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Determination of Benzo[a]pyrene in Edible Oil Using Nickel Oxide Deposited Silica-Based Solid-Phase Extraction Coupled with High-Performance Liquid Chromatography–Diode Array Detector

Yuejiao Yang [1,†], Yingjie Guo [1,†], Guanglin Huang [2,*] and Qiongwei Yu [1,*]

[1] College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China; 2023202030015@whu.edu.cn (Y.Y.); 18378837511@163.com (Y.G.)
[2] State Key Laboratory of Material Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
* Correspondence: guanglinhuang@hust.edu.cn (G.H.); qwyu@whu.edu.cn (Q.Y.)
† These authors contributed equally to this work.

Abstract

A simple, rapid, and cost-effective method for the determination of benzo[a]pyrene (BaP) in edible oil was developed and validated. Nickel oxide-deposited silica (SiO_2@NiO) was employed as a solid-phase extraction (SPE) adsorbent for the extraction of BaP from edible oil, followed by high-performance liquid chromatography–diode array detector (HPLC-DAD) analysis of BaP. The edible oil was diluted with n-hexane and directly loaded to SiO_2@NiO for SPE. The n-hexane was also used to clean the fat-soluble interference substance in the edible oil, and BaP was selectively captured using SiO_2@NiO through the electron donor–acceptor interaction. The SPE conditions, including the amount of adsorbent, volume of washing solvent, and type and volume of desorption solvent, were optimized. This SiO_2@NiO-based SPE coupled with the HPLC-DAD method demonstrated good linearity within a BaP concentration range of 6–1875 ng/g in edible oils, with a limit of detection of 1.3 ng/g, spiked recovery of 97.4–105.1%, and relative standard deviation (RSD) of <3.0%. The method was applied to the analysis of BaP in 11 real oil samples (soybean oil, olive oil, corn germ oil, flaxseed oil, walnut oil, sunflower kernel oil, peanut oil, unrefined oil, and high-temperature frying oil), and the results show that the unrefined oil and high-temperature frying oil were at risk of BaP exceeding acceptable level.

Keywords: nickel oxide deposited silica; benzo[a]pyrene; high performance liquid chromatography-diode array detector; edible oil

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1. Introduction

Benzo[a]pyrene (BaP) is a high-molecular-weight polycyclic aromatic hydrocarbon (PAH) composed of fused aromatic rings, and it is recognized as a marker for carcinogenic PAH in food [1,2]. It enters the human body mainly through the consumption of BaP-contaminated foods [3–6]. Edible oil is an essential component of human diet, rich in triglycerides, fatty acids, fat soluble vitamins, and other nutrients [7,8], and it is highly vulnerable to BaP contamination in its preparation process, such as through seed drying, smoking, charcoal grilling, and roasting [9–11]. In addition, during the application of edible oil to food processing, high-temperature pyrolysis, mainly including alkali refinement, deodorization, and frying, tends to generate BaP [12–14]. To reduce the risk

to human health, a permissible level of BaP in edible oil has been set legislatively. For example, the maximum permissible concentration of BaP in cooking oil is set to 10 μg/kg in China according to national standard GB 2762-2017 [15–20]. Therefore, it is essential to quantitatively monitor BaP in edible oil.

Currently, the development of a simple, low-cost, and selective quantification method for BaP in edible oil is challenging. Existing detection methods such as high-performance liquid chromatography (HPLC)–fluorescence and gas chromatography–mass spectrometry (GC-MS) are reliable but costly [15,16]. Due to its inexpensive and stable detection performance, HPLC coupled with a diode array or ultraviolet detector (HPLC-DAD/UV) is a desirable alternative [17,18]. However, BaP detection is difficult because of its low content in edible oil with complex composition [18]. This necessitates sample pretreatment to purify and enrich BaP from edible oils before instrumental analysis [18,19]. Solid-phase extraction (SPE) is a widely used sample pretreatment technology, characterized by simple operation, good reproducibility, and strong enrichment ability. SPE can capture and enrich target analytes through the selective interaction between adsorbent and target analytes, and thus, the adsorbent is the key to SPE [20–23]. However, the high lipophilicity of BaP and the edible oil matrix prevents the selective extraction of BaP from edible oil using a conventional solid-phase extraction adsorbent (such as C_{18}) via hydrophobic interaction, and therefore, it is necessary to develop new adsorbents with high extraction selectivity for BaP in edible oil [24]. In our previous work [25], a humic acid-bonded silica gel adsorbent was prepared and used for the selective extraction of BaP from edible oil through π-π interaction. Guo et al. [26] prepared tetraoxoacalix [2] arene [2] triazine as a SPE adsorbent for the detection of BaP in edible oil based on a complex mechanism. However, the preparation processes of the above adsorbents are extremely complex, requiring multi-step synthesis reactions.

