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One-step integrated sample pretreatment technique by Gas-Liquid Microextraction (GLME) to determine multi-class pesticide residues in plant-derived foods

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Abstract

Gas-liquid microextraction technique (GLME) has been integrated with dispersive solid phase extraction to establish a one-step sample pretreatment approach for rapid analysis of multi-class pesticides in different plant-derived foods. A 50 μL of organic solvent plus 40 mg of PSA were required throughout the 5-minute pretreatment procedure. Good trueness (recoveries of 67.2 – 105.4%) and precision (RSD ≤18.9%) were demonstrated by the one-step GLME method, with MLOQs ranged from 0.001-0.011 mg kg^{-1}. As high as 93.6% pesticides experienced low matrix effect through this method, and the overall matrix effects (ME%) were generally better or comparable to QuEChERS. This method successfully quantified 2-phenylphenol, quintozene, bifenthrin and permethrin in the range of 0.001 – 0.008 mg kg^{-1} in real food samples. The multiresidue analysis feature of GLME has been validated, which displays further potential for on-site determination of organic pollutants in order to safeguard food safety and human health.

Keywords: Multi-residue methods (MRMs); Fruits; Vegetables; Honey; Insecticides; Herbicides

1. Introduction

Different categories of pesticides comprising insecticides, herbicides, acaricides, fungicides, antimicrobials, etc. have been extensively applied in agriculture worldwide to increase crop production and pest control. Since the publication of *Silent Spring* by Rachel Carson in the 1960s, an increasing attention has been drawn on the environmental concerns associated to the applications of pesticides, and it initiated tighter regulation of pesticides in the United States and many other countries (Dunn, 2012). Numerous studies in past decades proved the likeliness of pesticides to cause cancer (Alavanja et al., 2004), immunotoxicity (Corsini et al., 2013), neurological dysfunction (Gangemi et al., 2016), endocrine disruption (Rattan et al., 2017), decreased fertility (Hu et al., 2018) and behavioral disorders in children (Viel et al., 2017). Since then, international food safety and quality standard such as Codex Alimentarius and different national standards have set the maximum residue limit (MRL) of multi-class pesticides in foods to minimize damage on the environment and consumer health.

Fresh produce, especially fruits and vegetables, provides essential nutrition such as vitamins and minerals for meeting the daily intake requirement recommended for human wellbeing. Unfortunately, approximately one-third of the global food production which account for about 1.3 billion tons per annual ended up lost or wasted, and unsafe food with unsatisfactory quality is one of the factors that leads to food loss (Gustavsson et al., 2011). Taking into the account the considerable short shelf life of vegetables and fruits, a rapid analytical technique to assure pesticide-free fresh produce in the market is imperative. Not only that a speedy inspection system is crucial for improving food security, it also helps to reduce food waste and to preserve human health. Nonetheless, the complex matrix compositions of vegetables and fruits pose a great challenge that hinder the realization of rapid analysis, as interferences like sugars, water, pigments (including chlorophyll and other natural dyes), fatty acids, non-volatile material and compounds containing acidic or basic groups are frequently co-extracted during the sample pretreatment process (Rutkowska et al., 2019), hence jeopardizing the accuracy of analytical results. Therefore, a highly efficient extraction method coupled with powerful clean-up approach is the key to achieve rapid qualitative and quantitative analysis of plant-derived foods with excellent precision.

At present, there are a substantial number of analytical methods being developed for determining pesticide residues in various food matrices. In particular, the sample pretreatment technologies known as multiresidue methods (MRMs) have been established lately for simultaneously analyzing varied classes of pesticide residues with distinctive physicochemical properties. In contrast to the conventional pretreatment techniques such as liquid-liquid extraction (LLE), solid-phase extraction (SPE) and ultrasonic assisted extraction (UAE), miniaturized analytical methods including solid-phase microextraction (SPME), liquid-phase microextraction (LPME) and stir bar sorptive extraction (SBSE) are the upcoming development trend to realize the objective of green analytical chemistry. Although these modern MRMs are fast, accurate and sensitive, most of them are labor-intensive, time-consuming and unsuitable for automation. A technique termed as quick, easy, cheap, effective, rugged and safe (QuEChERS) method have become the preferred MRMs for pesticide analysis in recent years, and it has been appropriately modified to meet the challenges of multiresidue analysis. However, QuEChERS technique that usually combined with d-SPE clean-up still exhibits some limitations, such as high matrix effects and the necessity for modification to perform better in analyzing certain analytes and matrices (Kittlaus et al., 2011; Bruzzoniti et al., 2014). Most importantly, the variance of physicochemical properties for co-extracts in different foods covering a wide range of polarity and boiling points require a combination of clean-up techniques to effectively eliminate these interferences prior to quantitative analysis.

The gas-liquid microextraction (GLME) technique (previously known as gas-purge microsyringe extraction, GP-MSE) was developed on the basis of headspace liquid phase microextraction (Yang et al., 2009). GLME was previously applied in the analyses of polycyclic aromatic hydrocarbons (PAHs), alkyl phenols, light hydrocarbons, phthalate esters and other organic pollutants in plant leaves, soil, sediments, crude oil, and foodstuffs, respectively (Yang et al., 2011; Wang et al., 2013; Zhao et al., 2015; He et al., 2015; Gao et al., 2016; Jin et al., 2020; Zhao et al., 2020; Kaw et al., 2021). The principle of the GLME technology is based on the utilization of distinctive boiling points between analytes and interferences to achieve effective separation. Hence, majority of the volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) including organic pollutants like pesticides that are amenable for GC-MS analysis, are well suited for GLME treatment. The main strength of the GLME method which integrates extraction and clean-up procedures into a single step demonstrates great potential for a speedy pretreatment process. Commonly, the GLME pretreatment can be completed within several minutes prior to GC-MS analysis.

In the present study, GLME plays a significant role as an integrated extraction and clean-up approach to simultaneously extract multi-class pesticides from different plant-derived food commodities, and at the same time, the high extraction temperature of GLME aims to remove high-boiling-point interferences like carbohydrates and pigments. Throughout the extraction process, dispersive solid phase extraction (d-SPE) sorbents were also added in the receiving phase of the GLME system to adsorb organic acids, sugars and lipids through different clean-up mechanisms including ionic interaction. Two most determining GLME parameters (extraction temperature and extraction time) were sequentially optimized, and the optimal quantity of d-SPE sorbents were methodically evaluated. Eventually, a single-step sample pretreatment technique that involves effective extraction and clean-up procedures can be completed within few minutes, and its analytical performance was validated for the determination of pesticide residues in foods of plant origin. Fast analysis of pesticide residues in commercial products that proposed by this study is especially important in the food safety, food import and export and food inspection industries to safeguard human health.

2. Materials and Methods

2.1 Chemicals and reagents

HPLC grade dichloromethane, acetone, hexane, ethyl acetate and acetonitrile were purchased from Thermo Fisher Scientific (San José, CA, USA). Different sorbents including anhydrous sodium sulfate (Na_2SO_4 with ≥ 99% purity), graphitized carbon black (GCB, 40-60 μm), primary secondary amine (PSA, 40-60 μm) and bonded octadecyl silica (C18, 40-60 μm) were obtained from Shanghai BioSun Sci & Tech Co., Ltd. Details of the pesticide reference standards and the preparation procedures can be found in Supplementary Materials and Methods section. Detailed information regarding the toxicity, chemical and physical properties of the selected pesticides in this study can be referred to Table S1 and S2 in the supporting material.

2.2 Sample preparation

The selected plant-derived foods in this study consisted of apple (pome fruit with high water content), leek (allium with high water content that is widely recognized as a type of vegetable with highly complex matrix), orange (citrus fruit with high acid content and high water content), and honey (high sugar and low water content) were chosen based on their representative properties according to the SANTE/12682/2019 guideline. These four kinds of food were purchased from a local supermarket in Yanji city, Northeastern China. Each type of samples (approximately 200 g) was homogenized using a Fluko FA25 homogeniser. The homogenized sample was placed in a prewashed amber bottle, then sealed and stored at -18°C until further analysis.

2.3 One-step GLME pretreatment procedures

A schematic diagram and a short video indicating the arrangement and operations of the GLME device are shown in Fig. S1 and supplementary video, and the detailed description regarding the procedures of GLME extraction has been published elsewhere (Yang et al., 2011). In brief, 0.3 g (± 0.01 g) of sample at room temperature was precisely weighed and put into the sample tube (two-way glass tube with an internal diameter of 4 mm and a length of 6 cm). Surrogate standard was added onto the sample (target analytes were added in spiked samples) for evaluation of laboratory quality assurance. An optimized amount of d-SPE sorbents and 50 µL of hexane were added to a 250 µL GC insert as the receiving phase. The parameters of the GLME extraction were set as follows: extraction temperature: 120°C for 1 min, 300 °C for 3min; gas flow rate (N_2, 99.999% purity): 2 mL min^{-1}; condensation temperature: 0 °C and extraction time: 3 min. When the extraction was completed, the extract was eluted with 80 µL dichloromethane, acetone and ethyl acetate (v:v:v = 1:1:1), then concentrated by a gentle stream of nitrogen to adjust the extract volume to 80 µL. The post-extract eluate was spiked with 20 µL internal standard and an adequate amount of anhydrous sodium sulphate was added to completely remove the water content in the extract. The final extract was withdrawn to a 100 µL GC insert for GC-MS analysis.

2.4 GC-MS analysis

The analysis of pesticide residues was performed on a GC2010 gas chromatograph (Shimadzu, Kyoto, Japan) fitted with a DB-5 fused-silica capillary column (30 m × 0.25 mm; 0.25 µm) and coupled to a QPMS 2010 quadrupole mass spectrometer (Shimadzu, Kyoto, Japan). Helium with a purity of 99.999% was used as the carrier gas and was held at a flow rate of 1.0 mL min^{-1}. A sample volume of 2 µL was injected in splitless mode with an injection temperature of 280 °C. The GC-MS interface temperature was held at 280 °C and the ion source temperature was set at 200 °C. The electron energy for ionization was set to 70 eV. The initial oven temperature was set as 40 °C and then ramped at a rate of 50 °C min^{-1} to 150 °C, followed by 5 °C min^{-1} ramp to 250 °C then a final ramp of 10 °C min^{-1} to 300 °C and maintained for 3 min. The solvent cut time was 3.0 min. Selected ion monitoring (SIM) mode with a sampling rate of 1.2 s was used.

2.5 Quality assurance/Quality control

All analysis processes were performed using quality assurance and control measures. In order to eliminate the risk of contamination, all glasswares, sorbents and glass wool were baked at 400 °C for 12 h. After cooling down to room temperature, glass wool and Na_2SO_4 were preserved in a vacuum desiccator until analysis. A minimum of triplicate experiments were conducted for each type of samples. Instrumental and procedural blanks for every set of samples were systematically evaluated throughout the experiments. Quantification was carried out by the internal standard method. Internal standard (triphenyl phosphate (TPP), 20 ng) was used for the correction of injection amount and performance assurance of GC-MS. Quality control of the complete procedure and quantification was performed using 20 ng each of tetrachloro-m-xylene (TCMX) and deuterated tebuconazole (TEB-d_9) as surrogate standards. Extraction recoveries were calculated based on the formula $R_A = Q_A(\text{yield})/Q_A(\text{orig})$, where $Q_A(\text{yield})$ and $Q_A(\text{orig})$ represent the recovered and original quantities of analyte A.

2.6 Validation of analytical performance

The analytical performance of the proposed one-step sample pretreatment method was validated by assessing the trueness, reproducibility, linearity and method limit of detection (MLOD) and method limit of quantification (MLOQ). The concentrations of all 47 pesticides ranged from 5 to 1000 ng mL^{-1} in spiked samples were used for linearity evaluation. The trueness of the one-step pretreatment method was verified by evaluating the average recoveries of multi-class pesticides in spiked food samples at different concentration levels, and each spiked concentration was repeated in five replicates. The precision of this integrated sample pretreatment technique was determined through examining the relative standard deviations (RSDs) of recoveries. The MLOD and MLOQ of the developed method was confirmed by the sample-spiked method and the stepwise dilution method, which were determined based on a signal-to-noise ratio (S/N) of 3 and 10, respectively (Dong et al., 2020). The recoveries of surrogate standards that ranged from 66.9% to 93.8% validated the trueness of this analytical method.

2.7 Data analysis

Spearman’s rank correlation analysis was conducted to investigate the relationships between matrix effect and the physical and chemical properties of target compounds. The significant analysis was performed using SPSS Statistics 17.0 for Windows (Chicago, IL, USA) with a significance of $p < 0.01$ and $p < 0.05$.

3. Results and Discussions

3.1 Optimization of the one-step pretreatment parameters

3.1.1 GLME extraction parameters

As indicated in previous studies, extraction temperature and extraction time are the most determining parameters that decide the analytical performance of the GLME technique. In order to examine the influence of these important parameters of GLME in extracting multi-class pesticides, temperatures in the range of 260 to 330°C and the extraction times of 1 to 5 min were systematically evaluated. The extraction time was set to 5 min throughout the process of optimizing extraction temperature, while extraction temperature of 300°C remained constant in the experiments for optimizing extraction time. The optimization results were denoted in the form of heat map in Fig. 1. An obvious and easily distinguishable pattern that represents higher recovery values between 80 and 120% for all tested pesticides can be observed when the extraction time and extraction temperature were over 3 min and 300 °C, respectively. Based on this indication, these optimized extraction parameters were employed in subsequent experimentations.

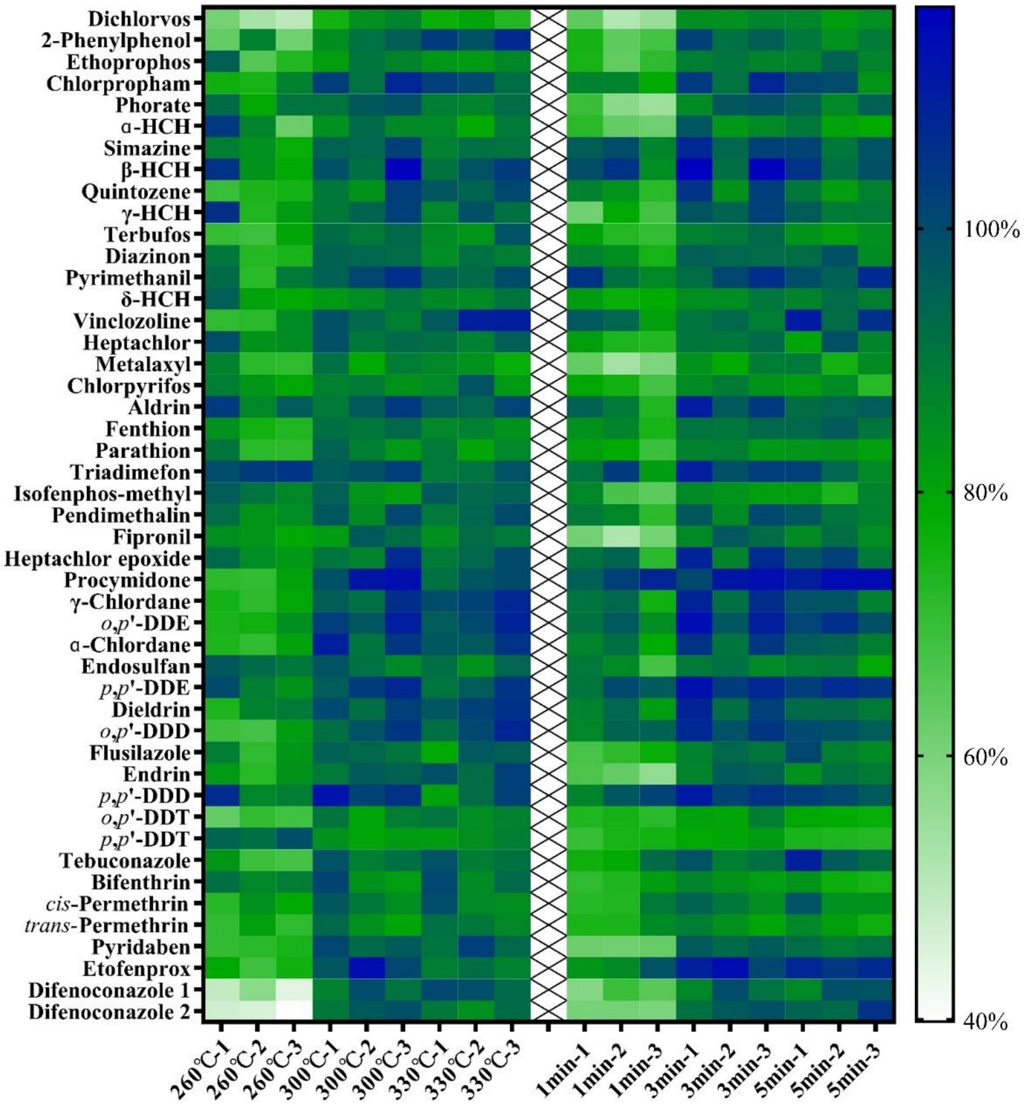

Fig. 1 Recoveries of 47 pesticides by using GLME under different extraction parameters (time and temperature).

3.1.2 Amount of clean-up sorbents

Due to boiling point difference between analytes and interfering substances, co-extracts with high boiling points such as chlorophyll with over 1000°C, can be priorly eliminated during GLME extraction. However, other low boiling point substances such as fatty acids, phenols and sugars were unavoidably co-extracted and remained in the post-GLME extract. Such co-extractants may bring about matrix effect that significantly interferes with the GC-MS analysis of target pesticides, thus resulting in inaccurate quantification. To overcome this problem, an additional clean-up step is indispensable. In this case, d-SPE technique is an ideal method as it can be flawlessly integrated with GLME. PSA, C18 and GCB were chosen as the sorbents for purifying sample extract as their clean-up effectiveness has been widely justified, especially for plant-derived food samples. Different amounts of each sorbents (10 - 50 mg with 10 mg interval for PSA, and 10 - 20 mg with 5 mg interval for GCB and C18) were sequentially evaluated. Results in Table S3 showed that PSA achieved excellent clean-up effect without imposing significant impact on the recoveries of 47 target pesticides (84.6 – 103.6%). Based on the weak anion exchange mechanism, PSA proved its effectiveness for adsorptive removal of organic acids, fatty acids and sugars that are commonly found in fruits and vegetables (VerÃ, 2017; Ferrentino et al., 2020; Klein et al., 2021), as shown in Fig. 2(A). This result is consistent with previous study (Oellig & Schmid, 2019). C18 and GCB, on the other hand, showed minimal clean-up effect (Fig. S2). The interferences in post-PSA clean-up extract were identified by using The National Institute of Standards and Technology (NIST) mass spectral library (please refer to Table S4 for detailed information), suggesting that most compounds were lipophilic substances with Log P values of > 5, and they were highly soluble in organic solvent. In comparison to PSA that forms hydrogen bond with fatty acids and sugars to achieve adsorption via chemical bonding, the adsorption mechanism for GCB and C18 is based on π-π interaction and hydrophobic effect to realize physical adsorption. In this study, the interaction between lipophilic interferences with DCM exhibited stronger effect than with the solid phases (sorbents), hence they were inclined to remain in the organic solvent instead of being adsorbed by GCB or C18 (Ly et al., 2020). GCB also substantially reduced the recoveries of several target compounds in a descending pattern that was inversely proportionate to the amount of GCB being added. For example, the recoveries of quintozene gradually decreased from 78.0% to 60.5% and 48.6% when the addition of GCB increased from 10 mg, 15 mg to 20 mg; likewise, pyrimethanil demonstrated a similar trend (a reduction of recoveries from 88.3% to 59.5%). This result is in line with published literatures, as GCB may adsorb low-polar pesticides with planar structure including quintozene and pyrimethanil (Pareja et al., 2011). Therefore, 40 mg of PSA was selected as the optimal d-SPE sorbent to be integrated with GLME technique as a one-step sample pretreatment approach. Clear peaks of multi-class pesticides can be effectively identified in chromatogram of GLME-d-SPE-treated spiked leek sample (Fig. 2(B)) and other plant-derived foods (Fig. S3), which was similar to the chromatogram of reference standard, suggesting the noteworthy clean-up performance of this method.

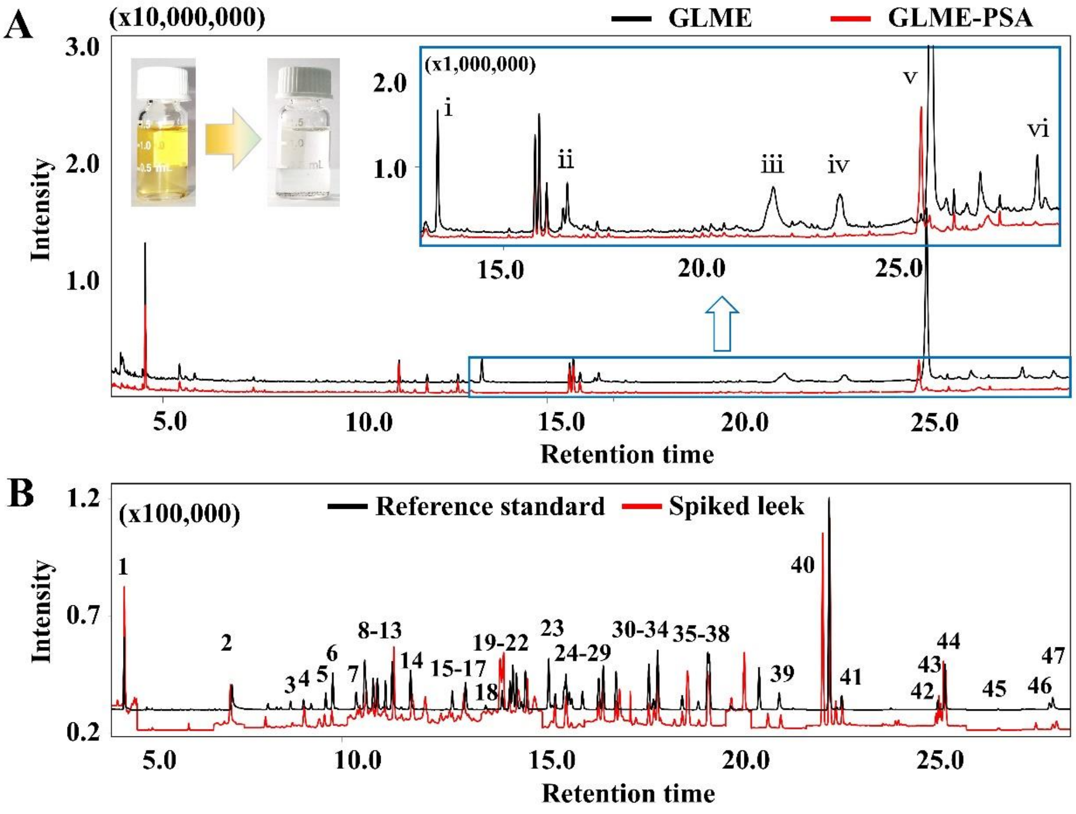

Fig. 2 Scan chromatograms that compare the clean-up performances by using GLME only and the combination of GLME with d-SPE sorbent (PSA) in leek (A), and the SIM chromatograms showing peaks of 47 pesticides in reference standard and spiked leek extract (B) (peaks were numbered according to the pesticides listed in Table 2). Additional information: (i): n-Hexadecanoic acid; (ii): Linoleic acid; (iii): 24-epicampesterol; (iv): Stigmasterol; (v): γ-Sitosterol; (vi): Cholestenone.

3.2 Matrix effect and its relationship with chemical properties of interferences

In order to establish a multiresidue method that is able to simultaneously analyze multi-class pesticides across different plant-derived food matrices, the clean-up performance of the one-step integrated GLME-d-SPE technique for accurate quantification of pesticide residues was examined by assessing the matrix effect (ME%) in post-treatment extracts. It is one of the critical criteria in chromatographic analysis as it significantly affects the accuracy of quantitative analysis, particularly in detection of trace-level pollutants in complex food or biological samples. In this study, ME% was calculated according to Eq. 1 to evaluate the influence of matrices on the analytical effectiveness.

$$\mathrm{ME}\ (\%) = 100 \times \left(\frac{S_m}{S_s} - 1\right) \qquad (1)$$

where S_m and S_s represent the slopes of calibration curve in sample matrix and solvent, respectively. In general, ME% within ±20% was categorized as weak matrix effect; otherwise, other values of ME% were considered as medium or high matrix effects. The calculated ME% of the present study was listed in Table 1, and the depictions of the overall ME% for all pesticides in each plant-derived food can be referred to Fig. S4 and Fig. S5. As high as 93.6% (44) detected pesticides were classified as weak matrix effect in apple, followed by orange with 85.1% (40) pesticides experienced minimal matrix interference during chromatographic analysis. The matrix effects for honey and leek samples were greater as these matrices are known to be more complex, in which leek contains various sulfur-containing compounds and the sugar level in honey is high (Xu et al., 2017; Cortese et al., 2020). Nonetheless, the pesticides with weak and medium matrix effects altogether accounted for approximately 81.0% (38) and 63.8% (30) in honey and leek, respectively.

