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Rapid Magnetic Solid-Phase Extraction Based on Magnetic Multiwalled Carbon Nanotubes for the Determination of Polycyclic Aromatic Hydrocarbons in Edible Oils

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ABSTRACT: In this study, magnetic multiwalled carbon nanotubes were fabricated by a simple method and applied to magnetic solid-phase extraction (MSPE) of eight heavy molecular weight polycyclic aromatic hydrocarbons (PAHs) including chrysene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenzo[*a*,*h*]-anthracene and benzo[*g*,*h*,*i*]perylene from edible oil samples. Several parameters affecting the extraction efficiency were investigated, including the type and volume of desorption solvent, extraction and desorption time, washing solution and the amount of sorbent. Under the optimized conditions, a simple and effective method for the determination of PAHs in edible oils was developed by coupling with gas chromatography−mass spectrometry (GC−MS). The whole pretreatment process was rapid, and it can be accomplished within 10 min. The limits of quantitation for the target PAHs were found to be 0.34−2.9 ng/g. The recoveries in oil sample were in the range 87.8−122.3% with the RSDs less than 6.8% (intraday) and 9.6% (interday). This method was successfully applied to the analysis of PAHs in seven kinds of edible oils from local markets.

KEYWORDS: *magnetic multiwalled carbon nanotubes, magnetic solid-phase extraction, GC−MS, polycyclic aromatic hydrocarbons, edible oil*

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), a large class of compounds originated from incomplete combustion or pyrolysis of organic matter,[1,2] are widespread in the environment. Because of their toxicity and carcinogenicity, close attention has been paid to them by scientists for a long time. In the last decades, many studies have identified food as an important contributor to the direct exposure of humans to PAHs, therefore their presence in food is a matter of concern.[3−7] Due to the lipophilic nature of these compounds, fats and oils can be highly contaminated.[1,8,9] Especially for edible oils, oilseed drying processes by direct combustion[8] or solvent extraction during their production may be an important source of contamination in a variety of edible oils. Different maximum residue limits are recommended by food authorities of many countries. The German Society for Fat Science has recommended maximum residue limits of 25 ppb for total PAHs and 5 ppb for heavy PAHs which contain five or more aromatic rings.[10] Some other countries (Spain, Italy, Portugal and Greece) have also established a maximum level of 2 μg/kg for these PAHs involving benzo[*a*]pyrene, benzo[*e*]pyrene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]-fluoranthene, dibenzo[*a*,*h*]anthracene, benzo[*g*,*h*,*i*]perylene, indeno[1,2,3-*c*,*d*]pyrene, and the sum of them cannot be above 5 μg/kg.[11]

It is well-known that high fat content may cause the main difficulties for the analysis of residue compounds with low concentration in edible oil matrices. PAHs exhibit strong affinity to the oil matrix due to their high hydrophobicity. Therefore, the extraction of PAHs from edible oils is usually a laborious and time-consuming stage. The reported methods on extraction of PAHs from edible oils mainly relied on two general strategies.[12] The first strategy was the combination of several conventional analytical processes involving the dilution of the sample, followed by several liquid−liquid extraction (LLE) processes and then a cleanup procedure by column chromatography or solid-phase extraction (SPE);[13−15] the other general methodology carried out extraction and cleanup with a single SPE[10,16,17] or tandem-SPE[18] after the sample dilution. However, by using these reported methods, some time-consuming steps such as LLE, SPE or concentration to dryness were required. Besides the general strategies, solid-phase microextraction (SPME) has also been used for the analysis of PAHs in head space,[9,19] or with direct immersion of the fiber into oil matrix.[20,21] However, the longstanding sorptive extraction in SPME is always a boring stage. Thus, a simple, rapid and effective method for the analysis of PAHs in edible oils is desirable.

In recent years magnetic solid-phase extraction (MSPE), a promising technique for sample preparation, has attracted much interest.[22−29] It is a new mode of extraction technique based on the use of magnetic or magnetizable adsorbents, which can be readily isolated from sample matrix with an

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external magnet. Hence, two of the significant advantages of MSPE are simplicity and convenience. Furthermore, in MSPE, the adsorbents can be uniformly dispersed into sample solution by vortex or shaking, which makes the contact area between the adsorbents and the analytes large enough to ensure a fast mass transfer. So it is favorable to achieve high extraction efficiency in a short time, which is desirable in high throughput sample preparations.[23] Generally, the adsorbents used in MSPE are Fe_3O_4-based materials with different functional groups, which are suitable for various analytes. Nevertheless, the surface modification of Fe_3O_4 was usually complicated and work-intensive.

