özütleme, bal

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INTRODUCTION

Sulfonamides are antibiotics which have been used as synthetic antimicrobial agents for preventing and treating various diseases [1,2]. Use of large amounts of sulfonamides in animal husbandry particularly as veterinary medicine cause to the hazardous effects on people's health and environment [3]. These antibiotics can produce allergic hypersensitivity effects or toxic reactions to human health. For these reasons, the residues of sulfonamides in the food chains must keep under control [4].

Several methods have been developed for the analysis of sulfonamides in different matrices such as milk, wastewater, urine, egg, fish, and honey [5-10]. HPLC has widely and effectively been utilized for the determination of sulfonamide residues in environmental samples. HPLC coupled with fluorescence detector [11], ultraviolet detector [12] or tandem mass spectrometry [13] has been used for the determination of these antibiotics. Due to the low concentration of sulfonamides in the food chains, these antibiotics must be enriched before their determinations. Solid phase extraction (SPE) has been frequently used technique for the separation and preconcentration of antibiotics from food matrices and environmental waters [6,7,14].

Recently, ionic surfactants coated metal oxides such as alumina, silica and ferric oxyhydroxides have been come up as excellent sorbent materials for solid phase extraction of analytes [15-19]. Due to high water permeability of the ionic surfactants, the solute incorporation was quite rapid comparing with the collection to hydrophobic sorbents [18]. Therefore the ionic surfactant-mediated SPE methods are extensively used for separation and preconcentration of hydrophobic organic compounds in the various matrices [19].

In the present study, silica-based ionic surfactant sorbent using cetyltrimethylammonium bromide were prepared and examined for the efficient preconcentration of sulfonamide antibiotics. The main effective factors were particularly optimized. The developed method was successfully applied to determination of sulfonamides in several honey samples.

MATERIALS AND METHODS

Reagents

Sulfadiazine (SDA), sulfamethazine (SMT), sulfamerazine (SMR), and sulphamethoxazole (SMX) were purchased from Sigma-Aldrich (Steinheim, Germany). HPLC grade acetonitrile and methanol were obtained from Sigma-Aldrich (St. Louis, MO, USA). Cetyltrimethyl ammonium bromide (CTAB), didecylmethyl ammonium bromide (DDAB) and tridodecylmethyl ammonium chloride (TDMAC) was obtained from Fluka. Silica (70-230 mesh, 60 Å and surface area > 500 m²/g) was supplied by Merck. Formic acid and silica (70-230 mesh, 60 Å and surface area > 500 m²/g) was supplied by Merck (Darmstadt, Germany). All other solvents were of analytical grade. Ultrapure water (Milli-Q plus system, Millipore Bedford, MA, USA) was used throughout the work.

Instruments

HPLC measurements were performed with a Shimadzu 20A model (Shimadzu, USA) liquid chromatographic system equipped with a diode array detector, (SPD-M20A) a quaternary pump. A Perkin Elmer Spectrum 100 model FTIR spectrometer was used to record the FTIR spectra of KBr discs in the range of 4000-700 cm⁻¹, 20 co-added interferograms were scanned at 2 cm⁻¹ resolution (Perkin Elmer, USA). A Philips SEM-XL-300 FEG scanning electron microscope (SEM) by operating at the accelerating voltage of 7 kV was used to study the morphology of the prepared sorbent. A Watson Marlow 323i (Falmouth, England) peristaltic pump was used to pass the analyte and the eluent solutions through the columns in the solid phase extraction experiments. A Selecta pH 2001 model pH meter was used for all pH adjustments. For solid phase extraction experiments, Varian cartridges (plastic container, 10 mm x 100 mm) equipped with 20 µm polypropylene frits were used.

Chromatographic conditions

A Hypersyl Gold C₁₈ column (250 mm x 4 mm i.d., 5 µm particle diameter) was used for the separation of the sulfonamides. The mobile phase was methanol: acetonitrile: 0.05 M formic acid (10:15:75, v:v:v) [20]. The wavelength of determination was set at 272 nm, and the mobile phase at isocratic condition was pumped at a flow

rate of 1.0 mL/min. The column temperature was controlled at 35°C. The injected sample volume was 20 µL.

