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Magnetic solid-phase extraction based on graphene oxide for the determination of lignans in sesame oil

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ABSTRACT

Graphene oxide was fabricated by a simple method and applied to magnetic solid-phase extraction. In a pretreatment procedure before the sesamol, sesamin and sesamolin in sesame oil were detected by high performance liquid chromatography. Several parameters affecting the extraction efficiency were investigated, including the type and volume of desorption solvent, desorption time and the amount of sorbent. Under the optimized conditions, the detection limits of sesamol, sesamin, and sesamolin were 0.05 μg/g, 0.02 μg/g, and 0.02 μg/g, respectively. The limits of quantification were all 0.2 μg/g. The average recoveries of sesamol, sesamin, and sesamolin were 84.55%, 85.47%, 86.83%, respectively and their relative standard deviations were 1.23%, 1.33%, and 0.84%, respectively.

1. Introduction

Sesame seeds were regarded as a healthy food containing lignans such as sesamol, sesamin and sesamolin, which improve the stability of sesame oil (Huang, Song, Sun, & Bao, 2011; Namiki, 1995; Zhang, Li, Wang, & Wang, 2005). Studies showed that the lignans in sesame oil had many physiological functions, such as alcohol metabolism promotion, lipid metabolism regulation, anticancer function, anti-mutation and liver protection (Hemalatha, Raghunath, & Ghafoorunissa, 2004; Kushiro, Masaoka, Hageshita, Akahashi, & Sugano, 2002; Ren, Yuan, Ling, & Li, 2012). The contents and types of lignan in sesame oil are not only an important index for evaluating sesame oil quality, but also a basis for determining high quality sesame varieties.

To eliminate the influence of lipid components on oil samples in the process of detecting lignans in sesame oil, pretreatment of oil samples is a key step. Solid phase extraction (Chen et al., 2012; Li & Zeng, 2011), liquid-liquid extraction (Rangkadilok et al., 2010; Reshma et al., 2010), thin layer chromatography (Kamal-Eldin, Yousif, & Appelqvist, 1991; Zhao, 2005), and saponification (Xue et al., 2006) are the main pretreatment methods. However, those methods have some disadvantages including high complexity, low sensitivity, and a long processing cycle. In recent years, magnetic solid phase extraction (MSPE) has received wide attention in the sample preparation field (He, Liu, Li, Zhou, & Wang, 2012; Mehdinia, Roohi, & Jabbari, 2011; Qin, Fang, & Luo, 2011; Wang, Huang, Yu, Wang, & Shen, 2013), as the sample treatment is simple with the magnetic extraction medium directly dispersed in the sample solution. It is especially suitable for samples containing suspended solids and biological samples (Huang, Ding, & Feng, 2012).

Graphene oxide is an important derivative of graphene with a similar structure, which is composed of carbon atoms in the single-atom layer of a sp^2 hybrid connection. The basic unit of graphene is the most stable structure of a hexatomic ring in organic materials (Dai, Shao, Ma, & Pei, 2010). In this study, few-layer graphene oxide and hydroxylated Fe_3O_4 were combined and after sesame oil was pretreated by MSPE in combination with the liquid chromatography (LC) technology, a detection method was established for sesamol, sesamin and sesamolin in sesame oil. This method is fast and simple and has a good application prospect in detection of main lignans in sesame oil.

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2. Experimental section

2.1. Instruments and reagents

Sesamol, sesamin and sesamolin were analyzed on Agilent 1200 high performance liquid chromatography (HPLC) system (Agilent Technologies, Santa Clara, CA) equipped with a diode array detector (DAD). Flake graphite of spectroscopically pure was obtained from Beijing DK Nano Technology Co., Ltd. $FeCl_3$-$6H_2O$ and sodium acetate were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethylene glycol, ethylenediamine, sulfuric acid (98%), potassium permanganate, dimethyl sulfoxide, dichloromethane, ethanol, acetonitrile, methanol, and hydrogen peroxide were obtained from Sinopharm Chemical Reagent Co., Ltd. Sesamol (purity 99%) was supplied by Nanjing Ze Lang Pharmaceutical Technology Co., Ltd. Sesamin and sesamolin spiked substances (99% purity) were obtained from China standard material network. All solvents used were of HPLC grade, unless otherwise specified. Sesame oil samples were purchased from local markets in Wuhan (China).

