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Rapid preparation of expanded graphite by microwave irradiation for the extraction of triazine herbicides in milk samples

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ABSTRACT

In this study, we proposed a rapid and efficient method for the preparation of the expanded graphite (EG). The exfoliation process was accelerated by microwave irradiation, and the preparation time was greatly shortened. The obtained EG was worm-like in shape and exhibits well exfoliated structure. It was successfully applied as solid-phase extraction (SPE) adsorbent to extract and clean up the triazine herbicides in milk, followed by liquid chromatography tandem mass spectrometry (LC–MS) analysis. The parameters affecting the performance of extraction and LC–MS analysis were evaluated. Under the optimal conditions, the detection limits of triazines are in the range of 0.03–0.12 ng mL^{-1}. At the spiked level (0.4 ng mL^{-1}), the recoveries of triazines are in the range of 82.5 ± 2.5% to 97.5 ± 7.5%. The proposed method was successfully applied to determine six triazines in six milk samples.

1. Introduction

Expanded graphite (EG) is a promising material. It has been used as adsorbent due to the abundant network pore structure (Cao, Shen, Wen, & Liu, 1996), which can increase the surface area of EG, and the introduction of intercalation compounds can improve the sorption capacity (Zhao, Zhou, Cao, Shen, & Zheng, 2002), especially for materials with large molecular size and weak polarity (Kang, Zheng, Wang, Nishi, & Inagaki, 2002). EG has been applied to remove heavy oil (Toyoda & Inagaki, 2000), methylene blue (Zhao & Liu, 2009) and DDT pesticides (Zhou, Wang, Kim, Li, & Yan, 2006). It is easy to insert atoms or molecules between the carbon layers in EG because the special porous structure and long distance between the carbon layers. Intercalation means organic or inorganic compounds enter into the graphite layer and form the graphite intercalation compounds (GICs). By inducing the vaporization or decomposition of the GICs, a significant expansion of the crystallographic c-axis will occur, and then porous EG can be obtained (Zhao & Liu, 2009). The vaporization or decomposition of the GICs will produce a thrust along the direction of *c*-axis of the graphite layer. Under the action of the thrust, the graphite layer will be pushed away and the interval between the layers will increase, which result in the volume increase. This is called exfoliation. In general, EG is prepared by rapid heating of GICs by flame/-muffle (Wei, Fan, Luo, Zheng, & Xie, 2008). However, the applications of microwave irradiation in the synthesis of EG were successively reported (Wei et al., 2008; Kwon, Choi, Park, & Kwon, 2003; Yu, Wu, Zhao, & Cheng, 2012; Zhao, Cheng, Wu, & Yu, 2014). Compared with the conventional heating method, microwave irradiation is more promising because it can be performed at room temperature in a short time with less consuming energy. Kwon OY et al. used microwave to prepare EG successfully, but the preparation of GIC is more than 5 h and the microwave treatment is 5 min (Kwon et al., 2003). Yu et al. prepared sulfur-free EG by microwave, however, the GICs were dried for 12 h (Yu et al., 2012). The GIC was prepared by mixing flake graphite, $KMnO_4$ and perchloric acid for 40 min and drying for 12 h by (Zhao et al., 2014). The intercalation time of the above methods is long. Therefore, in this work, we proposed a more rapid way to prepare EG by microwave. The intercalation and exfoliation of the precursors can be accomplished fast under microwave. The whole preparation process was accomplished in less than 4 min. And we use EG as SPE adsorbent to extract triazines in milk samples followed by LC–MS analysis.

