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A green method using micellar system for determination of sulfonamides in soil

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ABSTRACT

A green and simple method was developed for determination of sulfonamides (SAs) in soil samples. The procedure was based on the microwave-assisted extraction (MAE) of SAs from soil using non-ionic surfactant Triton X-114 as the extraction medium. Then sodium chloride was added into the MAE extract and the mixture was equilibrated for some time at high temperature. The analytes in the surfactant-rich phase were concentrated with the help of centrifugation and directly analyzed by high performance liquid chromatography with UV detection. None of potentially hazardous organic solvents was used in the whole sample preparation procedure. The significant variables for the performance of extraction and concentration were studied. The limits of detection of SAs obtained are in the range of 3.2–5.7 ng g^{-1}. The relative standard deviations of intra- and inter-day tests ranging from 3.5% to 7.7% and from 4.6% to 9.5% are obtained, respectively. This method was applied to the determination of SAs in some soil samples with different characteristics. The SAs recoveries obtained at fortified level of 100 ng g^{-1} for these samples are in the range of 81.2–93.7%. The effect of ageing time of spiked soil samples on the SAs recoveries was examined by the proposed method and a method reported in the literature. The recoveries of SAs decreased when the ageing time changed from 1 day to 4 weeks.

1. Introduction

Sulfonamides (SAs) belong to one class of synthetic antibiotics [1]. They have been widely used for treatment of many human and animal diseases, such as infectious diseases of digestive and respiratory tracts [2]. A significant fraction of the antibiotics can reach soil through application of animal wastes as fertilizers [3]. They can not only promote the generation and spread of drug resistant bacterial strains [4,5], but also cause the potentially detrimental long-term ecological effects [6].

Several methods have been developed for determining SAs in soil [7–13]. In the whole analytical procedure, sample preparation is an important and crucial step [14,15]. In general, SAs were firstly extracted from soil with organic solvents or the mixture of organic and aqueous solutions, such as acetonitrile/0.1 mol L^{-1} tris(hydroxymethyl)aminomethane buffer (15:85, v/v) [7], methanol/0.2 mol L^{-1} citric acid buffer (50:50, v/v) [8], methanol [9], methanol/0.1 mol L^{-1} McIlvaine buffer/0.1 mol L^{-1} Na_2EDTA (50:25:25, v/v/v) [10,11] and acetonitrile [12,13]. In order to improve extraction efficiency of SAs, pressurized liquid extraction (PLE) [7,8], ultrasound-assisted extraction (UAE) [9–11] and microwave-assisted extraction (MAE) [12,13] were usually used in these studies. Then the extracts were centrifugated and passed a solid-phase extraction (SPE) column for clean-up and concentration. In all these studies, most organic solvents were used in the sample preparation procedure, which may be dangerous to the operators [16] and increased the expenses due to the increasing the total amount of wastes generated in the lab.

It is well known that surfactants are amphiphilic molecules, the head of which is hydrophilic and the tail is hydrophobic [17]. When the surfactant concentration is increased above a certain threshold called critical micellar concentration, the surfactant molecules become associated to form molecular aggregates called micelles [18]. One of the most important properties of these organized structures is their good capacity to solubilise some compounds by the interactions of electrostatically, hydrophobically or combination of both effects [17]. Another important property is that when the micellar solution is heated, it becomes turbid over a narrow temperature range, which is referred to as its cloud-point temperature [19]. When the temperature rises above the cloud point, the solution is separated into two distinct phases: a surfactant-rich phase and an aqueous phase. The surfactant-rich phase volume is very

Abbreviations: HPLC, High performance liquid chromatography; LOD, Limit of detection; MAE, Microwave-assisted extraction; MAME, Microwave-assisted micellar extraction; PLE, Pressurized liquid extraction; RSDs, Relative standard deviations; SPE, Solid-phase extraction; SPME, Solid-phase microextraction; SDZ, Sulfadiazine; SDM, Sulfadimethoxine; SMR, Sulfamerazine; SMX, Sulfamethoxazole; SMD, Sulfamethoxydiazine; SMM, Sulfamonomethoxine; SQX, Sulfaquinoxaline; SAs, Sulfonamides; UAE, Ultrasound-assisted extraction.

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Table 1
The physicochemical properties of soil samples.