Carbon nanotubes (CNTs) are an electron-rich, hydrophobic nanomaterial with large specific area and $\pi-\pi$ electrostatic stacking property. It has served as an extraordinarily wonderful adsorbent or extraction material in both sample preparation and bioanalysis fields.[30] Recently, magnetic carbon nanotubes (mCNTs) have been prepared by filling CNTs with magnetic fluid or assembling magnetic nanoparticles (MNPs) via chemical or physical modification[31−35] and utilized as the adsorbent for MSPE. However, the reported preparation approaches, to some extent, are tedious and time-consuming. In addition, a change in CNT properties might occur due to the chemical modification, leading to a change in their adsorption abilities. Very recently, we reported a novel method for the fabrication of magnetic multiwalled carbon nanotubes (mMWCNTs) by simple vortex and ultrasonic agitation based on an "aggregation wrap" mechanism. The resultant mMWCNTs were applied as a sorbent for MSPE of estrogens from milk samples.[36] In the present study, the mMWCNTs were expanded to extract PAHs from edible oils in a process that was based on $\pi-\pi$ interaction. Parameters that affect the extraction efficiency were investigated and discussed in detail. By coupling with gas chromatography−mass spectrometry (GC−MS), under the optimal conditions, a rapid, simple and convenient MSPE−GC−MS method for the determination of PAHs in oil samples was established.

MATERIALS AND METHODS

Reagents and Chemicals. Acetic ester (HPLC grade) and *n*-hexane (HPLC grade) were obtained from CNW technologies GmbH (Dusseldorf, Germany). Acetone (HPLC grade) was obtained from J. T. Baker Chemical Company (Phillipsburg, NJ, USA). Ethylene glycol (EG), ethanol, toluene, ethylene diamine (ED), ferric trichloride hexahydrate ($FeCl_3{\cdot}6H_2O$), and sodium acetate (NaAc) were purchased from Sinopharm Chemical Reagent (Shanghai, China). Before use, toluene was distilled from sodium shavings under the protection of N_2. All the other chemicals were used directly without further purification.

PAHs standard solution, chrysene-d_{12} (internal standard (I.S.), 4 mg/mL in CH_2Cl_2) were bought from J&K Chemical Ltd. (Tianjin, China). Benzo[*a*]pyrene-d_{12} (I.S., BaP-d_{12} ≥ 98%) was bought from Sigma-Aldrich (St. Louis, MO, USA). The PAH standard solution contains chrysene (CHRY), benzo[*a*]anthracene (BaA), benzo[*b*]-fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (INPY), dibenzo[*a*,*h*]anthracene (DiahA) and benzo[*g*,*h*,*i*]perylene (BghiP), each at 0.2 mg/mL in methanol/methylene dichloride (1/1, v/v). The PAH stock solution and the I.S. stock solution were prepared in *n*-hexane (HPLC grade) at a concentration of 2 μg/mL. All the stock solutions were kept at 4 °C in darkness. Preliminary experimental results showed that the stock solutions were stable for almost three months. With the stock solutions, the sample solution was spiked to the desired concentration for the following experiments.

MWCNTs (length 5−15 μm, diameter 10−20 nm) were obtained from Nanotech Port Co. (Shenzhen, China). Before use, MWCNTs were washed with toluene by Soxhlet extraction for 48 h at 120 °C to avoid impurities influencing the following analysis. The resultant MWCNTs were dried under reduced pressure at 80 °C for 24 h.

Oil Samples. Several kinds of edible oils including blend oil, peanut oil, olive oil, maize oil, rapeseed oil, sunflower oil and soybean oil were purchased from local markets in Wuhan (China) and stored at room temperature. One of the olive oil samples was checked to be free of any target PAHs and used as blank oil for calibration and validation purposes. The eight PAHs were directly spiked into a 1 g oil sample over a range of 1−200 ng/g. After mixing evenly, the sample was diluted to 10 mL with *n*-hexane.