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Prior to the LC–MS analysis, the pretreatment and clean-up steps are necessary due to the complexity of samples, such as milk samples. SPE has been applied for the pretreatment of milk (Guy, Royer, Mottier, Gremaud, Perisset, & Stadler, 2004; Alexiadou, Maragou, Thomaidis, Theodoridis, & Koupparis, 2008; Maragou, Lampi, Thomaidis, & Koupparis, 2006), which is an efficient and solvent-saving pretreatment method with many advantages, such as reducing of analysis time and organic solvent consumption (See, Sanagi, Ibrahim, & Naim, 2010). In SPE procedure, to obtain good recovery and reduce the interfering substances, the adsorbent is very important. To date, a lot of materials were developed as adsorbents in SPE for the pretreatment of milk, such as silica-based sorbents (Tsai, Huang, Huang, Hsue, & Chuang, 2009), molecularly imprinted polymers (MIPs) (Zheng, Gong, Zhao, Feng, 2010), graphene (Wang, Ma, Wu, Wang, & Wang, 2013), carbon nanotubes (Lu, Shen, Dai, & Zhang,2010) and nanoparticles (Chi, Liu, Guan, Zhang, & Han, 2010; Ma et al., 2013). Most adsorbents above are expensive and the preparations are time-consuming. Hence, it is necessary to develop a cheaper and more efficient adsorbent in SPE for the pretreatment of milk. Recently, EG was used as SPE adsorbent for the determination of trace levels of DDTs in water samples (Zhou et al., 2006) due to the high adsorption capacity, low cost and rapid preparation. To the best of our knowledge, this is the first time to use EG as SPE adsorbent for the pretreatment of milk followed by LC–MS analysis.

As reported, triazines have been extensively applied to provide pre- and post-emergence of grasses, crops and many weeds by inhibiting photosynthesis (Ma, Fu, Cai, & Jiang, 2003; Wang et al., 2010; Herranz, Ramón-Azcón, Benito-Peña, Marazuela, Marco, & Moreno-Bondi, 2008). The increasing use of triazines has effect on the directly treated plants and the entire food chain (Liu et al., 2014). And the presence of triazines residues in foodstuffs may lead to potential health risks to humans, such as cancers, birth defects and interruption of hormone functions (Li, Jin, et al., 2013; Li, Yang, et al., 2013). Therefore, in order to ensure food safety, the determination and monitoring of triazines residues in foodstuffs is essential and crucial.

In this study, a fast and simple method based on microwave irradiation was proposed for the preparation of EG. The obtained EG was successfully applied as SPE adsorbent to extract and clean up the triazines in milk, followed by the LC–MS/MS analysis. The properties of EG prepared were then evaluated and the predominant experimental factors affecting the recoveries were examined.

2. Experiment

2.1. Chemicals and materials

The standards (purity > 98%) of ametryn, atrazine, desmetryn, prometryn, propazine, simazine and pirimicarb were obtained from the Dr. Ehrenstorfer (Augsburg, Germany). Their chemical structures are shown in supplementary material. Acetonitrile (ACN) of chromatographic grade was obtained from Fisher (Pittsburgh, PA, USA). Methanol, ethanol, ACN of analytical grade, potassium permanganate ($KMnO_4$), H_2SO_4, H_3PO_4 and sodium hydroxide were purchased from Beijing Chemical (Beijing, China). Flaky graphite (FG) was obtained from Aoyu Company (Heilongjiang, China). High purity water with a resistivity of 18.2 MΩ cm was obtained from a Milli-Q water system (Millipore, Billerica, MA).

Stock standard solutions (500 μg mL^{-1}) of triazines were prepared in methanol and stored at −18 °C. A mixed stock solution (20 μg mL^{-1}) of six triazines was prepared by diluting individual stock solutions with methanol and stored at 4 °C in a dark glass bottle. The mixed solution should be replaced every two weeks. Working standard solutions were daily prepared by diluting the mixed solution with deionized water.

The milk samples were randomly purchased from the local market in Changchun (China). One milk sample was checked to be free of any triazines and used as blank milk sample. The spiked milk samples were obtained by adding certain amounts of triazine standard solutions to the blank milk samples.

2.2. The preparation of the EG

Firstly, FG (0.4 g), H_2SO_4 (0.652 mL), $KMnO_4$ (0.6 g) and H_3PO_4 (200 μL) were mixed by a glass bar in a beaker at room temperature for 3 min. Then, the beaker was directly placed into a domestic microwave oven (Midea China) and irradiated at 350 W for 30 s. Subsequently, the EG obtained was ground and washed thoroughly with water and alcohol several times until the solution became neutral. Finally, the powders obtained were dried at 80 °C.

