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Liquid-phase extraction coupled with metal–organic frameworks-based dispersive solid phase extraction of herbicides in peanuts

Na Li [a], Zhibing Wang [b], Liyuan Zhang [c], Li Nian [d], Lei Lei [a], Xiao Yang [a], Hanqi Zhang [a], Aimin Yu [a,*]

[a] College of Chemistry, Jilin University, Qianjin Street 2699, Changchun 130012, PR China
[b] College of Chemistry and Life Science, Changchun University of Technology, Yanan Street 2055, Changchun 130012, PR China
[c] College of Food, Heilongjiang Bayi Agricultural University, Xinfeng Lu 5, Daqing 163319, PR China
[d] Institude of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, PR China

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ABSTRACT

Liquid-phase extraction coupled with metal–organic frameworks-based dispersive solid phase extraction was developed and applied to the extraction of pesticides in high fatty matrices. The herbicides were ultrasonically extracted from peanut using ethyl acetate as extraction solvent. The separation of the analytes from a large amount of co-extractive fat was achieved by dispersive solid-phase extraction using MIL-101(Cr) as sorbent. In this step, the analytes were adsorbed on MIL-101(Cr) and the fat remained in bulk. The herbicides were separated and determined by high-performance liquid chromatography. The experimental parameters, including type and volume of extraction solvent, ultrasonication time, volume of hexane and eluting solvent, amount of MIL-101(Cr) and dispersive solid phase extraction time, were optimized. The limits of detection for herbicides range from 0.98 to 1.9 μg/kg. The recoveries of the herbicides are in the range of 89.5–102.7% and relative standard deviations are equal or lower than 7.0%. The proposed method is simple, effective and suitable for treatment of the samples containing high content of fat.

1. Introduction

Peanuts contain high content of protein and fat, and are good source of niacin, folate, fiber, vitamin E, magnesium and phosphorus. The peanuts can be eaten raw, used in recipes, made into peanut butter and oils as well as many other uses. Peanuts are popular all over the world. To improve the yield of peanuts, pesticides are usually used to protect crops from weeds, diseases and pests. Unfortunately, the agricultural products can be contaminated with pesticides by the improper and abusive use of pesticides as well as uptake from contaminated water and soil [1–3]. Pesticides residues in food could pose a risk to human health [4]. Nowadays food safety in terms of pesticide residues has attracted more and more attention. The European Union (EU) legislation has established maximum residue limits (MRLs) for pesticide residues in agricultural products and MRLs of some triazine and phenylurea herbicides in peanuts are in the range of 0.02–0.1 mg/kg (Commission Directive 2008/149/EC). These herbicides were detectable in agricultural products, even in vegetable oil and animal-origin food [1,5–7]. So the determination of triazine and phenylurea herbicides in peanuts is essential. To the best of our knowledge, the available literature on determination of pesticide in peanuts is very limited.

Due to the inherent complexity of the high fatty matrices, the determination of pesticide residues in the matrices is challenging. It is imperative to effectively remove fat before chromatographic analysis. The fat may affect separation efficiency and harm the separation system [8]. The common extraction method for pesticides in fatty matrices is liquid-phase extraction with organic solvent followed by clean-up procedures. Acetonitrile (ACN) is usually used in terms of its limited solubility of fat. The most common methods of clean-up are liquid–liquid partitioning (LLP) [9,10], low-temperature fat precipitation (LTFP) [6,11–13], gel-permeation chromatography (GPC) [5,14], solid-phase extraction (SPE) [9,10,15] and dispersive-SPE (DSPE) [11,12,16]. LLP is a traditional method with the main drawbacks of consumption of time and large amounts of organic solvent and tendency of emulsion formation. In LTFP, fat is precipitated in the freezer below −20 °C and then easily removed. However, this method is time-consuming and it usually takes several hours [6,11–13]. In addition, the two methods are inadequate to remove fat and thus some further clean-up is usually necessary [9–13]. Koesukwiwat

* Corresponding author. Tel.: +86 431 85168399; fax: +86 431 85112355.
E-mail address: analchem@jlu.edu.cn (A. Yu).

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et al. found that compared with DSPE, when GPC was applied, the removal of co-extractive fat is not complete and the peaks of fat partly overlap with those of the analytes in GPC [16]. SPE and DSPE are conventional sorbent-based clean-up procedures and the sorbents are usually octadecylsilane(C18), primary–secondary amine (PSA), graphitized carbon black (GCB), florisil and silica gel (Si) [9–16]. Recently, Rajski et al. used Z-Sep as sorbent for the clean-up of the extract of avocado and almonds [17]. Compared with PSA/C18 and Si, Z-Sep can remove more fat and provide higher recoveries. But they found that Z-Sep does nothing to ethyl acetate(EA) extract containing high content of fat. In addition, the SPE procedures with C18/florisil or alumina (Al_2O_3) were ineffective in treatment of high content of fat and provided poor recovery and precision [14]. In these methods, the co-extractive fat was removed by adsorption on sorbents and the removal of interfering substances is related to the capacity of the sorbent. So the common sorbent-based clean-up may not be suitable for extract containing high content of fat and also very much limits the choice of extraction solvent. In the literature, ACN was found to be ineffective for the extraction of some pesticides in high fatty matrices [6,14,17]. So the extending of various extraction solvents used in high fatty matrices is meaningful. EA was proved to be an effective solvent in extraction of most pesticides in non-fatty samples [18–20]. In addition, compared with ACN, EA is cheaper and safer. For high fatty matrices, the main problem associated with EA is co-extraction of large amount of fat which is difficult to be removed satisfactorily with common sorbents. So the reports on application of EA to fatty matrices are limited. Metal–organic frameworks (MOFs) are hybrid inorganic–organic microporous crystalline materials self-assembled straightforwardly from metal ions with organic linkers via coordination bonds. They exhibit fascinating structures and unique properties, including diverse structures and pore topologies, uniform structured nanoscale cavities, high surface area and good thermal stability [21]. MOFs have been used successfully as stationary phases for gas and liquid chromatography and sorbents in aqueous system in analytical chemistry [22–24]. MOFs could be effective sorbents for the analytes in fatty matrices. Up to now, the MOFs-based extraction of the analytes from fatty matrices has not been developed. MIL-101 first reported by Ferey et al. in 2005 is built up from a hybrid supertetrahedral building unit formed by terephthalate ligands and trimeric chromium octahedral clusters [21]. MIL-101 contains two types of mesoporous quasi-spherical cages, a small cage of 20 supertetrahedra with free diameter of 2.9 nm accessible through pentagonal windows of 1.2 nm and a large cage of 28 supertetrahedra with free diameter of 3.4 nm accessible through hexagonal/pentagonal windows of $1.47 \times 1.6\ nm^2$. The large windows make it accessible to relatively large molecules, not merely limited to gaseous molecules. These properties, including high surface area, large pore windows, mesoporous pores, accessible coordinative unsaturated sites and excellent chemical and solvent stability, make MIL-101 outstanding among MOFs and make it attractive as a sorbent for extraction. MIL-101(Cr) has been successfully applied to the extraction of targets in aqueous samples [25,26]. The unsaturated metal sites in MIL-101 can play an important role in sorption process besides the interaction between the organic ligand network of MIL-101 and targets [25,26]. MIL-101 can be used as a stationary phase for liquid chromatography in normal-phase mode [23]. So MIL-101 could be chosen as an attractive sorbent for the extraction of triazine and phenylurea herbicides in a nonpolar system.