Liquid-phase deposition (LPD) is a simple method for preparing oxide coatings, and this method can uniformly deposit different nano-oxides on various substrates to form oxide coatings [27]. Various metal oxide coatings have been prepared via LPD and used as separation media [27–30]. NiO-related adsorbents exhibit high selectivity for imidazoles based on the coordination interaction between Ni(II) in the material and imidazole groups [30–32]. It has been demonstrated that PAHs can interact with metal ion-containing surfaces via interfacial electron transfer [33]. In addition, metal cations have been reported to serve as adsorption active sites to interact with aromatic rings through π-complexation interactions, thereby facilitating the adsorption and extraction of PAHs [34]. Ni (II) with vacancies and BaP with abundant π electrons make NiO a potential adsorbent for the selective extraction of BaP. However, NiO has not been used as an adsorbent to selectively extract BaP from a hydrophobic matrix such as edible oil.

In this work, NiO nanoparticles were deposited on silica using the LPD method and then used for the SPE of BaP from edible oil. Finally, a simple, selective, and reliable method for determining BaP in edible oils was established.

2. Materials and Methods

2.1. Chemicals and Reagents

Analytical-grade dichloromethane, n-hexane, acetone, acetonitrile, methanol, and ethanol were purchased from Wuhan Freton Co., Ltd. (Wuhan, China). Dimethylglyoxume, nickel fluoride tetrahydrate ($NiF_2 \cdot 4H_2O$), boric acid (H_3BO_3), and hydrochloric acid (HCl, 36%) were all of analytical grade and sourced from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Benzo(a)pyrene (BaP, 96%) was obtained from YuanYe Biotechnology (Shanghai, China). Purified water was prepared with a Milli-Q apparatus (Millipore, Bedford, MA, USA). The silica (200–300 mesh) used for SPE adsorbent preparation was obtained from Qingdao Marine Chemical Plant (Qingdao, China).

2.2. Equipment and Chromatographic Analysis Conditions

A field emission scanning electron microscope (FE-SEM, Zeiss Merlin Compact, Jena, Germany) with EDS mapping (X-MaxN, Oxford Instruments, Abingdon, UK) was used for the characterization of adsorbent morphology and composition. The specific surface areas and pore sizes were determined through nitrogen adsorption analysis with a TriStar II 3020 specific surface area analyzer (Micromeritics, Norcross, GA, USA). Materials were dried in a drying oven (LC-DZF-6050AB, LICHEN, Changsha, China). The separation of BaP from edible oils was conducted using a Inertsil ODS-4 column (150 mm × 4.6 mm, GL Sciences, Tokyo, Japan) in the HPLC system (LC-20A, Shimadzu, Kyoto, Japan) equipped with a quaternary pump and a diode array detector (SPD-M20A, Shimadzu, Kyoto, Japan). The separation conditions were as follows: room temperature, injection volume of 20 µL, detection wavelength of 295 nm, and mobile phases consisting of acetonitrile and water (80/20, *v*/*v*) at a flow rate of 1.0 mL/min.

2.3. Preparation of SiO_2@NiO

The LPD method involves the slow hydrolysis of metal fluorides $[MF_n]^{m-n}$ in the presence of water, boric acid (H_3BO_3), or Al to generate metal oxides. Water directly facilitates the formation of oxides, while H_3BO_3 or Al, serving as fluoride ion scavengers, promotes the hydrolysis of $[MF_n]^{m-n}$, thereby depositing metal oxides on the substrate surface [27].

