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Determination of triazine herbicides in cereals using dynamic microwave-assisted extraction with solidification of floating organic drop followed by high-performance liquid chromatography

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ABSTRACT

A simple and cost-effective method of dynamic microwave-assisted extraction (DMAE) combined with solidification of floating organic drop (SFO) was developed for determining the five triazine herbicides in cereals. The approach combines the advantages of DMAE and SFO technique, and up to 15 samples can be treated simultaneously in 16 min. Firstly, triazine herbicides were extracted with 1 mL of methanol containing 90 μL of 1-dodecanol and following with 10 mL of water under the action of microwave energy. After that, 1.5 g sodium chloride was added into the obtained extract, and the mixture was centrifuged and cooled. The 1-dodecanol drop which contained the target analytes was solidified and transferred for analysis by HPLC-UV. Limits of detection of the five triazines obtained were in the range of 1.1–1.5 ng g^{-1}. Relative standard deviations of intra- and inter-day tests ranging from 5% to 7% were obtained. The method was successfully applied to the analysis of ten cereals and the recoveries of the triazines for the spiked samples were in the range of 80–102%. The proposed method is an alternative approach to the analysis of triazine herbicides in complex solid samples, being more rapid and simpler compared with the traditional extraction method.

1. Introduction

Triazine herbicides are among primary common agrochemicals applied to pre- and post-emergence weed control for agricultural and non-agricultural purposes [1–4]. A number of studies have explored the mammalian toxicity of triazine herbicides, which were proven to be toxic at inappropriately high levels [5]. For most agriculture products, the Environmental Protection Agency (EPA) requires that the tolerance of triazine herbicides is 0.25 mg/kg, while the European Union (EU) dictates that the concentration of atrazine and simazine must not exceed maximal admissible values of 0.01 mg/kg and 0.1 mg/kg for cereals, respectively. Therefore, a simple, rapid and sensitive analytical method for determination of triazine herbicides in cereals is required.

Sample preparation is one of the most important steps of the analytical process especially for analyzing complex samples [6]. Generally speaking, the preparation procedure of the cereal samples included two steps, such as an extraction procedure that provides suitable recovery for the analyte, and a clean-up step to remove some of the co-extracted compounds. Carabias-Martínez et al. [7] reported an extraction method of triazine herbicides in wheat samples by pressurized liquid extraction, and the total time of extraction was 21 min. Then the extract was evaporated to dryness, and the residue was reconstituted and subjected to a cleanup step with solid phase extraction (SPE) using Oasis MCX adsorbents. Lawrence et al. [8] described a method employing immunoaffinity cartridge as clean-up cartridge for triazine herbicides in the crop samples. The method involved extraction of the triazines by homogenization with methanol (20 mL) for 2 min, and then the mixture was centrifuged for 10 min. The supernatant obtained was evaporated to 0.2 mL, and diluted in aqueous phosphate buffered saline (PBS). The PBS diluent was cleaned up sequentially using a strong anion-exchange SPE cartridge followed by the immunoaffinity cartridge. In recent years, ultrasonication coupled with molecular imprinted polymers (MIP) technology was employed to selective extraction and cleanup of triazine herbicides in cereal samples [9–12]. These methods included three separate steps: firstly, the cereal sample was extracted with organic solvent (methanol or acetonitrile) by ultrasonication for 10–30 min, then the extract was centrifuged, filtered and evaporated, followed by the residue was reconstituted and used for solid phase microextraction or SPE procedure with MIP. More recently, a method based on polymer monolith microextraction has been proposed by Su et al. for the analysis of triazines in cereal samples [13]. The cereal samples were extracted with acetone by shaking (50 min) and ultrasonication (30 min). Then, the extract was centrifuged,

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concentrated, reconstituted, and passed through the monolithic capillary for cleanup and concentration. However, in these studies, the extraction and clean up were performed separately, so processing time was prolonged, and organic solvent consumption and manual handling were enhanced.

Microwave-assisted extraction (MAE) is a rather green sample preparation technique which shows lower solvent consumption, excellent extraction yields, and relatively short extraction time. There are a few publications about the application of MAE for the extraction of herbicides in cereals or cereal-based foods [14–18]. Whereas, some triazine herbicides may be partially decomposed under the both high temperature and high pressure conditions [14]. In addition, when the extraction process was finished, the vessels must be cooled to room temperature before opening, and the extract has to be filtered or centrifugated. Thus, overall extraction time was increased considerably. To overcome these weaknesses, dynamic MAE (DMAE) [17,19–22] has been developed, which can continuously supply the extraction vessel with fresh extraction solvent, and the analytes were transferred out of the extraction vessel as soon as they were extracted. It was especially important to avoid degradation or contamination of analytes. Moreover, the extract could be filtered on-line and DMAE could be coupled with other sample pretreatment techniques.