2.2. Methods

2.2.1. Preparation of hydroxylated Fe_3O_4 magnetite nanoparticles (MNPs)

Monodisperse Fe_3O_4 MNPs with mesoporous structure were synthesized via a solvothermal process according to a previously reported method (Wei et al., 2013). In Brief, after 5 g $FeCl_3{\cdot}6H_2O$ was completely dissolved in 100 mL ethylene glycol, 15 g sodium acetate and 50 mL of ethylenediamine were added and vortex stirred for 30 min before reaction in a Teflon-lined stainless steel autoclave (200 mL) for 8 h under 200 °C. The product was washed with 50 mL of water/ethanol (1:1, v/v) five times and vacuum-dried at 60 °C for 6 h.

2.2.2. Preparation of graphene oxide

The synthesis of graphene oxide was performed using $KMnO_4$ and a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 as oxidizing agents according to the method reported by Marcano and coworkers (Marcano et al., 2010). Briefly, 3.0 g of flake graphite was added to 400 mL of mixture of sulfuric acid and phosphoric acid (volume ratio 9:1). After stirring for 10 min, 18.0 g of potassium permanganate was added into the mixture. Potassium permanganate was added slowly in case of the reaction temperature exceeded 20 °C. Then the mixture was heated to 50 °C and stirred for 12 h. After the reaction was completed, the mixture was cooled to room temperature, and 400 mL of ice water was poured in and stirred continuously for half an hour. Then, 30% hydrogen peroxide was added dropwise into the reaction system until the solution turned into bright yellow. The mixture was kept overnight and then the supernatant was discarded. The solution was washed with 1 L 5–10% hydrochloric acid three times and with 1 L of deionized water five times so as to remove metal ions, sulfate and chloride ions. Finally, the solid was freezing dried and then placed in deionized water for preparation of 1 mg/mL water solution. Later it was ultrasonic for 1 h. When oxidized graphene was dissociated into graphene oxide, the solution was centrifuged for 30 min at 1000 rpm and then the supernatant was removed. The sediment was then dried at 50 °C and the graphene oxide powder was obtained.

2.2.3. Synthesis of magnetic graphene oxide

The synthesis of magnetic graphene oxide was performed according to the method reported by Ding et al. (2011) and Luo, Shi, Gao, and Feng (2011). After 0.1 g of hydroxylation Fe_3O_4 MNPs and 0.04 g of graphene oxide were mixed by 40 mL of dimethyl sulfoxide, the mixture was ultrasonic treated in a water bath for 30 min at room temperature. Then, materials were obtained and the enrichment concentrations became 3.5 mg/mL.

2.2.4. Sample extraction process

2.2.4.1. Magnetic solid-phase extraction. Sesame oil of 0.1 g was added into a test tube (10 mL), in which 4 mL dichloromethane was mixed, vortexed and dissolved. Then, 1.4 mg magnetic graphene oxide was added and vortexed intensively for 3 min. Sesamol, sesamin and sesamolin were adsorbed onto the surface of magnetic graphene oxide. And then an external magnetic field was applied at the bottom of the tube to gather adsorption agents before the supernatant was discarded. After cleanup by 1 mL dichloromethane solution, the supernatant was removed by the magnetic field. Later, 1.7 mL methanol was added into the remaining precipitate and vortex-shaken for 1.5 min for desorption. They were then separated by the external magnetic field, and the supernatant was collected for HPLC analysis.

2.2.4.2. Saponification method. The saponification method in previous literatures were used (Xue et al., 2006). The oil was extracted from the prepared sesame seeds with hexanes for 4–5 h in a Soxhlet apparatus. The organic solvent was removed from the extract under vacuum using a water bath. Sodium hydroxide (1 g) dissolved in distilled water (5 mL) and pure ethanol (10 mL) were added into the oil sample (0.5 g). The mixture was stirred for 30 min at 80 °C and then extracted trice by petroleum ether (100 mL). The solvent was removed from emerged extracts under vacuum using rotary evaporation. Finally, the concentrate was suspended in 50 mL of methanol.