Soils	pH	Organic C (%)	Cation-exchange capacity (cmol kg^{-1})	Sand (%) ($2 > d > 0.05$)[a]	Silt (%) ($0.05 > d > 0.002$)[a]	Clay (%) ($d < 0.002$)[a]
Sample 1	6.2	2.5	62.5	36.1	29.4	34.5
Sample 2	6.3	2.8	67.2	32.7	36.9	30.4
Sample 3	6.8	1.2	33.8	45.2	28.6	26.2
Sample 4	5.7	1.6	53.9	50.4	17.8	31.8

[a] d: particle diameter (mm).

small, thus a high enrichment factor can be obtained. This leads to an enhanced sensitivity of the analysis without further sample clean-up or evaporation steps [20].

MAE is an effective technique in reducing sample preparation time and solvent consumption. The mechanism of MAE is based on the direct effect of microwave on molecules by ionic conduction and dipole rotation [21]. In resent years, microwave-assisted micellar extraction (MAME) which using micellar system to substitute organic solvent as extractant in MAE has been applied to the extraction of different compounds from solid samples [22–27]. This method combined the advantages of MAE and micellar extraction. In most of these studies, SPE [24,25] and solid-phase microextraction (SPME) [25–27] were used for subsequent clean-up and concentration of MAME extract.

The aim of the study is to develop a green method to improve the analysis of SAs in soil. The MAME was used for the extraction of SAs from soil sample, and then the analytes in the MAME extract were concentrated with the help of centrifugation after equilibrium some time at high temperature and adding sodium chloride. The analytes in the surfactant-rich phase were directly injected into high performance liquid chromatography (HPLC) for subsequent separation and detection.

According to the previous studies [16,22], some variables including Triton X-114 concentration, extractant volume, extractant pH, extraction time, extraction temperature, sodium chloride amount, equilibration time and equilibration temperature would influence the performance of extraction and concentration, so these significant variables were studied in this paper. The time and temperature are interrelated parameters and their influence on the extraction and concentration efficiency was investigated by applying a statistical approach using a central composite design.

2. Experimental

2.1. Chemicals and samples

The standards of sulfadiazine (SDZ), sulfamerazine (SMR), sulfamethoxydiazine (SMD), sulfamonomethoxine (SMM), sulfadimethoxine (SDM), sulfamethoxazole (SMX) and sulfaquinoxaline (SQX) were purchased from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Chromatographic grade methanol and acetic acid were obtained from Fisher (Pittsburgh, PA, USA). Non-ionic surfactant Triton X-114 was purchased from Sigma–Aldrich (St. Louis, MO, USA). Sodium chloride, sodium hydroxide and hydrochloric acid were of analytical grade and purchased from Beijing Chemical (Beijing, China). High purity water with a resistivity of 18.2 MΩ cm^{-1} was obtained from a Milli-Q water system (Millipore, Billerica, MA, USA).

Stock solutions of the standards (1.0 mg mL^{-1}) were prepared by dissolving each SAs in acetonitrile. They were stored in a refrigerator at 4 °C and found to be stable for two months. Working solutions were freshly prepared by diluting the stock solutions with water. The dilution procedure was done by volume measuring.

Soil samples were collected randomly from four agricultural fields in Changchun (China). Some physicochemical properties of these samples are shown in Table 1. The soils were air-dried, powdered and sieved through a 10-mesh sieve. They stored in the dark before analysis. For recovery studies, spiked samples were prepared by adding 1.0 mL of SAs standard solution to 2 g soil sample. The mixture was equilibrated by shaking for 15 min and then dried with a stream of nitrogen in order to completely remove the organic solvent. Subsequently, the spiked soil samples were left to stand 24 h at room temperature in the dark before analysis.

2.2. Apparatus

Chromatographic analysis was performed on an Agilent 1100 liquid chromatograph (Palo Alto, CA, USA) which was equipped with a quaternary pump, a heated column compartment, a UV detector, a LC workstation and a 7725 injection valve. A Zorbax SB-C18 column (250 mm × 4.6 mm I.D., 5 μm) was used as analytical column (Palo Alto, CA, USA).