In the work, liquid-phase extraction coupled with MIL-101(Cr)-based dispersive solid-phase extraction was developed and applied to the extraction of herbicides in peanuts. EA was used as an extraction solvent. The principle of removal of fat with MOF is contrary to that with common sorbents. The herbicides were adsorbed on MIL-101(Cr) and the fats remained in the non-polar solvent. Then the analytes were eluted from MIL-101(Cr) with ACN. The herbicides were separated and determined by high performance liquid chromatography.

2. Material and methods

2.1. Chemicals and reagents

Monuron, atraton, chlortoluron, atrazine, terbumeton, ametryn and terbuthylazine were obtained from the National Institutefor the Control of Pharmaceutical and Biological Products (Beijing, China). The structures of the herbicides are shown in Fig. 1. Standard stock solutions for the herbicides at the concentration level of 100 μg/mL were prepared in ACN. All of the stock standard solutions were stored in a refrigerator at 4 °C. Working and mixed working standard solutions were prepared every week by diluting stock standard solutions in ACN. Chromatographic grade ACN was purchased from Fisher Scientific Company (Pittsburgh, PA, USA). $Cr(NO_3)_3 \cdot 9H_2O$ (> 99.0%) was purchased from XLong chemical Co., Ltd. (Guangdong, China). 1,4-Benzene dicarboxylic acid (H_2BDC, ≥ 98.5%) was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Hydrofluoric acid (HF, ≥ 40%) was purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). PSA was purchased from Beijing Agela Technologies Inc. (Beijing, China). Si was purchased from Qingdao Ocean Chemical Factory (Qingdao, China). Al_2O_3 was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Pure water was obtained with a Milli-Q water purification system (Millipore Co., USA). All other reagents were of analytical-reagent grade and purchased from Beijing Chemical Factory (Beijing, China).

2.2. Instruments

Chromatographic separation and determination of the herbicides were carried out on the 1100 series liquid chromatograph (Agilent Technologies Inc., USA) equipped with diode-array detector (DAD) and quaternary gradient pump. Eclipse XDB-C18 column (3.5 μm, 4.6 mm × 150 mm, Agilent, USA) was used. The KQ3200E ultrasonic cleaner was purchased from Kunshan Ultrasonic Instrument Co., Ltd. (Kunshan, China). The frequency and output power of the ultrasonic cleaner are 40 kHz and 150 W, respectively. The HC-2006 high speed centrifuge was purchased from AnHui USTC Zonkia Scientific Instruments Co., Ltd. (Anhui, China).

The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2550 diffractometer equipped with a graphite monochromator (Rigaku, Japan) and Cu Kα radiator (λ = 1.5418 Å). Transmission electron microscopic (TEM) characterization was performed on a Tecnai G2 F20 S-Twin (Philips, Holland). BET surface area was measured on an ASAP 2020 micropore physisorption analyzer (Micromeritics, Norcross, GA) using nitrogen adsorption at 77 K.

2.3. Synthesis of MIL-101(Cr)

MIL-101(Cr) was synthesized according to the method reported by Ferey et al. [21]. $Cr(NO_3)_3 \cdot 9H_2O$ (800 mg), terephthalic acid (322 mg) and HF (0.1 mL) were mixed with ultrapure water (9.6 mL) in a Teflon autoclave. The Teflon autoclave was then sealed and placed in an oven at 220 °C for 8 h. The Teflon autoclave was then cooled down to room temperature. The resulting green crystalline solid was washed thoroughly with dimethyl formamide and hot ethanol and collected by centrifugation at 10,000 rpm for 5 min. The washing was repeated at least three times to remove the unreacted terephthalic acid from MIL-101(Cr) pores. Finally, the obtained solid was dried in an oven at 150 °C overnight.

