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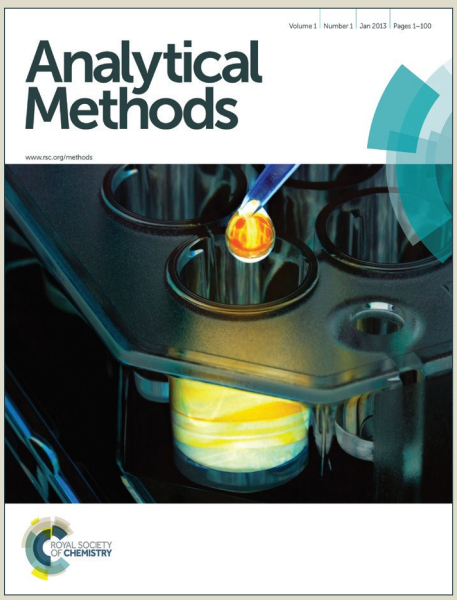

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Development and validation of a modified QuEChERS method based on magnetic zirconium dioxide microspheres for the determination of 52 pesticides in oil crops by gas chromatography tandem mass spectrometry

Wei Lu [a], Xitian Peng [b,*], Jing Shen [b], Xizhou Hu [b], Lijun Peng [b], Yuqi Feng[a,*]

[a] Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), Department of Chemistry,Wuhan University, Wuhan 430072, China

[b] Institute of Agricultural Quality Standards and Testing Technology Research, Hubei Academy of Agricultural Science, Wuhan, 430064, China

*Corresponding author, Xitian Peng, Tel.:+86-27-87389808, fax: +86-27-87389482, E-mail address: pxitian@aliyun.com.cn; Yuqi Feng, Tel.:+86-27-68755595, fax: +86-27-68755595, E-mail address: yqfeng@whu.edu.cn.

Abstract: The residue analysis of pesticide in high-fat oil crops is a challenging task because of the high amount of lipid co-extracts, which could seriously affect the extraction efficiency and the performance of the instruments. In this study, a modified QuEChERS (quick, easy, cheap, effective, rugged and safe) method based on magnetic mesoporous ZrO_2 microspheres (m-ZrO_2@Fe_3O_4) and n-octadecylphosphonic acid modified magnetic microsphere (Fe_3O_4-OPA) was established for the determination of 52 pesticides in oil crops by gas chromatography coupled to tandem mass spectrometry (GC-MS/MS). The ability of m-ZrO_2@Fe_3O_4 to remove fatty acids from acetonitrile extracts of oil crops has been evaluated. The results indicated that m-ZrO_2@Fe_3O_4 had better performance on the removal of fatty acids than that of PSA, a commonly used sorbent to remove acidic co-extracts in QuEChERS method. The parameters affecting the cleanup performance were also investigated, including the amounts of m-ZrO_2@Fe_3O_4 and Fe_3O_4-OPA. Under the optimal condition, the method was validated in four kinds of oil crops (peanuts, rapeseed, soybean and sesame) by GC-MS/MS. The linear correlation coefficients (R^2) of all four oil crops were higher than 0.9904. Limits of detection (LODs) were found to be in the range of 0.1–4.1 μg/kg. The average recoveries of all analytes ranged from 69.1% to 120.0% (except p,p'-DDE, p,p'-DDD, o,p'-DDT and p,p'-DDT) with the intra-day and inter-day relative standard deviations (RSDs) less than 14.7% and 14.9%, respectively.

1. Introduction

Vegetable oils, as the main source of human body fat, have become an irreplaceable component of our balanced diet [1-2]. Generally, vegetable oils are extracted by mechanical pressure or organic solvents from oil crops, such as peanuts, rapeseed, soybean and sesame. Nowadays, various classes of pesticides have been widely used in the production of oil crops to increase faming yield [3]. However, because many pesticides retain in the crops up to harvest stage, they can easily contaminate the final vegetable oil products, causing great threat to human health. Therefore, development of simple, effective and sensitive analytical methods for analysis of pesticide residues in oil crops is very significant, which can help to effectively prevent vegetable oils being polluted by pesticides.

For the fat-free or low-fat fruits and vegetables such as tomato, lettuce, apple, citrus, etc., there have been some reliable methods developed for analysis of pesticide [4-5]. However, for high fatty samples such as oil crops, the analysis of pesticide residues is always a challenging problem, because high amount of lipid co-extracts can seriously affect the extraction efficiency and performance of analytical instruments [6-7]. Even small amount of lipids could cause significant damage to column, source and detector [8-9]. Additionally, fatty acids also interfere with the analysis because they produce broad peaks overlapping the analytes and increase matrix effects [10-11]. Therefore, sample pretreatment techniques are required to remove the lipid co-extractives prior to chromatography and/or mass spectrometry analysis.

Traditionally, low-temperature fat precipitation, liquid–liquid extraction (LLE),

and gel permeation chromatography (GPC) are usually used as a cleanup procedure for removing fatty matrices. Among them, freezing-out is the simplest method, of which fat can be precipitated in the freezer and subsequently separated by centrifugation. However, this method is time-consuming and unable to remove all of fat, and other cleanup approaches are still required to further purify samples [12-14]. LLE is another easy-to-operate approach, but the large consumption of solvents and low selectivity of the extraction limit its applications [15]. GPC can be used to the separation of low molecular mass pesticides from high molecular mass compounds such as lipids. However, some pesticides with high molecular mass (e.g. pyrethroids) can not be separated from lipids by GPC [16-17]. Additionally, GPC also consumes large volume of solvents and takes much time and labor, which reduces laboratory efficiency and sample throughput. In order to improve the removal efficiency of lipids and the selectivity for the target analytes, some other kinds of sample preparation methods such as matrix solid-phase dispersion extraction [18], solid phase microextraction [19], microwave assisted extraction [20], supercritical fluid extraction [21] and solid-phase extraction based on carbon nanotubes [22] have been applied to oily matrices for extraction and cleanup.

Quick, easy, cheap, effective, rugged and safe (QuEChERS) method originally developed by Anastassiades et al. in 2003 has been widely applied for pesticide multi-residues analysis in fruits and vegetables [23]. Recently, this technique has been extended to determine multiple pesticides in oil crops [24-25]. Koesukwiwat et al. firstly evaluated a modified QuEChERS method for determination of pesticide residues in

flaxseeds, doughs and peanuts [24]. In this approach, the traditional dispersive solid-phase extraction (d-SPE) and primary-secondary amine (PSA) adsorbent have been applied. Later on, amine modified graphene has been successfully synthesized and used to remove lipids from four oil crops [25]. However, the adsorption capacity of amino-based adsorbent is limited, and the removal efficiency is reduced in the present of abundant lipids [11]. Furthermore, in conventional QuEChERS methods, adsorbents are separated from the acetonitrile extract by centrifugation, which takes extra time and is not conducive to the high-throughput detection of a large number of samples. Therefore, development of modified QuEChERS methods based on novel adsorbents of lipid matrices is highly desired to achieve rapid, high-throughput and sensitive detection of pesticide residues in oil crops.

Zirconium dioxide (ZrO_2) has an amphoteric characteristic and its surface possess large amount of Lewis acid sites, which makes it a good adsorbent for Lewis bases such as fatty acids and glycerides. It has been reported that ZrO_2-based sorbents can be used as adsorbents of QuEChERS methods in some high fatty matrices, such as avocado, almonds [10]. The reported results indicate that the matrix components such as fatty acids and glycerides can be efficiently removed from sample extracts by ZrO_2 composite. Recently, our group has prepared and evaluated a novel mesoporous ZrO_2 magnetic microsphere (m-ZrO_2@Fe_3O_4) and n-octadecylphosphonic acid modified magnetic microspheres (Fe_3O_4-OPA) for the multi-residues analysis of 42 pesticides and 7 polychlorinated biphenyls (PCBs) in fishes by a modified QuEChERS method combined with gas chromatography tandem mass spectrometry (GC-MS/MS) [26].

