Dispersive Solid-Phase Extraction Using Microporous Sorbent UiO-66 Coupled to Gas Chromatography−Tandem Mass Spectrometry: A QuEChERS-Type Method for the Determination of Organophosphorus Pesticide Residues in Edible Vegetable Oils without Matrix Interference

Xuejin Mao,[†] Aiping Yan,[‡] Yiqun Wan,*[,†,‡] Dongmei Luo,[‖] and Hongshun Yang*[,§]

[†]State Key Laboratory of Food Science and Technology and [‡]Center of Analysis and Testing, Nanchang University, Nanchang 330047, People's Republic of China

[§]Food Science and Technology Programme, c/o Department of Chemistry, National University of Singapore, Singapore 117543, Singapore

[‖]College of Chemistry and Chemical Engineering, Chifeng University, Chifeng 024000, People's Republic of China

S *Supporting Information*

ABSTRACT: A QuEChERS-type method without matrix interference was designed and developed to determine organophosphorus pesticide residues in edible vegetable oils, based on dispersive solid-phase extraction with cleanup using UiO-66 as sorbent. Microporous UiO-66 directly and selectively adsorbed organophosphorus pesticides and excluded interfering compounds. Clean analytes were obtained by elution and analyzed using gas chromatography−tandem mass spectrometry. The dispersive solid-phase extraction conditions (amount of adsorbent, extraction time, desorption solvent volume, and elution time) were optimized. The limits of detection of the pesticides in vegetable oils were 0.16−1.56 ng/g. Under optimized conditions, the average pesticide recoveries were 81.1−113.5%. The intraday and interday relative standard deviations for analyte recovery were <8.2 and <13.9%, respectively. Thus, the method is reliable and could detect organophosphorus pesticide residues in edible vegetable oils. Furthermore, UiO-66 can be easily recycled and reused at least 10 times, reducing the cost of analysis.

KEYWORDS: UiO-66, dispersive solid-phase extraction, organophosphorus pesticides, gas chromatography−tandem mass spectrometry, vegetable oil

INTRODUCTION

Edible oils have been widely used in food processing and cooking because of their high nutritional value. Every year, a vast quantity of edible oil is consumed worldwide; it has been reported that the consumption of edible oils in China was 3406 million tons in 2015.[1] To fulfill demand, pesticides are usually used to increase yields by protecting oil crops from weeds, diseases, and pests, which results in a high risk of pesticide contamination of edible oils. The presence of pesticides in edible oil is harmful to human health.[2] Therefore, monitoring the residual levels of pesticides in edible oils is necessary.

Quantification of pesticide residues in foods is often performed by gas chromatography (GC) and liquid chromatography (LC) coupled with various detectors.[3] GC or LC analysis may result in false analysis results. In recent years, GC and LC equipped with mass analyzers have been commonly used for pesticide analysis, including GC and LC coupled with single quadrupole (GC−MS, LC−MS) or triple quadrupole mass spectrometry (GC−QqQ-MS/MS, LC−QqQ-MS/MS).[4−7] The accuracy and sensitivity of pesticide analysis can be significantly improved by these techniques through the selected ion monitoring (SIM) mode or multiple reaction monitoring (MRM) mode.[8] Nevertheless, they still usually suffer the interference from matrix compounds.[2,7] As is well-known, food samples have a complex matrix, and interference compounds from the matrix, even in small amounts, may result in false positive analysis results and cause harm to the instruments.[9] Therefore, the development of methods to prepare clean analytes is a current focus in the safety assessment of foods. Edible oils mainly comprise various fats, possessing a very complex matrix, and the pesticides generally have a similar polarity to the oil matrix. Therefore, the separation of pesticides from complex oil samples remains a challenge in monitoring the quality of edible oils.[10] To date, a number of studies on the extraction of pesticide residues from a complex lipid matrix have been reported.[11−19] The most commonly used sample preparation method for the pesticides in fatty matrices is solvent extraction (SE) followed by liquid–liquid extraction (LLE),[11,15,16] gel permeation chromatography (GPC),[17] and low-temperature fat precipitation (LTFP)[15,16] cleanup procedures. In these cleaning procedures, the LLE

technique is time-consuming and requires large amounts of organic solvents.[20] GPC is a high-cost cleanup technique that includes the drawbacks of LLE.[1] For LTFP, fat can be easily removed by precipitation in a freezer below −20 °C; however, it demands that the analytes and extraction solvents cannot be frozen at the low temperature and usually takes several hours.[20] In addition, the three methods cannot remove fat entirely, and further cleanup is usually necessary, resulting in a tedious operation, long analysis time, and increased cost.[21,22] Therefore, to better monitor the quality of edible oils, the development of a quick, easy, cheap, effective, rugged, and safe sample preparation method (QuEChERS-type) has received increased attention in recent years. The sorbent-based cleanup procedure, dispersive solid-phase extraction (d-SPE), has been widely used to develop QuEChERS methods to monitor food quality because of its simple operation. Commonly used sorbents in d-SPE are primary secondary amine (PSA), graphitized carbon black (GCB), octadecylsilane (C18), florisil, silica gel, and alumina. More recently, the new and commercially available sorbents such as Z-Sep, EMR-Lipid, Oasis-HLB Prime, and LipiFltr have been used to remove lipids from lipid-rich foods.[4−6,13,23] Even though significant progress has been achieved by these adsorbents, some issues remain to be addressed. For example, matrix effects cannot be suppressed well, because it is hard to completely remove the interference compounds.[5,13] In some cases, the sorbents have high capacity to adsorb the analytes, leading to poor recoveries.[23,24] Moreover, most of these used sorbents cannot be recycled. Thus, it remains a challenge to establish a reliable method to monitor the quality of edible oils.[10,20]

Metal−organic frameworks (MOFs), synthesized by assembling metal ions with organic ligands, have emerged as a class of very promising ordered porous materials. They are widely used in catalysis, gas storage/capture, drug delivery, and sensor.[25] As a result of their inorganic−organic compositions as well as high porosity, MOFs show good adsorption affinity and capacity to many compounds via various interactions such as π−π stacking, hydrogen-bonding, coordination bonding, and van der Waals as well as electrostatic interaction.[25−27] Moreover, the uniform pores of MOFs can exclude large compounds but allow small compounds to enter, resulting in the separation of compounds with different molecular sizes.[27] Additionally, it is generally acknowledged that the interference compounds in edible oil matrices, such as fats, pigments, and vitamins, usually are large molecules, while the molecular size of pesticide is relatively small. It means that the pesticides can be separated from the edible oil matrices by MOFs with a proper pore size. Inspired by these, we employed a stable and cheap Zr-MOF, UiO-66, and evaluated it as the sorbent in the current study. UiO-66 comprises a ZrO_x cluster and terephthalic acid (BDC)[28] and possesses an ordered microporous structure with high surface area (>1000 m^2/g) and pore sizes of 0.7 and 0.9 nm.[29,30] In recent years, UiO-66 has been used as an outstanding adsorbent to remove small organic contaminants such as rhodamine B,[31] methylchlorophenoxypropionic acid,[32] the anticonvulsant carbamazepine, and the antibiotic tetracycline hydrochloride[33] and selectively extract neonicotinoid insecticides in aqueous media,[34] via weak interactions (hydrogen bonding, π−π stacking, electrostatic interaction) between the substrates and UiO-66 (ZrO_x cluster or BDC linker). Nevertheless, to the best of our knowledge,

UiO-66 has not been used as a sorbent to selectively extract the pesticides from a hydrophobic matrix such as edible oil.