2.3. Characterizations of the EG

X-ray diffraction (XRD) measurements (on a Rigaku D/max-2500 diffractometer with a graphite monochromator by using Cu Ka radiation operating at 200 mA and 40 kV) were employed to investigate the phase and structures of the FG and the synthesised EG. The morphology of EG was analyzed using the JSM-6700F SEM instrument (JEOL, Tokyo, Japan). The chemical function groups in the samples were analyzed by the Fourier-transform infrared spectrometry (FTIR 360, Nicolet, Madison, WI, USA) from 4000 to 500 cm^{-1}. The Brunauer–Emmet–Teller (BET) surface area and pore size distribution of the EG was measured using an auto N_2 absorption instrument (ASAP 2420, Micrometrics, USA).

2.4. The measure of expanded volume

The expanded volume was measured using a 50 ml graduated cylinder and the operation went as follows: EG was transferred into graduated cylinder lightly, then the volume (V) and quantity (m) of EG were recorded and the expanded volume was calculated by V/m (ml g^{-1}).

2.5. Sample preparation

To remove the protein which might affect the analysis of the triazines, the milk sample was deproteinized as follows: first, 15 % trichloroacetic acid (2 ml) aqueous solution was added to 5 mL of milk sample, which was diluted with 10 mL of distilled water previously. Then the sample was shaken for 30 s and centrifuged at 4500 rpm for 5 min. Finally, the supernatant (17 mL) was transferred and the pH was adjusted to 6 with 5% sodium hydroxide solution for further use.

2.6. Extraction procedure

The SPE column was prepared by packing 80 mg of EG into a 1 mL SPE cartridge. Two sieve plates were placed at the bottom end and the top end of the cartridge respectively in order to keep the sorbents steady. Prior to the sample loading, the cartridge was consecutively preconditioned with 3 mL of methanol (1.5 mL × 2) and 2 mL of deionized water. Subsequently, the supernatant obtained in Section 2.5 (about 17 mL) was passed through the cartridge. The cartridge was washed with 3 mL water, and then the analytes were eluted with 3 mL of ACN solution. Then the eluate was evaporated to dryness under nitrogen gas at 40 °C. The remaining residue was dissolved in 1.0 mL ACN and filtered through microfilters with a pore size of 0.22 μm for subsequent

LC–MS/MS analysis. The time of the whole extraction procedure was less than 15 min.

2.7. LC–MS/MS analysis

A Q-Trap MS (Applied Biosystems/MDS Sciex, Concord, ON, Canada) equipped with an electrospray ionization (ESI) source was connected to an Agilent 1100 liquid chromatograph (PaloAlto, CA). The separation of triazines was performed on an Aglient 1100 HPLC system equipped with an XTerra MS C_{18}. The mobile phase is ACN – water (65:35, v/v). The flow rate of mobile phase is 0.8 mL min^{-1} and the column temperature was kept at 40 °C. The mobile phase was split and then introduced into MS detector at the flow rate of 0.2 mL min^{-1}.

The ESI-MS/MS detection conditions were as follows: scan type, multiple reaction monitoring (MRM); ionization mode, positive; curtain gas, N_2 (30 psi); collision gas, N_2 (medium); gas 1, N_2 (55 psi); gas 2, N_2 (50 psi); ion spray voltage, 4500 V; source temperature, 400 °C. The results of the precursor ion, product ion, and corresponding declustering potential (DP), entrance potential (EP), collision energy (CE), collision cell entrance potential (CEP) and collision cell exit potential (CXP) are shown in supplementary material.

3. Results and discussion

3.1. The preparation of the EG

When the microwave power is more than 350 W or the microwave time is more than 30 s, the preparation process will be accompanied by fuming and lightening, which is not safe enough. On the other hand, when the microwave power or the microwave time is less, the expanded volume of the EG will be reduced, even the exfoliation will not occur. Therefore, the preparation of EG is accomplished in 30 s under 350 W microwave power, which is safe and the expanded volume of EG is satisfactory.

During the preparation of EG, $KMnO_4$ was used as oxidizing agent while H_2SO_4 and H_3PO_4 were used as intercalating agents and provide acidity to promote the oxidation ability of $KMnO_4$. The amount of FG, H_2SO_4 and $KMnO_4$ has been investigated.

The exfoliation volume was determined by measuring the volume of EG prepared from 0.4 g FG. The maximum expanded volume (70 mL g^{-1}) is obtained for No. 7 in Table 1.

