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QuEChERS Method Combined with Gas- and Liquid-Chromatography High Resolution Mass Spectrometry to Screen and Confirm 237 Pesticides and Metabolites in Cottonseed Hull

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Abstract: Cottonseed hull is a livestock feed with large daily consumption. If pesticide residues exceed the standard, it is easy for them to be introduced into the human body through the food chain, with potential harm to consumer health. A method for multi-residue analysis of 237 pesticides and their metabolites in cottonseed hull was developed by gas-chromatography and liquid-chromatography time-of-flight mass spectrometry (GC-QTOF/MS and LC-QTOF/MS). After being hydrated, a sample was extracted with 1% acetic acid in acetonitrile, then purified in a clean-up tube containing 400 mg $MgSO_4$, 100 mg PSA, and 100 mg C18. The results showed that this method has a significant effect in removing co-extracts from the oily matrix. The screening detection limit (SDL) was in the range of 0.2–20 μg/kg, and the limit of quantification (LOQ) was in the range of 0.2–20 μg/kg. The recovery was verified at the spiked levels of 1-, 2-, and 10-times LOQ (n = 6), and the 237 pesticides were successfully verified. The percentages of pesticides with recovery in the range of 70–120% were 91.6%, 92.8%, and 94.5%, respectively, and the relative standard deviations (RSDs) of all pesticides were less than 20%. This method was successfully applied to the detection of real samples. Finally, this study effectively reduced the matrix effect of cottonseed hull, which provided necessary data support for the analysis of pesticide residues in oil crops.

Keywords: QuEChERS; gas-chromatography high resolution mass spectrometry; liquid-chromatography high resolution mass spectrometry; pesticide residues; cottonseed hull

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1. Introduction

The composition of cottonseed hull is similar to that of soybean concentrate, with a high content of cellulose that can enhance the digestive systems of ruminants. Cottonseed hull has been widely used as an alternative feed for ruminants, due to its low price, easy availability, and excellent mixing performance [1–3]. The excessive and illegal use of pesticides during forage planting makes it easy for pesticides to enter the food chain and accumulate in animal adipose tissue [4], and human consumers may indirectly experience food safety problems through contact with livestock products. The composition of the oily matrix is complex: in addition to fat, it contains polysaccharides, proteins, pigments, and other substances. In the process of residue analysis, problems such as matrix enhancement, matrix inhibition, and retention-time shifts may occur in the detection of pesticides, which

will hinder the detection of target compounds [5,6]. Therefore, it is urgent to develop a detection technique for the oily matrix to solve these problems.

The analysis of pesticide residue usually includes the following steps: (1) extraction of the target compound; (2) removal of interference from the extract; and (3) qualitative and quantitative detection of the target compound [4]. Lipophilic pesticides tend to be concentrated in fat. Improper pretreatment will affect the detection sensitivity, recovery, and sample throughput [7]. The current pretreatment methods for plant-derived oil substrates mainly include dispersion liquid-liquid micro-extraction (DLLME) [8], matrix solid phase dispersion (MSPD) [9,10], low temperature fat precipitation (LTFP) [11], solid phase extraction (SPE) [5], and QuEChERS [12–16]. The QuEChERS method requires fewer reagent consumables and short pretreatment time, so it is accepted by more and more experimenters [17]. Theurillat et al. established the QuEChERS method to determine the residues of various pesticides and verified the method for 176 pesticides in six oily matrices [12]. Rutkowska et al. investigated the matrix effect and recovery of four seed samples of cress, fennel, flax, and hemp. The final method verified 248 pesticides, and the LOQs reached 0.005 mg/kg [14]. Banerjee et al. used the QuEChERS method to analyze more than 220 pesticide residues in sesame seeds. This method can effectively reduce the interference of the matrix effect by freezing and degreasing at −80 °C and then purifying the oil.

The current trend of separation science is to develop new chromatographic mass spectrometry methods that can detect multiple compounds at the same time after a single injection, thereby reducing analysis time and cost [18]. The current detection technology for the detection of pesticide residues in oily matrices is mainly triple quadrupole mass spectrometry (MS/MS) [13,19–21]. The data was collected according to the specific nucleocytoplasmic ratio of the specified compound, but other compounds that were not in the list could not be identified. When analyzing a large number of compounds, the sensitivity and selectivity are limited. Due to their high resolution, precise mass accuracy, outstanding full-scan sensitivity, and complete mass spectrometry information, high-resolution mass spectrometry (HRMS), such as time-of-flight mass spectrometry (TOF/MS) and quadrupole Orbitrap mass spectrometry (Obitrap/MS), can be used without additional sample injection. Under retrospective analysis, with these advantages, HRMS has been widely used in the field of food analysis [22,23]. Lehotay et al. used GC-TOF to analyze 34 pesticides in flaxseed, dough, and peanuts [15]. Amadeo et al. used GC-QTOF to verify 166 pesticide residues in avocados and almonds [24].

To ensure the safety of livestock feed and to prevent pesticide residues from being introduced into the human body through the food chain, this work established a QuEChERS multi-residue analysis method, and used GC- and LC-QTOF/MS techniques to verify 237 pesticides in cottonseed hull. By optimizing the hydration volume, extraction solvent, salting-out agent, and clean-up sorbents, the influence of the matrix effect was reduced and the pesticide recovery was optimized. Finally, this method was successfully applied to the analysis of actual samples, providing data support for the risk of pesticide residues in oily substrate monitoring.

2. Materials and Methods

2.1. Chemicals and Reagents

Pesticide standards (purity $\geq$ 98%) were obtained from Tianjin Alta Scientific (Tianjin, China). Sodium chloride, magnesium sulfate, and sodium sulfate (analytical purity) were obtained from Tianjin Fuchen Chemical Reagent Ltd. (Tianjin, China). Primary secondary amine (PSA) and C18 were purchased from Agilent Technologies (Santa Clara, CA, USA). Methanol, acetonitrile, and toluene (chromatographic purity) were obtained from Anpel Laboratory Technology (Shanghai, China). Formic acid and ammonium acetate (mass spectrometry grade) were obtained from Honeywell (Muskegon, MI, USA).

2.2. Apparatus

HPLC-QTOF/MS Agilent 1290 and Agilent 6550 equipped with Agilent Dual Jet Stream ESI and GC-QTOF/MS Agilent 7890B and Agilent 7200 were obtained from Agilent Technologies (Santa Clara, CA, USA). A Milli-QTM Ultrapure Water System was obtained from Millipore (Milford, MA, USA). An N-EVAP112 Nitrogen Blowing Concentrator was obtained from Organomation Associates (Worcester, MA, USA). An AH-30 Automatic homogenizer was obtained from RayKol Group Corp., Ltd. (Xiamen, China). An MS204S Electronic Analytical Balance was obtained from Mettler Toledo (Shanghai, China).

2.3. Standard Solution

Ten mg of the standard substance was accurately weighed into a 10 mL brown volumetric flask. a suitable reagent was selected according to the solubility of the compound in the organic reagent. It was dissolved by ultrasound and diluted to the mark to a standard solution of 1 mg/L. The standard solution was stored at −18 °C in the dark. As needed, a pipette with an appropriate amount of the standard stock solution was diluted with methanol to prepare a working solution of appropriate concentration, and stored at 4 °C in the dark.

2.4. Sample Preparation Method

Based on other oily matrix sample preparation methods [12,16], a modified QuEChERS method was used for the detection of cottonseed hull. Two g (accurate to ±0.01 g) of sample were transferred into a 50 mL centrifuge tube; 2 mL of ultrapure water were added for hydration and then extracted with 10 mL of 1% acetic acid in acetonitrile. The homogenizer was used to homogenize the sample for 1 min at 13,500× *g*; then, 4 g $MgSO_4$, 1 g NaCl and a ceramic homoproton were added. The mixture was shaken for 10 min and centrifuged at 3155× *g* for 5 min; then, 3 mL of supernatant was transferred to a clean-up tube containing 400 mg $MgSO_4$, 100 mg PSA, and 100 mg C18. After shaking for 10 min and being centrifuged at 3155× *g* for 5 min, 1 mL of supernatant was dried under nitrogen, then ultrasonically redissolved with ethyl acetate containing internal heptachlor-exo-epoxide for GC-QTOF/MS analysis, and ultrasonically redissolved with acetonitrile aqueous solution (2:3, *v*/*v*) containing internal standard atrazine D5 for LC-QTOF/MS analysis.

2.5. Instrument Parameters

The instrument parameters of LC-QTOF/MS and GC-QTOF/MS were configurated according to a previous paper published by our laboratory [25].

An LC-QTOF/MS: ZORBAX SB-C18 column (100 mm × 2.1 mm, 3.5 µm, Agilent Technologies) was used for separation at 40 °C; 5 mmol/L ammonium acetate with 0.1% (*v*/*v*) formic acid aqueous solution and acetonitrile were applied as phase A and phase B. The flow rate was set at 0.4 mL/min. The gradient program was set as follows: 0 min, 1% B; 3 min, 30% B; 6 min, 40% B; 9 min, 40% B; 15 min, 60% B; 19 min, 90% B; 23 min, 90% B; 23.01 min, 1% B. The equilibrium time was 4 min. The injection volume was 5 µL.

The Agilent Dual Jet Stream (AJS) ESI source (Agilent Technologies) was set in positive full scan (m/z 50–1000) mode; the capillary voltage was 4 kV; nitrogen was used as the nebulizer gas at 0.14 MPa; the sheath gas temperature was set at 375 °C with 11.0 L/min; the drying gas flow rate was 12.0 L/min; the drying gas temperature was 225 °C; the fragmentation voltage was 345 V. In all ions Mass/Mass mode, the collision energy was 0 V at 0 min, and 0, 15, and 35 V at 0.5 min, respectively. The total program duration was 27.01 min.

GC-QTOF/MS: HP-5 MS UI (30 m × 0.25 mm, 0.25 µm, Agilent Technologies) was used for separation at 40 °C. The oven temperature gradient was started at 40 °C for 1 min, increased at 30 °C/min to 130 °C, heated at 5 °C/min to 250 °C, ramped to 300 °C at 10 °C/min, and maintained for 7 min. Helium (purity > 99.999%) was used as the carrier gas with a constant flow rate of 1.2 mL/min. The injection temperature was set to 270 °C

and the injection volume was 1 μL. The injection mode was not split injection, and the purge valve was opened after 1 min.

The ion source was an electronic ionization source (70 eV, 280 °C), and the temperatures of the transfer line and the quadrupole were 250 °C and 180 °C, respectively. Solvent delay was set to 3 min; the ion monitoring mode was full scan; scanning ranged (m/z) from 45 to 550; the scan rate was 5 Hz. The total program duration was 42 min.

Mass calibration was required before sample acquisition, and the instrument was tuned at intervals to ensure stability.

2.6. Method Validation

The screening method of high-resolution mass spectrometry can be validated through screening detection limits (SDL), and the quantitative method can be validated through limit of quantitation (LOQ). The SDL, LOQ, linearity, recovery, and precision of this experiment were verified by SANTE/12682/2019 guidelines. SDL is the minimum concentration at which more than 95% of a series of concentration levels meets the detection requirements (20 additional experiments were conducted in parallel for each concentration). When the SDL and recovery were validated, all the target pesticides were spiked to the sample and the spiked samples were placed at room temperature for 30 min, then treated according to the above method. After the 10-point matrix matching calibration was constructed, its linearity was evaluated with the coefficient of determination (R^2). The recovery and precision were investigated in three different levels of spiked blank samples with 1-, 2-, and 10-times LOQ.