Hence, the aim of this study was to develop a selective and sensitive QuEChERS-type method to monitor pesticides in edible vegetable oils. As a major group of pesticides, organophosphorus pesticides (OPPs) are cost-effective and widely applied. The OPPs can accumulate in the seeds,[2] and some of them have been found in edible oils.[22,35] In the present study, a UiO-66-based d-SPE method was designed to monitor OPPs in edible vegetable oils. The ordered microporous UiO-66 could selectively adsorb the OPPs from the edible vegetable oils by excluding most of interference compounds. This procedure is different from many d-SPE methods, where the sorbents are used to adsorb the interference compounds, and the analytes remain in bulk.[36] The UiO-66-based d-SPE conditions were further optimized with an orthogonal array experimental design. A perfect multiresidue analysis technique, GC−MS/MS, was employed to determine the OPPs in the final extracts, Finally, a selective and sensitive QuEChERS-type method to determine OPPs in edible vegetable oils was established. In addition, most of the sorbents used in d-SPE cannot be recycled.[1,2,11,18,19,22,35] However, the UiO-66 used in the present method can be easily recycled.

■ MATERIALS AND METHODS

Reagents and Materials. Four pesticide standards including dichlorovos, dimethoate, malathion, and methidathion, were offered by the Agro-Environment Protection Institute (Tianjin, China). The purity of each pesticide standard was 99.99%. The standard working solutions were prepared with a suitable dilution of the stock standard solution in *n*-hexane. Matrix-matched standard solutions were prepared by an appropriate dilution of stock standard solutions with blank vegetable oil sample extracts. All the solutions were stored in the refrigerator at 4 °C. The analytical reagent (AR) grade acetone, terephthalic acid, N,N-dimethylformamide (DMF), methanol, and ammonia solution ($NH_3 \cdot H_2O$) were purchased from Sinopharm Chemical Reagent Limited Company (Shanghai, China). High-performance liquid chromatography (HPLC) grade *n*-hexane was purchased from TEDIA Company (Fairfield, OH, USA). HPLC grade ethyl acetate, acetonitrile, and methanol were purchased from Merck Company (Darmstadt, Germany). Ultrapure water was produced by a Milli-Q system (Millipore, Burlington, MA, USA). The AR grade $ZrCl_4$ was provided by Aladdin Biotechnology Limited Company (Shanghai, China). Five different edible vegetable oils, including corn oil, blend oil, soybean oil, rapeseed oil, and peanut oil, were purchased from different supermarkets in Nanchang, China.

Synthesis of UiO-66. UiO-66 was synthesized according to the previously reported method with some modification.[37] Zirconium chloride (0.18 g) was dissolved in 2 mL of DMF by stirring for 30 min. In another beaker, 0.127 g of terephthalic acid was dissolved in 2 mL of DMF by stirring for 15 min; 0.065 mL of ammonia aqueous (2 mol L^{-1}) was then added. The terephthalic acid solution was slowly added to the dissolved zirconium chloride, and then, 6 mL of DMF was added and stirred for 20 min. After this, the mixture was transferred to a 15 mL Teflon liner stainless steel autoclave tube and placed in an oven at 120 °C for 24 h. The final products were separated by centrifugation (9000g for 3 min), washed with DMF, activated by methanol exchange (immersing in methanol for 12 h at room temperature and repeating the procedure three times), and then dried under a vacuum at 100 °C overnight.

Characterization of UiO-66. Powder X-ray diffraction (XRD) was performed on a Puxi XD-3 diffractometer with Cu Kα radiation (λ = 0.15418 nm, 40 kV/30 mA) at a scanning step of 2°/min in the 2θ range from 5 to 45°. The N$_2$ adsorption−desorption isotherm was determined on a Micrometrics ASAP 2020 instrument analyzer at 77 K. Before the analysis, the sample was activated on a Micrometrics

Table 1. Gas Chromatography−Tandem Mass Spectrometry (GC−MS/MS) Acquisition Parameters Used To Measure Four Pesticides

time segment window (min)	pesticide	t_R (min)	quantification transition	collision energy (eV)	confirmation transition	collision energy (eV)
4.0−6.5	dichlorovos	5.252	184.9 > 93.0	10	184.9 > 109.1	20
6.5−8.5	dimethoate	8.236	229.0 > 87.1	5	229.0 > 42.0	25
8.5−10.5	malathion	9.145	173.0 > 99.1	15	173.0 > 127.2	5
10.5−13.0	methidathion	11.578	144.9 > 85.1	5	144.9 > 58.2	10

Smart VacPrep System at 200 °C for 12 h. The surface areas were calculated using the multipoint BET (Brunauer−Emmett−Teller) method. Fourier transform infrared (FT-IR) spectra were recorded as KBr discs on a Nicolet iS10 spectrophotometer in the 4000−650 cm^{-1} regions. The ultraviolet−visible diffuse reflectance spectra (UV−vis DRS) were collected using a Cary-60 spectrophotometer. BaSO$_4$ was used as a reflectance standard.

Sample Preparation. The extraction experiments were carried out using a 5 mL centrifuge tube. To perform the extraction, 1.0 g of oil sample and 2 mL of *n*-hexane were added to the tube, and then, 30 mg UiO-66 was dispersed and mixed to produce a homogeneous solution. The extraction was conducted under vortexing for 20 min at 2500 rpm in an MS2 mini shaker (Guangzhou Yike Lab Technology LTM Co., Guangzhou, Guangdong, China). Then, the 5 mL microcentrifuge tube was centrifuged at 6000g for 2 min. After the supernatant was removed, 4 mL of acetone was added to the tube as an eluent under ultrasonication for 20 min (Kunshan Ultrasonic Instrument Co., Ltd., Kunshan, China). After centrifugation, the collected eluent was transferred into a round-bottomed flask and evaporated to dryness with an RE-52A rotary vacuum evaporator (Shanghai Yarong Biochemistry Instrument Factory, Shanghai, China) in a water bath at 40 °C. Then, 1 mL of *n*-hexane was added. The reconstituted solution was shaken for 1 min at 2500 rpm using an MS2 mini shaker. Subsequently, the solution was filtered through a 0.22 μm organic membrane. Finally, the solution was transferred into a 2.0 mL sample vial and analyzed with a GC−MS/MS system.

GC−MS/MS Analysis. Analysis was carried out on an Agilent 7890A GC system connected to a triple quadrupole mass spectrometer. A DB-35MS capillary column (30 m × 0.25 mm i.d., film thickness = 0.25 μm) was used for GC separation. The injector port temperature was kept at 250 °C, and sample injection was implemented in splitless mode. Helium (99.999%) at a flow rate of 1.0 mL min^{-1} was used as the carrier gas. The oven temperature program was applied as follows: 80 °C, held for 1 min; increased at a rate of 30 °C min^{-1} up to 200 °C; then increased at a rate of 25 °C min^{-1} up to 250 °C and held for 6 min. Mass spectrometry was performed using electron impact (EI) ionization (70 eV) in MRM mode under the temperature of 230 °C. The transfer-line temperature was set at 280 °C. Helium was also used as the quench gas at a flow rate of 2.25 mL min^{-1}. Nitrogen (99.999%) was used as the collision gas at a flow rate of 1.5 mL min^{-1}. The solvent delay was set for 4 min, and the injection volume was 1 μL.

For both identification and quantification of the results, one precursor ion and two product ions for each target compound in MRM mode was employed. Groupings were set to obtain adequate sensitivity and low background noise. The analysis parameters used to measure pesticides are presented in Table 1. A representative GC−MS/MS chromatogram of the OPPs in mixture standard solution is shown in Figure 1A.