Sample extraction was performed using a WR-3TA microwave extraction system (Meicheng, Beijing, China) equipped with 10 Teflon lined extraction vessels. A DK-98-IIA thermostatic bath (Taisite, Tianjin, China) was used to implement the concentration procedure. A SH-36 vortex mixer (Zhenghui, Shanghai, China) was used to mix the micellar solution. A SC-3610 centrifuge (Keda, Beijing, China) was used to accelerate the phase separation process. All glassware and plastic-ware used in this work were washed with methanol and high pure water, and then dried at 60 °C for at least 10 h.

2.3. MAME procedure

A 2.0 g soil sample was added into a Teflon lined vessel, and then 20 mL Triton X-114 (5.0%, v/v) was also added into it. The control vessel was connected with the temperature control device after putting the vessel into the microwave oven. Then the temperature in the extraction vessel was gradually increased until it reached the preset value. When completing the microwave heating, the sample vessels were cooled down to the room temperature before opening. The mixture was transferred into a centrifuge tube.

2.4. Concentration procedure

The sodium chloride (6.0 g) was added into the centrifuge tube containing MAME extract. The mixture was stirred in the vortex for 2 min, and then incubated in the thermostatic bath at 80 °C for 23 min. The phase separation was then accelerated by centrifugation at 4000 rpm for 5 min. The surfactant-rich phase was directly injected into the HPLC system for subsequent analysis.

2.5. MAE-SPE procedure

The MAE-SPE method developed by Raich-Montiu et al. [12] was also used for the comparative study. In summary, 1.0 g soil sample was extracted with 3 mL acetonitrile under the irradiation of microwave at 115 °C for 15 min. After the centrifugation, the supernatant was diluted with formic aqueous solution (pH

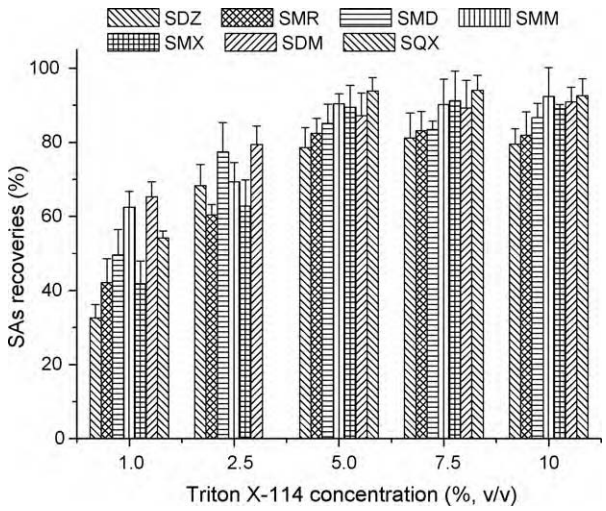

Fig. 1. Effect of Triton X-114 concentration on the SAs recoveries. Extractant volume, 20 mL; pH, 7; extraction temperature, 76 °C; extraction time, 13 min ($n = 3$).

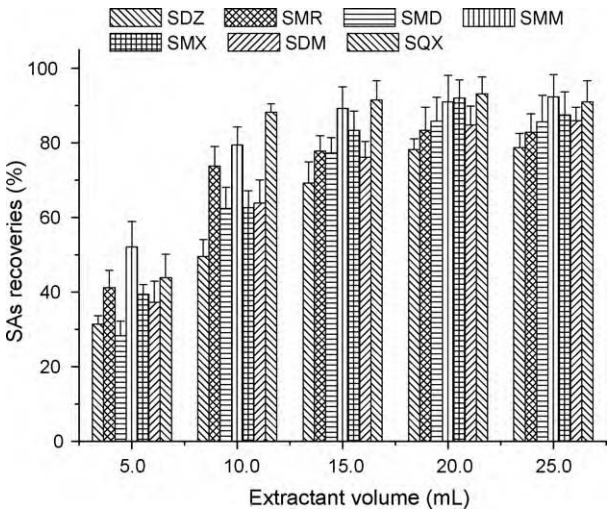

Fig. 2. Effect of extractant volume on the SAs recoveries. Triton X-114 concentration, 5.0% (v/v); pH, 7; extraction temperature, 76 °C; extraction time, 13 min ($n = 3$).

3.5) to reduce the acetonitrile content to 5% and passed through a hydrophilic–lipophilic balanced SPE cartridge which was preconditioned in sequence with 5 mL methanol and 5 mL formic acid aqueous solution (pH 3.5). The cartridge was rinsed with 10 mL water, air-dried and eluted with 1 mL acetonitrile.