2.2.4.3. Alumina column chromatography method. Alumina column chromatography was referred to previously published literature (Liu, Wang, & Jin, 2004). Alumina used for chromatography was activated at the temperature of 190 °C. After the activated alumina was added into the column which contained a certain amount of petroleum ether, the column was washed twice by elution solution for column equilibrium. Sesame oil sample (5 g) dissolved by petroleum ether was applied to a chromatographic column packed with alumina and eluted first with 100 mL of petroleum ether, and then 150 mL of ethyl acetate. The eluate was collected and vacuum evaporated to remove the adsorbed solvent. Then it was diluted by 50 mL of acetone for HPLC analysis.

2.2.5. Liquid chromatography conditions

Chromatographic separation was performed on a Kromasil C-18 column: (4.6 mm × 150 mm, 5 μm) with a methanol water (75:25, V/V) mobile phase at a flow rate of 0.8 mL/min and the injection volume was 20 μL. UV detection wavelength was 290 nm.

3. Results and discussion

3.1. Optimization of extraction conditions

3.1.1. Types of desorption solvents

Different amounts of sesamol, sesame and sesamolin standards were added into sesame oil of known contents, each gram of which contained 0.030 mg of sesamol, 0.025 mg of sesamin and 0.030 mg of sesamolin. According to the sample extraction method described in Section 2.2.4, the sesamol, sesamin and sesamolin recoveries were respectively determined when the desorption solvents were pure methanol, acetonitrile and ethanol. Each level of extraction condition was measured 4 times and their average were separately obtained. The calculation formula was as follows:

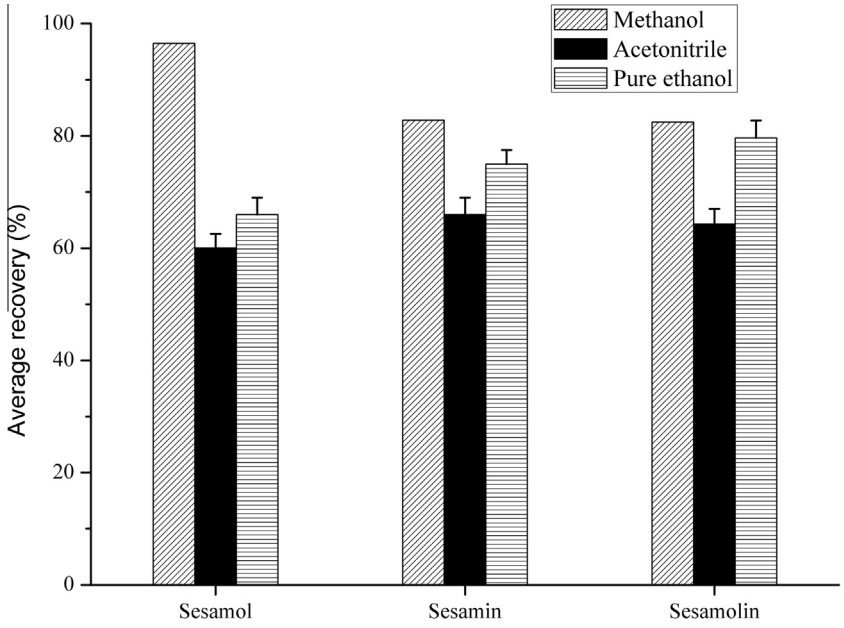

Fig. 1. The effects of the desorption solvents on extraction efficiency.

$$Recovery = \frac{observed\ value - background}{addition\ amount} \times 100\%$$

As shown in Fig. 2, for those three kinds of desorption solvents, the desorption effects were arranged in a descending order: methanol > ethanol > acetonitrile. Therefore, pure methanol was selected as the desorption solvent (Fig. 1).

3.1.2. Volume of the desorption solvent

According to the spiked amounts in the background, when methanol was used as the desorption solvent, the recoveries of sesamol, sesamin and sesamolin were determined when the volumes of methanol were 0.5, 0.7, 1.0, 1.5, 1.7 and 2.0 mL, respectively. The recoveries of sesamol, sesamin and sesamolin became higher with the solvent volume increase and almost reached the maximum when the volume was 1.7 mL, and the average recoveries varied insignificantly when the volume was further increased. Therefore, 1.7 mL was the optimal volume of the desorption solvent, as shown in Fig. 2.