The matrix effect (ME) is the interference of other components in the matrix with the target compounds. The formula is:

$$\text{ME (\%)} = (\text{bm} - \text{bs})/\text{bs} \times 100\% \quad (1)$$

where bm is the slope of the matrix standard curve and bs is the slope of the solvent standard curve.

Based on previous studies, we established several hundred kinds of pesticide databases on gas and liquid high resolution mass spectrometry, respectively [25]. According to the recovery and precision, 237 pesticides were divided into pesticides suitable for GC or LC detection.

3. Results

3.1. Optimization of Hydration Volume

For the oily matrix, adding an appropriate amount of water for hydration during sample pretreatment was conducive to the softening of the matrix epidermis, making it easier for residual pesticides in the matrix to be extracted. This experiment explored the effect of different hydration volumes on the recovery of multiple pesticides. The experiment results show that the proportion of pesticides that met the recovery requirements (70–120%) under a non-hydration condition was 74.9%, which was less than under the conditions with water additions of 2 mL and 5 mL. Under the condition of a 2 mL water addition, the number of pesticides meeting the recovery requirements was the most numerous, accounting for 83.5%. As shown in Figure 1, the average recovery under the 2 mL condition was 88.3%, which was higher than that under the other two conditions. The results were in line with our expectations. The oil-water partition coefficient (logP) is an important parameter for the solubility of compounds, which is a simulated value based on the soil sorption coefficient normalized to organic carbon content (log Koc) [26]. The smaller the logP value, the better the water solubility of the compound. The effect of hydration volume on recovery with different logP was investigated, showing that hydration had a great impact on recovery with a low logP. The overall recovery of 54 pesticides with hydrophilic compounds (logP < 2.0) was low under a non-hydration condition, with the pesticides meeting the requirements accounting for 42.6%. When the hydration volume was 5 mL, the pores were opened due to the increase in the hydration volume, and multiple interferents

in the matrix could be extracted together. The matrix promotion effect was enhanced, so that the overall recovery of pesticides with logP < 2.0 was higher than the recovery under the other two conditions. When the hydration volume was 2 mL, the pesticides that met the requirements of recovery were most numerous, accounting for 70.4%; therefore, 2 mL was finally selected as the optimal hydration volume.

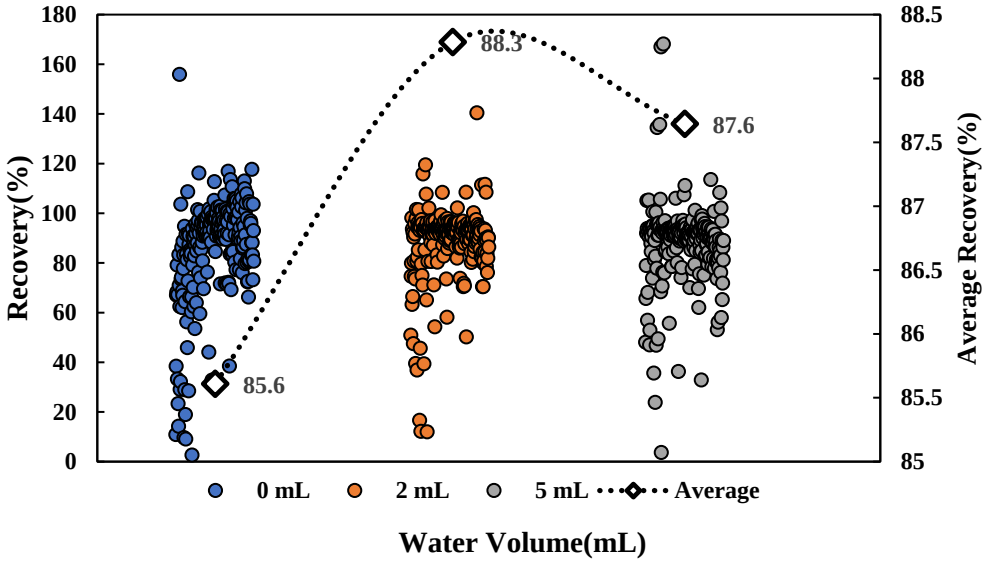

Figure 1. Effects of hydration volumes on pesticide recovery.

3.2. Optimization of Extraction Solvent Volume

The extraction of target compounds is a critical step in pesticide residue analysis. Mol et al. [27] tested a series of solvents for extraction and found that methanol usually extracts too many compounds in the matrix, and further matrix removal steps were required. Acetonitrile has low solubility in fat and a low matrix effect when extracting from complex matrices. Therefore, acetonitrile was selected as the extraction solvent of cottonseed hull in this experiment. Three different extraction volumes of 10 mL, 16 mL, and 20 mL (i.e., a hydration volume and extraction volume ratio of 1:5, 1:8, and 1:10) were compared to explore the effect of different extraction volumes on the recovery of pesticide residues. The results are shown in Figure 2. It was found that when the extract volume was 10 mL, 16 mL, and 20 mL, the proportion of pesticides meeting the recovery requirements was similar, at 81.0%, 80.7% and 81.3% respectively. However, at the spiked level, the volume of the extraction solution decreased, the pesticide concentration per unit volume increased, and more pesticide compounds had better peak shapes. In addition, a lower organic reagent amount was recommended from the perspective of green environmental protection, so the final extraction volume was 10 mL.

3.3. Optimization of Salting-Out Agent

The salting-out agents commonly used in pesticide residue screening were EN buffer salt (4 g $MgSO_4$, 1 g NaCl, 0.5 g disodium hydrogen citrate, and 1 g sodium citrate), the QuEChERS method for fruits and vegetables (4 g $MgSO_4$ and 1 g NaCl), and AOAC buffer salt (6 g $MgSO_4$ and 1.5 g NaAc). In this work, the effects of the above three salting-out agents on the recovery of pesticides were compared. As shown in Figure 3, although EN or AOAC salt forms a buffer system in the solution state, the results showed that the recovery using an $MgSO_4$ + NaCl combination best met the requirements, accounting for 78%. The reason for this result was that the volume of the extract from the QuEChERS method was relatively small. If the amount of extraction salt was too large, the heat emitted during water absorption destroys the structure of thermally unstable pesticides and affects their

recovery. Therefore, 4 g $MgSO_4$ and 1 g NaCl with less salt consumption were finally selected as the salting-out agents.

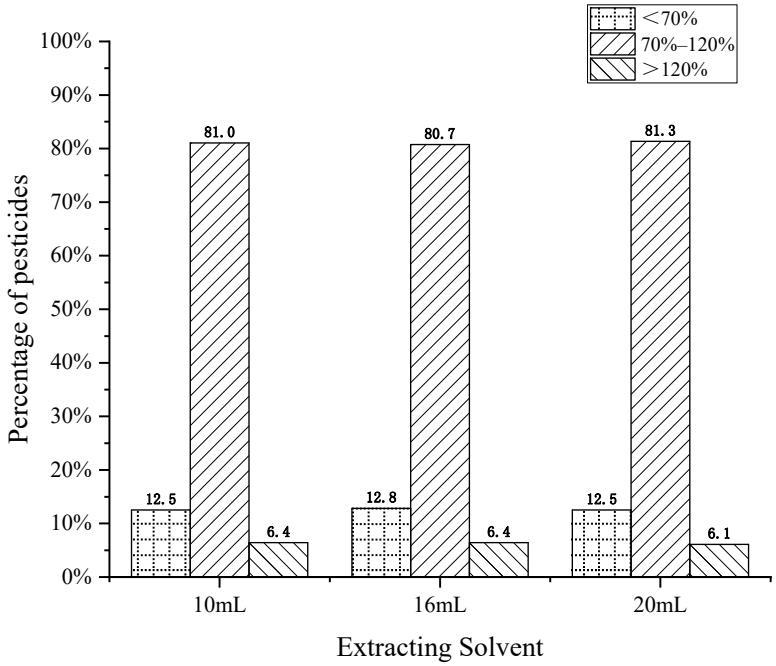

Figure 2. Effect of extraction solvent volume on pesticide recovery.

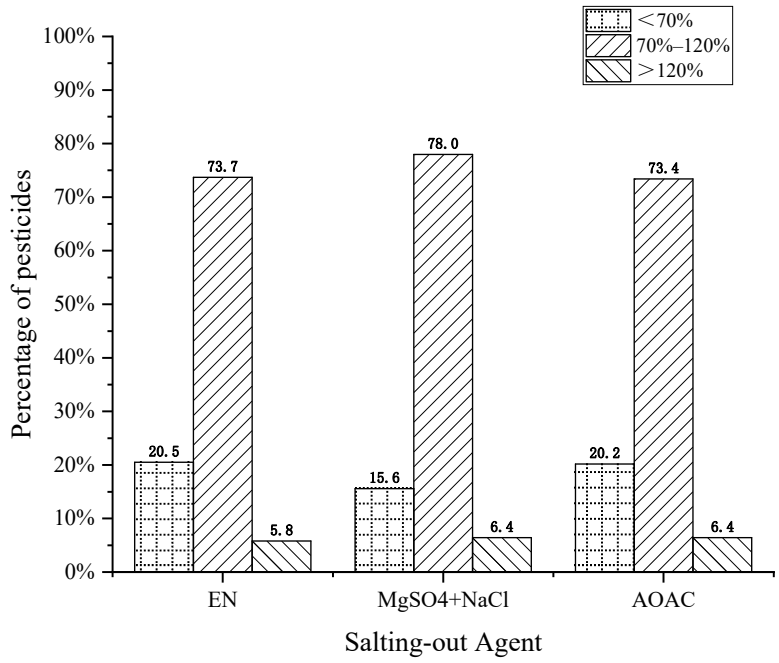

Figure 3. Effect of salting-out agents on pesticide recovery.

3.4. Optimization of Types and Amounts of Clean-Up Sorbents

A clean-up procedure was a key step in the pretreatment of the oily matrix. Its purpose was to effectively purify the analyzed matrix, and most of target pesticides had acceptable recovery, precision, and matrix effect [14]. Although acetonitrile had low liposolubility, which can slightly reduce the interference of a fat-soluble matrix on target compounds [15], in order to effectively reduce the influence of high-fat matrix co-extraction on the detection sensitivity of pesticides, as well as instrument loss, the clean-up procedure was necessary.

Theurillat established a d-SPE clean-up method containing 150 mg C18 and 150 mg PSA to determine 176 pesticide residues in fatty foods [12]. Therefore, this study was optimized on this basis.

In this work, the ability of $MgSO_4$ + PSA + C18 + Z-sep and $MgSO_4$ + PSA + C18 sorbents were compared. The structure of PSA had -NH_2, which can form a strong hydrogen bond with -COOH, so it was often used to adsorb polar compounds, such as fatty acids, lipids, and carbohydrates. C18 was often used to adsorb non-polar compounds, such as long-chain aliphatic compounds and sterols [8,25]. Z-sep was a new adsorbent, based on zirconia, which can be used for the adsorption of hydrophobic compounds in the fat matrix [28]. It was seen that the bottom of the purification tube after Z-sep purification was dark yellow, while the sample without Z-sep purification was light yellow, indicating that Z-sep had an obvious effect on degreasing.