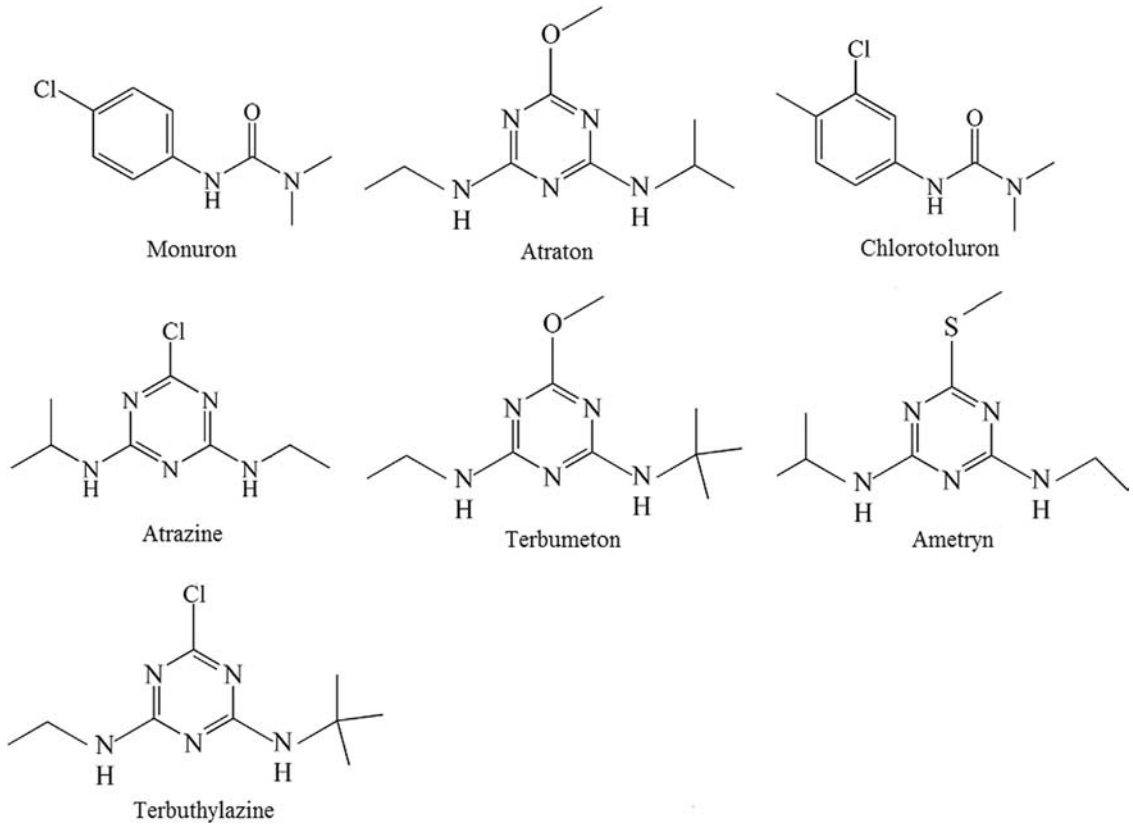

Fig. 1. Structures of triazine and phenylurea herbicides.

2.4. Sample preparation

Peanuts were collected from local markets. The samples (sample 1–8) were triturated with a pulverizer and stored at 4 °C in freezer. The fresh spiked samples were prepared by spiking appropriate volume of mixed working solution into samples, mixed homogenously and left for 24 h. The aged spiked samples were prepared by the method mentioned above except that the spiked sample was stored for 1, 2, 3 and 4 weeks in a freezer at 4 °C. All results were obtained with sample 1 except for those mentioned in Section 3.4.2.

2.5. Extraction procedure

1 g of peanut sample and 7 mL of EA were added into a 10 mL centrifuge tube. The mixture was referred to as sample solution and ultrasonicated for 15 min followed by centrifugation for 5 min at 10,000 rpm. Then the supernatant was transferred into a flask and evaporated to near "dryness". The residue was dissolved with hexane and transferred into another centrifuge tube. 7 mg of MIL-101 was added into the tube and the tube was shaken for 5 min. The resulting mixture was centrifuged for 3 min at 10,000 rpm and the supernatant was removed. 2 mL of ACN was added into the tube and the ultrasonic elution of the analytes was carried out. After centrifugation, the obtained eluate was dried under a nitrogen stream and dissolved in 150 μL of methanol. The obtained solution filtered with 0.22 μm PTFE filter was referred to as an analytical solution and 20 μL of the solution was injected into the HPLC system.

2.6. HPLC analysis

The HPLC analysis was conducted in gradient modes. Mobile phases A and B are water and acetonitrile, respectively. The gradient conditions are as follows: 0–6 min, 37–45% B; 6–8 min, 45% B; 8–12 min, 45–50% B; 12–18 min, 50–72% B; 18–19 min, 72%B; 19–20 min, 72–37% B. The column temperature was kept at 30 °C and the flow rate of the mobile phase was kept at 0.5 mL/min. Injection volume of analytical solution was 20 μL. The monitoring wavelength was 244 nm for monuron and chlortoluron and 222 nm for the other herbicides. The effect of flow rate ranging from 0.5 to 0.7 mL/min was investigated. The retention time of terbuthylazine was 18.48, 16.52 and 15.01 min at the flow rate of 0.5, 0.6, and 0.7 mL/min, respectively. The retention times of the analytes are shortened and the peak widths of the analytes decrease with the increase of flow rate. The peak of inferent overlapped with the peak of ametry when the flow rate is higher than 0.5 mL/min (the detailed information can be found in Fig. S1). So the flow rate of 0.5 mL/min was chosen.

The herbicides in real sample was determined by LC/DAD and further identified by LC/MS. The HPLC conditions are the same as those mentioned above. Mass spectrometric conditions are as follows: nitrogen (99.999%) was used for nebulizer gas and curtain gas. The ion polarity was set to positive mode. The source temperature was set to 450 °C. The curtain gas 1 (nebulizer gas) and gas 2 (turbo gas) were 40 and 45 psi, respectively. The ion spray and entrance potential were 5200 and 10 V, respectively. The declustering potential, collision energy and collision cell exit potential were 50 V, 20 eV and 35 V, respectively. Both Q1 and Q3 were set to unit resolution. The data was acquired in IDA mode.

