Hindawi
Journal of Analytical Methods in Chemistry
Volume 2022, Article ID 7684432, 17 pages
https://doi.org/10.1155/2022/7684432

Research Article

Rapid Screening of 352 Pesticide Residues in Chrysanthemum Flower by Gas Chromatography Coupled to Quadrupole-Orbitrap Mass Spectrometry with Sin-QuEChERS Nanocolumn Extraction

Yuanyuan Wang,[1] **Zhijuan Meng**,[2] **Chunyan Su**,[3] **Sufang Fan**,[2] **Yan Li**,[2] **Haiye Liu**,[1] **Xuan Zhang**,[1] **Pingping Chen**,[1] **Yunyun Geng**,[1] **and Qiang Li**[2]

[1]*Department of Pharmacology, College of Basic Medicine, Hebei University of Chinese Medicine, Shijiazhuang, 050200 Hebei, China*
[2]*Hebei Food Inspection and Research Institute, Key Laboratory of Food Safety of Hebei Province, Shijiazhuang, 050091 Hebei, China*
[3]*School of Pharmacy, Hebei University of Chinese Medicine, Shijiazhuang, 050200 Hebei, China*

Correspondence should be addressed to Yuanyuan Wang; wangyy0830@iccas.ac.cn and Qiang Li; liqiang@nepp.com.cn

Received 31 January 2022; Revised 13 April 2022; Accepted 10 May 2022; Published 15 June 2022

Academic Editor: Eliseo Herrero Hernandez

To analyze pesticide residues, GC coupled with quadrupole-Orbitrap MS (GC-Orbitrap-MS) has become a powerful tool because of its unique characteristics of accurate mass full-spectrum acquisition, high resolution, fast acquisition rates, and overcoming matrix interference. This paper presents an efficiency evaluation of GC-Orbitrap-MS for identification and quantitation in the 352 pesticide residues analysis of chrysanthemum flowers in full-scan mode. A streamlined pretreatment approach using one-step extraction and dilution was used, which provided high-throughput processing and excellent recovery. The samples were extracted using acetonitrile. The extracted solution was purified by a Sin-QuEChERS Nano column to suppress the matrix in chrysanthemum flowers and determined by GC-Orbitrap-MS. The calibration curves for the 352 pesticides obtained by GC-Orbitrap-MS were linear in the range of 0.5–200 $\mu g \cdot kg^{-1}$, with the correlation coefficients higher than 0.99. The limits of detection (LODs) and the limits of quantification (LOQs) for the 352 pesticide residues were 0.3–3.0 $\mu g \cdot kg^{-1}$ and 1.0–10.0 $\mu g \cdot kg^{-1}$, respectively. The average recoveries in chrysanthemum flower at three levels were 95.2%, 88.6%, and 95.7%, respectively, with relative standard deviations (RSDs) of 7.1%, 7.5%, and 7.2%, respectively. Lastly, the validated method and retrospective analysis was applied to a total of 200 chrysanthemum flower samples bought in local pharmacies. The proposed method can simultaneously detect multipesticide residues with a good performance in qualitative and quantitative detection.

1. Introduction

Chrysanthemum flower (*Dendranthema grandiflora*) is one of the most common Chinese herbal medicines, and it has been consumed as food for health care and disease prevention since ancient times. It is mainly used for the treatment of respiratory and cardiovascular diseases and shows significant activities, such as antimicrobial, anti-inflammatory, and anti-cancer and neuroprotective and cardiovascular system [1]. Because of its efficacy in alleviating chronic diseases, some consumers often drink chrysanthemum tea as a health food [2]. The chrysanthemum flower, as a good product of the "integration of medicine and food" [3], has a huge consumer group.

However, in order to minimize the loss of crops during planting, pesticides are widely used to control many plant diseases and insects, such as gray mold, rust, aphids, thrips, leaf pickers, leaf folding insects, and spider mites [4]. Therefore, chrysanthemum flowers may be exposed to a variety of pesticides and contain pesticide residues. However, with the widespread use of pesticides, overuse, abuse, and misuse of pesticides also occur from time to time, which

will lead to pesticide residues in chrysanthemum flowers, thus constituting a potential threat to human health and adversely affecting international trade.

Because of the potential of pesticide contamination in current agricultural products, many countries and world organizations (e.g., Codex Alimentarius Commission, European Union (EU), United States, Japan, China, Republic of Korea, Canada) have prescribed stringent stipulations for maximum residue limits (MRLs) for pesticides. For instance, there are 162,248 MRL items that cover 465 pesticides in the EU, 39,147 MRL items that cover 351 pesticides in the United States, and 51,600 MRL items that cover 579 pesticides in Japan, and the residue limit level is as low as $10\,\mu g{\cdot}kg^{-1}$, and 10,092 MRLs for 564 pesticides in 376 kinds of food was stipulated in China National standards for food safety. Implementing these laws and regulations has strengthened supervision over pesticides and ensured the standard use of pesticides to protect human health. However, laws and regulations of such a multitude of MRLs pose a new challenging issue for the monitoring and controlling of pesticide residues.

At present, the commonly used pesticide residues pretreatment methods include solid-phase extraction [5], solid-phase microextraction [6], gel permeation chromatography [7], and the QuEChERS [8–10]. Among them, the QuEChERS method is widely used, but in most studies, there are many kinds of purification materials with a large amount, low purification efficiency, and large matrix effect, which is not conducive to the rapid and accurate analysis of the experiment [11, 12]. Therefore, the selection of suitable purification materials is conducive to the high-throughput treatment of complex matrices. Sin-QuEChERS Nano column is a new type of rapid sample pretreatment purification column developed and optimized based on the QuEChERS method. Based on the basic principle of reversed dispersion solid-phase extraction, multiwalled carbon nanotubes (MWCNTs), PSA, and C_{18} solid-phase materials are filled into the column tube to achieve one-step purification. MWCNTs have the characteristics of the nanoscale hollow tubular structure and large specific surface area, small dosage, strong adsorption capacity, stability, and durability, which are suitable for the treatment of complex matrices and have better purification and adsorption effect [13–15].

In the past 10 years, most pesticide food control laboratories have shifted from GC-MS to GC-MS/MS as the preferred analytical technology for the treatment of GC amenable compounds. The main reason for this change is that the interference of eluting matrix compounds has a negative impact on single-stage GC-MS analysis. In recent years, the demand for nontargeted detection methods of LC and GC combined with full-scan (FS) MS is increasing, so as to better cover the scope of pesticides and detect them more easily. In GC-MS, FS measurement has been realized for decades, but quadrupole (Q), ion trap, nominal mass time of flight (TOF), and early-generation high-resolution TOF instruments lack sensitivity and/or selectivity. The improvement of high-resolution mass spectrometry (HRMS) in resolution and obtaining appropriate selectivity by improving mass resolution provides new opportunities for residue analysis. Initially, GC and Q-TOF instruments were coupled through the atmospheric pressure chemical ionization (APCI) interface to achieve this goal [16–18], but recently, a special GC and electron ionization (EI) Orbitrap MS system was introduced. The system combines the peak capacity and chromatographic resolution of gas chromatography with the sub-ppm mass accuracy of the Orbitrap system to provide higher resolution (15,000, 30,000, 60,000, and 120,000 at half-maximum (FWHM) at m/z 200). The collected data are traceable, which is convenient for retrospective analysis and screening of more interested unknown compounds. Compared with the instrument based on APCI, EI is a more general ionization technology. Because multiple ions for quantification and identification can be obtained in one scanning event, the acquisition is also simpler.

In this study, the potential of GC-Orbitrap-MS in nontarget full-scan independent acquisition mode was evaluated for identification and quantitation purposes. A total of 352 pesticides were selected as the target analytical compounds from the 2020 edition of Chinese Pharmacopoeia. An improved QuEChERS method based on Sin-QuEChERS Nano column purification was used [19, 20]. Method validation in chrysanthemum flowers samples was carried out in terms of sensitivity, linearity, ME, and LOQ. Lastly, the validated method and retrospective analysis was applied to a total of 200 chrysanthemum flower samples bought in local pharmacies (Shijiazhuang, China). This method is suitable for the rapid screening and quantitative analysis of multipesticide residues in chrysanthemum flower and provides data and technical support for the safety evaluation of chrysanthemum flowers.

2. Materials and Methods

2.1. Instruments and Reagents. Analytical standards of the 352 pesticides ($10\,\mu g{\cdot}mL^{-1}$) were purchased from Alta Scientific Ltd. (Tianjin, China). A total of 352 kinds of pesticide mixed standard stock solution were prepared with acetonitrile at a concentration of $10\,\mu g{\cdot}mL^{-1}$ and stored in the refrigerator at −18°C. HPLC-grade acetonitrile was purchased from Merck (Darmstadt, Germany). HPLC-grade water was from Milford Super Pure Water System (Milford, MA). Two types of traditional QuEChERS purification were purchased from Thermo Fisher Scientific (Massachusetts, USA). QuEChERS purification package (simple matrix), includes 50.0 mg PSA and 150.0 mg MgSO4; QuEChERS purification package (complex matrix), includes 50.0 mg PSA, 150.0 mg MgSO4, 50 mg C18, and 50 mg GCB. We used two kinds of salting-out for the QuEChERS method: an unbuffered salt system, including 6 g $MgSO_4$ and 1.5 g NaCl, and an acetate buffer salt system, including 6 g $MgSO_4$ and 1.5 g sodium acetate, purchased from Thermo Fisher Scientific Inc. (Fair Lawn, NJ). Sin-QuEChERS Nano column, including 2 g Na_2SO_4, 0.6 g $MgSO_4$, 90 mg PSA, 10 mg C18, and 15 mg MWCNTs, were purchased from China

Agricultural University (Beijing, China). All the chrysanthemum flower materials were purchased from local pharmacies (Shijiazhuang, China).

2.2. Sample Extraction Methods. The samples were crushed by FW100 High-Speed Universal Crusher (Tianjin Tester instrument Co. Ltd.) and mixed well. Two grams of chrysanthemum flower powder (±0.01 g) were then added into a 50 ml plug centrifuge tube; 10 ml of water was added for redissolution; the tube was vortexed for 1 min; and then the sample was allowed to fully soak and evenly disperse. Then, 10 ml acetonitrile was added, mixed well, and vortexed for 1 min. Next, an acetate buffer salt system containing 6 g anhydrous $MgSO_4$ and 1.5 g sodium acetate was added; the tube was vortexed for 1 min, put into an ice water bath for 10 min, and centrifuged for 2 min at 4°C, 9,500 r·min^{-1}, and the supernatant was taken for use.

2.3. Sample Purification Methods

(1) Traditional QuEChERS purification: we tested the purification efficiency of two QuEChERS purification packages: one was a simple matrix, including 50.0 mg PSA and 150.0 mg $MgSO_4$, and the other was a complex matrix, including 50.0 mg PSA, 150.0 mg $MgSO_4$, 50 mg C18, and 50 mg GCB. We transferred 2 ml of the extracted supernatant into a QuEChERS purification centrifuge tube, mixed this by oscillation for 1 min, centrifuged it at 9,500 r·min^{-1} for 3 min, absorbed the supernatant, passed this through a 0.22 μm nylon filter membrane to an injection bottle, and waited for sample analysis by the GC-Orbitrap-MS.