In recent years, a novel microextraction method based on the solidification of floating organic drop (SFO) has been applied for the analysis of trace organic compound in the environment and biological samples [23–29]. A small volume of an organic solvent with low density and the proper melting point was used for concentration of target analyte [30–32]. With the help of centrifugation and cooling, the organic solvent drop was solidified and transferred easily. The advantages of the SFO technique include simplicity of operation, low cost, and high enrichment factors. Up to now, the SFO has been employed extensively for determination of agricultural pesticides in aqueous samples [32–34].

This paper describes a rapid analytical method based on DMAE–SFO combined with HPLC-UV for determination of five triazine residues in cereal samples. The approach combines the benefits of DMAE and SFO technology, up to 15 samples can be treated simultaneously in 16 min. Some experimental parameters which could affect the extraction efficiency were studied and optimized.

2. Experimental

2.1. Chemicals and samples

The standards (purity > 98.5%) of ametryn, atrazine, desmetryn, propazine and simazine were provided by Dr. Ehrenshtofer (Augsburg, Germany). Their chemical structures are shown in Fig. 1. Chromatographic grade acetonitrile was obtained from Fisher (Pittsburgh, PA, USA). The Milli-Q water was obtained from a Millipore purification system (Billerica, MA, USA) operating at a resistivity of 18.2 MΩ cm^{-1}. Analytical grade 1-dodecanol, methanol, acetonitrile, ethanol, acetic acid and ammonia water were purchased from Beijing Chemical (Beijing, China). Quartz sand (25–50 mesh) was obtained from Sinopharm (Shanghai, China), which was heated in a muffle furnace at 550 °C for 1 h to eliminate organic matter before used.

Individual triazine stock solutions (200 μg mL^{-1}) were prepared in methanol and stored at −18 °C. A mixed stock solution (10 μg mL^{-1}) of five triazines was prepared by diluting individual stock solutions with methanol and stored at 4 °C in dark glass bottles. The mixed solution should be replaced every two weeks in order to prevent the decomposition of triazines.

Ten cereal samples were purchased from a local supermarket (Changchun, China). Cereal samples were powdered to pass through a 40 mesh sieve, and then stored in a sealed brown bottle at room temperature. All samples were analyzed. The sample 1 shows the absence of the triazines and used as the blank sample in the recovery studies.

For recovery studies, spiked cereal samples were prepared by adding the different volumes of the triazine standard solution into the sample 1. The mixture was equilibrated by shaking for 15 min and then left to stand at room temperature in the dark for more than 24 h until methanol has volatilized completely.

2.2. Apparatus

The DMAE–SFO system is represented in Fig. 2, which was modified based on our previous work [17]. The system consisted of a vacuum pump (HPD-25, Beijing, China), a vacuum SPE manifold (Waters, Milford, MA, USA), a centrifuge (Keda, Beijing, China) and a flat countertop microwave oven (Panasonic, Shanghai, China) which a microwave antenna rotates underneath to evenly distribute the microwaves to every part of the oven for consistent heat. Fifteen screw-cap glass centrifuge tubes were used as collection tubes. The extraction vessels were polyethylene tubes (100.0 mm long, 10.0 mm i.d.), which were static in the whole experimental process. The upper ends and the bottoms were connected with the solvent container and the ports of the vacuum SPE manifold by tubes (T1 and T2) (polyethylene, 500.0 mm long, 0.5 mm i.d.), respectively (Fig. 2).

2.3. Analytical procedure

2.3.1. Dynamic microwave-assisted extraction coupled with solidification of floating organic drop

Firstly, the cereal sample was accurately weighed (1.000 g) and mixed thoroughly with quartz sand (4.0 g) which was used as dispersant. The mixture was placed between two absorbent cotton plugs in the extraction vessel, and then compressed carefully. Fifteen samples were loaded by the same method and arranged systematically in the microwave oven, and connected with the solvent container and the ports of the vacuum SPE manifold by T1 and T2.

Subsequently, the vacuum pump was activated and 1 mL of methanol containing 90 μL of 1-dodecanol was passed through the extraction vessels. When methanol was pumped into the extraction vessel thoroughly, microwave heating was started with the power of 600 W, and water was pumped into the extraction vessel at a flow rate of 1.5 mL min^{-1}. When the volume of the extract in the collection tubes was 10 mL, the vacuum pump and microwave irradiation were stopped, and the extraction process was completed.

Finally, 1.5 g sodium chloride was added to the collection tube. After centrifugation for 3 min at 4000 rpm, the 1-dodecanol contained analytes droplet was floated on the top of the extract. The collection tubes were put into an ice bath for 5 min. Then the 1-dodecanol was solidified and attached to the wall of the tube, and then transferred to a conical vial and melted immediately at the room temperature. The 1-dodecanol was diluted to 200 μL with methanol for HPLC analysis.