There were significant correlations between the numbers of hydrogen-bond donors of target molecules and the ME% in apple, orange and leek (0.455, $p < 0.01$; 0.458, $p < 0.01$; 0.368, $p < 0.05$), suggesting that ME% in these matrices was closely associated to the formation of hydrogen bond between analytes and coextracts with greater electronegative functional groups such as N, O or Cl. As for honey sample, the ME% of 47 pesticides and the numbers of hydrogen bond donor or acceptor showed insignificant correlation. Instead, the ME% in honey was significantly correlated to polarizability and Log P values (0.458, $p < 0.01$; -0.450, $p < 0.01$), which was likely due to the abundance of coextracts that derived from alkane- or alkene groups in honey extract. This result indicated that the ME% in honey was influenced by the electrostatic interaction between pesticide molecules and the alkane- or alkene-group interferences. As elaborated in previous study (Gomez-Ramos et al., 2016), the chemical compositions of leek are extremely complex, thus there were multiple interactions between coextracts and pesticide molecules which eventually caused much stronger ME% in leek (referred to Table S5 for detailed information). In light of the quick and effective sample pretreatment performance of the one-step GLME-d-SPE method without jeopardizing the accurate quantification of multi-class pesticides, the slightly higher ME% in leek was compromised.

A summary of ME% for the representative orange (relatively simpler matrix) and leek samples (comparatively more complex matrix) was demonstrated in Fig. 3, which also showed a comparison of ME% in these matrices after treated by GLME-d-SPE and QuEChERS. It can be observed that identical if not slightly better clean-up effects were achieved by GLME-d-SPE than QuEChERS. Fig. S6 similarly justified the visibly better purification performance of the proposed one-step pretreatment technology in treated food samples. Chromatograms in Fig. 3(B) and (C) indicated the difference in clean-up effects between these two methods, which highlighted the robust purification performance of GLME-d-SPE regardless of different food types.

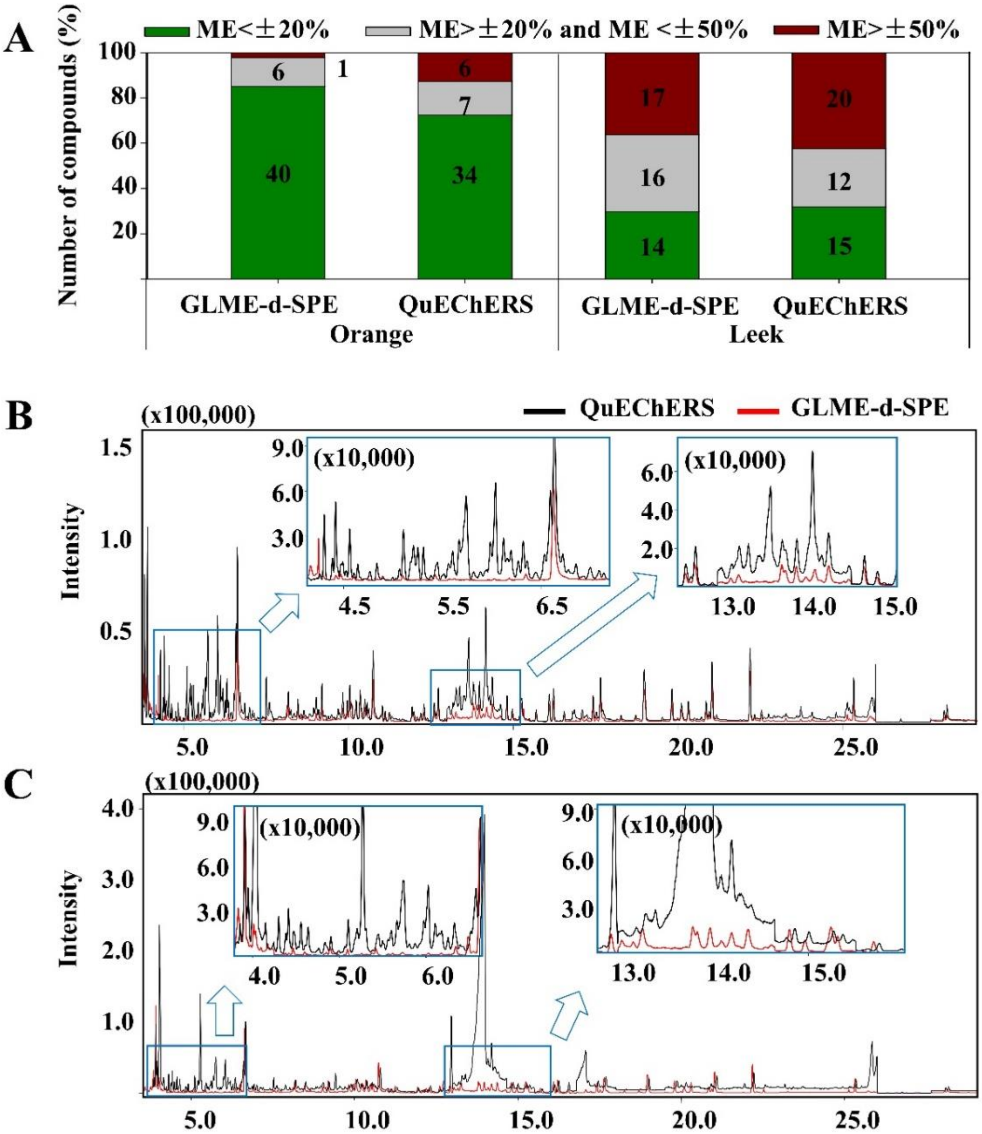

Fig. 3 Comparison of matrix effects (ME%) for orange and leek samples by using GLME-d-SPE and QuEChERS methods (A), and the chromatograms that demonstrated the post-treatment effects in orange (B) and leek (C).

3.3 Performance validation of the one-step GLME-d-SPE method

The analytical performance of the single step GLME-d-SPE pretreatment method under optimized condition was systematically validated through assessing the method sensitivity, linearity, trueness and precision. As shown in Table 1, the method limit of quantification (MLOQ) of this technique for analyzing pesticides in four representative food matrices generally ranged from 0.001 to 0.01 mg kg^{-1}, except for β-HCH, γ-chlordane and triadimefon with MLOQ of 0.011 mg kg^{-1} in honey. This range of MLOQs fulfils the detection requirements of MRLs set by the EU and China for multiresidue pesticide analysis. The calibration curves of all 47 pesticides showed good linearity, with determination coefficients (R^2) higher than 0.999 (Table S6). The trueness of the one-step pretreatment method was verified by evaluating the average recoveries of multi-class pesticides in spiked food samples at different concentration levels, and each spiked concentration was repeated in five replicates. The precision of this integrated sample pretreatment technique was determined through examining the relative standard deviations (RSDs) of recoveries. Both the recoveries at different spiked levels and their associated RSDs are recorded in Table 2. Results revealed the recoveries and RSDs (in parentheses) of 71.6-105.4% (2.4-18.3%), 64.2-99.7% (2.2-18.9%), 67.2-103.9% (3.2-16.4%) and 68.3-96.1% (0.6-15.4%) in apple, orange, honey and leek, respectively, suggesting the up to par analytical performance of the GLME-d-SPE method. A comparison between the proposed one-step integrated sample pretreatment method with other techniques was shown in Table 3, which suggested the advantageous of this newly developed approach.

Table 1 Method limit of quantification (MLOQ) and matrix effect (ME%) for 47 multi-class pesticides in the representative plant-derived foods by using the one-step GLME-d-SPE method, and the relevant maximum residue levels (MRLs) as reference.

	Pesticide	Family *	MLOQ (mg kg^{-1})				MRLs (EU/China)** mg kg^{-1}	ME%			
			Apple	Orange	Honey	Leek	Apple/Orange/Honey/Leek	Apple	Orange	Honey	Leek
1	Dichlorvos	OP	0.001	0.001	0.007	0.001	0.01/0.01/-/0.01	1	8	80	132
2	2-Phenylphenol	UN	0.001	0.001	0.002	0.001	0.01/10.0/0.05-0.01	18	29	103	120
3	Ethoprophos	OP	0.004	0.004	0.005	0.004	0.02/0.02/-/0.02	-7	-1	26	53
4	Chlorpropham	GI	0.004	0.004	0.004	0.004	0.01/0.01/0.05/0.01	6	12	45	68
5	Phorate	OP	0.001	0.001	0.007	0.001	0.01/0.01/0.01/0.01	-5	8	-65	56
6	Simazine	CT	0.005	0.005	0.007	0.005	0.01/0.01/0.01/0.01	16	23	-5	88
7	α-HCH	OC	0.002	0.001	0.002	0.002	0.01/0.01/0.01/0.01***	-16	-1	20	59
8	β-HCH	OC	0.004	0.004	0.011	0.004		-10	-4	6	38
9	γ-HCH	OC	0.003	0.003	0.007	0.005		-16	-1	10	56
10	δ-HCH	OC	0.003	0.002	0.003	0.004		-15	-5	-2	40
11	Quintozene	AF	0.009	0.009	0.009	0.009	0.02/0.02/0.01/0.02	-1	25	80	107
12	Terbufos	OP	0.001	0.001	0.005	0.001	0.01/0.01/-/0.01	-10	3	-75	52
13	Diazinon	OP	0.003	0.003	0.003	0.003	0.01/0.01/0.01/0.01	5	3	9	27
14	Pyrimethanil	PF	0.001	0.001	0.002	0.001	15.0/8.0/0.05/4.0	16	26	19	96
15	Vinclozoline	DC	0.003	0.003	0.003	0.003	0.01/0.01/0.05/0.01	3	1	13	26
16	Heptachlor	OC	0.002	0.002	0.002	0.004	0.01/0.01/0.01/0.01***	-13	2	30	68
17	Heptachlor epoxide	OC	0.002	0.002	0.007	0.002		-19	-12	-4	17
18	Metalaxyl	AN	0.008	0.004	0.008	0.005	1.0/0.7/0.05/0.03	-11	-8	-6	21
19	Chlorpyrifos	OP	0.003	0.003	0.003	0.003	0.01/1.5/0.05/0.01	1	3	15	36
20	Aldrin	OC	0.003	0.004	0.005	0.004	0.01/0.01/0.01/0.01	-15	0	20	51
21	Fenthion	OP	0.001	0.001	0.007	0.001	0.01/0.01/0.01/0.01	-2	3	-81	32
22	Parathion	OP	0.009	0.009	0.009	0.009	0.01/0.01/-/0.01	36	59	143	120
23	Triadimefon	CF	0.006	0.006	0.011	0.006	0.01/0.01/0.05/0.01	-10	-7	-6	30
24	Isofenphos-methyl	OP	0.003	0.003	0.003	0.006	0.01/0.01/-/0.01	-14	-6	-13	28
25	Pendimethalin	DA	0.003	0.003	0.003	0.003	0.05/0.05/0.05/0.05	28	41	98	103
26	Fipronil	PP	0.002	0.002	0.005	0.002	0.005/0.005/0.005/0.005	1	4	13	20
27	Procymidone	DC	0.004	0.004	0.004	0.004	0.01/0.01/0.05/0.01	-2	-3	3	17
28	γ-Chlordane	OC	0.002	0.002	0.011	0.002	0.01/0.01/0.01/0.01***	-17	-7	6	27
29	α-Chlordane	OC	0.002	0.002	0.002	0.002		-15	-10	4	16
30	*o,p*'-DDE	OC	0.001	0.001	0.005	0.001	0.05/0.05/0.05/0.05***	-12	-5	8	27
31	*p,p*'-DDE	OC	0.001	0.001	0.001	0.001		-5	-1	8	12
32	*o,p*'-DDD	OC	0.001	0.001	0.001	0.001		-14	-7	1	9
33	*p,p*'-DDD	OC	0.001	0.001	0.001	0.002		-8	-1	12	29
34	*o,p*'-DDT	OC	0.001	0.001	0.001	0.002		-5	0	13	21
35	*p,p*'-DDT	OC	0.001	0.001	0.001	0.002		6	12	28	53
36	Endosulfan	OC	0.006	0.005	0.009	0.010	0.05/0.05/0.01/0.05	-17	-9	0	26
37	Dieldrin	OC	0.008	0.007	0.009	0.010	0.01/0.01/0.01/0.01***	-17	-10	5	22

38	Endrin	OC	0.004	0.004	0.005	0.008		-16	-4	7	37
39	Flusilazole	CF	0.010	0.010	0.010	0.010	0.01/0.01/0.05/0.01	-6	-15	-16	-7
40	Tebuconazole	CF	0.003	0.003	0.003	0.003	0.3/0.9/0.05/0.6	8	11	9	25
41	Bifenthrin	PY	0.001	0.001	0.001	0.002	0.01/0.05/-/0.05	-16	-18	-8	-1
42	cis-Permethrin	PY	0.004	0.005	0.006	0.009	0.05/0.05/-/0.05***	-13	-18	-4	-6
43	trans-Permethrin	PY	0.001	0.001	0.001	0.003		-9	-18	-5	-4
44	Pyridaben	UN	0.004	0.004	0.005	0.004	0.9/0.3/0.05/0.01	6	-22	9	-34
45	Etofenprox	PY	0.003	0.003	0.003	0.003	0.6/1.5/0.05/0.01	-3	-10	20	-50
46	Difenoconazole 1	CF	0.007	0.007	0.007	0.007	0.5/0.5/0.05/0.6***	33	13	55	30
47	Difenoconazole 2	CF	0.004	0.004	0.004	0.004		-7	-2	24	4

* OC: Organochlorine insecticide; OP: Organophosphate insecticide; PY: Pyrethoid insecticide; GI: Growth inhibitor; CT: Chlorotriazine herbicide; AF: Aromatic fungicide; PF: Pyrimidine fungicide; DC: Dicarboximide fungicide; AN: Anilide fungicide; CF: Conazole fungicide; DA: Dinitroaniline herbicide; PP: Phenylpyrazole acaricide; UN: Unclassified.

** The listed MRLs in each food type were displayed according to the lower MRL values set by EU and China.

*** MRLs refer to the sum of isomers.

Table 2 Trueness (mean recovery) and precision (relative standard deviation, RSD) of the one-step GLME-d-SPE method to analyze 47 pesticides spiked at three concentrations in different plant-derived foods.

		Apple						Orange						Honey						Leek					
		Spiked level (mg kg^{-1})																							
		20		50		200		20		50		200		20		50		200		20		50		200	
		R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)
1	Dichlorvos	79.9	6.0	89.5	6.5	75.2	5.7	73.5	9.2	82.9	4.8	80.5	13.2	90.0	12.6	74.3	12.9	71.3	4.4	75.4	6.4	70.4	7.2	75.3	6.5
2	2-Phenylphenol	85.0	11.2	91.8	8.9	93.4	2.4	79.9	6.0	81.2	3.4	77.0	8.3	86.4	5.4	86.9	14.4	87.8	12.5	89.4	5.8	83.0	13.9	79.3	6.0
3	Ethoprophos	80.9	9.6	87.5	5.2	88.6	9.6	95.2	5.7	86.6	4.4	80.7	14.0	80.0	10.6	74.4	13.8	78.7	9.7	82.8	4.9	89.8	14.6	73.1	5.1
4	Chlorpropham	91.4	9.0	88.4	8.9	89.9	11.7	87.5	3.8	87.1	6.6	99.7	11.5	103.9	4.6	82.1	8.3	88.8	9.0	91.7	9.5	77.2	9.7	84.5	10.2
5	Phorate	87.9	4.5	83.6	8.6	80.8	2.5	86.5	7.9	85.6	11.0	76.3	14.3	90.8	8.8	77.2	8.9	76.5	6.7	96.1	3.7	92.2	0.6	82.9	4.8
6	α-HCH	83.1	16.9	95.6	9.6	89.9	15.6	84.3	11.1	75.2	13.4	88.8	12.0	82.0	7.0	81.8	11.7	81.0	8.9	71.0	8.9	70.5	6.0	82.4	10.4
7	Simazine	85.5	10.7	88.9	6.9	97.5	6.3	94.2	9.5	95.1	1.8	84.2	6.7	99.9	10.6	88.8	10.1	77.0	8.5	81.0	5.6	88.8	9.3	90.6	4.4
8	β-HCH	77.5	8.1	85.5	5.8	87.6	4.9	80.4	10.8	74.8	3.2	77.1	12.7	84.4	9.6	79.2	6.9	77.5	10.1	84.5	12.5	83.6	12.8	82.3	10.1
9	Quintozene	77.4	18.3	91.1	3.2	90.2	3.9	85.7	18.0	95.0	12.8	74.2	11.1	74.7	7.6	86.5	7.1	82.2	6.4	87.6	7.0	71.5	9.7	72.4	10.2
10	γ-HCH	83.5	10.3	86.5	7.2	87.9	9.5	77.6	4.8	73.7	16.3	82.3	8.1	67.2	12.1	84.9	10.7	75.2	10.5	83.0	3.2	85.2	12.0	77.7	10.9
11	Terbufos	83.5	6.5	89.7	7.6	102.2	13.2	100.0	13.0	86.4	11.5	96.8	9.1	87.7	12.0	90.2	12.4	84.6	7.1	81.0	13.5	90.9	10.7	85.6	5.8
12	Diazinon	77.6	4.8	83.1	9.5	87.7	5.9	75.7	8.0	72.4	10.7	79.3	3.2	77.4	10.3	87.9	7.1	90.1	10.6	88.3	3.0	77.2	8.5	87.3	5.8
13	Pyrimethanil	90.0	9.9	80.0	9.9	90.0	9.9	82.4	12.6	92.4	12.6	82.4	12.6	87.6	8.1	91.2	5.4	81.5	7.6	79.3	2.2	79.1	9.1	83.2	10.7
14	δ-HCH	94.5	12.8	83.4	2.4	84.1	5.5	90.9	8.3	85.0	5.4	70.6	13.0	75.8	5.6	91.9	4.9	85.4	7.8	85.0	8.6	72.8	13.8	82.2	3.4
15	Vinclozoline	92.8	10.8	88.3	13.0	87.3	6.6	92.8	10.8	88.0	13.4	98.2	14.9	89.6	14.7	79.1	11.0	81.5	5.8	89.0	3.2	90.8	6.1	91.2	3.6
16	Heptachlor	89.9	11.3	89.5	17.8	95.5	4.4	83.8	15.0	85.2	9.9	76.9	14.8	75.5	6.3	98.6	10.9	88.4	9.9	88.8	9.3	87.2	11.7	91.6	10.0
17	Metalaxyl	92.5	5.9	79.1	4.0	96.6	8.4	91.2	4.7	88.7	4.7	87.4	7.7	85.0	16.4	80.9	5.3	73.7	5.0	75.2	7.6	71.5	5.6	72.9	11.2
18	Chlorpyrifos	86.3	18.0	79.7	13.3	98.7	13.0	68.1	14.5	70.2	3.1	87.7	16.2	81.8	7.3	67.8	7.6	92.2	8.8	73.7	3.2	78.0	10.1	84.3	4.4
19	Aldrin	90.0	11.5	83.4	6.2	87.8	4.2	82.5	11.9	70.0	8.3	75.0	18.5	79.7	10.9	70.1	11.4	84.4	5.8	81.1	14.2	77.4	3.5	71.7	6.4
20	Fenthion	74.6	8.8	89.4	6.2	96.2	6.7	76.1	15.5	83.0	13.5	78.4	9.9	74.7	16.4	81.2	7.4	72.9	9.8	79.9	5.0	81.2	10.9	78.5	0.9
21	Parathion	80.2	8.3	73.5	7.1	93.3	10.5	82.9	6.0	70.6	10.0	82.5	11.4	84.5	12.2	87.1	9.5	80.7	9.4	86.4	11.4	80.4	7.8	77.6	7.0
22	Triadimefon	81.7	10.5	73.0	11.5	86.3	6.3	91.4	6.0	86.7	8.1	80.1	4.4	83.4	10.5	86.9	10.6	89.1	13.5	89.1	5.9	89.5	6.7	85.9	9.0
23	Isofenphos-methyl	79.2	7.5	80.2	12.8	84.2	12.9	89.2	7.5	77.3	17.7	78.9	18.9	74.1	7.3	92.8	8.0	90.8	7.1	81.6	7.2	93.8	7.7	81.8	7.1

24	Pendimethalin	84.0	17.1	84.0	11.9	89.3	3.1	84.0	17.1	71.9	14.2	79.3	3.1	79.9	8.5	84.5	11.3	95.3	9.5	77.8	5.1	79.9	7.1	90.2	6.9
25	Fipronil	71.6	9.1	82.1	5.8	105.4	4.5	74.6	12.8	83.1	5.0	78.6	3.2	76.4	7.5	79.7	9.9	84.1	8.1	73.1	4.1	80.1	11.9	73.7	6.6
26	Heptachlor epoxide	83.0	10.9	86.6	11.0	96.1	5.7	98.2	6.1	77.1	15.7	79.8	15.5	80.2	6.5	75.0	11.0	78.9	10.5	68.3	5.3	83.7	5.7	73.7	6.1
27	Procymidone	92.5	12.0	77.0	10.8	74.9	5.8	73.0	10.9	79.4	6.2	77.3	11.5	80.0	8.3	95.1	11.3	84.1	5.1	86.1	14.6	81.8	10.0	92.7	10.5
28	γ-Chlordane	77.9	8.9	80.0	7.9	90.0	13.7	80.1	7.1	89.4	12.9	74.7	6.6	89.5	7.4	84.4	12.0	73.1	7.9	83.1	5.7	75.0	10.0	71.1	5.2
29	*o,p*'-DDE	81.2	7.9	78.1	11.4	99.5	5.5	64.2	12.3	72.3	3.6	81.9	7.5	84.4	14.6	83.5	12.8	76.2	10.2	82.6	5.2	72.4	5.2	78.2	8.1
30	α-Chlordane	94.1	10.8	79.4	12.2	96.2	6.3	103.3	3.8	83.6	5.8	79.6	9.8	98.9	5.6	85.3	5.2	86.6	7.2	85.2	10.8	87.7	9.6	74.8	5.9
31	Endosulfan	75.3	13.2	86.3	11.8	83.4	12.4	82.6	9.0	78.2	11.3	89.2	18.1	79.6	7.1	73.6	9.6	73.3	7.4	70.6	8.1	73.8	7.9	73.9	4.5
32	*p,p*'-DDE	86.9	18.0	79.7	3.2	93.0	4.6	89.4	2.2	86.4	4.8	87.3	7.7	88.2	4.7	74.5	5.2	93.1	11.4	77.1	8.9	88.1	5.1	80.7	6.0
33	Dieldrin	89.4	12.2	86.4	4.8	97.3	7.7	80.7	10.4	82.3	17.4	90.5	10.5	89.8	6.1	68.3	7.4	91.7	7.8	85.0	10.7	78.3	10.1	78.6	6.7
34	*o,p*'-DDD	89.4	12.2	81.7	4.6	88.1	10.4	91.2	4.9	92.7	7.2	90.0	11.8	86.8	10.2	82.1	8.7	82.2	8.0	73.7	9.9	91.1	4.9	80.7	6.0
35	Flusilazole	82.6	9.0	87.9	5.2	77.3	9.7	79.9	9.0	75.4	3.9	71.2	9.9	92.7	11.1	88.9	9.4	88.8	11.2	81.8	8.3	70.6	7.7	92.1	9.7
36	Endrin	78.8	3.2	88.6	11.7	84.5	8.4	76.6	5.5	78.2	11.9	87.4	9.2	93.6	10.3	71.8	6.7	85.8	10.8	72.9	9.0	77.9	15.4	91.8	5.6
37	*p,p*'-DDD	86.6	5.5	96.0	5.7	90.0	11.8	79.1	9.2	87.0	5.7	84.9	7.3	79.9	6.7	78.4	14.5	80.0	4.1	74.5	9.3	81.3	8.3	81.8	10.0
38	*o,p*'-DDT	92.0	8.5	77.4	10.3	98.8	8.2	70.0	10.3	74.1	10.8	77.0	17.7	78.2	11.8	86.9	13.0	91.3	11.2	77.8	8.4	84.5	7.5	72.4	9.3
39	*p,p*'-DDT	85.7	13.6	82.1	11.3	75.7	7.1	79.1	14.0	70.6	16.1	84.0	5.0	91.9	13.8	74.5	10.1	84.9	3.2	74.9	10.8	75.1	5.0	75.2	9.8
40	Tebuconazole	84.6	8.6	77.4	4.9	92.2	10.9	82.2	9.3	80.0	4.3	70.0	5.0	80.3	6.9	88.0	11.3	82.1	8.1	84.2	5.8	87.2	6.5	90.4	8.8
41	Bifenthrin	82.2	9.3	88.7	13.4	84.0	5.0	91.9	4.9	87.0	15.5	81.2	18.1	90.5	16.2	74.7	11.9	86.8	4.2	75.5	12.0	83.2	13.1	86.6	7.2
42	cis-Permethrin	80.1	6.7	85.6	4.9	90.6	6.0	82.2	4.1	90.8	5.1	91.8	5.4	76.6	9.9	84.8	6.0	82.5	14.1	84.4	8.7	80.5	7.8	83.4	10.9
43	trans-Permethrin	82.3	8.4	84.1	6.5	89.5	9.0	80.1	6.7	89.3	16.8	80.6	6.0	87.0	15.9	82.8	10.4	85.2	4.8	88.6	7.3	83.7	3.9	80.7	6.0
44	Pyridaben	88.8	10.6	79.5	8.8	100.6	7.7	84.8	10.3	85.2	5.5	98.1	9.8	88.0	10.2	76.7	7.4	79.0	3.3	81.1	12.5	76.5	8.1	71.1	5.9
45	Etofenprox	81.0	13.0	88.0	8.7	90.8	11.4	73.8	6.2	98.9	8.0	74.3	11.3	72.2	11.8	71.1	5.0	78.9	7.1	89.5	9.9	78.2	10.5	77.8	10.9
46	Difenoconazole 1	85.7	13.9	97.3	15.5	72.6	3.6	81.2	10.0	89.6	7.4	88.2	11.0	87.0	7.7	87.4	8.4	84.3	8.1	77.1	8.2	84.1	8.0	79.3	9.4
47	Difenoconazole 2	80.0	9.3	84.4	8.4	92.4	4.1	83.8	14.3	80.8	13.4	81.4	10.4	84.9	12.5	80.6	10.2	86.1	6.0	81.9	8.0	81.2	12.2	85.1	5.0

*R% denotes average recovery (%)

Table 3 Comparison of the analytical performances between different methods for multiresidue pesticide analysis in plant-derived food.