Spiking Procedure. Before the corresponding sample spiking procedure, the samples were detected following the procedure described above. A corn oil sample without the target analyte was selected as a blank sample for the preparation of matrix-matched standards and the recovery experiment. For the recovery study, 1.0 g of blank oil sample and 2 mL of *n*-hexane were transferred into a 5 mL screw cap centrifuge and spiked with the mixture standard solution at various concentrations. The mixture was then blended using an MS2 mini vortex shaker and stood at room temperature for 2 h.
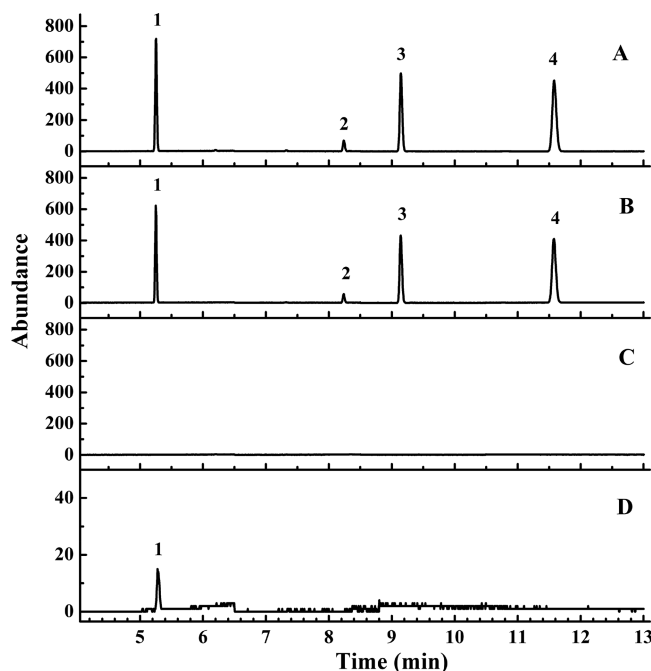

Figure 1. Gas chromatography−tandem mass spectrometry (GC−MS/MS) chromatograms of the pesticide matrix-matched standard mixture solution (50 ng/g) (A), spiked corn oil sample (50 ng/g) (B), corn oil sample (C), and blended oil sample (D). Peak identification: (1) dichlorovos, (2) dimethoate, (3) malathion, (4) methidathion.

Method Validation. The validation of the analytical method was carried out using the following parameters: linearity, calibration data, limit of detection (LOD), limit of quantification (LOQ), matrix effect (ME), accuracy, and precision. The calibration curves were estimated with matrix-matched standard calibration in blank extracts of corn oil. Three injections were carried out at each concentration level. The peak areas of each analyte were plotted against the concentration level, and then, linear regressions were performed on the resulting curves with the minimum least-square method. The LOD and LOQ were estimated based on signal-to-noise ratios of 3 and 10, respectively. For sample matrix spiking testing, 1.0 g of edible vegetable oil was separately spiked and measured for accuracy and precision at three fortification levels. Six replicate experiments were carried out at each of fortification levels.

Statistical Analysis. Each optimization experiment was performed in triplicate, and the average mean recovery of the pesticides was selected as the experimental response. The data were analyzed statistically using analysis of variance (ANOVA) with the IBM SPSS software (Version 18), and means were compared using the least significant difference (LSD) method to determine significant differences. In addition, differences with $P \leq 0.05$ were considered significant. The results are presented in histograms.

■ RESULTS AND DISCUSSION

Material Characterization. Figure S1A presents the XRD pattern of the as-synthesized UiO-66, which showed intensive

diffraction peaks that are in good agreement with the simulated pattern reported in the literature,[28,29] revealing the successful synthesis of highly crystalline UiO-66. The pore structure of the as-synthesized UiO-66 was evaluated using an N_2 sorption isotherm at 77 K. As revealed in Figure S1B, the as-synthesized UiO-66 exhibited a typical type-I isotherm, indicating the microporous structure of UiO-66. The as-synthesized UiO-66 showed a high BET surface area of 1514 m^2 g^{-1}, which was calculated from the isotherm. The pore structure of UiO-66 was similar to that reported previously.[28,29]

Optimization of Sample Preparation. To improve the extraction efficiency of the d-SPE process, the effect of experimental variables including the type and volume of dilution solvents, the amount of adsorbent, extraction time, the type and volume of desorption solvents, and elution time were selected for optimization.

Selection of the Dilution Solvent. The viscosity of oil samples hinders the dispersion of the sorbent in d-SPE. Thus, dilution has an important effect on the extraction efficiency. In this study, *n*-hexane, acetone, ethyl acetate, and acetonitrile were investigated as dilution solvents. The experimental results showed that analytes were adsorbed on UiO-66 only in the nonpolar *n*-hexane solution. The possible reason is that the polar solvents (acetone, ethyl acetate, and acetonitrile) could prevent the adsorption of OPPs by occupying the adsorption sites in UiO-66. Figure 2 shows the effect of the amount of *n*-
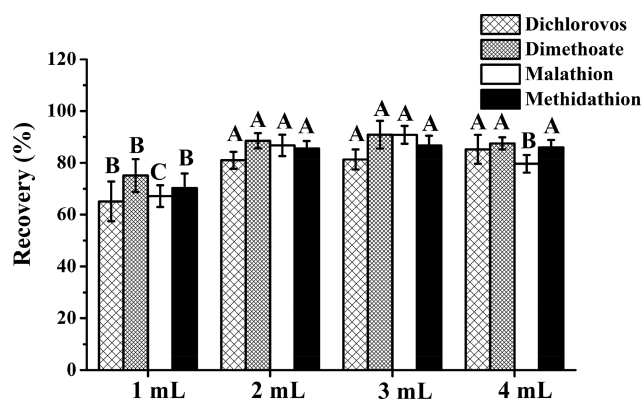

Figure 2. Effect of the volume of *n*-hexane in oil samples on the recovery of organophosphorus pesticides (OPPs) from corn oil. Within each pesticide, means with different capital letters are significantly different ($P \leq 0.05$) among different groups.

hexane. The recoveries of OPPs increased with an increase in the volume of *n*-hexane, and the highest recoveries were obtained when the dilution volume was 2 mL. Further increasing the volume of *n*-hexane did not improve recovery; therefore, 2 mL of *n*-hexane was selected.

Selection of the Desorption Solvent. The type of desorption solvent is an important factor that influences the recovery of the analyte.[10] Acetone, ethyl acetate, methanol, and acetonitrile are commonly used solvents for pesticide analysis. To test their desorption abilities, parallel experiments were carried out. The results were plotted as a histogram in Figure 3. The results showed that acetone was the most suitable desorption solvent in this trial. This is because acetone has a strong dissolving ability toward the analytes and could interact with the UiO-66 adsorption sites that weaken the interaction between UiO-66 and the analytes. Besides, acetone has a lower boiling point, meaning that the concentration step takes less
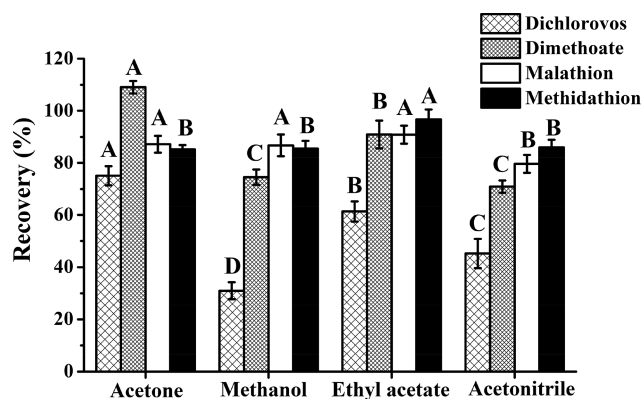

Figure 3. Effect of the elution solvent type on the recovery of organophosphorus pesticides (OPPs) from corn oil. Within each pesticide, means with different capital letters are significantly different ($P \leq 0.05$) among different groups.

time and can be easily removed from UiO-66. Thus, acetone was chosen as the desorption solvent.

Optimization of d-SPE Conditions. To obtain good extraction efficiency, the extraction conditions needed to be carefully tested and proven. In this study, the extraction conditions were investigated using an orthogonal array experimental design. It is a cost-effective optimization tactic using a minimum number of experiments.[24] The effects of four factors on recovery were evaluated and optimized using an L_9 (3^4) orthogonal array design. Table 2 shows the factors allocation for the orthogonal matrix. In the matrix, the factors A, B, C, and D denote the amount of adsorbent, adsorption time, volume of desorption solvent, and elution time, respectively. The numbers 1, 2, and 3 indicate different experimental levels.