3. Results and discussion

3.1. Characterization of the synthesized MIL-101(Cr)

The experimental XRD pattern of the synthesized MIL-101(Cr) crystals is shown in Fig. 2A. The XRD pattern of the as-synthesized

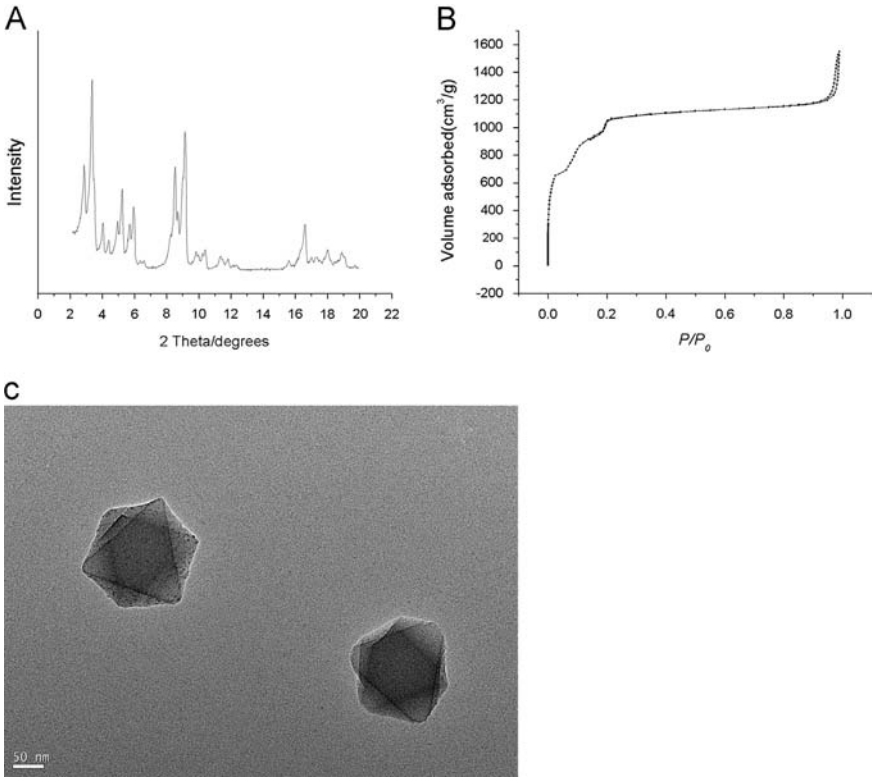

Fig. 2. XRD pattern (A), N_2 adsorption–desorption isotherm (B), and TEM image (C) of the preparaed MIL-101(Cr).

MIL-101 was in good agreement with the simulated XRD pattern of MIL-101 reported previously [21,27], showing the successful preparation of MIL-101(Cr). The N_2 sorption–desorption isotherm is shown in Fig. 2B. P is gas pressure and P^0 is saturation pressure. The N_2 sorption isotherm of the prepared MIL-101(Cr) is of type I with secondary uptakes at $P/P^0 \sim 0.1$ and $P/P^0 \sim 0.2$ characteristic of the presence of two kinds windows. It is in good accordance with that reported in the literature [21]. The BET surface area of MIL-101 (Cr) is 3023 m^2/g which is similar to that of MIL-101(Cr) reported [26,27]. The TEM image is shown in Fig. 2C and exhibits cubic shaped crystals of MIL-101(Cr).

3.2. Optimization of liquid phase extraction

3.2.1. Type of extraction solvent

The effect of types of extraction solvents including methanol (MeOH), ACN, acetone, EA and hexane was investigated. The results are shown in Fig. 3A. It can be seen that the recoveries obtained with ACN, acetone and EA was obviously higher than those obtained with MeOH and hexane. The extraction recoveries obtained with MeOH are lowest. The experimental results indicate that both the polar solvents, such as MeOH, and the non-polar solvents, such as hexane, are not beneficial to the extraction of the analytes. Methanol could not permeate through the fatty sample effectively due to the high polarity. Non-polar hexane has limited capacity to extract the medium polarity herbicides. Although the co-extractive substances in the extract obtained with EA and acetone are obviously more than those obtained with ACN, the extraction recoveries obtained with ACN, acetone and EA are close, because the co-extractive fat is kept in hexane solution and the herbicides are effectively adsorbed on MOFs. Compared with ACN and acetone, EA is cheaper, safer and easier to be evaporated. In addition, the chromatogram obtained with EA is cleaner than those obtained with ACN and acetone (the detailed information can be found in Fig. S2). Therefore, EA was used as an extraction solvent.

3.2.2. Volume of EA

The effect of the volume of EA ranging from 2 to 8 mL was investigated. The results shown in Fig. 3B indicate that recoveries increase with the increase of the volume of EA from 2 to 6 mL and changed slightly with the further increase of EA volume. It was insufficient to extract the analytes when the volume of extraction solvent is small. To ensure a complete extraction, 7 mL of EA was chosen for the subsequent experiments.

To further optimize the extraction conditions, the extraction was repeated and the extracts were combined. However, the extraction efficiency was improved slightly and the baseline noise was amplified obviously. It can be deduced that most of the analytes were extracted in the first extraction. Therefore, the extraction was carried out once with 7 mL EA.

3.2.3. Ultrasonication time

The effect of ultrasonication time was evaluated by performing assays in the range of 1–30 min. The results are shown in Fig. 3C. The recoveries increase obviously with the increase of ultrasonication time from 1 to10 min, increasing slowly from 10 to 15 min and changing slightly when extraction time is further prolonged. The increase of ultrasonic time is beneficial to the diffusion of analytes from sample to extraction solvent and the dissolution of analytes in the extraction solvent. So the recovery increases within 15 min. But a further increase of ultrasonic time has slight effect on the recoveries because the extraction equilibrium is achieved. Therefore, 15 min of ultrasonic time was selected.