Preparation of mMWCNTs. The preparation procedure of mMWCNTs is depicted in Figure 1.

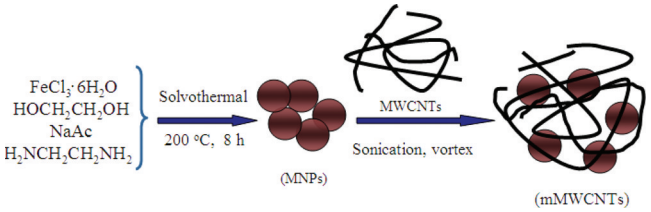

Figure 1. Preparation scheme of mMWCNTs.

Magnetite nanoparticles (MNPs) were synthesized via a solvothermal process according to our previously used method.[23] Briefly, $FeCl_3{\cdot}6H_2O$ (5.0 g) was dissolved in EG (100 mL), and then NaAc (15.0 g) and ED (50 mL) were added to the solution. After vigorous stirring for 30 min, the homogeneous mixture was sealed in a Teflon-lined stainless-steel autoclave (200 mL). The autoclave was heated to 200 °C and maintained for 8 h, and allowed to cool to room temperature. The product was magnetically collected, washed with water/ethanol several times and vacuum-dried at 60 °C for 6 h.

The fabrication of mMWCNTs was similar to the procedure described in our previous work with minor modification:[36] the resultant MNPs (400 mg) were dispersed in acetone (20 mL) by ultrasonic agitation (20 min). Then, MWCNTs (100 mg) were added into the resultant suspension with ultrasonic agitation for another 5 min. Finally, the mixture was vortexed for about 10 min. In the whole process, the MWCNTs and MNPs could spontaneously assemble as mMWCNTs.

Magnetic Solid-Phase Extraction Procedure. Ten milliliters of 0.1 g/mL oil sample was added into a 15 mL vial, and then mMWCNT solution (200 μL, 5 mg mMWCNTs) was added. The mixture was vortexed vigorously for 1 min, and in the process, PAHs were adsorbed onto mMWCNTs through $\pi-\pi$ interaction. The supernatant was discarded; meanwhile the sorbent was gathered to the vial bottom by placing a strong magnet on the outwall of the vial. Then, the PAH-adsorbed mMWCNTs were washed with 0.5 mL of acetone by vortexing for 15 s. After discarding the washing solution, PAHs were desorbed with 100 μL of toluene by ultrasonic agitation for 1 min. The desorption solution was separated from mMWCNTs by a magnet and collected in a vial. Ultimately, 1 μL of the desorption solution was supplied to GC−MS for analysis.

It is worth noting that we employed two ways for the addition of internal standard in our experiments. When investigating the effect of experimental conditions on extraction performance of mMWCNTs toward the target compounds, the internal standard was added to the eluate, which was just to eliminate the deviation of GC−MS analysis. However, when we validated the proposed analytical method, the internal standard was added into the sample solution before MSPE.

GC−MS Analysis. The gas chromatography−mass spectroscopy (GC−MS) analysis was performed on a Shimadzu GC−MS QP2010plus which was equipped with an AOC-20i+s autosampler (Kyoto, Japan). The GC separation was achieved on a Rxi-5 ms column (30 m × 0.25 mm ×0.25 μm) purchased from Restek (Bellefonte, PA, USA). The oven temperature was held at 70 °C for

2.0 min, then increased to 190 °C at a rate of 15 °C/min and held for 1.0 min, then increased to 260 °C at a rate of 10 °C/min and to 320 °C at a rate of 5 °C/min. Finally it was held at 320 °C for another 10.0 min. The injection volume was 1.0 μL in splitless mode. Helium (purity ≥99.999%) was used as carrier gas at a flow rate of 1.2 mL/min. The temperatures of injection port, detector and interface were held at 270 °C, 200 °C and 320 °C, respectively. The selective ion monitoring (SIM) mode was adopted for the quantitative analysis. The information of qualitative and quantitative ions for each PAHs is listed in Table 1.