3.1.3. Content of the adsorbents

The concentration of the prepared magnetic graphene oxide was 3.5 mg/mL. According to the spiked amount in Section 3.1.1 and sample extraction method in Section 2.2.4, 0.35 mg (100 μL), 0.70 mg (200 μL), 1.4 mg (400 μL), 1.75 mg (500 μL) and 2.1 mg (600 μL) adsorbents were added respectively. The results showed that the average recoveries of sesamin and sesamolin increased when the adsorbent content was less than 1.4 mg and decreased when the adsorbent content was more than 1.4 mg. When the content was 1.4 mg, the recoveries of sesamin and sesamolin reached the maximum although that of sesamol was not the highest. The optimal content of the adsorbent was selected as 1.4 mg, as illustrated in Fig. 3.

3.1.4. Desorption time

According to the spiked amounts in Section 3.1.1 and sample extraction method in Section 2.2.4, average recoveries of sesamol, sesamin and sesamolin were determined when the desorption

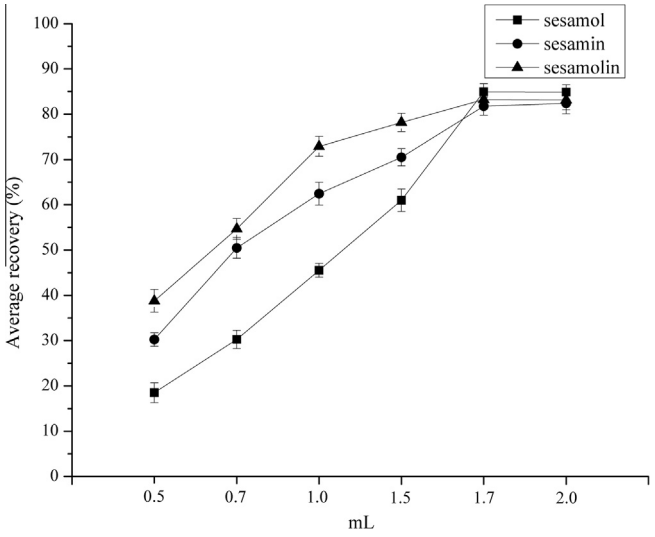

Fig. 2. The effects of the desorption volumes on extraction efficiency.

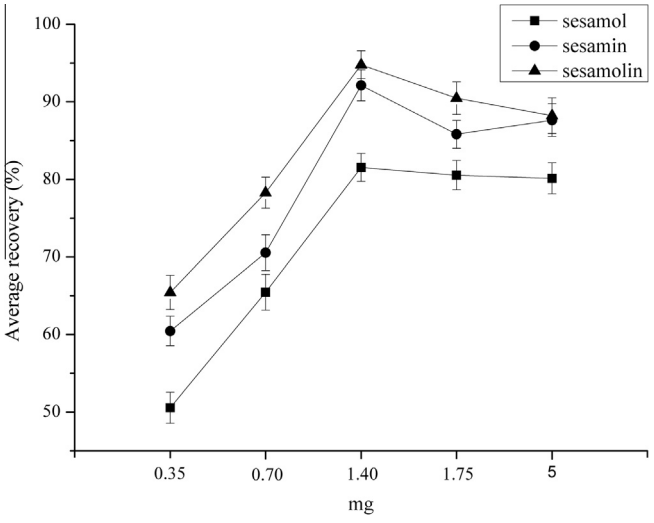

Fig. 3. The effects of magnetic graphene oxide amounts on extraction efficiency.

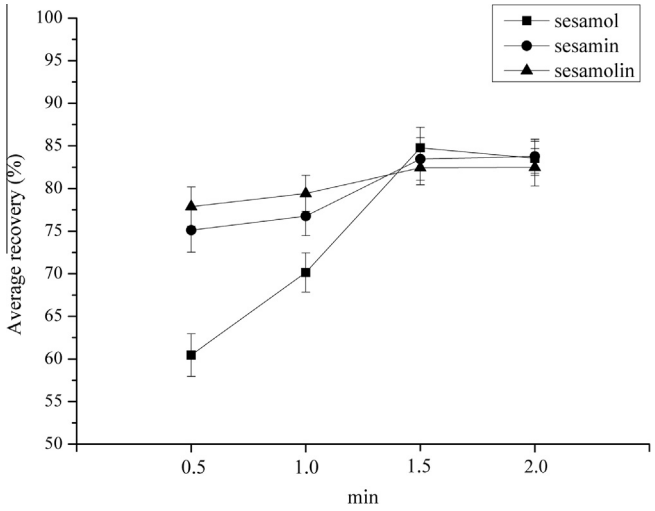

Fig. 4. The effects of desorption time on extraction efficiency.