In order to further verify the ability of sorbents, the spiked experiments were carried out. As shown in Figure 4, A was the sorbent combination of $MgSO_4$ + PSA + C18 + Z-sep, and B was the sorbent combination of $MgSO_4$ + PSA + C18. As a result, the sorbent combination without Z-sep accounted for more pesticides that meet the requirements, reaching 81.04%. The reason for this result was that Z-sep adsorbs some target pesticides while removing lipids. According to the Lewis theory, the affinities of Z-sep on the analyte containing different substituent characteristics can be sorted in the following order: chloride < formate < acetate < sulphate< citrate < fluoride < phosphate < hydroxide [25]. In this work, a variety of pesticides, such as trinexapac-ethyl, abamectin containing -OH, fenamiphos sulfoxide containing phosphate, and sulfoxaflor containing sulphate, had substituents with a strong affinity to Z-sep. Therefore, the recovery of sorbent combinations with Z-sep was significantly lower than that without Z-sep. Although Z-sep was more efficient in removing lipid compounds, the sorbent combination of $MgSO_4$ + PSA + C18 was finally selected as the purification filler in this work, from the perspective of method versatility.

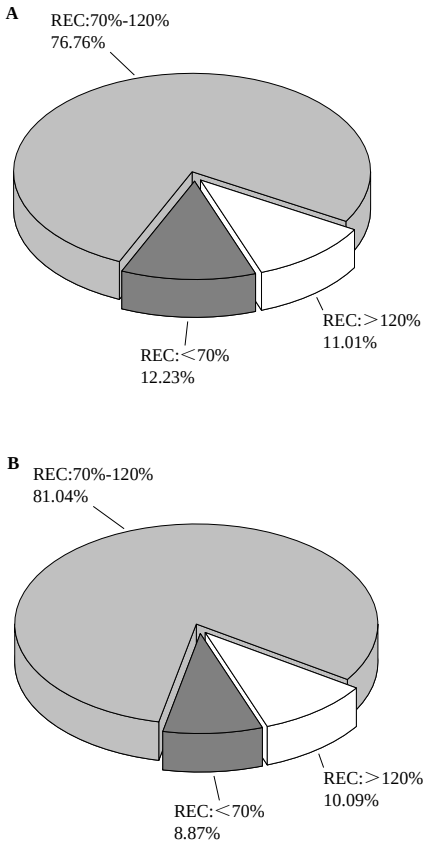

Figure 4. Effect of clean-up sorbents on pesticide recovery. (**A**) $MgSO_4$ + PSA + C18 + Z-sep; (**B**) $MgSO_4$ + PSA + C18.

The amount of PSA and C18 was also optimized. The effects of PSA (50–150 mg) and C18 (100–300 mg) on the recovery of various pesticides were optimized by controlling other variables. The results showed that when the amount of PSA was 100 mg, the greatest number of pesticides with satisfactory recovery was obtained, accounting for 73.7%. With the increase in PSA amount, the recovery of organic nitrogen pesticides, such as propanil and fenbuconazole, and carbamate pesticides, such as aldicarb-sulfone and thiophanate-methyl, gradually decreased. When the amount of C18 was 100 mg, the proportion of pesticides that met satisfactory recovery was 82.0%. With an increase in the C18 amount, the recovery of various organic nitrogen pesticides obviously decreased, especially the chlorides with a benzene ring structure, such as monolinuron, novaluron, propanil, and pretilachlor. Therefore, 100 mg PSA and 100 mg C18 were finally selected as the optimal amounts of clean-up sorbents.

3.5. Evaluation of Matrix Effect

Analysis of pesticide residues in the oil matrix may be adversely affected by the matrix effect. The main result of the matrix effect is to increase or decrease the analyte signal when the same analyte exists in the solvent [29]. The methods for eliminating or reducing the matrix effect include: (1) optimizing the sample preparation method and reducing co-extraction; (2) changing the chromatographic mass spectrometry conditions; (3) diluting the samples; and (4) using matrix-matched standards or an additional standard method [30]. In this work, the purifying agent was optimized, and the matrix-matched standard was used to reduce the interference of the matrix effect on target compounds. The matrix effect distribution of 237 pesticides is shown in Figure 5. Among the 237 pesticides investigated in cottonseed hull samples, the proportion of pesticides with a negative matrix effect accounted for 81.4%, indicating that the substrate had a suppression effect on the tested pesticides as a whole. The matrix effect can be divided into three categories: no matrix effect ($|ME| \leq 20\%$); a weak matrix effect ($20\% < |ME| < 50\%$); and a strong matrix effect ($|ME| \geq 50\%$). In this work, only 8% of the pesticides in the cottonseed hull matrix showed a strong matrix effect; the weak matrix effect and no matrix effect accounted for 13.1% and 78.9%, respectively, indicating that this research method had a strong anti-matrix interference ability.

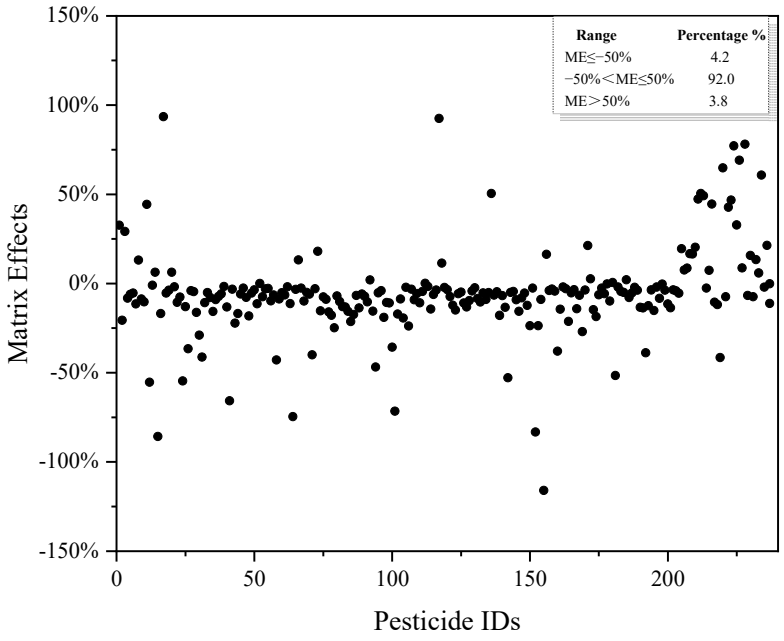

Figure 5. Matrix effect distribution of 237 pesticides.

3.6. Method Validation and Method Performance

3.6.1. SDL, LOQ, and Standard Curve

The method validation was carried out under the optimal sample preparation procedure, and the results are shown in Table 1. The typical extraction ion chromatograms of GC-Q TOF/MS and LC-Q TOF/MS are shown in Figures 6 and 7, respectively. The SDLs were in the range of 0.2–20 μg/kg, of which 224 pesticides (accounting for 94.5%) were in the range of 0.2–5 μg/kg. The LOQs were in the range of 0.2–20 μg/kg; 215 pesticides (accounting for 90.7%) had an LOQ range of 0.2–5 μg/kg. Shinde developed and verified 222 and 220 multi-pesticides residue analysis methods in sesame seeds, using LC-MS/MS and GC-MS/MS, respectively, and most pesticides offered an LOQ of 10 μg/kg for most compounds [16]. Kuzukiran et al. developed an SPE sample preparation method, combined with GC-MS, GC-MS/MS and LC-MS/MS, to analyze the residues of 322 organic pollutants in bats [31]. The LOQ of the method was in the range of 0.27–19.26 μg/kg, which was similar to that in our work; however, they paid more attention to environmental pollutants. This indicated that this method had high sensitivity in the detection of pesticide residues in cottonseed hull matrix. It is noteworthy that due to the large number of pesticides spiked, the retention time of some pesticides may overlap or be very close; for example, the RTs of Chloridazon and Mevinphos were 3.62 min. However, the excellent resolution of high-resolution mass spectrometry was sufficient to separate compounds that had a similar RT but a different mass (the quantitative ion mass of Chloridazon and that of Mevinphos were 222.04287 and 225.05230, respectively).

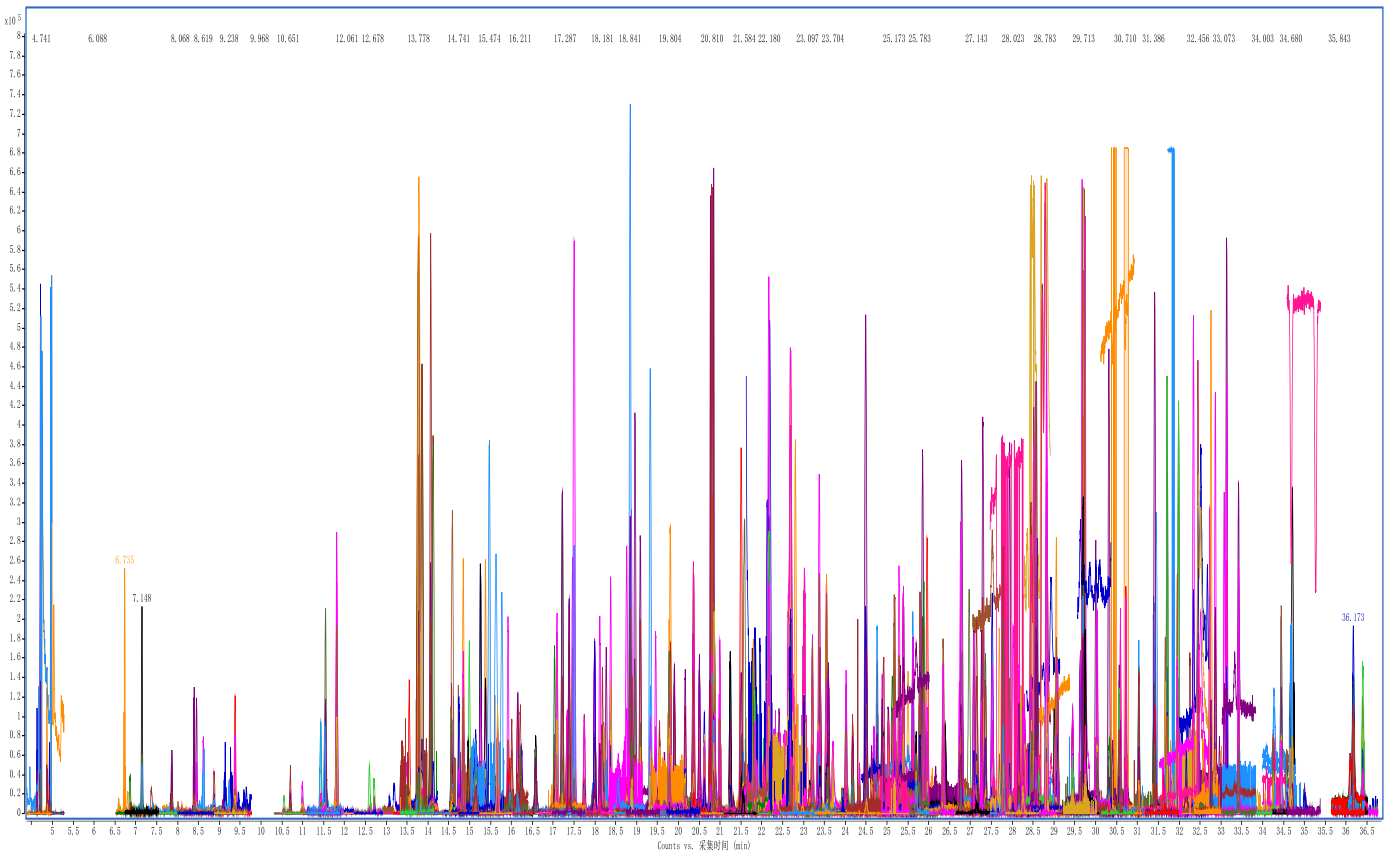

Figure 6. Overlay extraction ion chromatograms of GC-Q TOF/MS of cottonseed hull sample at spiking level of 200 μg/kg.