2.3.2. Column solid-phase extraction

The classical sample preparation technique for extraction of triazines from cereals was performed according to the Chinese national standard [35]. Ten grams of cereal samples was placed in a 50 mL centrifuge tube, and 40 mL acetonitrile was added into it. The mixture was homogenated for 2 min and shook for 30 min, and then centrifuged at 4000 rpm for 5 min. The supernatant was added into a 100 mL round bottomed flask. Another 40 mL acetonitrile was added into the centrifuge tube and repeated the

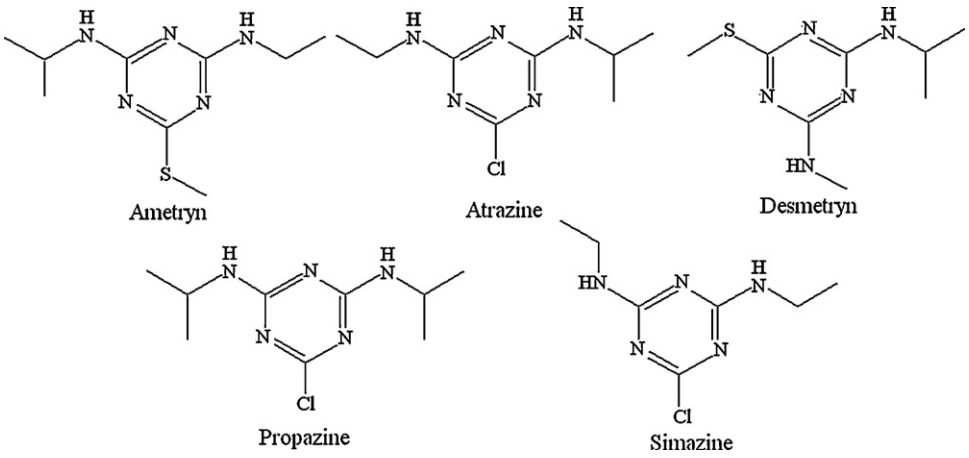

Fig. 1. Chemical structures of five triazine herbicides.

previous treatment. Then two extracts were combined and evaporated to dryness on a rotary evaporator at 35 °C. A SPE column which was packed with medium alumina (1000 mg, 6 mL) was activated with 5 mL dichloromethane. The residue was reconstituted with 10 mL dichloromethane and transferred into the SPE column at a flow rate of 1.0 mL min^{-1}, the effluent was collected. Another 5 mL dichloromethane was used for washing the SPE column, and was combined with the previous effluent, subsequently evaporated to dryness under a stream of N_2. The residue was reconstituted with 1 mL acetonitrile–water (40%, v/v) and filtered through a 0.45 μm membrane. Then 20 μL aliquots were injected into the HPLC system for analysis.

2.4. HPLC analysis

The triazines were separated and quantified using an Agilent 1100 liquid chromatograph (Palo Alto, CA, USA), which was equipped with a quaternary pump, a heated column compartment, an HPLC workstation and a UV detector monitoring at 228 nm. The analytical column was an XTerra MS C_{18} column (250 mm × 4.6 mm i.d., 5 μm) (Waters, Milford, MA, USA). A gradient elution solvent was applied which contained acetonitrile as mobile phase A and water as mobile phase B. The mobile-phase gradient profile (where refers to the time in minutes) was as follows: t_0, A = 40%; $t_{4\,min}$, A = 50%; $t_{12\,min}$, A = 80%; $t_{13\,min}$, A = 40%. The total flow rate was 1.0 mL min^{-1}. The column temperature was set at 40 °C and injection volume was 20 μL.

3. Results and discussion

3.1. The optimization of DMAE conditions

3.1.1. Effect of microwave power

The effect of microwave power on the recoveries of triazines in the spiked sample was studied by varying the power between 0 and 1000 W. Fig. 3(a) shows that the recoveries of triazines increased with the increase of the microwave power from 0 to 600 W, and then decreased from 600 to 1000 W. It is worth noting that simazine has the highest recovery at 800 W. Too high microwave power was not useful to increase the recoveries of the other triazines and may result in the degradation of the analyte [14,36]. Thus, 600 W of microwave power was selected.

3.1.2. Effect of extraction solvent

Firstly, the type of extraction solvent was investigated. The extraction solvent should be miscible with both water and 1-dodecanol, and be able to absorb microwave energy to accelerate the extraction. The dissipation factor (tan δ) is a measure of the ability of the solvent to absorb microwave energy and dissipate that energy in the form of heat [37]. The dissipation factor is expressed as the quotient:

$$\tan\delta = \frac{e''}{e'},$$

where e'' is the dielectric loss factor, indicative of the efficiency of converting electromagnetic radiation to heat and e' is the