(2) Sin-QuEChERS Nano column purification: we tested the purification efficiency of the Sin-QuEChERS Nano column, including 2 g Na_2SO_4, 0.6 g $MgSO_4$, 90 mg PSA, 10 mg C18, and 15 mg MWCNTs. The purification column of the Sin-QuEChERS Nano purification tube is vertically inserted into the 50 ml centrifuge tube containing the extract, and the top of the purification column is slowly pressed down so that the upper organic extract in the centrifuge tube passes through the water blocking filter and column filler in the purification column from bottom to top, and finally enters into the Sin-QuEChERS Nano storage tank for about 4 ml of supernatant. After mixing the purified liquid, the supernatant is sucked over a 0.22 μm nylon filter membrane to the injection bottle for analysis by GC-Orbitrap-MS.

By comparing the purification effects, total ions, and recovery rates of these three purification methods, the Sin-QuEChERS Nano column was finally selected as the purification method for method validation and real sample analysis. See Section 3.2 "Selection of Purification Conditions" for the comparison results.

2.4. Preparation of Standard Solution. The mixed standard stock solutions of 352 pesticides were diluted with the blank extract of the matrix, and a series of standard solutions with concentrations of 0.005, 0.02, 0.05, 0.1, and 0.2 μg·ml^{-1} were prepared. The matrix mixed standard solution was prepared and used immediately.

2.5. Instrument Conditions. We followed and optimized the methods of previous works [21, 22]. A GC-Orbitrap-MS system (Thermo Scientific, Bremen, Germany) consisting of an AI/AS 1310 TriPlus RSH™ autosampler was used. TRACE 1300 Series GC with a hot split/splitless injector, an EI source, and a hybrid quadrupole Orbitrap mass spectrometer with an HCD (higher energy collision-induced dissociation) cell was used.

GC separation was performed on a 30 m × 0.25 mm id, 0.25 μm Thermo Scientific TG-5MS column using the following temperature program: 40°C, 1.5 min; 25°C·min^{-1} to 90°C, 1.5 min; 25°C·min^{-1} to 180°C, 0 min; 5°C·min^{-1} to 280°C, 0 min; and 10°C·min^{-1} to 310°C, 3 min. Helium 5.0 (99.999%; Linde Gas, Schiedam, The Netherlands) was used as carrier gas at a constant flow of 1 mL·min^{-1}. The transfer line was maintained at 280°C. EI was performed at 70 eV, with the source temperature set at 280°C. FS MS acquisition was done in profile mode using an m/z range of 50–550. The nitrogen gas supply for the C-trap was 5.0 grade (99.999%; Linde Gas). The resolving power was set at 60,000 (FWHM at m/z 200) to ensure high mass accuracy. The automatic gain control (AGC) target was set at $5e^6$ ions, with the maximum ion injection time set to 25 ms.

2.6. Establishment of Database. In this experiment, 352 pesticide compounds were selected and prepared into 1.0 μg·ml^{-1} mixed standard solutions. The retention time of the corresponding compounds, the accurate molecular weight, and the chemical formula of the fragment ions were obtained under the full-scan mode. Three fragment ions of each compound were selected to obtain ion information (accurate mass and chemical formula). The data were imported into TraceFinder (4.1) software, and the relevant database was established. The TraceFinder software not only can realize the rapid batch and automatic processing of data but also can set the functions of qualitative, quantitative, and method establishment. According to the established database, it can realize the rapid screening of target substances. The database mainly contains the compounds' names, CAS registration numbers, fragment ion information, retention times, and other information (Table 1).

3. Results and Discussion

3.1. Optimization of Extraction Conditions. According to the list of pesticides involved in the 2020 edition of Chinese Pharmacopoeia, combined with pesticides, herbicides, and fungicides that may be used in chrysanthemum flower planting, 352 pesticides were selected as the target analytical

Table 1: Information of the 352 pesticides detected in chrysanthemum flower samples by GC-Orbitrap-MS screening.

Pesticides	CAS	Molecular formula	Retention time (min)	Quantitative ion (m/z)	Qualitative ion (m/z)	
					1	2
Clopyralid	1702-17-6	$C_6H_3Cl_2NO_2$	6.38	146.96	76.02	111.99
Dichlorvos	62-73-7	$C_4H_7O_4PCl_2$	7.99	184.98	186.97	144.98
Methamidophos	10265-92-6	$C_2H_8NO_2PS$	8.02	141.00	112.01585	125.98
Thiofanox	39196-18-4	$C_9H_{18}N_2O_2S$	8.20	115.10	161.09	83.07
Allidochlor	93-71-0	$C_8H_{12}NOCl$	8.27	138.09	132.02	96.08
Dichlobenil	1194-65-6	$C_7H_3Cl_2N$	8.68	170.96	100.02	172.96
EPTC	759-94-4	$C_9H_{19}NOS$	8.71	128.11	132.08	160.08
Dichlormid	37764-25-3	$C_8H_{11}Cl_2NO$	8.72	172.05	108.08	165.98
2,4,6-Trichlorophenol	88-06-2	$C_6H_3OCl_3$	8.73	195.92	199.92	197.92
3,5-Dichloroaniline	626-43-7	$C_6H_5Cl_2N$	9.05	160.98	162.98	126.01
O-phthalimide	85-41-6	$C_8H_5NO_2$	9.15	147.03	103.04	104.03
Mevinphos	7786-34-7	$C_7H_{13}O_6P$	9.18	192.02	164.02	127.01
Acephate	30560-19-1	$C_4H_{10}NO_3PS$	9.25	136.02	112.02	94.00
Vernolate	1929-77-7	$C_{10}H_{21}NOS$	9.30	86.06	161.09	146.10
Propham	122-42-9	$C_{10}H_{13}NO_2$	9.37	137.05	179.09	120.08
Etridiazole	2593-15-9	$C_5H_5N_2OSCl_3$	9.40	210.95	212.95	182.92
Pebulate	1114-71-2	$C_{10}H_{21}NOS$	9.40	128.11	72.04	161.09
cis-1,2,3,6-Tetrahydrophthalimide	1469-48-3	$C_8H_9NO_2$	9.57	151.06	123.07	122.06
Chloroneb	2675-77-6	$C_8H_8O_2Cl_2$	9.77	190.97	192.96	205.99
Tebuthiuron	34014-18-1	$C_9H_{16}N_4OS$	9.86	156.06	89.02	171.08
Fenobucarb	3766-81-2	$C_{12}H_{17}NO_2$	9.93	121.06	91.05	93.07
Pentachlorobenzene	608-93-5	C_6HCl_5	9.95	247.85	251.85	249.85
Isoprocarb	2631-40-5	$C_{11}H_{15}NO_2$	9.98	121.06	136.09	103.05
Molinate	2212-67-1	$C_9H_{17}NOS$	10.01	126.09	187.10	98.10
Heptenophos	23560-59-0	$C_9H_{12}CLO_4P$	10.30	124.00	215.05	200.02
Chlorfenprop-methyl	14437-17-3	$C_{10}H_{10}O_2Cl_2$	10.43	165.01	196.03	167.00
Omethoate	1113-02-6	$C_5H_{12}NO_4PS$	10.47	156.00	110.01	140.98
Propoxur	114-26-1	$C_{11}H_{15}NO_3$	10.57	110.04	82.04	152.08
Tecnazene	117-18-0	$C_6HNO_2CL_4$	10.59	200.88	177.91	260.87
Propachlor	1918-16-7	$C_{11}H_{14}NOCl$	10.61	120.08	176.11	169.03
Diphenylamine	122-39-4	$C_{12}H_{11}N$	10.70	169.09	167.07	168.08
Ethoprophos	13194-48-4	$C_8H_{19}O_2PS_2$	10.77	157.96	199.00	200.01
Tributyl phosphate	126-73-8	$C_{12}H_{27}O_4P$	10.78	98.98	155.05	124.10
Cycloate	1134-23-2	$C_{11}H_{21}NOS$	10.79	154.12	155.13	72.04
2,3,5,6-Tetrachloroaniline	3481-20-7	$C_6H_3Cl_4N$	10.80	230.90	232.90	157.96
Atrazine-desethyl	6190-65-4	$C_6H_{10}N_5Cl$	11.00	172.04	145.01	187.06
Dicrotophos	141-66-2	$C_8H_{16}NO_5P$	11.07	127.02	193.03	111.07
Methabenzthiazuron	18691-97-9	$C_{10}H_{11}N_3OS$	11.07	136.02	164.04	135.01
Trifluralin	1582-09-8	$C_{13}H_{16}N_3O_4F_3$	11.08	264.02	306.07	248.03
Bendiocarb	22781-23-3	$C_{11}H_{13}NO_4$	11.09	151.04	126.03	223.08
Benfluralin	1861-40-1	$C_{13}H_{16}F_3N_3O_4$	11.12	292.05	276.06	318.11
Sulfotep	3689-24-5	$C_8H_{20}O_5P_2S_2$	11.20	322.02	209.90	173.96
Cadusafos	95465-99-9	$C_{10}H_{23}O_2PS_2$	11.25	158.97	130.94	213.02
Tebutam	35256-85-0	$C_{15}H_{23}NO$	11.27	91.05	190.12	233.18
Promecarb	2631-37-0	$C_{12}H_{17}NO_2$	11.27	135.08	107.09	150.10
Phorate	298-02-2	$C_7H_{17}O_2PS_3$	11.34	75.03	230.97	260.01
α-Hexachlorocyclohexane	319-84-6	$C_6H_6Cl_6$	11.95	180.94	145.97	218.91
Atratone	1610-17-9	$C_9H_{17}N_5O$	11.61	169.10	154.07	211.14
3,4,5-Trimethacarb	2686-99-9	$C_{11}H_{15}NO_2$	11.69	121.06	91.05	136.09
Dicloran	99-30-9	$C_6H_4Cl_2N_2O_2$	11.70	175.97	159.97	207.96
Pentachloroanisole	1825-21-4	$C_7H_3Cl_5O$	11.72	264.84	238.84	279.86

Table 1: Continued.