Table 1. Compound information, screening detection limits (SDLs), limit of quantification (LOQ), linear range, R^2, recovery, and RSD of 237 pesticides (n = 6).

No	Compound	Formula	RT (Min)	Quantitative Ion	Qualitative Ion	R^2	Linearity (ng/g)	SDL (ng/g)	LOQ (ng/g)	1-LOQ		2-LOQ		10-LOQ		Detecting Instrument
										REC (%)	RSD (%)	REC (%)	RSD (%)	REC (%)	RSD (%)	
1	1-(2-chloro-4-(4-chlorophenoxy)phenyl)-2-(1H-1,2,4-triazol-1-yl)ethanol	C16H13Cl2N3O2	10.16	350.04580	70.03997	0.9995	10–200	10	10	81.3	2.9	71.5	7.8	76.9	11.5	LC
2	1-(2-Chloro-pyridin-5-yl-methyl)-2-imino-imidazolidine hydrochloride	C9H11ClN4	2.28	211.07450	90.03383	0.9992	1–200	1	1	71.4	1.4	58.7	4.7	54.4	1.1	LC
3	1-methyl-3-(tetrahydro-3-furylmethyl) urea	C7H14N2O2	1.87	159.11280	58.02874	0.9986	2–200	2	2	84.1	17.2	78.2	11.8	87.3	7.9	LC
4	2,4-D butylate	C12H14O3Cl2	19.45	185.00000	276.03146	0.9992	1–200	1	1	71.7	14.3	90.8	5.3	77.6	4.6	GC
5	3-(Trifluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide	C6H6F3N3O	2.63	194.05360	134.03488	0.9911	20–200	5	20	104.7	8.7	105.4	12.8	79.6	3.2	LC
6	5-hydroxy Imidacloprid	C9H10ClN5O3	3.05	272.05450	225.05377	0.9976	10–200	5	10	72.0	7.8	78.2	8.5	70.2	7.8	LC
7	Acetamiprid	C10H11ClN4	3.93	223.07450	126.01051	0.9938	1–200	1	1	93.5	11.7	110.3	11.0	89.6	7.2	LC
8	Acetamiprid-N-desmethyl	C9H9ClN4	3.57	209.05890	126.01051	0.9950	1–200	1	1	113.2	9.4	105.6	8.8	96.3	6.4	LC
9	Acetochlor	C14H20ClNO2	12.57	270.12553	133.08861	0.9992	1–200	1	1	115.3	13.8	99.2	10.5	86.4	3.1	LC
10	Alachlor	C14H20ClNO2	12.45	270.12553	238.09932	0.9995	1–200	1	1	99.2	15.1	70.1	7.9	84.8	4.1	LC
11	Aldicarb-sulfone	C7H14N2O4S	2.63	223.07470	62.98991	0.9987	10–200	10	10	73.7	7.5	86.5	8.3	84.2	2.7	LC
12	Aldrin	C12H8Cl6	19.52	262.85641	264.85352	0.9994	1–200	1	1	79.7	4.5	80.8	7.4	66.3	3.5	GC
13	Allidochlor	C8H12ClNO	4.94	174.06800	98.09643	0.9995	0.2–200	0.2	0.2	93.1	19.9	70.7	15.3	83.8	8.1	LC
14	Alpha-HCH	C6H6Cl6	16.14	182.93437	180.93732	0.9904	1–200	1	1	99.6	10.4	71.6	8.2	87.7	8.2	GC
15	Ametryn	C9H17N5S	6.70	228.12774	186.08080	0.9997	1–200	1	1	82.6	2.5	91.2	1.1	79.3	1.9	LC
16	Atrazine	C8H14ClN5	6.38	216.10105	174.05409	0.9999	1–200	1	1	82.7	3.9	93.1	3.1	78.1	1.5	LC
17	Atrazine D5 (Ethylamino D5)	C8H9D5ClN5	6.47	221.13310	69.03060	0.9965	1–200	1	1	97.7	3.5	100.0	0.9	98.6	1.4	LC
18	Avermectin B1a	C48H72O14	18.66	895.48140	751.40521	0.9983	2–200	1	2	90.9	11.6	83.7	3.3	110.0	6.5	LC
19	Azoxystrobin	C22H17N3O5	11.07	404.12410	329.07950	0.9996	1–200	1	1	94.8	8.1	93.9	2.8	82.2	1.3	LC
20	Benalaxyl	C20H23NO3	14.04	326.17507	91.05423	0.9999	1–200	1	1	91.6	5.6	96.9	3.2	83.2	2.2	LC
21	Bendiocarb	C11H13NO4	5.74	224.09173	81.03349	1.0000	2–200	1	2	85.9	8.2	84.5	17.1	120.0	8.7	LC
22	Benfluralin	C13H16F3N3O4	15.37	292.05396	264.02267	1.0000	50–200	2	20	96.7	5.2	73.7	2.4	73.7	7.9	GC
23	Benfuracarb	C20H30N2O5S	17.27	411.19482	102.00081	0.9999	1–200	1	1	64.2	5.0	71.9	9.4	44.3	2.6	LC
24	Benzovindiflupyr	C18H15Cl2F2N3O	14.33	398.06400	159.03644	0.9999	1–200	1	1	95.9	5.0	98.1	2.2	83.0	1.8	LC
25	beta-Endosulfan	C9H6Cl6O3S	27.04	236.84077	242.90135	0.9950	1–200	1	1	103.9	14.0	91.7	5.7	70.3	9.0	GC
26	Beta-HCH	C6H6Cl6	20.76	182.93437	180.93732	0.9964	1–200	1	1	72.3	17.2	70.5	15.6	74.2	7.7	GC
27	Bifenazate	C17H20N2O3	12.18	301.15467	198.09134	0.9999	1–200	1	1	89.5	18.7	83.4	12.2	88.0	6.3	LC

Table 1. *Cont.*

No	Compound	Formula	RT (Min)	Quantitative Ion	Qualitative Ion	R^2	Linearity (ng/g)	SDL (ng/g)	LOQ (ng/g)	1-LOQ		2-LOQ		10-LOQ		Detecting Instrument
										REC (%)	RSD (%)	REC (%)	RSD (%)	REC (%)	RSD (%)	
28	Bifenthrin	C23H22ClF3O2	28.81	181.10118	166.07770	0.9939	10–200	10	10	106.6	16.2	45.7	2.6	82.8	2.0	GC
29	Bioresmethrin	C22H26O3	19.09	339.19550	143.08553	0.9978	20–200	20	20	84.9	17.6	71.6	6.6	77.7	6.0	LC
30	Bitertanol	C20H23N3O2	12.68	338.18630	70.03997	0.9928	5–200	5	5	77.1	10.6	79.2	10.2	75.8	14.2	LC
31	Boscalid	C18H12Cl2N2O	11.18	343.03994	271.08658	0.9997	2–200	1	2	100.9	9.9	91.1	10.5	88.0	7.9	LC
32	Bromobutide	C15H22BrNO	13.75	312.09575	119.08553	0.9998	1–200	1	1	91.3	18.0	92.3	14.9	70.3	7.0	LC
33	Bromophos-methyl	C8H8BrCl2O3PS	21.82	330.87753	328.87982	0.9941	1–200	1	1	75.4	15.6	81.2	10.8	78.4	14.3	GC
34	Bromopropylate	C17H16Br2O3	29.69	340.89948	342.89755	0.9989	1–200	1	1	87.1	10.5	90.6	6.9	76.6	7.2	GC
35	Bupirimate	C13H24N4O3S	12.61	317.16419	44.04948	0.9998	1–200	1	1	95.0	8.2	95.3	2.6	82.3	1.0	LC
36	Buprofezin	C16H23N3OS	17.38	306.16346	57.06988	0.9975	1–200	1	1	101.4	3.6	101.9	17.7	78.7	3.1	LC
37	Butachlor	C17H26ClNO2	17.47	312.17250	57.06988	0.9987	1–200	1	1	115.3	19.9	95.0	19.9	80.4	6.5	LC
38	Butamifos	C13H21N2O4PS	16.45	333.10350	95.96675	0.9981	1–200	1	1	86.8	14.4	110.6	9.5	74.7	6.5	LC
39	Butylate	C11H23NOS	16.60	218.15731	57.06988	0.9992	10–200	5	10	61.4	10.4	82.4	6.5	70.4	15.9	LC
40	Cadusafos	C10H23O2PS2	14.61	271.09498	96.95076	0.9998	1–200	1	1	73.3	9.4	86.1	9.1	77.3	1.8	LC
41	Carbaryl	C12H11NO2	6.21	202.08626	127.05423	0.9927	10–200	10	10	102.3	17.1	112.5	16.9	107.1	17.2	LC
42	Carbendazim	C9H9N3O2	2.67	192.07675	160.05054	0.9999	1–200	1	1	111.8	19.1	79.8	9.6	71.5	12.1	LC
43	Carbofuran	C12H15NO3	5.80	222.11247	123.04406	0.9944	1–200	1	1	107.5	3.6	91.3	6.1	112.5	2.4	LC
44	Carbofuran-3-Hydroxy	C12H15NO4	3.55	238.10738	107.04914	0.9997	0.2–200	0.2	0.2	82.7	17.6	70.6	11.0	86.9	9.3	LC
45	Carbosulfan	C20H32N2O3S	19.82	381.22064	76.02155	0.9994	2–200	2	2	79.8	18.9	34.2	11.0	51.7	12.0	LC
46	Carfentrazone-ethyl	C15H14Cl2F3N3O3	14.18	412.04350	345.99561	0.9998	1–200	1	1	115.9	14.3	85.8	7.5	84.7	4.0	LC
47	Chlorantraniliprole	C18H14BrCl2N5O2	8.23	481.97807	283.92160	1.0000	1–200	1	1	93.0	16.9	99.8	10.3	81.1	4.9	LC
48	Chlorfenapyr	C15H11BrClF3N2O	27.57	363.94073	361.94278	0.9913	1–200	1	1	85.1	6.6	109.8	17.5	112.4	13.6	GC
49	Chlorfenvinphos	C12H14Cl3O4P	13.67	358.97681	98.98434	0.9999	1–200	1	1	89.8	10.9	103.8	9.8	86.5	4.2	LC
50	Chloridazon	C10H8ClN3O	3.62	222.04287	77.03857	0.9977	1–200	1	1	77.7	6.2	84.4	4.1	79.2	3.4	LC
51	Chlormequat	C5H12ClN	0.70	122.07310	58.06512	0.9983	1–200	1	1	90.8	14.7	93.6	4.7	113.3	8.4	LC
52	Chloroneb	C8H8Cl2O2	11.81	190.96611	192.96324	0.9945	2–200	2	2	127.8	19.3	54.8	13.8	69.5	8.8	GC
53	Chlorotoluron	C10H13ClN2O	6.10	213.07892	72.04488	0.9998	1–200	1	1	96.1	6.1	102.1	5.0	82.2	2.2	LC
54	Chlorpropham	C10H12ClNO2	15.92	127.01833	213.05511	0.9989	5–200	5	5	138.2	19.7	88.1	15.8	84.0	8.3	GC
55	Chlorpyrifos	C9H11Cl3NO3PS	17.72	349.93356	96.95076	0.9998	5–200	1	5	100.9	19.3	84.9	8.9	85.1	5.3	LC
56	Chlorpyrifos-methyl	C7H7Cl3NO3PS	19.32	285.92557	287.92316	0.9949	1–200	1	1	93.6	7.9	79.4	10.6	78.7	13.1	GC
57	Cis-Chlordane (alpha)	C10H6Cl8	23.58	372.82544	374.82251	0.9996	1–200	1	1	85.7	7.4	83.5	6.9	70.5	6.5	GC
58	Clodinafop-propargyl	C17H13ClFNO4	15.05	350.05899	91.05423	0.9999	1–200	1	1	109.5	7.4	94.4	4.1	83.1	3.0	LC
59	Clofentezine	C14H8Cl2N4	15.32	303.01988	102.03383	0.9997	5–200	5	5	81.2	17.4	72.2	12.4	104.2	7.5	LC
60	Clomazone	C12H14ClNO2	7.91	240.07858	125.01525	0.9999	1–200	1	1	112.3	18.4	99.8	12.7	78.5	3.6	LC
61	Clothianidin	C6H8ClN5O2S	3.50	250.01600	131.96692	0.9995	2–200	1	2	101.9	19.4	103.9	15.1	89.4	6.9	LC
62	Cyanazine	C9H13ClN6	5.16	241.09630	214.08540	0.9998	1–200	1	1	78.9	11.9	89.0	8.2	85.9	13.9	LC
63	Cyanofenphos	C15H14NO2PS	29.06	156.98715	169.04129	0.9996	1–200	1	1	77.3	14.9	100.8	13.9	81.2	6.1	GC