Food type	Number of analytes	Extraction	Clean-up	MLOQ ($\mu g\ kg^{-1}$)	Recoveries (%)	References
Apple, orange, honey, leek	47	GLME-d-SPE		0.2 – 10.9	67.2 – 105.4	This study
Cabbage, leek radicchio	45	MSPD		0.4 - 4.0*	89 - 106	(Chatzimitakos et al., 2019)
Apple, tomato, cucumber, cabbage	14	HS-SPME		1.15 – 27.76	73 - 118	(Abdulra'uf & Tan, 2015)
Peach and canned peach	10	QuEChERS		1 - 10	69 - 146	(Costa et al., 2014)
Honey	4	LLE	LTP	28 – 33	84.6 – 100.9	(de Pinho et al., 2010)
Peach, lettuce, wheat grain	25	SLE	Two-step SPE	5 – 10	73 - 117	(Balinova et al., 2007)
15 types of vegetables	8	QuEChERS – DLLME-SFO		0.9 – 4.7	61.6 – 119.4	(Mao et al., 2020)

* Concentrations were displayed in ng mL^{-1}. Additional information: MSPD: matrix solid-phase dispersion; HS-SPME: headspace solid phase microextraction; LLE: liquid-liquid extraction; LTP: low temperature purification; SLE: solid-liquid extraction; DLLME-SFO: dispersive liquid–liquid microextraction based on solidification of floating organic droplet.

3.4 Application in real samples

Under optimized condition, the one-step GLME-d-SPE method was employed to analyze 47 multi-class pesticides in real plant-derived food samples. Based on the results (Table S7) obtained by using matrix-match calibration curves (Table S8), 2-phenylphenol was detected at the concentration of 0.004 mg kg^{-1} in apple and 0.006 mg kg^{-1} in orange, while quintozene was identified in honey and leek at 0.008 mg kg^{-1} and 0.010 mg kg^{-1}, respectively. Bifenthrin and permethrin were also detected in apple at the concentrations of 0.001 and 0.005 mg kg^{-1}, respectively. Fipronil, chlordane and p-p'-DDE were detected in apple and orange, but the concentrations were below MLOQ, hence they were not quantified. In spite of the fact that several pesticides have been detected in chosen foods, the concentrations were all below permitted MRLs, indicating the low risk that may impose on human health. Nevertheless, the detected pesticides in selected food commodities in this study were previously identified at high concentration (2.16 mg kg^{-1} of 2-phenylphenol was found in orange (Blasco et al., 2002); while *trans*-permethrin were detected at 1.35 and 0.21 mg kg^{-1} in lettuce and apple, respectively) (Li et al., 2016), signifying the significance of developing rapid detection system for continual surveillance of food quality in the market.

4. Conclusions

The extraction and purification processes by GLME, in addition to the integration of d-SPE clean-up were simultaneously completed within a single sample pretreatment procedure to analyze multi-class pesticide residues in plant-derived foods. This one-step GLME-d-SPE method has been validated for its notable advantages of speedy, environmentally-friendly and time-saving features. The one-step pretreatment feature of this method offers a promising prospect for the rapid determination of pesticide residues in varying food matrices. In view of the great sensitivity of this technique that meets the detection requirements of allowable MRLs in varied countries, it is applicable for routine and on-site monitoring of food quality, therefore help to safeguard human health.

Conflict of interest

There are no conflicts to declare.

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One-step integrated sample pretreatment technique by Gas-Liquid Microextraction (GLME) to determine multi-class pesticide residues in plant-derived foods

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Abstract

Gas-liquid microextraction technique (GLME) has been integrated with dispersive solid phase extraction to establish a one-step sample pretreatment approach for rapid analysis of multi-class pesticides in different plant-derived foods. A 50 µL of organic solvent plus 40 mg of PSA were required throughout the 5-minute pretreatment procedure. Good trueness (recoveries of 67.2 – 105.4%) and precision (RSD ≤18.9%) were demonstrated by the one-step GLME method, with MLOQs ranged from 0.001-0.011 mg kg^{-1}. As high as 93.6% pesticides experienced low matrix effect through this method, and the overall matrix effects (ME%) were generally better or comparable to QuEChERS. This method successfully quantified 2-phenylphenol, quintozene, bifenthrin and permethrin in the range of 0.001 – 0.008 mg kg^{-1} in real food samples. The multiresidue analysis feature of GLME has been validated, which displays further potential for on-site determination of organic pollutants in order to safeguard food safety and human health.

Keywords: Multi-residue methods (MRMs); Fruits; Vegetables; Honey; Insecticides; Herbicides

1. Introduction

Different categories of pesticides comprising insecticides, herbicides, acaricides, fungicides, antimicrobials, etc. have been extensively applied in agriculture worldwide to increase crop production and pest control. Since the publication of *Silent Spring* by Rachel Carson in the 1960s, an increasing attention has been drawn on the environmental concerns associated to the applications of pesticides, and it initiated tighter regulation of pesticides in the United States and many other countries (Dunn, 2012). Numerous studies in past decades proved the likeliness of pesticides to cause cancer (Alavanja et al., 2004), immunotoxicity (Corsini et al., 2013), neurological dysfunction (Gangemi et al., 2016), endocrine disruption (Rattan et al., 2017), decreased fertility (Hu et al., 2018) and behavioral disorders in children (Viel et al., 2017). Since then, international food safety and quality standard such as Codex Alimentarius and different national standards have set the maximum residue limit (MRL) of multi-class pesticides in foods to minimize damage on the environment and consumer health.

Fresh produce, especially fruits and vegetables, provides essential nutrition such as vitamins and minerals for meeting the daily intake requirement recommended for human wellbeing. Unfortunately, approximately one-third of the global food production which account for about 1.3 billion tons per annual ended up lost or wasted, and unsafe food with unsatisfactory quality is one of the factors that leads to food loss (Gustavsson et al., 2011). Taking into the account the considerable short shelf life of vegetables and fruits, a rapid analytical technique to assure pesticide-free fresh produce in the market is imperative. Not only that a speedy inspection system is crucial for improving food security, it also helps to reduce food waste and to preserve human health. Nonetheless, the complex matrix compositions of vegetables and fruits pose a great challenge that hinder the realization of rapid analysis, as interferences like sugars, water, pigments (including chlorophyll and other natural dyes), fatty acids, non-volatile material and compounds containing acidic or basic groups are frequently co-extracted during the sample pretreatment process (Rutkowska et al., 2019), hence jeopardizing the accuracy of analytical results. Therefore, a highly efficient extraction method coupled with powerful clean-up approach is the key to achieve rapid qualitative and quantitative analysis of plant-derived foods with excellent precision.

At present, there are a substantial number of analytical methods being developed for determining pesticide residues in various food matrices. In particular, the sample pretreatment technologies known as multiresidue methods (MRMs) have been established lately for simultaneously analyzing varied classes of pesticide residues with distinctive physicochemical properties. In contrast to the conventional pretreatment techniques such as liquid-liquid extraction (LLE), solid-phase extraction (SPE) and ultrasonic assisted extraction (UAE), miniaturized analytical methods including solid-phase microextraction (SPME), liquid-phase microextraction (LPME) and stir bar sorptive extraction (SBSE) are the upcoming development trend to realize the objective of green analytical chemistry. Although these modern MRMs are fast, accurate and sensitive, most of them are labor-intensive, time-consuming and unsuitable for automation. A technique termed as quick, easy, cheap, effective, rugged and safe (QuEChERS) method have become the preferred MRMs for pesticide analysis in recent years, and it has been appropriately modified to meet the challenges of multiresidue analysis. However, QuEChERS technique that usually combined with d-SPE clean-up still exhibits some limitations, such as high matrix effects and the necessity for modification to perform better in analyzing certain analytes and matrices (Kittlaus et al., 2011; Bruzzoniti et al., 2014). Most importantly, the variance of physicochemical properties for co-extracts in different foods covering a wide range of polarity and boiling points require a combination of clean-up techniques to effectively eliminate these interferences prior to quantitative analysis.

The gas-liquid microextraction (GLME) technique (previously known as gas-purge microsyringe extraction, GP-MSE) was developed on the basis of headspace liquid phase microextraction (Yang et al., 2009). GLME was previously applied in the analyses of polycyclic aromatic hydrocarbons (PAHs), alkyl phenols, light hydrocarbons, phthalate esters and other organic pollutants in plant leaves, soil, sediments, crude oil, and foodstuffs, respectively (Yang et al., 2011; Wang et al., 2013; Zhao et al., 2015; He et al., 2015; Gao et al., 2016; Jin et al., 2020; Zhao et al., 2020; Kaw et al., 2021). The principle of the GLME technology is based on the utilization of distinctive boiling points between analytes and interferences to achieve effective separation. Hence, majority of the volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) including organic pollutants like pesticides that are amenable for GC-MS analysis, are well suited for GLME treatment. The main strength of the GLME method which integrates extraction and clean-up procedures into a single step demonstrates great potential for a speedy pretreatment process. Commonly, the GLME pretreatment can be completed within several minutes prior to GC-MS analysis.

In the present study, GLME plays a significant role as an integrated extraction and clean-up approach to simultaneously extract multi-class pesticides from different plant-derived food commodities, and at the same time, the high extraction temperature of GLME aims to remove high-boiling-point interferences like carbohydrates and pigments. Throughout the extraction process, dispersive solid phase extraction (d-SPE) sorbents were also added in the receiving phase of the GLME system to adsorb organic acids, sugars and lipids through different clean-up mechanisms including ionic interaction. Two most determining GLME parameters (extraction temperature and extraction time) were sequentially optimized, and the optimal quantity of d-SPE sorbents were methodically evaluated. Eventually, a single-step sample pretreatment technique that involves effective extraction and clean-up procedures can be completed within few minutes, and its analytical performance was validated for the determination of pesticide residues in foods of plant origin. Fast analysis of pesticide residues in commercial products that proposed by this study is especially important in the food safety, food import and export and food inspection industries to safeguard human health.

2. Materials and Methods

2.1 Chemicals and reagents

HPLC grade dichloromethane, acetone, hexane, ethyl acetate and acetonitrile were purchased from Thermo Fisher Scientific (San José, CA, USA). Different sorbents including anhydrous sodium sulfate (Na_2SO_4 with $\geq$ 99% purity), graphitized carbon black (GCB, 40-60 μm), primary secondary amine (PSA, 40-60 μm) and bonded octadecyl silica (C18, 40-60 μm) were obtained from Shanghai BioSun Sci & Tech Co., Ltd. Details of the pesticide reference standards and the preparation procedures can be found in Supplementary Materials and Methods section. Detailed information regarding the toxicity, chemical and physical properties of the selected pesticides in this study can be referred to Table S1 and S2 in the supporting material.

2.2 Sample preparation

The selected plant-derived foods in this study consisted of apple (pome fruit with high water content), leek (allium with high water content that is widely recognized as a type of vegetable with highly complex matrix), orange (citrus fruit with high acid content and high water content), and honey (high sugar and low water content) were chosen based on their representative properties according to the SANTE/12682/2019 guideline. These four kinds of food were purchased from a local supermarket in Yanji city, Northeastern China. Each type of samples (approximately 200 g) was homogenized using a Fluko FA25 homogeniser. The homogenized sample was placed in a prewashed amber bottle, then sealed and stored at -18°C until further analysis.

2.3 One-step GLME pretreatment procedures

A schematic diagram and a short video indicating the arrangement and operations of the GLME device are shown in Fig. S1 and supplementary video, and the detailed description regarding the procedures of GLME extraction has been published elsewhere (Yang et al., 2011). In brief, 0.3 g (± 0.01 g) of sample at room temperature was precisely weighed and put into the sample tube (two-way glass tube with an internal diameter of 4 mm and a length of 6 cm). Surrogate standard was added onto the sample (target analytes were added in spiked samples) for evaluation of laboratory quality assurance. An optimized amount of d-SPE sorbents and 50 µL of hexane were added to a 250 µL GC insert as the receiving phase. The parameters of the GLME extraction were set as follows: extraction temperature: 120°C for 1 min, 300 °C for 3min; gas flow rate (N_2, 99.999% purity): 2 mL min^{-1}; condensation temperature: 0 °C and extraction time: 3 min. When the extraction was completed, the extract was eluted with 80 µL dichloromethane, acetone and ethyl acetate (v:v:v = 1:1:1), then concentrated by a gentle stream of nitrogen to adjust the extract volume to 80 µL. The post-extract eluate was spiked with 20 µL internal standard and an adequate amount of anhydrous sodium sulphate was added to completely remove the water content in the extract. The final extract was withdrawn to a 100 µL GC insert for GC-MS analysis.

2.4 GC-MS analysis

The analysis of pesticide residues was performed on a GC2010 gas chromatograph (Shimadzu, Kyoto, Japan) fitted with a DB-5 fused-silica capillary column (30 m × 0.25 mm; 0.25 µm) and coupled to a QPMS 2010 quadrupole mass spectrometer (Shimadzu, Kyoto, Japan). Helium with a purity of 99.999% was used as the carrier gas and was held at a flow rate of 1.0 mL min^{-1}. A sample volume of 2 µL was injected in splitless mode with an injection temperature of 280 °C. The GC-MS interface temperature was held at 280 °C and the ion source temperature was set at 200 °C. The electron energy for ionization was set to 70 eV. The initial oven temperature was set as 40 °C and then ramped at a rate of 50 °C min^{-1} to 150 °C, followed by 5 °C min^{-1} ramp to 250 °C then a final ramp of 10 °C min^{-1} to 300 °C and maintained for 3 min. The solvent cut time was 3.0 min. Selected ion monitoring (SIM) mode with a sampling rate of 1.2 s was used.

2.5 Quality assurance/Quality control

All analysis processes were performed using quality assurance and control measures. In order to eliminate the risk of contamination, all glasswares, sorbents and glass wool were baked at 400 °C for 12 h. After cooling down to room temperature, glass wool and Na_2SO_4 were preserved in a vacuum desiccator until analysis. A minimum of triplicate experiments were conducted for each type of samples. Instrumental and procedural blanks for every set of samples were systematically evaluated throughout the experiments. Quantification was carried out by the internal standard method. Internal standard (triphenyl phosphate (TPP), 20 ng) was used for the correction of injection amount and performance assurance of GC-MS. Quality control of the complete procedure and quantification was performed using 20 ng each of tetrachloro-m-xylene (TCMX) and deuterated tebuconazole (TEB-d_9) as surrogate standards. Extraction recoveries were calculated based on the formula $R_A = Q_A(\text{yield})/Q_A(\text{orig})$, where $Q_A(\text{yield})$ and $Q_A(\text{orig})$ represent the recovered and original quantities of analyte A.

2.6 Validation of analytical performance

The analytical performance of the proposed one-step sample pretreatment method was validated by assessing the trueness, reproducibility, linearity and method limit of detection (MLOD) and method limit of quantification (MLOQ). The concentrations of all 47 pesticides ranged from 5 to 1000 ng mL^{-1} in spiked samples were used for linearity evaluation. The trueness of the one-step pretreatment method was verified by evaluating the average recoveries of multi-class pesticides in spiked food samples at different concentration levels, and each spiked concentration was repeated in five replicates. The precision of this integrated sample pretreatment technique was determined through examining the relative standard deviations (RSDs) of recoveries. The MLOD and MLOQ of the developed method was confirmed by the sample-spiked method and the stepwise dilution method, which were determined based on a signal-to-noise ratio (S/N) of 3 and 10, respectively (Dong et al., 2020). The recoveries of surrogate standards that ranged from 66.9% to 93.8% validated the trueness of this analytical method.

2.7 Data analysis

Spearman's rank correlation analysis was conducted to investigate the relationships between matrix effect and the physical and chemical properties of target compounds. The significant analysis was performed using SPSS Statistics 17.0 for Windows (Chicago, IL, USA) with a significance of $p < 0.01$ and $p < 0.05$.

3. Results and Discussions

3.1 Optimization of the one-step pretreatment parameters

3.1.1 GLME extraction parameters

As indicated in previous studies, extraction temperature and extraction time are the most determining parameters that decide the analytical performance of the GLME technique. In order to examine the influence of these important parameters of GLME in extracting multi-class pesticides, temperatures in the range of 260 to 330°C and the extraction times of 1 to 5 min were systematically evaluated. The extraction time was set to 5 min throughout the process of optimizing extraction temperature, while extraction temperature of 300°C remained constant in the experiments for optimizing extraction time. The optimization results were denoted in the form of heat map in Fig. 1. An obvious and easily distinguishable pattern that represents higher recovery values between 80 and 120% for all tested pesticides can be observed when the extraction time and extraction temperature were over 3 min and 300 °C, respectively. Based on this indication, these optimized extraction parameters were employed in subsequent experimentations.

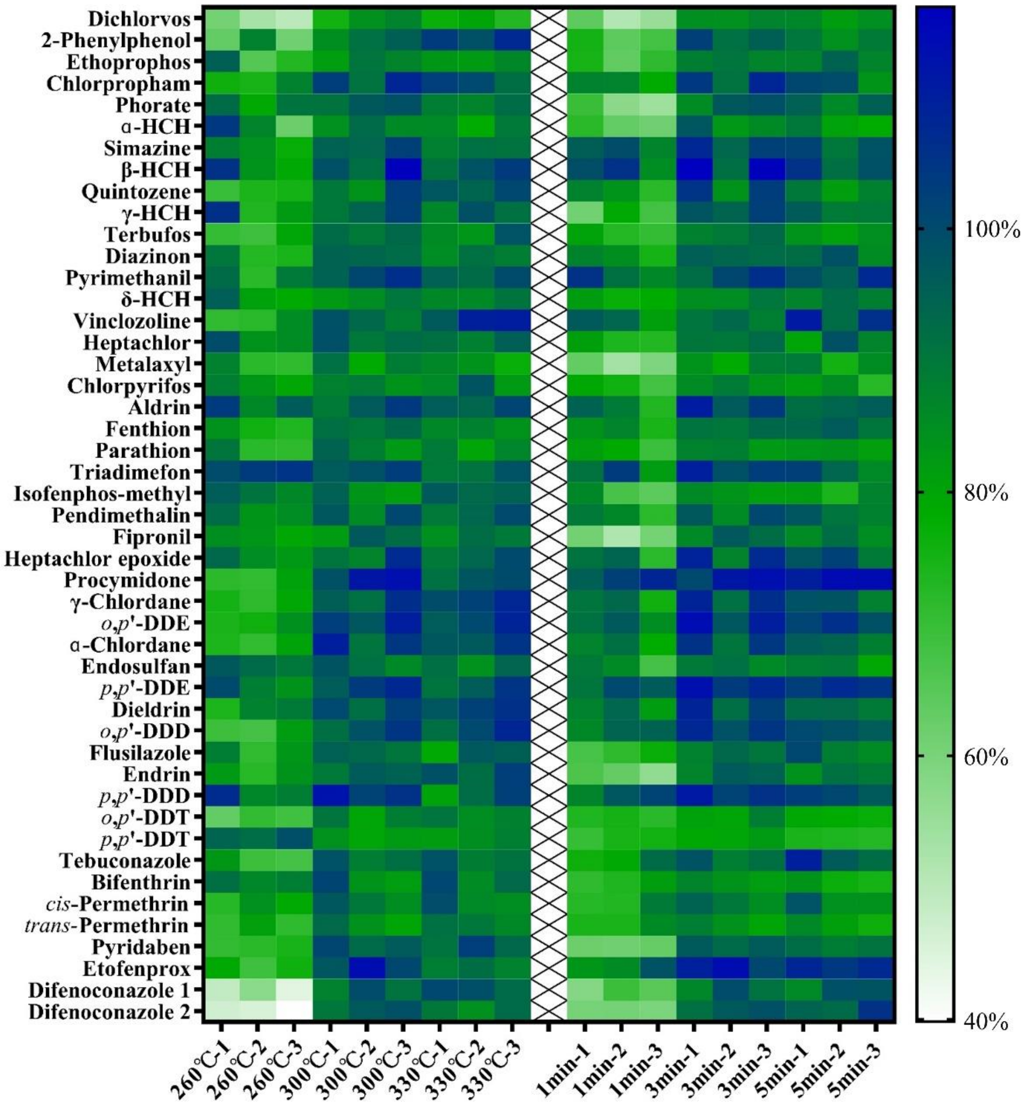

Fig. 1 Recoveries of 47 pesticides by using GLME under different extraction parameters (time and temperature).

3.1.2 Amount of clean-up sorbents

Due to boiling point difference between analytes and interfering substances, co-extracts with high boiling points such as chlorophyll with over 1000°C, can be priorly eliminated during GLME extraction. However, other low boiling point substances such as fatty acids, phenols and sugars were unavoidably co-extracted and remained in the post-GLME extract. Such co-extractants may bring about matrix effect that significantly interferes with the GC-MS analysis of target pesticides, thus resulting in inaccurate quantification. To overcome this problem, an additional clean-up step is indispensable. In this case, d-SPE technique is an ideal method as it can be flawlessly integrated with GLME. PSA, C18 and GCB were chosen as the sorbents for purifying sample extract as their clean-up effectiveness has been widely justified, especially for plant-derived food samples. Different amounts of each sorbents (10 - 50 mg with 10 mg interval for PSA, and 10 - 20 mg with 5 mg interval for GCB and C18) were sequentially evaluated. Results in Table S3 showed that PSA achieved excellent clean-up effect without imposing significant impact on the recoveries of 47 target pesticides (84.6 – 103.6%). Based on the weak anion exchange mechanism, PSA proved its effectiveness for adsorptive removal of organic acids, fatty acids and sugars that are commonly found in fruits and vegetables (VerÃ, 2017; Ferrentino et al., 2020; Klein et al., 2021), as shown in Fig. 2(A). This result is consistent with previous study (Oellig & Schmid, 2019). C18 and GCB, on the other hand, showed minimal clean-up effect (Fig. S2). The interferences in post-PSA clean-up extract were identified by using The National Institute of Standards and Technology (NIST) mass spectral library (please refer to Table S4 for detailed information), suggesting that most compounds were lipophilic substances with Log P values of > 5, and they were highly soluble in organic solvent. In comparison to PSA that forms hydrogen bond with fatty acids and sugars to achieve adsorption via chemical bonding, the adsorption mechanism for GCB and C18 is based on π-π interaction and hydrophobic effect to realize physical adsorption. In this study, the interaction between lipophilic interferences with DCM exhibited stronger effect than with the solid phases (sorbents), hence they were inclined to remain in the organic solvent instead of being adsorbed by GCB or C18 (Ly et al., 2020). GCB also substantially reduced the recoveries of several target compounds in a descending pattern that was inversely proportionate to the amount of GCB being added. For example, the recoveries of quintozene gradually decreased from 78.0% to 60.5% and 48.6% when the addition of GCB increased from 10 mg, 15 mg to 20 mg; likewise, pyrimethanil demonstrated a similar trend (a reduction of recoveries from 88.3% to 59.5%). This result is in line with published literatures, as GCB may adsorb low-polar pesticides with planar structure including quintozene and pyrimethanil (Pareja et al., 2011). Therefore, 40 mg of PSA was selected as the optimal d-SPE sorbent to be integrated with GLME technique as a one-step sample pretreatment approach. Clear peaks of multi-class pesticides can be effectively identified in chromatogram of GLME-d-SPE-treated spiked leek sample (Fig. 2(B)) and other plant-derived foods (Fig. S3), which was similar to the chromatogram of reference standard, suggesting the noteworthy clean-up performance of this method.