Under the magnetic field, magnetic materials can be easily separated from the solution, avoiding tedious centrifugation and filtration steps, which greatly save the extraction time and labor cost.

In this work, the m-ZrO_2@Fe_3O_4 and Fe_3O_4-OPA microspheres were used as QuEChERS adsorbents for the analysis of 52 pesticides in four oil crops. By using this modified QuEChERS combined with GC-MS/MS, a rapid, high-throughput and sensitive pesticide multi-residues detection method for oil crops was successfully established.

2. Materials and methods

2.1 Reagents and materials

Sodium chloride (NaCl), anhydrous magnesium sulfate ($MgSO_4$), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) anhydrous sodium acetate (NaOAc), ethanol (EtOH), ethylene glycol (EG), ammonium hydroxide (NH_4OH), tetrahydrofuran (THF), potassium hydroxide (KOH), sodium bisulfate, ethylenediamine and isooctane were all of analytical reagent grade and supplied by Shanghai General Chemical Reagent Factory (Shanghai, China). n-Octadecylphosphonic acid was purchased from TCI (Shanghai, China). PSA was supplied by Agela Technologies. Acetonitrile (ACN), methanol (MeOH) and acetone of HPLC grade were obtained from Tedia (Ohio, USA). Purified water was obtained from a Millipore Milli-Q apparatus (Bedford, MA, USA).

The standard solutions of 52 pesticides (1000 μg/mL) were provided by the

Agro-Environmental Protection Institute, Ministry of Agriculture (Tianjin, China). The standard stock solution of a mixture 52 pesticides was made up to 10 μg/mL with acetone and stored at -18 ^{o}C. The working standard solutions were prepared daily.

2.2 Preparation of m-ZrO_2@Fe_3O_4 and Fe_3O_4-OPA magnetic microspheres

The magnetite microspheres were prepared through the solvothermal reaction [27], as described as follows: $FeCl_3 \cdot 6H_2O$ (5.4 g) was dissolved in ethylene glycol (160 mL) under magnetic stirring for 0.5 h. Then NaOAc (14.4 g) and polyethylene glycol (4.0 g) were added to the solution. After stirring for another 0.5 h, the resultant solution was transferred into a 200 mL Teflon lined stainless-steel autoclave. The autoclave was sealed and heated at 200 ^{o}C for 24 h and then cooled to room temperature. The magnetic microspheres were collected with the help of magnet, followed by washing with ethanol and deionized water 4 times. The product was dried in vacuum at 60 ^{o}C for 8 h.

Mesoporous ZrO_2 was directly coated onto the surface of magnetic Fe_3O_4 by the hydrolysis of $ZrOCl_2$ and using cethyltrimetylammonium bromide (CTAB) as the mesoporous template reagent according to our previous report [26]. Fe_3O_4 microspheres (0.5 g) were dispersed in a solution containing 1.5 g CTAB, 400 mL of deionized water, 7.5 mL of concentrated NH_4OH solution (28%) and 300 mL of ethanol. The mixture was stirred continuously for 30 min to form a homogenized dispersion. To the above dispersed solution, an aqueous solution of $ZrOCl_2$ (3.1 g dissolved in the minimum volume of water) was added drop-wise and then the reaction mixture was

stirred for 6 h. Then the product was collected by a hand-held magnet and washed repeatedly with ethanol. The obtained particles were redispersed in 250 mL of acetone and refluxed at 80 ^{o}C for 60 h. The resultant particles were then washed with deionized water, separated through magnetic decantation and dried in vacuum at 60 ^{o}C for 12 h. At last, the obtained m-ZrO_2@Fe_3O_4 was further calcined at 300 ^{o}C for 6 h to age.

The Fe_3O_4-OPA was prepared according to the previously described method [26]. OPA (1.0 g) was dissolved in 50 mL THF, then bare Fe_3O_4 (5.0 g) was added into the solution. The mixture was refluxed at 80 ^{o}C for 12 h. The final product was magnetically collected and washed by water/ethanol/acetone/n-hexane successively and repeatedly, followed by drying at 60 ^{o}C for 6 h.

2.3 Sample preparation

Commercial oil crops (peanut, rapeseed, soybean and sesame) were cut into small pieces and comminuted with an electric grinder to achieve good sample homogeneity. The thoroughly homogenized sample (2.5 g) was then weighted into an Eppendorf vial (50 mL). ACN (10 mL) and deionized water (10 mL) were added and the vial was shaken vigorously for 1 min to ensure that the solvent interacted well with the entire sample. Subsequently, anhydrous NaCl (1.0 g) and anhydrous $MgSO_4$ (4.0 g) were added to the mixture and the shaking step was repeated for 1 min. After centrifugation (5000 rpm, 5 min), the extract was transferred to an Eppendorf vial (15 mL) containing 1.0 g anhydrous $MgSO_4$. The vial was shaken by hand followed by

standing for 1 min, and the supernatant was collected for the subsequent steps.

The cleanup procedure was performed by magnetic solid-phase extraction using m-ZrO_2@Fe_3O_4 and Fe_3O_4-OPA as co-adsorbents. 0.5 mL extract was added into a 1.5 mL centrifugal tube containing a certain amount of magnetic adsorbents (m-ZrO_2@Fe_3O_4 and Fe_3O_4-OPA), then the mixture was shaken vigorously for 0.5 min. The adsorbents were then separated rapidly from the solution by an external magnet. Finally, the above solution (1 μL) was supplied to GC-MS/MS analysis.

2.4 Instrumentation and analytical conditions

GC-MS/MS analysis was performed using a Shimadzu GCMS-TQ8030 equipped with an AOC-20i auto-sampler (Kyoto, Japan). Data acquisition and analysis were performed using software from GCMS Solution (Shimadzu, Kyoto, Japan). The separation was achieved on a fused silica capillary column (Rtx–5MS, 30 m × 0.25 mm i.d., film thickness 0.25 μm) (Restek, Pennsylvania, USA). The oven temperature was programmed at 40 ^{o}C for 4.0 min, increased to 125 ^{o}C at a rate of 25 ^{o}C min^{-1}, and then increased to 300 ^{o}C at a rate of 10 ^{o}C min^{-1} and held for 6.0 min. The solvent cut time was 7 min. The injection volume was 1.0 μL and splitless injection mode was used. The splitless time was 1.0 min. Helium (purity 99.999%) was used as the carrier gas at a flow rate of 1.0 mL min^{-1}. Argon (purity 99.999%) was used as a collision cell gas. The injection port, ion source and interface temperatures were set at 250, 230 and 250 ^{o}C, respectively. The QqQ mass spectrometer was operated in selected reaction monitoring mode detecting two transitions per analyte,

which are listed together with the particular collision energies in **Table 1**.

3. Results and Discussion

3.1 Selection of target analytes and optimization of GC-MS/MS conditions

Nowdays, a variety of pesticides have been widely applied in oil crops. In order to establish a universal method for multi-residues analysis of pesticides in oil crops, 52 kinds of commonly used pesticides were selected in the present work, including organochlorine, organophosphorus, organonitrogen, dimethrin and so on.