Preparation of the standard solutions

A stock solution of each studied sulfonamide (200 mg L⁻¹) was prepared in methanol and stored at 4°C in refrigerator. They were stable at least one month. A mixed stock solution contained SDA, SMT, SMR, and SMX was prepared as 10 µg mL⁻¹. The standard solutions with sulfonamide concentrations from 0.010 to 2.0 µg mL⁻¹ at 12 concentration levels were prepared by dilution stock mixed solution with eluent [methanol:water (1:1)] solution.

Preparation of ionic surfactant coated silica sorbent

To prepare sorbent, 50 mg CTAB was added to an aqueous suspension of 2 g of silica gel with gentle mixing. Total volume was completed to 25 mL with doubly deionized water. The pH of solution was adjusted to 9 by using 0.01 mol L⁻¹ of Tris-HCl. The final mixture was stirred using magnetic stirrer for 1 h. The supernatant solution was discarded and the filtered residue was dried at 110 °C for 2 h and used as solid phase sorbent.

Preconcentration procedure

A 250 mg of prepared sorbent was put on a polyethylene SPE cartridge. It was conditioned with firstly 5 mL of deionized water and then 5 mL of pH 6 phosphate buffer solution. After mixing 5 mL of sample solution with 5 mL of pH 6 phosphate buffer solution, it was passed through the cartridge at a flow rate 1.5 mL min⁻¹ and then rinsed with 3 mL of 0.01 mol L⁻¹ of Tris-HCl. Finally, the sulfonamides were eluted with 4 mL of methanol-water (1:1) mixture. A 20 µL aliquot of eluate was injected into the HPLC system. All studies were done in three replicates.

Preparation of honey samples

Honey samples (pine, flower, lavender) were purchased from the local market in Izmir, Turkey. A 2 g of honey sample was added to 50 mL of polyethylene tube containing 5 mL of 2 mol L⁻¹ HCl solution and then the last mixture was stirred for 30 min at room temperature. A 20 mL of 30% (w/v) NaCl aqueous solution was added to this

solution and the final solution was transferred to a separation funnel. Then the mixture was shaken for 5 minute after adding 25 mL of dichloromethane. After separation of phase, a 25 mL of lower aqueous phase was transferred to a test tube and a 5 mL portion of this phase was used for solid phase extraction procedure [21]. A 0.1 and 0.25 µg mL⁻¹ of mixed sulfonamide standard solutions were spiked to honey samples for accuracy of extraction experiments.

RESULTS AND DISCUSSION

Type of surfactants

Three different cationic surfactants were evaluated for highest sorption capacity of sulfonamides. These surfactants are CTAB, DDAB and TDMAC. CTAB has the mono longest alkyl group while the other surfactants have more than one but shorter alkyl groups. The mono alkylated CTAB has less hydrophobic property than di- and tri-alkylated cationic surfactants. Therefore, it could be concluded that CTAB showed the greatest extractability.

Characterization of sorbent

The FTIR spectrum of the CTAB-silica gel was compared to that of silica gel and CTAB-silica gel/sulfonamide (Table 1). The band at 2820 cm⁻¹ in CTAB-silica gel appeared at 2910 cm⁻¹ in CTAB-silica gel/sulfonamide. The bands at 3065 and 1646 cm⁻¹ in CTAB-silica gel/sulfonamide seemed as bands of aryl H and S=O that are related to sulfonamides. These results clearly indicated the sorption of antibiotic to the prepared sorbent.

The SEM micrographs of silica gel and CTAB-silica gel and CTAB-silica gel/sulfonamide were shown in Figure 1 to clarify the change in

Table 1. Some frequencies (cm⁻¹) of silica gel, CTAB-silica gel and CTAB-silica gel/sulfonamide.