The SiO_2@NiO material was prepared using the LPD method, as previously described [29]. Briefly, a certain amount of silica (200–300 mesh) was added into a 6 mol/L hydrochloric acid aqueous solution and stirred for 24 h to remove metal ions from SiO_2 surface. The treated SiO_2 was washed with deionized water until neutral pH, and then dried in the oven.

The 20.0 g of treated SiO_2 was added into the mixture of 150 mL of saturated NiF_2 aqueous solution and 250 mL of 0.6 mol/L H_3BO_3 aqueous solution, shaken at 40 °C for 72 h, filtered, washed with deionized water, and dried at 60 °C in the oven.

Finally, the resulting SiO_2@NiO was calcined at 200 °C for 1 h in a muffle furnace (SX2-2.5-10, Jianli Electric Furnace Manufacturing Co., Ltd., Changzhou, China) to obtain the SiO_2@NiO adsorbent. The SPE cartridges were prepared by packing a 5 mL polypropylene syringe with 100 mg of SiO_2@NiO adsorbent, with the packed materials fixed with two polyethylene frits.

2.4. Sample Preparation

The stock standard solution of BaP (500 µg/mL) was prepared with acetonitrile and then stored at −20 °C. The working solution was freshly prepared daily using an appropriate dilution of stock solution using n-hexane to the desired concentration.

Eight edible oils (soybean oil, 2 types of olive oil, corn germ oil, flaxseed oil, walnut oil, sunflower kernel oil, and peanut oil) were purchased online in China. Two unrefined oil samples were directly obtained from oil presses, and frying oil was collected from a street food vendor. The 2.0 g edible oil was diluted with n-hexane in 10 mL volumetric flask for subsequent SPE.

The diluted edible oil (2 mL) was directly loaded onto the SiO_2@NiO cartridge, which was sequentially pre-activated by 2 mL of dichloromethane and 2 mL of n-hexane. The cartridge was then rinsed with 3 mL of n-hexane to eliminate the impurities in oil. BaP was eluted with 4 mL of dichloromethane. Finally, the eluate was concentrated to dryness under nitrogen gas at 40 °C, redissolved in 200 µL ACN/H_2O (80/20, *v*/*v*), and subjected to HPLC-DAD analysis. SPE was conducted at a flow rate of 1.0 mL/min.

2.5. Optimization of SPE Conditions

To achieve better extraction efficiency, the SPE parameters such as the amount of adsorbent (50, 100, 200, 300, 400 mg), cleaning solvent volume (2, 3, 4, 5, 6 mL), desorption solvent type (acetone, dichloromethane, methanol, ethanol, acetonitrile), and volume (2, 3, 4, 5, 6 mL) were optimized. Each parameter was initially explored through the one-factor-at-a-time (OFAT) method by changing one variable while maintaining the others at a constant level. The influence of these individual variable changes on the recovery of BaP was evaluated. The specific details of these parameters are presented in Supplementary Table S1. All optimization experiments were carried out in triplicate (n = 3), and the blank soybean oil spiked with 50 ng/mL BaP was used as a representative sample. In addition, one-way analysis of variance (ANOVA), followed by Waller-Duncan's post hoc test, was performed to evaluate the statistical significance of each parameter' s effect on recovery, and $p < 0.05$ was considered statistically significant. To evaluate the extraction efficiency, the BaP recoveries were calculated.

In SPE optimization, recovery was calculated as (peak area of BaP in spiked sample/peak area of BaP in standard solution) × 100% under identical injection volume and instrumental conditions. While in method evaluation, recovery was calculated following the formula Recovery (%) = (concentration measured/concentration actually spiked) × 100%.

3. Results and Discussion

3.1. Characterization of SiO_2@NiO

The morphology of SiO_2 and SiO_2@NiO was examined via field emission scanning electron microscopy (FE-SEM). As shown in Figure 1, after NiO deposition, the particle sizes of SiO_2@NiO exhibited no significant difference from those of SiO_2. EDS mapping confirmed the presence of nickel in SiO_2@NiO and not in SiO_2, indicating the successful preparation of SiO_2@NiO. EDS further demonstrated that SiO_2@NiO consisted of carbon, oxygen, silica, and nickel elements, with their weight percentages being 4.81%, 47.38%, 19.05%, and 28.76%, respectively.