Compared with other analytical instruments, GC-MS/MS possesses the advantages of higher sensitivity, specificity and selectivity. Therefore, it was employed in this work, and multiple reaction monitoring (MRM) acquisition methods were used. To optimize the triple quadrupole MS/MS, the relevant conditions were considered for the best response, such as the choice of precursor ions, product ions, and optimization of collision energies [28]. The mass spectrometric parameters option was initially performed by full scan for the compounds. After that, the precursor ion for each analyte was selected, and then the collision energy voltages (potential on second quadrupole) were optimized to generate MS/MS product ions. The characteristic ion transition and collision energy for each compound during MRM acquisition are listed in **Table 1**. The collision energy was optimized for two selective ion transitions for every pesticide. Both pairs of MRM transitions were used for confirmation analysis, which meets the EU Decision (European Council 2002/657/EC, implementing council directive 96/23/EC concerning the performance of analytical

methods and the interpretation of results, 2002), and the most sensitive transitions were selected for quantification analysis.

3.2 Compared with other QuEChERS adsorbents

In order to test the purification efficiency of the m-ZrO_2@Fe_3O_4, it was compared with PSA, a commonly used QuEChERS absorbent to remove acidic co-extracts. Twelve kinds of common fatty acids (chain length was C_{18}:3, C_{16}:1, C_{22}:2, C_{18}:1, C_{17}:0, C_{20}:2, C_{20}:1 C_{18}:2, C_{24}:1, C_{24}:0, C_{16}:0; C_{18}:0, respectively) were detected in the peanuts blank extract, which was then purified by m-ZrO_2@Fe_3O_4 and PSA, respectively. The purification efficiency of two sorbents was relative to the change of relative content of total fatty acids. The relative concentrations of fatty acids in QuEChERS acetonitrile extracts of peanut after cleanup with different sorbents and without cleanup were determined in three replicates according to the method of GB/T 17376-2008/ISO 5509. As shown in **Figure 1**, after cleanup with m-ZrO_2@Fe_3O_4, the relative content of fatty acids, which was equal to the sum of peak areas of 12 fatty acids after cleanup divided that of without cleanup, was less than 20%, while it was 68% for PSA. Therefore, the purification efficiency of m-ZrO_2@Fe_3O_4 is much better compared with that of PSA.

3.3 Optimization of sample pretreatment

The lipid contents of peanut, rapeseed, sesame seeds, soybean were 49.24%, 40.71%, 49.67% and 21.62%, respectively [25]. In this study, we used a blank peanut QuEChERS extract that has relatively high lipid content to optimize the amounts of

m-ZrO_2@Fe_3O_4 and Fe_3O_4-OPA. We believed that the optimized results could be used to analyze other three oil crops, which have less or equivalent lipid contents. In the cleanup process of modified QuEChERS method, m-ZrO_2@Fe_3O_4 and Fe_3O_4-OPA microspheres were mixed and the resultant material can be separated from solvent rapidly and conveniently by applying an external magnetic field (**Figure 2**). Therefore, this magnetic property enables easy and rapid separation of solid adsorbents, simplifying the sample preparation process with manipulative convenience.

Optimization of the amount of m-ZrO_2@Fe_3O_4. The surface of m-ZrO_2@Fe_3O_4 has many Lewis acid sites, which could adsorb Lewis bases such as fatty acids in QuEChERS extract of oil crops. The amount of m-ZrO_2@Fe_3O_4 was optimized. The experiment was performed using 0.5 mL of ACN extract that was placed into an Eppendorf vial (1.5 mL) which was containing different amounts of m-ZrO_2@Fe_3O_4 (i.e. 10, 15, 35 and 50 mg). After cleanup, the samples were analyzed by GC–MS in full scan mode. As shown in **Figure 3**, the wide peak of interfering substances gradually disappeared with the increase of amount of m-ZrO_2@Fe_3O_4. The wide spectrum bands in chromatograms were identified as fatty acids by GC-MS . At last, 35 mg of m-ZrO_2@Fe_3O_4 was enough to remove those fatty acids, and thus it was chosen for the following experiments.

Optimization of the amount of OPA-Fe_3O_4. Not only lipid co-extracts but also some apolar compounds have great effects on the matrix interference. OPA-Fe_3O_4 with hydrophobic C_{18} groups was used to remove the apolar matrix components.

Therefore, the quantity of OPA-Fe_3O_4 was optimized. m-ZrO_2@Fe_3O_4 (35 mg) and different amounts of OPA-Fe_3O_4 (i.e. 20, 30, 50, 70 mg) were used as co-adsorbents for the cleanup process in QuEChERS method. It was found that 30 mg OPA-Fe_3O_4 was enough to remove the corresponding matrix components and obtain satisfactory recovery of all pesticides. Therefore, 30 mg OPA-Fe_3O_4 was chosen as the optimal condition.

Under the optimal condition, typical GC-MS/MS chromatograms of a fortified peanut sample are shown in **Figure 4**. There were no interference peaks in the region of the chromatograms of all pesticides, indicating the good cleanup performance.

3.4 Validation of the method

Calibration curves, detection limits, limits of quantification. To verify the accuracy and precision of the established method, several basic analytical parameters were evaluated, including recovery, linear range, limit of detection (LOD) and limit of quantitation (LOQ). Calibration curves were calculated with a matrix-matched standard calibration in blank samples to avoid matrix effects, which were always observed in the form of signal enhancement in GC-MS/MS analysis, leading to unacceptable high recoveries. For the construction of the calibration curves, triplicate measurements were performed, and the calibration curves were generated by plotting the mean peak areas versus analytes concentration. The corresponding results are listed in **Table 2**. For all of the four oil crops, the linear correlation coefficients (R^2) are higher than 0.9904 in the range from 5 to 1000 μg/kg. The LOD and LOQ were

calculated as the concentration giving a signal-to-noise ratio of 3 (S/N = 3) and 10 (S/N = 10), respectively. As shown in **Table 2**, the LODs and LOQs for all analytes are found to be in the range of 0.1–4.1 μg/kg and 0.2–13.5 μg/kg, respectively.

Accuracy and precision. To assay the accuracy of the method, peanut was also used as a representative sample. The recoveries at three different spiking concentrations were obtained by comparing the amount calculated from the calibration curves with the corresponding spiking amount. The precision of the method was assessed by determining the intra-day and inter-day relative standard deviations (RSDs) at three concentration levels. The recoveries and precisions are summarized in **Table 3**. Except p,p'-DDE, p,p'-DDD, o,p'-DDT and p,p'-DDT, the average recoveries of most target pesticides ranged from 69.1% to 120.0% with the relative standard deviation less than 15.1%. The recoveries of p,p'-DDE, p,p'-DDD, o,p'-DDT and p,p'-DDT range from 41.1% to 64.0%, which is relatively low because of their high lipid solubility in the lipid matrix [5, 29]. Simultaneously, the intra-day and inter-day RSDs were below 14.7% and 14.9%, respectively (**Table 4**). The results demonstrated that the accuracy of the present method was acceptable. Additionally, the recoveries of other three kinds of oil crops (sesame, soybean and rapeseed) were also verified. As shown in **Table 5**, the recoveries of 48 pesticides in the three samples were in the range from 69.6 to 118.5% with the RSDs less than 14.3%, while the recoveries of p,p'-DDE, p,p'-DDD, o,p'-DDT and p,p'-DDT were in the range of 41.1% to 94.9%.

Comparison with the previous methods. The comparison of the method

performance and cleanup time developed in this research with the previous methods was studied. As illustrated in **Table 6**, our method took less cleanup time, had satisfactory precisions and recoveries, and showed better sensitivity than the previous methods. The experimental and comparative results well indicated that our method could be used to effectively monitor pesticides in oil crops.

3.5 Application to commercial oil crops samples

Under the optimized conditions, the developed QuEChERS method was applied to the analysis of the pesticide residues in oil crops including peanuts, sesame, soybean and rapeseed. All the oil crops samples collected from local markets and supermarkets in Wuhan. No analytes were detectable in those samples.