Silica gel	CTAB-silica gel	CTAB-silica gel/sulfonamide
3643 (-OH)	3465 (-OH)	3463 (-OH, NH)
-	2820 (-CH ₂ -)	2910 (-CH ₂ -)
-	-	3095 (aryl H)
-	-	1646 (S=O)
1094 (-Si-O)	1090 (-Si-O)	1084 (-Si-O)

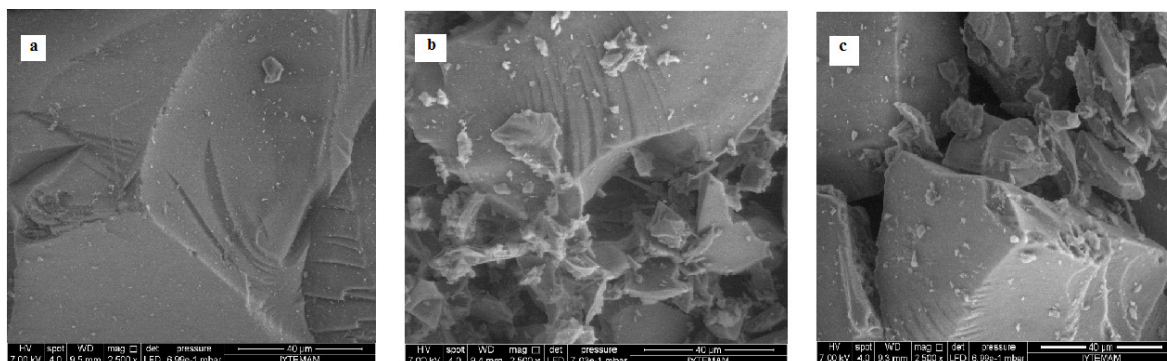


Fig. 1. SEM micrographs of silica gel (a), CTAB-silica gel (b), and CTAB-silica gel/sulfonamide (c) at 2500 times of magnification.

morphological features. It was seen that the surface morphology of the prepared sorbent was different from that silica gel and the prepared CTAB-silica gel/sulfonamide.

Influences of pH

A pH of the sample solution is one of the most important parameters in the extraction procedure [22]. Thus to investigate the effect of pH on the sorption of sulfonamides on the prepared sorbent, the pH of the 10 mL of sample solution containing $0.5 \mu\text{g mL}^{-1}$ of the sulfonamides was adjusted from 4 to 8 using the phosphate buffer solutions. The investigated sulfonamides were sorbed as 70-100% by the CTAB-silica gel sorbent in the pH range of 5-8. The pK_a values of these sulfonamides are approximately around 6 and 7.5 and so, it could be thought that they are partially in their protonated and neutral forms. The pH 6 has been selected as the best sorption pH value for the subsequent work.

Amounts of CTAB

The influence of amounts of CTAB on the sorption of sulfonamides was investigated in the range of 0 - 60 mg CTAB. In the absence of CTAB, SDA,

SMT, SMR and SMX were retained on the silica between 10-15 %. The sorption percentage of all studied sulfonamides was found between 80 and 100 when the amount of CTAB was changing from 40 to 60 mg. For completeness of sorption, CTAB as 50 mg was used for further studies.

Eluent type

Different solvent and solvent mixtures as 2 mL were attempted to use as the eluent solution to desorb the sulfonamides from the CTAB-silica gel sorbent (Table 2). It was eventually found that the mixture of methanol:water (1:1) provided the effective elution of sulfonamides from CTAB coated on silica sorbent. Later, the volume of methanol:water (1:1) mixture was also studied. As it was concluded from Table 2, the mixture of methanol:water (1:1) as 4 mL was selected as the eluent solution for the complete desorption of sulfonamides in the all concentrations studied.

Effect of flow rate of sample solution

The rate of flow of sample solution through the column was one of the factors affecting the process of the determination and directly related to the contact of the solution with the solid phase

Table 2. Effect of type of and volume of eluting agent on recovery of sulfonamides (N=3)^a.

Eluent	Recovery (%)			
	SDA	SMT	SMR	SMX
Methanol:Acetonitrile:Formic acid (1:1.5:7.5)	33±2	33±2	37±2	61±1
Methanol:Water (1:1)	72±1	57±1	57±2	57±1
Methanol:Acetonitrile (7.5:2.5)	20±2	56±1	30±2	39±2
Methanol:Ammonia (1:1)	83±1	6±3	10±3	17±3
Dichloromethane	26±2	15±3	20±2	23±2
Methanol:Water (1:1)	72±1	57±1	57±2	57±1
Methanol:Water (1:1) ^b	95±1	100±1	95±1	102±1
Methanol:Water (1:1) ^c	95±1	95±1	93±1	98±1

^a sulfonamides, $0.5 \mu\text{g mL}^{-1}$, sample volume 10 mL, sample pH 6, volume of elution: 2 mL, sample flow rate 1.5 min^{-1} .