Pesticides	CAS	Molecular formula	Retention time (min)	Quantitative ion (m/z)	Qualitative ion (m/z)	
					1	2
Ethoxyquin	91-53-2	$C_{14}H_{19}NO$	11.72	202.12	174.09	203.13
Prometon	1610-18-0	$C_{10}H_{19}N_5O$	11.73	168.09	210.13	225.16
Atrazine	1912-24-9	$C_8H_{14}ClN_5$	11.84	200.07	202.07	173.05
Monolinuron	1746-81-2	$C_9H_{11}ClN_2O_2$	11.89	126.01	152.10	214.05
Propazine	139-40-2	$C_9H_{16}N_5Cl$	11.92	214.08	187.06	229.11
Clomazone	81777-89-1	$C_{12}H_{14}ClNO_2$	11.94	204.10	89.04	125.02
Terbumeton	33693-04-8	$C_{10}H_{19}N_5O$	11.95	210.13	169.10	225.16
β-Hexachlorocyclohexane	319-85-7	$C_6H_6Cl_6$	11.99	180.94	145.97	218.91
Aminocarb	2032-59-9	$C_{11}H_{16}N_2O_2$	12.04	151.10	136.08	150.09
Isocarbamid	30979-48-7	$C_8H_{15}N_3O_2$	12.05	142.06	130.06	113.03
Cyromazine	66215-27-8	$C_6H_{10}N_6$	12.06	151.07	165.09	166.10
γ-Hexachlorocyclohexane	58-89-9	$C_6H_6Cl_6$	12.12	180.94	145.97	218.91
Propetamphos	31218-83-4	$C_{10}H_{20}NO_4PS$	12.12	138.01	193.98	222.03
Cycluron	2163-69-1	$C_{11}H_{22}N_2O$	12.13	198.17	127.09	169.13
Terbuthylazine	5915-41-3	$C_9H_{16}N_5Cl$	12.14	186.05	188.05	201.08
Terbufos	13071-79-9	$C_9H_{21}O_2PS_3$	12.16	230.97	174.91	202.94
Cyanophos	2636-26-2	$C_9H_{10}NO_3PS$	12.17	243.01	124.98	109.00
Trietazine	1912-26-1	$C_9H_{16}N_5Cl$	12.17	200.07	214.09	229.11
Quintozene	82-68-8	$C_6NO_2Cl_5$	12.23	213.87	248.84	294.83
Fonofos	944-22-9	$C_{10}H_{15}OPS_2$	12.27	246.03	137.02	108.99
Pyroquilon	57369-32-1	$C_{11}H_{11}NO$	12.28	173.08	144.08	172.08
Dinoterb	1420-07-1	$C_{10}H_{12}N_2O_5$	12.35	225.05	177.04	161.05
Pyrimethanil	53112-28-0	$C_{12}H_{13}N_3$	12.35	198.10	199.11	183.08
Diazinon	333-41-5	$C_{12}H_{21}N_2O_3PS$	12.36	179.12	199.06	304.10
Flufenoxuron	101463-69-8	$C_{21}H_{11}CLF_6N_2O_3$	12.46	331.00	268.04	296.03
Disulfoton	298-04-4	$C_8H_{19}O_2PS_3$	12.51	88.03	153.01	141.97
Paraoxon-methyl	950-35-6	$C_8H_{10}NO_6P$	12.52	230.02	247.02	200.02
Secbumeton	26259-45-0	$C_{10}H_{19}N_5O$	12.52	196.12	169.10	210.13
Aziprotryne	4658-28-0	$C_7H_{11}N_7S$	12.53	182.05	139.01	225.08
Dinitramine	29091-05-2	$C_{11}H_{13}F_3N_4O_4$	12.53	305.09	244.06	261.06
Fenfuram	24691-80-3	$C_{12}H_{11}NO_2$	12.57	201.08	184.05	109.03
δ-Hexachlorocyclohexane	319-86-8	$C_6H_6Cl_6$	12.61	180.94	145.97	218.91
Mexacarbate	315-18-4	$C_{12}H_{18}N_2O_2$	12.63	165.11	164.11	222.14
Isazofos	42509-80-8	$C_7H_{13}N_3O_3PSCl$	12.66	162.04	161.03	177.01
Chlorothalonil	1897-45-6	$C_8Cl_4N_2$	12.71	263.88	193.94	228.91
Triallate	2303-17-5	$C_{10}H_{16}CL_3NOS$	12.71	268.03	270.03	142.92
Tebupirimfos	96182-53-5	$C_{13}H_{23}N_2O_3PS$	12.82	234.02	261.05	276.07
Musk ambrette	83-66-9	$C_{12}H_{16}N_2O_5$	12.83	253.08	251.10	268.10
Oxabetrinil	74782-23-3	$C_{12}H_{12}N_2O_3$	12.85	73.03	103.04	114.03
Iprobenfos	26087-47-8	$C_{13}H_{21}O_3PS$	12.87	204.00	171.02	246.05
Fluroxypyr	69377-81-7	$C_7H_5N_2O_3FCl_2$	12.92	180.97	208.97	195.96
Pirimicarb	23103-98-2	$C_{11}H_{18}N_4O_2$	12.95	238.14	166.10	137.07
Monalide	7287-36-7	$C_{13}H_{18}NOCl$	12.95	197.06	127.01	239.11
Furmecyclox	60568-05-0	$C_{14}H_{21}NO_3$	12.98	123.04	251.15	124.05
Benoxacor	98730-04-2	$C_{11}H_{11}NO_2C_{l2}$	12.99	120.04	259.02	261.01
Pentachloroaniline	527-20-8	$C_6H_2C_{l5}N$	13.14	262.86	191.92	229.89
Benfuresate	68505-69-1	$C_{12}H_{16}O_4S$	13.17	163.08	121.06	256.08

Table 1: Continued.

Pesticides	CAS	Molecular formula	Retention time (min)	Quantitative ion (m/z)	Qualitative ion (m/z)	
					1	2
Dioxacarb	6988-21-2	$C_{11}H_{13}NO_4$	13.17	121.03	165.05	166.06
Cyprazine	22936-86-3	$C_9H_{14}N_5Cl$	13.24	212.07	170.02	226.08
Phosphamidon	13171-21-6	$C_{10}H_{19}NO_5PCl$	13.25	138.09	193.02	264.10
Dichlorprop	120-36-5	$C_9H_8O_3Cl_2$	13.26	161.96	132.96	188.99
Dichlofenthion	97-17-6	$C_{10}H_{13}CL_2O_3PS$	13.26	222.94	250.97	279.00
Fenthion	55-38-9	$C_{10}H_{15}O_3PS_2$	13.26	222.94	250.97	279.00
Propanil	709-98-8	$C_9H_9NOCl_2$	13.26	160.98	162.98	219.00
2,4-DB	94-82-6	$C_{10}H_{10}O_3C_{l2}$	13.26	161.96	125.99	97.99
Chlorthiamid	1918-13-4	$C_7H_5Cl_2NS$	13.29	169.98	171.98	204.95
Dimethachlor	50563-36-5	$C_{13}H_{18}NO_2Cl$	13.29	197.06	148.08	134.10
Metribuzin	21087-64-9	$C_8H_{14}N_4OS$	13.31	198.07	144.05	182.04
Dimethenamid	87674-68-8	$C_{12}H_{18}NO_2SCl$	13.32	154.07	230.04	232.04
Bromobutide	74712-19-9	$C_{15}H_{22}NOBr$	13.35	119.09	120.08	232.17
Terbucarb	1918-11-2	$C_{17}H_{27}NO_2$	13.44	205.16	177.13	220.18
Malaoxon	1634-78-2	$C_{10}H_{19}O_7PS$	13.46	268.02	194.99	238.98
Vinclozolin	50471-44-8	$C_{12}H_9Cl_2NO_3$	13.48	178.04	212.00	285.10
Parathion-methyl	298-00-0	$C_8H_{10}NO_5PS$	13.49	263.00	124.98	245.99
Chlorpyrifos-methyl	5598-13-0	$C_7H_7Cl_3NO_3PS$	13.50	285.93	287.92	289.92
Transfluthrin	118712-89-3	$C_{15}H_{12}O_2F_4Cl_2$	13.54	163.02	127.03	335.05
Simetryn	1014-70-6	$C_8H_{15}N_5S$	13.56	213.10	155.04	170.05
Fuberidazole	3878-19-1	$C_{11}H_8N_2O$	13.57	184.06	156.07	183.06
Tolclofos-methyl	57018-04-9	$C_9H_{11}O_3PSCL_2$	13.61	264.98	249.96	266.98
Alachlor	15972-60-8	$C_{14}H_{20}NO_2Cl$	13.67	188.11	202.12	160.11
Ametryn	834-12-8	$C_9H_{17}N_5S$	13.67	227.12	170.05	185.07
Heptachlor	76-44-8	$C_{10}H_5CL_7$	13.72	269.81	100.01	336.85
Prometryn	7287-19-6	$C_{10}H_{19}N_5S$	13.75	241.13	184.07	199.09
Acetochlor	34256-82-1	$C_{14}H_{20}NO_2Cl$	13.76	223.08	162.10	174.10
Paraoxon-ethyl	311-45-5	$C_{10}H_{14}NO_6P$	13.77	275.05	247.02	139.05
Metalaxyl	57837-19-1	$C_{15}H_{21}NO_4$	13.78	160.11	206.12	146.10
Tridiphane	58138-08-2	$C_{10}H_7OC_{l5}$	13.84	186.97	172.96	284.92
Octachlorodipropyl ether	127-90-2	$C_6H_6OCl_8$	13.89	129.91	108.96	142.92
Prosulfocarb	52888-80-9	$C_{14}H_{21}NOS$	13.89	128.11	86.06	251.13
Fenpropidin	67306-00-7	$C_{19}H_{31}N$	13.97	98.10	273.24	258.22
1-naphthylacetamide	86-86-2	$C_{12}H_{11}NO$	14.05	141.07	142.08	185.08
Dithiopyr	97886-45-8	$C_{15}H_{16}NO_2F_5S_2$	14.05	306.05	258.05	354.06
Orbencarb	34622-58-7	$C_{12}H_{16}NOSCl$	14.08	222.09	125.02	100.08
Terbutryn	886-50-0	$C_{10}H_{19}N_5S$	14.08	226.11	185.07	170.05
Spiroxamine	118134-30-8	$C_{18}H_{35}NO_2$	14.11	100.11	126.13	198.15
Methiocarb	2032-65-7	$C_{11}H_{15}NO_2S$	14.15	168.06	153.04	154.04
Fenitrothion	122-14-5	$C_9H_{12}NO_5PS$	14.16	260.01	124.98	277.02
Pirimiphos-methyl	29232-93-7	$C_{11}H_{20}N_3O_3PS$	14.19	290.07	276.06	305.10
Methiocarb sulfone	2179-25-1	$C_{11}H_{15}NO_4S$	14.22	200.05	197.03	197.03
Ethofumesate	26225-79-6	$C_{13}H_{18}O_5S$	14.22	207.10	161.06	179.07
Linuron	330-55-2	$C_9H_{10}N_2O_2Cl_2$	14.27	159.97	61.05	248.01

Table 1: Continued.