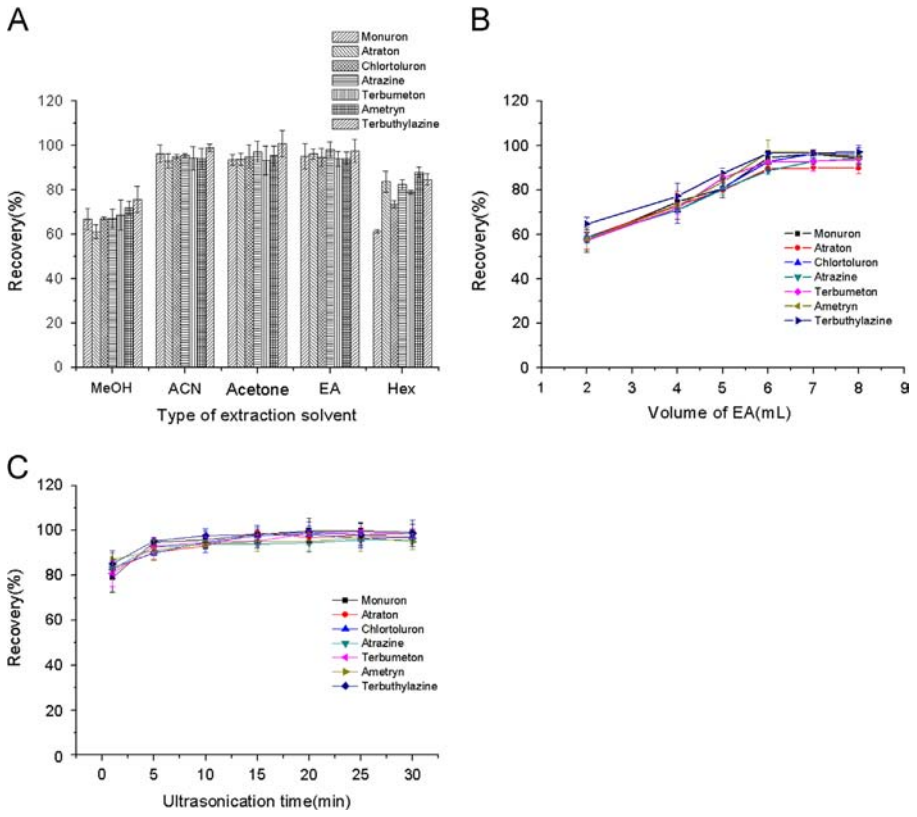

Fig. 3. Effects of type of extraction solvent (A), volume of EA (B) and ultrasonication time (C) on recovery of the analytes. Volume of hexane, 5 mL; amount of MIL-101(Cr), 7 mg; extraction time of MIL-101(Cr), 5 min; volume of eluting solvent, 2 mL of ACN; and spiked concentration, 80 μg/kg.

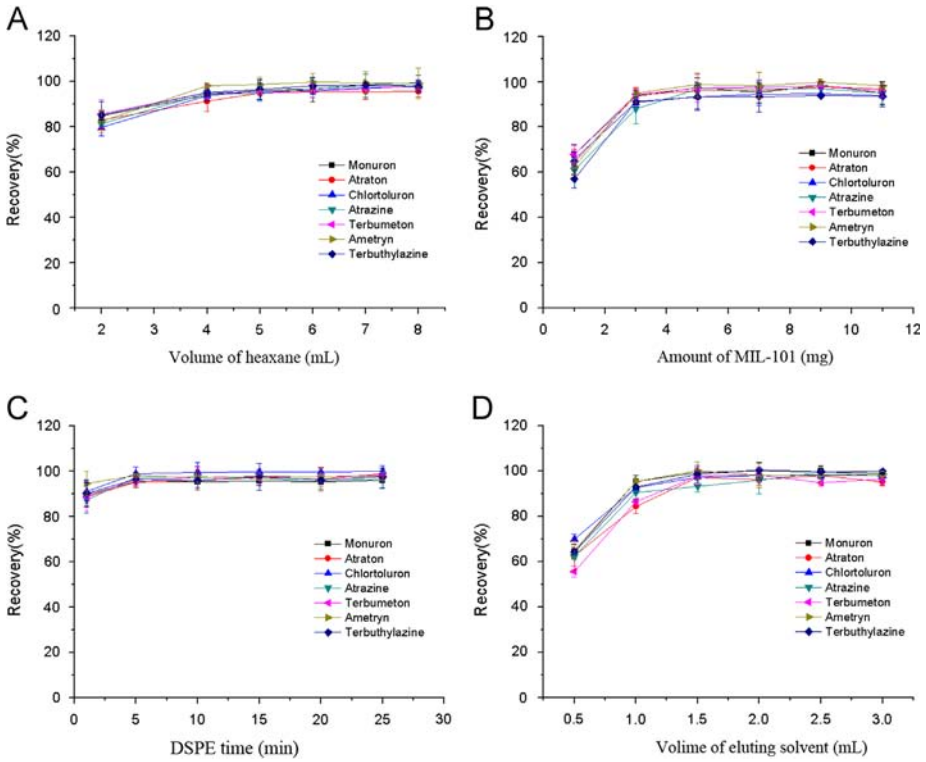

Fig. 4. Effects of hexane volume (A), MIL-101(Cr) amount (B), DSPE time (C) and volume of eluting solvent (D) on recovery of the analytes. Extraction solvent, 7 mL of EA; ultrasonication time, 15 min; and spiked concentration, 80 μg/kg.

3.3. Optimization of DSPE

3.3.1. Volume of hexane

In the work, hexane was used to dissolve fat and keep fat in bulk. The effect of volume of hexane ranging from 2 to 8 mL was investigated. The results are shown in Fig. 4A. It can be seen that the recoveries increase obviously with the increase of the volume of hexane from 2 to 5 mL and change slightly with the further increase of hexane volume. The reason may be that the viscosity of solution decreases with the increase of hexane which is beneficial to the dispersion of sorbent and thus improvement of the extraction efficiency. So 5 mL of hexane was used in the following experiments.

3.3.2. Amount of MIL-101(Cr)

The effect of the amount of MIL-101(Cr) ranging from 1 to 11 mg on recovery was studied. The results shown in Fig. 4B indicate that the recoveries increase with the increase of the amount of MIL-101(Cr) from 1 to 5 mg and change slightly when the amount of MIL-101(Cr) is larger than 5 mg. Because the extraction capacity of MIL-101 is limited, the extraction of analytes was insufficient when the amount of MIL-101 was smaller than 5 mg. The analytes were efficiently adsorbed on MIL-101 when 5 mg of MIL-101 was used and thus the recoveries of analytes changed slightly with a further increase of MIL101. To ensure sufficient extraction, 7 mg of MIL-101(Cr) was selected.

3.3.3. DSPE time

The effect of DSPE time from 1 to 25 min on the recoveries of the analytes was examined. The results are shown in Fig. 4C. It can be seen that the recoveries increase with the increase of extraction time from 1 to 5 min and change slightly with a further increase of extraction time. The increase of DSPE time is beneficial to the adsorption of analytes and thus the recoveries increase. When the extraction equilibrium is achieved, the recoveries change slightly. Therefore, 5 min was chosen as DSPE time.