Table 1. *Cont.*

No	Compound	Formula	RT (Min)	Quantitative Ion	Qualitative Ion	R^2	Linearity (ng/g)	SDL (ng/g)	LOQ (ng/g)	1-LOQ		2-LOQ		10-LOQ		Detecting Instrument
										REC (%)	RSD (%)	REC (%)	RSD (%)	REC (%)	RSD (%)	
64	Cycloate	C11H21NOS	15.35	216.14166	55.05423	0.9998	2–200	2	2	117.4	15.3	85.0	16.2	79.6	5.7	LC
65	Cycloxydim	C17H27NO3S	16.22	326.17844	107.04914	0.9996	1–200	1	1	62.6	11.6	100.4	5.7	74.1	4.2	LC
66	Cyprodinil	C14H15N3	22.15	224.11823	225.12605	0.9999	1–200	1	1	92.3	15.9	89.1	4.1	75.3	5.9	GC
67	Cyromazine	C6H10N6	0.75	167.10400	85.05087	0.9927	5–200	1	5	58.2	6.0	56.2	10.1	51.5	5.8	LC
68	Delta-HCH	C6H6Cl6	21.60	180.93732	182.93437	0.9943	2–200	2	2	158.1	19.5	162.4	19.8	181.8	19.4	GC
69	Desmetryn	C8H15N5S	5.21	214.11209	172.06514	0.9994	1–200	1	1	84.7	3.7	93.5	0.7	78.6	1.9	LC
70	Diallate	C10H17Cl2NOS	16.66	270.04810	86.06004	0.9992	10–200	5	10	70.6	19.0	107.5	9.7	85.9	19.9	LC
71	Diazinon	C12H21N2O3PS	14.97	305.10833	96.95076	0.9998	1–200	1	1	89.5	3.6	87.7	3.4	78.5	1.5	LC
72	Dichlofenthion	C10H13Cl2O3PS	18.86	279.00061	222.93800	0.9938	1–200	1	1	76.6	17.7	82.0	10.5	73.0	7.0	GC
73	Dichlorvos	C4H7Cl2O4P	7.85	184.97650	109.00491	0.9954	10–200	1	10	116.2	12.6	108.9	17.6	78.1	16.0	GC
74	Dicloran	C6H4Cl2N2O2	18.20	205.96443	207.96156	0.9946	2–200	2	2	89.3	15.9	89.7	14.5	86.0	8.9	GC
75	Difenoconazole	C19H17Cl2N3O3	14.63	406.07200	251.00250	0.9998	1–200	1	1	77.3	4.8	94.0	2.8	79.6	2.2	LC
76	Diflubenzuron	C14H9ClF2N2O2	12.11	311.03934	141.01465	0.9938	10–200	10	10	64.8	5.6	83.7	10.3	92.2	10.0	LC
77	Dimethenamid	C12H18ClNO2S	9.58	276.08195	244.05574	0.9997	1–200	1	1	90.6	3.6	84.8	5.5	82.8	4.6	LC
78	Dimethoate	C5H12NO3PS2	3.78	230.00690	198.96469	0.9941	2–200	1	2	70.4	10.0	89.8	9.0	84.7	6.0	LC
79	Dimethylvinphos (Z)	C10H10Cl3O4P	10.47	330.94550	127.01547	0.9999	1–200	1	1	92.1	16.9	80.7	10.3	108.7	7.9	LC
80	Diniconazole	C15H17Cl2N3O	12.97	326.08210	70.03997	1.0000	2–200	1	2	89.1	4.0	84.2	7.1	85.5	5.5	LC
81	Dinotefuran	C7H14N4O3	2.31	203.11387	58.05255	0.9994	20–200	20	20	80.0	5.6	86.8	4.5	77.1	3.3	LC
82	Dioxabenzofos	C8H9O3PS	10.47	217.00830	77.03857	1.0000	2–200	1	2	97.3	5.0	88.0	5.7	87.0	2.9	LC
83	Dipropetryn	C11H21N5S	11.46	256.15904	102.01205	0.9999	1–200	1	1	74.3	5.0	94.6	4.2	76.3	3.1	LC
84	Diuron	C9H10Cl2N2O	6.63	233.02429	72.04488	0.9989	1–200	1	1	105.7	17.6	124.8	11.1	70.6	5.3	LC
85	Edifenphos	C14H15O2PS2	13.46	311.03238	109.01065	0.9998	1–200	1	1	92.6	4.6	93.3	3.6	81.5	0.8	LC
86	Emamectin B1a	C49H75NO13	16.88	886.53112	158.11755	0.9996	1–200	1	1	83.1	12.3	82.3	6.6	75.2	10.3	LC
87	Endosulfan-sulfate	C9H6Cl6O4S	29.05	271.80963	273.80667	0.9999	1–200	1	1	61.7	7.1	61.1	6.0	51.4	2.7	GC
88	Ethalfluralin	C13H14F3N3O4	14.96	276.05905	316.09036	0.9981	1–200	1	1	93.0	9.6	106.1	16.4	73.9	9.5	GC
89	Ethion	C9H22O4P2S4	17.95	384.99489	199.00108	1.0000	1–200	1	1	119.9	8.3	89.1	16.0	78.1	3.3	LC
90	Ethoprophos	C8H19O2PS2	10.86	243.06368	96.95076	0.9998	1–200	1	1	90.3	11.8	87.3	6.6	78.7	1.5	LC
91	Etrimfos	C10H17N2O4PS	14.56	293.07194	124.98206	0.9999	1–200	1	1	76.9	4.5	92.3	4.6	81.6	3.0	LC
92	Fenamidone	C17H17N3OS	30.72	268.09030	238.11006	0.9994	1–200	1	1	77.7	11.7	89.6	17.0	87.1	6.1	GC
93	Fenamiphos	C13H22NO3PS	10.46	304.11308	201.98480	0.9998	1–200	1	1	83.6	2.6	96.2	2.9	84.2	0.9	LC
94	Fenamiphos-sulfone	C13H22NO5PS	5.59	336.10291	266.02466	0.9999	1–200	1	1	94.6	18.1	91.1	4.4	83.4	2.0	LC
95	Fenamiphos-sulfoxide	C13H22NO4PS	4.61	320.10799	108.05727	0.9999	1–200	1	1	90.3	5.0	100.2	6.5	83.9	1.1	LC
96	Fenarimol	C17H12Cl2N2O	10.59	331.03994	81.04472	0.9998	2–200	1	2	102.8	11.0	90.7	9.7	76.6	6.8	LC
97	Fenbuconazole	C19H17ClN4	12.38	337.12150	70.03997	0.9999	1–200	1	1	116.4	11.7	74.0	19.3	75.1	7.0	LC
98	Fenchlorphos	C8H8Cl3O3PS	19.80	284.93033	286.92749	0.9968	1–200	1	1	86.2	7.0	102.3	6.6	75.3	9.4	GC
99	Fenobucarb	C12H17NO2	8.80	208.13321	77.03857	0.9982	5–200	5	5	87.9	12.4	104.7	8.0	84.0	2.7	LC