Pesticides	CAS	Molecular formula	Retention time (min)	Quantitative ion (m/z)	Qualitative ion (m/z)	
					1	2
Probenazole	27605-76-1	$C_{10}H_9NO_3S$	14.33	130.07	103.04	158.06
Noruron	18530-56-8	$C_{13}H_{22}N_2O$	14.34	153.10	193.13	207.15
Quinoclamine	2797-51-5	$C_{10}H_6NO_2Cl$	14.37	172.04	144.04	207.01
Dipropetryn	4147-51-7	$C_{11}H_{21}N_5S$	14.38	255.15	222.17	184.07
Malathion	121-75-5	$C_{10}H_{19}O_6PS_2$	14.41	124.98	99.01	173.08
Thiobencarb	28249-77-6	$C_{12}H_{16}ClNOS$	14.44	257.06	100.08	125.02
Diethofencarb	87130-20-9	$C_{14}H_{21}NO_4$	14.51	267.15	225.10	168.03
Phorate sulfoxide	2588-03-6	$C_7H_{17}O_3PS_3$	14.57	124.93	170.97	199.00
Metolachlor	51218-45-2	$C_{15}H_{22}NO_2Cl$	14.61	162.13	211.08	238.10
Fenpropimorph	67564-91-4	$C_{20}H_{33}NO$	14.67	128.11	110.10	173.13
Cyanazine	21725-46-2	$C_9H_{13}ClN_6$	14.69	225.07	212.06	240.09
Chlorpyrifos	2921-88-2	$C_9H_{11}CL_3NO_3PS$	14.71	196.92	257.90	313.96
Parathion	56-38-2	$C_{10}H_{14}NO_5PS$	14.73	291.03	155.00	185.99
Flufenacet	142459-58-3	$C_{14}H_{13}N_3O_2F_4S$	14.79	210.98	136.06	151.08
Rabenzazol	40341-04-6	$C_{12}H_{12}N_4$	14.79	212.11	170.07	195.08
4,4′-Dichlorobenzophenone	90-98-2	$C_{13}H_8Cl_2O$	14.80	138.99	110.99	249.99
Triadimefon	43121-43-3	$C_{14}H_{16}ClN_3O_2$	14.80	208.03	210.02	181.02
Chlorthal-dimethyl	1861-32-1	$C_{10}H_6CL_4O_4$	14.86	300.88	298.88	331.90
Dicapthon	2463-84-5	$C_8H_9NO_5PSCl$	14.86	261.99	124.98	216.00
Isofenphos-oxon	31120-85-1	$C_{15}H_{24}NO_5P$	14.87	200.99	229.03	272.07
Isocarbophos	24353-61-5	$C_{11}H_{16}NO_4PS$	14.90	135.99	230.00	121.03
Tetraconazole	112281-77-3	$C_{13}H_{11}Cl_2F_4N_3O$	14.92	336.05	136.01	170.98
Isobenzan	297-78-9	$C_9H_4CL_8O$	15.00	407.78	274.86	310.83
Flurochloridone	61213-25-0	$C_{12}H_{10}Cl_2F_3NO$	15.01	174.05	311.01	313.01
Fenson	80-38-6	$C_{12}H_9O_3SCl$	15.03	267.99	141.00	269.99
Pyracarbolid	24691-76-7	$C_{13}H_{15}NO_2$	15.13	125.06	217.11	97.03
Dodemorph	1593-77-7	$C_{18}H_{35}NO$	15.13	154.12	238.22	281.27
Mgk 264	113-48-4	$C_{17}H_{25}NO_2$	15.14, 15.45	164.07	209.14	210.15
Butralin	33629-47-9	$C_{14}H_{21}N_3O_4$	15.16	266.11	236.10	220.11
Carbaryl	63-25-2	$C_{12}H_{11}NO_2$	15.16	144.06	115.05	116.06
Diphenamid	957-51-7	$C_{16}H_{17}NO$	15.21	167.09	165.07	152.06
Pirimiphos-ethyl	23505-41-1	$C_{13}H_{24}N_3O_3PS$	15.29	168.06	318.10	333.13
Isodrin	465-73-6	$C_{12}H_8C_{l6}$	15.36	192.94	361.88	194.93
Aldrin	309-00-2	$C_{12}H_8CL_6$	15.36	260.86	290.93	326.91
Isopropalin	33820-53-0	$C_{15}H_{23}N_3O_4$	15.36	280.13	238.08	264.13
Cyprodinil	121552-61-2	$C_{14}H_{15}N_3$	15.41	224.12	225.13	208.09
Isofenphos-methyl	99675-03-3	$C_{14}H_{22}NO_4PS$	15.42	199.02	230.99	241.06
Octachlorostyrene	29082-74-4	C_8Cl_8	15.54	305.81	270.84	379.74
Metazachlor	67129-08-2	$C_{14}H_{16}ClN_3O$	15.56	209.06	133.09	211.06
Dimethametryn	22936-75-0	$C_{11}H_{21}N_5S$	15.58	212.10	185.07	240.13
Pendimethalin	40487-42-1	$C_{13}H_{19}N_3O_4$	15.60	252.10	191.07	162.08
Disulfoton-sulfone	2497-6-5	$C_8H_{19}O_4PS_3$	15.62	153.01	124.98	213.02
Phorate sulfone	2588-04-7	$C_7H_{17}O_4PS_3$	15.62	199.00	124.98	170.97
Terbufos sulfone	56070-16-7	$C_9H_{21}O_4PS_3$	15.62	153.01	199.00	263.97

Table 1: Continued.

Pesticides	CAS	Molecular formula	Retention time (min)	Quantitative ion (m/z)	Qualitative ion (m/z)	
					1	2
Paclobutrazol	76738-62-0	$C_{15}H_{20}ClN_3O$	15.64	236.06	138.02	167.03
Penconazole	66246-88-6	$C_{13}H_{15}N_3Cl_2$	15.64	248.09	160.97	158.98
Chlozolinate	84332-86-5	$C_{13}H_{11}NO_5Cl_2$	15.72	186.96	260.98	188.96
Pyrifenox	88283-41-4	$C_{14}H_{12}N_2OCl_2$	15.72	262.01	186.96	227.04
Tolylfluanid	731-27-1	$C_{10}H_{13}N_2O_2FS_2Cl_2$	15.75	237.97	181.08	239.96
Fosthiazate	98886-44-3	$C_9H_{18}NO_3PS_2$	15.80	195.01	166.02	226.98
Phosfolan	947-02-4	$C_7H_{14}NO_3PS_2$	15.80	139.96	167.99	266.98
Allethrin	584-79-2	$C_{19}H_{26}O_3$	15.84	123.12	91.05	136.09
Isofenphos	25311-71-1	$C_{15}H_{24}NO_4PS$	15.84	213.03	184.99	216.97
Captan	133-06-2	$C_9H_8NO_2SCl_3$	15.85	149.05	105.03	116.91
Fipronil	120068-37-3	$C_{12}H_4Cl_2F_6N_4OS$	15.88	366.94	368.94	212.95
Diclocymet	139920-32-4	$C_{15}H_{18}N_2OCl_2$	15.90, 16.38	221.05	172.99	277.11
Quinalphos	13593-03-8	$C_{12}H_{15}N_2O_3PS$	15.92	146.05	157.08	173.07
Phenthoate	2597-03-7	$C_{12}H_{17}O_4PS_2$	15.93	273.99	121.01	245.99
Triadimenol	55219-65-3	$C_{14}H_{18}N_3O_2Cl$	15.94	168.11	112.05	169.12
Dinobuton	973-21-7	$C_{14}H_{18}N_2O_7$	16.00	211.03	163.03	205.06
Furalaxyl	57646-30-7	$C_{17}H_{19}NO_4$	16.03	242.12	152.07	146.10
Crotoxyphos	7700-17-6	$C_{14}H_{19}O_6P$	16.06	193.03	127.02	105.07
Procymidone	32809-16-8	$C_{13}H_{11}NO_2Cl_2$	16.11	283.02	96.06	255.02
Chlorbenside	103-17-3	$C_{13}H_{10}SCl_2$	16.15	125.02	127.01	267.99
Chlorflurenol-methyl	2536-31-4	$C_{15}H_{11}O_3Cl$	16.22	215.03	152.06	274.04
Chlordane	5103-71-9	$C_{10}H_6Cl_8$	16.32, 16.58	372.83	376.82	374.82
Methidathion	950-37-8	$C_6H_{11}N_2O_4PS_3$	16.33	145.01	85.04	147.00
Haloxyfop-methyl	69806-40-2	$C_{16}H_{13}ClF_3NO_4$	16.39	375.05	288.00	179.98
Bromophos-ethyl	4824-78-6	$C_{10}H_{12}O_3PSCl_2Br$	16.41	300.85	241.87	358.91
Procyazine	32889-48-8	$C_{10}H_{13}N_6Cl$	16.43	210.05	212.05	252.09
Disulfoton-sulfoxide	2497-07-6	$C_8H_{19}O_3PS_3$	16.61	183.98	124.98	167.98
Tetrachlorvinphos	22248-79-9	$C_{10}H_9O_4PCl_4$	16.63	328.93	203.93	239.89
Endosulfan	959-98-8	$C_9H_6O_3SCl_6$	16.67, 18.37	236.84	169.97	159.98
Mepanipyrim	110235-47-7	$C_{14}H_{13}N_3$	16.69	222.10	221.09	223.11
Butachlor	23184-66-9	$C_{17}H_{26}NO_2Cl$	16.74	176.11	188.11	160.11
Ditalimfos	5131-24-8	$C_{12}H_{14}NO_4PS$	16.81	242.98	208.97	271.00
TCMTB	21564-17-0	$C_9H_6N_2S_3$	16.87	179.99	166.99	237.97
Trans-nonachlor	39765-80-5	$C_{10}H_5Cl_9$	16.90	408.78	404.79	271.81
Chlorfenson	80-33-1	$C_{12}H_8CL_2O_3S$	16.94	174.96	176.96	301.96
Fenamiphos	22224-92-6	$C_{13}H_{22}NO_3PS$	16.95	303.11	260.05	217.01
Picoxystrobin	117428-22-5	$C_{18}H_{16}NO_4F_3$	16.96	303.05	173.06	335.08
Napropamide	15299-99-7	$C_{17}H_{21}NO_2$	17.00	271.16	72.08	115.05
Hexaconazole	79983-71-4	$C_{14}H_{17}Cl_2N_3O$	17.06	213.99	231.03	174.97
Flutolanil	66332-96-5	$C_{17}H_{16}NO_2F_3$	17.07	173.02	281.07	323.11

Table 1: Continued.