Table 1. The Qualitative and Quantitative Ions for the Analysis of PAHs

analytes	qualitative ions	quantitative ion
BaA	226, 228, 229	228
CHRY	226, 228, 229	228
BbF	250, 252, 253	252
BkF	250, 252, 253	252
BaP	250, 252, 253	252
INPY	276, 277, 278	276
DiahA	276, 277, 278	278
BghiP	276, 277, 278	276
chrysene-d_{12} (I.S.)	240	240
benzo[a]pyrene-d_{12} (I.S.)	264	264

RESULTS AND DISCUSSION

Optimization of Conditions for MSPE. In order to evaluate the feasibility of mMWCNTs for the extraction of PAHs from oil samples, the parameters that might affect the performance of MSPE needed to be optimized. In this study, six major factors, namely, the type and volume of desorption solvent, extraction and desorption time, washing solution and the amount of sorbent, were investigated by using spiked oil samples (20 ng/mL) as matrix, and all the optimization experiments were conducted three times.

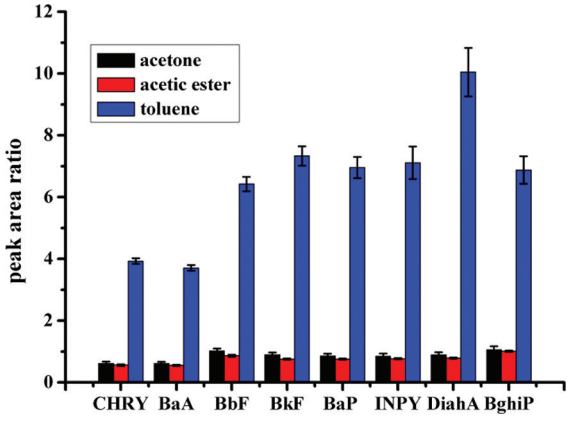

Figure 2. The effect of desorption solvent on extraction efficiency with the concentration 20 ng/mL of each PAH.

Effect of the Type and Volume of Desorption Solvent. The type and volume of desorption solvent are vital for the desorption efficiency. So the choice of desorption solvent and its optimum volume should be carefully taken into account. Figure 2 shows the peak area ratio of the analytes obtained with three organic solvents including acetone, acetic ester, and toluene tested as desorption solvents. Obviously, the best desorption efficiency was obtained when toluene was used, which may be ascribed to toluene's being a π-electon rich molecule that exhibited stronger π−π interaction with mMWCNTs than that of the polar solvents (acetone and acetic ester). Thus, it may be expected that the π−π interaction was dominant in the retention of PAHs on mMWCNTs. Therefore, toluene was selected as desorption solvent in the following experiments.

Moreover, the influence of volume of toluene was also studied (as shown in Figure 3). It can be seen that the smaller the volume of toluene used, the higher concentration of PAHs

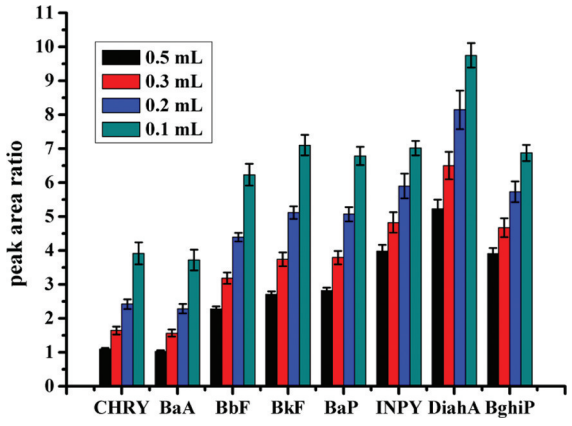

Figure 3. The effect of desorption volume on extraction efficiency with the concentration 20 ng/mL of each PAH.

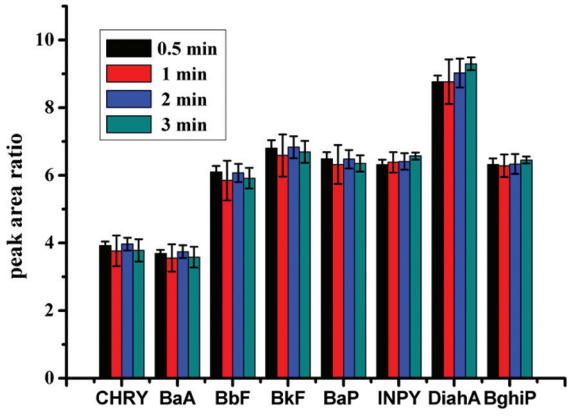

Figure 4. The effect of extraction time on extraction efficiency with the concentration 20 ng/mL of each PAH.