^b volume of elution: 4 mL

^c volume of elution: 6 mL

[23]. Therefore, a 10 mL of sample solutions containing $0.5 \mu\text{g mL}^{-1}$ of the sulfonamides were passed through the column at four different flow rate levels ranging from 1 to 2.5 mL min^{-1} . It was observed that the sorption yields of SMR and SMX were not changed at these flow rates. However, the sorption percentages of SDA and SMT were slightly influenced above 1.5 mL min^{-1} . Hence, the flow rate was selected as 1.5 mL min^{-1} for all the experiments.

Sample volume

The maximal preconcentration volume of sulfonamides solutions was determined using a series of different volumes of solutions (10-250 mL) containing $1 \mu\text{g}$ of sulfonamides. The recoveries of sulfonamides (95-100%) were satisfactory with sample volume ranging from 10 to 100 mL. At the sample volume above 100 mL, the recoveries decreased gradually. Thus, the sample volume as 100 mL conceived to be a maximal preconcentration volume sample when a 250 mg CTAB-silica gel sorbent was used for the extraction of sulfonamides. It was understood that the preconcentration factor was obtained as 25.

Analytical performance

Under the optimized conditions, the analytical performance of proposed SPE method for the analysis of sulfonamides was evaluated. The linear ranges were studied by using 10 different concentration levels ranging from 0.01 to $2 \mu\text{g mL}^{-1}$ for each sulfonamide. The curves were linear over these concentration ranges with the regression coefficients between 0.9982 and 0.9996 (Table 3). The reproducibility of the method was evaluated by the analysis of five replicates of sample solutions containing $0.1 \mu\text{g mL}^{-1}$ of the each sulfonamide. The relative standard deviations

(RSD%) were found to be in the range of 1.98-5.91%. The limits of detection (LOD) and the limits of quantitation (LOQ) were calculated by using a signal-to-noise ratio 3 and 10 (the ratio between the peak area of each sulfonamide and peak area of noise), respectively. The LOD and LOQ were calculated from 10 independent complete determinations of $0.1 \mu\text{g mL}^{-1}$ of each sulfonamide. The LOD and LOQ for sulfonamides obtained by the proposed method were in the range of $3 \mu\text{g L}^{-1}$ to $13 \mu\text{g L}^{-1}$ and $8 \mu\text{g L}^{-1}$ to $23 \mu\text{g L}^{-1}$ respectively. Surfactant loaded silica sorbent could be used as high as greater than 15 experiments without any loss in its sorption behavior.

Honey analysis

Applicability of the proposed method was evaluated by processing spiked four honey samples with 0.1 and $0.25 \mu\text{g mL}^{-1}$ of mixture of sulfonamides throughout the entire procedure. Unspiked honey samples were previously analyzed using the proposed method. According to the obtained results (Table 4), the sulfonamide contents of the investigated honey samples were in the range of 0 - $1.30 \mu\text{g mL}^{-1}$. The amount of SDA and SMR of lavender honey was higher than the others, but SMT was not detected in this honey. The sulfonamide contents of two flower honeys were different from each other because they were from different regions of Turkey. However, the sulfonamide contents of the studied honey samples were mostly above the maximum residue limit of European Union [24]. As can be seen from Table 4, all the sulfonamides were determined in all tested spiked samples with the recoveries over 70%. In Figure 2, the chromatograms of the standard sulfonamides, the non-spiked and the spiked pine honey sample under the optimized conditions were shown.

Table 3. Analytical performance of the proposed method.

Compounds	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	Linear range ($\mu\text{g mL}^{-1}$)	Correlation coefficient (R^2)	RSD (%)
SDA	5	11	0.010-2.0	0.9989	5.91
SMR	13	23	0.010-2.0	0.9996	3.33
SMT	3	11	0.010-2.0	0.9983	2.84
SMX	4	8	0.010-2.0	0.9982	1.98

Table 4. Analysis of the honey samples (N=3).