4. Conclusion

In this work, a simple and rapid method for the multi-residues analysis of 52 pesticides in four oil crops samples was developed based on a modified QuEChERS method coupled with GC–MS/MS analysis. Two magnetic microspheres, m-ZrO_2@Fe_3O_4 and Fe_3O_4-OPA, were used as cleanup co-adsorbents for the removal of interferents from different oil crops matrices in the QuEChERS method. Compared to traditional QuEChERS methods in which phase separation must be achieved by centrifugation, the modified QuEChERS method using magnetic adsorbents endows the cleanup procedure with manipulative convenience through applying an external magnetic field. Furthermore, our results indicate that m-ZrO_2@Fe_3O_4 has better

cleanup performance on the removing of fatty acids than that of PSA, a commonly used sorbent to remove acidic co-extracts in QuEChERS method. This study demonstrates that the QuEChERS method combined with GC–MS/MS analysisis a simple, rapid, effective and sensitive method for pesticide multi-residues analysis in oil crops and will have broad applications in food analysis.

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Figure captions

Figure 1 Relative concentrations of the content of fatty acids for blank peanut extracts after different QuEChERS sorbents cleanup.

Figure 2 The photo of m-ZrO_2@Fe_3O_4 and Fe_3O_4-OPA dispersed in peanut extract (a) and collected by a magnet (b).

Figure 3 Effect of the amount of m-ZrO_2@Fe_3O_4 on the cleanup performance.

Figure 4 GC-MS/MS chromatograms of a blank peanut sample spiked with 52 pesticides at 100 μg/kg level.

Tables

Table 1 Optimized GC-MS/MS acquisition method parameters for the 52 pesticides.

Pesticide	Retention time (min)	Quantication ion (m/z)	CE1	Confirmation ion (m/z)	CE2
Dichlorvos	10.046	185.00>93.00	14	185.00>109.00	14
Trifluralin	14.632	306.10>264.10	8	306.10>206.10	14
Phorate	14.907	260.00>75.00	8	260.00>231.00	4
alpha-HCH	15.072	218.90>182.90	8	218.90>144.90	20
Dimethoate	15.309	125.00>79.00	8	125.00>47.00	14
beta-HCH	15.629	218.90>182.90	8	218.90>144.90	20
Gamma-HCH	15.758	218.90>182.90	8	218.90>144.90	20
Quintozine	15.853	294.80>236.80	16	294.80>264.80	12
Pyrimethanil	15.965	198.10>183.10	14	198.10>158.10	18
Diazinon	15.978	304.10>179.10	10	304.10>162.10	8
delta-HCH	16.246	218.90>182.90	10	218.90>144.90	20
Chlorothalonil	16.336	265.90>230.80	14	265.90>168.00	22
Vinclozolin	16.973	285.00>212.00	12	285.00>178.00	14
Parathion-methyl	17.007	263.00>109.00	14	263.00>136.00	8
Chlorpyrifos-methyl	17.002	285.90>93.00	22	285.90>270.90	14
Metalaxyl	17.232	249.20>190.10	8	249.20>146.10	22
Fenitrothion	17.538	277.00>260.00	6	277.00>109.10	14
Malathion	17.697	173.10>99.00	14	173.10>127.00	6
Fenthion	17.909	278.00>109.00	20	278.00>125.00	20
Clorpyrifos	17.94	313.90>257.90	14	313.90>285.90	8
Parathion	17.961	291.10>109.00	14	291.10>137.00	6
Triadimefon	18.001	208.10>181.00	10	208.10>127.00	14
Dicofol	18.035	250.00>139.00	14	250.00>215.00	8
Isocarbophos	18.086	289.10>136.00	14	289.10>113.00	6
Isofenphos-methyl	18.435	199.00>121.00	14	199.00>167.00	22
Pendimethalin	18.579	252.10>162.10	10	252.10>191.10	8
Fipronil	18.714	366.90>212.90	30	366.90>254.90	22
Procymidone	18.936	283.00>96.00	10	283.00>255.00	12
Profenofos	19.677	336.90>266.90	14	336.90>308.90	6
p,p'-DDE	19.772	246.00>176.00	30	246.00>211.00	22
Chlorfenapyr	20.214	247.10>200.10	15	247.10>227.10	15
p,p'-DDD	20.566	235.00>165.00	24	235.00>199.00	14
o,p'-DDT	20.641	235.00>165.00	24	235.00>199.00	16
Triazophos	20.847	257.00>162.00	8	257.00>134.00	22
p,p'-DDT	21.262	235.00>165.00	24	235.00>199.00	16
Iprodione	21.941	314.00>245.00	12	314.00>56.00	22
Phosmet	22.170	160.00>133.00	14	160.00>77.00	24
Bromopropylate	22.156	340.90>182.90	18	340.90>184.90	20

Bifenthrin	22.115	181.10>166.10	12	181.10>153.10	8
Fenpropathrin	22.264	265.10>210.10	12	265.10>172.10	10
Phosalone	22.845	182.00>111.00	14	182.00>138.00	8
Cyhalothrin-1	22.899	197.00>161.00	8	197.00>141.00	12
Cyhalothrin-2	23.092	197.00>161.00	8	197.00>141.00	12
Permethrin-1	23.860	183.10>168.10	14	183.10>165.10	14
Permethrin-2	23.983	183.10>168.10	14	183.10>165.10	14
Pyridaben	24.033	147.10>117.10	22	147.10>132.10	14
Cyfluthrin-1	24.427	226.10>206.10	14	226.10>199.10	6
Cyfluthrin-2	24.509	226.10>206.10	14	226.10>199.10	6
Cyfluthrin-3	24.626	226.10>206.10	14	226.10>199.10	6
Cyfluthrin-4	24.626	226.10>206.10	14	226.10>199.10	6
Cypermethrin-1	24.748	181.10>152.10	22	181.10>127.10	22
Cypermethrin-2	24.835	181.10>152.10	22	181.10>127.10	22
Flucythrinate-1	24.938	199.10>157.10	10	199.10>107.10	22
Cypermethrin-3	24.940	181.10>152.10	22	181.10>127.10	22
Cypermethrin-4	25.128	181.10>152.10	22	181.10>127.10	22
Flucythrinate-2	25.128	199.10>157.10	10	199.10>107.10	22
Phenvalerate-1	25.740	419.10>225.10	6	419.10>167.10	12
Fluvalinate-1	25.906	250.10>55.00	20	250.10>200.00	20
Phenvalerate-2	25.963	419.10>225.10	6	419.10>167.10	12
Fluvalinate-2	25.962	250.10>55.00	20	250.10>200.00	20
Difenoconazole-1	26.271	323.00>265.00	14	323.00>202.00	28
Difenoconazole-2	26.357	323.00>265.00	14	323.00>202.00	28
Deltamethrin-1	26.374	252.90>93.00	20	252.90>171.90	8
Deltamethrin-2	26.644	252.90>93.00	20	252.90>171.90	8
Azoxystrobin	27.033	344.00>329.10	15	344.00>183.10	15

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Table 2 Determination coefficients (R^2), limit of detection (LOD) and limit of quantification (LOQ) of the target pesticides in peanut, rapeseed, soybean, sesame.