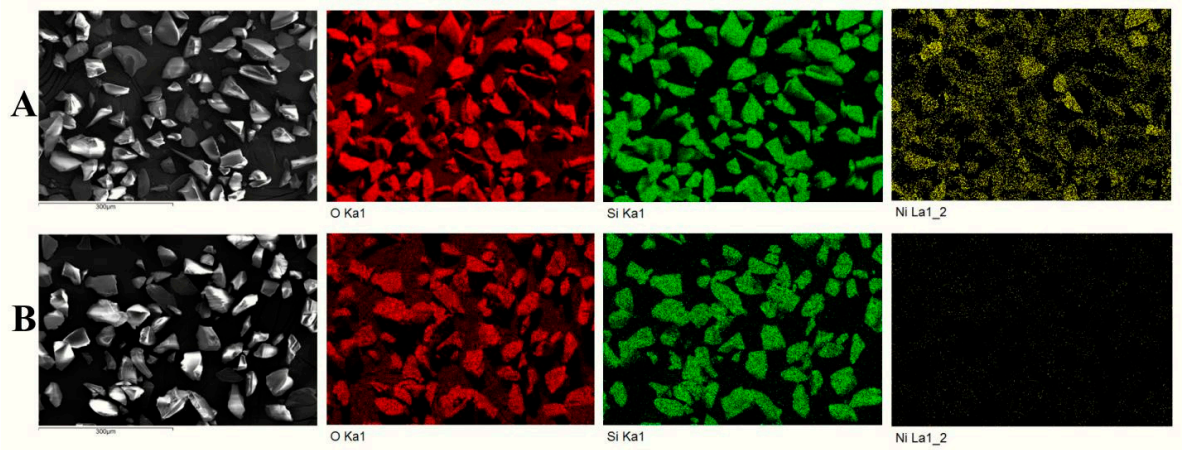


Figure 1. FE-SEM and EDS mapping images of SiO_2@NiO (**A**) and blank silica (SiO_2) (**B**).

To evaluate the specific surface area and pore characteristics of the adsorbent before and after NiO deposition, nitrogen adsorption analysis was performed. Table 1 shows no significant differences in specific surface area, pore volume, or pore diameter between SiO_2@NiO and SiO_2, and thus, a large specific surface area remained after NiO deposition, making SiO_2@NiO suitable as an SPE adsorbent.

Table 1. Specific surface area, pore volume, and pore size of SiO_2 and SiO_2@NiO.

Adsorbent	Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
SiO_2	391.9	0.9	9.8
SiO_2@NiO	396.4	0.9	9.6

3.2. Optimization of SPE

3.2.1. Influence of Adsorbent Amount

The adsorbent amount is one of the important factors affecting extraction efficiency. Various amounts of adsorbent ranging from 5 to 400 mg (5, 100, 200, 300, 400 mg) were investigated. As shown in Figure 2A, the recovery was at its maximum when the amount of SiO_2@NiO was 100 mg. Therefore, the optimal SiO_2@NiO amount was determined to be 100 mg for the subsequent experiments.