Sulfonamide	Added ($\mu\text{g mL}^{-1}$)	Found ($\mu\text{g mL}^{-1}$)	R (%)	RSD (%)
Pine honey sample				
SDA	-	0.78 \pm 0.02		1.35 \pm 0.02
	0.10	0.85 \pm 0.02	97 \pm 1	1.02 \pm 0.03
	0.25	1.02 \pm 0.03	99 \pm 1	6.22 \pm 0.09
SMR	-	0.29 \pm 0.01		1.05 \pm 0.03
	0.10	0.41 \pm 0.01	105 \pm 1	1.10 \pm 0.03
	0.25	0.53 \pm 0.02	98 \pm 1	6.59 \pm 0.09
SMT	-	0.26 \pm 0.01		0.85 \pm 0.02
	0.10	0.33 \pm 0.01	92 \pm 1	0.90 \pm 0.02
	0.25	0.41 \pm 0.01	80 \pm 2	4.25 \pm 0.04
SMX	-	0.15 \pm 0.01		0.95 \pm 0.02
	0.10	0.22 \pm 0.01	88 \pm 1	0.94 \pm 0.02
	0.25	0.29 \pm 0.01	73 \pm 2	1.55 \pm 0.03
Lavender honey sample				
SDA	-	1.30 \pm 0.03		3.46 \pm 0.04
	0.10	1.38 \pm 0.03	99 \pm 1	1.10 \pm 0.02
	0.25	1.60 \pm 0.04	103 \pm 1	1.22 \pm 0.03
SMR	-	0.80 \pm 0.02		3.53 \pm 0.04
	0.10	0.75 \pm 0.02	83 \pm 2	1.14 \pm 0.02
	0.25	1.04 \pm 0.03	99 \pm 1	2.09 \pm 0.03
SMT	-	-		-
	0.10	0.07 \pm 0.01	70 \pm 3	1.05 \pm 0.02
	0.25	0.20 \pm 0.01	80 \pm 2	6.05 \pm 0.09
SMX	-	0.18 \pm 0.01		4.46 \pm 0.04
	0.10	0.27 \pm 0.02	96 \pm 1	1.07 \pm 0.02
	0.25	0.45 \pm 0.02	105 \pm 1	1.28 \pm 0.02
Flower 1 honey samples				
SDA	-	0.31 \pm 0.01		0.11 \pm 0.01
	0.10	0.39 \pm 0.01	95 \pm 1	0.78 \pm 0.02
	0.25	0.56 \pm 0.02	100 \pm 1	2.90 \pm 0.04
SMR	-	0.04 \pm 0.01		0.98 \pm 0.03
	0.10	0.10 \pm 0.01	71 \pm 3	0.95 \pm 0.03
	0.25	0.28 \pm 0.01	97 \pm 1	2.85 \pm 0.04
SMT	-	0.06 \pm 0.01		1.14 \pm 0.02
	0.10	0.13 \pm 0.01	81 \pm 2	1.02 \pm 0.03
	0.25	0.26 \pm 0.01	84 \pm 1	1.49 \pm 0.03
SMX	-	0.23 \pm 0.01		1.28 \pm 0.02
	0.10	0.30 \pm 0.01	91 \pm 1	1.08 \pm 0.02
	0.25	0.45 \pm 0.02	94 \pm 1	2.46 \pm 0.04
Flower 2 honey samples				
SDA	-	0.12 \pm 0.01		5.88 \pm 0.04
	0.10	0.20 \pm 0.01	91 \pm 1	1.05 \pm 0.02
	0.25	0.38 \pm 0.01	103 \pm 1	2.12 \pm 0.02
SMR	-	0.11 \pm 0.01		3.33 \pm 0.03
	0.10	0.18 \pm 0.01	82 \pm 2	0.65 \pm 0.02
	0.25	0.37 \pm 0.01	103 \pm 1	0.96 \pm 0.02
SMT	-	-		-
	0.10	0.09 \pm 0.01	90 \pm 1	0.72 \pm 0.01
	0.25	0.26 \pm 0.01	104 \pm 1	0.98 \pm 0.02
SMX	-	0.04 \pm 0.01		3.28 \pm 0.03
	0.10	0.14 \pm 0.01	100 \pm 1	0.85 \pm 0.01
	0.25	0.31 \pm 0.02	107 \pm 1	0.96 \pm 0.02