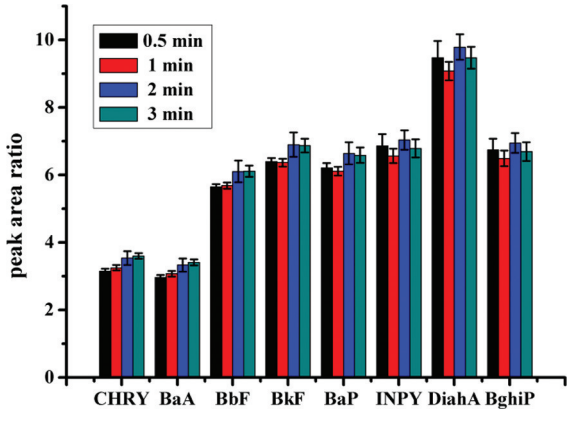

Figure 5. The effect of desorption time on extraction efficiency with the concentration 20 ng/mL of each PAH.

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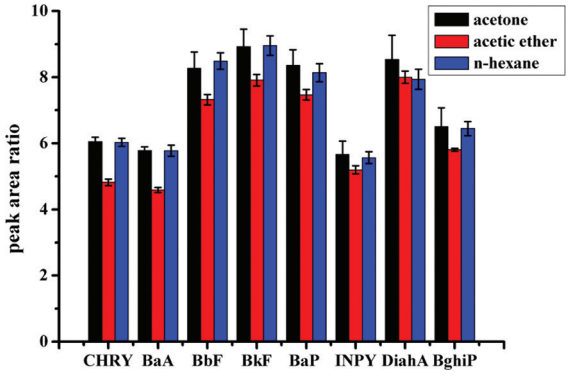

Figure 6. The effect of washing solution on extraction efficiency with the concentration 20 ng/mL of each PAH.

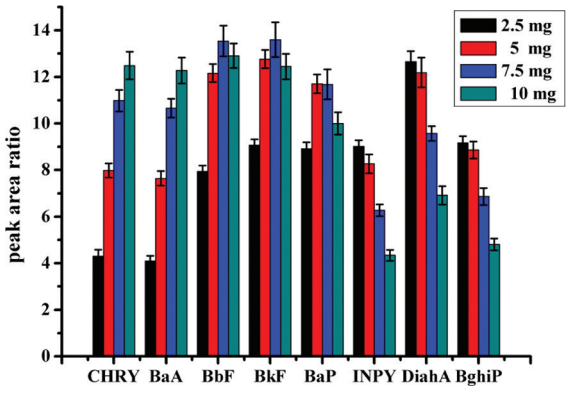

Figure 7. The effect of mMWCNTs amount on extraction efficiency with the concentration 20 ng/mL of each PAH.

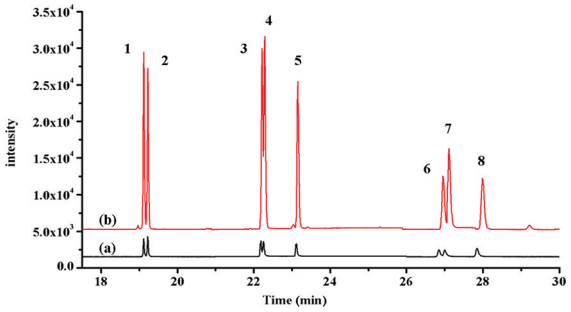

Figure 8. Chromatogram of standard mixture of eight PAHs at a concentration of 20 ng/mL (a). Chromatogram of oil sample spiked at 20 ng/mL of eight PAHs and then extracted by the mMWCNTs (b). Peak identification: (1) CHRY, (2) BaA, (3) BbF, (4) BkF, (5) BaP, (6) INPY, (7) DiahA, (8) BghiP.

can be obtained in the desorption solution. Finally, 100 μL of toluene was adopted for the desorption of PAHs from mMWCNTs for further work.