A portion (50 μL) of the mixture standard solutions (1.0 mg/L) was added to 1.0 g of corn oil. For each test, triplicate samples were performed; thus, 27 samples were prepared and extracted according to the L_9 (3^4) orthogonal array design. Table 2 shows the average recoveries for the four pesticides used in each trial as well as the mean effects (K_1, K_2, and K_3) for each factor at three different levels. The importance of these factors was evaluated using range values (the difference quantity between maximal and minimal means within three levels of each factor). A variable with a greater R value was more crucial to the extraction efficiency. As listed in Table 2, the range in K observed with the changes in A was 141.7, which was greater than the 15.9, 18.6, and 19.6 that resulted from changes in B, C, and D, respectively. In other words, the amount of adsorbent was the most significant factor. Deduced from the orthogonal array design, the optimum extraction conditions were $A_3B_2C_1D_2$, namely, 30 mg of adsorbent, 20 min extraction time, 4 mL of desorption solvent, and 20 min elution time. The current method took 20 min for the adsorption and desorption, respectively; this was mainly due to the relatively slow mass transfer rate of analytes in the small pores of UiO-66.

Reusability of the UiO-66. The reusability of the sorbent in a d-SPE procedure can reduce the cost of analysis. In this work, the reusability of the UiO-66 was examined. Used UiO-66 was eluted again with 4 mL of acetone, followed by the same elution procedure as mentioned in the Sample Preparation section. The elution concentration solution was analyzed with GC–MS/MS, and there was no analyte residue

Table 2. Assignment of Factors and Levels of Optimization Experiments Obtained Using an L_9 (3^4) Orthogonal Array Design, along with the Average Recoveries of Four Pesticides

trial NO.	factor				mean recovery (%) ± SD (n = 3)			
	A^a	B^b	C^c	D^d	dichlorovos	dimethoate	malathion	methidathion
1	1	1	1	1	72.4 ± 4.4	88.9 ± 5.5	61.3 ± 3.2	71.5 ± 3.6
2	1	2	2	2	72.6 ± 3.0	96.8 ± 14.5	65.4 ± 3.9	75.0 ± 4.0
3	1	3	3	3	66.8 ± 4.6	63.5 ± 9.9	70.7 ± 5.9	68.8 ± 5.3
4	2	1	2	3	80.1 ± 7.5	112.7 ± 7.3	104.8 ± 5.9	103.8 ± 3.9
5	2	2	3	1	83.3 ± 9.9	115.6 ± 13.5	110.8 ± 8.0	103.5 ± 4.1
6	2	3	1	2	91.9 ± 13.7	115.9 ± 13.7	118.0 ± 8.1	106.8 ± 4.8
7	3	1	3	2	88.1 ± 12.7	122.2 ± 9.9	117.1 ± 8.0	106.4 ± 2.7
8	3	2	1	3	91.2 ± 15.0	120.6 ± 14.5	123.7 ± 7.7	110.5 ± 7.5
9	3	3	2	1	93.2 ± 14.5	101.2 ± 11.3	123.5 ± 7.5	101.1 ± 4.2
K_1	291.3	376.5	390.9	375.4				
K_2	415.7	389.7	376.8	392.1				
K_3	433.0	373.8	372.3	372.5				
range	141.7	15.9	18.6	19.6				
optimization level	A_3	B_2	C_1	D_2				

^{a}Factor A, amount of adsorbent; level 1, 10 mg; level 2, 20 mg; level 3, 30 mg. ^{b}Factor B, extraction time; level 1, 10 min; level 2, 20 min; level 3, 30 min. ^{c}Factor C, volume of desorption solvent; level 1, 4 mL; level 2, 6 mL; level 3, 8 mL. ^{d}Factor D, elution time; level 1, 10 min; level 2, 20 min; level 3, 30 min. $^e K_i$, the mean effect of each factor at level i (i = 1, 2, 3).

in UiO-66. Afterward, the same batch of recycled UiO-66 was used to conduct the extraction experiments 10 times. After each run, UiO-66 was collected and put into the oven at 100 °C to bake for 1 h. As can be seen from Table 3, no significant

Table 3. Reusability of the UiO-66 Sorbent

number of recycle	recoveries (%) (mean ± SD, n = 3)			
	dichlorovos	dimethoate	malathion	methidathion
1	80.5 ± 3.8	87.2 ± 3.2	85.6 ± 4.8	88.9 ± 1.7
2	78.7 ± 2.8	109.1 ± 4.1	77.2 ± 4.6	85.2 ± 3.2
3	80.6 ± 2.9	93.0 ± 3.7	76.9 ± 4.1	74.6 ± 3.1
4	79.9 ± 1.0	93.4 ± 6.4	79.9 ± 4.9	83.9 ± 5.7
5	83.7 ± 5.5	92.2 ± 4.6	84.0 ± 6.5	87.9 ± 2.9
6	86.7 ± 4.1	88.4 ± 4.0	90.8 ± 3.9	80.4 ± 5.1
7	81.1 ± 3.6	97.7 ± 5.3	86.0 ± 2.9	87.0 ± 1.8
8	87.3 ± 3.7	91.8 ± 6.0	87.6 ± 0.6	86.5 ± 0.4
9	83.0 ± 4.2	82.9 ± 4.6	78.6 ± 3.6	76.6 ± 2.8
10	92.1 ± 3.8	90.2 ± 5.6	82.9 ± 3.9	77.6 ± 3.0

changes in recovery were found after 10 runs. In addition, the recyclable UiO-66 was characterized by XRD (Figure 4). XRD revealed that the reused UiO-66 was comparable to the fresh sorbent, indicating the stability of UiO-66. These results suggest the excellent reusability of UiO-66.

Matrix Effect. The matrix effect (ME) is a significant factor in multiresidue analysis. Matrix-induced effects including suppression and enhancement are usually reported in analytical detection methods.[24] In particular, the matrix-induced enhancement effect is more common in GC analysis, because the interference components might compete for the active site in the glass liner, weakening the interaction between the analyte and active site, and thus permitting a larger amount of analyte to be transferred to the chromatographic column. It will result in an inaccurate quantification result if using standard curves for quantitation. In this work, the ME was calculated from calibration curve slopes in matrix and in solvent according to the following equation.[38]
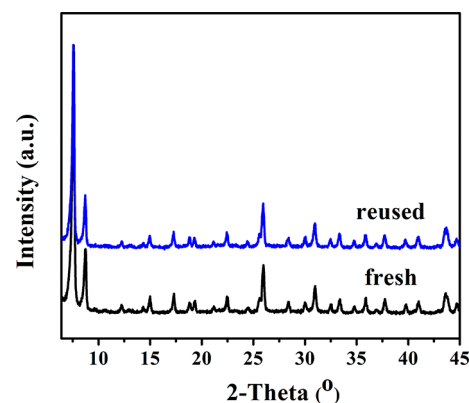
Figure 4. X-ray diffraction (XRD) spectra of reused UiO-66 and fresh UiO-66.

$$ME\ (\%) = \left(\left(\frac{\text{slope of calibration curve in matrix}}{\text{slope of calibration curve in solvent}} \right) - 1 \right) \times 100$$

As shown in Table 4, the results revealed that the signals of the pesticides showed no matrix effect in this case (−20% < no ME < 20%).[39] This means that the analytes did not suffer from interference of the matrixes in real sample analysis. This was further proven by the phenomenon that oil samples and sorbent UiO-66 showed no color changes before and after adsorption (Figure 5). The current designed sample preparation method provides clean analytes without matrix interference to monitor the quality of edible vegetable oils. Therefore, matrix-matched standard curves or normal standard curves can also be performed in the quantitative analysis. The matrix-matched standard curves were selected in this study.