2.6. HPLC-UV analysis

The separation and determination of SAs were carried out by a HPLC-UV system. The HPLC-UV conditions used in this work were developed from another work [28]. The mobile phase was a mixture of 1.0% acetic acid aqueous solution and methanol. The gradient elution was carried out starting from 20% to 50% methanol in 20 min, then back to 20% methanol in 1 min, held for 5 min to equilibrate the column. The flow rate was 1.0 mL min^{-1}. The column temperature was 30 °C and the injection volume was 20 μL. The SAs were monitored at the wavelength of 270 nm.

3. Results and discussion

3.1. Optimization of MAME conditions

Triton X-114 was chosen as the extraction medium because it is easily commercially available and has been successfully applied to the extraction of several organic compounds before HPLC analysis [17]. Moreover, its low cloud-point temperature and high density which facilitate the following concentration procedure [17]. Other parameters affecting the performance of the MAME, such as Triton X-114 concentration, extractant volume and pH, extraction time and temperature were investigated. All experiments were performed using 2.0 g of soil sample 1 spiked with 1000 ng g^{-1} SAs. When one parameter was changed, the other parameters were fixed at their optimized values.

3.1.1. Effect of Triton X-114 concentration

The surfactant concentration should be large enough to lead the high recovery. The effect of Triton X-114 concentration from 1.0% to 10.0% (v/v) on SAs recoveries was investigated (Fig. 1). The recoveries of SAs increased with the increase of surfactant concentration from 1.0% to 5.0%, and then remained constant. In principle, the small surfactant concentration is suitable for obtaining the high concentration factor [29]. So 5.0% (v/v) was chosen as the optimum surfactant concentration for further studies.

3.1.2. Effect of extractant volume

The MAME was evaluated by varying the extractant volume between 5 and 25 mL (Fig. 2). The experimental results demonstrated that the recoveries of SAs increased with the increase of the extractant volume from 5 to 20 mL, and then remained constant from 20 to 25 mL. The small extractant volume is not enough to extract the SAs from the soil sample completely. Twenty milliliters of extractant was chosen in this work.

3.1.3. Effect of pH

The extraction process might also be influenced by the pH of the extractant as it can alter the ionic form of the analytes. The effect of pH which was adjusted with 0.1 mol L^{-1} hydrochloric acid or sodium hydroxide on the recovery of SAs was studied over the pH range 2.0–11.0 (Fig. 3). The experimental results indicated that the SAs recoveries (82.9–94.1%) were satisfactory over the pH range 2.0–7.0. In the following experiments, the pH of the extractant was not adjusted, and its value is about 7.0.

3.1.4. Extraction time and temperature

The influence of extraction time and temperature on the recovery was investigated using a central composite design. The experimental design parameters and the response values are

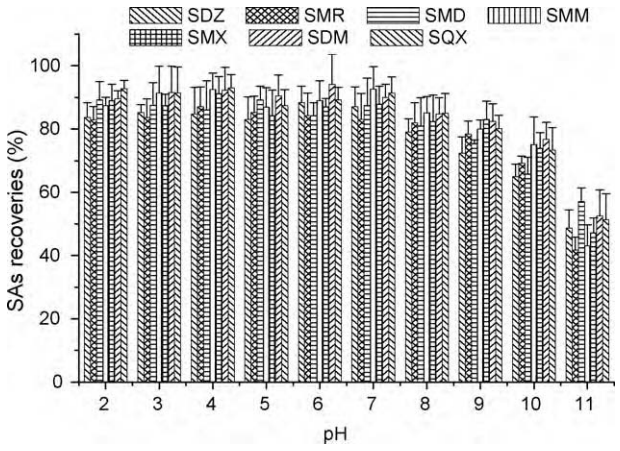

Fig. 3. Effect of pH on the SAs recoveries. Triton X-114 concentration, 5.0% (v/v); extractant volume, 20 mL; extraction temperature, 76 °C; extraction time, 13 min ($n = 3$).

Table 2
Design matrix and response values in the screening design for evaluation of extraction time and temperature.