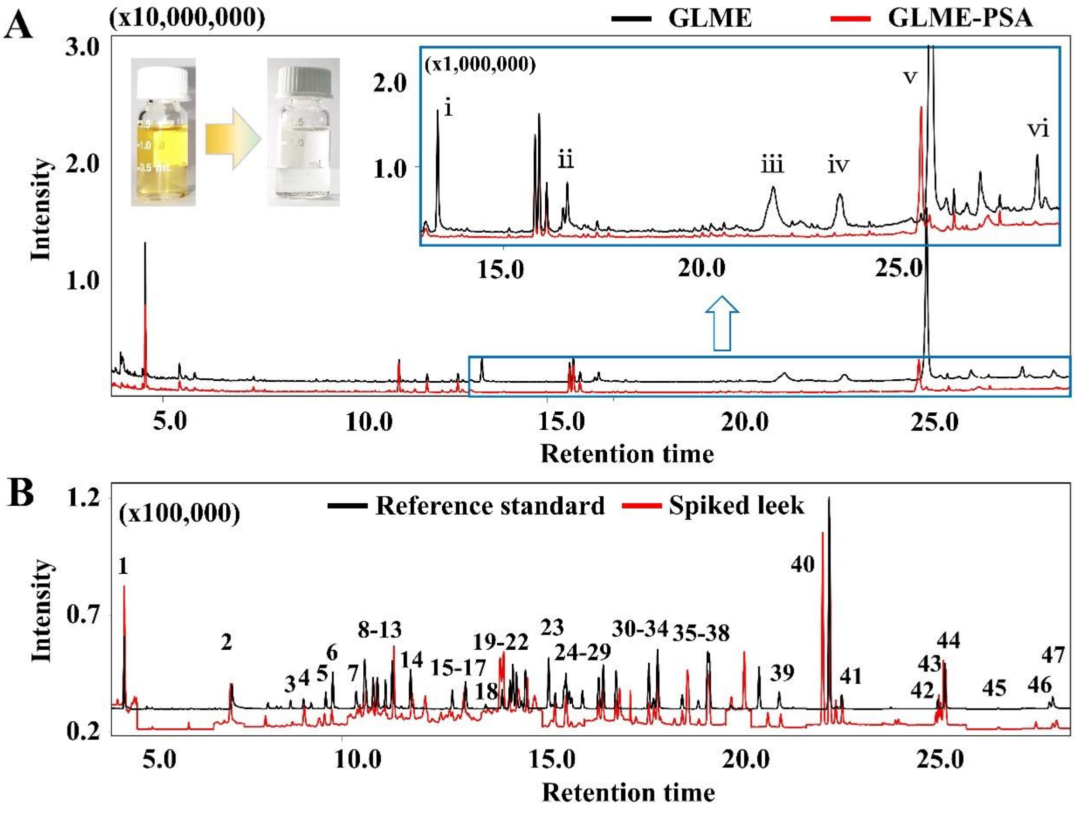

Fig. 2 Scan chromatograms that compare the clean-up performances by using GLME only and the combination of GLME with d-SPE sorbent (PSA) in leek (A), and the SIM chromatograms showing peaks of 47 pesticides in reference standard and spiked leek extract (B) (peaks were numbered according to the pesticides listed in Table 2). Additional information: (i): n-Hexadecanoic acid; (ii): Linoleic acid; (iii): 24-epicampesterol; (iv): Stigmasterol; (v): γ-Sitosterol; (vi): Cholestenone.

3.2 Matrix effect and its relationship with chemical properties of interferences

In order to establish a multiresidue method that is able to simultaneously analyze multi-class pesticides across different plant-derived food matrices, the clean-up performance of the one-step integrated GLME-d-SPE technique for accurate quantification of pesticide residues was examined by assessing the matrix effect (ME%) in post-treatment extracts. It is one of the critical criteria in chromatographic analysis as it significantly affects the accuracy of quantitative analysis, particularly in detection of trace-level pollutants in complex food or biological samples. In this study, ME% was calculated according to Eq. 1 to evaluate the influence of matrices on the analytical effectiveness.

$$\mathrm{ME}\ (\%) = 100 \times \left(\frac{S_m}{S_s} - 1\right) \qquad (1)$$

where S_m and S_s represent the slopes of calibration curve in sample matrix and solvent, respectively. In general, ME% within ±20% was categorized as weak matrix effect; otherwise, other values of ME% were considered as medium or high matrix effects. The calculated ME% of the present study was listed in Table 1, and the depictions of the overall ME% for all pesticides in each plant-derived food can be referred to Fig. S4 and Fig. S5. As high as 93.6% (44) detected pesticides were classified as weak matrix effect in apple, followed by orange with 85.1% (40) pesticides experienced minimal matrix interference during chromatographic analysis. The matrix effects for honey and leek samples were greater as these matrices are known to be more complex, in which leek contains various sulfur-containing compounds and the sugar level in honey is high (Xu et al., 2017; Cortese et al., 2020). Nonetheless, the pesticides with weak and medium matrix effects altogether accounted for approximately 81.0% (38) and 63.8% (30) in honey and leek, respectively.

There were significant correlations between the numbers of hydrogen-bond donors of target molecules and the ME% in apple, orange and leek (0.455, $p < 0.01$; 0.458, $p < 0.01$; 0.368, $p < 0.05$), suggesting that ME% in these matrices was closely associated to the formation of hydrogen bond between analytes and coextracts with greater electronegative functional groups such as N, O or Cl. As for honey sample, the ME% of 47 pesticides and the numbers of hydrogen bond donor or acceptor showed insignificant correlation. Instead, the ME% in honey was significantly correlated to polarizability and Log P values (0.458, $p < 0.01$; -0.450, $p < 0.01$), which was likely due to the abundance of coextracts that derived from alkane- or alkene groups in honey extract. This result indicated that the ME% in honey was influenced by the electrostatic interaction between pesticide molecules and the alkane- or alkene-group interferences. As elaborated in previous study (Gomez-Ramos et al., 2016), the chemical compositions of leek are extremely complex, thus there were multiple interactions between coextracts and pesticide molecules which eventually caused much stronger ME% in leek (referred to Table S5 for detailed information). In light of the quick and effective sample pretreatment performance of the one-step GLME-d-SPE method without jeopardizing the accurate quantification of multi-class pesticides, the slightly higher ME% in leek was compromised.

A summary of ME% for the representative orange (relatively simpler matrix) and leek samples (comparatively more complex matrix) was demonstrated in Fig. 3, which also showed a comparison of ME% in these matrices after treated by GLME-d-SPE and QuEChERS. It can be observed that identical if not slightly better clean-up effects were achieved by GLME-d-SPE than QuEChERS. Fig. S6 similarly justified the visibly better purification performance of the proposed one-step pretreatment technology in treated food samples. Chromatograms in Fig. 3(B) and (C) indicated the difference in clean-up effects between these two methods, which highlighted the robust purification performance of GLME-d-SPE regardless of different food types.

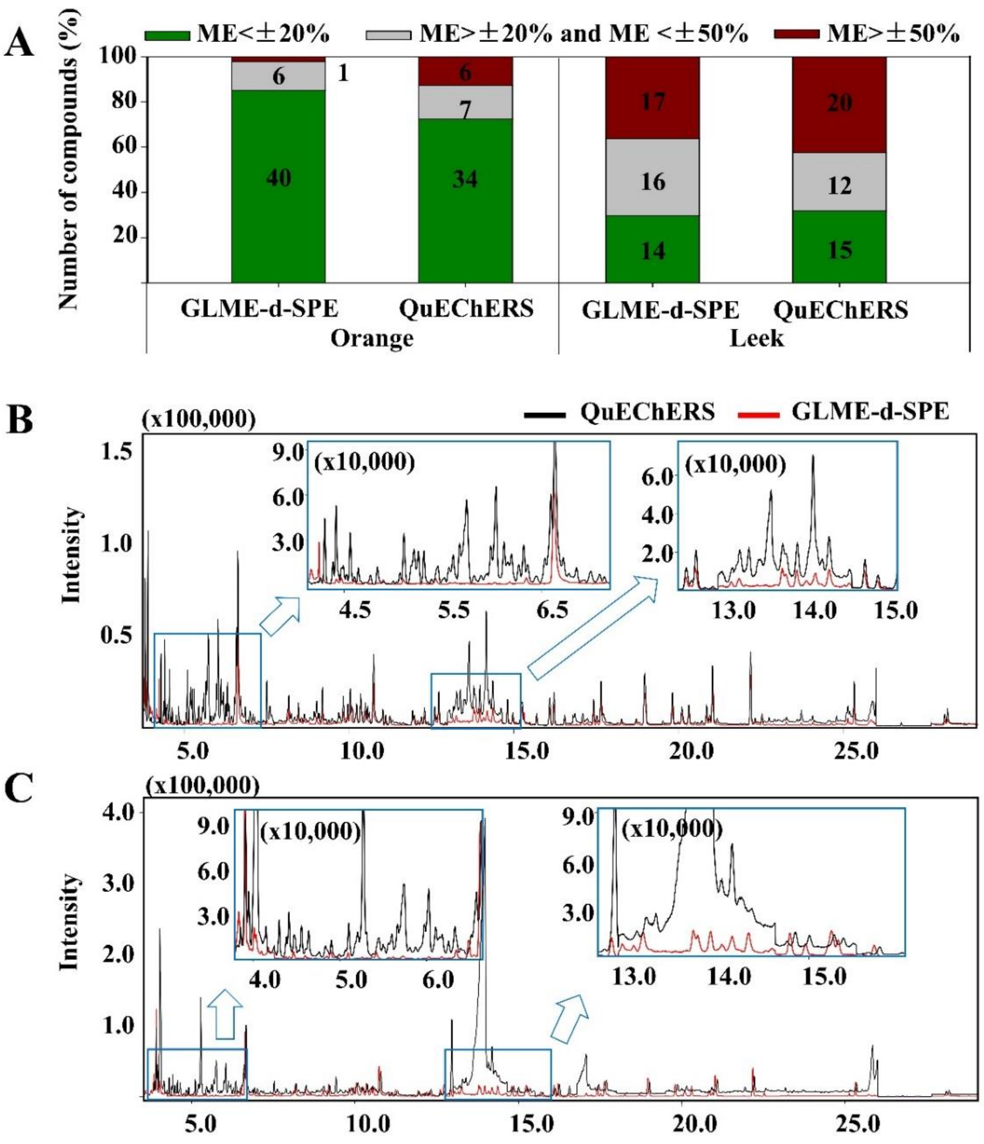

Fig. 3 Comparison of matrix effects (ME%) for orange and leek samples by using GLME-d-SPE and QuEChERS methods (A), and the chromatograms that demonstrated the post-treatment effects in orange (B) and leek (C).

3.3 Performance validation of the one-step GLME-d-SPE method

The analytical performance of the single step GLME-d-SPE pretreatment method under optimized condition was systematically validated through assessing the method sensitivity, linearity, trueness and precision. As shown in Table 1, the method limit of quantification (MLOQ) of this technique for analyzing pesticides in four representative food matrices generally ranged from 0.001 to 0.01 mg kg^{-1}, except for β-HCH, γ-chlordane and triadimefon with MLOQ of 0.011 mg kg^{-1} in honey. This range of MLOQs fulfils the detection requirements of MRLs set by the EU and China for multiresidue pesticide analysis. The calibration curves of all 47 pesticides showed good linearity, with determination coefficients (R^2) higher than 0.999 (Table S6). The trueness of the one-step pretreatment method was verified by evaluating the average recoveries of multi-class pesticides in spiked food samples at different concentration levels, and each spiked concentration was repeated in five replicates. The precision of this integrated sample pretreatment technique was determined through examining the relative standard deviations (RSDs) of recoveries. Both the recoveries at different spiked levels and their associated RSDs are recorded in Table 2. Results revealed the recoveries and RSDs (in parentheses) of 71.6-105.4% (2.4-18.3%), 64.2-99.7% (2.2-18.9%), 67.2-103.9% (3.2-16.4%) and 68.3-96.1% (0.6-15.4%) in apple, orange, honey and leek, respectively, suggesting the up to par analytical performance of the GLME-d-SPE method. A comparison between the proposed one-step integrated sample pretreatment method with other techniques was shown in Table 3, which suggested the advantageous of this newly developed approach.

Table 1 Method limit of quantification (MLOQ) and matrix effect (ME%) for 47 multi-class pesticides in the representative plant-derived foods by using the one-step GLME-d-SPE method, and the relevant maximum residue levels (MRLs) as reference.

			MLOQ (mg kg^{-1})				MRLs (EU/China)** mg kg^{-1}	ME%			
	Pesticide	Family *	Apple	Orange	Honey	Leek	Apple/Orange/Honey/Leek	Apple	Orange	Honey	Leek
1	Dichlorvos	OP	0.001	0.001	0.007	0.001	0.01/0.01/-/0.01	1	8	80	132
2	2-Phenylphenol	UN	0.001	0.001	0.002	0.001	0.01/10.0/0.05-0.01	18	29	103	120
3	Ethoprophos	OP	0.004	0.004	0.005	0.004	0.02/0.02/-/0.02	-7	-1	26	53
4	Chlorpropham	GI	0.004	0.004	0.004	0.004	0.01/0.01/0.05/0.01	6	12	45	68
5	Phorate	OP	0.001	0.001	0.007	0.001	0.01/0.01/0.01/0.01	-5	8	-65	56
6	Simazine	CT	0.005	0.005	0.007	0.005	0.01/0.01/0.01/0.01	16	23	-5	88
7	α-HCH	OC	0.002	0.001	0.002	0.002	0.01/0.01/0.01/0.01***	-16	-1	20	59
8	β-HCH	OC	0.004	0.004	0.011	0.004		-10	-4	6	38
9	γ-HCH	OC	0.003	0.003	0.007	0.005		-16	-1	10	56
10	δ-HCH	OC	0.003	0.002	0.003	0.004		-15	-5	-2	40
11	Quintozene	AF	0.009	0.009	0.009	0.009	0.02/0.02/0.01/0.02	-1	25	80	107
12	Terbufos	OP	0.001	0.001	0.005	0.001	0.01/0.01/-/0.01	-10	3	-75	52
13	Diazinon	OP	0.003	0.003	0.003	0.003	0.01/0.01/0.01/0.01	5	3	9	27
14	Pyrimethanil	PF	0.001	0.001	0.002	0.001	15.0/8.0/0.05/4.0	16	26	19	96
15	Vinclozoline	DC	0.003	0.003	0.003	0.003	0.01/0.01/0.05/0.01	3	1	13	26
16	Heptachlor	OC	0.002	0.002	0.002	0.004	0.01/0.01/0.01/0.01***	-13	2	30	68
17	Heptachlor epoxide	OC	0.002	0.002	0.007	0.002		-19	-12	-4	17
18	Metalaxyl	AN	0.008	0.004	0.008	0.005	1.0/0.7/0.05/0.03	-11	-8	-6	21
19	Chlorpyrifos	OP	0.003	0.003	0.003	0.003	0.01/1.5/0.05/0.01	1	3	15	36
20	Aldrin	OC	0.003	0.004	0.005	0.004	0.01/0.01/0.01/0.01	-15	0	20	51
21	Fenthion	OP	0.001	0.001	0.007	0.001	0.01/0.01/0.01/0.01	-2	3	-81	32
22	Parathion	OP	0.009	0.009	0.009	0.009	0.01/0.01/-/0.01	36	59	143	120
23	Triadimefon	CF	0.006	0.006	0.011	0.006	0.01/0.01/0.05/0.01	-10	-7	-6	30
24	Isofenphos-methyl	OP	0.003	0.003	0.003	0.006	0.01/0.01/-/0.01	-14	-6	-13	28
25	Pendimethalin	DA	0.003	0.003	0.003	0.003	0.05/0.05/0.05/0.05	28	41	98	103
26	Fipronil	PP	0.002	0.002	0.005	0.002	0.005/0.005/0.005/0.005	1	4	13	20
27	Procymidone	DC	0.004	0.004	0.004	0.004	0.01/0.01/0.05/0.01	-2	-3	3	17
28	γ-Chlordane	OC	0.002	0.002	0.011	0.002	0.01/0.01/0.01/0.01***	-17	-7	6	27
29	α-Chlordane	OC	0.002	0.002	0.002	0.002		-15	-10	4	16
30	*o*,*p*'-DDE	OC	0.001	0.001	0.005	0.001	0.05/0.05/0.05/0.05***	-12	-5	8	27
31	*p*,*p*'-DDE	OC	0.001	0.001	0.001	0.001		-5	-1	8	12
32	*o*,*p*'-DDD	OC	0.001	0.001	0.001	0.001		-14	-7	1	9
33	*p*,*p*'-DDD	OC	0.001	0.001	0.001	0.002		-8	-1	12	29
34	*o*,*p*'-DDT	OC	0.001	0.001	0.001	0.002		-5	0	13	21
35	*p*,*p*'-DDT	OC	0.001	0.001	0.001	0.002		6	12	28	53
36	Endosulfan	OC	0.006	0.005	0.009	0.010	0.05/0.05/0.01/0.05	-17	-9	0	26
37	Dieldrin	OC	0.008	0.007	0.009	0.010	0.01/0.01/0.01/0.01***	-17	-10	5	22

38	Endrin	OC	0.004	0.004	0.005	0.008		-16	-4	7	37
39	Flusilazole	CF	0.010	0.010	0.010	0.010	0.01/0.01/0.05/0.01	-6	-15	-16	-7
40	Tebuconazole	CF	0.003	0.003	0.003	0.003	0.3/0.9/0.05/0.6	8	11	9	25
41	Bifenthrin	PY	0.001	0.001	0.001	0.002	0.01/0.05/-/0.05	-16	-18	-8	-1
42	cis-Permethrin	PY	0.004	0.005	0.006	0.009	0.05/0.05/-/0.05***	-13	-18	-4	-6
43	trans-Permethrin	PY	0.001	0.001	0.001	0.003		-9	-18	-5	-4
44	Pyridaben	UN	0.004	0.004	0.005	0.004	0.9/0.3/0.05/0.01	6	-22	9	-34
45	Etofenprox	PY	0.003	0.003	0.003	0.003	0.6/1.5/0.05/0.01	-3	-10	20	-50
46	Difenoconazole 1	CF	0.007	0.007	0.007	0.007	0.5/0.5/0.05/0.6***	33	13	55	30
47	Difenoconazole 2	CF	0.004	0.004	0.004	0.004		-7	-2	24	4

* OC: Organochlorine insecticide; OP: Organophosphate insecticide; PY: Pyrethoid insecticide; GI: Growth inhibitor; CT: Chlorotriazine herbicide; AF: Aromatic fungicide; PF: Pyrimidine fungicide; DC: Dicarboximide fungicide; AN: Anilide fungicide; CF: Conazole fungicide; DA: Dinitroaniline herbicide; PP: Phenylpyrazole acaricide; UN: Unclassified.

** The listed MRLs in each food type were displayed according to the lower MRL values set by EU and China.

*** MRLs refer to the sum of isomers.

Table 2 Trueness (mean recovery) and precision (relative standard deviation, RSD) of the one-step GLME-d-SPE method to analyze 47 pesticides spiked at three concentrations in different plant-derived foods.

		Apple						Orange						Honey						Leek					
		Spiked level (mg kg^{-1})																							
		20		50		200		20		50		200		20		50		200		20		50		200	
		R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)	R% *	RSD (%)
1	Dichlorvos	79.9	6.0	89.5	6.5	75.2	5.7	73.5	9.2	82.9	4.8	80.5	13.2	90.0	12.6	74.3	12.9	71.3	4.4	75.4	6.4	70.4	7.2	75.3	6.5
2	2-Phenylphenol	85.0	11.2	91.8	8.9	93.4	2.4	79.9	6.0	81.2	3.4	77.0	8.3	86.4	5.4	86.9	14.4	87.8	12.5	89.4	5.8	83.0	13.9	79.3	6.0
3	Ethoprophos	80.9	9.6	87.5	5.2	88.6	9.6	95.2	5.7	86.6	4.4	80.7	14.0	80.0	10.6	74.4	13.8	78.7	9.7	82.8	4.9	89.8	14.6	73.1	5.1
4	Chlorpropham	91.4	9.0	88.4	8.9	89.9	11.7	87.5	3.8	87.1	6.6	99.7	11.5	103.9	4.6	82.1	8.3	88.8	9.0	91.7	9.5	77.2	9.7	84.5	10.2
5	Phorate	87.9	4.5	83.6	8.6	80.8	2.5	86.5	7.9	85.6	11.0	76.3	14.3	90.8	8.8	77.2	8.9	76.5	6.7	96.1	3.7	92.2	0.6	82.9	4.8
6	α-HCH	83.1	16.9	95.6	9.6	89.9	15.6	84.3	11.1	75.2	13.4	88.8	12.0	82.0	7.0	81.8	11.7	81.0	8.9	71.0	8.9	70.5	6.0	82.4	10.4
7	Simazine	85.5	10.7	88.9	6.9	97.5	6.3	94.2	9.5	95.1	1.8	84.2	6.7	99.9	10.6	88.8	10.1	77.0	8.5	81.0	5.6	88.8	9.3	90.6	4.4
8	β-HCH	77.5	8.1	85.5	5.8	87.6	4.9	80.4	10.8	74.8	3.2	77.1	12.7	84.4	9.6	79.2	6.9	77.5	10.1	84.5	12.5	83.6	12.8	82.3	10.1
9	Quintozene	77.4	18.3	91.1	3.2	90.2	3.9	85.7	18.0	95.0	12.8	74.2	11.1	74.7	7.6	86.5	7.1	82.2	6.4	87.6	7.0	71.5	9.7	72.4	10.2
10	γ-HCH	83.5	10.3	86.5	7.2	87.9	9.5	77.6	4.8	73.7	16.3	82.3	8.1	67.2	12.1	84.9	10.7	75.2	10.5	83.0	3.2	85.2	12.0	77.7	10.9
11	Terbufos	83.5	6.5	89.7	7.6	102.2	13.2	100.0	13.0	86.4	11.5	96.8	9.1	87.7	12.0	90.2	12.4	84.6	7.1	81.0	13.5	90.9	10.7	85.6	5.8
12	Diazinon	77.6	4.8	83.1	9.5	87.7	5.9	75.7	8.0	72.4	10.7	79.3	3.2	77.4	10.3	87.9	7.1	90.1	10.6	88.3	3.0	77.2	8.5	87.3	5.8
13	Pyrimethanil	90.0	9.9	80.0	9.9	90.0	9.9	82.4	12.6	92.4	12.6	82.4	12.6	87.6	8.1	91.2	5.4	81.5	7.6	79.3	2.2	79.1	9.1	83.2	10.7
14	δ-HCH	94.5	12.8	83.4	2.4	84.1	5.5	90.9	8.3	85.0	5.4	70.6	13.0	75.8	5.6	91.9	4.9	85.4	7.8	85.0	8.6	72.8	13.8	82.2	3.4
15	Vinclozoline	92.8	10.8	88.3	13.0	87.3	6.6	92.8	10.8	88.0	13.4	98.2	14.9	89.6	14.7	79.1	11.0	81.5	5.8	89.0	3.2	90.8	6.1	91.2	3.6
16	Heptachlor	89.9	11.3	89.5	17.8	95.5	4.4	83.8	15.0	85.2	9.9	76.9	14.8	75.5	6.3	98.6	10.9	88.4	9.9	88.8	9.3	87.2	11.7	91.6	10.0
17	Metalaxyl	92.5	5.9	79.1	4.0	96.6	8.4	91.2	4.7	88.7	4.7	87.4	7.7	85.0	16.4	80.9	5.3	73.7	5.0	75.2	7.6	71.5	5.6	72.9	11.2
18	Chlorpyrifos	86.3	18.0	79.7	13.3	98.7	13.0	68.1	14.5	70.2	3.1	87.7	16.2	81.8	7.3	67.8	7.6	92.2	8.8	73.7	3.2	78.0	10.1	84.3	4.4
19	Aldrin	90.0	11.5	83.4	6.2	87.8	4.2	82.5	11.9	70.0	8.3	75.0	18.5	79.7	10.9	70.1	11.4	84.4	5.8	81.1	14.2	77.4	3.5	71.7	6.4
20	Fenthion	74.6	8.8	89.4	6.2	96.2	6.7	76.1	15.5	83.0	13.5	78.4	9.9	74.7	16.4	81.2	7.4	72.9	9.8	79.9	5.0	81.2	10.9	78.5	0.9
21	Parathion	80.2	8.3	73.5	7.1	93.3	10.5	82.9	6.0	70.6	10.0	82.5	11.4	84.5	12.2	87.1	9.5	80.7	9.4	86.4	11.4	80.4	7.8	77.6	7.0
22	Triadimefon	81.7	10.5	73.0	11.5	86.3	6.3	91.4	6.0	86.7	8.1	80.1	4.4	83.4	10.5	86.9	10.6	89.1	13.5	89.1	5.9	89.5	6.7	85.9	9.0
23	Isofenphos-methyl	79.2	7.5	80.2	12.8	84.2	12.9	89.2	7.5	77.3	17.7	78.9	18.9	74.1	7.3	92.8	8.0	90.8	7.1	81.6	7.2	93.8	7.7	81.8	7.1