Table 1. *Cont.*

No	Compound	Formula	RT (Min)	Quantitative Ion	Qualitative Ion	R^2	Linearity (ng/g)	SDL (ng/g)	LOQ (ng/g)	1-LOQ		2-LOQ		10-LOQ		Detecting Instrument
										REC (%)	RSD (%)	REC (%)	RSD (%)	REC (%)	RSD (%)	
100	Fenpropimorph	C20H33NO	18.52	128.10699	129.11012	0.9948	5–200	5	5	66.6	19.4	70.7	16.3	76.9	3.2	GC
101	Fensulfothion	C11H17O4PS2	7.42	309.03786	140.02904	0.9996	1–200	1	1	87.9	2.9	94.5	1.5	84.0	1.2	LC
102	Fenthion-sulfoxide	C10H15O4PS2	6.02	295.02221	109.00491	0.9998	1–200	1	1	87.3	3.7	93.5	3.7	84.1	1.1	LC
103	Fipronil	C12H4Cl2F6N4OS	28.19	366.94296	368.94003	0.9970	1–200	1	1	80.1	19.1	75.7	11.4	72.0	7.6	GC
104	Fipronil Desulfinyl	C12H4Cl2F6N4	25.54	332.99609	387.97116	0.9951	2–200	2	2	107.4	12.3	67.2	18.7	117.8	19.5	GC
105	Fipronil-sulfide	C12H4Cl2F6N4S	27.81	350.94803	352.94510	0.9999	1–200	1	1	75.5	2.9	75.5	3.0	71.2	2.0	GC
106	Fluacrypyrim	C20H21F3N2O5	16.67	427.14753	145.06479	0.9992	1–200	1	1	109.3	15.5	111.5	6.5	77.6	6.8	LC
107	Fluazifop-butyl	C19H20F3NO4	17.62	384.14172	91.05423	0.9999	1–200	1	1	76.7	5.6	91.6	3.3	80.5	3.0	LC
108	Flubendiamide	C23H22F7IN2O4S	14.52	705.01250	530.97986	0.9999	1–200	1	1	88.5	3.1	93.2	3.4	83.2	1.7	LC
109	Flumiclorac-pentyl	C21H23ClFNO5	17.47	441.15930	308.04843	0.9973	2–200	1	2	26.4	19.5	75.0	19.5	79.0	18.1	LC
110	Fluopicolide	C14H8Cl3F3N2O	11.85	382.97271	172.95555	0.9999	1–200	1	1	90.7	9.5	95.1	6.7	83.8	2.4	LC
111	Fluquinconazole	C16H8Cl2FN5O	11.40	376.01630	306.98358	0.9996	5–200	5	5	82.4	6.4	88.9	6.3	94.9	4.3	LC
112	Fluridone	C19H14F3NO	9.19	330.11003	309.09598	0.9989	1–200	1	1	92.3	8.5	94.2	1.4	84.3	2.0	LC
113	Flusilazole	C16H15F2N3Si	12.36	316.10761	165.06967	0.9997	1–200	1	1	82.1	6.5	97.4	9.5	79.8	2.3	LC
114	Flutriafol	C16H13F2N3O	6.40	302.10994	70.03997	0.9996	1–200	1	1	89.3	9.1	96.2	5.3	76.0	3.2	LC
115	Fluxapyroxad	C18H12F5N3O	11.39	382.09730	342.08487	1.0000	1–200	1	1	93.0	7.8	94.4	4.5	84.2	3.4	LC
116	Fonofos	C10H15OPS2	15.23	247.03747	80.95585	0.9976	5–200	1	5	72.0	1.5	100.3	16.0	105.8	4.3	LC
117	Fosthiazate	C9H18NO3PS2	6.37	284.05385	104.01646	0.9998	1–200	1	1	96.0	11.1	94.6	4.3	87.1	2.2	LC
118	Furathiocarb	C18H26N2O5S	17.26	383.16352	195.04742	0.9999	1–200	1	1	74.3	6.7	82.6	4.4	64.9	1.2	LC
119	Haloxyfop	C15H11ClF3NO4	23.54	316.03467	375.04797	0.9997	20–200	1	20	96.0	4.8	77.0	6.3	73.3	6.9	GC
120	Haloxyfop-2-ethoxyethyl	C19H19ClF3NO5	17.06	434.09766	91.05423	0.9983	1–200	1	1	92.3	2.4	110.3	3.5	83.7	3.2	LC
121	Haloxyfop-methyl	C16H13ClF3NO4	16.23	376.05460	272.00845	0.9985	1–200	1	1	91.7	11.5	90.2	5.9	83.0	2.6	LC
122	Heptachlor	C10H5Cl7	18.48	271.80963	273.80667	0.9979	1–200	1	1	106.4	18.9	76.3	6.1	74.9	10.0	GC
123	Hexachlorobenzene	C6Cl6	14.03	283.80963	285.80670	0.9918	1–200	1	1	61.6	2.1	60.1	4.1	54.3	6.4	GC
124	Hexaconazole	C14H17Cl2N3O	12.19	314.08250	70.03997	0.9996	2–200	1	2	98.4	11.4	85.7	9.5	97.2	10.8	LC
125	Hexythiazox	C17H21ClN2O2S	17.70	353.10850	168.05696	0.9992	2–200	1	2	70.6	10.4	120.0	9.3	82.0	4.1	LC
126	Imazalil	C14H14Cl2N2O	25.76	172.95555	215.00250	0.9998	1–200	1	1	92.1	6.8	73.2	7.6	84.1	3.9	GC
127	Imazapyr	C13H15N3O3	3.07	262.11862	69.06988	0.9998	5–200	5	5	24.8	2.0	23.1	11.0	25.3	6.7	LC
128	Imidacloprid	C9H10ClN5O2	3.68	256.05958	209.05885	0.9967	1–200	1	1	117.5	0.2	181.6	6.6	87.1	12.1	LC
129	Imidacloprid-Olefin	C9H8ClN5O2	3.07	254.04390	171.06653	0.9997	10–200	5	10	94.8	13.7	91.1	7.3	78.1	9.6	LC
130	Iprobenfos	C13H21O3PS	12.36	289.10218	91.05423	0.9994	2–200	1	2	104.1	14.5	100.1	15.0	101.6	5.7	LC
131	Iprovalicarb	C18H28N2O3	10.44	321.21727	119.08553	0.9999	1–200	1	1	111.8	13.5	106.4	9.2	89.1	2.3	LC
132	Isazofos	C9H17ClN3O3PS	13.62	314.04895	119.99574	0.9998	1–200	1	1	86.0	4.6	91.2	3.4	83.4	2.0	LC
133	Isofenphos	C15H24NO4PS	16.48	346.12364	121.02872	0.9996	5–200	2	5	76.4	15.6	80.4	17.8	108.1	16.7	LC
134	Isoproturon	C12H18N2O	6.66	207.14919	72.04439	0.9990	0.5–200	0.5	0.5	96.2	7.9	89.2	1.7	84.0	2.2	LC
135	Isopyrazam	C20H23F2N3O	15.58	360.18950	320.17575	0.9998	1–200	1	1	86.9	5.8	96.8	4.1	79.9	1.2	LC

Table 1. *Cont.*

No	Compound	Formula	RT (Min)	Quantitative Ion	Qualitative Ion	R^2	Linearity (ng/g)	SDL (ng/g)	LOQ (ng/g)	1-LOQ		2-LOQ		10-LOQ		Detecting Instrument
										REC (%)	RSD (%)	REC (%)	RSD (%)	REC (%)	RSD (%)	
136	Kresoxim-methyl	C18H19NO4	14.26	314.13868	116.04948	0.9998	5–200	2	5	72.0	15.1	79.3	12.3	89.8	4.7	LC
137	Lactofen	C19H15ClF3NO7	17.70	479.08210	343.99319	0.9972	20–200	20	20	90.5	5.1	111.6	17.1	77.7	12.5	LC
138	Lindane	C6H6Cl6	17.74	180.93732	182.93437	0.9989	1–200	1	1	62.9	16.7	116.5	18.3	110.8	7.9	GC
139	Linuron	C9H10Cl2N2O2	9.10	249.01921	132.96063	0.9990	5–200	2	5	73.1	10.3	84.4	8.9	94.2	3.2	LC
140	Malaoxon	C10H19O7PS	5.72	315.06619	99.00767	0.9998	1–200	1	1	74.4	17.4	93.9	12.3	89.4	10.2	LC
141	Malathion	C10H19O6PS2	12.53	331.04334	99.00767	0.9983	1–200	1	1	82.9	11.0	83.7	10.3	77.8	3.4	LC
142	Mepanipyrim	C14H13N3	24.48	222.10257	223.11040	0.9998	5–200	1	5	84.5	9.9	77.6	8.7	79.4	4.8	GC
143	Metaflumizone	C24H16F6N4O2	17.39	507.12502	178.04628	0.9973	10–200	2	10	80.3	4.6	86.7	16.9	82.8	8.0	LC
144	Metalaxyl	C15H21NO4	6.70	280.15433	45.03349	0.9993	1–200	1	1	95.0	8.6	98.4	2.2	81.8	1.1	LC
145	Metconazole	C17H22ClN3O	12.66	320.15242	70.03997	0.9998	2–200	1	2	80.5	8.7	86.5	5.8	86.1	6.8	LC
146	Methiocarb	C11H15NO2S	8.73	226.08960	121.06479	0.9939	20–200	5	20	84.1	15.4	86.1	16.2	85.3	5.1	LC
147	Methiocarb-sulfoxide	C11H15NO3S	3.42	242.08454	122.07262	0.9980	1–200	1	1	101.1	14.8	87.6	6.8	84.0	4.0	LC
148	Metolachlor	C15H22ClNO2	12.32	284.14118	252.11497	0.9999	1–200	1	1	97.1	9.1	105.6	3.2	84.0	1.4	LC
149	Metrafenone	C19H21BrO5	16.24	409.06451	209.08084	0.9998	1–200	1	1	91.0	4.6	92.7	3.6	79.1	1.9	LC
150	Metribuzin	C8H14N4OS	5.26	215.09611	49.01065	0.9999	5–200	2	5	87.5	13.9	80.6	3.0	93.6	1.2	LC
151	Mevinphos	C7H13O6P	3.62	225.05230	127.01547	0.9992	2–200	1	2	70.3	11.8	118.8	10.5	90.0	7.6	LC
152	Mirex	C10Cl12	29.05	271.80963	273.80667	0.9999	1–200	1	1	64.6	2.1	62.6	6.0	57.1	2.9	GC
153	Monocrotophos	C7H14NO5P	2.77	224.06824	58.02874	0.9995	1–200	1	1	99.3	17.3	110.1	12.7	81.7	3.4	LC
154	Myclobutanil	C15H17ClN4	10.56	289.12145	70.03997	0.9996	5–200	1	5	110.7	15.3	93.8	6.3	83.1	5.2	LC
155	Napropamide	C17H21NO2	11.63	272.16451	171.08044	0.9999	1–200	1	1	84.6	2.7	94.7	2.1	83.9	1.6	LC
156	Norflurazon	C12H9ClF3N3O	7.06	304.04590	140.03062	0.9998	1–200	1	1	87.7	2.8	95.0	2.7	82.4	1.0	LC
157	Omethoate	C5H12NO4PS	2.08	214.02974	182.98755	0.9988	1–200	1	1	85.5	8.5	92.2	5.6	80.2	2.7	LC
158	Oxadiazon	C15H18Cl2N2O3	25.39	174.95862	258.03214	0.9999	2–200	2	2	98.2	15.3	81.3	17.4	84.2	2.1	GC
159	Oxadixyl	C14H18N2O4	4.99	279.13393	132.08078	0.9999	1–200	1	1	84.8	19.7	117.3	11.0	93.9	3.3	LC
160	Paclobutrazol	C15H20ClN3O	25.79	236.05852	125.01525	0.9996	2–200	1	2	86.4	2.7	82.0	9.3	81.8	2.6	GC
161	Pentachloroaniline	C6H2Cl5N	18.83	264.85950	266.85657	0.9975	1–200	1	1	72.1	6.9	70.9	5.6	71.5	1.6	GC
162	Pentachloroanisole	C7H3Cl5O	14.82	264.83569	279.85919	0.9945	1–200	1	1	72.6	9.2	71.0	2.6	71.2	1.5	GC
163	Penthiopyrad	C16H20F3N3OS	14.47	360.13620	256.03506	0.9998	1–200	1	1	97.1	8.3	91.1	4.1	83.4	1.1	LC
164	Phenthoate	C12H17O4PS2	14.95	321.03786	79.05423	0.9999	2–200	2	2	84.7	11.0	74.6	18.2	100.6	7.8	LC
165	Phorate-Sulfone	C7H17O4PS3	8.56	293.00970	96.95076	0.9933	5–200	5	5	76.4	0.5	70.5	11.2	70.3	11.8	LC
166	Phorate-Sulfoxide	C7H17O3PS3	6.30	277.01502	96.95076	0.9998	1–200	1	1	99.7	7.2	97.6	5.5	85.6	1.2	LC
167	Phosalone	C12H15ClNO4PS2	15.96	367.99414	110.99960	0.9929	20–200	20	20	118.3	12.9	116.0	11.7	88.8	2.4	LC
168	Phosphamidon	C10H19ClNO5P	4.68	300.07621	127.01547	0.9997	1–200	1	1	88.2	7.1	91.8	3.1	84.7	1.2	LC
169	Phoxim	C12H15N2O3PS	15.98	299.06138	77.03889	0.9917	10–200	5	10	71.1	10.9	74.2	17.6	110.9	14.9	LC
170	Picoxystrobin	C18H16F3NO4	14.65	368.11042	145.06479	0.9993	1–200	1	1	101.0	16.6	94.6	8.8	84.0	5.2	LC
171	Piperonyl butoxide	C19H30O5	17.06	356.24230	119.08553	0.9994	1–200	1	1	93.5	10.4	82.4	7.7	78.2	1.6	LC