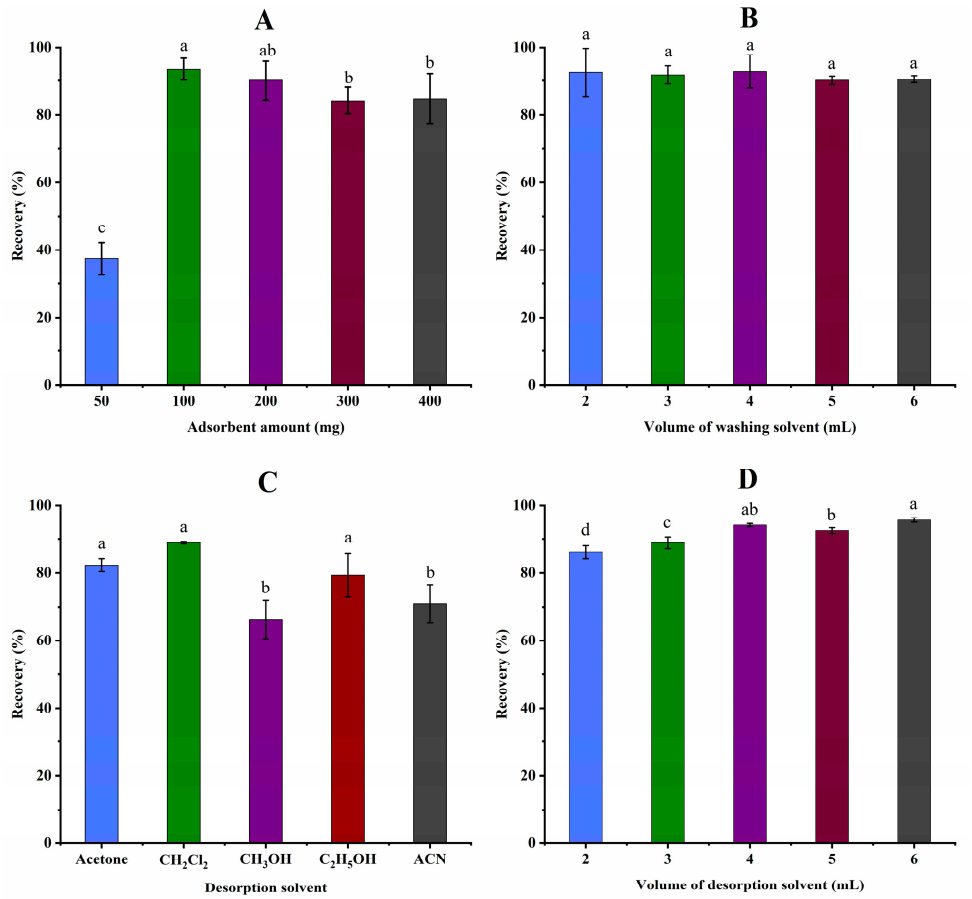


Figure 2. Optimization of SPE conditions including adsorbent amount (**A**), washing solvent volume (**B**), desorption solvent type (**C**), and desorption solvent volume (**D**). The error bars represent the standard deviation (SD) of three replicates. Different letters above the bars indicate statistically significant differences at $p < 0.05$, as determined via one-way analysis of variance (ANOVA) followed by Waller-Duncan's post hoc test. Bars sharing the same letter are not significantly different.

3.2.2. Influence of Washing Solvent Volume

Since polar solvents such as acetone, ethyl acetate, and acetonitrile could occupy the adsorption sites in SiO_2@NiO, leading to BaP elution, the nonpolar n-hexane solution capable of dissolving fat-soluble substances in the edible oil was used as the loading and cleaning solvents. Various volumes (2, 3, 4, 5 and 6 mL) of the cleaning solvents were used for optimization experiments. As shown in Figure 2B, the volume of the cleaning

solvent had little effect on the extraction recovery. In order to thoroughly eliminate impurities and shorten the extraction time, 3 mL of n-hexane was finally selected as the washing solvent volume.

3.2.3. Influence of Desorption Solvent

Both the type and volume of the desorption solvent affect the extraction recovery. Acetone, dichloromethane, methanol, ethanol, and acetonitrile were selected as desorption solvents. As shown in Figure 2C, dichloromethane demonstrated the optimal desorption performance. A possible reason might be that the moderate polarity of dichloromethane results in the easy solubility of BaP in dichloromethane and the competitive adsorption on polar SiO_2@NiO [35]. Additionally, dichloromethane is easily evaporated to dryness, thus greatly facilitating subsequent analysis. Therefore, dichloromethane was determined to be an optimal desorption solvent. Further, the desorption solvent volume ranging from 2 to 6 mL was optimized. As shown in Figure 2D, 4 mL dichloromethane achieved the maximum BaP elution (95%). When the volume of dichloromethane was more than 4 mL, the BaP recoveries stopped increasing, and thus 4.0 mL was determined as the optimal volume.

One-way ANOVA results show that all other parameters (except wash solvent volume) exhibited a significant effect on BaP recovery ($p < 0.05$). Taken together, an adsorbent amount of 100 mg, washing solvent volume of 3 mL n-hexane, and desorption solvent volume of 4.0 mL dichloromethane were determined to be the optimal conditions for SiO_2@NiO SPE.