When the ratio of m (H_2SO_4) increased, more H_2SO_4 was intercalated into the gallery of FG which resulted in that the expanded volume would be larger (Nos.1–4 in Table 1). However, excess H_2SO_4 could decrease the expanded volume (No. 5 in Table 1), which may result from that the acidity have effect on the oxidation ability of $KMnO_4$ (Wei et al., 2008). On the other hand, the oxidation ability of $KMnO_4$ has relation with its concentration. Therefore, the expanded volume increased with the increasing of the amount of $KMnO_4$ (No. 6, No. 4 and No. 7 in Table 1). When the m ($KMnO_4$) is less than 0.2 g, there is no expansion (No. 6 in Table 1). Strong oxidation of superfluous $KMnO_4$ would damage the structure of the graphite layers (No. 8 and No. 9 in Table 1) (Avdeev, Monyakina, Nikol'skaya, Sorokina, & Semenenko, 1992).

Table 1
Expanded volume of the EG prepared.

Nos.	m(FG): m(H_2SO_4): m($KMnO_4$)	Expanded volume (mL g^{-1})
1	1:1:1	17
2	1:2:1	35
3	1:2.5:1	37
4	1:3:1	38
5	1:3.5:1	29
6	1:3:0.5	–
7	1:3:1.5	70
8	1:3:2	51
9	1:3:3	29

Due to the volume of H_3PO_4 added in the EG preparation procedure was small, it didn't have too much effect on the expanded volume of EG. However, in the experiment, we found that the volume of H_3PO_4 added during the preparation of EG had effect on the recoveries of triazines. As shown in Fig. 2a, the recoveries increased until the volume of H_3PO_4 is 200 μL, further increasing the volume of H_3PO_4, the recoveries decreased. That could be attributed to the fact that the co-intercalation of H_2SO_4 and H_3PO_4 can provide more function groups which is favorable for the combination between the analytes and the adsorbent. Also, H_2SO_4 and H_3PO_4 can improve the efficiency of the oxidation process (Marcano, Kosynkin, Berlin, Sinitskii, & Sun, 2010). However, when the volume of H_3PO_4 is more than 200 μL, strong oxidation would damage the structure of the graphite layers, which might affect the intercalation and extraction. Therefore, we added 200 μL H_3PO_4 during the preparation process.

3.2. Characterization of the EG

The phase and structures of FG and the synthesised EG were investigated by XRD. As shown in Fig. 1a, the FG showed a strong peak at $2\theta = 26.60°$, which was resulted from the diffraction of 002 planes. After the intercalation and microwave treatment, the XRD pattern of the synthesised EG shows a broad peak at $2\theta = 26.66°$ (Fig. 1b), corresponding to the reflection of EG.

The SEM images of FG and the synthesised EG are shown in Fig. 1(c–f). It can be clearly seen that the surface of FG is smooth in Fig. 1c and Fig. 1d. After microwave, the lamellar structure of FG was transformed to a vermicular structure by expansion along the c-axis of graphite crystal. The morphology of EG is worm-like and exhibits well exfoliated structure as shown in Fig. 1e and f. Therefore, it is expected that the EG might have a greater surface for adsorption.

The FTIR spectrum of FG (g) and EG (h) in Fig. 1 illustrated their structures. The peaks at about 1716 cm^{-1} and 1174 cm^{-1} represent the C=O stretch vibration and C–O–C stretch vibration, respectively. The peaks at 1286 cm^{-1} and 1068 cm^{-1} correspond to the stretch vibration of S=O and P–O asymmetric stretch vibration. The characteristic peaks at 2917 cm^{-1} is related to $-CH_3$ stretch vibration.

In order to investigate the absorbability of the prepared EG, its BET surface area and pore size distribution were measured. The measurement results showed that the BET surface area of the expanded graphite was 18.975 $m^2 g^{-1}$ The pore size distribution of EG is shown in Fig. 1i. The prepared EG had a wide pore size distribution, which mainly consisted of mesopores and macropores. Organic compounds are easily absorbed into mesopores and macropores of EG (Zhang & Fang, 2006). It is advantageous for the rapid establishment of adsorption equilibrium. Therefore, the prepared EG had a high sorption capacity and can be used as a good adsorbent.