Experiments	Coded levels		Responses: SAs recoveries						
	Extraction temperature (°C)	Extraction time (min)	SDZ	SMR	SMD	SMM	SMX	SDM	SQX
1	60	5	35.3	46.5	55.6	80.0	52.5	42.6	51.8
2	100	5	63.8	69.5	72.0	65.3	82.3	88.0	64.8
3	60	15	78.6	66.5	69.2	80.9	64.2	84.7	72.3
4	100	15	51.8	60.3	58.8	62.5	63.8	58.8	64.8
5	51.7	10	54.7	63.6	57.2	62.1	57.9	57.7	63.1
6	108.3	10	44.4	56.0	50.8	55.2	47.4	39.4	40.2
7	80	2.9	42.1	36.7	59.2	58.4	54.6	51.8	41.0
8	80	17.1	72.3	78.7	89.6	89.7	91.9	75.0	86.4
9	80	10	71.2	81.3	72.3	87.4	87.7	69.1	86.9
10	80	10	72.3	70.8	88.4	95.2	85.6	92.8	90.7
11	80	10	71.8	89.8	90.8	97.9	82.3	85.8	83.1
12	80	10	74.1	84.2	92.0	88.3	96.1	89.1	92.8
13	80	10	84.9	75.1	78.4	84.1	102.0	82.0	103.6

shown in Table 2. The *P* values of the model obtained by Design Expert software (Trial Version 7.1.3, Stat-Ease Inc., Minneapolis, MN, USA) are in the range of 0.0007–0.0376 for all analytes. These model terms are significant ($P < 0.0500$ indicate that the model term is significant), which confirmed that the model fitness was good.

Fig. 4 shows the response surface for SMX. The effect of extraction time was positive which indicated that the longer extraction time was suitable for the extraction process. The recoveries increased with the extraction temperature initially, but decreased at high temperature. This behavior is similar for the other target compounds. The extraction performed at 76 °C for 13 min can obtain the highest recoveries by prediction with computing program using Design Expert software. The thermostability of SAs was investigated by heating the standard solution of SAs with microwave irradiation at 76 °C for 13 min. The content of the target analytes was not decreased in this condition.

3.2. Optimization of concentration conditions

When the MAME was completed, the salt was added into the extract, and then the mixture was heated and separated into two distinct phases: a surfactant-rich phase and an aqueous phase. The analytes were extracted into the surfactant-rich phase. Compared to the initial sample solution volume, the surfactant-rich phase volume is small, thus a high enrichment factor would be obtained. There was no or very little loss of analytes due to no evaporation step. Moreover, surfactant-rich phase is compatible with the mobile phase used in HPLC. The concentration conditions were evaluated using 20 mL SAs standard solution (100 ng mL^{-1}) containing 5.0% Triton X-114 (v/v).

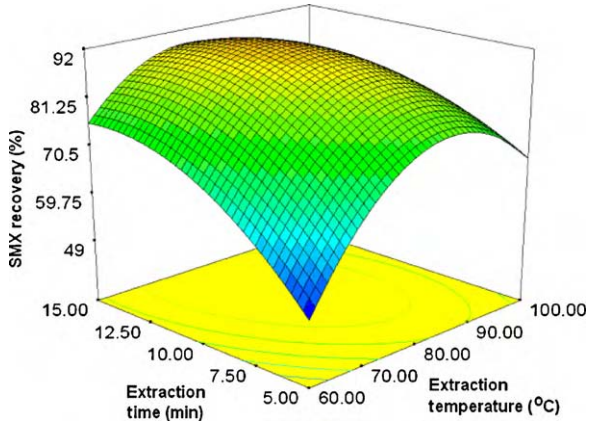

Fig. 4. 3D-surface plot showing the effect of extraction time and temperature on the SMX recovery. Triton X-114 concentration, 5.0% (v/v); extractant volume, 20 mL; pH 7.

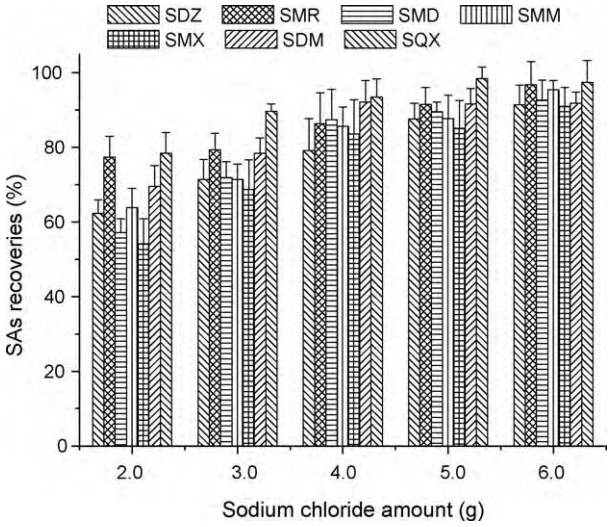

Fig. 5. Effect of sodium chloride amount on the SAs recoveries. Equilibration temperature, 80 °C; equilibration time, 23 min ($n = 3$).