Performance Evaluation of the Method. The calibration curves showed excellent linearity, with a correlation coefficient in the range of 0.9987−0.9998 (Table 4). Pesticides were detected at the level of 0.16−1.56 ng/g, depending on the type of analyte, and the LOQ values ranged from 0.61 to 5.00 ng/g (Table 4). Furthermore, these values are lower than the maximum residue limits set by the National Food Safety Standard of China, the Agri-Food & Veterinary Authority of

Table 4. Calibration Data of Four Organophosphorus Pesticides (OPPs) in Matrix-Free Solvent and Oil Matrix

pesticide	linear range (mg/L)	calibration data in solvent	R^2	calibration data in matrix	R^2	LOD (ng/g)	LOQ (ng/g)	MRL[a] (ng/g)	MRL[b] (ng/g)	MRL[c] (ng/g)	ME (%)
dichlorovos	0.005–0.5	$y = 17228.8016x - 13.7594$	0.9999	$y = 18306.7941x + 114.0747$	0.9993	0.16	0.61	100	-	-	6.3
dimethoate	0.005–0.5	$y = 2060.3408x + 5.2914$	0.9942	$y = 2242.2420x + 11.2343$	0.9987	1.56	5.00	50	-	-	8.8
malathion	0.005–0.5	$y = 15312.0253x - 44.2003$	0.9990	$y = 14681.2334x + 104.1939$	0.9993	0.24	0.81	8000	-	13000	−4.1
methidathion	0.005–0.5	$y = 32207.5416x - 155.1970$	0.9985	$y = 29765.7799x + 162.9042$	0.9998	0.25	0.84	-	1000	2000	−7.6

[a]Source: National Food Safety Standard of China, Maximum Residue Limits for Pesticides in Food. [b]Source: AVA, Agri-Food & Veterinary Authority of Singapore, Food with Maximum Amounts of Pesticides. [c]Source: CAC, Codex Alimentarius Commission, Codex Alimentarius Commission Pesticide Residues in Food Online Database.
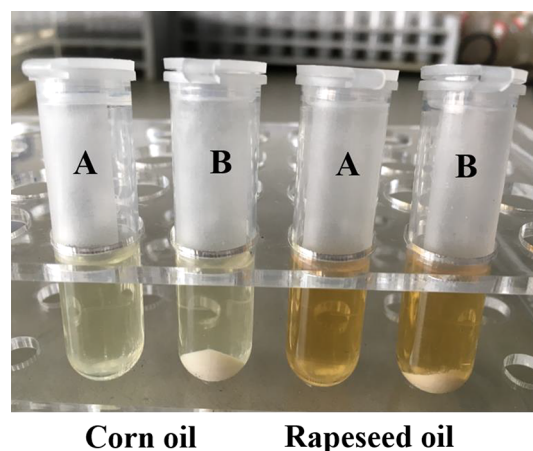

Figure 5. Color changes of oil samples and sorbent UiO-66 before (A) and after adsorption (B).

Singapore, and the Codex Alimentarius Commission (shown in Table 4). These results demonstrated that the LOQs of the present work are sufficient to safeguard public health.

Accuracy and precision were investigated using a recovery experiment. Recovery validation experiments were conducted in the matrix at three fortified levels (10, 20, and 50 ng/g). Repeatability (intraday) and reproducibility (interday) conditions were applied to determine the precision of the method. The experiments for intraday precision determination were performed within the same day and comprised six replicates at each fortified level. To determine interday precision, six replicate experiments at each fortified level were performed on six successive days. The average recoveries and relative standard deviations (RSDs) from the experiments are shown in Table 5. The representative GC−MS/MS chromatograms of

Table 5. Intra and Interday Method Precisions at Three Spiked Levels

pesticides	spiked level (ng/g)	intraday ($n = 6$)		interday ($n = 36$)	
		recovery (%)	RSD (%)	recovery (%)	RSD (%)
dichlorovos	10.0	103.8	5.0	107.0	7.9
	20.0	81.1	4.4	84.4	11.5
	50.0	84.2	5.6	88.3	12.4
dimethoate	10.0	87.7	6.8	102.7	13.9
	20.0	113.5	5.6	93.3	12.9
	50.0	95.4	8.2	96.8	13.2
malathion	10.0	101.7	4.6	107.4	9.1
	20.0	91.2	3.7	82.8	8.9
	50.0	86.8	2.4	82.4	5.8
methidathion	10.0	100.5	5.5	104.9	10.4
	20.0	89.5	4.4	81.7	9.4
	50.0	86.8	1.4	81.9	6.6

the OPPs obtained from the fortified samples and the blank sample chromatogram obtained from the corn oil sample without the target analyte are shown in Figure 1B and C, respectively. The recoveries of most pesticides (81.1−113.5%) were in the range of 70−120% set by the European Commission, Health & Consumer Protection Directorate-General.[40] The RSDs for the intraday and interday experiments were below 13.9%, meeting the requirements of

Table 6. Comparison of Methods for the Determination of Organophosphorus Pesticides in Oils

matrix	major sample preparation procedure	solvent amount (mL)	adsorbent amount (mg)	adsorbent reusability	pretreatment time (min)	analytical technique	recovery (%)	RSD (%)	LOD (ng/g)	LOQ (ng/g)	matrix effect	ref
rapeseed oil	(1) LLE (2) LTFP (12 h)	10	5000	no	>720	LC–MS/MS	25–139	1–31	not reported	0.5–18	not reported	18
edible oil	(1) LLE (2) RLTFP (10 min) (3) d-SPE	13	490	no	>32	GC–MS/MS	83–119	1–10	0.01–0.2	0.05–1	yes	2
olive oil	(1) LLE (2) LTFP (12 h) (3) d-SPE	10	1062.5	no	>720	GC–MS/MS and LC–MS/MS	70–120	<20	3	10	yes	22
olive oil	(1) LLE (2) d-SPE	10	6500	no	>3.5	LC–MS	70–130 % for 72 % of analytes	0.54–27.57	0.12–84	0.4–277.2	yes	11
olive oil	(1) LLE (2) MSPD	67	4000	no	-[a]	LC–MS	70–130 % for 57 % of analytes	1.49–18.54	0.16–50	0.53–165	yes	11
olive oil	(1) MAE2. SPE	16	500	no	-[a]	GC–FPD	60–104	1–10	not reported	7–20	yes	35
blended oil	(1) LLE (2) LTFP (4 h) (3) d-μ-SPE	10	100	no	>240	GC–MS	74–118	1–12	0.6–1.2[b]	2–40[b]	not reported	1
peanut oil	(1) LLE (2) LTFP (12h) (3) d-SPE	11.7	1600	no	>720	GC–MS	85.9–114.3	1.22–8.48	0.7–1.6	not reported	not reported	19
cold-pressed vegetable oils	dispersive microextraction ("magnetic water")	1.19	30	no	<15	GC–MS	76.0–135.9	1.2–11.6	0.21–0.38	0.70–1.27	not reported	41
edible oil	d-SPE	6	30	yes	>40	GC–MS/MS	81.1–113.5	1.4–13.9	0.16–1.56	0.61–5.00	no	this method

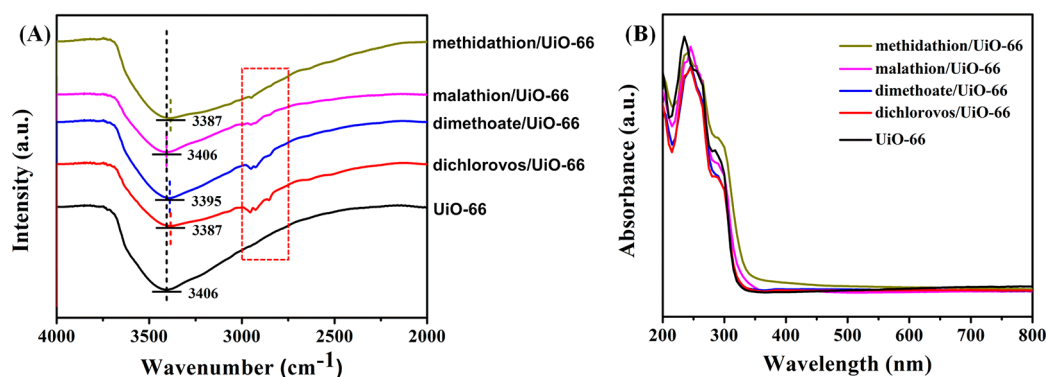[a]No detailed data of pretreatment time. [b]The unit of LOD is ng/mL.

Figure 6. FT-IR spectra (A) and UV−vis DRS spectra (B) of UiO-66 and pesticide/UiO-66 samples.