3.3. Optimization of the extraction conditions

After removing the protein of milk sample, diluting with distilled water and adjusting the pH, the sample (about 17 mL) was used for SPE procedure. The extraction conditions were optimized by analyzing spiked milk samples (2 μg mL^{-1}), using EG as adsorbents. The parameters affecting the performance of the extraction, such as the amount of EG, pH of diluted milk samples, washing solvent and desorption conditions were investigated and optimized. When one parameter was changed, the other parameters were fixed at their optimal values.

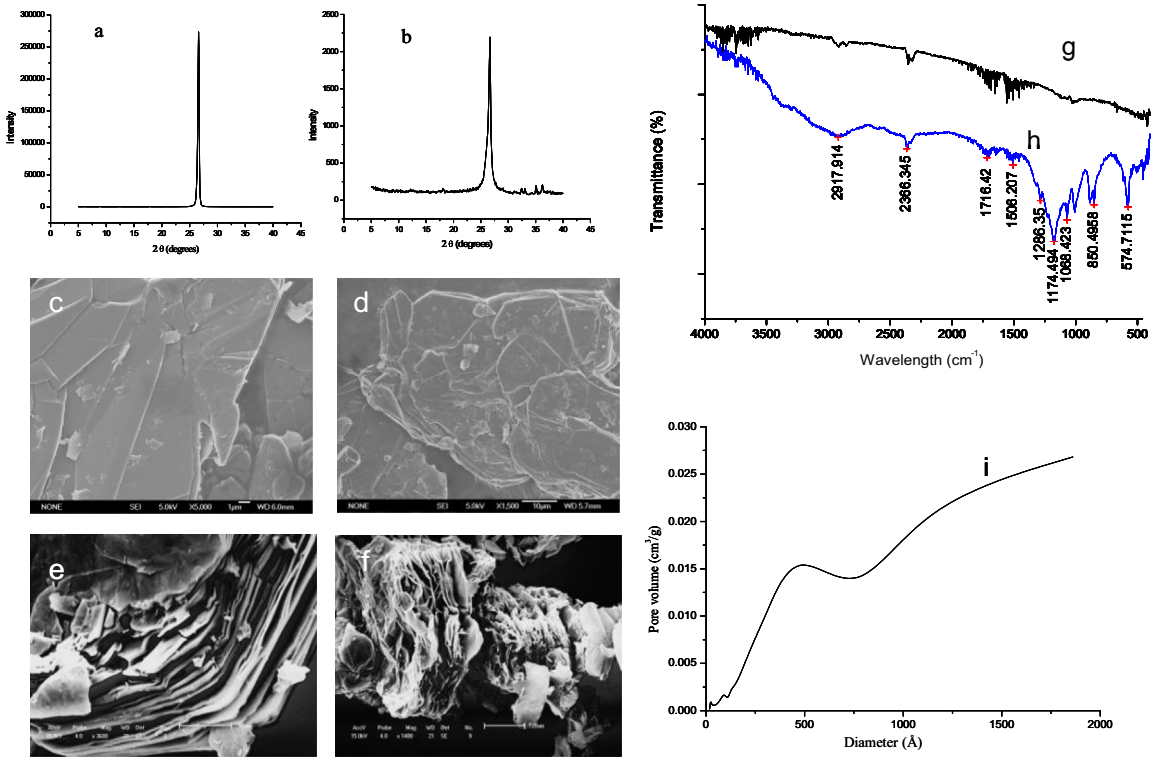

Fig. 1. Characterization of the EG: XRD patterns of FG (a) and EG (b); SEM images of FG (c, d) and EG (e, f); FT-IR spectras of FG (g) and EG (h); Pore size distribution of EG (i).