Pesticide	Peanut			Rapeseed			Soybean			Sesame		
	R^2	LOD	LOQ	R^2	LOD	LOQ	R^2	LOD	LOQ	R^2	LOD	LOQ
Dichlorvos	0.9994	2.3	7.6	0.9908	0.3	0.9	0.9939	0.4	1.3	0.9975	0.2	0.5
Trifluralin	0.9972	0.2	0.7	0.9929	0.1	0.2	0.9963	0.2	0.7	0.9961	0.2	0.5
Phorate	0.9964	0.8	2.8	0.9914	0.2	0.7	0.9932	0.4	1.3	0.9972	0.4	1.5
alpha-HCH	0.9975	0.3	1.0	0.9919	0.1	0.3	0.9954	0.2	0.6	0.9968	0.3	0.9
Dimethoate	0.9932	2.7	8.8	0.9910	1.6	5.3	0.9980	4.1	13.5	0.9988	1.1	3.6
beta-HCH	0.9949	0.2	0.8	0.9953	0.1	0.3	0.9962	0.2	0.7	0.9977	0.2	0.7
gamma-HCH	0.9942	0.4	1.2	0.9934	0.1	0.4	0.9943	0.3	0.9	0.9972	0.3	0.9
Quintozine	0.9936	0.9	3.0	0.9930	0.3	0.9	0.9932	0.6	2.1	0.9978	0.6	2.1
Pyrimethanil	0.9953	2.4	7.9	0.9904	2.7	9.0	0.9969	3.1	10.4	0.9981	0.4	1.3
Diazinon	0.9914	0.2	0.6	0.9944	0.1	0.4	0.9951	0.3	0.9	0.9956	0.2	0.7
delta-HCH	0.9942	0.5	1.6	0.9906	0.3	0.9	0.9956	0.3	1.1	0.9969	0.3	0.9
Chlorothalonil	0.9930	1.8	6.1	0.9921	0.2	0.7	0.9974	1.4	4.6	0.9934	1.1	3.8
Vinclozolin	0.9956	0.2	0.7	0.9957	0.1	0.5	0.9947	0.5	1.8	0.9978	0.5	1.5
Parathion-methyl	0.9932	0.7	2.5	0.9968	1.6	5.3	0.9975	0.3	1.2	0.9979	0.5	1.6
Chlorpyrifos-methyl	0.9924	0.4	1.3	0.9914	0.3	0.9	0.9957	0.3	0.9	0.9967	1.5	5.0
Metalaxyl	0.9961	0.3	0.9	0.9955	0.1	0.4	0.9974	0.5	1.6	0.9981	0.3	0.8
Fenitrothion	0.9923	2.5	8.2	0.9948	0.7	2.3	0.9979	0.3	1.1	0.9979	0.4	1.4
Malathion	0.9923	0.2	0.8	0.9941	0.5	1.7	0.9982	0.1	0.5	0.9984	0.1	0.3
Fenthion	0.9937	0.1	0.5	0.9933	0.1	0.3	0.9970	0.1	0.4	0.9984	0.1	0.2
Clorpyrifos	0.9921	0.1	0.2	0.9954	0.1	0.2	0.9967	0.1	0.3	0.9976	0.1	0.3
Parathion	0.9915	0.9	3.0	0.9946	0.3	0.9	0.9990	0.3	0.9	0.9973	0.4	1.2
Triadimefon	0.9915	0.6	2.1	0.9956	0.8	2.7	0.9951	0.4	1.4	0.9992	1.2	4.1
Dicofol	0.9967	0.3	1.0	0.9972	0.1	0.3	0.9967	0.3	0.9	0.9990	0.3	0.8
Isocarbophos	0.9912	1.3	4.3	0.9924	0.3	0.9	0.9987	0.4	1.4	0.9991	0.4	1.4
Isofenphos-methyl	0.9931	0.1	0.2	0.9951	0.1	0.4	0.9963	0.1	0.2	0.9990	0.1	0.2
Pendimethalin	0.9911	0.4	1.2	0.9961	2.1	6.9	0.9969	1.7	5.5	0.9968	0.1	0.4
Fipronil	0.9929	0.3	0.9	0.9905	0.1	0.3	0.9990	3.4	11.2	0.9978	1.4	4.8
Procymidone	0.9967	0.2	0.7	0.9969	0.8	2.7	0.9950	0.2	0.6	0.9998	0.1	0.5
Profenofos	0.9988	1.1	3.6	0.9943	0.2	0.6	0.9958	0.3	1.0	0.9998	0.2	0.6
p,p'-DDE	0.9981	0.1	0.2	0.9965	0.1	0.3	0.9957	0.1	0.2	0.9998	0.1	0.2
Chlorfenapyr	0.9985	0.4	1.3	0.9952	0.8	2.6	0.9988	1.3	4.5	0.9997	0.9	2.9
p,p'-DDD	0.9985	0.1	0.3	0.9956	0.1	0.3	0.9964	0.1	0.2	0.9996	0.1	0.3
o,p'-DDT	0.9941	0.4	1.3	0.9965	0.2	0.6	0.9973	0.1	0.2	0.9997	0.1	0.4
Triazophos	0.9952	0.3	1.0	0.9940	0.4	1.3	0.9971	0.1	0.4	0.9992	0.1	0.3
p,p'-DDT	0.9932	0.2	0.8	0.9959	0.2	0.5	0.9973	0.1	0.2	0.9998	0.1	0.3
Iprodione	0.9993	1.7	5.6	0.9967	0.3	0.9	0.9969	0.3	1.0	0.9968	0.4	1.4
Phosmet	0.9967	2.3	7.7	0.9969	0.3	0.9	0.9990	1.1	3.5	0.9976	0.4	1.3
Bromopropylate	0.9983	0.1	0.3	0.9955	0.1	0.3	0.9977	0.8	2.8	0.9983	0.1	0.2

Bifenthrin	0.9967	0.4	1.3	0.9961	0.5	1.7	0.9973	0.2	0.8	0.9988	0.2	0.8
Fenpropathrin	0.9968	0.3	1.0	0.9966	0.2	0.5	0.9957	0.2	0.6	0.9979	0.1	0.4
Phosalone	0.9958	0.1	0.4	0.9966	0.7	2.4	0.9980	0.7	2.3	0.9964	0.4	1.3
Cyhalothrin	0.9971	0.8	2.7	0.9975	0.2	0.8	0.9968	0.2	0.6	0.9963	0.1	0.5
Permethrin	0.9992	1.9	6.4	0.9980	2.2	7.3	0.9971	2.0	6.5	0.9944	0.8	2.6
Pyridaben	0.9965	0.3	1.1	0.9964	0.3	1.0	0.9974	0.2	0.8	0.9963	0.2	0.8
Cyfluthrin	0.9978	1.7	5.6	0.9987	0.2	0.7	0.9989	0.4	1.4	0.9939	0.4	1.5
Cypermethrin	0.9964	1.3	4.3	0.9959	1.2	4.1	0.9985	1.1	3.8	0.9936	1.2	4.1
Flucythrinate	0.9955	1.2	4.1	0.9969	0.7	2.5	0.9988	0.8	2.7	0.9936	0.4	1.5
Phenvalerate	0.9954	0.9	3.1	0.9957	0.2	0.6	0.9977	0.4	1.4	0.9943	0.3	1.0
Fluvalinate	0.9979	0.5	1.6	0.9978	0.1	0.4	0.9993	0.2	0.5	0.9943	0.1	0.4
Difenoconazole	0.9989	0.2	0.7	0.9972	0.1	0.2	0.9982	0.1	0.4	0.9915	0.3	1.2
Deltamethrin	0.9968	2.1	6.9	0.9978	1.2	3.9	0.9978	1.8	6.1	0.9953	1.7	5.6
Azoxystrobin	0.9993	1.3	4.3	0.9971	2.5	8.2	0.9984	3.1	10.3	0.9908	1.2	3.9

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Table 3 Average recoveries and RSDs of 52 pesticides spiked in peanut at three different concentration levels via GC–MS/MS analysis (n=4).