3.3.4. Elution conditions

In the work, ACN was used as an eluting solvent in terms of its great ability to dissolve the analytes. The effect of volume of ACN ranging from 0.5 to 3 mL was investigated. The results are shown in Fig. 4D. The recoveries increase when the volume of ACN increases from 0.5 to 1.5 mL and change slightly when the volume of ACN is larger than 1.5 mL. The reason is that the herbicides were incompletely eluted when the volume of ACN was smaller than 1.5 mL. To elute analytes completely, 2 mL of ACN was used in the following experiments. The effect of eluting time was investigated in the range of 0.5–10 min. The recoveries increase with the increase of the time from 0.5 to 1 min and change slightly with a further increase of the time. Ultrasonic irradiation could facilitate the elution of analytes from sorbent and thus the recoveries of analytes increase with the increase of ultrasonic time from 0.5 to 1 min. The recoveries change slightly with a further increase of ultrasonic time after the analytes are almost completely eluted. Therefore, 3 min is adequate for elution.

3.3.5. Comparison with other sorbents

The effect of type of sorbents, including MIL-101, HKUST-1, Si, PSA and Al_2O_3, were studied. HKUST-1 was synthesized according to the method reported by Chui et al. [28]. MIL-101 showed higher extraction efficiency than the others. The recoveries of analytes ranged from 89.0 to 97.9% when MIL-101 was used. When HKUST-1was used, the recoveries of monuron and chlortoluron were 84.0 and 92%, respectively, and the recoveries of the triazine herbicides were lower than 30%. The recoveries of analytes ranged from 4.3 to 54.1% when Si was used. When PSA and Al_2O_3 were used, the herbicides were nearly unrecovered probably due to the weak interaction of the two sorbents and analytes. The difference of extraction efficiency obtained by MIL-101 and HKUST-1 may be related to the pore size. HKUST-1 forms face-centered-cubic crystals that contain a three-dimensional system of large square-shaped pores (0.9×0.9 nm^2) [28]. It contains three types of pores, of which two larger square-shaped pores (1.2 nm in diameter) are reported to penetrate the basic structure in all three dimensions and are connected with pore windows about 0.8 nm in diameter [28,29]. The kinetic diameters of monuron, atraton, chlortoluron, atrazine, terbumeton, ametryn and terbuthylazine were 1.041, 0.971, 1.050, 0.934, 1.035, 1.036 and 0.964 nm, respectively. All calculations of kinetic diameter are carried out with the Gaussian 09 A.02 package. The configuration of molecular was optimized with the molecular mechanics method under the uff force field. The relative small pore is not beneficial to the filling of analytes, so the extraction efficiency is poor. The high recoveries of monuron and chlortoluron were obtained probably due to their relative planar configuration which makes them enter the pore easily. Due to the large pores and windows of MIL-101, the herbicides can enter the pore of MIL-101 easily and thus the recoveries of analytes are high. The different extraction efficiencies between MIL-101 and Si can be attributed to the different interactions between sorbent and analytes. The herbicides can be adsorbed on MIL-101 mainly by the interaction between heteroatoms in herbicides and the unsaturated metal sites, π–π interaction between the herbicides and the framework terephthalic acid molecular and the π-complexation between the π-electrons of herbicides and Lewis acid sites in the pore of MIL-101. The hydrogen-bonding plays a main role in adsorption of analytes on Si, which is relatively weak and results in low recovery. The experimental results demonstrate that compared with other sorbents MIL-101 is efficient to extract herbicides in oily solution.

3.4. Evaluation of the proposed method

3.4.1. Analytical performances

The working curves were constructed by plotting the peak areas measured versus the concentrations of analytes in spiked samples. The linear regression equations and the correlation

Table 1
Working curve.

Analyte	Regression equation	Correlation coefficient	Linear range (μg/kg)	LOD (μg/kg)	LOQ (μg/kg)
Monuron	$A=0.91377c+0.00913$	0.9999	6.3–200.0	1.9	6.2
Atraton	$A=1.70551c+0.06484$	0.9999	3.1–200.0	0.99	3.3
Chlortoluron	$A=0.94348c+0.03956$	0.9999	6.3–200.0	1.8	6.1
Atrazine	$A=1.70397c-0.22268$	0.9999	3.1–200.0	1.0	3.4
Terbumeton	$A=1.52254c+0.81379$	0.9999	3.1–200.0	0.98	3.3
Ametryn	$A=1.34351c-0.92771$	0.9999	5.0–200.0	1.5	5.1
Terbuthylazine	$A=1.53531c-1.04555$	0.9999	5.0–200.0	1.5	4.9

coefficients are listed in Table 1. The lowest concentration of the linear range was determined by experiment. The chromatographic peak corresponding to the lowest concentration can be precisely measured and correlation coefficient of the regression equation including the concentration should be acceptable. The limits of detection (LODs) and quantification (LOQs) are determined as the concentrations yielding a signal-to-noise (S/N) ratio of 3 and 10, respectively. As shown in Table 1, the LODs for herbicides range from 0.98 to1.9 μg/kg. The LOQs for herbicides ranging from 3.3 to 6.2 μg/kg are far lower than the MRLs established by EU.

The intra- and inter-day precision of the present method were obtained by analyzing the spiked sample at a spiking concentration of 80 μg/kg. The intraday precision was obtained by analyzing a sample six times during a working day. The inter-day precision was obtained by analyzing the same sample once each day over six working days. Table 2 shows the RSDs and recoveries. The intra- and inter-day RSDs range from 0.5 to 5.1% and from 2.7 to 5.7%, respectively. The recoveries range from 95.6 to 102.0%.

In order to further evaluate the performance of the proposed method, the enrichment factor (EF) was investigated. Because the sample is solid, EF was calculated based on the ratio of the concentration of analytes in analytical solution to the concentration of analytes in sample solution. In the proposed method, the EFs for monuron, atraton, chlortoluron, atrazine, terbumeton, ametryn and terbuthylazine, were 31.7, 38.0, 34.7, 37.5, 36.0, 31.7 and 32.5, respectively.