Pesticides	CAS	Molecular formula	Retention time (min)	Quantitative ion (m/z)	Qualitative ion (m/z)	
					1	2
Prothiophos	34643-46-4	$C_{11}H_{15}O_2PS_2Cl_2$	17.18	308.99	238.92	266.95
Isoprothiolane	50512-35-1	$C_{12}H_{18}O_4S_2$	17.19	117.99	161.98	290.06
Profenofos	41198-08-7	$C_{11}H_{15}BrClO_3PS$	17.26	338.96	205.91	207.91
Tricyclazole	41814-78-2	$C_9H_7N_3S$	17.35	189.03	135.01	161.02
Pretilachlor	51218-49-6	$C_{17}H_{26}NO_2Cl$	17.36	162.13	202.12	238.10
Dieldrin	60-57-1	$C_{12}H_8CL_6O$	17.44	262.86	81.03	260.86
Oxadiazon	19666-30-9	$C_{15}H_{18}N_2O_3Cl_2$	17.51	174.96	302.02	344.07
Iprovalicarb	140923-17-7	$C_{18}H_{28}N_2O_3$	17.52, 17.82	134.10	116.07	158.12
Carboxin	5234-68-4	$C_{12}H_{13}NO_2S$	17.60	235.07	218.04	143.02
Myclobutanil	88671-89-0	$C_{15}H_{17}ClN_4$	17.60	179.02	150.01	245.06
p,p'-Dichlorodiphenyldichloroethylene	72-55-9	$C_{14}H_8Cl_4$	17.64	315.94	247.99	245.99
Buprofezin	69327-76-0	$C_{16}H_{23}N_3OS$	17.68	175.09	171.10	249.11
Imazalil	35554-44-0	$C_{14}H_{14}Cl_2N_2O$	17.70	174.95	172.96	158.98
Flusilazole	85509-19-9	$C_{16}H_{15}N_3F_2Si$	17.70	233.06	206.05	314.10
Methoprotryne	841-06-5	$C_{11}H_{21}N_5OS$	17.72	256.12	184.07	212.10
Azaconazole	60207-31-0	$C_{12}H_{11}N_3O_2Cl_2$	17.75	216.98	144.96	174.95
Bupirimate	41483-43-6	$C_{13}H_{24}N_4O_3S$	17.79	208.14	193.14	273.10
Imazamethabenz-methyl	81405-85-8	$C_{16}H_{20}N_2O_3$	17.82	144.04	176.07	245.09
Kresoxim-methyl	143390-89-0	$C_{18}H_{19}NO_4$	17.83	116.05	131.07	206.08
Metamitron	41394-05-2	$C_{10}H_{10}N_4O$	17.85	174.09	173.08	202.08
Isoxathion	18854-01-8	$C_{13}H_{16}NO_4PS$	17.97	177.02	159.01	313.05
Aramite	140-57-8	$C_{15}H_{23}O_4SCl$	17.98	185.00	175.11	319.08
Nitrofen	1836-75-5	$C_{12}H_7Cl_2NO_3$	18.02	282.98	284.98	202.02
Endrin	72-20-8	$C_{12}H_8CL_6O$	18.09	242.95	280.93	316.90
Endrin aldehyde	7421-93-4	$C_{12}H_8OCl_6$	18.09	242.95	280.93	344.90
Ancymidol	12771-68-5	$C_{15}H_{16}N_2O_2$	18.12	228.90	107.02	215.08
Perthan	72-56-0	$C_{18}H_{20}Cl_2$	18.15	223.15	178.08	167.09
Chlorfenapyr	122453-73-0	$C_{15}H_{11}BRCLF_3N_2O$	18.19	247.05	363.94	361.94
Chloropropylate	5836-10-2	$C_{17}H_{16}O_3Cl_2$	18.38	138.99	110.99	251.00
Chlorobenzilate	510-15-6	$C_{16}H_{14}O_3Cl_2$	18.38	138.99	251.00	252.99
Fenthion sulfoxide	3761-41-9	$C_{10}H_{15}O_4PS_2$	18.51	294.01	278.99	152.98
Diniconazole	83657-24-3	$C_{15}H_{17}N_3OCl_2$	18.55	268.00	234.04	165.01
Flamprop-isopropyl	52756-22-6	$C_{19}H_{19}NO_3FCl$	18.63	276.06	105.03	156.00
p,p'-Dichlorodiphenyldichloroethane	72-54-8	$C_{14}H_{10}Cl_4$	18.66	235.01	199.03	165.07
Aclonifen	74070-46-5	$C_{12}H_9CLN_2O_3$	18.68	264.03	182.06	212.06
o,p'-Dichlorodiphenyltrichloroethane	789-02-6	$C_{14}H_9Cl_5$	18.76	235.00	165.07	237.00
Oxadixyl	77732-09-3	$C_{14}H_{18}N_2O_4$	18.78	233.09	163.10	132.08
Ethion	563-12-2	$C_9H_{22}O_4P_2S_4$	18.82	230.97	202.94	153.01
Mepronil	55814-41-0	$C_{17}H_{19}NO_2$	19.07	119.05	210.07	269.14
Triazophos	24017-47-8	$C_{12}H_{16}N_3O_3PS$	19.22	162.07	257.00	172.09
Azamethiphos	35575-96-3	$C_9H_{10}ClN_2O_5PS$	19.34	182.99	214.97	323.97
Ofurace	58810-48-3	$C_{14}H_{16}NO_3Cl$	19.39	232.10	186.09	281.08
Carbophenothion	786-19-6	$C_{11}H_{16}O_2PS_3Cl$	19.47	341.97	170.97	199.00
Benalaxyl	71626-11-4	$C_{20}H_{23}NO_3$	19.55	148.11	176.11	206.12

Table 1: Continued.

Pesticides	CAS	Molecular formula	Retention time (min)	Quantitative ion (m/z)	Qualitative ion (m/z)	
					1	2
Tepraloxydim	149979-41-9	$C_{17}H_{24}NO_4Cl$	19.55	164.07	136.04	108.04
Diofenolan	63837-33-2	$C_{18}H_{20}O_4$	19.56, 19.77	186.07	131.05	225.09
Cyanofenphos	13067-93-1	$C_{15}H_{14}NO_2PS$	19.60	141.01	169.04	185.02
Edifenphos	17109-49-8	$C_{14}H_{15}O_2PS_2$	19.60	172.98	186.05	310.02
Quinoxyfen	124495-18-7	$C_{15}H_8NOFC_{l2}$	19.63	306.99	237.06	161.00
Endosulfan sulfate	1031-07-8	$C_9H_6CL_6O_4S$	19.69	271.81	236.84	269.81
Propiconazol	60207-90-1	$C_{15}H_{17}Cl_2N_3O_2$	19.70, 19.91	172.95	259.03	261.03
Norflurazon	27314-13-2	$C_{12}H_9N_3OF_3Cl$	19.74	303.04	173.03	302.03
Fenhexamid	126833-17-8	$C_{14}H_{17}Cl_2NO_2$	19.79	176.97	178.97	301.06
p,p'-Dichlorodiphenyltrichloroethane	50-29-3	$C_{14}H_9Cl_5$	19.84	235.00	199.03	165.07
Trifloxystrobin	141517-21-7	$C_{20}H_{19}F_3N_2O_4$	19.92	116.05	190.05	186.05
Hexazinone	51235-04-2	$C_{12}H_{20}N_4O_2$	20.17	171.09	71.06	128.08
Tebuconazol	107534-96-3	$C_{16}H_{22}ClN_3O$	20.26	250.07	125.02	163.03
Chloridazon	1698-60-8	$C_{10}H_8ClN_3O$	20.26	220.03	221.04	222.02
Nuarimol	63284-71-9	$C_{17}H_{12}N_2OFCl$	20.28	235.03	203.06	314.06
Diclofop-methyl	51338-27-3	$C_{16}H_{14}Cl_2O_4$	20.39	340.03	254.98	252.98
Triphenyl phosphate	115-86-6	$C_{18}H_{15}O_4P$	20.49	325.06	169.06	233.04
Piperonyl butoxide	51-03-6	$C_{19}H_{30}O_5$	20.62	176.08	161.06	177.09
Oxycarboxin	5259-88-1	$C_{12}H_{13}NO_4S$	20.68	175.01	250.03	267.06
Resmethrin	10453-86-8	$C_{22}H_{26}O_3$	20.70	143.09	128.06	171.08
Zoxamide	156052-68-5	$C_{14}H_{16}NO_2Cl_3$	20.83	186.97	258.04	242.01
Mefenpyr-diethyl	135590-91-9	$C_{16}H_{18}Cl_2N_2O_4$	21.02	271.00	227.01	299.03
Benzoylprop-ethyl	22212-55-1	$C_{18}H_{17}NO_3Cl_2$	21.12	105.03	292.03	260.02
Spiromesifen	283594-90-1	$C_{23}H_{30}O_4$	21.14	254.13	231.10	226.13
Endrin ketone	53494-70-5	$C_{12}H_8OCl_6$	21.16	314.91	281.93	242.95
Fenamiphos sulfone	31972-44-8	$C_{13}H_{22}NO_5PS$	21.27	292.04	320.07	214.06
Bromuconazole	116255-48-2	C13H12BrCl$_2$N$_3$O	21.31, 22.12	172.95	294.91	174.95
Fenpiclonil	74738-17-3	$C_{11}H_6N_2Cl_2$	21.32	235.99	201.02	237.99
Phosmet	732-11-6	$C_{11}H_{12}NO_4PS_2$	21.37	160.04	104.03	133.03
Bromopropylate	18181-80-1	$C_{17}H_{16}O_3Br_2$	21.48	184.94	182.94	338.90
Tetramethrin	7696-12-0	$C_{19}H_{25}NO_4$	21.61	164.07	107.05	123.12
Picolinafen	137641-05-5	$C_{19}H_{12}N_2O_2F_4$	21.61	238.05	145.03	376.08
Bifenthrin	82657-04-3	$C_{23}H_{22}ClF_3O_2$	21.64	181.10	165.07	182.10
Piperophos	24151-93-7	$C_{14}H_{28}NO_3PS_2$	21.68	122.10	140.11	320.14
4,4′-Methoxychlor	72-43-5	$C_{16}H_{15}O_2CL_3$	21.73	227.11	212.08	228.11
Bifenazate	149877-41-8	$C_{17}H_{20}N_2O_3$	21.73	300.15	258.10	196.08
Fenpropathrin	39515-41-8	$C_{22}H_{23}NO_3$	21.83	181.06	209.08	265.07
Etoxazole	153233-91-1	$C_{21}H_{23}F_2NO_2$	21.91	300.12	187.11	330.13

Table 1: Continued.

Pesticides	CAS	Molecular formula	Retention time (min)	Quantitative ion (m/z)	Qualitative ion (m/z)	
					1	2
Tebufenpyrad	119168-77-3	$C_{18}H_{24}N_3OCl$	21.94	333.16	171.03	276.09
Fenamidone	161326-34-7	$C_{17}H_{17}N_3OS$	21.95	268.09	206.07	238.11
Dicofol	115-32-2	$C_{14}H_9CL_5O$	21.98	138.99	199.03	140.99
Metconazole	125116-23-6	$C_{17}H_{22}N_3OCl$	21.99	125.02	145.06	250.11
Fenazaquin	120928-09-8	$C_{20}H_{22}N_2O$	22.00	145.10	117.07	160.12
Tetradifon	116-29-0	$C_{12}H_6O_2SCl_4$	22.36	226.89	228.89	158.97
Furathiocarb	65907-30-4	$C_{18}H_{26}N_2O_5S$	22.54	163.08	194.04	325.13
Phosalone	2310-17-0	$C_{12}H_{15}NO_4PS_2Cl$	22.68	182.00	121.04	366.99
Pyriproxyfen	95737-68-1	$C_{20}H_{19}NO_3$	22.88	136.08	226.10	137.08
Mirex	2385-85-5	$C_{10}Cl_{12}$	22.96	271.81	269.81	331.81
Mefenacet	73250-68-7	$C_{16}H_{14}N_2O_2S$	23.04	192.01	136.02	120.08
Cyhalothrin	68085-85-8	$C_{23}H_{19}ClF_3NO_3$	23.13, 23.49	141.05	197.03	161.06
Tralkoxydim	87820-88-0	$C_{20}H_{27}NO_3$	23.17	137.04	227.13	283.16
Fenarimol	60168-88-9	$C_{17}H_{12}N_2OCl_2$	23.58	251.00	219.03	252.99
Trifenmorph	1420-06-0	$C_{23}H_{23}NO$	23.65	243.12	228.09	239.09
Azinphos-ethyl	2642-71-9	$C_{12}H_{16}N_3O_3PS_2$	23.85	132.04	104.05	160.05
Pyrazophos	13457-18-6	$C_{14}H_{20}N_3O_5PS$	23.88	221.08	265.09	193.05
Acrinathrin	101007-06-1	$C_{26}H_{21}F_6NO_5$	23.90	181.06	208.08	289.07
Fluoroglycofen-ethyl	77501-90-7	$C_{18}H_{13}NO_7F_3Cl$	23.96	343.99	223.04	447.03
Fenoxaprop-ethyl	66441-23-4	$C_{18}H_{16}NO_5Cl$	24.25	288.04	182.06	361.07
Bitertanol	55179-31-2	$C_{20}H_{23}N_3O_2$	24.59	170.07	168.11	171.08
Spirodiclofen	148477-71-8	$C_{21}H_{24}Cl_2O_4$	24.74	259.05	312.03	156.96
Permethrin	61949-76-6	$C_{21}H_{20}CL_2O_3$	24.78, 25.03	183.08	163.01	127.03
Pyridaben	96489-71-3	$C_{19}H_{25}ClN_2OS$	24.96	147.12	117.07	309.08
Fluquinconazole	136426-54-5	$C_{16}H_8N_5OFC_{l2}$	25.13	340.04	298.02	286.02
Coumaphos	56-72-4	$C_{14}H_{16}CLO_5PS$	25.16	362.01	210.01	225.98
Prochloraz	67747-09-5	$C_{15}H_{16}N_3O_2Cl_3$	25.28	180.11	265.95	308.00
Butafenacil	134605-64-4	$C_{20}H_{18}N_2O_6F_3Cl$	25.63	331.01	123.99	179.98
Prallethrin	23031-36-9	$C_{19}H_{24}O_3$	25.83	123.12	81.07	105.07
Cyfluthrin	68359-37-5	$C_{22}H_{18}NO_3FCl_2$	25.94, 26.13, 26.26, 26.35	206.06	199.06	163.01
Cypermethrin	52315-07-8	$C_{22}H_{19}Cl_2NO_3$	26.51, 26.71, 26.83, 26.93	181.06	163.01	127.03
Boscalid	188425-85-6	$C_{18}H_{12}Cl_2N_2O$	26.53	342.03	111.99	139.99
Quizalofop-ethyl	76578-14-8	$C_{19}H_{17}CLN_2O_4$	26.75	372.09	243.03	163.01
Flucythrinate	70124-77-5	$C_{26}H_{23}F_2NO_4$	26.93, 27.30	157.05	199.09	225.08
Etofenprox	80844-07-1	$C_{25}H_{28}O_3$	27.03	163.11	135.08	164.12
Pyridalyl	179101-81-6	$C_{18}H_{14}NO_3F_3Cl_4$	27.18	204.06	148.04	176.03
Fenvalerate	51630-58-1	$C_{25}H_{22}NO_3Cl$	28.21, 28.61	419.13	125.02	167.06