Analytes	10 ng/g spiked level		50 ng/g spiked level		200 ng/g spiked level	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Dichlorvos	75.2	2.6	106.7	5.8	100.7	3.7
Trifluralin	98.7	8.3	76.1	5.5	88.6	2.0
Phorate	100.4	7.8	86.6	4.7	101.7	0.9
alpha-HCH	96.0	7.0	84.2	5.0	95.8	2.9
Dimethoate	100.4	8.6	95.3	4.2	112.6	8.0
beta-HCH	97.8	7.8	87.3	5.1	98.8	1.9
gamma-HCH	93.9	4.0	86.2	5.4	96.6	2.2
Quintozine	70.4	9.4	70.2	3.5	69.6	0.9
Pyrimethanil	105.9	4.2	86.0	4.4	95.2	1.8
Diazinon	107.4	10.9	92.1	5.2	107.5	2.1
delta-HCH	93.2	4.3	85.0	4.7	97.6	2.7
Chlorothalonil	93.8	13.0	85.2	4.5	104.3	8.7
Vinclozolin	110.3	9.6	96.3	4.2	109.1	1.3
Parathion-methyl	111.5	6.5	93.3	4.0	112.4	2.0
Chlorpyrifos-methyl	93.4	7.9	83.7	5.5	98.9	1.3
Metalaxyl	120.0	6.0	100.3	2.1	119.3	4.1
Fenitrothion	103.1	2.5	93.5	5.3	111.6	1.4
Malathion	109.2	2.8	96.7	4.4	115.9	4.1
Fenthion	102.3	2.5	94.7	3.3	107.8	1.5
Clorpyrifos	106.6	12.0	76.0	2.3	87.9	1.2
Parathion	110.7	6.4	91.8	4.8	111.2	2.1
Triadimefon	117.5	5.9	102.3	3.1	115.2	2.8
Dicofol	90.4	1.4	82.3	11.8	86.3	13.3
Isocarbophos	114.1	11.5	99.3	4.8	115.3	3.4
Isofenphos-methyl	109.8	3.0	96.7	4.3	112.9	2.2
Pendimethalin	92.6	5.8	71.4	4.4	83.6	1.2
Fipronil	99.8	3.3	88.7	5.5	109.5	2.6
Procymidone	108.5	6.1	101.4	2.8	110.6	2.0
Profenofos	86.8	2.8	94.3	2.2	96.0	0.7
p,p'-DDE	58.1	7.9	41.1	1.8	44.3	0.6
Chlorfenapyr	91.0	6.2	93.5	3.1	103.3	5.6
p,p'-DDD	79.8	8.0	63.3	1.5	70.2	0.8
o,p'-DDT	64.0	1.5	44.4	1.7	49.1	0.4
Triazophos	103.2	4.7	100.7	3.5	115.1	3.7
p,p'-DDT	61.9	6.8	45.7	2.0	51.0	0.9
Iprodione	92.4	6.4	102.9	3.4	115.1	3.6
Phosmet	89.6	6.2	99.9	2.5	110.1	10.6

Bromopropylate	89.8	6.3	82.0	1.9	89.1	0.7
Bifenthrin	76.1	11.1	73.4	3.5	70.5	1.0
Fenpropathrin	102.2	15.1	79.9	4.7	89.0	1.5
Phosalone	102.9	3.9	95.2	4.3	108.0	3.5
Cyhalothrin	91.4	6.8	79.5	5.2	90.1	1.5
Permethrin	79.9	11.7	77.9	2.4	75.2	1.1
Pyridaben	83.1	8.1	70.7	3.2	78.8	0.9
Cyfluthrin	97.9	8.6	78.8	6.1	87.7	1.4
Cypermethrin	96.4	8.2	71.3	5.8	81.5	1.7
Flucythrinate	102.7	5.8	90.1	5.7	102.3	1.0
Phenvalerate	90.9	9.4	70.2	7.3	79.8	1.4
Fluvalinate	91.6	14.7	71.3	5.0	80.1	1.2
Difenoconazole	105.7	8.5	104.9	4.7	115.8	6.9
Deltamethrin	85.1	11.8	69.1	5.8	80.1	1.6
Azoxystrobin	111.1	15.0	106.9	4.7	116.5	12.6

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406 **Table 4** Method precisions at three different concentrations for determination 52

407 pesticides in peanut samples.

Analytes	Intra-day precision (RSD%, n=4)			Inter-day precision (RSD%, n=4)		
	Low	Middle	High	Low	Middle	High
Dichlorvos	2.7	7.6	3.0	2.7	8.6	5.1
Trifluralin	1.4	5.6	2.0	4.0	7.4	4.4
Phorate	6.7	6.9	0.9	8.8	9.5	4.0
alpha-HCH	2.6	4.4	1.5	2.3	5.4	4.4
Dimethoate	11.9	13.1	9.7	9.8	14.9	6.0
beta-HCH	3.0	3.3	1.6	1.8	5.5	3.9
gamma-HCH	3.0	3.8	0.8	3.7	5.7	4.6
Quintozine	4.1	4.7	0.9	6.0	6.1	4.0
Pyrimethanil	0.3	2.3	1.9	5.5	5.2	4.7
Diazinon	8.6	6.6	1.0	1.1	9.5	4.3
delta-HCH	4.8	2.7	1.9	4.2	5.3	5.1
Chlorothalonil	10.3	3.1	8.5	12.6	6.8	8.8
Vinclozolin	7.2	2.2	0.8	12.0	4.4	5.1
Parathion-methyl	5.2	9.4	2.4	6.1	12.7	4.9
Chlorpyrifos-methyl	5.5	4.7	1.3	7.0	7.2	4.5
Metalaxyl	3.3	5.4	1.5	5.4	5.6	3.7
Fenitrothion	2.1	10.1	0.6	3.1	13.4	5.6
Malathion	2.4	10.7	3.9	2.4	13.6	5.4
Fenthion	0.7	4.4	0.4	2.3	6.4	4.4
Clorpyrifos	8.1	3.4	1.5	6.9	4.5	4.7
Parathion	6.8	7.4	1.8	8.6	10.4	7.0
Triadimefon	3.7	2.0	2.9	3.6	4.1	3.8
Dicofol	3.2	3.0	14.7	1.9	12.5	10.7
Isocarbophos	12.1	11.7	3.4	10.2	14.5	5.8
Isofenphos-methyl	1.2	7.5	0.5	2.9	9.9	4.9
Pendimethalin	5.2	4.9	1.2	3.0	6.8	6.0
Fipronil	2.1	9.6	3.1	6.4	13.9	2.9
Procymidone	2.7	4.0	1.1	4.0	4.1	4.4
Profenofos	3.8	2.9	0.1	3.9	3.8	4.6
p,p'-DDE	0.9	2.0	0.4	2.4	3.1	4.3
Chlorfenapyr	7.4	4.5	2.0	8.5	4.7	8.4
p,p'-DDD	1.1	3.2	0.5	2.9	3.8	4.9
o,p'-DDT	0.7	2.1	0.4	2.1	3.1	4.0
Triazophos	4.6	6.7	3.6	5.6	9.5	5.2
p,p'-DDT	1.6	2.1	0.4	1.0	3.3	5.0
Iprodione	14.0	1.6	4.2	12.3	2.8	5.7
Phosmet	6.1	8.2	12.0	6.6	11.2	9.3
Bromopropylate	1.7	3.0	0.9	1.2	3.6	5.9

Bifenthrin	0.2	1.9	0.7	0.7	3.4	4.5
Fenpropathrin	3.3	6.0	2.0	5.2	6.7	4.7
Phosalone	4.4	4.6	3.5	4.2	7.5	5.7
Cyhalothrin	1.8	6.5	1.5	4.2	8.6	4.8
Permethrin	0.6	2.0	0.7	1.2	4.0	3.7
Pyridaben	3.3	3.0	1.2	3.5	4.1	5.4
Cyfluthrin	6.6	7.4	0.9	9.8	8.7	4.3
Cypermethrin	8.1	6.6	2.3	6.5	8.5	4.7
Flucythrinate	1.6	10.7	0.2	1.8	10.7	4.4
Phenvalerate	10.3	10.2	1.5	5.8	12.2	5.2
Fluvalinate	4.8	6.1	0.5	0.7	7.8	4.8
Difenoconazole	1.5	8.9	7.4	7.1	9.1	6.2
Deltamethrin	9.0	7.2	1.9	2.6	8.5	4.8
Azoxystrobin	10.6	7.6	14.6	4.6	8.3	9.3

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410 **Tables 5** Average recoveries and RSDs of 52 pesticides spiked in other three oil crops

411 (sesame, soybean, rapeseed) via GC–MS/MS analysis (n=4).