3.2.1. Effect of sodium chloride amount

The addition of salt can facilitate the phase separation process for some micellar systems, since it increases the density of the bulk aqueous phase [30,31]. In addition, hydrophobic analyte may become less soluble in the aqueous solution at higher salt concentration and thus contribute to higher concentration efficiency [32]. To study the influence of electrolyte, different amounts of sodium chloride ranging from 2 to 6 g were investigated (Fig. 5). It was observed that the satisfactory recoveries of SAs were obtained with the sodium chloride amount in the range of 4–6 g. However, the higher concentration factor was obtained with large amount of sodium chloride due to the decreased volume of surfactant-rich phase. The sodium chloride amount of 6 g was chosen in this study.

3.2.2. Effect of equilibration temperature and time

It is known that two phases are formed when aqueous solution of a non-ionic surfactant is heated above the cloud-point temperature [33]. As the equilibration temperature increases, the volume of the surfactant-rich phase decreases because hydrogen bonds are disrupted and dehydration occurs [32]. The amount of water in surfactant-rich phase also decreases. Moreover, enough time was needed for getting the satisfactory recovery, because the ana-

Table 3
Design matrix and response values in the screening design for evaluation of equilibration time and temperature.

Experiments	Coded levels		Responses: SAs recoveries						
	Equilibration temperature (°C)	Equilibration time (min)	SZ	SMR	SMD	SMM	SMX	SDM	SQX
1	50	10	50.4	41.1	44.5	55.0	54.7	36.9	54.6
2	80	10	72.5	80.9	72.6	87.3	87.9	78.2	94.8
3	50	30	57.4	54.7	60.1	57.6	66.1	46.8	59.2
4	80	30	87.6	95.0	88.8	91.3	96.4	92.4	97.0
5	43.8	20	50.9	42.1	39.3	37.2	44.5	39.1	34.7
6	86.2	20	85.0	93.1	92.5	90.9	94.5	88.5	99.4
7	65	5.9	45.5	34.9	54.4	45.7	53.3	44.4	45.0
8	65	34.1	70.2	81.7	56.1	70.8	66.1	70.5	72.7
9	65	20	85.5	74.5	80.5	91.1	77.0	68.1	83.0
10	65	20	81.9	83.7	83.5	84.5	86.8	77.0	88.6
11	65	20	87.6	77.3	74.3	74.1	80.4	66.9	77.9
12	65	20	86.8	84.2	78.9	81.6	72.7	74.1	67.8
13	65	20	74.3	82.0	86.6	89.6	75.5	71.0	83.0

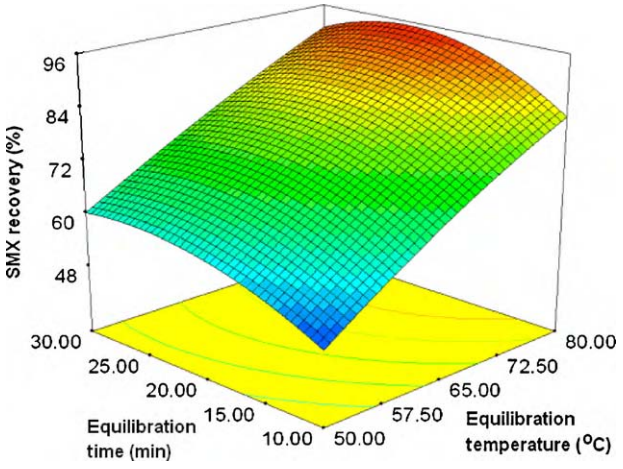

Fig. 6. 3D-surface plot showing the effect of equilibration time and temperature on the SMX recovery. Sodium chloride amount, 6 g.

lytes have to interact with the micelles and get into their core [34]. The influence of equilibration temperature and time on the concentration was investigated using a central composite design. The experimental design parameters and the response values in the screening design are shown in Table 3. The *P* values of the model obtained by Design Expert software are in the range of 0.0001–0.0474 for all analytes. These model terms are significant, which confirmed that the model fitness was good.