time was 0.5, 1, 1.5 and 2.0 min, respectively. The results showed that the average recoveries of sesamol, sesamin and sesamolin reached their maximum when the desorption time was 1.5 min, and the average recoveries varied insignificantly when the desorption time further increased. To shorten the detection time, 1.5 min was selected as the optimal desorption time, which was shown in Fig. 4.

3.2. Linear range, quantitative limit and detection limit of the method

The mixed standard solution with a concentration of 50 μg/mL was prepared by 200 μg/mL sesamol, 200 μg/mL sesamin and 200 μg/mL sesamolin. It was further diluted with methanol, and mixed standard solutions were obtained until a series of concentrations of 50, 25, 12.5, 6.25, 3.125 and 1.5625 μg/mL. The standard curve was established with the peak area (Y) as the vertical coordinate and concentration (X) as the horizontal coordinate. The coefficients of correlation (R^2) were higher than 0.99994. The limit of detection (LOD) of the sample was determined by a signal-to-noise ratio (S/N) of 3, and the limit of quantity (LOQ) was determined by the concentration at which standards were diluted until an obvious computable peak appeared. The linear regression equation, correlation coefficient (R^2), LOD and LOQ of sesamol, sesamin and sesamolin were shown in Table 1. The results showed that the LODs and LOQs of the three target lignans ranged from 0.02 to 0.05 μg/g and 0.2 μg/g, respectively. The relative differences in LOD and LOQ of the different lignans may be attributed to the different interactions between the different lignans and the Fe_3O_4 MNPs and the different responses of the different lignans with HPLC-DAD. Additionally, the present method consumed a relatively small amount of extraction sorbent.

Table 1
Calibration curves, LOD and LOQ of the sesamol, sesamin and sesamolin.

Analytes	Regression equation	Correlation coefficient (R^2)	LOD (S/N = 3) (mg/g)	LOQ (mg/g)
Sesamol	Y = 11.5271X-1.4287	0.99994	0.05	0.20
Sesamin	Y = 16.1252X-3.1278	0.99996	0.02	0.20
Sesamolin	Y = 10.7254X-1.7709	0.99996	0.02	0.20

Table 2
Spiked recoveries and RSDs of the sesamol, sesamin and sesamolin in sesame oil.

Analytes	Spiked amount (mg/g)	Recovery (%)				Average recovery (%)	RSD (%, n = 4)
		1	2	3	4		
Sesamol	0.14	82.15%	85.26%	83.78%	85.74%	84.23%	1.92
	0.35	83.23%	82.25%	84.12%	81.21%	82.70%	1.52
	0.56	84.79%	85.45%	84.78%	86.21%	85.31%	0.80
	0.65	85.48%	85.64%	86.78%	85.97%	85.97%	0.67
Sesamin	0.21	85.74%	86.48%	83.79%	83.80%	84.75%	1.61
	0.36	80.88%	81.25%	81.21%	83.58%	81.73%	1.52
	0.58	84.75%	83.99%	83.24%	82.15%	83.53%	1.33
	0.77	91.48%	91.13%	92.96%	91.86%	91.86%	0.86
Sesamolin	0.15	84.54%	85.75%	83.59%	84.12%	84.50%	1.09
	0.25	84.59%	86.55%	86.32%	87.45%	86.23%	1.39
	0.42	83.24%	82.84%	82.58%	83.66%	83.08%	0.57
	0.49	93.63%	93.54%	93.78%	93.12%	93.52%	0.30

Table 3
Comparison of recoveries among different pretreatment methods for the determination of sesamol, sesamin and sesamolin in sesame oil.