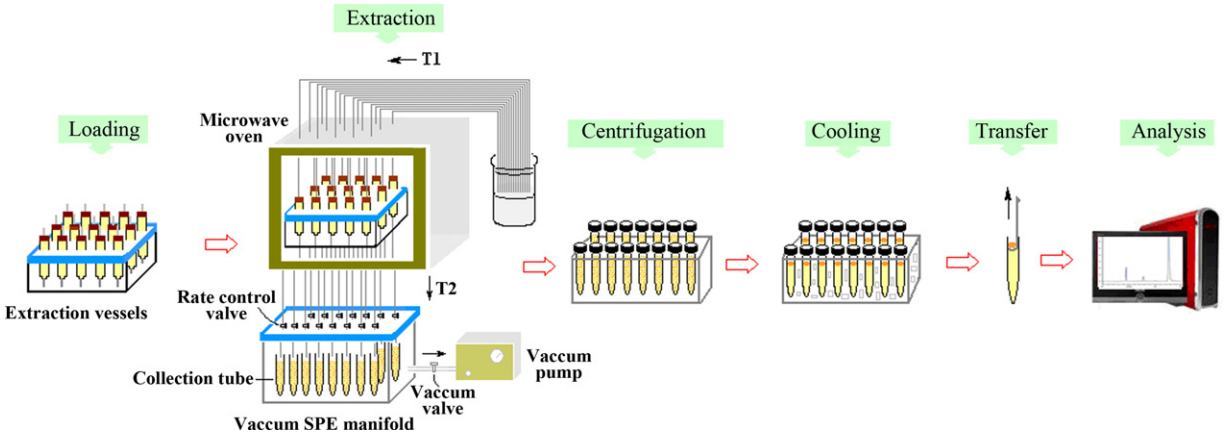

Fig. 2. Schematic diagram of DMAE–SFO system.

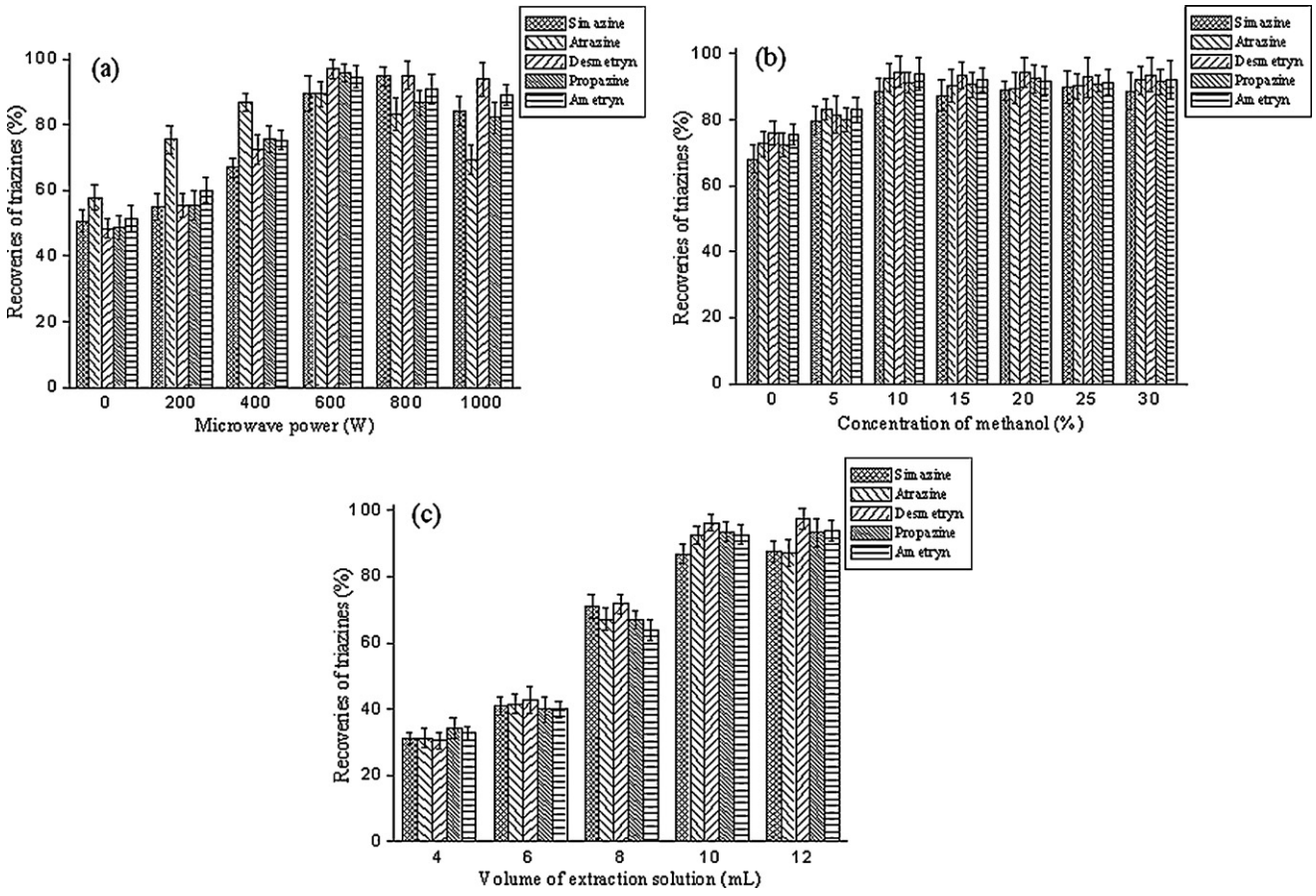

Fig. 3. The optimization of DMAE conditions ($n = 3$): the effect of (a) microwave power, (b) concentration of methanol and (c) volume of extraction solution on the recoveries of triazine herbicides.

dielectric constant describing the ability of molecules to be polarized by the electric field [38,39]. In this work, methanol, acetonitrile and ethanol are selected as extraction solvents. Methanol has a relatively higher dissipation factor, which means that it could transform microwave energy into heat better than other solvents. And the results also demonstrated that the best recoveries of triazines were achieved with methanol as the extraction solvent.