Fig. 6 shows the response surface for SMX. The equilibration temperature had a significant effect on the SAs recoveries and its effect was positive. The recoveries of SAs increased with the equilibration time from 10 to 20 min, and then remain constant. This behavior is similar for the other target compounds. The concentration performed at 80 °C for 23 min can obtain the highest SAs recoveries by prediction with computing program using Design Expert software. The thermostability of SAs was also investigated in this condition, and the content of the target analytes was not decreased.

3.3. Analytical performance

The chromatograms obtained by the analysis of blank and spiked soil sample 1 (20 ng g^{-1}) are illustrated in Fig. 7. The calibration curves were constructed in the SAs concentration range of 20–2000 ng g^{-1}. The correlation coefficients ranging from 0.9975 to 0.9991 are obtained. Limit of detection (LOD) is considered as the minimum concentration of analyte that can be confidently identified. The LODs estimated as the analyte concentration producing

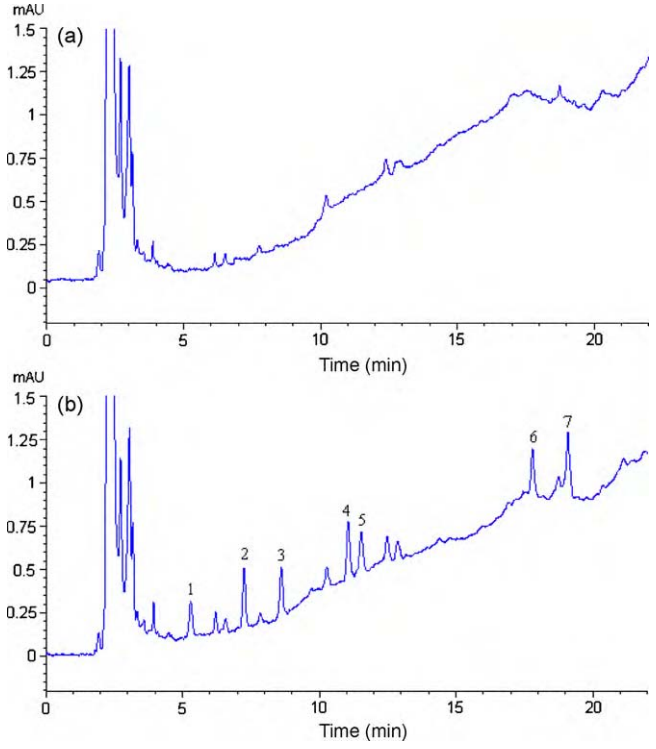

Fig. 7. Chromatograms obtained by the analysis of blank (a) and spiked (20 ng g^{-1}) (b) soil sample 1. 1, SDZ; 2, SMR; 3, SMD; 4, SMM; 5, SDM; 6, SMX; 7, SQX.

signal/noise ratio of 3:1 are 5.7, 3.2, 4.9, 4.6, 4.5, 3.5 and 4.0 ng g^{-1} for SDZ, SMR, SMD, SMM, SDM, SMX and SQX, respectively.

Precision was evaluated by measuring relative standard deviations (RSDs) of intra- and inter-day tests. The intra-day precision was performed by analyzing spiked soil sample 1 five times in 1 day at three different fortified concentrations of 20, 100 and 500 ng g^{-1}. The inter-day precision was performed over 5 days by analyzing spiked soil sample 1 at three different fortified concentrations of 20, 100 and 500 ng g^{-1}. The results obtained are shown in Table 4. RSDs of intra- and inter-day tests ranging from 3.5% to 7.7% and from 4.6% to 9.5% are obtained. In all three fortified levels, recoveries of the six SAs are in the range of 79.6–93.2%.

3.4. Application of the method

In order to study the influence of soil characteristics on the extraction, the proposed method was applied for analyzing the soil samples with different physicochemical properties (Table 1).

Table 4
The intra- and inter-day precisions and recoveries of the assay ($n = 5$).