Analytes	Sesame		Soybean		Rapeseed	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Dichlorvos	107.6	9.4	108.0	4.4	100.1	0.7
Trifluralin	73.2	11.9	83.3	1.1	101.9	9.5
Phorate	74.0	0.8	96.3	1.9	101.0	3.7
alpha-HCH	78.6	8.5	91.8	2.3	97.7	2.2
Dimethoate	95.7	14.3	104.1	7.4	113.2	5.8
beta-HCH	84.7	3.5	94.1	4.6	99.2	4.9
gamma-HCH	86.6	5.3	93.7	3.1	97.3	2.7
Quintozine	74.8	10.2	71.5	3.1	96.7	6.0
Pyrimethanil	83.9	11.4	111.2	0.7	101.5	7.7
Diazinon	93.7	7.4	104.4	1.9	99.8	3.7
delta-HCH	88.2	3.7	98.4	3.7	101.3	4.4
Chlorothalonil	100.7	8.8	102.2	7.2	85.6	0.1
Vinclozolin	93.6	9.5	110.7	2.0	102.6	6.0
Parathion-methyl	81.1	0.9	111.6	5.3	104.7	11.8
Chlorpyrifos-methyl	80.7	6.2	98.0	2.3	100.0	3.1
Metalaxyl	110.7	6.6	114.3	3.6	102.1	6.5
Fenitrothion	88.6	13.6	115.5	4.3	104.4	4.7
Malathion	109.8	6.0	117.9	3.2	99.2	6.7
Fenthion	93.1	1.3	107.3	2.9	101.0	4.4
Clorpyrifos	81.1	1.5	94.8	1.2	97.5	3.4
Parathion	90.6	11.7	112.1	1.1	100.7	5.0
Triadimefon	109.2	1.7	117.3	2.4	100.9	3.0
Dicofol	94.5	5.2	96.4	4.5	99.3	7.7
Isocarbophos	100.5	9.4	110.0	6.1	100.6	2.4
Isofenphos-methyl	95.8	6.8	110.0	2.4	100.1	4.4
Pendimethalin	69.8	11.8	83.4	1.3	100.6	7.9
Fipronil	107.6	9.0	113.4	2.7	97.7	10.3
Procymidone	97.3	3.0	118.5	3.3	101.8	6.9
Profenofos	92.0	4.1	106.0	0.9	99.0	0.4
p,p'-DDE	48.6	1.6	41.1	0.6	58.8	4.1
Chlorfenapyr	92.9	2.1	106.7	11.6	95.0	5.0
p,p'-DDD	64.6	2.1	63.4	1.5	67.1	9.8
o,p'-DDT	52.5	0.6	49.7	1.4	45.9	10.6
Triazophos	95.5	9.5	101.4	3.1	103.6	5.1
p,p'-DDT	55.3	0.6	50.8	2.3	94.9	5.8
Iprodione	105.2	3.7	116.8	3.7	100.7	12.9
Phosmet	97.8	7.0	104.0	6.3	91.9	1.1

Bromopropylate	72.9	2.5	84.5	1.5	99.2	7.7
Bifenthrin	70.3	2.2	77.7	0.9	96.4	11.0
Fenpropathrin	74.8	3.4	84.2	2.7	98.5	9.6
Phosalone	85.5	7.2	117.2	2.8	105.1	12.9
Cyhalothrin	76.4	11.4	78.5	1.1	95.9	7.4
Permethrin	80.1	4.1	78.0	1.9	95.0	9.5
Pyridaben	83.2	6.2	78.3	1.1	96.4	9.0
Cyfluthrin	83.8	8.6	84.8	3.4	96.6	6.3
Cypermethrin	72.6	8.3	96.2	1.7	97.0	5.1
Flucythrinate	69.6	5.8	95.1	4.4	93.7	6.9
Phenvalerate	88.2	5.3	71.3	3.3	106.2	11.9
Fluvalinate	86.2	5.7	76.3	3.3	94.4	6.8
Difenoconazole	87.8	9.4	116.7	5.6	90.0	2.0
Deltamethrin	88.3	6.1	80.2	6.4	91.9	8.0
Azoxystrobin	97.5	3.2	116.6	8.1	84.7	1.8

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414 **Table 6** Comparison of method performance and the time with the previous method