24	Pendimethalin	84.0	17.1	84.0	11.9	89.3	3.1	84.0	17.1	71.9	14.2	79.3	3.1	79.9	8.5	84.5	11.3	95.3	9.5	77.8	5.1	79.9	7.1	90.2	6.9
25	Fipronil	71.6	9.1	82.1	5.8	105.4	4.5	74.6	12.8	83.1	5.0	78.6	3.2	76.4	7.5	79.7	9.9	84.1	8.1	73.1	4.1	80.1	11.9	73.7	6.6
26	Heptachlor epoxide	83.0	10.9	86.6	11.0	96.1	5.7	98.2	6.1	77.1	15.7	79.8	15.5	80.2	6.5	75.0	11.0	78.9	10.5	68.3	5.3	83.7	5.7	73.7	6.1
27	Procymidone	92.5	12.0	77.0	10.8	74.9	5.8	73.0	10.9	79.4	6.2	77.3	11.5	80.0	8.3	95.1	11.3	84.1	5.1	86.1	14.6	81.8	10.0	92.7	10.5
28	γ-Chlordane	77.9	8.9	80.0	7.9	90.0	13.7	80.1	7.1	89.4	12.9	74.7	6.6	89.5	7.4	84.4	12.0	73.1	7.9	83.1	5.7	75.0	10.0	71.1	5.2
29	*o,p*'-DDE	81.2	7.9	78.1	11.4	99.5	5.5	64.2	12.3	72.3	3.6	81.9	7.5	84.4	14.6	83.5	12.8	76.2	10.2	82.6	5.2	72.4	5.2	78.2	8.1
30	α-Chlordane	94.1	10.8	79.4	12.2	96.2	6.3	103.3	3.8	83.6	5.8	79.6	9.8	98.9	5.6	85.3	5.2	86.6	7.2	85.2	10.8	87.7	9.6	74.8	5.9
31	Endosulfan	75.3	13.2	86.3	11.8	83.4	12.4	82.6	9.0	78.2	11.3	89.2	18.1	79.6	7.1	73.6	9.6	73.3	7.4	70.6	8.1	73.8	7.9	73.9	4.5
32	*p,p*'-DDE	86.9	18.0	79.7	3.2	93.0	4.6	89.4	2.2	86.4	4.8	87.3	7.7	88.2	4.7	74.5	5.2	93.1	11.4	77.1	8.9	88.1	5.1	80.7	6.0
33	Dieldrin	89.4	12.2	86.4	4.8	97.3	7.7	80.7	10.4	82.3	17.4	90.5	10.5	89.8	6.1	68.3	7.4	91.7	7.8	85.0	10.7	78.3	10.1	78.6	6.7
34	*o,p*'-DDD	89.4	12.2	81.7	4.6	88.1	10.4	91.2	4.9	92.7	7.2	90.0	11.8	86.8	10.2	82.1	8.7	82.2	8.0	73.7	9.9	91.1	4.9	80.7	6.0
35	Flusilazole	82.6	9.0	87.9	5.2	77.3	9.7	79.9	9.0	75.4	3.9	71.2	9.9	92.7	11.1	88.9	9.4	88.8	11.2	81.8	8.3	70.6	7.7	92.1	9.7
36	Endrin	78.8	3.2	88.6	11.7	84.5	8.4	76.6	5.5	78.2	11.9	87.4	9.2	93.6	10.3	71.8	6.7	85.8	10.8	72.9	9.0	77.9	15.4	91.8	5.6
37	*p,p*'-DDD	86.6	5.5	96.0	5.7	90.0	11.8	79.1	9.2	87.0	5.7	84.9	7.3	79.9	6.7	78.4	14.5	80.0	4.1	74.5	9.3	81.3	8.3	81.8	10.0
38	*o,p*'-DDT	92.0	8.5	77.4	10.3	98.8	8.2	70.0	10.3	74.1	10.8	77.0	17.7	78.2	11.8	86.9	13.0	91.3	11.2	77.8	8.4	84.5	7.5	72.4	9.3
39	*p,p*'-DDT	85.7	13.6	82.1	11.3	75.7	7.1	79.1	14.0	70.6	16.1	84.0	5.0	91.9	13.8	74.5	10.1	84.9	3.2	74.9	10.8	75.1	5.0	75.2	9.8
40	Tebuconazole	84.6	8.6	77.4	4.9	92.2	10.9	82.2	9.3	80.0	4.3	70.0	5.0	80.3	6.9	88.0	11.3	82.1	8.1	84.2	5.8	87.2	6.5	90.4	8.8
41	Bifenthrin	82.2	9.3	88.7	13.4	84.0	5.0	91.9	4.9	87.0	15.5	81.2	18.1	90.5	16.2	74.7	11.9	86.8	4.2	75.5	12.0	83.2	13.1	86.6	7.2
42	cis-Permethrin	80.1	6.7	85.6	4.9	90.6	6.0	82.2	4.1	90.8	5.1	91.8	5.4	76.6	9.9	84.8	6.0	82.5	14.1	84.4	8.7	80.5	7.8	83.4	10.9
43	trans-Permethrin	82.3	8.4	84.1	6.5	89.5	9.0	80.1	6.7	89.3	16.8	80.6	6.0	87.0	15.9	82.8	10.4	85.2	4.8	88.6	7.3	83.7	3.9	80.7	6.0
44	Pyridaben	88.8	10.6	79.5	8.8	100.6	7.7	84.8	10.3	85.2	5.5	98.1	9.8	88.0	10.2	76.7	7.4	79.0	3.3	81.1	12.5	76.5	8.1	71.1	5.9
45	Etofenprox	81.0	13.0	88.0	8.7	90.8	11.4	73.8	6.2	98.9	8.0	74.3	11.3	72.2	11.8	71.1	5.0	78.9	7.1	89.5	9.9	78.2	10.5	77.8	10.9
46	Difenoconazole 1	85.7	13.9	97.3	15.5	72.6	3.6	81.2	10.0	89.6	7.4	88.2	11.0	87.0	7.7	87.4	8.4	84.3	8.1	77.1	8.2	84.1	8.0	79.3	9.4
47	Difenoconazole 2	80.0	9.3	84.4	8.4	92.4	4.1	83.8	14.3	80.8	13.4	81.4	10.4	84.9	12.5	80.6	10.2	86.1	6.0	81.9	8.0	81.2	12.2	85.1	5.0

*R% denotes average recovery (%)

Table 3 Comparison of the analytical performances between different methods for multiresidue pesticide analysis in plant-derived food.

Food type	Number of analytes	Extraction	Clean-up	MLOQ (μg kg^{-1})	Recoveries (%)	References
Apple, orange, honey, leek	47	GLME-d-SPE		0.2 – 10.9	67.2 – 105.4	This study
Cabbage, leek radicchio	45	MSPD		0.4 - 4.0*	89 - 106	(Chatzimitakos et al., 2019)
Apple, tomato, cucumber, cabbage	14	HS-SPME		1.15 – 27.76	73 - 118	(Abdulra'uf & Tan, 2015)
Peach and canned peach	10	QuEChERS		1 - 10	69 - 146	(Costa et al., 2014)
Honey	4	LLE	LTP	28 – 33	84.6 – 100.9	(de Pinho et al., 2010)
Peach, lettuce, wheat grain	25	SLE	Two-step SPE	5 – 10	73 - 117	(Balinova et al., 2007)
15 types of vegetables	8	QuEChERS – DLLME-SFO		0.9 – 4.7	61.6 – 119.4	(Mao et al., 2020)

* Concentrations were displayed in ng mL^{-1}. Additional information: MSPD: matrix solid-phase dispersion; HS-SPME: headspace solid phase microextraction; LLE: liquid-liquid extraction; LTP: low temperature purification; SLE: solid-liquid extraction; DLLME-SFO: dispersive liquid–liquid microextraction based on solidification of floating organic droplet.

3.4 Application in real samples

Under optimized condition, the one-step GLME-d-SPE method was employed to analyze 47 multi-class pesticides in real plant-derived food samples. Based on the results (Table S7) obtained by using matrix-match calibration curves (Table S8), 2-phenylphenol was detected at the concentration of 0.004 mg kg^{-1} in apple and 0.006 mg kg^{-1} in orange, while quintozene was identified in honey and leek at 0.008 mg kg^{-1} and 0.010 mg kg^{-1}, respectively. Bifenthrin and permethrin were also detected in apple at the concentrations of 0.001 and 0.005 mg kg^{-1}, respectively. Fipronil, chlordane and p-p'-DDE were detected in apple and orange, but the concentrations were below MLOQ, hence they were not quantified. In spite of the fact that several pesticides have been detected in chosen foods, the concentrations were all below permitted MRLs, indicating the low risk that may impose on human health. Nevertheless, the detected pesticides in selected food commodities in this study were previously identified at high concentration (2.16 mg kg^{-1} of 2-phenylphenol was found in orange (Blasco et al., 2002); while *trans*-permethrin were detected at 1.35 and 0.21 mg kg^{-1} in lettuce and apple, respectively) (Li et al., 2016), signifying the significance of developing rapid detection system for continual surveillance of food quality in the market.

4. Conclusions

The extraction and purification processes by GLME, in addition to the integration of d-SPE clean-up were simultaneously completed within a single sample pretreatment procedure to analyze multi-class pesticide residues in plant-derived foods. This one-step GLME-d-SPE method has been validated for its notable advantages of speedy, environmentally-friendly and time-saving features. The one-step pretreatment feature of this method offers a promising prospect for the rapid determination of pesticide residues in varying food matrices. In view of the great sensitivity of this technique that meets the detection requirements of allowable MRLs in varied countries, it is applicable for routine and on-site monitoring of food quality, therefore help to safeguard human health.

Conflict of interest

There are no conflicts to declare.

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CRediT Author statement

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Table 1 Method limit of quantification (MLOQ) and matrix effect (ME%) for 47 multi-class pesticides in the representative plant-derived foods by using the one-step GLME-d-SPE method, and the relevant maximum residue levels (MRLs) as reference.

	Pesticide	Family *	MLOQ (mg kg^{-1})				MRLs (EU/China)** mg kg^{-1}	ME%			
			Apple	Orange	Honey	Leek	Apple/Orange/Honey/Leek	Apple	Orange	Honey	Leek
1	Dichlorvos	OP	0.001	0.001	0.007	0.001	0.01/0.01/-/0.01	1	8	80	132
2	2-Phenylphenol	UN	0.001	0.001	0.002	0.001	0.01/10.0/0.05-0.01	18	29	103	120
3	Ethoprophos	OP	0.004	0.004	0.005	0.004	0.02/0.02/-/0.02	-7	-1	26	53
4	Chlorpropham	GI	0.004	0.004	0.004	0.004	0.01/0.01/0.05/0.01	6	12	45	68
5	Phorate	OP	0.001	0.001	0.007	0.001	0.01/0.01/0.01/0.01	-5	8	-65	56
6	Simazine	CT	0.005	0.005	0.007	0.005	0.01/0.01/0.01/0.01	16	23	-5	88
7	α-HCH	OC	0.002	0.001	0.002	0.002	0.01/0.01/0.01/0.01***	-16	-1	20	59
8	β-HCH	OC	0.004	0.004	0.011	0.004		-10	-4	6	38
9	γ-HCH	OC	0.003	0.003	0.007	0.005		-16	-1	10	56
10	δ-HCH	OC	0.003	0.002	0.003	0.004		-15	-5	-2	40
11	Quintozene	AF	0.009	0.009	0.009	0.009	0.02/0.02/0.01/0.02	-1	25	80	107
12	Terbufos	OP	0.001	0.001	0.005	0.001	0.01/0.01/-/0.01	-10	3	-75	52
13	Diazinon	OP	0.003	0.003	0.003	0.003	0.01/0.01/0.01/0.01	5	3	9	27
14	Pyrimethanil	PF	0.001	0.001	0.002	0.001	15.0/8.0/0.05/4.0	16	26	19	96
15	Vinclozoline	DC	0.003	0.003	0.003	0.003	0.01/0.01/0.05/0.01	3	1	13	26
16	Heptachlor	OC	0.002	0.002	0.002	0.004	0.01/0.01/0.01/0.01***	-13	2	30	68
17	Heptachlor epoxide	OC	0.002	0.002	0.007	0.002		-19	-12	-4	17
18	Metalaxyl	AN	0.008	0.004	0.008	0.005	1.0/0.7/0.05/0.03	-11	-8	-6	21
19	Chlorpyrifos	OP	0.003	0.003	0.003	0.003	0.01/1.5/0.05/0.01	1	3	15	36
20	Aldrin	OC	0.003	0.004	0.005	0.004	0.01/0.01/0.01/0.01	-15	0	20	51
21	Fenthion	OP	0.001	0.001	0.007	0.001	0.01/0.01/0.01/0.01	-2	3	-81	32
22	Parathion	OP	0.009	0.009	0.009	0.009	0.01/0.01/-/0.01	36	59	143	120
23	Triadimefon	CF	0.006	0.006	0.011	0.006	0.01/0.01/0.05/0.01	-10	-7	-6	30
24	Isofenphos-methyl	OP	0.003	0.003	0.003	0.006	0.01/0.01/-/0.01	-14	-6	-13	28
25	Pendimethalin	DA	0.003	0.003	0.003	0.003	0.05/0.05/0.05/0.05	28	41	98	103
26	Fipronil	PP	0.002	0.002	0.005	0.002	0.005/0.005/0.005/0.005	1	4	13	20
27	Procymidone	DC	0.004	0.004	0.004	0.004	0.01/0.01/0.05/0.01	-2	-3	3	17
28	γ-Chlordane	OC	0.002	0.002	0.011	0.002	0.01/0.01/0.01/0.01***	-17	-7	6	27
29	α-Chlordane	OC	0.002	0.002	0.002	0.002		-15	-10	4	16
30	*o,p*'-DDE	OC	0.001	0.001	0.005	0.001	0.05/0.05/0.05/0.05***	-12	-5	8	27
31	*p,p*'-DDE	OC	0.001	0.001	0.001	0.001		-5	-1	8	12
32	*o,p*'-DDD	OC	0.001	0.001	0.001	0.001		-14	-7	1	9
33	*p,p*'-DDD	OC	0.001	0.001	0.001	0.002		-8	-1	12	29
34	*o,p*'-DDT	OC	0.001	0.001	0.001	0.002		-5	0	13	21
35	*p,p*'-DDT	OC	0.001	0.001	0.001	0.002		6	12	28	53
36	Endosulfan	OC	0.006	0.005	0.009	0.010	0.05/0.05/0.01/0.05	-17	-9	0	26
37	Dieldrin	OC	0.008	0.007	0.009	0.010	0.01/0.01/0.01/0.01***	-17	-10	5	22

38	Endrin	OC	0.004	0.004	0.005	0.008		-16	-4	7	37
39	Flusilazole	CF	0.010	0.010	0.010	0.010	0.01/0.01/0.05/0.01	-6	-15	-16	-7
40	Tebuconazole	CF	0.003	0.003	0.003	0.003	0.3/0.9/0.05/0.6	8	11	9	25
41	Bifenthrin	PY	0.001	0.001	0.001	0.002	0.01/0.05/-/0.05	-16	-18	-8	-1
42	cis-Permethrin	PY	0.004	0.005	0.006	0.009	0.05/0.05/-/0.05***	-13	-18	-4	-6
43	trans-Permethrin	PY	0.001	0.001	0.001	0.003		-9	-18	-5	-4
44	Pyridaben	UN	0.004	0.004	0.005	0.004	0.9/0.3/0.05/0.01	6	-22	9	-34
45	Etofenprox	PY	0.003	0.003	0.003	0.003	0.6/1.5/0.05/0.01	-3	-10	20	-50
46	Difenoconazole 1	CF	0.007	0.007	0.007	0.007	0.5/0.5/0.05/0.6***	33	13	55	30
47	Difenoconazole 2	CF	0.004	0.004	0.004	0.004		-7	-2	24	4

* OC: Organochlorine insecticide; OP: Organophosphate insecticide; PY: Pyrethoid insecticide; GI: Growth inhibitor; CT: Chlorotriazine herbicide; AF: Aromatic fungicide; PF: Pyrimidine fungicide; DC: Dicarboximide fungicide; AN: Anilide fungicide; CF: Conazole fungicide; DA: Dinitroaniline herbicide; PP: Phenylpyrazole acaricide; UN: Unclassified.

** The listed MRLs in each food type were displayed according to the lower MRL values set by EU and China.

*** MRLs refer to the sum of isomers

Table 2 Trueness (mean recovery) and precision (relative standard deviation, RSD) of the one-step GLME-d-SPE method to analyze 47 pesticides spiked at three concentrations in different plant-derived foods.

	Apple						Orange						Honey						Leek					
	Spiked level (ng g^{-1})																							
	20		50		200		20		50		200		20		50		200		20		50		200	
	R%*	RSD (%)	R%*	RSD (%)	R%*	RSD (%)	R%*	RSD (%)	R%*	RSD (%)	R%*	RSD (%)	R%*	RSD (%)	R%*	RSD (%)	R%*	RSD (%)	R%*	RSD (%)	R%*	RSD (%)	R%*	RSD (%)
Dichlorvos	79.9	6.0	89.5	6.5	75.2	5.7	73.5	9.2	82.9	4.8	80.5	13.2	90.0	12.6	74.3	12.9	71.3	4.4	75.4	6.4	70.4	7.2	75.3	6.5
2-Phenylphenol	85.0	11.2	91.8	8.9	93.4	2.4	79.9	6.0	81.2	3.4	77.0	8.3	86.4	5.4	86.9	14.4	87.8	12.5	89.4	5.8	83.0	13.9	79.3	6.0
Ethoprophos	80.9	9.6	87.5	5.2	88.6	9.6	95.2	5.7	86.6	4.4	80.7	14.0	80.0	10.6	74.4	13.8	78.7	9.7	82.8	4.9	89.8	14.6	73.1	5.1
Chlorpropham	91.4	9.0	88.4	8.9	89.9	11.7	87.5	3.8	87.1	6.6	99.7	11.5	103.9	4.6	82.1	8.3	88.8	9.0	91.7	9.5	77.2	9.7	84.5	10.2
Phorate	87.9	4.5	83.6	8.6	80.8	2.5	86.5	7.9	85.6	11.0	76.3	14.3	90.8	8.8	77.2	8.9	76.5	6.7	96.1	3.7	92.2	0.6	82.9	4.8
α-HCH	83.1	16.9	95.6	9.6	89.9	15.6	84.3	11.1	75.2	13.4	88.8	12.0	82.0	7.0	81.8	11.7	81.0	8.9	71.0	8.9	70.5	6.0	82.4	10.4
Simazine	85.5	10.7	88.9	6.9	97.5	6.3	94.2	9.5	95.1	1.8	84.2	6.7	99.9	10.6	88.8	10.1	77.0	8.5	81.0	5.6	88.8	9.3	90.6	4.4
β-HCH	77.5	8.1	85.5	5.8	87.6	4.9	80.4	10.8	74.8	3.2	77.1	12.7	84.4	9.6	79.2	6.9	77.5	10.1	84.5	12.5	83.6	12.8	82.3	10.1
Quintozene	77.4	18.3	91.1	3.2	90.2	3.9	85.7	18.0	95.0	12.8	74.2	11.1	74.7	7.6	86.5	7.1	82.2	6.4	87.6	7.0	71.5	9.7	72.4	10.2
γ-HCH	83.5	10.3	86.5	7.2	87.9	9.5	77.6	4.8	73.7	16.3	82.3	8.1	67.2	12.1	84.9	10.7	75.2	10.5	83.0	3.2	85.2	12.0	77.7	10.9
Terbufos	83.5	6.5	89.7	7.6	102.2	13.2	100.0	13.0	86.4	11.5	96.8	9.1	87.7	12.0	90.2	12.4	84.6	7.1	81.0	13.5	90.9	10.7	85.6	5.8
Diazinon	77.6	4.8	83.1	9.5	87.7	5.9	75.7	8.0	72.4	10.7	79.3	3.2	77.4	10.3	87.9	7.1	90.1	10.6	88.3	3.0	77.2	8.5	87.3	5.8
Pyrimethanil	90.0	9.9	80.0	9.9	90.0	9.9	82.4	12.6	92.4	12.6	82.4	12.6	87.6	8.1	91.2	5.4	81.5	7.6	79.3	2.2	79.1	9.1	83.2	10.7
δ-HCH	94.5	12.8	83.4	2.4	84.1	5.5	90.9	8.3	85.0	5.4	70.6	13.0	75.8	5.6	91.9	4.9	85.4	7.8	85.0	8.6	72.8	13.8	82.2	3.4
Vinclozoline	92.8	10.8	88.3	13.0	87.3	6.6	92.8	10.8	88.0	13.4	98.2	14.9	89.6	14.7	79.1	11.0	81.5	5.8	89.0	3.2	90.8	6.1	91.2	3.6
Heptachlor	89.9	11.3	89.5	17.8	95.5	4.4	83.8	15.0	85.2	9.9	76.9	14.8	75.5	6.3	98.6	10.9	88.4	9.9	88.8	9.3	87.2	11.7	91.6	10.0
Metalaxyl	92.5	5.9	79.1	4.0	96.6	8.4	91.2	4.7	88.7	4.7	87.4	7.7	85.0	16.4	80.9	5.3	73.7	5.0	75.2	7.6	71.5	5.6	72.9	11.2
Chlorpyrifos	86.3	18.0	79.7	13.3	98.7	13.0	68.1	14.5	70.2	3.1	87.7	16.2	81.8	7.3	67.8	7.6	92.2	8.8	73.7	3.2	78.0	10.1	84.3	4.4
Aldrin	90.0	11.5	83.4	6.2	87.8	4.2	82.5	11.9	70.0	8.3	75.0	18.5	79.7	10.9	70.1	11.4	84.4	5.8	81.1	14.2	77.4	3.5	71.7	6.4
Fenthion	74.6	8.8	89.4	6.2	96.2	6.7	76.1	15.5	83.0	13.5	78.4	9.9	74.7	16.4	81.2	7.4	72.9	9.8	79.9	5.0	81.2	10.9	78.5	0.9
Parathion	80.2	8.3	73.5	7.1	93.3	10.5	82.9	6.0	70.6	10.0	82.5	11.4	84.5	12.2	87.1	9.5	80.7	9.4	86.4	11.4	80.4	7.8	77.6	7.0
Triadimefon	81.7	10.5	73.0	11.5	86.3	6.3	91.4	6.0	86.7	8.1	80.1	4.4	83.4	10.5	86.9	10.6	89.1	13.5	89.1	5.9	89.5	6.7	85.9	9.0
Isofenphos-methyl	79.2	7.5	80.2	12.8	84.2	12.9	89.2	7.5	77.3	17.7	78.9	18.9	74.1	7.3	92.8	8.0	90.8	7.1	81.6	7.2	93.8	7.7	81.8	7.1