Effect of Extraction and Desorption Time. As shown in Figures 4 and 5, the effect of both extraction and desorption time was examined in the range of 30 s to 3 min. No significant influence on the extraction efficiency was observed for the change of the two parameters. Ultimately, 1 min was selected as extraction and desorption time, which might be enough for both effective extraction and desorption.

Effect of Washing Solution and the Amount of Sorbent. The removal of lipid which was adsorbed on mMWCNTs is essential not only to minimize its maintenance

Table 2. Calibration Curves, LOD and LOQ Data of Eight PAHs in Oil Sample

	linearity and sensitivity characteristics				
		regression line			
analytes	linear dynamic range (ng/g)	linear eq	R^2 value	LOD (ng/g)	LOQ (ng/g)
BaA	1−200	$Y = 0.0602 + 0.0374X$	0.9996	0.13	0.43
CHRY	1−200	$Y = 0.1043 + 0.0370X$	0.9993	0.10	0.34
BbF	1−200	$Y = 0.0972 + 0.0190X$	0.9980	0.23	0.76
BkF	1−200	$Y = 0.0913 + 0.0212X$	0.9994	0.14	0.47
BaP	1−200	$Y = 0.0196 + 0.0169X$	0.9995	0.37	1.2
INPY	2−200	$Y = -0.0414 + 0.0089X$	0.9927	0.84	2.8
DiahA	2−200	$Y = -0.0374 + 0.0101X$	0.9933	0.37	1.2
BghiP	2−200	$Y = -0.0129 + 0.0129X$	0.9952	0.88	2.9

Table 3. Recoveries of Eight PAHs Spiked into Oil Samples at Three Different Concentrations[a]

	recovery (%, $n = 6$)		
analytes	low (10 ng/g)	medium (50 ng/g)	high (100 ng/g)
BaA	89.7 ± 1.5	113.1 ± 2.8	101.8 ± 3.3
CHRY	92.0 ± 2.1	114.8 ± 3.1	103.4 ± 3.3
BbF	114.4 ± 3.1	122.3 ± 6.7	98.4 ± 2.4
BkF	87.8 ± 2.1	113.2 ± 7.0	95.8 ± 2.2
BaP	108.8 ± 3.4	118.6 ± 7.2	103.8 ± 2.7
INPY	114.3 ± 7.1	103.1 ± 7.0	105.3 ± 3.3
DiahA	112.2 ± 5.5	102.9 ± 6.6	105.0 ± 3.9
BghiP	92.3 ± 3.9	108.1 ± 5.7	108.8 ± 3.2

[a]Recoveries are given as average values ± standard deviations of sextuple analysis.

Table 4. Method Precisions at Three Different Concentrations for the Extraction of PAHs from Oil Samples

	precision (RSD %)					
	intraday ($n = 6$)			interday ($n = 3$)		
analytes	low (10 ng/g)	medium (50 ng/g)	high (100 ng/g)	low (10 ng/g)	medium (50 ng/g)	high (100 ng/g)
BaA	1.7	2.5	3.2	0.7	1.8	0.8
CHRY	2.3	2.7	3.2	1.3	0.5	1.5
BbF	2.7	5.4	2.4	6.6	9.6	8.9
BkF	2.4	6.2	2.3	5.4	5.0	3.2
BaP	3.1	6.1	2.6	5.1	8.4	9.0
INPY	6.2	6.8	3.1	2.3	6.3	7.5
DiahA	4.9	6.4	3.7	3.3	5.7	7.6
BghiP	4.2	5.3	2.9	2.9	6.5	6.3

in the chromatographic system (especially when using GC) but also to obtain low detection limits. In this work, acetone, acetic ester, and *n*-hexane were tested as washing solution and their effect on the peak area ratio of PAHs is shown in Figure 6. It can be seen that the better cleaning performance was obtained when acetone and *n*-hexane were used. However, when *n*-hexane was used as washing solution, a small quantity of mMWCNTs were readily adsorbed on the glass wall, which