3.3. Comparison of BaP SPE on SiO_2@NiO and SiO_2 Materials

In order to investigate BaP adsorption via NiO coating on SiO_2, the extraction efficiency of BaP on SiO_2@NiO and SiO_2 materials was compared under the same SPE conditions. The results show that the BaP recovery on SiO_2 was only 9.2% (RSD = 0.3%), while that on SiO_2@NiO was 87.5% (RSD = 0.4%), indicating that BaP was mainly captured by the NiO coating on the SiO_2@NiO material. This might be attributed to adsorption-related interactions between donor (π electron-rich aromatic structure of BaP) and acceptor (electron-deficient Ni(II) surface sites) at the NiO–BaP interface [33,34].

3.4. Reproducibility of SiO_2@NiO Preparation

The extraction stability and preparation reproducibility of SiO_2@NiO were investigated by comparing the extraction recoveries of BaP on SiO_2@NiO materials from the same batch (n = 5, intra-batch) and different batches (n = 5, inter-batch). As shown in Figure 3, the RSDs of BaP extraction recoveries on intra-batch and inter-batch SiO_2@NiO were less than 3.2% and 1.5%, respectively, indicating the good reproducibility of the prepared SiO_2@NiO adsorbents.

No visible green powder or green solution was observed in the effluent during SPE with SiO_2@NiO as the adsorbent, indicating no obvious release of NiO particles or ionic Ni. Furthermore, 0.1 mL of 1% dimethylglyoxume ethane solution was added to the treated effluent solution (first dried and then dissolved in 2 mL ammonia water to reach pH 8.0–9.0). No red color was observed, suggesting that no nickel ions were detected under the SPE conditions. These results demonstrate that the SiO_2@NiO adsorbent was stable during SPE, with negligible Ni leaching.

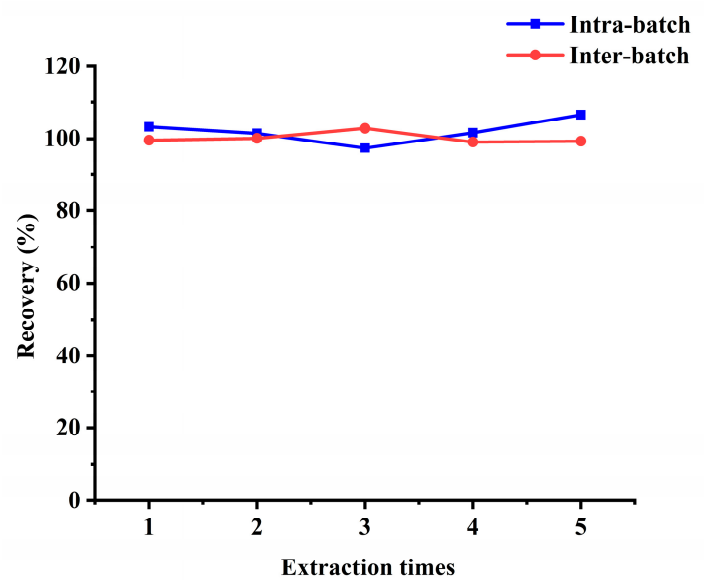


Figure 3. BaP extraction efficiency on intra-batch and inter-batch SiO_2@NiO adsorbent.

3.5. Method Validation

Figure 4 shows HPLC chromatograms of a blank soybean oil sample, a soybean oil sample spiked with 500 ng/mL BaP, and 500 ng/mL BaP standard solution. Although SiO_2@NiO SPE reduced impurities in sample solution, a matrix effect might also exist. In this study, the matrix effect (ME) was calculated by comparing the BaP peak area of the BaP-spiked soybean oil sample with that of the BaP standard solution. The results show that the ME was 81.7%, indicating that the SiO_2@NiO-based SPE-HPLC-DAD method displayed slight signal suppression. Therefore, the matrix-matched calibration curve was constructed to reduce the influence of the matrix on BaP quantification.