Method	Analytes	Spiked amount (mg/g)	Recovery (%)				Average recovery (%)	RSD (%, n = 4)
			1	2	3	4		
Saponification method	Sesamol	0.81	78.12%	80.22%	78.89%	80.33%	79.39%	1.35
	Sesamin	0.97	78.25%	76.49%	81.54%	80.04%	79.08%	2.77
	Sesamolin	0.61	80.45%	80.22%	78.55%	79.64%	79.72%	1.06
Alumina column chromatography method	Sesamol	0.81	82.44%	81.88%	79.54%	80.49%	81.09%	1.63
	Sesamin	0.97	81.50%	78.45%	81.22%	80.58%	80.44%	1.72
	Sesamolin	0.61	80.44%	82.95%	80.45%	81.36%	81.30%	1.45
MSPE	Sesamol	0.65	85.48%	85.64%	86.78%	85.97%	85.97%	0.67
	Sesamin	0.77	91.48%	91.13%	92.96%	91.86%	91.86%	0.86
	Sesamolin	0.49	93.63%	93.54%	93.78%	93.12%	93.52%	0.30

3.3. Precision and accuracy of the method

The method precision and accuracy were measured based on the analyses of different amounts of sesamol, sesamin and sesamolin spiked in sesame oil. Samples were pretreated and quantitatively analyzed by the chromatography method. Each of the added scalar quantity was repeated four times, and their recoveries were calculated and averaged. The average recovery of sesamol was 82.70–85.97%, the average value of sesamin was 81.73–91.86%, and that of sesamolin was 83.08–93.52%. The relative standard deviations (RSDs) were 0.67–1.92%, 0.86–1.61% and 0.30–1.39%, respectively. The results shown in Table 2 illustrated that the method was reproducible, accurate and reliable.

3.4. Comparison of the recoveries of this method and other published methods

The method in this paper and sesame oil pretreatment methods in previous literatures were used, the latter of which included the saponification method (Xue et al., 2006), and alumina column chromatography (Liu, Wang, & Jin, 2004). Different amounts of sesamol, sesamin and sesamolin were added into sesame oil of known contents, which was the background. Average recoveries of sesamol, sesamin and sesamolin were determined when three different pretreatment methods were used. The results were shown in Table 3.

From Table 3, we found that the average recovery of the method in this paper was significantly higher than that of the saponification method and alumina column chromatography method. It also demonstrated that the accuracy of the method in this paper was reliable. The poor recoveries of sesamol and sesamin of the last two methods may be caused by more operation steps and prolonged time of the saponification method, as well as large capacity of adsorption to the weak acid substance of alumina. The procedure of the saponification method is complicated, time consuming and low efficiency. There were more influence factors during alumina column chromatography method, such as more solvent consumption and the poor consistency of column filling, which would affect the separation efficiency. However, the developed method was convenient and rapid; the whole procedure of our proposed MSPE-HPLC method could be completed within 20 min, while it took no less than 30 min for just the extraction process for the other two methods. Many oil samples could be pretreated and analyzed simultaneously, and not only total lignans in oils can be determined, but each lignan as well. By comparison, the Fe_3O_4 @GO could provide high enrichment efficiencies toward lignans within a short time, making it desirable for high-throughput sample preparations because the adsorbents can be dispersed uniformly into a sample solution by vortexing, making the contact area between the adsorbents and the analytes large enough to ensure a fast mass transfer (Ding, Gao, Luo, Shi, & Feng, 2010; Gao, Luo, Bai, Chen, & Feng, 2011). The newly developed method proposed a fast, simple, sensitive, accurate, solvent-saving and reliable analytical procedure. Therefore, the method in this paper was superior to the last two methods in terms of pretreatment.

3.5. Sample analysis

To demonstrate the applicability of the method, the developed MSPE method was applied for the determination of sesamol, sesamin and sesamolin in real sesame oil samples. Ten kinds of edible sesame oil samples from retail markets located in Wuhan (China) were analyzed. The graphs of the standard solution were shown in Fig. 5 and graphs of the actual samples were shown in Fig. 6. The results were shown in Table 4, from which we found that the concentrations of sesamin and sesamolin were high in the majority of the market-sold sesame oil. Sesamin and sesamolin accounted for 61.70% and 31.60% of the total amount of lignans. The contents of sesamin and sesamolin were both significantly positively correlated with the total amount of lignans (r = 0.760 and r = 0.490, respectively). Among the three lignans, the concentration of sesamol was low and significantly negatively correlated