Furthermore, the effect of the methanol concentration in the extraction solvent was researched. The experiments were performed with 10 mL various concentration methanol–water solutions (0–30%, v/v) and the results are shown in Fig. 3(b). The recoveries of triazines increased from 0 to 10%, and then remained relatively constant when the methanol concentration was higher than 10%. So methanol–water (10%, v/v) was chosen.

Lastly, the volume of the extraction solvent was investigated. It can be seen from Fig. 3(c) that 10 mL extraction solvent offers the highest recoveries of triazines in the cereal sample. When the volume of extraction solvent was above 10 mL, the increase of the volume did not result in any noticeable improvement on the recoveries of triazines. Therefore, 10 mL methanol–water solutions (10%, v/v) were used.

3.1.3. Effect of extraction flow rate

The extraction process was investigated with the extract flow rate from 0.5 to 3.0 mL min^{-1}. The results indicated that the extract flow rate in the range of 1.0–2.0 mL min^{-1} had no significant effect on the recoveries of triazines. The recoveries of triazines were deceased when the flow rate was higher than 2.0 mL min^{-1}. On the contrary, the overall extraction time was prolonged when the flow rate was lower than 1.0 mL min^{-1}. In this study, 1.5 mL min^{-1} of the extract flow rate was chosen.

3.2. The optimization of SFO conditions

It has been pointed out that the solvent used for the SFO should have a low volatility, lower density than water and a melting point near room temperature. Generally, 1-undecanol, 1-dodecanol, 2-dodecanol and 1-tetradecanol have been recommended. In this study, 1-dodecanol was selected as the enriched solvent which provided excellent enrichment efficiency for the triazines in the cereal extracts. The parameters of the SFO such as volume of the 1-dodecanol, pH value and the salt effect were optimized.

3.2.1. Effect of volume of the 1-dodecanol

In this study, the 1-dodecanol was employed in the DMAE: 40 μL 1-dodecanol was dispersed into 1 mL methanol and the mixture was immediately injected into 10 mL water. A cloudy suspension was formed and used for the extraction of triazines in the spiked cereal samples. The results demonstrated that the volume of the collected 1-dodecanol was too small, because the most 1-dodecanol was attached to the cereal sample. If the methanol and water were pumped into the extraction vessel, respectively, the 1-dodecanol attached to the sample will be transported by flowing water and the volume of the collected 1-dodecanol could increase.

Different volumes of 1-dodecanol in the range of 50–110 μL (10 μL intervals) were mixed with 1 mL methanol, and the mixture was pumped into the extraction vessel. Then microwave heating was started and 10 mL water was pumped following into the vessel. As shown in Fig. 4(a), the recoveries of triazines increased