Table 7. Analysis of Organophosphorus Pesticides in Real Vegetable Oils

pesticides	blended oil detected (ng/g)	recovery (%) ± SD	soybean oil detected (ng/g)	recovery (%) ± SD	rapeseed oil detected (ng/g)	recovery (%) ± SD	peanut oil detected (ng/g)	recovery (%) ± SD
dichlorovos	1.1	81.1 ± 3.6	ND	87.3 ± 3.7	ND	83.0 ± 4.2	ND	92.1 ± 3.8
dimethoate	ND	94.3 ± 8.1	ND	96.5 ± 9.0	ND	80.6 ± 6.7	ND	91.2 ± 7.2
malathion	ND	86.0 ± 2.9	ND	87.6 ± 0.6	ND	78.6 ± 3.6	ND	82.9 ± 3.9
methidathion	ND	87.0 ± 1.8	ND	86.5 ± 0.4	ND	76.6 ± 2.8	ND	77.6 ± 3.0

[a]ND: not detected. Spiked level: 50 ng/g.

pesticide residue analysis (RSD ≤ 20%).[40] Thus, the developed method could reliably detect OPPs in edible vegetable oils.

Method Comparison. To estimate the developed method objectively and comprehensively, a comparison between this method and several other reported methods to determine OPPs in oils was performed. Important impacting factors, including sample pretreatment procedure, usage of organic solvent, adsorbent used per test, reusability of adsorbent, pretreatment time, instrumental requirements, recoveries, RSD, LODs, LOQs, and ME, are presented in Table 6. The results showed that the present method could achieve desirable recovery and precision. The LODs and LOQs obtained by the present method were lower than or comparable to those of previously reported methods.[1,2,11,18,19,22,35,41] This indicated that the present method provides satisfactory accuracy and sensitivity. In addition, most of the methods in Table 6 should combine two or more steps to separate the analytes and coextraction compounds, resulting in a tedious and time-consuming sample pretreatment (usually need several hours).[1,23,24,27] In contrast, our developed approach can selectively and directly extract the analytes from oils without any additional steps. The time consumed by the current method was 40 min, shorter than or comparable to most of the reported methods. There is no matrix effect in our designed sample preparation method, which is superior to that of the reported methods.[2,11,22,35] Moreover, the disposable sorbents used directly or packed in cartridges in the reported methods could add additional expense and extra risk of pollution to the environment.[1,2,15,23,24,27,47] The sorbent used in the present method showed excellent performance and can be reused. This suggests that the present method is both economical and environmentally friendly. Although the current method for the extraction of the pesticides from oil is not the official QuEChERS approach, it still presents quick, easy, cheap, effective, rugged, and safe features. Therefore, this developed method is referred to as the QuEChERS-type method. Furthermore, to examine the scope of the designed method,

the pyrethroid residues were also determined in apple juice. The analysis results revealed that the current method showed excellent extraction and cleanup efficiency. The matrix effect was well-suppressed, and the LODs, LOQs, recoveries, and RSDs met the requirement of routine analysis of pesticide residue (Table S1).

Adsorption Mechanism. Fats are the main components in the edible oil matrix; they possess long alkyl chains and are usually present in oligomers larger than 10 nm.[42] While pesticides have a smaller molecular size, the widths of the four OPPs were estimated, and they are all less than 0.9 nm (Figure S2, dichlorovos: 0.30 nm, dimethoate: 0.69 nm, malathion: 0.87 nm, and methidathion: 0.69 nm). As described above, UiO-66 exhibits a highly porous structure with uniform micropores of 0.7 and 0.9 nm.[29,30] It means that the uniform micropores of UiO-66 can effectively block the large compounds in oil matrix and permit relatively small OPPs to enter,[27] which is a good suppression effect of the matrix. Moreover, FT-IR and UV−vis DRS were employed to inspect the adsorption behavior (Figure 6). The samples used for FT-IR and UV−vis DRS analysis were prepared by an immersion method (Supporting Information). As presented in the FT-IR spectra, the bands in the range of 2750−3000 cm^{-1} could be assigned to the vibration of −CH$_3$,[43] which suggests that the OPPs were adsorbed on UiO-66. The UiO-66 is composed of a Zr$_6$O$_4$(OH)$_4$ cluster and terephthalic acid. The stretching vibration of −OH in Zr$_6$O$_4$(OH)$_4$ was located in the 3000−4000 cm^{-1} region. After OPPs were adsorbed, the shape and position of the −OH vibration band were changed, revealing the possible formation of a hydrogen-bonding interaction between the −OH and heteroatoms (O, N) of OPPs.[44,45] The UV−vis DRS demonstrate that UiO-66 shows a light absorption band edge at 330 nm originating from the excitation of terephthalic acid,[46] and the light absorption exhibits a clear red shift while adsorbing methidathion and malathion. The shift of the light absorption indicates that the π−π stacking interaction probably occurs between unsaturated

bonds of methidathion/malathion and the phenyl group of terephthalic acid.[47,48] Furthermore, the large surface area of UiO-66 may facilitate the adsorption of OPPs because of the van der Waals interaction.[49] That is, the uniform micropores of UiO-66, hydrogen-bonding interaction, $\pi-\pi$ stacking interaction, and van der Waals interaction cause the selective adoption of OPPs from edible oil.

Analysis of Commercial Samples. To evaluate the feasibility and applicability of the developed method, it was applied to determine pesticides in four other different types of vegetable oil samples, including a blended oil sample, soybean oil sample, rapeseed oil sample, and peanut oil sample. To achieve reliable results, each experiment was carried out in triplicate, independently, and spiked samples at a concentration of 50 ng/g were also tested. From the analytical results (Table 7), residue of the pesticide dichlorovos was detected in one blended oil sample at a concentration of 1.1 ng/g, which was lower than the limit set by the National Food Safety Standard of China. The GC–MS/MS chromatogram obtained from the blended oil is presented in Figure 1D. The results confirmed the feasibility of the proposed method, which could be easily performed for routine testing and monitoring of pesticide residues in various oil samples.

In conclusion, a d-SPE technique using the ordered microporous UiO-66 as the sorbent was introduced to analyze pesticide residues in edible vegetable oils. In contrast to most of d-SPE method, the pesticides are directly adsorbed on the UiO-66, and matrix interference compounds are excluded via size exclusion interactions in the current method. The clean analytes are obtained by ultrasonication elution and determined by GC–MS/MS in MRM mode. This method greatly simplifies the analysis procedure and avoids matrix interference. The analysis results showed excellent linearity and acceptable precision and accuracy for all pesticides analyzed. The LOD and LOQ values ranged from 0.16 to 1.56 ng/g and 0.61 to 5.00 ng/g, respectively. Pesticides recovery was between 81.1 and 113.5%. Desirable reproducibility was achieved, with inter and intraday RSD values lower than 13.9%. Thus, we developed a reliable QuEChERS-type method to determine pesticides in edible vegetable oils without matrix interference. Notably, the sorbent UiO-66 was easily recycled and reused at least 10 times in the present method, which reduces the cost of analysis. We believe that the results of the present study will inspire further development of advanced analysis methods to monitor food quality.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.8b04980.

> Preparation of samples for FT-IR and UV–vis DRS analysis. LODs, LOQs, recoveries, RSDs, and matrix effect for the determination of pyrethroids in apple juice (Table S1). XRD patterns of as-synthesized UiO-66 and simulated UIO-66, and N_2 sorption isotherm of the as-synthesized UiO-66 (Figure S1). The pesticide structures optimized by the Gaussian 09W program package together with Gview 5.0 (Figure S2) (PDF)

■ AUTHOR INFORMATION

Corresponding Authors
*Tel: +86 791 88321370; Fax: +86 791 88321370; E-mail: yqwanoy@sina.com (Y.W.)
*Tel: 65-6516 4695; Fax: 65-6775 7895; E-mail: chmynghs@nus.edu.sg (H.Y.)

ORCID Ⓓ

Hongshun Yang: 0000-0002-2965-4353

Notes
The authors declare no competing financial interest.