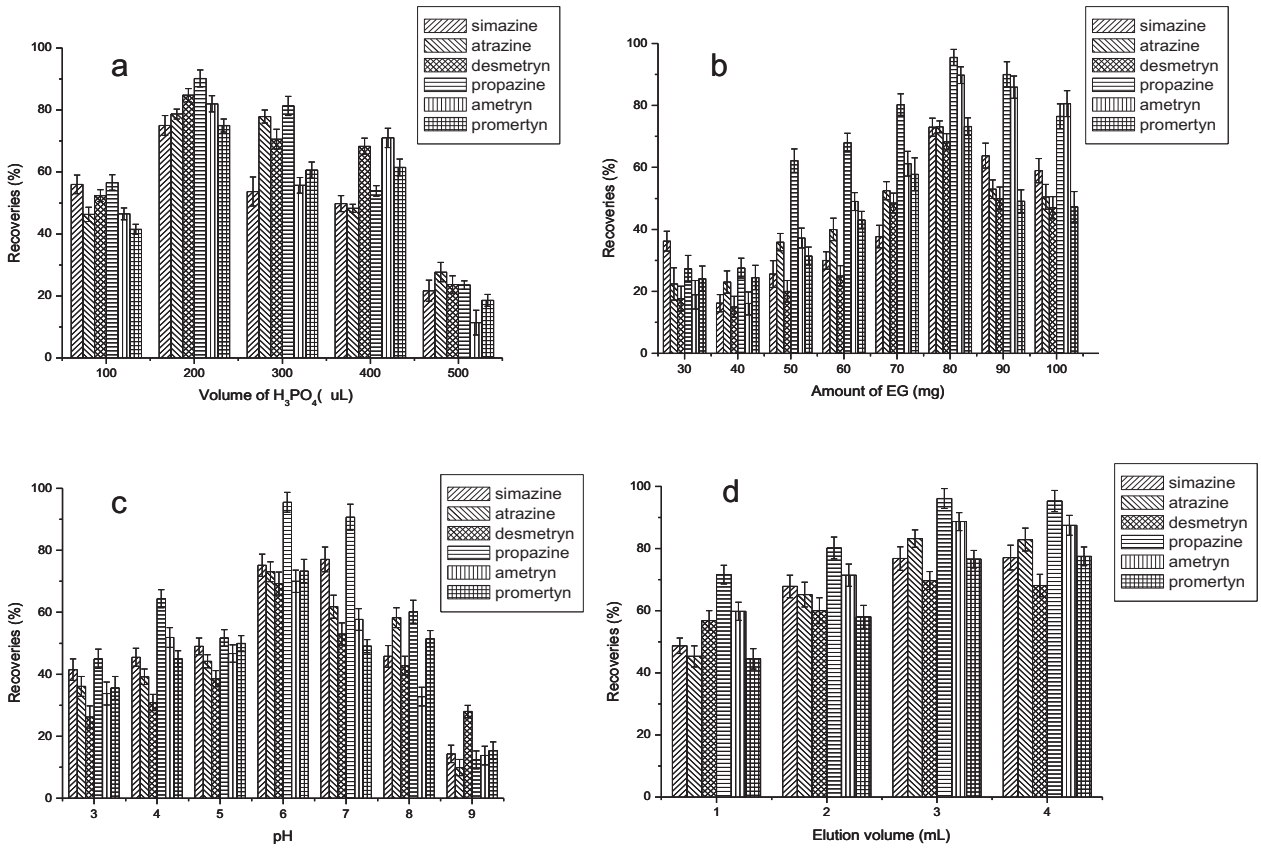

Fig. 2. (a) Effect of volume of H_3PO_4 on the recoveries of triazines. (b) Effect of amount of EG on the recoveries of triazines. (c) Effect of pH on the recoveries of triazines. (d) Effect of elution volume on the recoveries of triazines.

3.3.1. The EG amount in SPE cartridge

Different EG amounts ranging from 30 mg to 100 mg were packed in SPE cartridge to evaluate the adsorption efficiency. It was demonstrated in Fig. 2b that 80 mg was enough to extract triazines with the recoveries from 73.0% to 95.5%. The recoveries increased with the increasing of the EG amount from 30 to 80 mg, further increasing the amount of EG gave no significant improvement for the recoveries. On the contrary, excessive amount of EG require more organic solvents for elution which make the sample pretreatment more time-consuming. Therefore, 80 mg was selected as the final amount of adsorbents used in the following studies.

3.3.2. Sample pH

The sample pH is one of the important influencing factors on the recoveries of triazines. Different sample pH (3–9) was investigated for the extraction of triazines from milk samples. As shown in Fig. 2c, with the pH increasing, the recoveries of triazines rose until the pH was 6 and then it showed a downward trend. That may be attributed to that under acidic condition, the triazines (pKa 1.65–4.1) will be protonated. The protonated triazines could interact with the acidic groups, such as $-SO_3H$ and –COOH on the surface of EG by weak ion exchange, which was favorable for improving the recoveries of triazines. However, strongly acidic environment was not in favor of the weak ion exchange and also would lead to the hydrolysis of trazines. When the sample pH was 6, it was suitable for the weak ion exchange. Besides, there also exist π–π interactions between the groups of the analytes and carbon layers of EG, which is favorable for the adsorption of triazines. When the alkalinity is high, the surface of EG would be modified by alkaline ion, which might result in a weak interaction between target analytes and the adsorbents. Therefore, the solution pH of 6 was selected for the next studies.