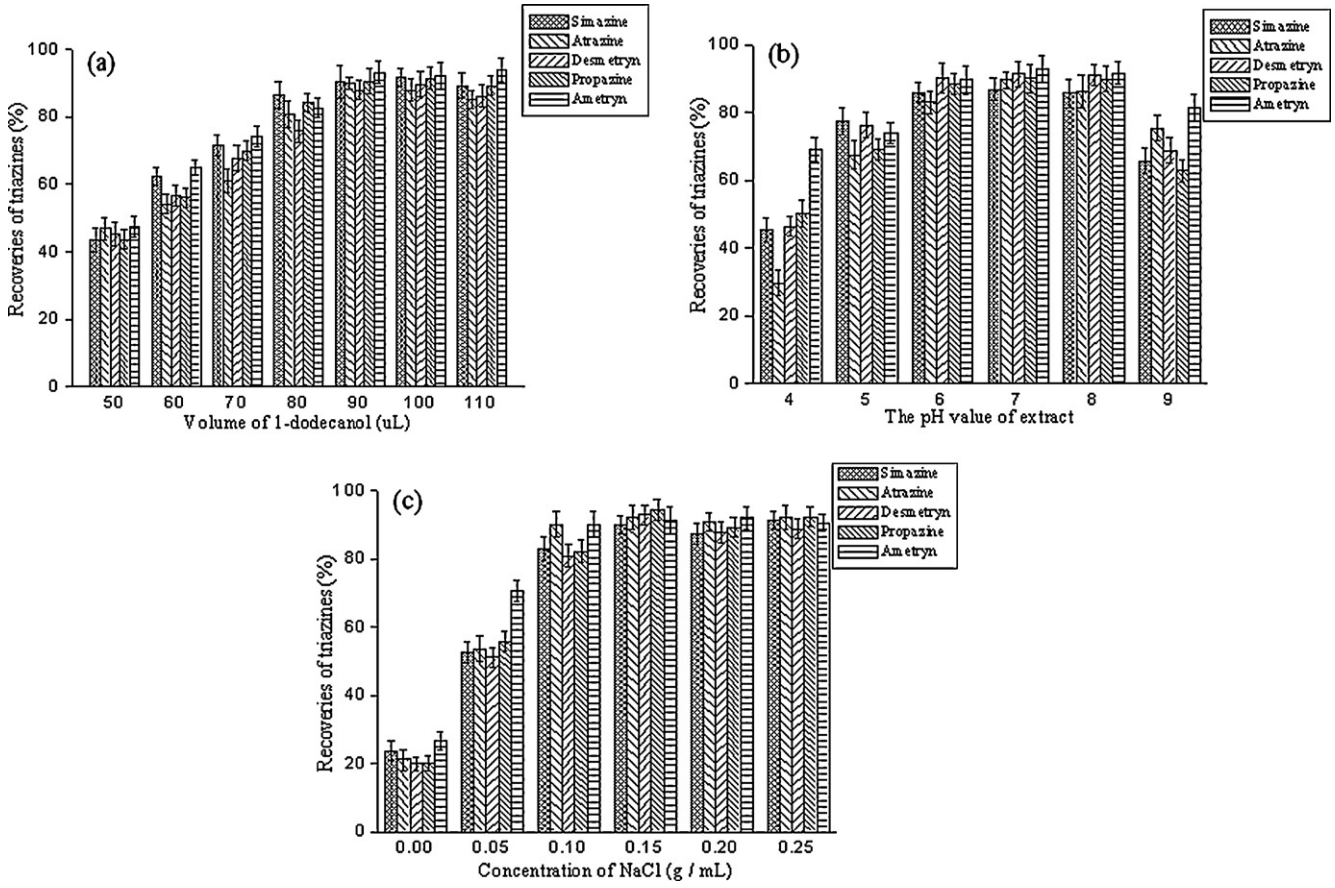

Fig. 4. The optimization of SFO conditions ($n = 3$): the effect of (a) volume of the 1-dodecanol, (b) pH value of extract and (c) salt concentration on the recoveries of triazine herbicides.

with the increasing volume of 1-dodecanol, when the volume of 1-dodecanol was 90 μL, the recoveries reached a maximum value and remained approximately constant in the range of 90–110 μL. Therefore, 90 μL 1-dodecanol was used in the subsequent studies.

3.2.2. Effect of pH

The cereal extracts with different pH values in the range of 4–9 were evaluated to obtain higher triazine recoveries. It can be seen from Fig. 4(b) that the recoveries of triazines were nearly constant in the pH range of 6–8. The pH of the extract obtained was 7, so the pH of the extract did not need to adjust.

3.2.3. Effect of salt

The addition of salt to the extract is usually made to improve the enrichment efficiency of the analytes, because the increased ionic strength of the aqueous phase could aid the partition of the analyte to the organic phase [26]. In this study, the NaCl concentration was varied between 0 and 0.25 g mL^{-1}, and the effect on the recoveries of triazines is illustrated in Fig. 4(c). Recoveries improved as the salt concentration increased from 0 to 0.15 g mL^{-1} and were approximately constant in the range of 0.15–0.25 g mL^{-1}. So, 1.5 g NaCl was added into the extract.

In brief, the best experimental conditions for all the target analytes were: 600 W of microwave power; 1 mL methanol and 10 mL of water as the extraction solvent; 1.5 mL min^{-1} of the extraction solvent flow rate; 90 μL 1-dodecanol of enrichment solvent and 0.15 g mL^{-1} of salt concentration.

3.3. Validation of the method

The chromatograms which were obtained by the analysis of the sample 1, spiked sample 1 (25 ng g^{-1}) and the sample 8 are illustrated in Fig. 5. The calibration curves were constructed in the triazine concentration range of 5–1000 ng g^{-1}. Correlation coefficients ranging from 0.9983 to 0.9994 were obtained. Limit of detection (LOD) and limit of quantification (LOQ) were estimated as triazine concentration producing a signal/noise ratio of 3 and 10, respectively. The details of the calibration curves, correlation coefficients, LODs and LOQs of the proposed method are shown in Table 1.

Precisions were evaluated by measuring intra- and inter-day relative standard deviations (RSDs). Intra-day precision was performed by analyzing spiked samples six times in one day at three different fortified concentrations of 10, 25 and 500 ng g^{-1}. The mean values of RSDs (%) were in the range of 5–7%. Inter-day precision was performed over six days by analyzing spiked samples and the mean values of RSDs (%) were in the range of 5–7%. In addition, the microwave energy distribution within the 15 samples was evaluated. Fifteen spiked samples (25 ng g^{-1}) were treated simultaneously by the proposed method. The recoveries of triazines were in the range of 78–101% and the RSDs were in the range of 7–8%.