Table 1: Continued.

Pesticides	CAS	Molecular formula	Retention time (min)	Quantitative ion (m/z)	Qualitative ion (m/z)	
					1	2
Flumioxazin	103361-09-7	$C_{19}H_{15}FN_2O_4$	28.25	354.10	259.05	326.11
Pyraclostrobin	175013-18-0	$C_{19}H_{18}N_3O_4Cl$	28.34	132.04	104.05	164.07
Tau-fluvalinate	102851-06-9	$C_{26}H_{22}ClF_3N_2O_3$	28.62, 28.75	250.06	252.06	205.99
Difenoconazole	119446-68-3	$C_{19}H_{17}N_3O_3Cl_2$	28.95, 29.07	323.02	266.98	264.98
Deltamethrin	52918-63-5	$C_{22}H_{19}Br_2NO_3$	29.21, 29.56	171.99	173.99	252.90
Azoxystrobin	131860-33-8	$C_{22}H_{17}N_3O_5$	30.02	344.10	372.10	388.09
Dimethomorph	110488-70-5	$C_{21}H_{22}ClNO_4$	30.06	301.06	303.06	387.12

compounds. Because it contains many pesticides, including organophosphorus, organochlorine, pyrethroids, triazoles, carbamates, and other insecticides, there are many kinds and polarity differences. At the same time, chrysanthemum flower contains pigments, amino acids, and volatile components, so it is particularly important to choose the appropriate extraction solvent. The QuEChERS method uses acetonitrile as the extraction solvent, which is due to the good solubility, permeability, and versatility of acetonitrile and high extraction efficiency for most pesticides. The results showed that the recovery rate of some pesticides with poor stability was low by adding ordinary salt, which was related to the pH value of the matrix; the recovery of 280 pesticides was between 70% and 120%; 38 pesticides were less than 70%; and 34 pesticides were more than 120%. Because carbamates are sensitive to pH value, they are more stable under acidic conditions and easily to decompose under alkaline conditions. Therefore, adding acetate buffer salt makes the sample extract weak acidic, thus improving the recovery rate of acid-base-sensitive pesticides. The recovery rate of all pesticides is between 70% and 125%.

Using the QuEChERS method, adding the appropriate amount of water is conducive to the full contact between organic solvent and sample, improves the extraction efficiency, and helps achieve better recovery. However, adding too much water will lead to the dissolution of water-soluble pigment and other soluble matrix components. The effects of 0, 10, and 15 ml of water on the recovery of the target were compared, and the extraction efficiency of 10 ml water was higher than that of the other two groups. There were only 34 pesticides with a recovery rate of more than 120% in the nonwater group. Therefore, in this method, 10 ml water was added.

Some organophosphorus pesticides (such as parathion and fenitrothion) are unstable in chemical properties and easy to decompose at high temperatures. Because there is anhydrous $MgSO_4$ in the acetic acid buffer salt system, a lot of heat will be released in the process of water absorption. Therefore, after adding acetic acid buffer salt, we put the centrifuge tube of extracting sample into an ice water bath for 10 min to improve the recovery rate of pesticides with poor thermal stability.

3.2. Selection of Purification Conditions. It is important to select suitable purification adsorption materials for the efficient purification of complex substrates. The ideal purification adsorption material should achieve the purification effect required by the experiment and ensure that it does not adsorb the target analyte in the extraction solvent. In this experiment, the purification effects of QuEChERS purification and Sin-QuEChERS Nano column were compared (Figures 1 and 2). Mixed reference materials ($10\,\mu g{\cdot}kg^{-1}$) were added to the chrysanthemum flower sample and then extracted. The extracts were purified by QuEChERS purification (simple matrix), QuEChERS purification (complex matrix), and Sin-QuEChERS Nano column. It can be seen from Figure 1 that the color of samples purified by QuEChERS purification (simple matrix) is dark, the color of samples purified by Sin-QuEChERS Nano column is lighter, and QuEChERS purification (complex matrix) is almost colorless. It can be seen from the total ions in Figure 2 that the samples purified by QuEChERS purification (simple matrix) have more impurities and greater interference, while the samples purified by the Sin-QuEChERS Nano column are less interfered with, and the peak of QuEChERS purification (complex matrix) is less after 25 min, which is due to the adsorption of the target substance with late peak, making it look cleaner. Meanwhile, the recovery rates of target compounds were 72.7–118.9% in QuEChERS purification (simple matrix), 72.8–123.4% with the Sin-QuEChERS Nano column, and 62.4–120.7% by QuEChERS purification (complex matrix). The results showed little difference in the recovery rate between QuEChERS purification (simple matrix) and Sin-QuEChERS Nano column, but the recovery rate of QuEChERS purification (complex matrix) was relatively low. Primary-secondary amine (PSA), which plays the main role in QuEChERS purification (simple matrix), is a weak anion exchange adsorbent. It can effectively remove polar pigments, organic acids, sugars, fatty acids, and other

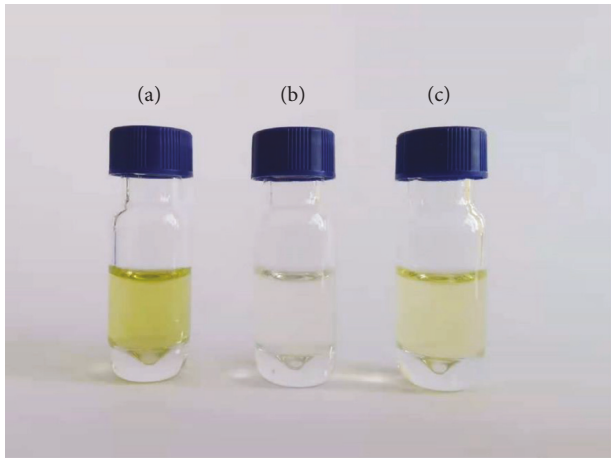

Figure 1: Purification effect maps of chrysanthemum flower samples cleaned up by different purification conditions. (a) QuEChERS purification (simple matrix), (b) QuEChERS purification (complex matrix), and (c) Sin-QuChERS Nano column.

components that are easy to form hydrogen bonds in the sample, but its adsorption capacity is limited. In addition to PSA, QuEChERS purification (complex matrix) also contains graphitized carbon black (GCB). GCB can remove pigments from chrysanthemum flower, such as chlorophyll, radish-like hormone, and sterol, but the strong adsorption force will absorb the target of a benzene ring, which leads to a low recovery rate. In addition to PSA, 15 mg MWCNTs (particle size length: 10–50 μm, outer diameter: 30–60 nm, and specific surface area: 280 $m^2 \cdot g^{-1}$) was added to the Sin-QuEChERS Nano column. MWCNTs are nano hollow tubes with high mechanical strength, strong acid-base resistance, stronger adsorption, and purification capacity but do not affect the recovery rate of the target substance [23–25]. This experiment shows that the combination of PSA and MWCNTs can effectively remove impurities in the sample, reduce the interference to the target substance, improve the recovery rate of the target substance, and protect the analytical instrument from pollution and damage. At the same time, the high-resolution mass spectrometer can detect low concentration pesticide residues in a complex matrix, so the Sin-QuEChERS Nano column was selected for purification.

3.3. Optimization of Instrument Resolution. As a high-resolution mass spectrometer, Orbitrap mass spectrometer can fully scan acquisition and collect data in the range of m/z 50–550, ensuring the retrospective data analysis. Resolution is an important parameter in high-resolution mass spectrometry. In the presence of matrix interference, the resolution will affect the accuracy of quality measurement. Therefore, the key to qualitative analysis is to choose the appropriate resolution. High resolution can improve the accuracy of mass determination and can effectively identify compounds with very close accurate mass. In the experiment, the content of trifloxystrobin in chrysanthemum flower was 10 $\mu g \cdot kg^{-1}$, which was determined at three different resolutions (15,000, 30,000, and 60,000). In Figure 3, the qualitative ion m/z 186.05251 is the qualitative ion of trifloxystrobin, and m/z 186.06752 is the interference ion. Only when the resolution is 60,000 or above, the two ions with the same mass can be clearly distinguished. At the same time, the accurate qualitative and quantitative analysis can be carried out, and the screening accuracy will be greatly improved; the quality accuracy is less than 2.0 ppm; and the high sensitivity can still be maintained, so it fully meets the requirements of pesticide residue detection in chrysanthemum flower. Also, the accurate mass number and deviation, retention time window, isotopic distribution, and isotopic abundance information were used simultaneously in this method to realize the rapid and accurate screening of target substances.

3.4. Matrix Effect. Matrix effects (MEs) are very common in GC-MS/MS and should be assessed at the method validation stage. MEs were estimated via the ratio of the calibration curve slopes of matrix to solvent. Studies recommend that MEs can be ignored when the ME values are in the range of 0.9–1.1 [15]. If the ME cannot be ignored, using a matrix-matched standard is the most effective way to compensate for MEs.

The MEs in this study are listed in Table S1. The MEs of the Sin-QuEChERS Nano method were in the range of 1.01–1.86; the MEs of the QuEChERS (simple matrix) and QuEChERS (complex matrix) method ranged between 1.05 and 2.38 and between 1.08 and 2.89, respectively. As for the matrix suppression or enhancement effect, QuEChERS (simple matrix) was the strongest, while Sin-QuEChERS nano was the weakest. This indicated that the Sin-QuEChERS Nano method reduced the matrix effect more efficiently than QuEChERS (simple matrix) and QuEChERS (complex matrix).