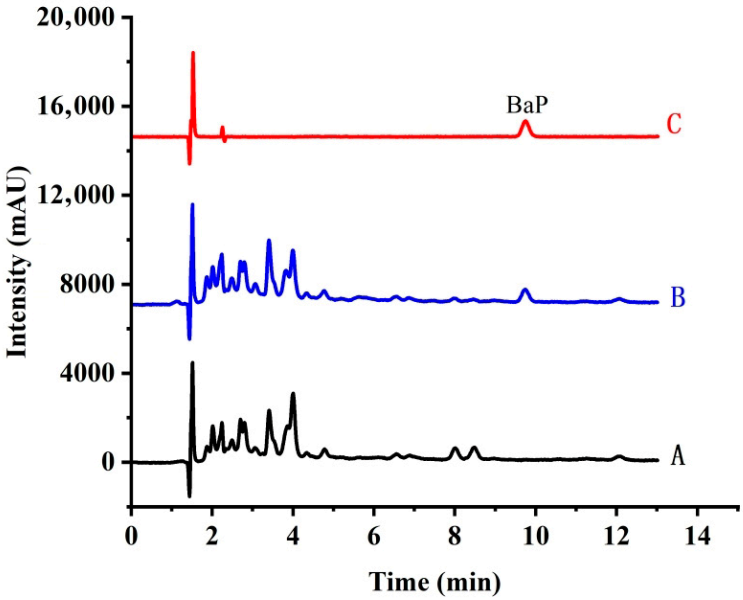


Figure 4. HPLC chromatograms of blank soybean oil sample (A), soybean oil sample spiked with 500 ng/mL BaP (B), and 500 ng/mL BaP standard solution (C).

Varying amounts of BaP (12 ng, 30 ng, 60 ng, 150 ng, 300 ng, 750 ng, 1500 ng, and 3750 ng) were spiked into 2 g of soybean oil, followed by dilution with n-hexane to prepare matrix-spiked sample solution with final BaP concentrations ranging from 6 to 1875 ng/g.

Under the optimized SPE conditions, the matrix-matched calibration curve was plotted with regard to the peak area of the BaP versus oil sample BaP concentrations (Table 2). The linear correlation coefficient was calculated to be 0.9999. The limits of detection (LOD) and limits of quantification (LOQ) of the method were calculated to be 3 and 10 times the signal-to-noise ratio, respectively. The results show that the LOD and LOQ of BaP were 1.3 and 4.4 ng/g, respectively, indicating that the method sensitivity was qualified for the detection of BaP in edible oils. The samples spiked with three BaP concentrations (30 ng/g, 150 ng/g, and 750 ng/g) were analyzed using the matrix-matched calibration curve. The intra- and inter-day RSDs of the spiked samples were investigated six times within one day (intra-day) and three times for three successive days (inter-day), respectively. As shown in Table 3, the intra- and inter-day RSDs were less than 3.0% and 2.6%, respectively, implying the desirable reproducibility of the method. The BaP recoveries of spiked samples varied from 97.4% to 105.1% (Table 3). The above results jointly indicate that the established method had good precision and accuracy, and thus, it could be used for the analysis of BaP in real oil samples.

Table 2. Linearity, limits of detection (LOD), limits of quantification (LOQ) for determination of BaP in oil samples.

Analyte	Linearity Range (ng/g)	Linear Regression		LOD (ng/g)	LOQ (ng/g)
		Linear Equation	R^2		
BaP	6–1875	Y = 227.3147X − 38.9316	0.9999	1.3	4.4

Table 3. Method's accuracy and precision (intra-day and inter-day) at three BaP concentrations.

Analyte (BaP)	Concentration	RSD (%)	Recovery (%)
Intra-day (n = 6)	Low concentration (30 ng/g)	3.0	97.4
	Medium concentration (150 ng/g)	0.3	100.6
	High concentration (750 ng/g)	1.2	105.1
Inter-day (n = 3)	Low concentration (30 ng/g)	2.6	100.1
	Medium concentration (150 ng/g)	0.7	98.9
	High concentration (750 ng/g)	1.1	104.9

3.6. Comparison Between Reported Methods and Developed Method

Further, the developed method for detecting BaP in edible oils was compared with several of the reported methods (Table 4), Firstly, the preparation of the adsorbent is simple with our developed method, involving no complex synthesis steps. Secondly, most of the previous methods presented in Table 4 require a tedious and time-consuming liquid extraction step for BaP before SPE. In the developed method, oil was only diluted with n-hexane and then directly loaded on SiO_2@NiO for SPE, thus simplifying sample-processing steps. In addition, the DAD detection equipment used in this method is inexpensive. The developed method provides satisfactory accuracy and sensitivity. The LOD of BaP in this method is lower than the maximum permissible residual amount of BaP of edible oil in China national standard GB 2762-2017. All data indicate that the developed method for SiO_2@NiO-based SPE coupled with HPLC-DAD for the detection of BaP in edible oils is simple, economical, and accurate.