■ ABBREVIATIONS USED

GC, gas chromatography; LC, liquid chromatography; GC–MS, gas chromatography–mass spectrometry; LC–MS, Liquid chromatography–mass spectrometry; SE, solvent extraction; LLE, liquid–liquid extraction; GPC, gel permeation chromatography; LTFP, low-temperature fat precipitation; QuEChERS, quick, easy, cheap, effective, rugged, and safe; d-SPE, dispersive solid-phase extraction; C18, octadecylsilane; PSA, primary-secondary amine; GCB, graphitized carbon black; MOFs, metal–organic frameworks; OPPs, organophosphorus pesticides; MRM, multiple reaction monitoring; AR, analytical reagent; HPLC, high-performance liquid chromatography; DMF, N,N-dimethylformamide; XRD, X-ray diffraction; FT-IR, Fourier transform infrared; UV–vis DRS, ultraviolet–visible diffuse reflectance spectra; EI, electron impact; LOD, limit of detection; LOQ, limit of quantification; ME, matrix effect; RSDs, relative standard deviations

■ REFERENCES

(1) Fang, Y.; Tian, W.; Pei, F.; Li, P.; Shao, X.; Fan, Y.; Hu, Q. Simultaneous determination of pesticide residues and antioxidants in blended oil using a liquid-liquid extraction combined with dispersive solid phase extraction method. *Food Chem.* **2017**, *229*, 347−353.

(2) Deme, P.; Azmeera, T.; Prabhavathi Devi, B. L.; Jonnalagadda, P. R.; Prasad, R. B.; Vijaya Sarathi, U. V. An improved dispersive solid-phase extraction clean-up method for the gas chromatography-negative chemical ionisation tandem mass spectrometric determination of multiclass pesticide residues in edible oils. *Food Chem.* **2014**, *142*, 144−151.

(3) Nguyen, T. D.; Yun, M. Y.; Lee, G. H. A multiresidue method for the determination of 118 pesticides in vegetable juice by gas chromatography-mass spectrometry and liquid chromatography-tandem mass spectrometry. *J. Agric. Food Chem.* **2009**, *57*, 10095−10101.

(4) Hakme, E.; Lozano, A.; Ucles, S.; Gomez-Ramos, M. M.; Fernandez-Alba, A. R. High-throughput gas chromatography-mass spectrometry analysis of pesticide residues in spices by using the enhanced matrix removal-lipid and the sample dilution approach. *J. Chromatogr. A* **2018**, *1573*, 28−41.

(5) Dias, J. V.; Cutillas, V.; Lozano, A.; Pizzutti, I. R.; Fernandez-Alba, A. R. Determination of pesticides in edible oils by liquid

chromatography-tandem mass spectrometry employing new generation materials for dispersive solid phase extraction clean-up. *J. Chromatogr. A* 2016, *1462*, 8−18.

(6) He, Z.; Wang, Y.; Wang, L.; Peng, Y.; Wang, W.; Liu, X. Determination of 255 pesticides in edible vegetable oils using QuEChERS method and gas chromatography tandem mass spectrometry. *Anal. Bioanal. Chem.* 2017, *409*, 1017−1030.

(7) Chung, S. W.; Chen, B. L. Determination of organochlorine pesticide residues in fatty foods: a critical review on the analytical methods and their testing capabilities. *J. Chromatogr. A* 2011, *1218*, 5555−5567.

(8) Cajka, T.; Sandy, C.; Bachanova, V.; Drabova, L.; Kalachova, K.; Pulkrabova, J.; Hajslova, J. Streamlining sample preparation and gas chromatography-tandem mass spectrometry analysis of multiple pesticide residues in tea. *Anal. Chim. Acta* 2012, *743*, 51−60.

(9) Zainudin, B. H.; Salleh, S.; Mohamed, R.; Yap, K. C.; Muhamad, H. Development, validation and determination of multiclass pesticide residues in cocoa beans using gas chromatography and liquid chromatography tandem mass spectrometry. *Food Chem.* 2015, *172*, 585−595.

(10) Yu, X.; Ang, H. C.; Yang, H. S.; Zheng, C.; Zhang, Y. Q. Low temperature cleanup combined with magnetic nanoparticle extraction to determine pyrethroids residue in vegetables oils. *Food Control* 2017, *74*, 112−120.

(11) Gilbert-Lopez, B.; Garcia-Reyes, J. F.; Fernandez-Alba, A. R.; Molina-Diaz, A. Evaluation of two sample treatment methodologies for large-scale pesticide residue analysis in olive oil by fast liquid chromatography-electrospray mass spectrometry. *J. Chromatogr. A* 2010, *1217*, 3736−3747.

(12) Gilbert-Lopez, B.; Garcia-Reyes, J. F.; Lozano, A.; Fernandez-Alba, A. R.; Molina-Diaz, A. Large-scale pesticide testing in olives by liquid chromatography-electrospray tandem mass spectrometry using two sample preparation methods based on matrix solid-phase dispersion and QuEChERS. *J. Chromatogr. A* 2010, *1217*, 6022−6035.

(13) Parrilla Vazquez, P.; Hakme, E.; Ucles, S.; Cutillas, V.; Martinez Galera, M.; Mughari, A. R.; Fernandez-Alba, A. R. Large multiresidue analysis of pesticides in edible vegetable oils by using efficient solid-phase extraction sorbents based on quick, easy, cheap, effective, rugged and safe methodology followed by gas chromatography-tandem mass spectrometry. *J. Chromatogr. A* 2016, *1463*, 20−31.

(14) Muhamad, H.; Zainudin, B. H.; Abu Bakar, N. K. Comparative study of different clean-up techniques for the determination of lambda-cyhalothrin and cypermethrin in palm oil matrices by gas chromatography with electron capture detection. *Food Chem.* 2012, *134*, 2489−2496.

(15) Sobhanzadeh, E.; Nemati, K. Liquid-liquid extraction/low-temperature purification (LLE/LTP) followed by dispersive solid-phase extraction (d-SPE) cleanup for multiresidue analysis in palm oil by LC-QTOF-MS. *J. Chem.* 2013, *2013*, 1−9.

(16) Nguyen, T. D.; Lee, M. H.; Lee, G. H. Rapid determination of 95 pesticides in soybean oil using liquid−liquid extraction followed by centrifugation, freezing and dispersive solid phase extraction as cleanup steps and gas chromatography with mass spectrometric detection. *Microchem. J.* 2010, *95*, 113−119.

(17) Ballesteros, E.; Garcia Sanchez, A.; Ramos Martos, N. Simultaneous multidetermination of residues of pesticides and polycyclic aromatic hydrocarbons in olive and olive-pomace oils by gas chromatography/tandem mass spectrometry. *J. Chromatogr. A* 2006, *1111*, 89−96.

(18) Jiang, Y.; Li, Y.; Jiang, Y.; Li, J.; Pan, C. Determination of multiresidues in rapeseed, rapeseed oil, and rapeseed meal by acetonitrile extraction, low-temperature cleanup, and detection by liquid chromatography with tandem mass spectrometry. *J. Agric. Food Chem.* 2012, *60*, 5089−5098.

(19) Su, R.; Xu, X.; Wang, X.; Li, D.; Li, X.; Zhang, H.; Yu, A. Determination of organophosphorus pesticides in peanut oil by dispersive solid phase extraction gas chromatography-mass spectrom-

etry. *J. Chromatogr. B: Anal. Technol. Biomed. Life Sci.* 2011, *879*, 3423−3428.

(20) Li, N.; Wang, Z.; Zhang, L.; Nian, L.; Lei, L.; Yang, X.; Zhang, H.; Yu, A. Liquid-phase extraction coupled with metal-organic frameworks-based dispersive solid phase extraction of herbicides in peanuts. *Talanta* 2014, *128*, 345−353.

(21) Koesukwiwat, U.; Lehotay, S. J.; Mastovska, K.; Dorweiler, K. J.; Leepipatpiboon, N. Extension of the QuEChERS method for pesticide residues in cereals to flaxseeds, peanuts, and doughs. *J. Agric. Food Chem.* 2010, *58*, 5950−5958.