Table 2
Precision and recovery.

Analytes	Intra-day ($n=6$)		Inter-day ($n=6$)	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Monuron	99.0	0.5	98.4	3.5
Atraton	97.6	1.2	95.6	2.7
Chlortoluron	98.7	1.1	96.0	4.8
Atrazine	102.0	2.6	95.6	5.7
Terbumeton	96.9	5.1	97.3	4.1
Ametryn	99.1	3.4	96.1	5.1
Terbuthylazine	99.4	1.3	100.0	4.6

3.4.2. Analysis of real samples

The proposed method was applied to the analysis of 8 real samples. The analytes in potential positive samples were identified by comparing their retention times with those of authentic standard analytes. In addition, LC/MS was used to identify the analytes by comparing their fragmentation patterns with those of authentic standards. The comparison of mass spectral data of the analytes in spiked sample 1 and those in standard solution are shown in Table 3. Atraton was detectable in sample 6 and the concentration was lower than the LOQ. The herbicides in other samples were not detectable.

The practical applicability of the present method was evaluated by determining seven herbicides in four spiked peanut samples. The recoveries and precision of herbicides in four samples are listed in Table 4. The results indicate that the proposed method provides good recoveries ranging from 89.5 to 102.7%

Table 3
Comparison of mass spectral data of the analytes in spiked sample 1 and those in standard solution.

	Analytes	Mw[a]	Retention time (min)	Precursor ion m/z	Production ion m/z
Matrix solution spiked sample 1	Monuron	198.65	8.65	199.1	102.2, 72.1
	Atraton	211.26	9.43	212.2	170.2, 142.2
	Chlortoluron	212.68	11.58	213.1	140.1, 72.1
	Atrazine	215.72	12.99	216.2	174.2, 132.1
	Terbumeton	225.29	14.95	226.2	170.2, 142.1
	Ametryn	227.33	17.33	228.2	186.2, 158.2
	Terbuthylazine	229.71	18.92	230.2	174.1, 132.1
Standard solution	Monuron	198.65	8.69	199.1	102.2, 72.1
	Atraton	211.26	9.45	212.2	170.2, 142.2
	Chlortoluron	212.68	11.61	213.1	140.2, 72.1
	Atrazine	215.72	12.97	216.1	174.2, 132.1
	Terbumeton	225.29	14.99	226.2	170.2, 142.1
	Ametryn	227.33	17.33	228.2	186.2, 158.2
	Terbuthylazine	229.71	18.92	230.2	174.1, 132.1

[a] Mw: molecular weight.

Table 4
Analytical results for fresh spiked samples.

Sample	Added (μg/kg)	Monuron		Atraton		Chlortoluron		Atrazine		Terbumeton		Ametryn		Terbuthylazine	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
1	10	98.0	5.0	99.1	1.9	95.5	5.0	102.3	4.1	98.8	0.9	95.9	2.2	97.6	2.2
	100	96.8	3.6	100.0	0.8	99.4	1.1	98.9	3.8	99.6	1.6	96.5	5.1	102.7	2.7
2	10	94.0	2.3	97.7	2.9	94.5	1.7	99.3	0.6	93.3	1.6	95.1	1.5	92.5	3.1
	100	96.4	2.4	93.7	0.3	97.0	0.4	96.6	1.3	96.0	0.8	99.1	0.3	98.2	1.5
3	10	92.2	4.9	97.4	2.4	93.9	4.5	94.2	3.7	91.2	1.6	89.5	3.2	90.2	0.8
	100	92.2	3.5	94.2	1.8	94.5	1.3	91.1	6.2	93.3	1.1	95.8	0.6	95.6	2.6
4	10	95.1	1.1	98.9	1.2	95.0	1.1	97.8	2.7	98.2	1.2	94.3	2.9	96.7	6.1
	100	95.3	3.4	95.8	4.0	96.4	2.1	94.4	2.4	96.3	1.4	98.2	2.3	100.3	0.9

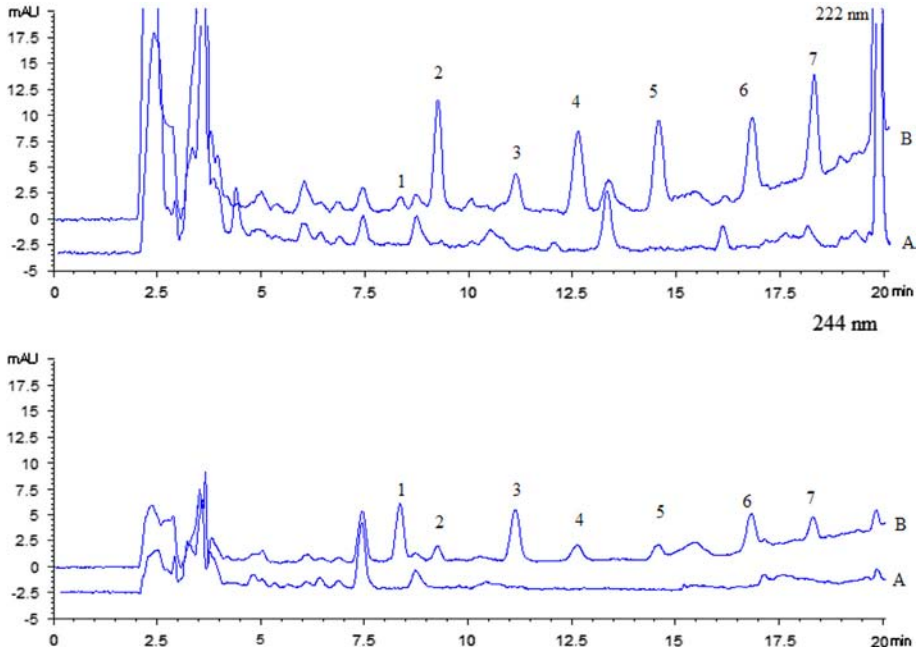

Fig. 5. Chromatograms of extracts of sample 1 (A) and spiked sample 1 (B). 1, Monuron; 2, atraton; 3, chlortoluron; 4, atrazine; 5, terbumeton; 6, ametryn and 7, terbuthylazine.