Pendimethalin	84.0	17.1	84.0	11.9	89.3	3.1	84.0	17.1	71.9	14.2	79.3	3.1	79.9	8.5	84.5	11.3	95.3	9.5	77.8	5.1	79.9	7.1	90.2	6.9
Fipronil	71.6	9.1	82.1	5.8	105.4	4.5	74.6	12.8	83.1	5.0	78.6	3.2	76.4	7.5	79.7	9.9	84.1	8.1	73.1	4.1	80.1	11.9	73.7	6.6
Heptachlor epoxide	83.0	10.9	86.6	11.0	96.1	5.7	98.2	6.1	77.1	15.7	79.8	15.5	80.2	6.5	75.0	11.0	78.9	10.5	68.3	5.3	83.7	5.7	73.7	6.1
Procymidone	92.5	12.0	77.0	10.8	74.9	5.8	73.0	10.9	79.4	6.2	77.3	11.5	80.0	8.3	95.1	11.3	84.1	5.1	86.1	14.6	81.8	10.0	92.7	10.5
γ-Chlordane	77.9	8.9	80.0	7.9	90.0	13.7	80.1	7.1	89.4	12.9	74.7	6.6	89.5	7.4	84.4	12.0	73.1	7.9	83.1	5.7	75.0	10.0	71.1	5.2
o,p'-DDE	81.2	7.9	78.1	11.4	99.5	5.5	64.2	12.3	72.3	3.6	81.9	7.5	84.4	14.6	83.5	12.8	76.2	10.2	82.6	5.2	72.4	5.2	78.2	8.1
α-Chlordane	94.1	10.8	79.4	12.2	96.2	6.3	103.3	3.8	83.6	5.8	79.6	9.8	98.9	5.6	85.3	5.2	86.6	7.2	85.2	10.8	87.7	9.6	74.8	5.9
Endosulfan	75.3	13.2	86.3	11.8	83.4	12.4	82.6	9.0	78.2	11.3	89.2	18.1	79.6	7.1	73.6	9.6	73.3	7.4	70.6	8.1	73.8	7.9	73.9	4.5
p,p'-DDE	86.9	18.0	79.7	3.2	93.0	4.6	89.4	2.2	86.4	4.8	87.3	7.7	88.2	4.7	74.5	5.2	93.1	11.4	77.1	8.9	88.1	5.1	80.7	6.0
Dieldrin	89.4	12.2	86.4	4.8	97.3	7.7	80.7	10.4	82.3	17.4	90.5	10.5	89.8	6.1	68.3	7.4	91.7	7.8	85.0	10.7	78.3	10.1	78.6	6.7
o,p'-DDD	89.4	12.2	81.7	4.6	88.1	10.4	91.2	4.9	92.7	7.2	90.0	11.8	86.8	10.2	82.1	8.7	82.2	8.0	73.7	9.9	91.1	4.9	80.7	6.0
Flusilazole	82.6	9.0	87.9	5.2	77.3	9.7	79.9	9.0	75.4	3.9	71.2	9.9	92.7	11.1	88.9	9.4	88.8	11.2	81.8	8.3	70.6	7.7	92.1	9.7
Endrin	78.8	3.2	88.6	11.7	84.5	8.4	76.6	5.5	78.2	11.9	87.4	9.2	93.6	10.3	71.8	6.7	85.8	10.8	72.9	9.0	77.9	15.4	91.8	5.6
p,p'-DDD	86.6	5.5	96.0	5.7	90.0	11.8	79.1	9.2	87.0	5.7	84.9	7.3	79.9	6.7	78.4	14.5	80.0	4.1	74.5	9.3	81.3	8.3	81.8	10.0
o,p'-DDT	92.0	8.5	77.4	10.3	98.8	8.2	70.0	10.3	74.1	10.8	77.0	17.7	78.2	11.8	86.9	13.0	91.3	11.2	77.8	8.4	84.5	7.5	72.4	9.3
p,p'-DDT	85.7	13.6	82.1	11.3	75.7	7.1	79.1	14.0	70.6	16.1	84.0	5.0	91.9	13.8	74.5	10.1	84.9	3.2	74.9	10.8	75.1	5.0	75.2	9.8
Tebuconazole	84.6	8.6	77.4	4.9	92.2	10.9	82.2	9.3	80.0	4.3	70.0	5.0	80.3	6.9	88.0	11.3	82.1	8.1	84.2	5.8	87.2	6.5	90.4	8.8
Bifenthrin	82.2	9.3	88.7	13.4	84.0	5.0	91.9	4.9	87.0	15.5	81.2	18.1	90.5	16.2	74.7	11.9	86.8	4.2	75.5	12.0	83.2	13.1	86.6	7.2
cis-Permethrin	80.1	6.7	85.6	4.9	90.6	6.0	82.2	4.1	90.8	5.1	91.8	5.4	76.6	9.9	84.8	6.0	82.5	14.1	84.4	8.7	80.5	7.8	83.4	10.9
trans-Permethrin	82.3	8.4	84.1	6.5	89.5	9.0	80.1	6.7	89.3	16.8	80.6	6.0	87.0	15.9	82.8	10.4	85.2	4.8	88.6	7.3	83.7	3.9	80.7	6.0
Pyridaben	88.8	10.6	79.5	8.8	100.6	7.7	84.8	10.3	85.2	5.5	98.1	9.8	88.0	10.2	76.7	7.4	79.0	3.3	81.1	12.5	76.5	8.1	71.1	5.9
Etofenprox	81.0	13.0	88.0	8.7	90.8	11.4	73.8	6.2	98.9	8.0	74.3	11.3	72.2	11.8	71.1	5.0	78.9	7.1	89.5	9.9	78.2	10.5	77.8	10.9
Difenoconazole 1	85.7	13.9	97.3	15.5	72.6	3.6	81.2	10.0	89.6	7.4	88.2	11.0	87.0	7.7	87.4	8.4	84.3	8.1	77.1	8.2	84.1	8.0	79.3	9.4
Difenoconazole 2	80.0	9.3	84.4	8.4	92.4	4.1	83.8	14.3	80.8	13.4	81.4	10.4	84.9	12.5	80.6	10.2	86.1	6.0	81.9	8.0	81.2	12.2	85.1	5.0

*R% denotes average recovery (%)

Table 3 Comparison of the analytical performances between different methods for multiresidue pesticide analysis in plant-derived food.

Food type	Number of analytes	Extraction	Clean-up	MLOQ (μg kg^{-1})	Recoveries (%)	References
Apple, orange, honey, leek	47	GLME-d-SPE		0.236 – 10.9	62.7 – 102.7	This study
Cabbage, leek radicchio	45	MSPD		0.4 - 4.0*	89 - 106	(Chatzimitakos et al., 2019)
Apple, tomato, cucumber, cabbage	14	HS-SPME		1.15 – 27.76	73 - 118	(Abdulra'uf & Tan, 2015)
Peach and canned peach	10	QuEChERS		1 - 10	69 - 146	(Costa et al., 2014)
Honey	4	LLE	LTP	28 – 33	84.6 – 100.9	(de Pinho et al., 2010)
Peach, lettuce, wheat grain	25	SLE	Two-step SPE	5 – 10	73 - 117	(Balinova et al., 2007)
15 types of vegetables	8	QuEChERS – DLLME-SFO		0.9 – 4.7	61.6 – 119.4	(Mao et al., 2020)

* Concentrations were displayed in ng mL^{-1}. Additional information: MSPD: matrix solid-phase dispersion; HS-SPME: headspace solid phase microextraction; LLE: liquid-liquid extraction; LTP: low temperature purification; SLE: solid-liquid extraction; DLLME-SFO: dispersive liquid–liquid microextraction based on solidification of floating organic droplet.

Figure 1

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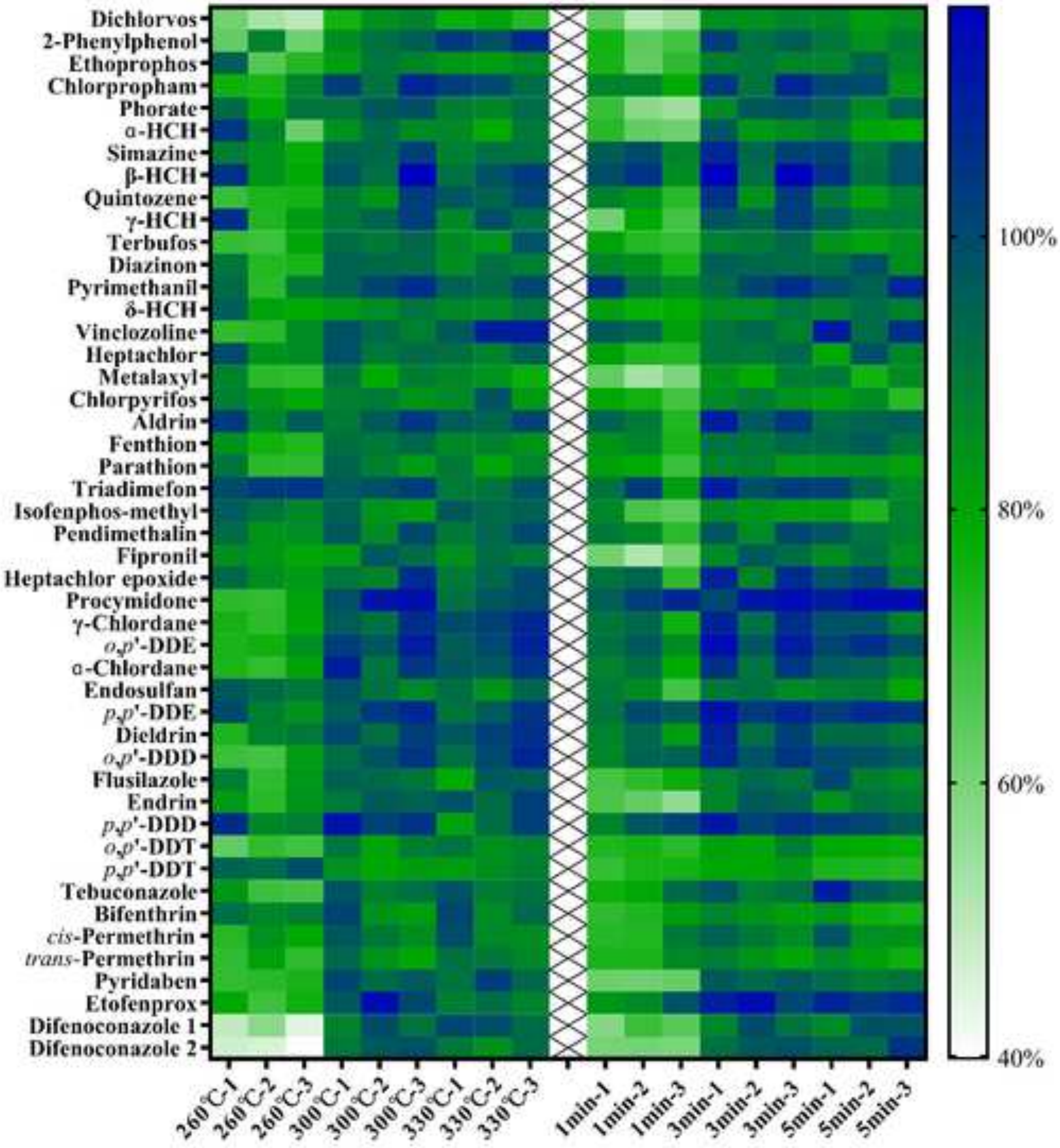

Figure 2

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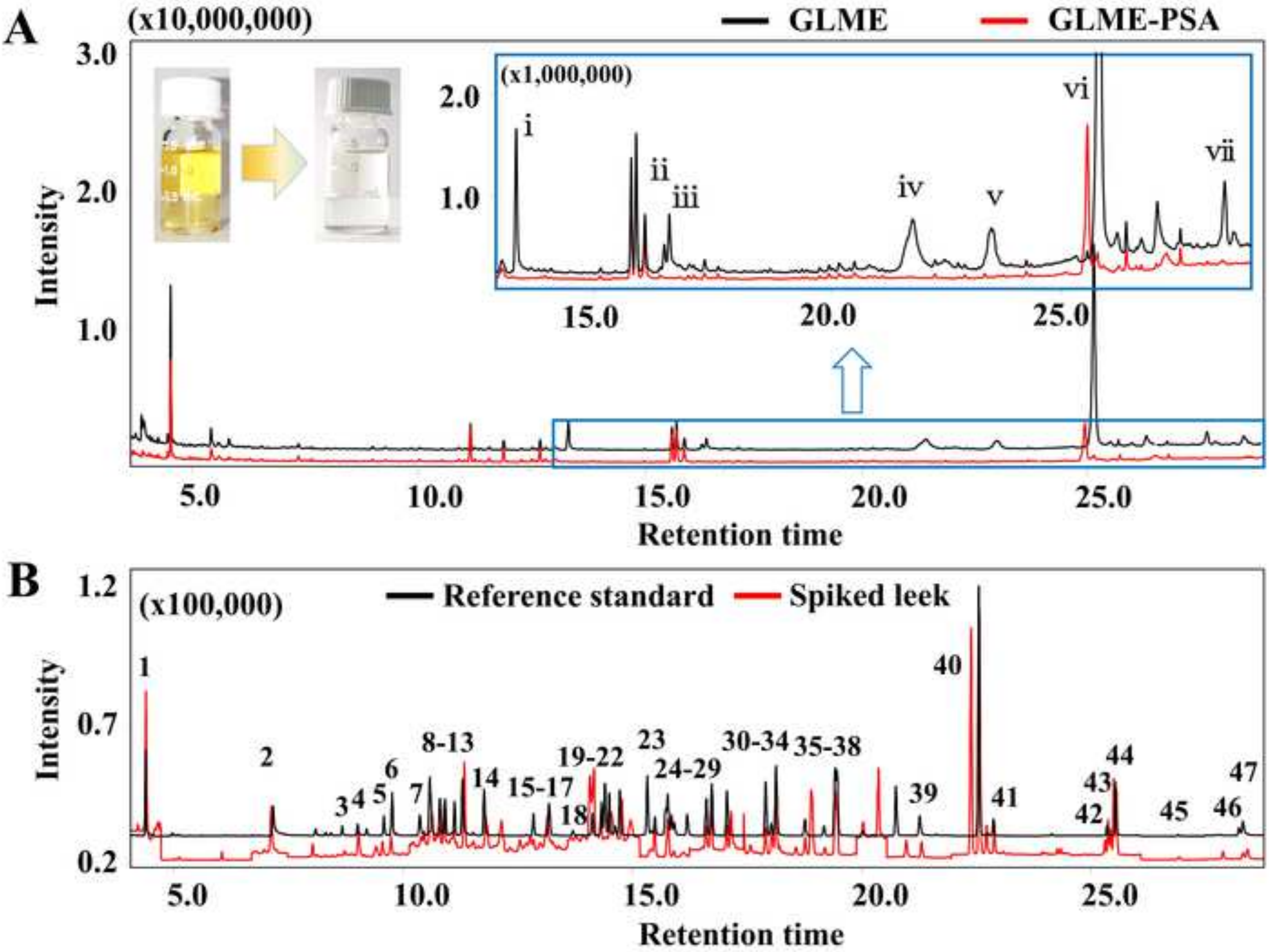

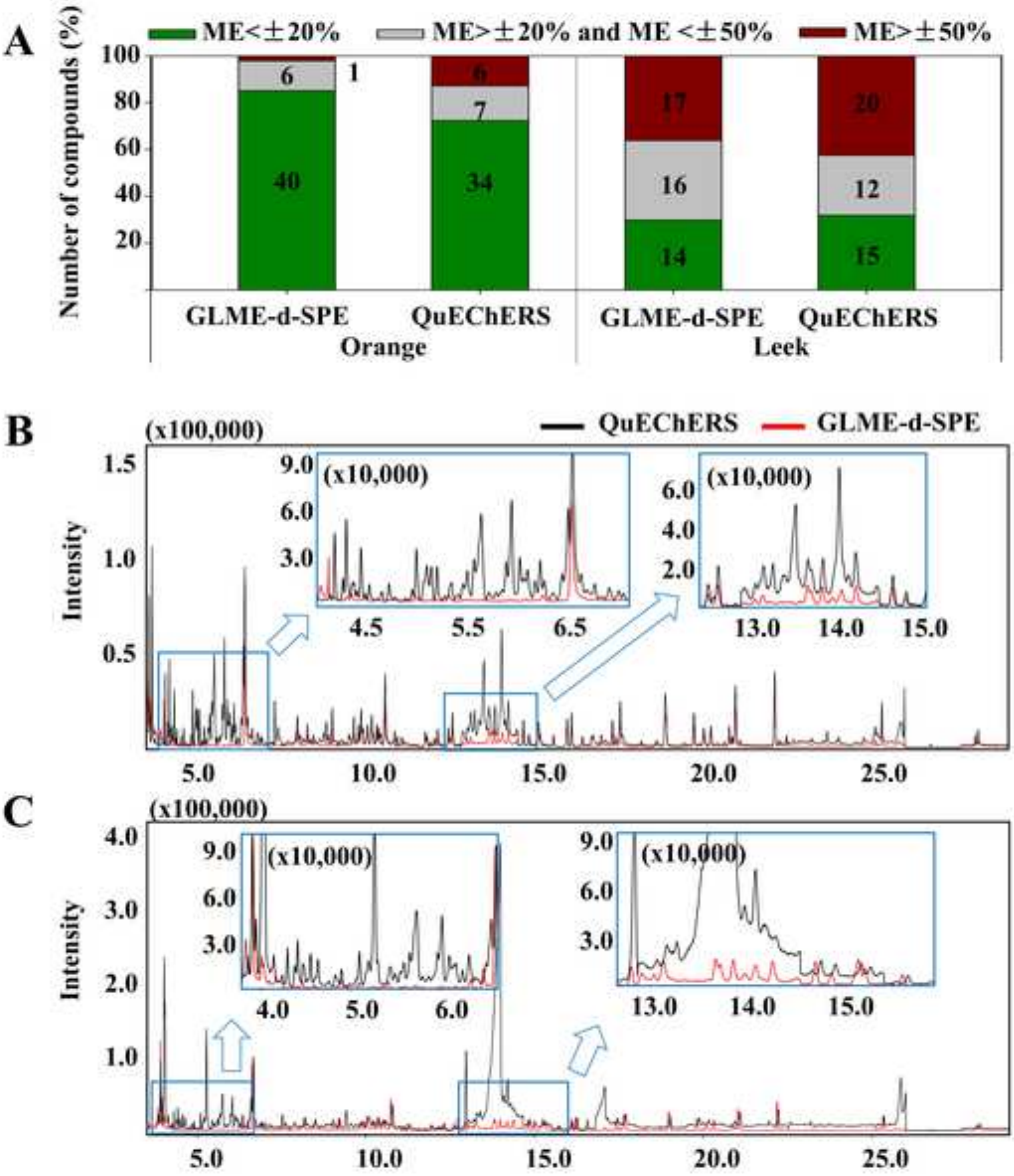
A
ME<±20%
ME>±20% and ME <±50%
ME>±50%
Number of compounds (%)
100
80
60
40
20
6
1
40
6
7
34
17
16
14
20
12
15
GLME-d-SPE
QuEChERS
Orange
GLME-d-SPE
QuEChERS
Leek
B
(x100,000)
QuEChERS
GLME-d-SPE
Intensity
1.5
1.0
0.5
(x10,000)
9.0
6.0
3.0
4.5
5.5
6.5
(x10,000)
6.0
4.0
2.0
13.0
14.0
15.0
5.0
10.0
15.0
20.0
25.0
C
(x100,000)
Intensity
4.0
3.0
2.0
1.0
(x10,000)
9.0
6.0
3.0
4.0
5.0
6.0
(x10,000)
9.0
6.0
3.0
13.0
14.0
15.0
5.0
10.0
15.0
20.0
25.0

Supplementary Material

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Supplementary material for publication in **Food Chemistry**

Supplementary Material

One-step integrated sample pretreatment technique by Gas-Liquid Microextraction (GLME) to determine multi-class pesticide residues in plant-derived foods

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Table of Contents

Supplementary materials and methods

Mixed OCPs standard containing aldrin, dieldrin, dichlorodiphenyldichloroethane (DDD) including both *p,p*'- and *o,p*'-DDD, dichlorodiphenyldichloroethylene (DDE) including both *p,p*'- and *o,p*'-DDE, dichlorodiphenyltrichloroethane (DDT) including both *p,p*'- and *o,p*'-DDT, endosulfan, endrin, heptachlor, heptachlor epoxide, α-HCH, β-HCH, γ-HCH (a.k.a Lindane), δ-HCH, α-chlordane and γ-chlordane was bought from AccuStandard (New Haven, CT, USA). Individual pesticide standards including dichlorvos, 2-phenylphenol, ethoprophos, chlorpropham, phorate, simazine, quintozene, terbufos, diazinon, pyrimethanil, vinclozoline, metalaxyl, chlorpyrifos, fenthion, parathion, triadimefon, isophenphos-methyl, pendimethalin, fipronil, procymidone, flusilazole, tebuconazole, bifenthrin, *cis*-permethrin, *trans*-permethrin, pyridaben, etofenprox, difenoconazole 1 and difenoconazole 2 were purchased from Aoke Biological Technology Co. Ltd. (Beijing, China). Both deuterated tebuconazole (TEB-d_9) and tetrachloro-m-xylene (TCMX) were used as surrogate standards, which were purchased from Toronto Research Chemicals (TRC; Toronto, ON, Canada). Triphenyl phosphate (TPP) was used as the internal standard, and it was also obtained from AccuStandard (New Haven, CT, USA).

The standard stock solution (100 mg L^{-1}) for each pesticide was prepared in acetone, and a mixed standard solution with all selected pesticides in this study was prepared at 10 mg L^{-1} by diluting the stock solution with dichloromethane. The calibration standards of different concentrations were prepared by diluting the mixed standard solution to 5, 10, 20, 50, 100, 200, 500 and 1000 ng mL^{-1} with dichloromethane, respectively, which were stored in the dark at 4 °C before use. The mixed surrogate standards containing TCMX and Teb-d_9, as well as TPP as the internal standard were prepared at 10 mg L^{-1} by diluting the stock solution with dichloromethane. The standard working solutions for spiked standard comprising 47 analytes, mixed surrogate standard and internal standard were freshly prepared by diluting the mixed standard solution to 1 mg L^{-1} with dichloromethane before experimentations.

The QuEChERS method was conducted according to Method AOAC, 2007. In brief, approximately 1 kg samples were cut into small pieces and about 200 g of subsample was homogenized with blender. A total of 15.0 g subsample was transferred into 50 mL Teflon tube, followed by the addition of 15 mL 1% HOAc in MeCN, 6 g anhydrous $MgSO_4$, 1.5 g anhydrous NaOAc and 75 µL internal standard to the tube. The tube was vigorously shaken by hand for 1 min, and then centrifuged at >1500 rcf for 1 min. 1-8 mL of the supernatant was transferred to a 15 mL tube containing 50 mg PSA sorbent and 150 mg $MgSO_4$ per mL extract. The tube was sealed and thoroughly mixed for 30 s, followed by the centrifugation at >1500 rcf for 1 min. 4 mL of the supernatant was withdrawn, evaporated with N_2 to 0.5 mL and GC-IS was added before subjected to GC-MS analysis."

Table S1 The classification and toxicity information of 47 multi-class pesticides in this study.

Pesticide	WHO Classification of hazardous pesticides *	WHO GHS **	Long-term effects **	Environmental. Toxicity **
Dichlorvos	Ib	√		√
2-Phenylphenol	III	—	—	—
Ethoprophos	Ia	√	√	
Chlorpropham	U	—	—	—
Phorate	Ia			√
α-HCH	II			
Simazine	U	—	—	—
β-HCH	II		√	
Quintozene	U			
γ-HCH	II		√	√
Terbufos	Ia			
Diazinon	II		√	√

Pyrimethanil	III	—	—	—
δ-HCH	II		√	
Isazofos	O			
Vinclozoline	U		√	
Heptachlor	O	—	—	—
Metalaxyl	II	—	—	—
Chlorpyrifos	II			√
Aldrin	O	—	—	—
Fenthion	II			√
Parathion	Ia			√
Triadimefon	II	—	—	—
Isofenphos-methyl	O	—	—	—
Pendimethalin	II			√
Fipronil	II			√
Heptachlor epoxide	O	—	—	—
Procymidone	U		√	
Chlordane	II		√	√
Endosulfan	II	√		
DDE	II	—	—	—
Dieldrin	O	—	—	—

DDD	II	一	一	一
Flusilazole	II		√	
Endrin	O	一	一	一
DDT	II		√	√
Tebuconazole	II	一	一	一
Bifenthrin	II		√	√
Permethrin	II		√	√
Pyridaben	II			√
Etofenprox	U			√
Difenoconazole	II	一	一	一

* Ia: Extremely hazardous; Ib: Highly hazardous; II: Moderately hazardous; III: Slightly hazardous; U: Unlikely to present acute hazard in normal use; O: Obsolete.

** √: Listed; 一: Deleted or not available; Blank: Not listed.

Information regarding the classification of the toxicity in the list was extracted from a publication entitled PAN International List of Highly Hazardous Pesticides by Pesticide Action Network International (PAN International), and it can be downloaded from pan-international.org/wp-content/uploads/PAN_HHP_List.pdf

Table S2 Chemical and physical properties of 47 pesticides in this study.