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Table 5. Comparison of Sample Preparation Procedures and LOQs among Different Methods

matrix	extraction	cleanup	determination	time	LOQs (ng/g)	ref
edible oils	LLE	C18 SPE	HPLC−FLD	>40 min	BaA, 0.3; CHRY, 0.3 BbF, 0.4; BkF, 0.3 BaP, 0.3; INPY, 0.3 DiahA, 0.6; BghiP, 0.4	13
edible oils	LLE	silica gel column	HPLC−FLD	>40 min	CHRY, 1.0; BaP, 1.0 BghiP, 1.3	15
olive pomace and vegetable oils	SPE (silica gel)	SPE (amino phase)	HPLC−FLD	>40 min	BaA, 0.1; CHRY, 0.1 BbF, 0.4; BkF, 0.1 BaP, 0.1; INPY, 0.8 DiahA, 0.2; BghiP, 0.4	18
edible fats and oils	SPE (polystyrene/DVB)	SPE (polystyrene/DVB)	HPLC−FLD	>40 min	BaA, 1.0; CHRY, 1.0 BbF, 2.7; BkF, 0.7 BaP, 0.7; INPY, 2.0 DiahA, 0.7; BghiP, 1.3	17
vegetable oils	SPME (Carbopack Z/ PDMS)	1 min rinse	GC×GC−TOF-MS	>31 min	BaA, 1.4; CHRY, 1.3 BaP, 0.7; INPY, 0.4 DiahA, 0.5; BghiP, 0.4	20
vegetable oils	SPME (Carbopack Z/ PDMS)	1 min rinse	GC−TOF-MS	>31 min	BaP, 0.46	21
edible oils	MSPE (mMWCNTs)	15 s vortex	GC−MS	<10 min	BaA, 0.4; CHRY, 0.3 BbF, 0.8; BkF, 0.5 BaP, 1.2; INPY, 2.8 DiahA, 1.2; BghiP, 2.9	this work

Table 6. Determination of PAHs in Seven Edible Oil Samples

	detected concn (ng/g, RSD% n = 3)						
analytes	blend oil	peanut oil	olive oil	maize oil	rapeseed oil	sunflower oil	soybean oil
BaA	nq[a]	1.55 (9.2)	nq	1.00 (2.6)	1.07 (10.0)	nq	0.90 (0.7)
CHRY	nq	1.56 (0.5)	nq	2.40 (5.8)	0.82 (1.7)	nq	0.81 (1.2)
BbF	0.94 (2.6)	2.03 (10.2)	nq	1.51 (6.6)	3.60 (10.8)	2.36 (6.5)	1.55 (1.8)
BkF	4.02 (6.1)	nq	nq	nq	nq	nq	nq
BaP	nq	nq	nd[b]	nq	1.75 (5.0)	1.40 (7.7)	nq
INPY	nd	nd	nd	nd	nd	nd	nd
DiahA	nd	nd	nd	nd	nd	nd	nd
BghiP	nd	nd	nd	nd	nd	nd	nd

[a]Not quantified. [b]Not detected.

were not easy to gather by a magnet. Therefore, acetone was chosen as washing solution in the following experiments.

The effect of the sorbent amount on extraction efficiency was studied in the range 2.5−10 mg. As shown in Figure 7, with the increase of mMWCNTs, the extraction efficiency enhanced for the PAHs containing fewer aromatic rings (BaA, CHRY) while the opposite trend was found for the heavier PAHs (INPY, DiahA, BghiP), and for the moderate PAHs (BbF, BkF, BaP), their extraction efficiency increased at first, then went down. To understand this phenomenon, two aspects (extraction and desorption) should be considered comprehensively. In the extraction stage, the investigations were carried out using the same sample solution. It can be expected that increasing the amount of sorbent would enhance the amount of analyte retained on mMWCNTs. However, in the desorption stage, when a given volume of desorption solvent was utilized, the more the sorbent was involved, the less the retained analyte could be desorbed, which was perhaps more prominent for the heavier PAHs due to their strong $\pi-\pi$ interaction with mMWCNTs; while for BaA and CHRY, due to their relatively week retention on mMWCNTs, they were easily desorbed from the sorbent, thus their extraction effiencies increased when increasing the sorbent amount as shown in Figure 7. Ultimately, taking all factors into consideration, 5 mg of magnetic sorbent was employed in the following experiments.