The recovery studies were carried out by spiking the cereal samples with five triazines in different fortified concentrations (10, 25 and 500 ng g^{-1}), and the recoveries of simazine, atrazine, desmetryn, propazine and ametryn were in the range of 80–97%, 85–94%, 83–100%, 82–98% and 83–102%, respectively (Table 2).

Table 1
Analytical parameters of the proposed method.

	Linearity range ($ng\,g^{-1}$)	Calibration equation	Correlation coefficient (r^2)	LOD ($ng\,g^{-1}$)	LOQ ($ng\,g^{-1}$)
Simazine	5–1000	$y = 0.18x - 2.21$	0.9993	1.3	4.3
Atrazine	5–1000	$y = 0.18x - 0.25$	0.9993	1.1	3.5
Desmetryn	5–1000	$y = 0.17x - 0.50$	0.9994	1.2	3.8
Propazine	5–1000	$y = 0.15x + 0.57$	0.9983	1.5	4.8
Ametryn	5–1000	$y = 0.15x + 0.68$	0.9989	1.5	4.8

Table 2
Recoveries of triazines by analyzing spiked real cereal samples ($n = 3$).

Cereal sample	Spiked ($ng\,g^{-1}$)	Simazine		Atrazine		Desmetryn		Propazine		Ametryn	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Sample 1	10	84	4	85	3	85	4	83	6	89	3
	25	86	5	88	3	86	4	86	5	88	4
	500	91	6	92	4	89	4	90	5	88	3
Sample 2	10	80	5	90	2	90	3	87	3	90	4
	25	91	5	85	3	90	3	89	3	88	4
	500	90	3	86	5	96	4	89	3	92	4
Sample 3	10	81	3	92	3	83	4	84	4	84	4
	25	86	3	87	3	86	3	82	3	86	4
	500	88	3	89	4	85	3	86	4	89	4
Sample 4	10	89	3	86	5	90	3	90	4	83	4
	25	93	2	93	4	93	4	95	4	87	3
	500	90	5	88	2	91	2	98	4	93	3
Sample 5	10	81	4	85	3	95	4	91	3	93	4
	25	85	4	87	4	98	4	96	3	94	4
	500	84	2	94	4	100	4	98	3	100	4
Sample 6	10	85	3	89	4	84	3	84	3	84	3
	25	86	5	88	4	88	4	84	5	86	3
	500	93	4	93	3	89	5	88	5	89	4
Sample 7	10	82	5	90	4	90	5	87	3	88	2
	25	90	4	93	3	94	4	89	4	93	3
	500	96	4	94	3	94	3	90	4	98	4
Sample 8	10	86	3	89	3	90	4	85	3	84	5
	25	92	5	86	4	95	5	89	3	90	4
	500	97	4	88	5	100	3	90	6	88	6
Sample 9	10	82	3	87	5	89	4	86	6	88	3
	25	87	5	94	5	96	3	89	4	93	3
	500	93	4	89	4	95	3	92	5	102	3
Sample 10	10	87	5	85	4	89	3	89	3	85	3
	25	89	2	92	3	86	4	91	4	91	3
	500	95	4	90	3	98	3	93	5	92	4

3.4. Application of the method

In order to demonstrate the applicability of the proposed method, it was used for the determination of triazines in ten cereals, including four rice samples, two maize samples, two millet samples and two wheat samples (Table 3). The result obtained by the proposed method was compared with that obtained by the column SPE method which was described in Section 2.3.2. The results were similar, and the triazines were detectable in five samples.

The proposed method was compared with the methods used in the literatures for analyzing triazines (Table 4). It is obvious that the proposed method reduces the volume of the organic solvent required, shortens the sample preparation time and increases the sample throughput. The entire sample preparation procedures, including extraction, centrifugation and cooling can be completed

Table 3
Determination of triazines in different cereals and comparison with the standard method.

Cereal sample	Contents of triazines in cereals ($ng\,g^{-1}$) ($n = 3$)									
	DMAE–SFO					Column SPE				
	Simazine	Atrazine	Desmetryn	Propazine	Ametryn	Simazine	Atrazine	Desmetryn	Propazine	Ametryn
Sample 1 (rice)	–	–	–	–	–	–	–	–	–	–
Sample 2 (rice)	–	–	23	–	8	–	–	18	–	8
Sample 3 (rice)	15	10	–	11	14	14	11	–	12	9
Sample 4 (rice)	–	–	–	–	–	–	–	–	–	–
Sample 5 (maize)	21	–	–	–	–	16	–	–	–	–
Sample 6 (maize)	–	7	–	21	–	–	8	–	24	–
Sample 7 (millet)	–	–	–	–	–	–	–	–	–	–
Sample 8 (millet)	28	–	6	–	–	21	–	–	–	–
Sample 9 (wheat)	–	–	–	–	–	–	–	–	–	–
Sample 10 (wheat)	–	–	–	–	–	–	–	–	–	–

Table 4
Comparisons of the proposed method with other methods used in the literatures.