3.5. Linear Range, Limit of Detection, Limit of Quantitation, and Recovery. The blank matrix standard solution is prepared according to the pretreatment method; the standard curve was drawn with the mass concentration of the compound as abscissa and the corresponding peak area as ordinate. The linear range of 352 compounds was 0.5–200 $\mu g \cdot kg^{-1}$, and the correlation coefficient (R) was greater than 0.99. The LODs and LOQs of the method were investigated by adding blank samples. The LODs were three times the signal-to-noise ratio ($S/N = 3$), and the LOQs were 10 times the signal-to-noise ratio ($S/N = 10$). The mixed standard solutions of 352 compounds were added to the negative samples of chrysanthemum flower at the levels of 10, 50, and 100 $\mu g \cdot kg^{-1}$, respectively, and each level was repeated six times. The results showed that the detection limits of 352 pesticides were 0.3–3 $\mu g \cdot kg^{-1}$, and the quantification limits were 1–10.0 $\mu g \cdot kg^{-1}$, which met the requirements of pesticide residue detection [26]. The average recovery rates of 352 compounds at three levels were 73.2–110.3%, 72.8–112.6%, and 77.6–123.4%, respectively. The average RSDs of 352 compounds at three levels were 3.2–9.6%, 4.0–9.7%, and 4.0–11.3%, respectively. The results showed that the method could be used for the determination

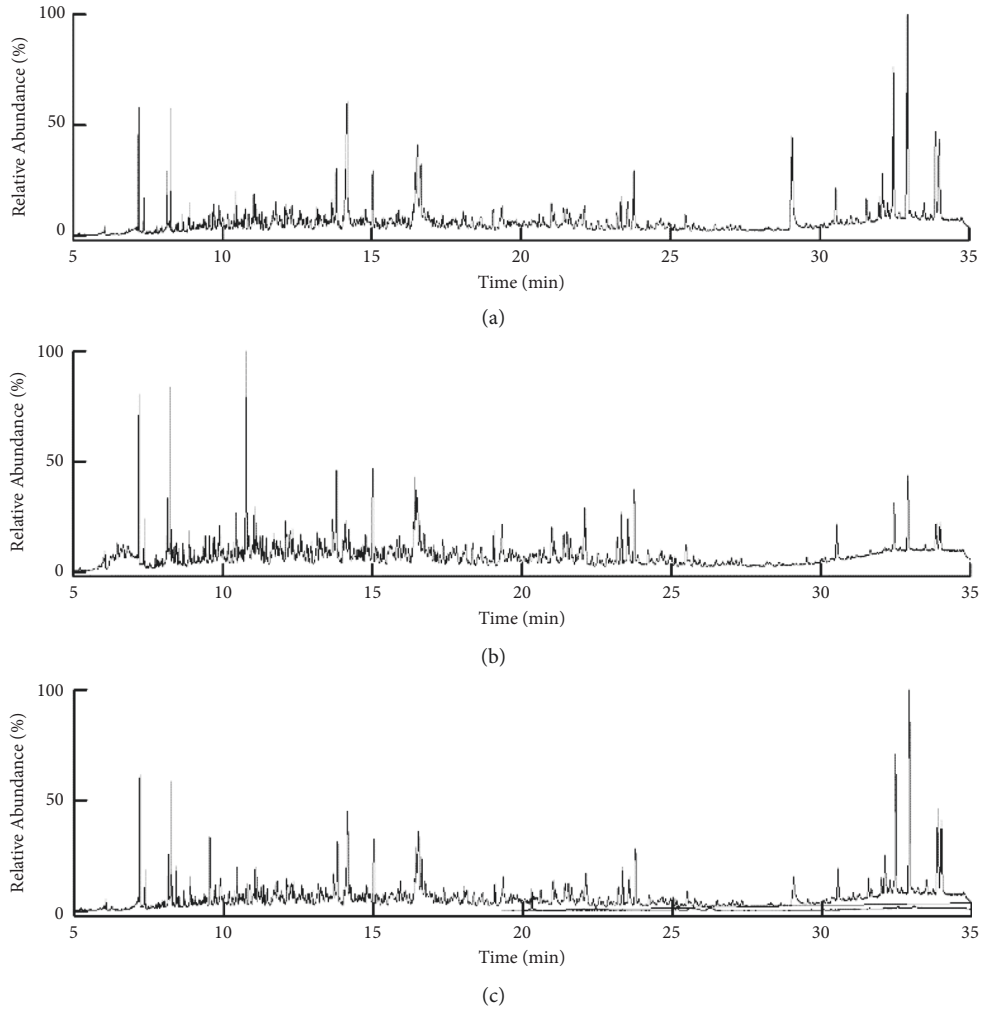

Figure 2: Total ion current chromatograms of the spiked ($10\,\mu g \cdot kg^{-1}$) chrysanthemum flower samples cleaned up by different purification conditions. (a) QuEChERS purification (simple matrix), (b) QuEChERS purification (complex matrix), and (c) Sin-QuChERS Nano column.

of pesticide residues in chrysanthemum flower. The correlation coefficients, limits of detection, limits of quantitation, spiked recovery rates, and relative standard deviations of 352 compounds in chrysanthemum flower are shown in Table S1.

3.6. Determination of Actual Samples. Two hundred samples were analyzed by the established method. Among them, 137 samples were detected with pesticide residues, and the chemical substances with a high detection rate were profenofos, procymidone, metalaxyl, chlorfenapyr, difenoconazole, dimethomorph, cypermethrin, tebuconazole, propiconazole, and pyrimethanil, among others (Table 2). Figure 4 is the mass spectrum of profenofos in the standard and chrysanthemum flower positive samples. The fragment ions (338.96369, 205.91286, and 207.91063) can be detected, and the ion ratio is highly matched. The results show that the method was also suitable for detecting 352 pesticide residues in chrysanthemum flowers, such as calendula and chamomile. The results showed that the nontarget rapid screening method established in this study could rapidly screen potential pesticide residues in chrysanthemum flower with high throughput.

3.7. Retrospective Analysis. GC-Orbitrap-MS often collects the full spectrum, which can collect data more comprehensively. The data collection has no relationship with the number of compounds in the database, so the data can be reviewed and reanalyzed to expand the target range. In the analysis of samples, we added the retention time, molecular formula, accurate relative molecular weight, and CAS number of new compounds pentachlorobenzonitrile, simazine, and simetone into 352 databases and verified them with actual samples. It was found that the linearity of these three compounds in each matrix was greater than 0.99, the average recovery rates were 72.8–123.4%, and the average RSD values were 3.2–11.3% at three levels (10, 50, and $100\,\mu g \cdot kg^{-1}$, respectively), which met the requirements of detection. Among 200 chrysanthemum flower samples, 5 chrysanthemum flower samples were detected with

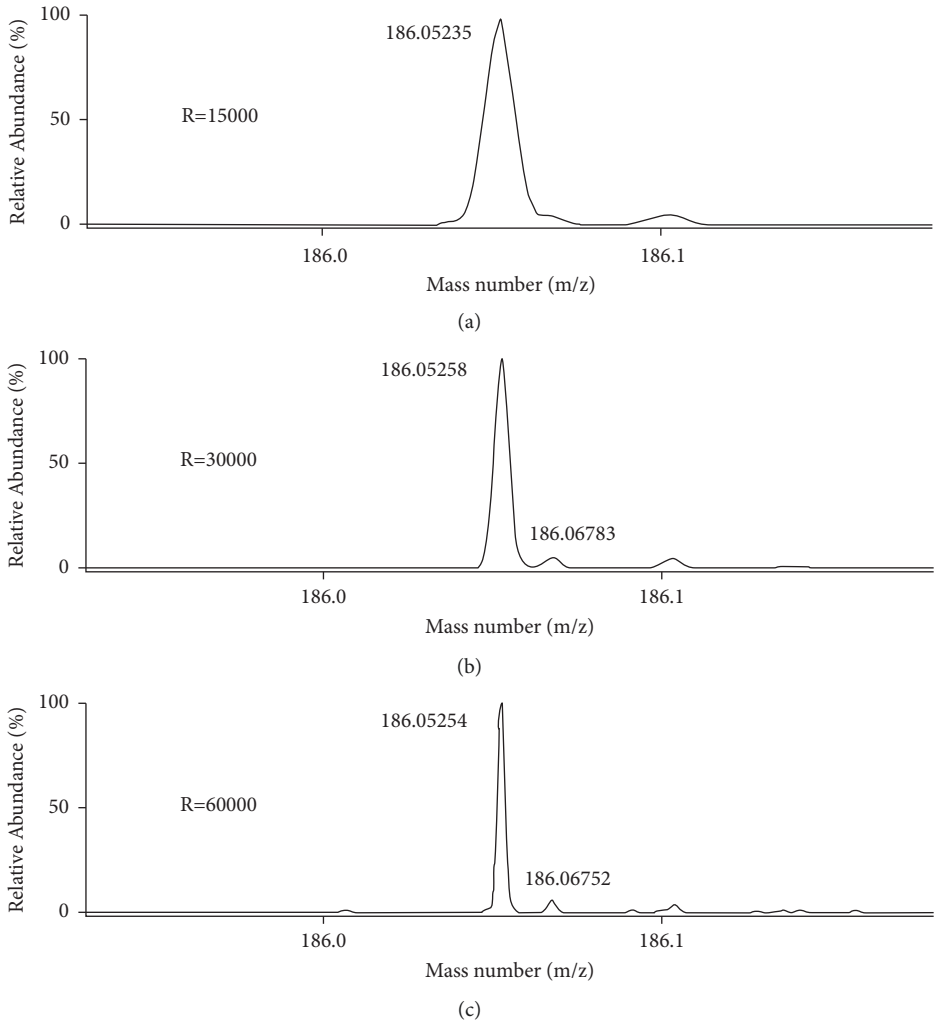

Figure 3: Effect of different resolutions ((a) 15,000, (b) 30,000, and (c) 60,000) on the quality accuracy of the qualitative ion (m/z 186.05251) of trifloxystrobin in chrysanthemum flower.

Table 2: Chemical substances with high detection rate detected in chrysanthemum samples.

Number	Pesticides	Number of detected samples	Detection rate	Value range (μg/kg)
1	Profenofos	50	31.5	0.12–40.8
2	Procymidone	18	14.5	0.10–177.9
3	Metalaxyl	36	24.5	0.29–108.9
4	Chlorfenapyr	48	26.0	0.25–35.7
5	Difenoconazole	39	19.5	0.27–40.5
6	Dimethomorph	33	16.5	0.18–280.4
7	Cypermethrin	42	21.0	6.2–199.6
8	Tebuconazol	29	14.5	0.45–76.8
9	Propiconazol	36	18.5	0.15–49.5
10	Pyrimethanil	44	22.0	1.2–110.4

pentachlorobenzonitrile with a detection value range of 0.048–0.22 mg·kg^{-1}; 3 chrysanthemum flower samples were detected with simetone, with a detection value range of 0.032–0.051 mg·kg^{-1}; and no samples were detected with simazine. Retrospective analyses can expand and analyze target compounds without recollecting data, which is flexible and is convenient for high-throughput screening and quantitative analysis of pesticide residues. It is the development direction of chrysanthemum flower risk monitoring technology in the future.