On the basis of the above discussion, the optimal extraction conditions were as follows: 100 μL of toluene as the desorption solution; 0.5 mL of acetone as the washing solution; 5 mg of mMWCNTs as the sorbent; both the extraction time and the desorption time were 1 min. Figure 8b showed the GC−MS chromatogram of eight PAHs extracted from oil sample (20 ng/mL) under the opitmized conditions, and for the comparsion, the chromatogram of the standard solution containing the same concentration of eight PAHs was also shown in Figure 8a. It could be seen that the peak area after extraction increased obviously, suggesting that the mMWCNTs exhibited high extraction efficiency toward the target PAHs in oil sample.

Analytical Performance. Under the optimal conditions mentioned above, PAHs were quantitatively analyzed using chrysene-d_{12} and benzo[a]pyrene-d_{12} as I.S. The linearity was studied using blank olive oil samples spiked with PAHs at eleven different concentrations ranging from 1 to 200 ng/g. In the construction of the calibration curve, triplicate measure-

ments of each concentration level of the calibration samples were performed, and the calibrations were obtained by plotting peak area ratios versus concentrations. As shown in Table 2, satisfactory correlation coefficients for the eight compounds were obtained ranging from 0.9927 to 0.9996. The sensitivity of the method was established by examining the limits of detection (LOD) and limits of quantitation (LOQ). LOD was defined as the lowest detectable concentration with a signal-to-noise ratio of at least 3, and the LOQ was defined as the lowest quantifiable concentration with a signal-to-noise ratio of at least 10. The LODs and LOQs data were in the range 0.10−0.88 ng/g and 0.34−2.9 ng/g, respectively.

The recoveries were obtained by comparing the amount calculated from the calibration curves with the corresponding spiking amount. At the same time, the recoveries were measured at three different concentrations, and the spiking levels ranged from 10 to 100 ng/g. The recoveries and standard deviations are summarized in Table 3. It could be seen that the average recoveries were in the range 87.8−122.3%, and the results demonstrate that the accuracy of the present method was acceptable.

The reproducibility of the method was determined by the intra- and interday precisions. The intraday precision was determined on the same day and consisted of three series and six replicates at each of three concentration levels. Interday precision was calculated with three replicates at the three fortification levels on three continuous days. The numerical value used was the relative standard deviation (RSD) of triplicate measurements of the analytes. Satisfactory precisions were obtained with RSD values less than 6.8% (intraday) and 9.6% (interday), as also shown in Table 4, illustrating the good reproducibility achieved by the method.

A comparative study of our developed method to other reported sample preparation procedures was performed, and the results are presented in Table 5. It can be seen that the developed method was convenient and rapid; the whole procedure of our proposed MSPE could be completed within 10 min.

Applications in Real Samples. To demonstrate the applicability of the method, seven kinds of edible oil samples from retail markets located in Wuhan (China) were analyzed. All samples obtained were analyzed in three replicates. The detailed results are outlined in Table 6. It was found that chrysene, benzo[*a*]anthracene, benzo[*b*]fluoranthene and benzo[*k*]fluoranthene were detected in all kinds of investigated oil samples and none of them contained detectable indeno-[1,2,3-*cd*]pyrene, dibenzo[*a*,*h*]anthracene and benzo[*g*,*h*,*i*]-perylene. The total concentration of the target PAHs in most of the investigated oils did not exceed 5 ng/g except rapeseed oil and peanut oil. The highest concentration of total PAHs was found in rapeseed oil, which was up to 7.24 ng/g. The results confirmed the feasibility of the proposed method for determination of PAHs in edible oils.

In conclusion, coupling with GC−MS analysis, the utilization of mMWCNTs for extraction of PAHs from edible oils by the mode of MSPE was proven to be a simple, rapid and effective method. The extraction and desorption were carried out quickly and the whole pretreatment process could be accomplished by simple vortex and ultrasonic agitation within 10 min. The LODs and LOQs of the target PAHs by this method were in the range 0.10−0.88 ng/g and 0.34−2.9 ng/g respectively. The recoveries in oil sample were in the range 87.8−122.3% with RSDs less than 6.8% (intraday) and 9.6% (interday). These results showed that the proposed method was suitable for routine analysis and the mMWCNTs based on "aggregation wrap" possessed great potential in sample preparation due to their good adsorption abilities and convenient construction method.

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