Pesticides	Molecular weight (g·mol^{-1})	Enthalpy of Vaporization (kJ mol^{-1})	Melting point (°C)	Vapor pressure (mm Hg at 25°C)	Log P	Polarizability (×10^{-24} cm^3)	Hydrogen Bond Donor Count	Hydrogen Bond Acceptor Count	Rotatable Bond Count
Dichlorvos	220.976	39.6	-60	1.58E-02	0.71	16.8	0	4	4
2-Phenylphenol	170.207	54.2	59	2.00E-03	2.94	20.9	1	1	1
Ethoprophos	242.339	52.9	-13	3.80E-04	3.59	25.3	0	4	8
Chlorpropham	213.661	59.8	42	1.80E-04	3.71	22.0	1	2	3
Phorate	260.377	51.4	-43	6.38E-04	3.67	27.2	0	5	8
α-Lindane	290.830	50.6	113	4.50E-05	3.99	22.5	0	0	0
Simazine	201.657	61.2	228	2.20E-08	2.28	21.4	2	5	4
β-HCH	290.830	50.6	113	4.50E-05	3.99	22.5	0	0	0
Quintozene	295.335	54.8	118.99	5.00E-05	4.16	22.7	0	2	0
γ-HCH	290.830	50.6	113	4.50E-05	3.99	22.5	0	0	0
Terbufos	288.431	53.9	-29	3.20E-04	4.37	30.7	0	5	8
Diazinon	304.345	57.5	25	9.01E-05	3.81	31.6	0	6	7
Pyrimethanil	199.252	60.9	96.3	1.65E-05	2.84	24.4	1	3	2
δ-HCH	290.830	50.6	113	4.50E-05	3.99	22.5	0	0	0
Vinclozoline	286.111	61.7	108	1.20E-07	3.19	27.3	0	3	2
Heptachlor	373.318	61.7	95	4.00E-04	5.46	29.9	0	0	0
Metalaxyl	279.332	64.4	72	5.62E-06	2.15	30.5	0	4	6
Chlorpyrifos	350.586	59.9	42	2.02E-05	4.77	30.6	0	5	6

Aldrin	364.910	60.9	104	1.20E-04	5.32	30.8	0	0	0
Fenthion	278.328	55	7	3.00E-04	3.21	28.6	0	5	5
Parathion	291.261	59.8	6	6.68E-06	3.84	28.1	0	6	6
Triadimefon	293.749	69.9	82	1.58E-08	2.77	31.3	0	4	5
Isofenphos-methyl	331.367	64.8	42	2.01E-05	3.59	34.6	1	6	8
Pendimethalin	281.308	67.5	56	9.40E-06	5.56	30.6	1	5	4
Fipronil	437.148	78.1	200	2.78E-09	4.76	32.5	1	11	2
Heptachlor epoxide	389.317	65.4	160	1.95E-05	5.47	29.8	0	1	0
Procymidone	284.138	74.2	166	1.40E-04	2.67	27.1	0	2	1
γ-Chlordane	409.779	65.3	106	9.75E-06	5.57	31.1	0	0	0
o,p'-DDE	318.025	60.7	75	6.20E-06	6.22	31.7	0	0	2
α-Chlordane	409.779	65.3	106	9.75E-06	5.57	31.1	0	0	0
Endosulfan	406.925	68.1	106	1.73E-07	3.13	31.1	0	4	0
p,p'-DDE	318.025	60.7	89	6.00E-06	6.37	31.7	0	0	2
Dieldrin	380.909	64.3	175	5.89E-06	4.88	30.7	0	1	0
o,p'-DDD	320.041	62.4	77	1.94E-06	5.39	31.6	0	0	3
Flusilazole	315.393	64.2	54	2.93E-07	3.84	34.6	0	4	4
Endrin	380.909	64.3	201	5.89E-06	4.88	30.7	0	1	0
p,p'-DDD	320.041	63.2	109	1.35E-06	5.39	31.6	0	0	3
o,p'-DDT	354.486	63.6	75	1.35E-06	5.92	33.5	0	0	2
p,p'-DDT	354.486	64.3	109	1.60E-07	5.92	33.5	0	0	2
Tebuconazole	307.818	78	105	1.30E-08	3.58	34.6	1	3	6

Bifenthrin	422.868	71.3	69	1.34E-08	7.30	43.2	0	5	6
cis-Permethrin	391.288	72.8	34	2.68E-08	7.15	41.9	0	3	7
trans-Permethrin	391.288	72.8	34	2.68E-08	7.15	41.9	0	3	7
Pyridaben	364.933	68.5	111	1.18E-06	4.73	41.7	0	3	5
Etofenprox	376.488	71.8	37	2.09E-07	7.34	44.9	0	3	9
Difenoconazole 1	406.263	76	206.96	1.82E-08	4.92	41.1	0	5	5
Difenoconazole 2	406.263	76	206.96	1.82E-08	4.92	41.1	0	5	5

Chemical and physical information was extracted from ChemSpider, which can be downloaded from http://www.chemspider.com.

Table S3 Evaluation on the recoveries of 47 pesticides in standard solution treated by different PSA amount.

		20 mg		40 mg		60 mg	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
1	Dichlorvos	94.8	2.1	99.4	6.2	94.4	2.7
2	2-Phenylphenol	92.3	2.8	87.2	5.0	84.6	5.4
3	Ethoprophos	93.0	1.7	99.5	4.1	97.2	3.1
4	Chlorpropham	92.5	0.1	95.4	1.1	94.7	2.7
5	Phorate	93.6	2.3	101.0	4.4	96.2	3.0
6	α-Lindane	94.1	1.8	98.0	0.5	91.2	2.4
7	Simazine	98.1	1.4	97.9	4.6	96.0	3.7
8	β-HCH	98.2	3.0	95.5	1.1	90.4	2.3
9	Quintozene	93.4	1.2	97.3	3.1	95.7	2.1
10	γ-HCH	94.6	1.9	98.7	1.0	97.2	2.3
11	Terbufos	94.0	2.4	96.1	1.4	100.7	2.4
12	Diazinon	100.4	3.3	97.1	0.8	101.0	1.5
13	Pyrimethanil	102.7	1.8	95.7	0.7	93.2	1.5
14	δ-HCH	98.8	3.8	93.7	4.2	85.7	2.0
15	Vinclozoline	97.4	2.6	99.0	1.2	101.3	1.1
16	Heptachlor	91.8	2.0	96.0	1.8	100.9	2.3
17	Metalaxyl	97.9	1.7	94.3	2.5	99.2	1.1
18	Chlorpyrifos	100.8	3.3	99.1	1.7	94.5	2.0
19	Aldrin	99.2	1.5	99.6	1.3	97.8	1.4
20	Fenthion	101.1	2.0	97.2	5.4	89.7	2.5
21	Parathion	96.1	1.3	91.8	3.0	94.4	4.1
22	Triadimefon	99.5	3.0	96.4	0.2	93.3	2.3
23	Isofenphos-methyl	101.4	1.9	98.2	2.8	91.3	1.1
24	Pendimethalin	97.7	4.0	95.0	3.3	97.9	0.9
25	Fipronil	98.3	3.9	97.6	6.5	87.5	0.7
26	Heptachlor epoxide	100.8	1.6	99.7	0.0	94.7	2.8
27	Procymidone	103.6	1.0	100.3	3.4	92.1	1.1
28	γ-Chlordane	101.8	4.5	97.3	6.5	93.0	1.0
29	*o,p*'-DDE	103.6	2.5	100.1	7.4	95.7	0.3
30	α-Chlordane	100.7	3.3	101.9	1.4	99.8	0.6
31	Endosulfan	101.9	0.5	99.6	5.0	97.7	0.8
32	*p,p*'-DDE	101.4	2.6	100.2	1.3	96.8	0.8
33	Dieldrin	102.4	3.3	98.6	4.7	93.4	1.7
34	*o,p*'-DDD	98.1	0.4	99.9	0.4	94.3	0.4
35	Flusilazole	100.7	2.0	96.6	4.8	98.8	0.5
36	Endrin	95.4	3.1	97.0	0.3	97.6	1.4
37	*p,p*'-DDD	99.8	4.4	97.4	1.2	98.9	1.6
38	*o,p*'-DDT	99.4	4.5	96.3	1.3	92.4	2.0
39	*p,p*'-DDT	91.9	3.3	89.7	4.5	92.9	1.4
40	Tebuconazole	96.5	3.0	94.2	0.7	84.7	1.9
41	Bifenthrin	100.2	3.6	96.1	3.9	98.0	2.1
42	*cis*-Permethrin	98.7	1.6	96.9	2.5	94.6	1.8

43	*trans*-Permethrin	102.6	2.7	95.6	4.3	99.7	0.9
44	Pyridaben	101.8	0.9	95.2	0.4	100.9	1.8
45	Etofenprox	101.3	3.9	96.4	8.3	97.8	1.2
46	Difenoconazole 1	90.9	3.5	101.8	1.6	100.1	2.1
47	Difenoconazole 2	93.5	1.5	95.8	0.5	91.8	3.3

Table S4 Qualitative analysis on the interferences in final extracts of different matrices.

Matrix	Co-extract	Retention time (min)	Molecular Formula	Log P
Apple	Ethyl palmitate	13.94	$C_{18}H_{36}O_2$	8.15
	Ethyl Linoleate	16.89	$C_{20}H_{36}O_2$	8.17
	Ethyl Oleate	17.00	$C_{20}H_{38}O_2$	8.69
	Hexatriacontane	26.89	$C_{36}H_{74}$	19.88
	Tetratriacontyl trifluoroacetate	28.76	$C_{36}H_{69}F_3O_2$	18.03
Orange	Nonacosane	18.64	$C_{29}H_{60}$	16.17
	Eicosane	19.27	$C_{20}H_{42}$	11.38
	Tetratetracontane	22.48	$C_{44}H_{90}$	24.14
	2-Methylhexacosane	25.97	$C_{27}H_{56}$	14.92
	Squalene	26.08	$C_{30}H_{50}$	13.09
Honey	2-Octylfuran	7.96	$C_{12}H_{20}O$	5.56
	17-Pentatriacontene	24.74	$C_{35}H_{70}$	18.83
	2-Methylhexacosane	25.97	$C_{27}H_{56}$	14.92
Leek	Neophytadiene	11.15	$C_{20}H_{38}$	9.83
	Methyl linoleate	15.80	$C_{19}H_{34}O_2$	7.64
	Phytol	15.97	$C_{20}H_{40}O$	8.66
	Palmitone	24.97	$C_{31}H_{62}O$	14.72

(The co-extracted compounds were identified by matching with the NIST mass spectral library, and the chemical and physical information was extracted from ChemSpider, which can be downloaded from http://www.chemspider.com.)

Table S5 Correlations between the matrix effects (ME%) of 47 pesticides with physical and chemical characteristics of pesticides in apple, orange, honey and leek matrices.

Physical and chemical property	Apple	Orange	Honey	Leek
Molecular weight	-.0.387**	-0.524**	-0.214	-0.646**
Enthalpy of vaporization	0.0093	-0.214	-0.082	-0.565**
Melting point	-0.026	-0.082	-0.010	-0.184
Vapor pressure	0.073	0.100	-0.330*	0.413**
Log P	-0.244	-0.330*	-0.450**	-0.523**
Polarizability	-0.074	-0.450**	0.458**	-0.762**
Hydrogen bond donor count	0.455**	0.458**	0.213	0.368*
Hydrogen bond accepter count	0.398	0.213	-0.010	0.022
Rotatable bond count	0.256	-0.010	0.649**	-0.221

* and ** signify the statistically significant difference ($p < 0.05$, $p < 0.01$) between ME% and physical or chemical properties.

Table S6 Retention time (RT), quantification ion (Quant.), qualifier ion (Qual.), linearity range, regression equation and the R^2 of pesticides.

	Pesticide	RT	Quant.	Qual.1	Qual.2	Linearity range (ng/mL)	Regression equation	R^2
	TCMX	8.26	**244**	207	209		-	
	TEB-d_9	21.14	**250**	163	252		-	
	TPP	21.66	**325**	326	233		-	
1	Dichlorvos	4.19	**109**	185	220	5-1000	Y = 0.4785698X – 0.02478608	0.9993
2	2-Phenylphenol	7.13	**170**	169	141	5-1000	Y = 2.197143X + 0.01198156	0.9998
3	Ethoprophos	8.70	**158**	200	242	5-1000	Y = 0.103628X + 0.003.345675	0.9998
4	Chlorpropham	9.07	**213**	171	154	20-1000	Y = 0.2141914X – 0.01162804	0.9990
5	Phorate	9.64	**260**	121	231	5-1000	Y = 0.2371548X + 0.005024683	0.9996
6	α-HCH	9.83	**219**	183	181	5-1000	Y = 0.2966105X + 0.01679804	0.9994

7	Simazine	10.45	**201**	186	173	20-1000	Y = 0.2499393X – 0.003637961	0.9993
8	β-HCH	10.64	**219**	183	181	5-1000	Y = 0.23763X + 0.02596978	0.9998
9	Quintozene	10.74	**295**	237	249	20-1000	Y = 0.08893083X – 0.000558777	0.9995
10	γ-HCH	10.89	**219**	183	181	5-1000	Y = 0.2333408X + 0.009924779	0.9996
11	Terbufos	11.03	**231**	153	288	5-1000	Y = 0.8088757X + 0.01836114	0.9998
12	Diazinon	11.23	**304**	276	289	10-1000	Y = 0.1953064X + 0.006969327	0.9997
13	Pyrimethanil	11.40	**198**	199	200	5-1000	Y = 1.437197X – 0.03244034	0.9997
14	δ-HCH	11.89	**219**	217	181	5-1000	Y = 0.2119227X + 0.002109898	0.9997
15	Vinclozoline	12.99	**285**	212	198	5-1000	Y = 0.1511521X + 0.001312981	0.9996
16	Heptachlor	13.37	**272**	274	270	5-1000	Y = 0.2780584X + 0.0065848	0.9999
17	Metalaxyl	13.37	**206**	249	279	10-1000	Y = 0.1230431X + 0.003219664	0.9995
18	Chlorpyrifos	14.54	**314**	258	197	10-1000	Y = 0.2084435X + 0.005182304	0.9999
19	Aldrin	14.63	**263**	265	293	5-1000	Y = 0.2159062X + 0.01150307	0.9996
20	Fenthion	14.71	**278**	279	94	5-1000	Y = 0.7613077X – 0.01092909	0.9999

21	Parathion	14.82	**291**	263	235	50-1000	Y = 0.08963665X – 0.005992036	0.9995
22	Triadimefon	14.93	**208**	210	181	10-1000	Y = 0.3125326X + 0.002440866	0.9997
23	Isofenphos-methyl	15.55	**199**	241	121	5-1000	Y = 0.655928X + 0.004639707	0.9998
24	Pendimethalin	15.73	**252**	281	162	10-1000	Y = 0.2836383X – 0.01630229	0.9990
25	Fipronil	15.96	**367**	369	351	5-1000	Y = 0.3361328X – 0.00719203	0.9999
26	Heptachlor epoxide	16.02	**353**	355	351	5-1000	Y = 0.3502664X + 0.01397809	0.9996
27	Procymidone	16.45	**283**	285	255	10-1000	Y = 0.2961204X + 0.003592299	0.9997
28	γ-Chlordane	16.88	**373**	375	377	10-1000	Y = 0.5199582X + 0.01810202	0.9995
29	*o,p*'-DDE	17.01	**246**	318	176	5-1000	Y = 0.9288046X + 0.03636354	0.9995
30	α-Chlordane	17.35	**373**	375	377	10-1000	Y = 0.57448604X + 0.003383311	0.9994
31	Endosulfan	17.35	**241**	277	339	10-1000	Y = 0.113719X + 0.00532571	0.9993
32	*p,p*'-DDE	18.20	**318**	316	246	5-1000	Y = 0.4566745X + 0.005864907	0.9999
33	Dieldrin	18.33	**263**	277	380	10-1000	Y = 0.1280253X + 0.1503029	0.9962
34	*o,p*'-DDD	18.43	**235**	237	165	5-1000	Y = 1.033868X + 0.02824158	0.9998

35	Flusilazole	18.44	**233**	206	315	20-1000	Y = 0.09631975X – 0.003997964	0.9993
36	Endrin	19.08	**263**	317	345	10-1000	Y = 0.1210101X + 0.003666413	0.9998
37	*p*,*p*'-DDD	19.79	**235**	237	165	5-1000	Y = 0.8527327X + 0.002550006	0.9994
38	*o*,*p*'-DDT	19.82	**235**	237	165	5-1000	Y = 0.6891307X – 0.0024842	0.9998
39	*p*,*p*'-DDT	21.08	**235**	237	246	5-1000	Y = 0.5102272X – 0.020245	0.9997
40	Tebuconazole	21.60	**125**	250	252	10-1000	Y = 0.5165352X – 0.03059378	0.9994
41	Bifenthrin	22.91	**181**	166	165	5-1000	Y = 2.077259X + 0.04815913	0.9996
42	*cis*-Permethrin	25.70	**183**	184	165	5-1000	Y = 0.1985953X + 0.0003587302	0.9998
43	*trans*-Permethrin	25.89	**183**	184	165	5-1000	Y = 0.8521885X + 0.002094915	0.9999
44	Pyridaben	25.90	**147**	309	364	10-1000	Y = 0.08686695X + 0.00002591288	0.9997
45	Etofenprox	27.27	**163**	376	183	10-1000	Y = 0.0754001X – 0.0002638079	0.9995
46	difenoconazole 1	28.59	**323**	325	265	20-1000	Y = 0.05348864X – 0.0036504	0.9993
47	Difenoconazole 2	28.68	**323**	325	265	20-1000	Y = 0.1340935X – 0.01637022	0.9993

Table S7 Concentrations (mg kg^{-1}) of 47 pesticides in plant-derived foods.

Pesticides	Apple	Orange	Honey	Leek
Dichlorvos	< MLOQ	< MLOQ	< MLOQ	< MLOQ
2-Phenylphenol	0.004	0.006	< MLOQ	< MLOQ
Ethoprophos	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Chlorpropham	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Phorate	< MLOQ	< MLOQ	< MLOQ	< MLOQ
α-HCH	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Simazine	< MLOQ	< MLOQ	< MLOQ	< MLOQ
β-HCH	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Quintozene	< MLOQ	< MLOQ	0.008	0.010
γ-HCH	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Terbufos	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Diazinon	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Pyrimethanil	< MLOQ	< MLOQ	< MLOQ	< MLOQ
δ-HCH	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Vinclozoline	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Heptachlor	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Metalaxyl	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Chlorpyrifos	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Aldrin	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Fenthion	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Parathion	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Triadimefon	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Isofenphos-methyl	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Pendimethalin	< MLOQ	< MLOQ	< MLOQ	< MLOQ

Fipronil	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Heptachlor epoxide	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Procymidone	< MLOQ	< MLOQ	< MLOQ	< MLOQ
γ-Chlordane	< MLOQ	< MLOQ	< MLOQ	< MLOQ
o,p'-DDE	< MLOQ	< MLOQ	< MLOQ	< MLOQ
α-Chlordane	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Endosulfan	< MLOQ	< MLOQ	< MLOQ	< MLOQ
p,p'-DDE	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Dieldrin	< MLOQ	< MLOQ	< MLOQ	< MLOQ
o,p'-DDD	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Flusilazole	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Endrin	< MLOQ	< MLOQ	< MLOQ	< MLOQ
p,p'-DDD	< MLOQ	< MLOQ	< MLOQ	< MLOQ
o,p'-DDT	< MLOQ	< MLOQ	< MLOQ	< MLOQ
p,p'-DDT	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Tebuconazole	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Bifenthrin	0.001	< MLOQ	< MLOQ	< MLOQ
cis-Permethrin	0.005	< MLOQ	< MLOQ	< MLOQ
trans-Permethrin	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Pyridaben	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Etofenprox	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Difenoconazole 1	< MLOQ	< MLOQ	< MLOQ	< MLOQ
Difenoconazole 2	< MLOQ	< MLOQ	< MLOQ	< MLOQ

Table S8 Regression equation and the R^2 of 47 pesticides in spiked apple, orange, honey and leek matrices.

	Pesticide	Apple		Orange		Honey		Leek	
		Regression equation	R^2	Regression equation	R^2	Regression equation	R^2	Regression equation	R^2
1	Dichlorvos	Y = 0.4828024X + 1.099865e-002	0.9985	Y = 0.5183879X + 2.343018e-002	0.9998	Y = 0.8600298X + 0.1302792	0.9988	Y = 1.108796X - 0.1193928	0.9960
2	2-Phenylphenol	Y = 2.591725X + 0.2060057	0.9995	Y =2.836736X + 0.585162	0.9996	Y = 4.466865X + 1.042498	0.9995	Y = 4.836842X - 0.5386015	0.9956
3	Ethoprophos	Y = 9.596433e-002X + 4.535824e-003	0.9986	Y = 0.1026748X + 6.987447e-003	0.9994	Y = 0.1301003X + 1.152159e-002	0.9999	Y = 0.1588949X - 1.359273e-002	0.9975
4	Chlorpropham	Y = 0.2261683X + 1.949207e-003	0.9991	Y = 0.2401865X + 1.090387e-002	0.9998	Y = 0.3115046X + 4.62661e-003	0.9999	Y = 0.3606004X - 2.794612e-002	0.9982
5	Phorate	Y = 0.2257425X + 4.42716e-003	0.9982	Y = 0.256827X + 2.333696e-003	0.9994	Y = 8.261067e-002X - 2.079347e-002	0.9892	Y = 0.3698496X - 2.01954e-002	0.9995
6	Simazine	Y = 0.2894193X + 7.341053e-003	0.9995	Y = 0.3072494X + 2.220866e-002	0.9996	Y = 0.2369185X + 0.1670373	0.9999	Y = 0.4687326X - 3.631309e-002	0.9981
7	alpha.-Lindane	Y = 0.2498324X + 5.651927e-003	0.9988	Y = 0.2930165X + 1.637438e-002	0.9996	Y = 0.3567291X + 2.513075e-002	0.9989	Y = 0.4720254X - 2.836617e-002	0.9991
8	beta.-HCH	Y = 0.2133201X + 6.725025e-003	0.9991	Y = 0.2274652X + 1.3027e-002	0.9994	Y = 0.2517053X + 7.368086e-002	0.9993	Y = 0.3284278X - 1.852538e-002	0.9990
9	r-HCH	Y = 0.1963785X + 4.007817e-003	0.9990	Y = 0.2305186X + 2.17853e-002	0.9994	Y = 0.2568114X + 0.1008234	0.9992	Y = 0.3633795X - 3.051646e-002	0.9976
10	d-HCH	Y = 0.1807701X + 2.226939e-002	0.9996	Y = 0.2013717X + 3.177244e-002	0.9995	Y = 0.2070253X + 0.9192887	0.9986	Y = 0.2960838X + 2.778197e-004	0.9986
11	Quintozene	Y = 8.764812e-002X + 4.966724e-003	0.9992	Y = 0.1116048X + 5.944601e-003	0.9997	Y = 0.160041X + 1.27073e-002	0.9992	Y = 0.1844179X - 1.07979e-002	0.9992
12	Terbufos	Y = 0.7263953X + 8.555584e-003	0.9989	Y = 0.8290994X + 3.646813e-002	0.9996	Y = 0.2038094X - 2.54301e-002	0.9951	Y = 1.229368X - 0.105238	0.9976
13	Diazinon	Y = 0.2048433X + 3.075625e-003	0.9996	Y = 0.2003195X - 4.679018e-004	0.9974	Y = 0.2136927X + 4.444291e-003	0.9997	Y = 0.2476579X - 1.560853e-002	0.9981
14	Pyrimethanil	Y = 1.664364X + 3.765675e-002	0.9993	Y = 1.815489X + 8.553036e-002	0.9996	Y = 1.71104X + 3.256161e-002	0.9993	Y = 2.821292X - 0.1472899	0.9994
15	Vinclozoline	Y = 0.1557556X + 2.046025e-003	0.9997	Y = 0.1526349X + 6.476869e-003	0.9996	Y = 0.1712175X + 6.34415e-003	0.9992	Y = 0.1901345X - 8.010438e-003	0.9993
16	Heptachlor	Y = 0.2408087X - 1.103505e-003	0.9984	Y = 0.2832373X + 2.021984e-002	0.9990	Y = 0.3617846X + 2.840645e-002	0.9988	Y = 0.466284X - 4.729808e-002	0.9966
17	Heptachlor epoxide	Y = 0.2828344X + 8.275054e-003	0.9981	Y = 0.3082104X + 2.026191e-002	0.9989	Y = 0.3368008X + 2.209285e-002	0.9995	Y = 0.4111507X - 1.48232e-002	0.9997
18	Metalaxyl	Y = 0.1099963X - 3.880618e-004	0.9998	Y = 0.1127066X + 4.39988e-003	0.9997	Y = 0.1151862X + 0.4175739	0.9947	Y = 0.1492795X - 7.486858e-003	0.9990
19	Chlorpyrifos	Y = 0.2094927X + 3.400552e-003	0.9994	Y = 0.2140187X + 5.253109e-003	0.9991	Y = 0.2398577X + 1.030998e-002	0.9995	Y = 0.2829274X - 1.975162e-002	0.9987
20	Aldrin	Y = 0.1840159X + 3.340505e-003	0.9990	Y = 0.2152992X + 1.831614e-002	0.9992	Y = 0.2599307X + 1.754583e-002	0.9993	Y = 0.3258195X - 1.689124e-002	0.9993
21	Fenthion	Y = 0.7437064X + 7.427344e-003	0.9997	Y = 0.7815892X + 1.869944e-002	0.9989	Y = 0.1448981X - 3.786673e-003	0.9950	Y = 1.006312X - 5.593081e-002	0.9990
22	Parathion	Y = 0.121982X - 9.03517e-003	0.9969	Y = 0.1424915X - 1.151111e-002	0.9894	Y = 0.217934X + 4.461415e-003	0.9999	Y = 0.1971949X - 1.445188e-002	0.9980
23	Triadimefon	Y = 0.2820919X - 7.128898e-004	0.9990	Y = 0.2904481X + 1.838252e-002	0.9993	Y = 0.2926582X + 4.113894e-002	0.9998	Y = 0.4074872X - 1.892433e-002	0.9996
24	Isofenphos-methyl	Y = 0.5647097X - 7.92334e-003	0.9999	Y = 0.6139269X + 3.773965e-002	0.9993	Y = 0.5729075X + 4.445425e-002	0.9998	Y = 0.8379323X - 2.188045e-002	0.9996
25	Pendimethalin	Y = 0.3641874X - 2.322678e-002	0.9975	Y = 0.3990776X - 2.006709e-002	0.9986	Y = 0.5613608X + 1.289077e-002	0.9999	Y = 0.5760302X - 4.279308e-002	0.9979
26	Fipronil	Y = 0.3382864X - 3.679045e-003	0.9999	Y = 0.3479446X + 1.393463e-003	0.9996	Y = 0.3793273X + 1.614153e-003	0.9997	Y = 0.4032667X - 1.586271e-002	0.9992
27	Procymidone	Y = 0.290144X + 4.620503e-003	0.9997	Y = 0.2872452X + 1.340636e-002	0.9998	Y = 0.3041272X + 2.5646e-002	0.9996	Y = 0.3478515X - 1.217223e-002	0.9995
28	g-Chlordane	= 4.296461X + 2.194871e-003	0.9994	Y = 4.824855X + 2.814088e-002	0.9996	Y = 5.510658X + 2.370366e-002	0.9996	Y = 6.619267X - 2.903335e-002	0.9995
29	a-Chlordane	Y = 6.296495e-002X + 1.180386e-003	0.9994	Y = 6.690884e-002X + 7.964503e-003	0.9995	Y = 7.772261e-002X + 7.51046e-003	0.9993	Y = 8.653045e-002X - 8.490699e-004	0.9993
30	o,p'-DDE	Y = 0.8151083X + 1.862052e-002	0.9992	Y = 0.8830543X + 6.790003e-002	0.9993	Y = 1.00552X + 5.535485e-002	0.9990	Y = 1.1842X - 4.674922e-002	0.9996
31	p,p'-DDE	Y = 0.4351963X + 9.774086e-003	0.9990	Y = 0.4534243X + 2.429448e-002	0.9998	Y = 0.4941892X + 1.299032e-002	0.9998	Y = 0.512547X - 1.408353e-002	0.9997