Table 5
Analytical results for aged spiked sample 1.

Store time (week)	Added (μg/kg)	Monuron		Atraton		Chlortoluron		Atrazine		Terbumeton		Ametryn		Terbuthylazine	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
1	10	96.1	6.5	101.6	0.4	97.5	4.6	99.8	2.5	97.7	3.4	96.4	2.8	98.2	7.0
	100	93.4	2.3	94.9	4.2	95.0	0.4	99.6	2.7	99.3	2.5	97.0	4.6	96.4	4.0
2	10	98.4	2.4	100.8	4.8	95.9	1.1	98.9	4.4	96.4	3.9	94.6	5.9	97.3	5.8
	100	93.6	5.5	98.3	3.1	94.5	4.2	99.1	1.9	98.9	3.6	97.0	2.8	98.0	5.8
3	10	97.2	4.1	100.8	4.9	95.9	1.6	94.9	4.7	95.2	2.6	93.8	4.1	97.1	6.4
	100	93.1	0.8	95.6	4.1	93.9	3.8	96.1	3.9	97.4	4.0	94.7	3.1	94.8	0.4
4	10	95.5	2.8	98.9	2.4	95.7	2.8	98.4	0.8	98.7	2.2	96.5	4.3	101.1	1.8
	100	92.5	1.9	96.3	2.1	93.3	0.3	97.9	2.3	98.8	1.8	94.4	3.6	99.4	0.6

Table 6
Comparison of the proposed method with other methods reported in the literatures.

Matrix	Extraction (min)	Clean-up procedure (time)	Removal amount of fat	Detection	Recovery (%)	RSD (%)	LOD (μg/kg)	LOQ (μg/kg)	Refs.
Peanuts	7 mL EA	DSPE: 7 mg MIL-101 (5 min)	High	LC-DAD	95.6–102.0	0.5–5.7	0.98–1.87	3.26–6.23	This work
Rapeseeds	2 mL H_2O+10 mL ACN with 1% acietic acid	LTFP (12 h)	Low	LC-MS/MS	61–91	1–10	–	0.7–2	[6]
Soybean oil	10 mL ACN	LTFP (4 h)+DSPE: 100 $MgSO_4$+500 mg florisil (2 min)	Low	GC-MS	84–106	2–10	–	8–20	[13]
Olive oil	10 mL ACN	GPC (23 min)	High	GC-MS/MS	92–109	3–6	0.2–1.4	0.6–3.4	[5]
Flaxseeds and peanuts	20 mL ACN/H_2O (v/v, 1/1)	DSPE: 150 mg $MgSO_4$+150 mg PSA+50 mg C_{18} (0.5 min)	Low	GC–TOF	101–114	5–6	5	–	[16]
Almond	10 mL ACN	DSPE: 750 mg MgSO4+175 mg Z-Sep (0.5 min)	Low	LC-MS/MS	82–94	2–7	–	10	[17]
Olive oil	20 mL ACN	SPE: 3000 mg florisil cartridge	Low	GC-ECD	92–98	3–5	–	50	[2]
Olive oil	20 mL ACN	SPE: 3000 mg florisil cartridge	Low	GC-MS	92–102	4–6	–	0.5–3	[2]
Olive oil	20 mL ACN	SPE: 500 mg ENVI-Carb cartridge	Low	GC-NPD	69.5–73.3	4.9–15.8	6.4–6.5	19.8–22.2	[9]

LTFP: low temperature fat precipitation; GPC: gel-permeation chromatography; SPE: solid-phase extraction; DSPE: dispersive-SPE; LC: liquid chromatography; GC: gas chromatography; DAD: diode array detection; MS: mass spectrometry; TOF: time-of-flight mass spectrometry; NPD: nitrogen–phosphorus detection; and ECD: electron capture detection.

and acceptable precision lower than 6.2% at two concentration levels. The chromatograms of sample 1 and spiked sample 1 are shown in Fig. 5.

3.4.3. Stability

The long term stability of the analytes in peanuts was evaluated. The extraction of herbicides in spiked peanut samples was carried out when the spiked samples were stored for 1, 2, 3 and 4 weeks. The results are shown in Table 5. The recoveries range from 92.5 to 101.6% and the RSDs were lower than 7.0%. It can be deduced that the analytes are stable and the interaction of the matrix and herbicides slightly affects extraction efficiency of analytes within four weeks.

3.4.4. Comparison with other methods

The proposed method was compared with the reported methods for the determination of triazine and phenylurea herbicides in fatty matrices [2,5,6,9,13,16,17]. The results are shown in Table 6. It can be seen that the consumption of sorbent in the proposed method is lower than that in other sorbent-based methods. Compared with the other methods, the consumption of organic solvent is acceptable. It also can be seen that the proposed method provided acceptable RSDs and satisfactory recoveries. The LODs obtained by the proposed method are similar to or lower than those obtained by other methods. In addition, a large amount of fat in the sample can be removed when the proposed method was applied. So it can be deduced that the proposed method is suitable to the determination of herbicides in peanuts.

4. Conclusion

A liquid-phase extraction coupled with MOF based dispersive solid phase extraction was developed to extract herbicides in peanuts. EA was used as extraction solvent. Compared with ACN, when EA was used, the cost was cheaper, the harm to the environment was slighter and obtained chromatogram was cleaner. The common methods removing fat are based on adsorbing fat with sorbents and the capacity of the sorbents is limited, which makes the analysis of the sample containing high content of fat difficult. In the work, MIL-101(Cr) was used as sorbent and the analytes were adsorbed on the sorbent and the fat was remained in the sample matrix. The proposed method is very effective in eliminating the fat interference and suitable for the treatment of sample containing high content of fat. It could be useful to extend different solvents to the extraction of pesticides in fatty matrices. The proposed method is simple, rapid and inexpensive. It is feasible to directly use MOFs to extract targets in various non-polar solvents by varying conditions and modifying MOFs.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.04.084.

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