415 for detection of pesticides in oil crops samples

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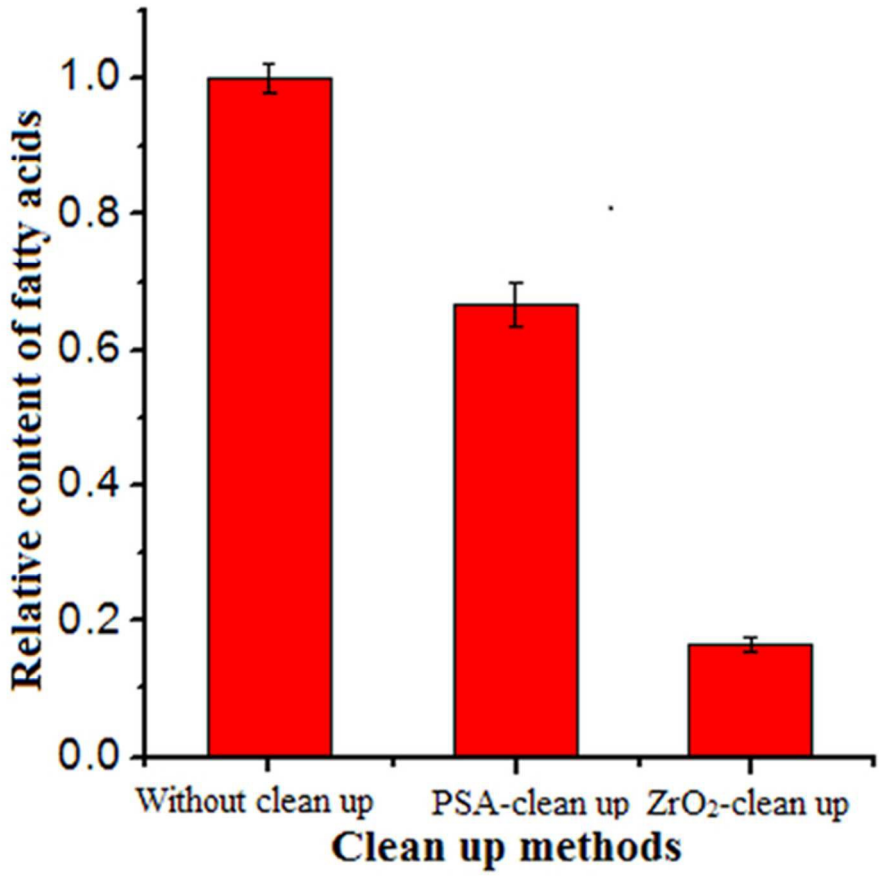
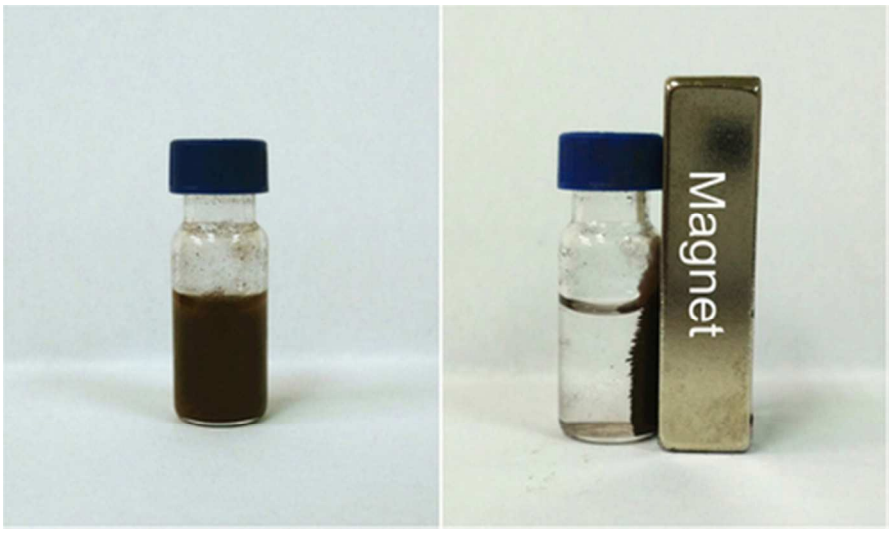
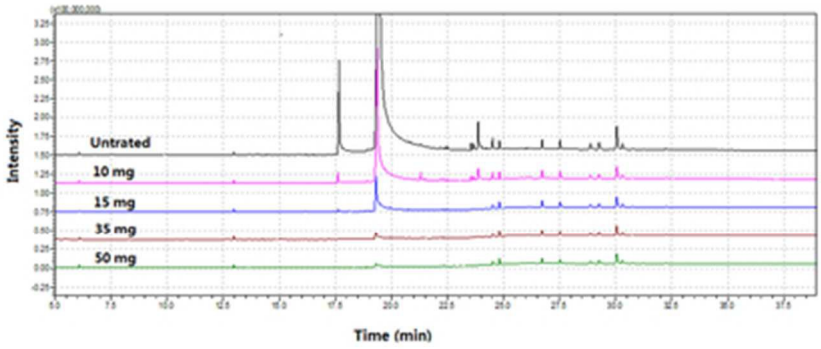
Technique	Commodity	Cleanup process	Determination method	Analytes and LODs	Recoveries (%)	RSD (%)	Time required (min)	Reference
QuEChERS	flaxseeds, peanut	d-SPE with 150 mg PSA and 50 mg C-18	GC–TOF-MS	34 pesticides: 5-300 μg/kg	22–113	＜26	＞5 min	24
	avocado, almond	d-SPE cleanups (Z-Sep, Z-Sep+, PSA + C18 and silica)	LC-MS/MS	113 pesticides: 3-15 μg/kg	70-120	＜20	＞15 min	7
	avocado, almond	d-SPE cleanups (Z-Sep, Z-Sep+)	GC–MS/MS	166 pesticides: 3-15 μg/kg	28-159	＜20	＞15 min	10
low temperature fat precipitation	rapeseed, rapeseed oil	12 h freezing	LC–MS/MS	27 pesticides: 0.1–6.0 μg/kg	70–118	＜27	12 h	13
	peanut oil	24 h freezing following by d-SPE with 100 mg MWCNTs and 1 g neutral alumina	GC–MS	9 pesticides: 0.7–1.6 μg/kg	85.9–114.3	＜ 8.84	＞24 h	14
ASE+LLE+ GPC+SPE	soybean	A combined method including LLE, GPC and SPE	Capillary electrophoresi sUV	6 herbicides 5.2–36 μg/kg	72–88.6	＜11	＞15 min	30
GPC	olive oil	Gel permeation chromatography (GPC) with ethyl acetate–ciclohexane (1:1) as mobile phase	GC–MS/MS	32 pesticides: 0.5-20 μg/kg	89-105	＜20	＞35 min	17
SPE	sesame seeds	MAE+SPE (florisil column)	GC/MS	16 pesticides: 1.5-3 μg/kg	86–103	＜12	＞20 min	20
Modified QuEChERS	rapeseed, peanut, soybean and sesame seeds	d-SPE with 35 mg m-ZrO_2@Fe_3O_4 and 40 mg C_{18}	GC–MS/MS	52 pesticides: 0.1-4.1 μg/kg	69.1-120.0 (except p,p'-DDE, p,p'-DDD, o,p'-DDT and p,p'-DDT range from 41.1% to 64.0%)	＜ 14.9	＜3min	This work



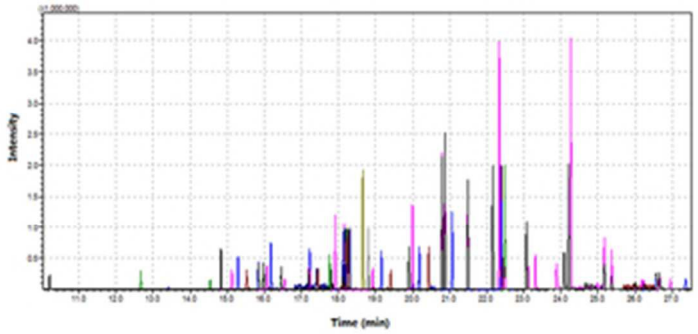
Relative concentrations of the content of fatty acids for blank peanut extracts after different QuEChERS sorbents cleanup
46x43mm (300 x 300 DPI)



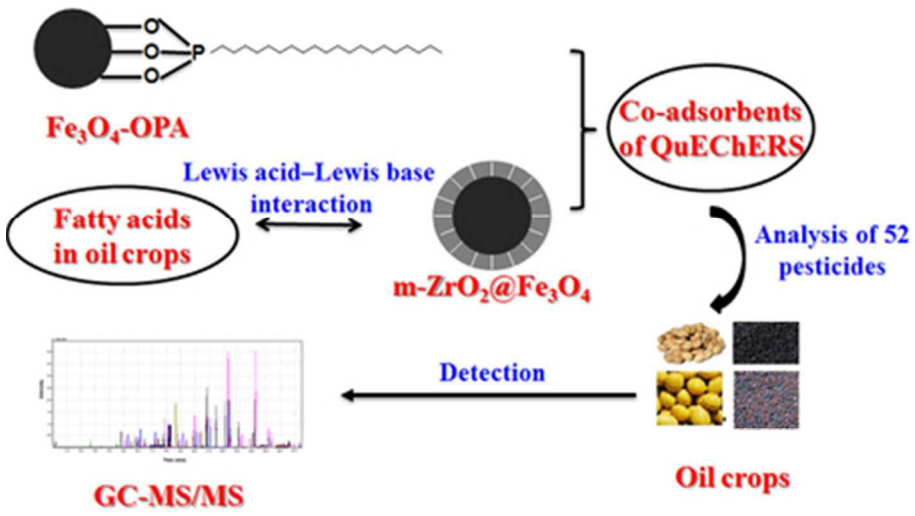
The photo of m-ZrO2@Fe3O4 and Fe3O4-OPA dispersed in peanut extract (a) and collected by a magnet (b)
37x22mm (300 x 300 DPI)



Effect of the amount of m-ZrO2@Fe3O4 on the cleanup performance
35x15mm (300 x 300 DPI)



GC-MS/MS chromatograms of a blank peanut sample spiked with 52 pesticides at 100 µg/kg level
30x14mm (300 x 300 DPI)



A modified QuEChERS method based on magnetic zirconium dioxide microspheres for the determination of 52 pesticides
in oil crops by gas chromatography tandem mass spectrometry was demonstrated
39x22mm (300 x 300 DPI)