32	o,p'-DDD	Y = 0.8937484X + 1.39848e-002	0.9990	Y = 0.9630849X + 6.570231e-002	0.9991	Y = 1.031968X + 7.92809e-003	0.9997	Y = 1.130138X - 1.047544e-002	0.9997
33	p,p'-DDD	Y = 0.7869428X - 4.268306e-003	0.9998	Y = 0.8462056X + 1.683978e-003	0.9992	Y = 0.9531636X + 4.140768e-002	0.9997	Y = 1.100065X - 5.207595e-002	0.9993
34	o,p'-DDT	Y = 0.6553986X - 1.154311e-002	0.9991	Y = 0.6917498X + 4.152971e-002	0.9991	Y = 0.7797451X + 1.222718e-002	0.9996	Y = 0.8326435X - 2.515772e-002	0.9997
35	p,p'-DDT	Y = 0.5394114X - 3.021643e-002	0.9993	Y = 0.5729122X + 1.039737e-002	0.9997	Y = 0.6549666X + 1.580869e-002	0.9996	Y = 0.7788066X - 5.270931e-002	0.9991
36	Endosulfan-1	Y = 9.415556e-002X + 1.423593e-002	0.9990	Y = 0.1031808X + 1.374516e-002	0.9979	Y = 0.1142805X + 6.887063e-003	0.9992	Y = 0.1433967X + 9.909676e-003	0.9993
37	Dieldrin	Y = 8.132736e-002X + 4.849355e-004	0.9988	Y = 8.81843e-002X + 1.058916e-002	0.9990	Y = 0.1019847X + 3.004728e-003	0.9993	Y = 0.1186089X - 1.728503e-003	0.9996
38	Endrin	Y = 0.1014699X - 8.263378e-004	0.9978	Y = 0.1161148X + 1.105303e-002	0.9971	Y = 0.1298771X + 6.126448e-003	0.9994	Y = 0.1657887X - 7.553933e-003	0.9995
39	Flusilazole	Y = 9.09546e-002X + 1.78541e-003	0.9991	Y = 8.199674e-002X + 1.426411e-003	0.9996	Y = 8.066e-002X - 1.986706e-003	0.9992	Y = 8.910267e-002X - 1.865103e-003	0.9998
40	Tebuconazole	Y = 0.5603725X - 2.033382e-002	0.9996	Y = 0.5722633X + 1.865024e-002	0.9994	Y = 0.5635538X + 3.477418e-003	0.9999	Y = 0.6446176X - 6.183693e-003	0.9999
41	Bifenthrin	Y = 1.739665X + 2.458311e-002	0.9990	Y = 1.708421X + 0.2943396	0.9885	Y = 1.902891X + 8.760693e-002	0.9994	Y = 2.05729X - 2.961614e-002	0.9998
42	Permethrin-1	Y = 0.1734583X + 1.193438e-002	0.9992	Y = 0.1619716X + 2.107225e-002	0.9966	Y = 0.1910168X + 2.747654e-003	0.9995	Y = 0.1871716X + 1.360615e-003	1.0000
43	Permethrin-2	Y = 0.7713714X - 1.101983e-002	0.9990	Y = 0.7020632X + 0.1146887	0.9829	Y = 0.8100916X + 1.380749e-002	0.9999	Y = 0.8196394X + 9.53706e-004	1.0000
44	Pyridaben	Y = 9.18147e-002X - 1.452594e-004	0.9998	Y = 6.78817e-002X + 6.68343e-003	0.9938	Y = 9.469913e-002X - 8.748421e-003	0.9960	Y = 5.716526e-002X + 4.999231e-003	0.9992
45	Etofenprox	Y = 7.304444e-002X + 6.071801e-003	0.9994	Y = 6.762157e-002X + 1.002958e-003	0.9972	Y = 9.045719e-002X - 3.780259e-003	0.9987	Y = 3.783463e-002X + 6.393394e-003	0.9932
46	Difenoconazole 1	Y = 7.122936e-002X - 8.471618e-003	0.9978	Y = 6.045877e-002X + 4.614969e-003	0.9960	Y = 8.270136e-002X - 3.557476e-003	0.9996	Y = 6.965197e-002X + 2.042378e-003	0.9997
47	Difenoconazole 2	Y = 0.1247075X - 1.147842e-002	0.9990	Y = 0.1318726X + 1.056394e-003	0.9989	Y = 0.1662166X - 1.969337e-002	0.9993	Y = 0.1401255X - 1.230822e-003	0.9998

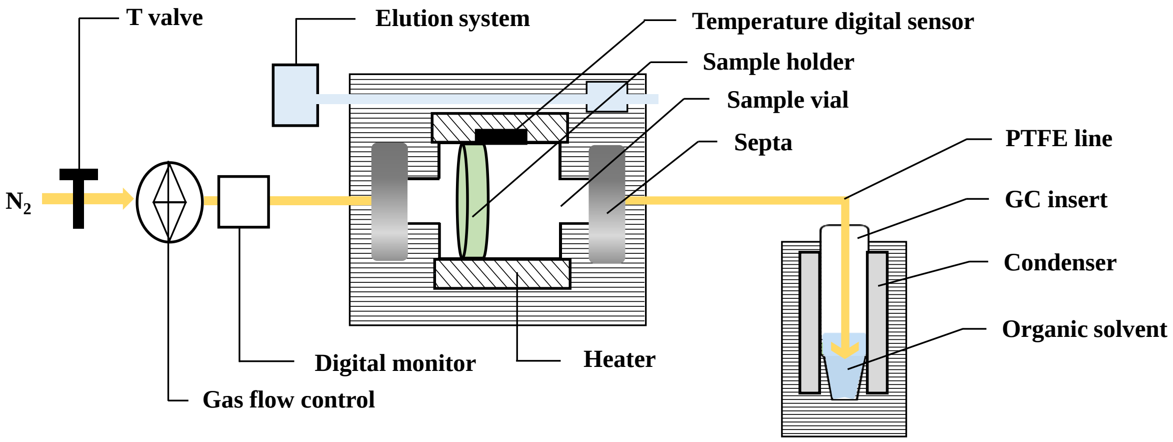

Fig S1 Schematic diagram of the GLME extraction system.

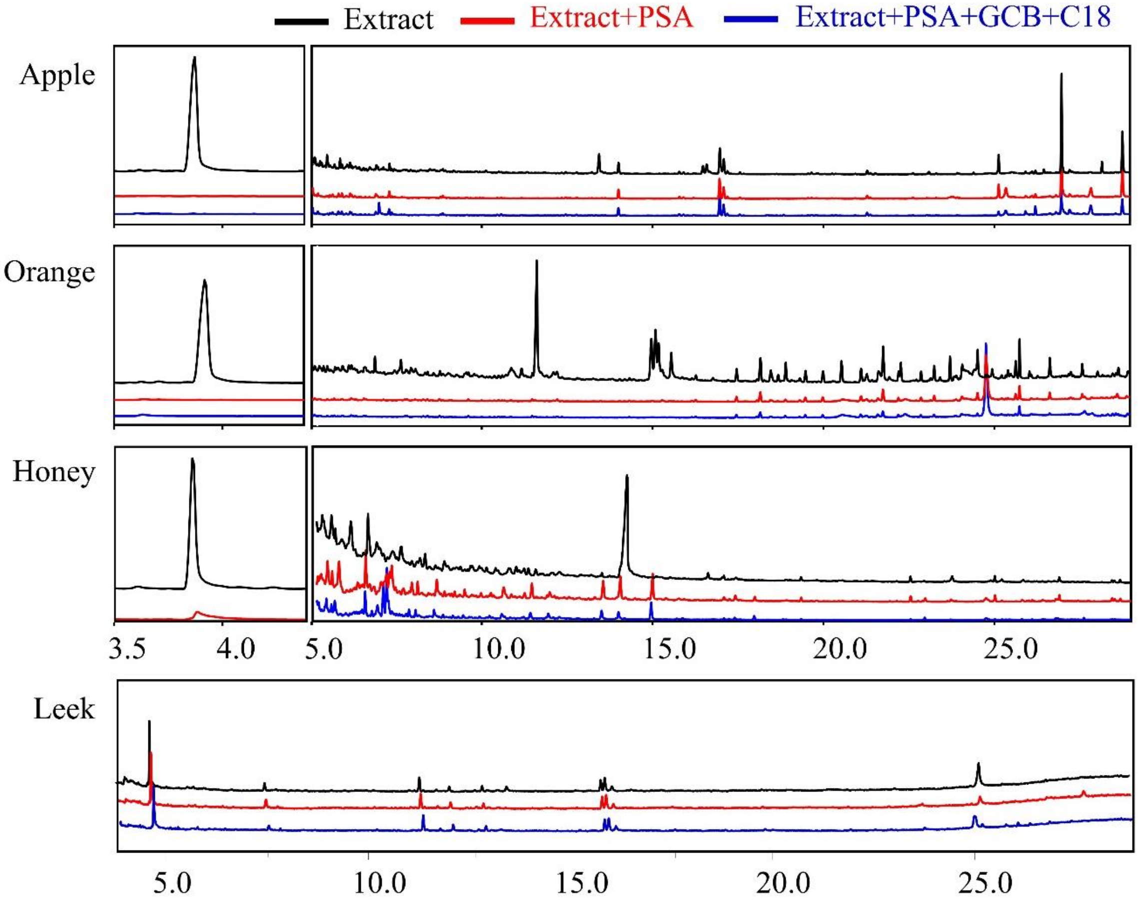

Fig S2 Chromatograms of GC-MS operated in SCAN mode that demonstrated the distinctive clean up effects by using PSA, GCB and C18 in the extracts of different matrices (apple, orange, honey and leek).

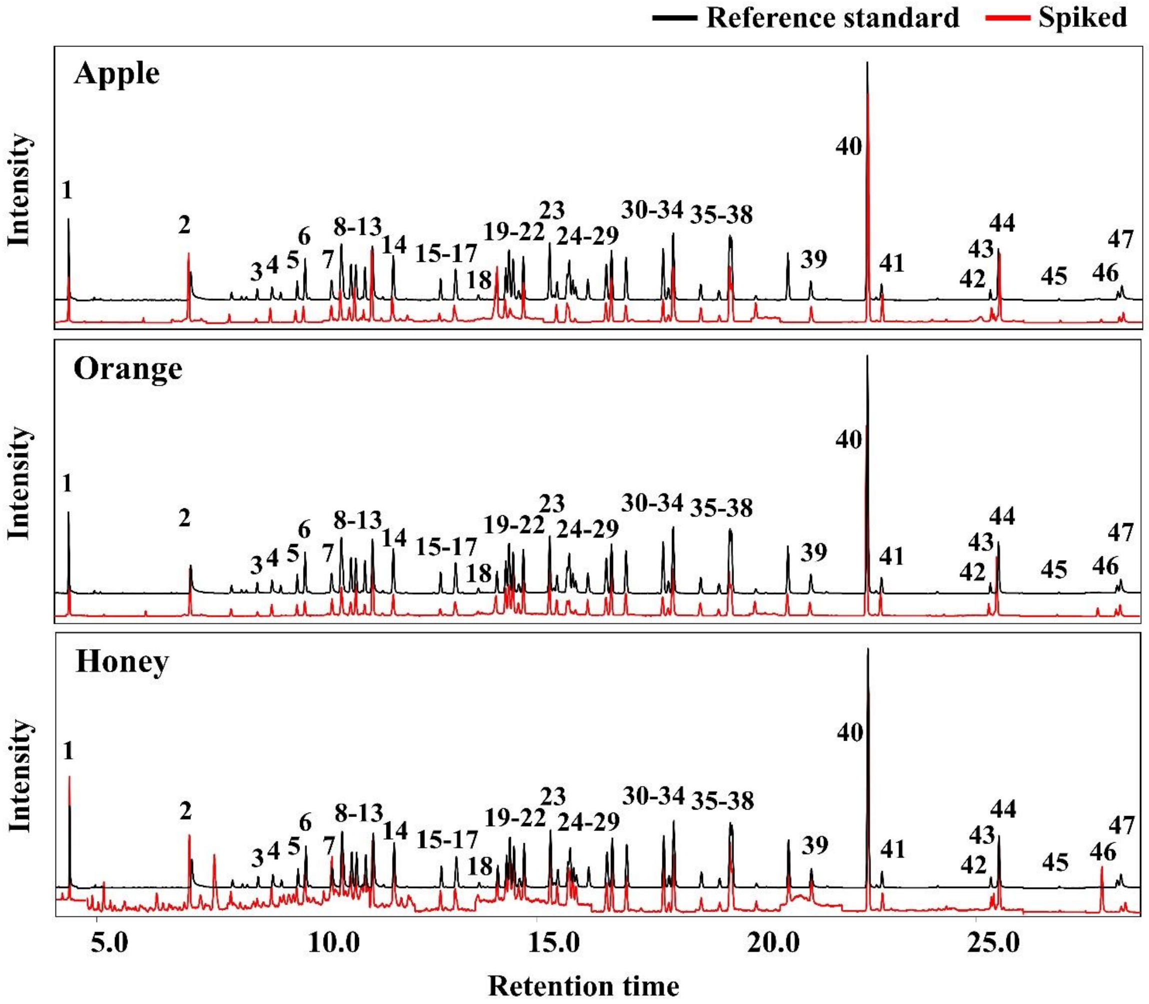

Fig. S3 SIM chromatograms showing peaks of 47 pesticides in reference standard (black) and spiked extracts from different matrices (red) (peaks were numbered according to the pesticides listed in Table 2).

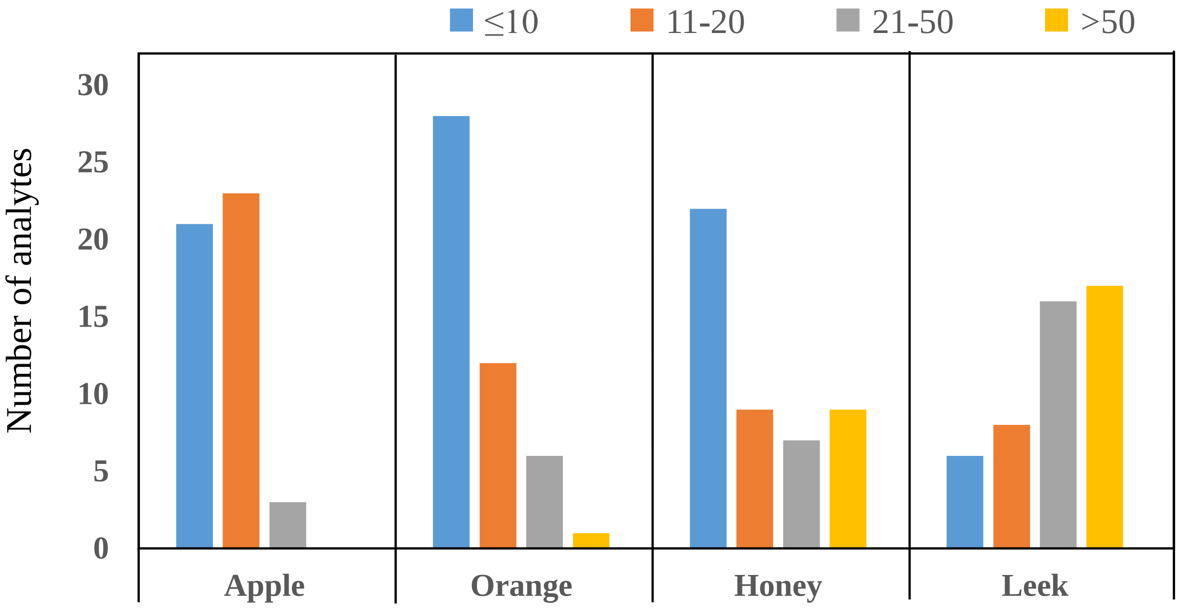

Fig. S4 Comparison of the matrix effect (ME%) for pesticides in different foods of plant origin, where ME% ≤ 10: no matrix effect; 11 – 20: low matrix effect; 21– 50: medium matrix effect and >50: high matrix effect.

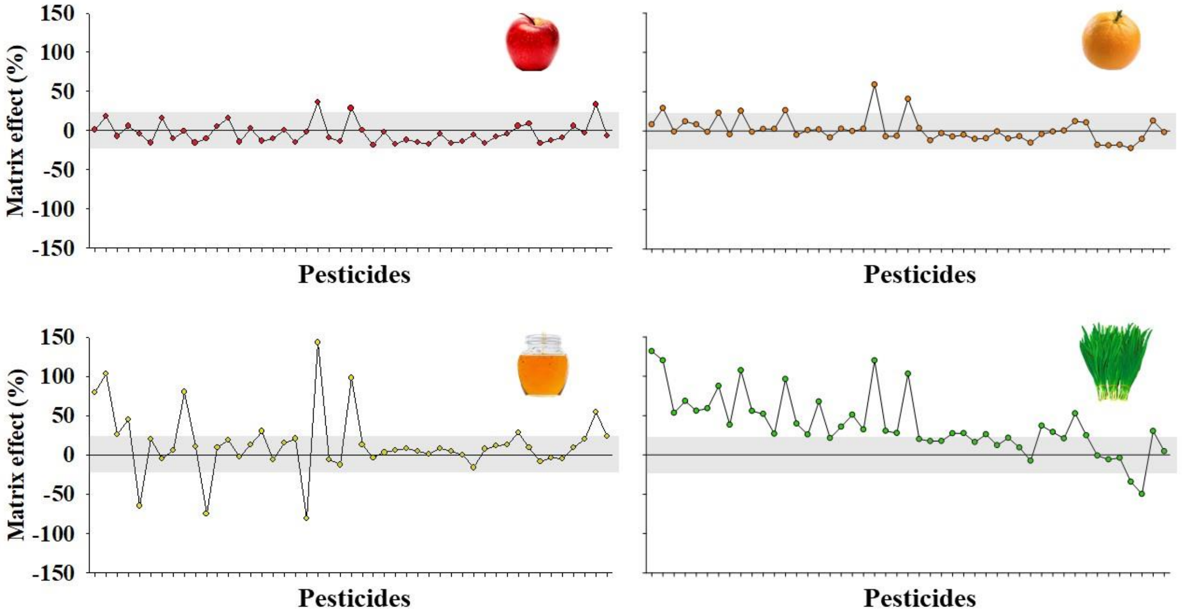

Fig. S5 Overview of matrix effects (ME%) for multi-class pesticides in apple, orange, honey and leek. (Grey zone depicts the ME% range of ±20%)

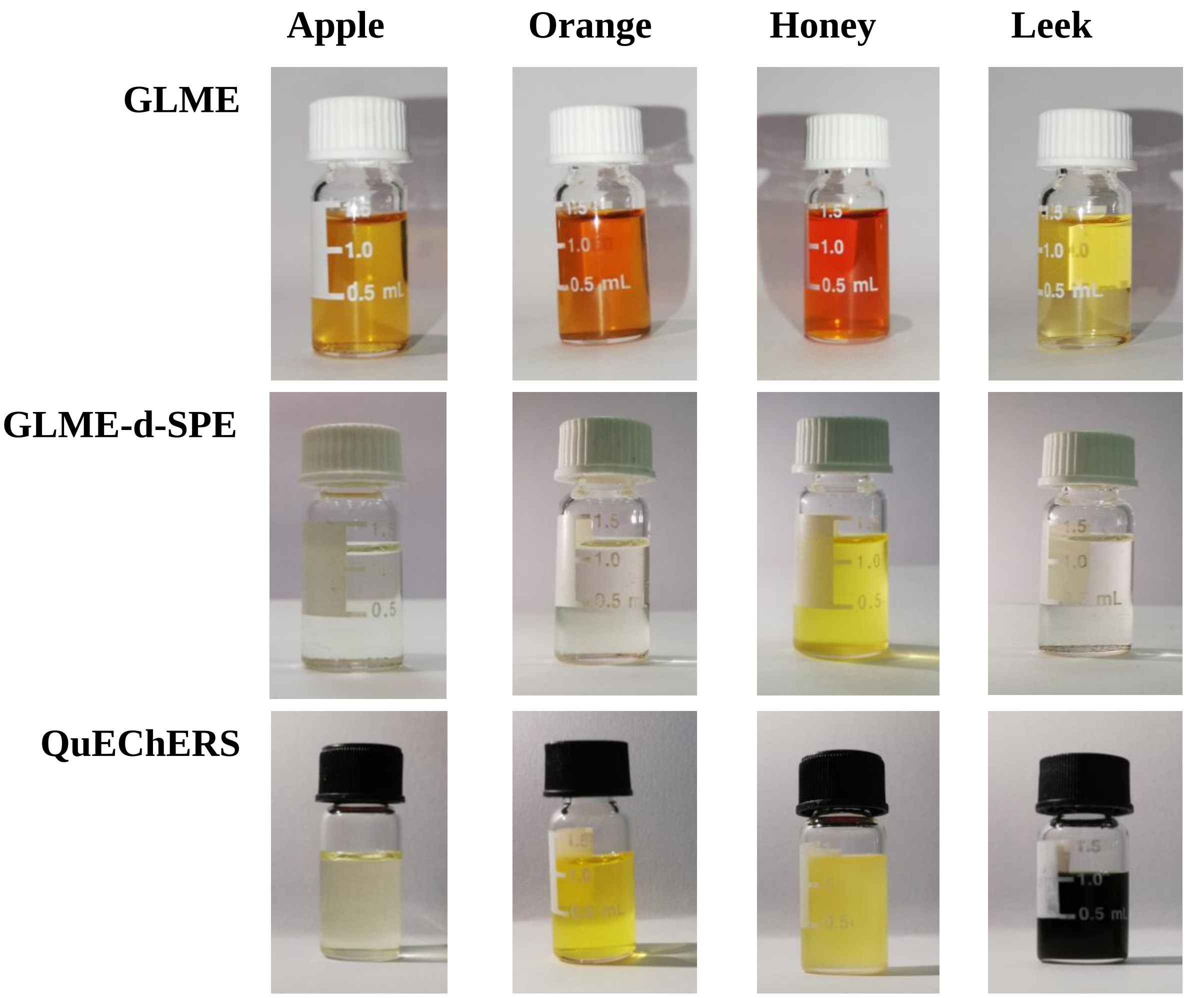

Fig. S6 A diagram showing the differences in clean-up effect by using different methods (GLME, GLME-d-SPE and QuEChERS).