Sample	Sample preparation	Total volume of organic solvent (mL)	Detection	LOD	LOQ	Recovery (%)	Precision (RSD, %)	Reference
Cereal-based food	Microwave-assisted extraction (10 min) → cooling (20 min) → evaporation → reconstitution → centrifugation (about 10 min)	20	LC–MS	No report	0.9–2.0 ng g^{-1}	66.2–88.6	≤12.62	[14]
Fruits and vegetables	Homogenizing (1 min) → centrifugation (10 min) → adding anhydrous $MgSO_4$ and PSA into the supernatant → vortexing (1 min) → centrifugation (5 min)	10	LC–MS	0.05–0.2 ng mL^{-1}	0.1–1 ng mL^{-1}	80–110	<10	[3]
Cereals and vegetables	Homogenizing → pre-extraction heating (5 min) → extraction and washing (21 min) → evaporation → reconstitution → SPE clean-up (10 min) → evaporation	65	Nonaqueous CE	10–15 ng g^{-1}	No report	87–114	10–15	[7]
Soil	Microwave-assisted extraction (4 min) → cooling (10 min) → filtering → evaporation at room temperature (an hour) → reconstitution → centrifugation (15 min)	53	LC-UV	0.16–0.3 μg mL^{-1}	0.5–1 μg mL^{-1}	83.3–96.3	<8	[4]
Soybean	Homogenizing (2 min) → shaking (30 min) → centrifugation (5 min) → shaking (30 min) → centrifugation (5 min) → evaporation (about 10 min) → reconstitution → SPE clean-up (10 min) → evaporation → reconstitution → filtering	90	LC-UV	No report	20 ng g^{-1}	71.9–101.9	2.2–10.7	[35]
			LC–MS	No report	5 ng g^{-1}	62.6–120.1	2.5–19.6	
Cereals	Dynamic microwave-assisted extraction (7 min) → adding NaCl into the extract → centrifugation (3 min) → cooling (5 min)	1.1	LC-UV	1.1–1.5 ng g^{-1}	3.5–4.8 ng g^{-1}	80–102	7–8	The proposed method

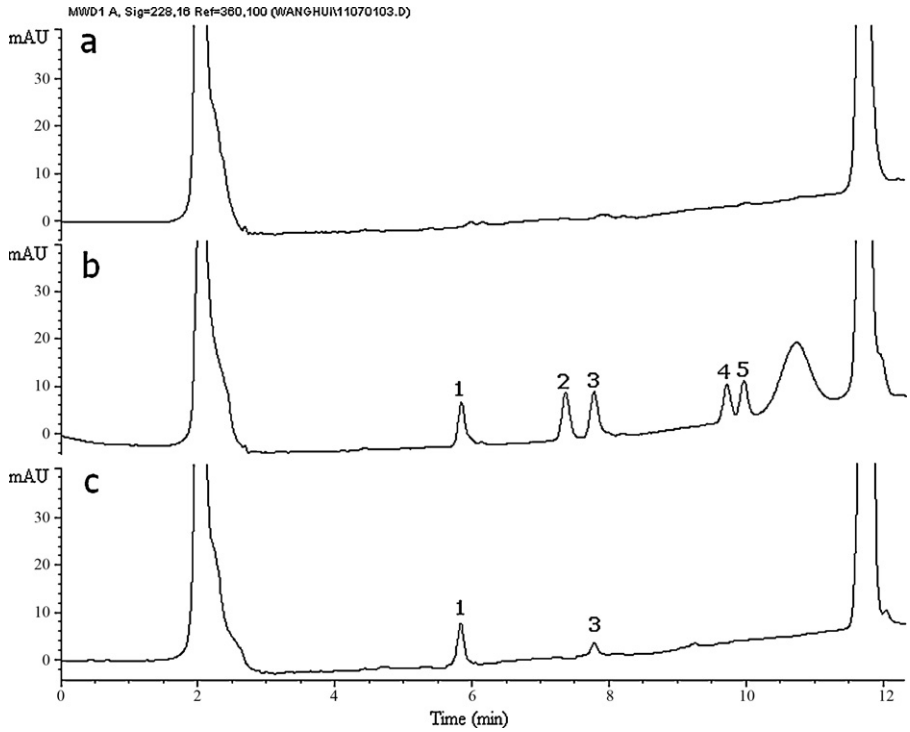

Fig. 5. Chromatograms were obtained by the analysis of the blank (a), spiked (25 ng g^{-1}) (b) and real (c) cereal sample (sample 8, millet). 1, simazine; 2, atrazine; 3, desmetryn; 4, propazine; 5, ametryn.

within 16 min, which suitable for analysis of trace triazine herbicides in the cereal samples.

4. Conclusions

This work has employed DMAE–SFO and HPLC for determination of triazine herbicides in cereals. The main benefits of the developed method were: minimum consumption of toxic organic solvent, simplification of sample treatment procedures and increase of sample throughput. Low cost, high enrichment factors and acceptable recoveries were achieved, and up to 15 samples can be treated simultaneously in 16 min. DMAE–SFO is an environmentally friendly technique and possesses the great potential for analysis of organic contaminants in solid samples.

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