Table 4. Comparison of our developed method with other methods.

Adsorbent	Detector	Recovery (RSD)	LOD (μg/kg)	LOQ (μg/kg)	Ref.
SPE (SiO_2-OCA)	HPLC-FLD	88.9–122.3% (9.2%)	0.03	0.1	[26]
SPE (ProElut C_{18})	HPLC-FLD	62.6–65.7% (4.9%)	0.05	0.15	[36]
MSPE (3D-IL@mGO)	GC-MS	84.4–96.6% (7.9%)	0.15	0.5	[37]
SPE (SiO_2@NiO)	HPLC-DAD	97.4–105.1% (3.0%)	1.3	4.4	This work

3.7. Real-Sample Analysis

To verify the practicability of the proposed method, it was applied to the analysis of BaP in 11 oil samples, and each sample was analyzed three times. As shown in Table 5, BaP was detected in two types of unrefined oil and frying oil. Since unrefined oils are not degummed, deacidified, or deodorized, their quality and safety cannot be guaranteed [38]. The presence of BaP in high-temperature frying oil may be because some substances in food are converted into BaP at high temperatures and dissolved in the oil [13]. Therefore, BaP in unrefined oil and high-temperature frying oil risk exceeding permissible limits, thus potentially damaging human health. Additionally, in order to obtain reliable results, 10 ng/g BaP was spiked into the above-mentioned 11 oil samples, and then, its recovery from the various oil samples was tested. BaP recovery was found to range from 87.6% to 111.0% with an RSD of 0.6–10.7%. The results demonstrate that the developed method was applicable for the analysis of BaP in various real edible oils.

Table 5. Concentrations before and after spiking and BaP recoveries of spiked oil samples.

Sample	Soybean Oil	Olive Oil (1)	Corn Oil	Olive Oil (2)	Linseed Oil	Walnut Oil	Sunflower Oil	Peanut Oil	Unrefined Oil (1)	Unrefined Oil (2)	Frying Oil
Concentration before spiking (ng/g, RSD%)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	13.1 (1.8)	8.3 (14.5)	8.6 (7.1)
Concentration after 10 ng/g BaP spiking (ng/g, RSD%)	11.1 (8.4)	10.5 (5.1)	9.9 (10.7)	9.9 (2.0)	10.8 (5.4)	10.9 (1.7)	9.7 (9.3)	9.5 (3.3)	22.9 (0.6)	18.4 (6.4)	17.2 (1.8)
Recovery (%)	111.0	104.9	99.3	99.1	108.9	109.6	97.6	95.0	99.2	103.0	87.6

Notes: N.D. indicates not detected.

4. Conclusions

A novel SPE-HPLC-DAD method for detecting BaP in edible oil was developed using SiO_2@NiO as the SPE adsorbent. SiO_2@NiO can selectively capture BaP through electron donor–acceptor interaction. It exhibited favorable recoveries (97.4–105.1%) and precisions (RSDs 0.3–3.0%). This method is characterized by its sample pretreatment simplicity, adsorbent preparation ease, and low cost, and thus, it can be applied to the monitoring of BaP in various edible oils. Although the method's sensitivity meets BaP detection requirements, the developed method is unsuitable for the determination of low-concentration PAHs. Therefore, future studies should combine the SiO_2@NiO adsorbent with a more sensitive detector to improve the detection sensitivity for a variety of PAHs in edible oils.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/separations13030087/s1: Table S1: Optimized parameters of SPE condition.

Author Contributions: Conceptualization, Y.G. and Q.Y.; methodology, Y.Y. and Y.G.; software, Y.G. and G.H.; validation, Y.G.; investigation, Y.Y. and Y.G.; resources, Q.Y.; data curation, Y.Y. and Y.G.; writing—original draft preparation, Y.Y. and Q.Y.; writing—review and editing, G.H. and Q.Y.; visualization, Y.Y. and Y.G.; supervision, Q.Y.; project administration, Q.Y. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

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