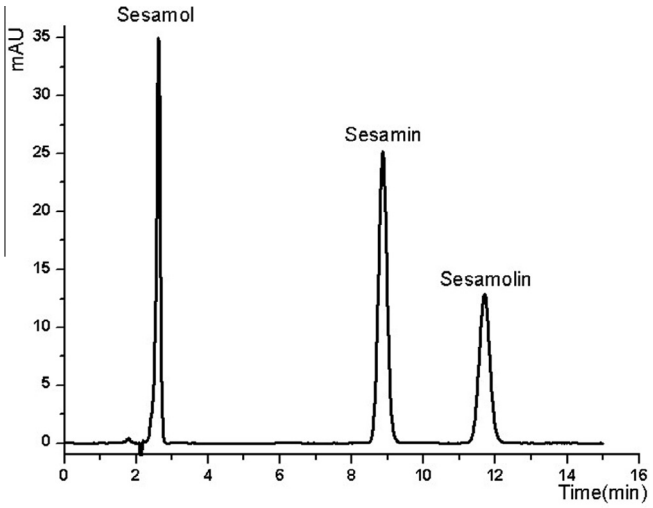

Fig. 5. Chromatograms of sesamol, sesamin and sesamolin standards.

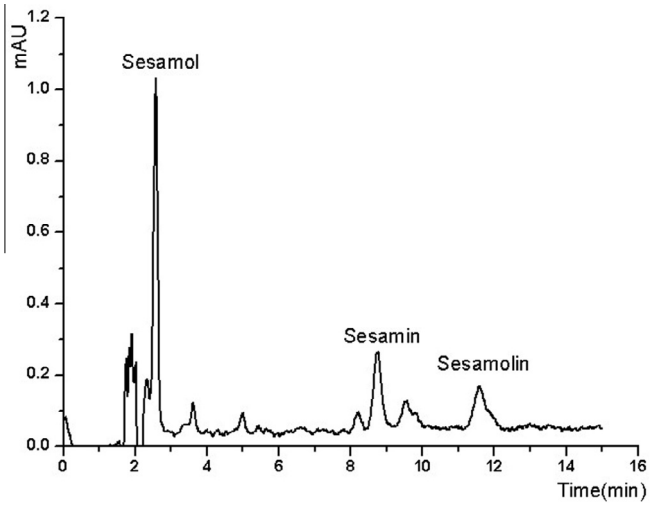

Fig. 6. Chromatograms of the sesamol, sesamin and sesamolin in samples.

Table 4
Detection results of samples.

Sesame oil	Sesamol amount (mg/g)	Sesamin amount (mg/g)	Sesamolin amount (mg/g)	Lignans (mg/g)
1	0.62	6.45	3.51	10.58
2	0.63	4.78	2.78	8.19
3	0.86	6.46	2.64	9.96
4	0.78	5.62	3.55	9.95
5	0.44	7.15	3.66	11.25
6	0.58	6.55	2.78	9.91
7	0.65	5.49	3.36	9.50
8	0.66	5.36	3.87	9.89
9	0.65	6.65	2.12	9.42
10	0.57	6.59	3.02	10.18
Average ± SD	0.644 ± 0.114	6.11 ± 0.745	3.129 ± 0.550	9.883 ± 0.795

with the total amount of lignans (r = −0.337). The results demonstrate the feasibility of the proposed method for the determination of sesamol, sesamin and sesamolin in edible oils.

4. Conclusions

A new method was established by the MSPE-HPLC method based on graphene oxide for simultaneously determining the contents of the three kinds of lignans including sesamol, sesamin and sesamolin in sesame oil. The innovation of this paper lay in the pretreatment technology of sesame oil samples. The target compounds in sesame oil were adsorbed and extracted through the combination of synthetic graphene oxide with hydroxylated Fe_3O_4 MNPs. The optimum adsorption solvent was methanol and the optimal desorption conditions were obtained, which were 1.5 min desorption time, 1.7 mL desorption volume and 1.4 mg adsorption dosage. The extraction and desorption were carried out quickly, and the whole pretreatment process could be accomplished by simple vortex within 5 min. Compared with traditional methods including the saponification method and alumina column chromatography method, the method in this paper had the advantages of fast sample pretreatment, a good purification effect, simple operation, and low cost. There are important and practical significance for the analysis of sesame oil and evaluation of the sesame oil quality.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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