Table 1. *Cont.*

No	Compound	Formula	RT (Min)	Quantitative Ion	Qualitative Ion	R^2	Linearity (ng/g)	SDL (ng/g)	LOQ (ng/g)	1-LOQ		2-LOQ		10-LOQ		Detecting Instrument
										REC (%)	RSD (%)	REC (%)	RSD (%)	REC (%)	RSD (%)	
172	Pirimicarb	C11H18N4O2	4.41	239.15025	72.04439	0.9975	1–200	1	1	78.3	14.4	95.3	4.3	78.0	3.7	LC
173	Pirimiphos-methyl	C11H20N3O3PS	15.87	306.10358	67.02908	0.9999	1–200	1	1	86.0	4.2	91.7	1.1	80.5	0.8	LC
174	Pretilachlor	C17H26ClNO2	16.17	312.17248	252.11497	0.9999	1–200	1	1	116.7	4.8	88.7	9.4	82.8	3.9	LC
175	Prochloraz	C15H16Cl3N3O2	13.20	376.03809	70.02874	0.9998	1–200	1	1	82.4	6.7	97.2	7.6	79.0	2.6	LC
176	Profenofos	C11H15BrClO3PS	16.14	372.94242	96.95094	0.9984	2–200	2	2	94.5	15.6	92.5	6.5	98.6	3.3	LC
177	Prometryn	C10H19N5S	8.73	242.14339	68.02432	0.9997	1–200	1	1	82.1	2.7	89.7	1.9	79.7	2.0	LC
178	Propamocarb	C9H20N2O2	2.18	189.15975	74.02366	0.9983	1–200	1	1	69.3	17.2	90.3	13.7	79.9	8.3	LC
179	Propanil	C9H9Cl2NO	7.97	218.01340	127.01784	0.9996	5–200	2	5	71.1	6.8	70.4	7.0	88.1	1.7	LC
180	Propaphos	C13H21O4PS	13.10	305.09709	44.97935	0.9998	1–200	1	1	83.3	5.4	83.7	2.8	81.4	1.5	LC
181	Propargite	C19H26O4S	18.28	368.18860	57.06988	0.9910	5–200	5	5	84.8	15.8	96.3	12.5	116.2	19.9	LC
182	Propazine	C9H16ClN5	8.11	230.11670	146.02280	0.9992	1–200	1	1	82.0	1.8	99.6	4.1	80.8	2.7	LC
183	Propiconazole	C15H17Cl2N3O2	13.23	342.07706	69.06988	0.9999	1–200	1	1	85.5	5.2	87.0	5.8	77.6	3.4	LC
184	Propyzamide	C12H11Cl2NO	11.01	256.02905	189.98210	0.9989	5–200	1	5	82.8	4.2	82.3	10.9	92.2	4.1	LC
185	Prothioconazole	C14H15Cl2N3OS	12.48	344.03860	102.01205	0.9942	5–200	5	5	70.2	0.8	117.9	18.9	70.4	10.6	LC
186	Prothioconazole-desthio	C14H15Cl2N3O	10.35	312.06640	70.03997	0.9999	1–200	1	1	87.0	6.6	89.6	5.0	80.2	1.7	LC
187	Pymetrozine	C10H11N5O	2.04	218.10364	105.04472	0.9943	1–200	1	1	113.0	9.8	81.7	8.7	71.3	11.5	LC
188	Pyraclostrobin	C19H18ClN3O4	15.40	388.10586	194.08118	0.9999	0.2–200	0.2	0.2	105.8	18.2	104.8	13.2	84.5	2.4	LC
189	Pyridaben	C19H25ClN2OS	18.83	365.14489	147.11682	0.9988	1–200	1	1	114.4	19.2	80.5	9.1	70.2	2.5	LC
190	Pyridaphenthion	C14H17N2O4PS	11.59	341.07194	92.04979	0.9998	1–200	1	1	72.5	9.5	92.7	6.8	85.6	1.5	LC
191	Pyrimethanil	C12H13N3	7.56	200.11822	77.03857	0.9995	5–200	1	5	84.9	6.6	76.3	2.2	90.8	3.4	LC
192	Pyriproxyfen	C20H19NO3	17.50	322.14377	96.04439	0.9998	1–200	1	1	87.7	15.8	86.4	3.4	76.5	3.5	LC
193	Quinalphos	C12H15N2O3PS	14.00	299.06138	96.95076	0.9999	1–200	1	1	90.3	10.2	100.0	2.9	79.9	2.4	LC
194	Quinoxyfen	C15H8Cl2FNO	16.79	308.00397	196.97887	0.9998	1–200	1	1	72.8	1.8	79.1	3.8	70.2	4.3	LC
195	Quintozene	C6Cl5NO2	16.21	236.84077	294.83371	0.9972	1–200	1	1	82.3	18.0	73.6	10.0	82.5	16.0	GC
196	Quizalofop-ethyl	C19H17ClN2O4	16.62	373.09496	91.05423	0.9997	1–200	1	1	105.5	15.8	103.8	9.9	76.0	0.9	LC
197	Saflufenacil	C17H17ClF4N4O5S	10.90	501.06170	348.99976	0.9994	1–200	1	1	112.6	17.7	83.8	17.3	82.7	6.0	LC
198	Simazine	C7H12ClN5	5.00	202.08540	68.02432	0.9997	1–200	1	1	93.1	1.7	96.5	5.2	84.2	2.3	LC
199	Spinosyn D	C42H67NO10	15.36	746.48377	142.12263	0.9998	1–200	1	1	88.0	8.6	98.9	9.1	80.1	5.2	LC
200	Spirodiclofen	C21H24Cl2O4	18.97	411.11244	71.08553	0.9992	0.5–200	0.5	0.5	73.9	19.9	119.8	12.3	103.1	13.8	LC
201	Spirotetramat	C21H27NO5	10.10	374.19620	302.17508	0.9996	5–200	2	5	81.0	12.2	70.5	7.6	77.3	5.3	LC
202	Spirotetramat-enol	C18H23NO3	5.29	302.17580	216.10190	0.9996	1–200	1	1	84.6	7.0	83.2	2.8	75.5	3.0	LC
203	Spirotetramat-enol-glucoside	C24H33NO8	2.86	464.22790	216.10190	0.9926	1–200	1	1	120.8	8.5	134.3	2.0	185.9	11.2	LC
204	Spiroxamine	C18H35NO2	8.76	298.27406	100.11208	0.9990	1–200	1	1	91.3	12.4	80.9	3.1	78.2	3.5	LC
205	Sulfentrazone	C11H10Cl2F2N4O3S	6.34	386.98915	306.99435	0.9988	5–200	5	5	76.7	5.3	83.6	4.9	94.0	4.3	LC
206	Sulfotep	C8H20O5P2S2	15.67	322.02219	237.92828	1.0000	1–200	1	1	95.4	16.1	91.2	9.3	79.1	9.5	GC