(22) Anagnostopoulos, C.; Miliadis, G. E. Development and validation of an easy multiresidue method for the determination of multiclass pesticide residues using GC-MS/MS and LC−MS/MS in olive oil and olives. *Talanta* 2013, *112*, 1−10.

(23) Moreno-Gonzalez, D.; Alcantara-Duran, J.; Addona, S. M.; Beneito-Cambra, M. Multi-residue pesticide analysis in virgin olive oil by nanoflow liquid chromatography high resolution mass spectrometry. *J. Chromatogr. A* 2018, *1562*, 27−35.

(24) Mao, X. J.; Wan, Y. Q.; Yan, A. P.; Shen, M. Y.; Wei, Y. L. Simultaneous determination of organophosphorus, organochlorine, pyrethriod and carbamate pesticides in Radix astragali by microwave-assisted extraction/dispersive-solid phase extraction coupled with GC-MS. *Talanta* 2012, *97*, 131−141.

(25) Xiao, Z.; He, M.; Chen, B.; Hu, B. Polydimethylsiloxane/metal-organic frameworks coated stir bar sorptive extraction coupled to gas chromatography-flame photometric detection for the determination of organophosphorus pesticides in environmental water samples. *Talanta* 2016, *156−157*, 126−133.

(26) Jiang, M.; Li, P.; Wu, P.; Zhang, F.; Tian, X.; Deng, C.; Wang, J. A squaramide-based metal-organic framework as a luminescent sensor for the detection of lactose in aqueous solution and in milk. *Chem. Commun.* 2018, *54*, 9131−9134.

(27) Hasan, Z.; Jhung, S. H. Removal of hazardous organics from water using metal-organic frameworks (MOFs): plausible mechanisms for selective adsorptions. *J. Hazard. Mater.* 2015, *283*, 329−39.

(28) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability. *J. Am. Chem. Soc.* 2008, *130*, 13850−13851.

(29) Han, Y.; Liu, M.; Li, K.; Zuo, Y.; Wei, Y.; Xu, S.; Zhang, G.; Song, C.; Zhang, Z.; Guo, X. Facile synthesis of morphology and size-controlled zirconium metal−organic framework UiO-66: the role of hydrofluoric acid in crystallization. *CrystEngComm* 2015, *17*, 6434−6440.

(30) Katz, M. J.; Brown, Z. J.; Colon, Y. J.; Siu, P. W.; Scheidt, K. A.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K. A facile synthesis of UiO-66, UiO-67 and their derivatives. *Chem. Commun.* 2013, *49*, 9449−9451.

(31) He, Q.; Chen, Q.; Lü, M.; Liu, X. Adsorption Behavior of Rhodamine B on UiO-66. *Chin. J. Chem. Eng.* 2014, *22*, 1285−1290.

(32) Seo, Y. S.; Khan, N. A.; Jhung, S. H. Adsorptive removal of methylchlorophenoxypropionic acid from water with a metal-organic framework. *Chem. Eng. J.* 2015, *270*, 22−27.

(33) Chen, C.; Chen, D.; Xie, S.; Quan, H.; Luo, X.; Guo, L. Adsorption behaviors of organic micropollutants on zirconium metal-organic framework UiO-66: analysis of surface interactions. *ACS Appl. Mater. Interfaces* 2017, *9*, 41043−41054.

(34) Cao, X.; Jiang, Z.; Wang, S.; Hong, S.; Li, H.; Zhang, C.; Shao, Y.; She, Y.; Jin, F.; Jin, M.; Wang, J. Metal-organic framework UiO-66 for rapid dispersive solid phase extraction of neonicotinoid insecticides in water samples. *J. Chromatogr. B: Anal. Technol. Biomed. Life Sci.* 2018, *1077−1078*, 92−97.

(35) Fuentes, E.; Báez, M. E.; Quinones, A. Suitability of microwave-assisted extraction coupled with solid-phase extraction for organo-phosphorus pesticide determination in olive oil. *J. Chromatogr. A* 2008, *1207*, 38−45.

(36) Anastassiades, M.; Lehotay, S. J.; Stajnbaher, D.; Schenck, F. J. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determi-

nation of pesticide residues in produce. *J. AOAC Int.* **2003**, *86*, 412−431.

(37) Abid, H. R.; Ang, H. M.; Wang, S. Effects of ammonium hydroxide on the structure and gas adsorption of nanosized Zr-MOFs (UiO-66). *Nanoscale* **2012**, *4*, 3089−94.

(38) Lozano, A.; Rajski, L.; Ucles, S.; Belmonte-Valles, N.; Mezcua, M.; Fernandez-Alba, A. R. Evaluation of zirconium dioxide-based sorbents to decrease the matrix effect in avocado and almond multiresidue pesticide analysis followed by gas chromatography tandem mass spectrometry. *Talanta* **2014**, *118*, 68−83.

(39) Song, S.; Zhu, K.; Han, L.; Sapozhnikova, Y.; Zhang, Z.; Yao, W. Residue analysis of 60 pesticides in red swamp crayfish using QuEChERS with high-performance liquid chromatography-tandem mass spectrometry. *J. Agric. Food Chem.* **2018**, *66*, 5031−5038.

(40) European Commission, Health & Consumer Protection Directorate-General. *Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed*; SANCO/12571/2013; 2013.

(41) Zhao, Q.; Lu, Q.; Yu, Q. W.; Feng, Y. Q. Dispersive microextraction based on "magnetic water" coupled to gas chromatography/mass spectrometry for the fast determination of organophosphorus pesticides in cold-pressed vegetable oils. *J. Agric. Food Chem.* **2013**, *61*, 5397−403.

(42) Kittirattanapiboon, K.; Krisnangkura, K. Separation of acylglycerols, FAME and FFA in biodiesel by size exclusion chromatography. *Eur. J. Lipid Sci. Technol.* **2008**, *110*, 422−427.

(43) Braun, D. E.; Karamertzanis, P. G.; Arlin, J. B.; Florence, A. J.; Kahlenberg, V.; Tocher, D. A.; Griesser, U. J.; Price, S. L. Solid-State Forms of β-Resorcylic Acid: How Exhaustive Should a Polymorph Screen Be? *Cryst. Growth Des.* **2011**, *11*, 210−220.

(44) Vecchio Ciprioti, S.; Bollino, F.; Tranquillo, E.; Catauro, M. Synthesis, thermal behavior and physicochemical characterization of ZrO2/PEG inorganic/organic hybrid materials via sol−gel technique. *J. Therm. Anal. Calorim.* **2017**, *130*, 535−540.

(45) Zhang, P.; Wang, L.; Yang, S.; Schott, J. A.; Liu, X.; Mahurin, S. M.; Huang, C.; Zhang, Y.; Fulvio, P. F.; Chisholm, M. F.; Dai, S. Solid-state synthesis of ordered mesoporous carbon catalysts via a mechanochemical assembly through coordination cross-linking. *Nat. Commun.* **2017**, *8*, 15020.

(46) Wu, X. P.; Gagliardi, L.; Truhlar, D. G. Cerium Metal-Organic Framework for Photocatalysis. *J. Am. Chem. Soc.* **2018**, *140*, 7904−7912.

(47) Balakrishnan, K.; Datar, A.; Naddo, T.; Huang, J.; Oitker, R.; Yen, M.; Zhao, J.; Zang, L. Effect of Side-Chain Substituents on Self-Assembly of Perylene Diimide Molecules: Morphology Control. *J. Am. Chem. Soc.* **2006**, *128*, 7390−7398.

(48) Wang, Q.; Weng, Q.; Chen, R.; An, Q.; Zhu, S.; An, Z.; Chen, X.; Chen, P. Effect of the thieno[3,4-c]pyrrole-4,6-dione on properties of the cyclic thiourea triphenylamine sensitizers. *Dyes Pigm.* **2019**, *161*, 197−204.

(49) Wu, M.; Chen, G.; Liu, P.; Zhou, W.; Jia, Q. Polydopamine-based immobilization of a hydrazone covalent organic framework for headspace solid-phase microextraction of pyrethroids in vegetables and fruits. *J. Chromatogr. A* **2016**, *1456*, 34−41.