3.3.3. The washing solution

Milk is a complicated biological sample. Hence, a wash step after the loading step is necessary to remove the interfering compounds. In the work, 3.0 mL different solutions including water, methanol aqueous solution (10%, 20%, 30%) and acetonitrile aqueous solution (10%, 20%, 30%) was evaluated as washing solvent. The washing efficiencies were evaluated by HPLC. The use of water can save organic solvents and the results showed that the interfering compounds can be removed. Also, the satisfactory recoveries of the triazines (83.2–95.4%) were obtained using 3.0 mL water as the washing solution, which indicated that water didn't result in loss of the analytes.

3.3.4. Elution solutions and volume

A series of elution solutions, such as methanol, ethanol and ACN were evaluated to obtain the recoveries of triazines. The experimental results indicated that the best recoveries of triazines (76.4–96.2%) were obtained using ACN as elution solutions.

Different volume of the eluting solution ranging from 1 mL to 4 mL was investigated. As shown in Fig. 2d, the recoveries increased with the increasing of the eluting solution volume from 1 to 3 mL, further increasing the eluting solution volume gave no obvious improvement for the recoveries. In conclusion, 3 mL ACN solution was selected as the eluting solution.

3.4. Evaluation of the method performance

3.4.1. Matrix effect

Matrix effects could greatly influence the accuracy of LC–MS/MS, which will lead to the suppression or enhancement of the signal. In order to evaluate the matrix effects, we compared the calibration curves of solvent and blank milk sample extract in the studied concentration range (0.2–100 ng mL^{-1} for simazine, atrazine, desmetryn and propazine, 0.39–100 ng mL^{-1} for ametryn and prometryn). The results showed that the matrix effects of the proposed method had signal enhancement (3.4% - 10.7%) for triazines. Therefore, in order to decrease the error resulted from the matrix effects, the matrix-matched calibration curves in this work were used for quantification of the triazines in milk samples.

3.4.2. Linearity and limit of detection

The linear range of the calibration curves were investigated by analyzing spiked milk samples. It showed good linearity. The data of correlation coefficient were showed in Table 2.

Limit of detection (LOD) and limit of quantification (LOQ) are considered as the analyte minimum concentrations which can be identified and quantified by the method. The LODs and LOQs were estimated as the analyte concentration producing signal/noise ratio of 3:1 and 10:1, respectively. The LODs and LOQs of the proposed method for six triazines were in the range of 0.03–0.12 ng mL^{-1} and 0.09–0.39 ng mL^{-1} (Table 2).

3.4.3. Precision and recovery

The precision of this method was evaluated by measuring intra- and inter-day relative standard deviations (RSDs) in this experiment. The intra-day RSD was performed by analyzing spiked milk samples six times in one day at three different fortified concentrations of 0.5, 5, and 50 ng mL^{-1}. The inter-day RSD was performed by analyzing spiked milk samples for six consecutive days at three different concentrations of 0.5, 5, and 50 ng mL^{-1}. The intra- and inter-day RSDs obtained were in the range of 2.2–5.6 % and 2.4–7.3 %, respectively. The results are shown in Table 3. At all fortified levels, the recoveries of triazines were in the range of 83.2–97.1%.

3.5. Application of the proposed method

To demonstrate the applicability of the proposed method, six different milk samples from local market in Changchun (China) were simultaneously analyzed by the proposed method. The triazines were detectable in two samples (shown in supplementary material). To further evaluate the accuracy and applicability of the proposed method, the recoveries of triazines were then carried out with adding the triazines standards to the six milk samples at the level of 0.4 ng mL^{-1} (shown in supplementary material). Satisfactory results of the recoveries were obtained which indicated that the proposed method was applicable for the detection of triazines in different milk samples.