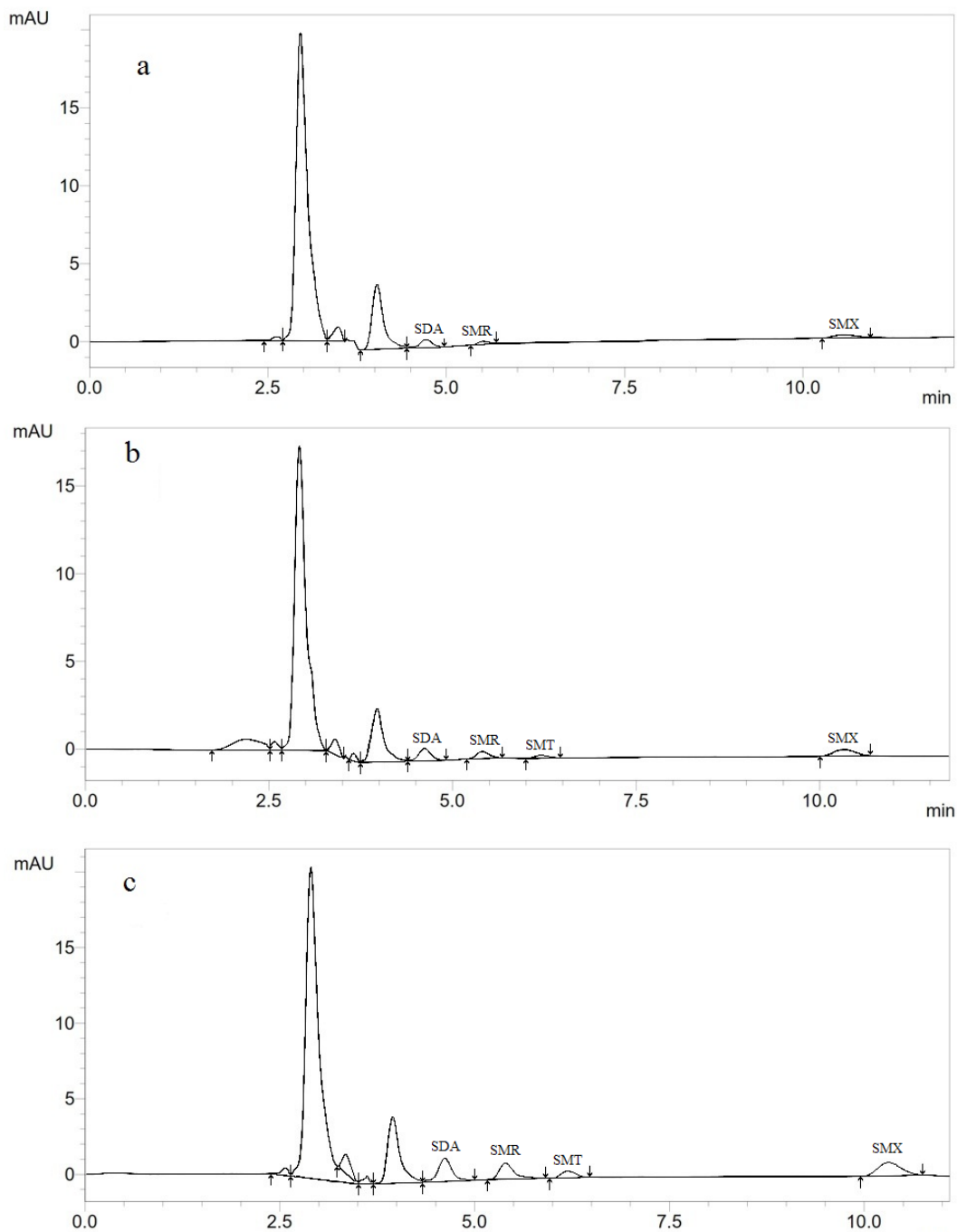


Fig. 2. HPLC chromatogram of the lavender honey sample after the extraction under the optimized conditions by the proposed method. (a) Non-spiked honey sample, (b) A honey sample spiked with $0.1 \mu\text{g mL}^{-1}$ sulfonamides, (c) A honey sample spiked with $0.25 \mu\text{g mL}^{-1}$ sulfonamides.

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