Table 1. *Cont.*

No	Compound	Formula	RT (Min)	Quantitative Ion	Qualitative Ion	R^2	Linearity (ng/g)	SDL (ng/g)	LOQ (ng/g)	1-LOQ		2-LOQ		10-LOQ		Detecting Instrument
										REC (%)	RSD (%)	REC (%)	RSD (%)	REC (%)	RSD (%)	
207	Sulfoxaflor	C10H10F3N3OS	4.48	278.05690	154.04628	0.9983	2–200	2	2	91.0	8.9	72.7	5.3	100.7	5.8	LC
208	Sulprofos	C12H19O2PS3	17.99	323.03575	218.96979	0.9997	2–200	1	2	72.4	14.0	89.1	10.9	86.6	5.5	LC
209	Tebuconazole	C16H22ClN3O	11.75	308.15240	70.03997	0.9999	2–200	1	2	95.8	5.9	80.8	6.7	87.3	6.0	LC
210	Tebufenozide	C22H28N2O2	13.92	353.22235	133.06479	0.9984	2–200	1	2	113.1	9.4	58.5	18.1	85.0	17.5	LC
211	Terbufos	C9H21O2PS3	17.05	289.05141	57.06988	0.9981	10–200	2	10	88.5	16.1	90.9	7.5	85.0	15.4	LC
212	Terbufos-Sulfone	C9H21O4PS3	11.57	321.04120	275.05353	0.9982	2–200	2	2	114.0	16.7	92.9	9.6	98.1	3.4	LC
213	Terbufos-Sulfoxide	C9H21O3PS3	8.23	305.04650	130.93848	0.9999	1–200	1	1	114.9	13.2	106.3	12.6	79.7	5.2	LC
214	Terbumeton	C10H19N5O	17.40	210.13493	169.09581	0.9986	1–200	1	1	111.8	18.6	79.2	6.9	85.4	2.4	GC
215	Terbuthylazine	C9H16ClN5	8.82	230.11670	174.05409	0.9998	1–200	1	1	89.3	18.9	98.2	8.4	79.8	3.4	LC
216	Terbutryn	C10H19N5S	9.10	242.14339	186.08080	0.9992	1–200	1	1	82.3	3.6	90.0	2.3	76.2	4.4	LC
217	Tetramethrin	C19H25NO4	17.04	332.18560	164.07060	0.9988	5–200	2	5	97.8	13.0	92.4	4.4	98.6	5.5	LC
218	Thiabendazole	C10H7N3S	2.90	202.04334	131.06038	0.9999	1–200	1	1	74.3	3.9	82.4	5.1	73.1	1.8	LC
219	Thiacloprid	C10H9ClN4S	4.51	253.03092	126.00867	0.9993	1–200	1	1	87.3	5.1	98.5	1.7	82.0	2.0	LC
220	Thiamethoxam	C8H10ClN5O3S	3.13	292.02656	131.96643	0.9950	1–200	1	1	79.4	11.6	81.3	5.6	74.7	6.9	LC
221	Thiobencarb	C12H16ClNOS	15.15	258.07139	125.01525	0.9985	2–200	2	2	84.6	18.6	89.5	13.2	90.6	1.3	LC
222	Thiophanate-methyl	C12H14N4O4S2	5.43	343.05292	151.03244	0.9992	1–200	1	1	102.4	5.6	82.9	2.0	73.9	3.0	LC
223	Tolfenpyrad	C21H22ClN3O2	16.91	384.14770	197.09608	0.9998	1–200	1	1	82.0	13.2	79.0	3.6	76.3	8.1	LC
224	Trans-Chlordane	C10H6Cl8	23.38	372.82544	374.82251	0.9997	1–200	1	1	78.6	6.2	71.2	6.4	70.6	4.5	GC
225	Triadimefon	C14H16ClN3O2	11.17	294.10038	57.06988	0.9996	1–200	1	1	90.9	10.0	85.9	8.2	83.1	3.9	LC
226	Triadimenol	C14H18ClN3O2	8.54	296.11580	70.03997	0.9998	5–200	5	5	90.6	14.0	74.5	11.0	84.3	4.3	LC
227	Triazophos	C12H16N3O3PS	12.72	314.07228	119.06037	0.9980	1–200	1	1	84.1	2.2	61.2	2.3	83.3	1.9	LC
228	Trichlorfon	C4H8Cl3O4P	3.33	256.92985	78.99452	0.9992	10–200	5	10	77.3	13.4	91.6	8.5	84.2	7.1	LC
229	Trifloxystrobin	C20H19F3N2O4	16.67	409.13697	145.02596	0.9992	1–200	1	1	88.2	3.8	89.0	3.7	81.4	1.3	LC
230	Triflumizole	C15H15ClF3N3O	14.98	346.09290	69.04472	1.0000	1–200	1	1	88.5	6.5	90.9	4.6	80.5	2.0	LC
231	Trifluralin	C13H16F3N3O4	15.26	264.02267	306.06961	0.9981	2–200	2	2	79.1	7.0	71.3	11.1	80.3	6.4	GC
232	Trinexapac-ethyl	C13H16O5	7.54	253.10705	69.03349	0.9996	5–200	5	5	75.4	9.5	60.1	12.4	73.4	3.4	LC
233	Uniconazole	C15H18ClN3O	10.58	292.12130	70.03997	0.9999	1–200	1	1	60.9	16.4	84.6	8.3	79.7	1.7	LC
234	Vinclozolin	C12H9Cl2NO3	20.63	212.00284	186.95862	0.9962	2–200	2	2	67.7	12.7	80.4	4.4	83.7	4.9	GC
235	Warfarin	C19H16O4	8.91	309.11214	163.03897	0.9997	0.5–200	0.5	0.5	98.7	15.0	99.5	6.0	91.0	6.7	LC
236	Zoxamide	C14H16Cl3NO2	14.92	336.03194	186.97119	0.9997	1–200	1	1	92.8	7.1	96.0	4.2	83.0	2.0	LC
237	Endrin	C12H8Cl6O	25.22	316.90341	262.85641	0.9962	5–200	5	5	63.7	19.8	76.5	5.5	78.2	4.5	GC

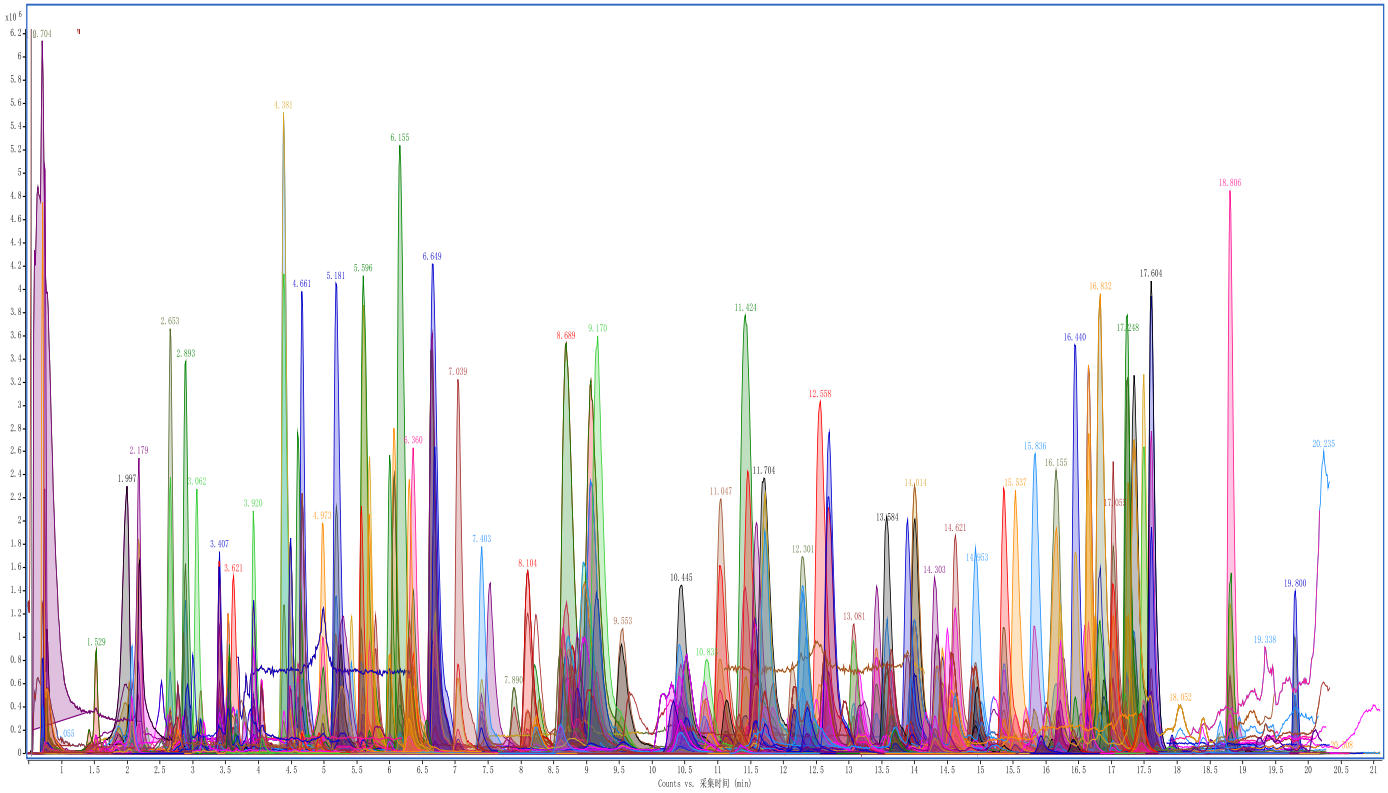

Figure 7. Overlay extraction ion chromatograms of LC-Q TOF/MS of cottonseed hull sample at spiking level of 200 µg/kg.

The calibration curve was plotted using the matrix matching calibration method and the target analytes at 10 spiked levels (0.2, 0.5, 1, 2, 5, 10, 20, 50, 100, and 200 µg/kg) were spiked to the blank cottonseed hull sample. The linear ranges of 237 pesticide analytes were 1–200 µg/L. All target pesticides showed good linearity in the concentration range, and R^2 was greater than 0.99, indicating that this method could meet the requirements of quantitative analysis.

3.6.2. Recovery and Precision

The recovery and precision of the method was evaluated by spiked standard solutions at the levels of 1-, 2-, and 10-times LOQ for the cottonseed hull samples with six parallels at each spiked level. The results are shown in Figure 8. At the levels of 1-, 2-, and 10-times LOQ, the recoveries of the 237 pesticides in the range of 70–120% were 91.6%, 92.8%, and 94.5%, respectively, and the RSD of all the pesticides was less than 20%, indicating that the method had satisfactory recovery and precision.

Among the 237 pesticides, 60 pesticides were detected by two detection techniques, and most of them showed similar performance; however, individual pesticides were different in the two techniques. For example, the average recovery (81.2%) of clodinafop-propargyl detected by GC-QTOF/MS was lower than that (95.7%) detected by LC-QTOF/MS. In terms of precision, the RSD (10.8%) of the compound detected by GC-QTOF/MS was higher than that (4.8%) detected by LC-QTOF/MS. For Propiconazole, the average recovery and RSD of GC-QTOF/MS (89.0%, 5.5%) were better than those of LC-QTOF/MS (80.0%, 6.4%). Therefore, appropriate detection techniques should be selected in pesticide residue analysis, especially when compounds are suitable for these two detection techniques.

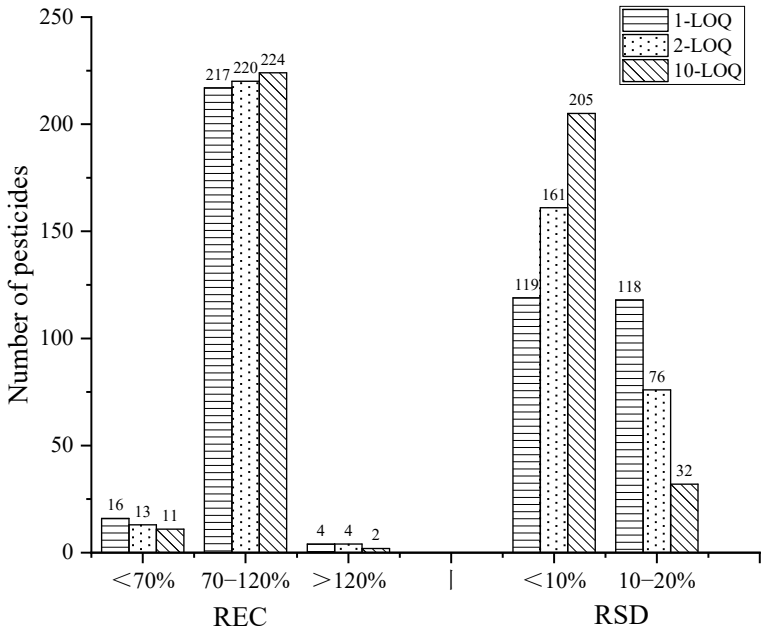

Figure 8. The recovery and RSD of the target pesticides at three spiked levels.

3.7. Analysis of Real Samples

The established method was applied to the analysis of 11 real cottonseed hull samples collected from several domestic pastures. The results showed that three pesticide residues were found in 11 cottonseed hull samples (butylate (three times), fenbuconazole (three times), and Diuron (two times)), with concentrations ranging from 10 to 28 μg/kg and above the LOQ. The determined three pesticides were slightly hazardous, according to WHO [32]. This method can be used for high-throughput trace detection of pesticide residues in cottonseed hull samples and improve the ability of risk-screening.

4. Conclusions

In this work, GC-QTOF/MS and LC-QTOF/MS were used to develop a high throughput method for qualitative screening and quantitative analysis of 237 pesticides in the cottonseed hull matrix. The modified QuEChERS extraction process seems to effectively eliminate the interference caused by the oily matrix, and the SDL, LOQ, recovery, and precision of the analysis method were verified under optimal conditions. In addition, compared with other methods for the oily matrix, this method has the advantages of being fast and simple, with high throughput and low solvent consumption. The results showed that the developed method could be applied to the screening of pesticide residues in the cottonseed hull matrix, effectively and generally.

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