Analytes	Intra-day precision						Inter-day precision					
	20 ng g^{-1}		100 ng g^{-1}		500 ng^{-1}		20 ng g^{-1}		100 ng g^{-1}		500 ng g^{-1}	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
SDZ	81.9	4.2	86.0	3.9	84.6	3.7	85.7	9.5	89.0	5.4	86.5	6.3
SMR	79.6	3.9	82.9	6.2	86.4	5.2	81.4	7.2	88.6	6.2	83.0	4.7
SMD	83.0	5.8	89.1	4.8	91.4	5.4	82.8	8.3	92.7	6.9	86.1	5.0
SMM	79.8	6.7	82.7	5.2	85.1	6.9	84.6	6.2	84.9	7.1	87.5	6.2
SDM	84.6	6.4	85.6	5.7	84.9	4.2	92.0	6.9	83.9	5.2	93.2	4.6
SMX	81.7	5.2	83.1	6.2	86.4	3.5	88.2	7.4	92.7	4.9	91.9	5.2
SQX	87.5	7.7	92.7	4.0	91.4	4.8	82.5	5.2	84.5	8.5	92.0	5.7

Table 5
The effect of ageing time of spiked soil sample on the SAs recoveries.

Analytes	SAs recoveries (%) obtained by the proposed method					SAs recoveries (%) obtained by the MAE-SPE method				
	1 day	1 week	2 weeks	3 weeks	4 weeks	1 day	1 week	2 weeks	3 weeks	4 weeks
SDZ	81.4	72.8	67.5	61.3	37.2	87.4	75.7	69.2	63.8	36.1
SMR	84.6	76.2	64.1	48.7	35.2	91.2	79.3	71.0	56.3	38.2
SMD	97.8	91.7	75.7	60.3	41.0	83.9	87.2	73.8	55.7	43.4
SMM	91.5	79.3	65.3	52.8	39.2	86.3	74.3	69.2	52.5	39.9
SDM	90.3	82.5	67.3	48.9	42.4	92.8	82.4	71.2	46.7	44.0
SMX	87.2	82.0	73.9	66.5	51.8	96.1	87.2	76.5	61.0	48.3
SQX	94.1	90.4	79.6	67.2	47.1	93.0	89.3	82.1	64.2	45.7

The optimized extraction and concentration conditions used in this work are as followed: Triton X-114 concentration, 5.0% (v/v); extractant volume, 20 mL; pH, 7; extraction temperature, 76 °C; extraction time, 13 min; sodium chloride amount, 6 g; equilibration temperature, 80 °C and equilibration time, 23 min. No SAs residues at detectable levels were found in these samples. The recovery study was then carried out by spiking soil samples with the SAs standards at level of 100 ng g^{-1}. The SAs recoveries obtained for different soil samples are not very significantly different and all in the range of 81.2–93.7%.

The recovery would be decreased with the increase of ageing time of spiked soil samples [35]. This is because the analytes are incorporated with soil by adsorption in short period and by sequestration in longer period [36]. The former phenomenon occurs at the early stages of sorption, where hydrogen bonding and Van der Waals forces prevail. On the other hand, sequestration involves sorption at remote microsites within the soil matrix [37].

Some studies also reported that the SAs recoveries decreased with the increasing of ageing time of spiked soil sample [38,39]. The soil sample 1 was selected as representative for this investigation, and was spiked with 500 ng g^{-1} of SAs and left to stand different times at room temperature in the dark before analysis. The MAE-SPE method developed by Raich-Montiu et al. [12] was also used for the comparative study. The results shown in Table 5 indicated that the values obtained by the two methods are quite similar. The SAs recoveries decreased from (81.4–94.1)% and (83.9–96.1)% to (35.2–51.8)% and (36.1–48.3)% with the two methods, respectively, when the ageing time changed from 1 day to 4 weeks. The reason may be the rapid increase of non-extractable amount or transformation of the SAs with increasing ageing time [7].

4. Conclusions

The proposed method based on micellar system was proved to be effective for extraction and concentration of SAs from soil samples. It presents significant advantages such as simple handling, small solvent and sample amount needed and high sensitivity when it was compared with other methods, such as LLE and SPE. More importantly, this method was a low cost and environmentally friendly method, because no organic solvents were used in the whole sample preparation process. It could be considered that this method is very promising and may be good alternatives to the traditional techniques.

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