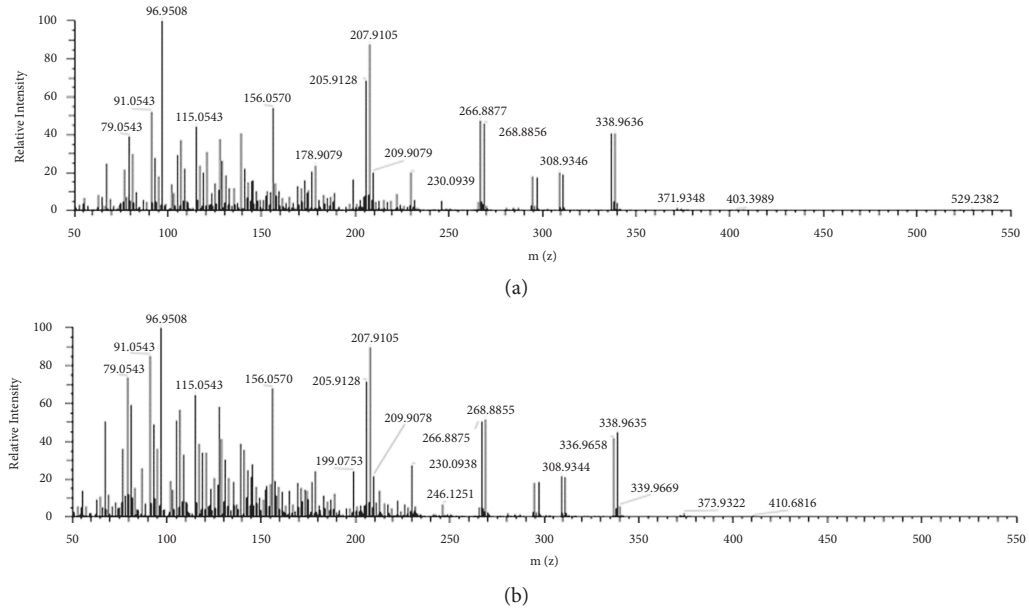

Figure 4: Mass spectrum of profenofos in the standard (a) and chrysanthemum flower positive samples (b).

4. Conclusion

The work presented a method that had been developed and validated for the simultaneous determination of 352 pesticide residues in chrysanthemum flower by GC-Orbitrap-MS, which was established based on the purification of the Sin-QuEChERS Nano column. The Sin-QuEChERS Nano column simplifies the pretreatment process and effectively improves the purification efficiency. After systematic validation for linearity, precision, accuracy, stability, and matrix effects, the developed method was successfully applied for qualitative confirmation and quantitative detection of 352 pesticide residues in 200 chrysanthemum flower samples bought from local pharmacies. No saturation phenomena were experienced in any case. The developed and validated method has proved to be robust and appropriate in sensitivity, mass accuracy, and quantification in full-scan mode and provide good results in the analysis of real samples. These good results show the advantages of full-scan analysis, which is applicable to other compounds that do not appear in selective and retrospective evaluation and easier range management than GC-MS/MS. This method has the advantages of simple pretreatment, high purification efficiency, high throughput, and accurate analysis. It can effectively reduce the amount of standard substances in the detection of multipesticide residues in chrysanthemum flowers, which provides technical support for rapid screening and analysis of potential pesticide residues in the chrysanthemum flower.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no potential conflicts of interest.

Authors' Contributions

Yuanyuan Wang and Zhijuan Meng contributed equally to this work.

Acknowledgments

This work was supported by the Program of Traditional Chinese Medicine Scientific Research foundation in Hebei Administration of Traditional Chinese Medicine (2019091, Hebei, China), the Project of Basic Scientific Research of Provincial Universities (JYZ2020003), Excellent Young Teacher Fundamental Research (YQ2020009), and Doctoral Foundation (BSZ2018008) of Hebei University of Chinese Medicine.

Supplementary Materials

Table S1 is included in the supplementary file. (*Supplementary Materials*)

References

[1] L.-Z. Lin and J. M. Harnly, "Identification of the phenolic components of chrysanthemum flower (chrysanthemum morifolium ramat)," *Food Chemistry*, vol. 120, no. 1, pp. 319–326, 2010.

[2] Q. Chu, L. Fu, Y. Guan, and J. Ye, "Determination and differentiation of flos Chrysanthemum based on characteristic

electrochemical profiles by capillary electrophoresis with electrochemical detection," *Journal of Agricultural and Food Chemistry*, vol. 52, no. 26, pp. 7828–7833, 2004.

[3] Y. Wu, X. Wang, J. Xue, and E. Fan, "Plant phenolics extraction from flos chrysanthemi: response surface methodology based optimization and the correlation between extracts and free radical Scavenging activity," *Journal of Food Science*, vol. 82, no. 11, pp. 2726–2733, 2017.

[4] J. Wu, H. Wei, and J. Xue, "Degradation of imidacloprid in chrysanthemi flos and soil," *Bulletin of Environmental Contamination and Toxicology*, vol. 88, no. 5, pp. 776–780, 2012.

[5] M. Shamsipur, N. Yazdanfar, and M. Ghambarian, "Combination of solid-phase extraction with dispersive liquid–liquid microextraction followed by GC–MS for determination of pesticide residues from water, milk, honey and fruit juice," *Food Chemistry*, vol. 204, pp. 289–297, 2016.

[6] L. B. Abdulra'uf and G. H. Tan, "Chemometric approach to the optimization of HS-SPME/GC-MS for the determination of multiclass pesticide residues in fruits and vegetables," *Food Chemistry*, vol. 177, pp. 267–273, 2015.

[7] B. Zhu, X. Xu, J. Luo et al., "Simultaneous determination of 131 pesticides in tea by on-line GPC-GC-MS/MS using graphitized multi-walled carbon nanotubes as dispersive solid phase extraction sorbent," *Food Chemistry*, vol. 276, pp. 202–208, 2019.

[8] O. Golge and B. Kabak, "Evaluation of QuEChERS sample preparation and liquid chromatography-triple-quadrupole mass spectrometry method for the determination of 109 pesticide residues in tomatoes," *Food Chemistry*, vol. 176, pp. 319–332, 2015.

[9] J. He, B. Zhang, H. Zhang et al., "Monitoring of 49 pesticides and 17 mycotoxins in wine by QuEChERS and UHPLC-MS/MS analysis," *Journal of Food Science*, vol. 84, no. 9, pp. 2688–2697, 2019.

[10] Y. Huang, T. Shi, X. Luo et al., "Determination of multi-pesticide residues in green tea with a modified QuEChERS protocol coupled to HPLC-MS/MS," *Food Chemistry*, vol. 275, pp. 255–264, 2019.

[11] C. V. Garcia and A. Gotah, "Application of QuEChERS for determining xenobiotics in foods of animal origin," *Journal of Analytical Methods in Chemistry*, vol. 2017, Article ID 2603067, 13 pages, 2017.

[12] B. Mekonnen, J. Siraj, and S. Negash, "Determination of pesticide residues in food premises using QuECHERS method in Bench-Sheko Zone, Southwest Ethiopia," *BioMed Research International*, vol. 2021, Article ID 6612096, 13 pages, 2021.

[13] M. González-Curbelo, A. V. Herrera-Herrera, J. Hernández-Borges, and M. Rodríguez-Delgado, "Analysis of pesticides residues in environmental water samples using multiwalled carbon nanotubes dispersive solid-phase extraction," *Journal of Separation Science*, vol. 36, no. 3, pp. 556–563, 2013.

[14] Y. Han, N. Zou, L. Song et al., "Simultaneous determination of 70 pesticide residues in leek, leaf lettuce and garland chrysanthemum using modified QuEChERS method with multi-walled carbon nanotubes as reversed-dispersive solid-phase extraction materials," *Journal of Chromatography B*, vol. 1005, pp. 56–64, 2015.

[15] P. Zhao, L. Wang, L. Zhou, F. Zhang, S. Kang, and C. Pan, "Multi-walled carbon nanotubes as alternative reversed-dispersive solid phase extraction materials in pesticide multi-residue analysis with QuEChERS method," *Journal of Chromatography A*, vol. 1225, pp. 17–25, 2012.

[16] X.-Y. Lu, Y.-Q. Ouyang, W.-Y. Zeng et al., "Effect of pretreatment on detection of 37 pesticide residues in chrysanthemum indicum," *Journal of Analytical Methods in Chemistry*, vol. 2021, Article ID 8854025, 12 pages, 2021.

[17] P. Tan, L. Xu, X.-C. Wei et al., "Rapid screening and quantitative analysis of 74 pesticide residues in Herb by retention index combined with GC-QQQ-MS/MS," *Journal of Analytical Methods in Chemistry*, vol. 2021, Article ID 8816854, 11 pages, 2021.

[18] G.-W. Zhou, Y.-M. Li, C.-N. Liu, H.-M. Ren, and H.-Y. Li, "Rapid simultaneous determination of 43 pesticide residues in schizonepeta tenuifolia by gas chromatography mass spectrometry," *International Journal of Analytical Chemistry*, vol. 2021, Article ID 8934998, 10 pages, 2021.

[19] J.-N. Chen, Y.-J. Lian, Y.-R. Zhou et al., "Determination of 107 pesticide residues in Wolfberry with acetate-buffered salt extraction and Sin-QuEChERS nano column purification coupled with ultra performance liquid chromatography tandem mass spectrometry," *Molecules*, vol. 24, no. 16, 2019.

[20] Y. Li, Q. An, C. Zhang, C. Pan, and Z. Zhang, "Comparison of Sin-QuEChERS nano and d-SPE methods for pesticide multi-residues in lettuce and Chinese chives," *Molecules*, vol. 25, no. 15, 2020.

[21] Z. Meng, Q. Li, J. Cong et al., "Rapid screening of 350 pesticide residues in vegetable and fruit juices by multi-plug filtration cleanup method combined with gas chromatography-electrostatic field orbitrap high resolution mass spectrometry," *Foods*, vol. 10, no. 7, 2021.

[22] M. Tienstra and H. G. J. Mol, "Application of gas chromatography coupled to quadrupole-orbitrap mass spectrometry for pesticide residue analysis in cereals and feed ingredients," *Journal of AOAC International*, vol. 101, no. 2, pp. 342–351, 2018.

[23] D. Moreno-González, J. Alcántara-Durán, S. M. Addona, and M. Beneito-Cambra, "Multi-residue pesticide analysis in virgin olive oil by nanoflow liquid chromatography high resolution mass spectrometry," *Journal of Chromatography A*, vol. 1562, pp. 27–35, 2018.

[24] S. Saito-Shida, T. Hamasaka, S. Nemoto, and H. Akiyama, "Multiresidue determination of pesticides in tea by liquid chromatography-high-resolution mass spectrometry: comparison between orbitrap and time-of-flight mass analyzers," *Food Chemistry*, vol. 256, pp. 140–148, 2018.

[25] Z. Wang, Y. Cao, N. Ge et al., "Wide-scope screening of pesticides in fruits and vegetables using information-dependent acquisition employing UHPLC-QTOF-MS and automated MS/MS library searching," *Analytical and Bioanalytical Chemistry*, vol. 408, no. 27, pp. 7795–7810, 2016.

[26] Z. Cheng, X. Zhang, X. Geng et al., "A target screening method for detection of organic pollutants in fruits and vegetables by atmospheric pressure gas chromatography quadrupole-time-of-flight mass spectrometry combined with informatics platform," *Journal of Chromatography A*, vol. 1577, pp. 82–91, 2018.