The proposed method was compared with the methods used in the literatures for analyzing triazines in milk samples (Table 4). It was confirmed that the proposed method was simpler and less time-consuming. Table 4 shown that compared with the methods detected triazines using LC–UV, the proposed method could provide lower LOD and LOQ, lower or similar RSD and higher or similar recoveries. Besides, compared with the methods detected triazines using GC–MS, the samples didn't need to be derived and the operation of the proposed method was more time-saving. Also, the

Table 2
Validation of the method.

	Linearity range (ng mL^{-1})	Correlation coefficient	LODs (ng mL^{-1})	LOQs (ng mL^{-1})
Simazine	0.20–100	0.9945	0.03	0.09
Atrazine	0.20–100	0.9992	0.06	0.20
Desmetryn	0.20–100	0.9997	0.06	0.20
Propazine	0.20–100	0.9931	0.05	0.18
Ametryn	0.39–100	0.9969	0.09	0.29
Prometryn	0.39–100	0.9987	0.12	0.39

Table 3
Intra- and inter-day precisions and recoveries of the method ($n = 6$).

Analytes	Intra-day precision (%)						Inter-day precision (%)					
	0.5 ng mL^{-1}		5 ng mL^{-1}		50 ng mL^{-1}		0.5 ng mL^{-1}		5 ng mL^{-1}		50 ng mL^{-1}	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
Ametryn	90.4	3.2	92.7	4.1	96.7	2.8	91.3	7.3	93.7	4.0	96.4	2.4
Atrazine	92.2	5.3	91.9	3.6	92.5	3.2	88.5	6.2	93.2	4.5	96.8	4.1
Desmetryn	90.2	3.3	93.2	4.3	95.4	3.2	90.4	4.3	93.8	5.2	93.5	5.0
Prometryn	88.4	4.7	94.4	2.9	96.5	2.2	90.1	4.5	94.5	3.8	97.1	4.2
Propazine	89.7	5.6	91.6	3.6	93.1	2.6	89.9	6.7	91.6	4.1	94.4	3.6
Simazine	84.2	4.1	85.4	3.8	87.4	3.4	83.2	5.6	84.3	4.6	85.9	3.5

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

Sample preparation time	Total volume of organic solvent	Detection	LOD	LOQ	Recovery (%)	Precision (RSD, %)	Reference
Several minutes for diluting + 10 min for shaking + 5 min for centrifugation + several tens minutes for diluting and filtering (>20 min)	>1.5 mL	LC–UV	2.1–2.8 (μg L^{-1})	6.9–9.4 (μg L^{-1})	86.3–120.6	<7.9	Yang et.al. (2014)
40 min for HFM-SPME + 5 or 10 min for homogeneity (about 50 min)	No report	GC–MS	0.003–0.013 (μg L^{-1})	0.006–0.021 (μg L^{-1})	57–107	4.3–12.37	Basheer and Lee (2004)
Several minutes for de-emulsification + 10 min for centrifugation + 30 min for incubating + 5 min for centrifugation (>45 min)	>2 mL (No details)	LC–UV	6.79–11.19 (μg L^{-1})	22.6–37.3 (μg L^{-1})	70.5–96.9	1.41–5.99	Liu et.al. (2014)
Several tens minutes for GCB SPE precondition and extraction + several minutes for washing + 3 min for drying (>30 min)	15 mL	GC–MS	No report	No report	58.64–63.22	1.01–4.75	Balduini et.al. (2003)
2 min for column precondition + 5 min for extraction + 1 min for clean-up + 1 min for elution + evaporation (<15 min)	6 mL	LC–MS	0.03–0.12 (ng mL^{-1})	0.09–0.39 (ng mL^{-1})	82.5–97.5	2.2–7.3	The proposed method

recoveries obtained were satisfactory. The consumption of organic solvent was not particularly much, which was environment-friendly. The sample preparation time used in the proposed method was very short, which were suitable for the rapid analysis of triazines in milk samples. Moreover, the extraction and enrichment were completed in one step in this study, therefore the pretreatment procedure was simple.

4. Conclusions

In this work, EG were prepared by microwave irradiation. The preparation process was accomplished in less than 4 min. The obtained product showed worm-like morphology and exhibited high adsorption capacity for triazines. The SPE based on EG was established and applied for the determination of the triazines in milk. Good recoveries and precisions of this method were obtained which indicates that this method has high analytical potential for the preconcentration of organic pollutants.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2015.11.056.

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