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SCHOLARENA

Journal of Food Technology and Food Chemistry

RESEARCH ARTICLE

ISSN: 2641-8118

Establishment of A High Throughput Pesticide Residue Detective Method Using Rapid Time-of-Flight Mass Spectrometer

Xuemei Wang[1#], Shanshan Sun[1#], JiaoYi Luo[1], Yi Hong[2] and Jin Cao[1*]

[1]*Key Laboratory of Food Quality and Safety, State Administration for Market Regulation, National Institutes for Food and Drug Control, Beijing, China*

[2]*Fundamental Research Department, Guangzhou Hexin Instrument. Co., Ltd., GuangZhou, China*

[*]**Corresponding author:** Jin Cao, Key Laboratory of Food Quality and Safety, State Administration for Market Regulation, National Institutes for Food and Drug Control, Beijing 100050, China, Tel: 18810956533, E-mail: caojin@nifdc.org.cn

Citation: Xuemei Wang, Shanshan Sun, JiaoYi Luo, Yi Hong, Jin Cao (2021) Establishment of A High Throughput Pesticide Residue Detective Method Using Rapid Time-of-Flight Mass Spectrometer. J Food Tech Food Chem 3: 101

Abstract

Objects food: We are aimed at detecting the pesticide residues in fruits and vegetables.

Aims: On-site, rapid and high throughput screening method for pesticide detection is urgently needed in Chinese local market. A new study based on time-of-flight mass spectrometer equipped with low-temperature plasma ionization combined with thermal analysis equipment (API-TOF/MS) is applied for pesticide multi-residue analysis in fruits and vegetables samples.

Methods: In this study, a TOF accurate mass database of 128 pesticides was established, and the parameters of the TOF database were optimized. The validation and verification of established database was tested by 381 batches of different types of fruits and vegetables.

Results: API-TOF/MS generated a good linear relationship between 2~100μg/L with the correlation coefficient (R^2)>0.99. Besides, the LODs were between 0.9~5μg/L, and the recoveries of pesticides were in the range of 70%-120% with RSDs<20%. By comparing, API-TOF/MS and UPLC-Q-TOF/MS provide detection rate of 37.11% and 40.68%, respectively. It was demonstrated a strong consistency between two methods by means of accessing Kappa value, which is 0.569 ($P<0.05$).

Conclusion: API-TOF/MS method is superior to other current rapid method in terms of sensitivity, specificity, precision, accuracy and throughput.

Keywords: Pesticide residue; Rapid detection; Atmospheric pressure ion source; High throughput

Introduction

With the widespread application of pesticides in the process of growing crops, vegetables and fruits, environmental pollution and food safety problems caused by pesticide residues are becoming more and more serious. Some pesticides would accumulate in the human body, which may cause chronic poisoning, carcinogenesis, teratogenicity and mutagenicity [1]. Thus, the inspection and supervision of the species and content of pesticide residues on the surface of vegetables or fruits become imperative and crucial. At present, the methods used for screening of multi-component pesticide residues in food mainly include chemical coloration, infrared spectroscopy [2], Raman spectroscopy [3], immunoassay [4], gas chromatography (GC), liquid chromatography (LC), gas chromatography-mass spectrometry (GC-MS) [5] and liquid chromatography-mass spectrometry (LC-MS) [6]. Among them, GC or LC combined with quadrupole-time-of-flight mass spectrometry(Q-TOF/MS) has become an effective way to detect pesticide residues in food due to its high sensitivity and low detection limit. However, considering the disadvantages of long time, high cost and complex pretreatment process [7], it is not suitable for on-site, rapid and high throughput screening of pesticide residues in food.

In recent years, rapid detection methods towards pesticide residues have attracted much attention. The ambient ionization mass spectrometry (AIMS) [8] proposed by Professor Cooks firstly combines the advantages of traditional MS methods such as high accuracy and high sensitivity and fast speed, uncomplicated sample pre-processing, high throughput and real-time direct analysis together. The more popular techniques are those commercially available including desorption electrospray ionization (DESI-MS) [9], direct analysis on real time (DART-MS) [10], paper spray (PS-MS) [11] and low-temperature plasma (LTP-MS) [12]. LTP-MS was first proposed by Harper and had been widely used in drug analysis [13], environmental analysis, explosives detection [14], food analysis [15], monitoring response [16] and other fields due to its simple structure, easy implementation and low cost. He and N2 are commonly used as discharge gases, the LTP probe can achieve direct ionization of molecules located on the surface, relying on the direct interaction between the plasma jet and the sample surface. Considering this characteristic, it is greatly affected by the surrounding environment (such as temperature, humidity and airflow) [17]. Besides, LTP-MS has low sensitivity for pesticides with low saturated vapor pressure. Thus, some researchers try to increase the surface temperature of the sample injector in order to increase the vapor pressure of the hard-to-volatile sample [18]. Therefore, the introduction of thermal desorption process before the plasma jet interacts with the sample can greatly increase its ionization efficiency, consequently increasing the sensitivity of LTP-MS. Notably, the peak signal in LTP experiments would be distinctly enhanced when the substrate is heated.

Based on requirements of real-time, rapid and accurate detection of pesticide residue, we have established a database of 128 pesticides using a time-of-flight mass spectrometer equipped with low-temperature plasma ionization combined with thermal desorption sample injector, and detected pesticide residues of 381 batches of different types of fruits and vegetables purchased from the market. The whole detecting process is simple, fast (within 5 minutes) and low-cost. We also made a comparative analysis between this method and UPLC-Q-TOF/MS, in order to verify the detection performances and to lay the foundation for the wide application of API-TOF/MS technology in rapid, accurate and broad-spectrum screening of pesticide residues.

Materials and Methods

Reagents and solvents

Acetonitrile and methanol (Merck, Germany), formic acid (Fluka) and ammonium acetate (Sigma-Aldrich, Germany) were chromatographically pure. Anhydrous magnesium sulphate ($MgSO_4$), sodium chloride (NaCl), adsorbents: octadecyl chemically bonded phase silica gel (C18, 43~60μm) and N-primary secondary amine (PSA, 40~60μm) were all of analytical grade. A Milli-Q Advantage A10 ultrapure water system from Millipore (Milford, MA) was used to obtain the HPLC-grade water during the analyses. All pesticide standards with purity greater than 97.0% were purchased from Dr. Ehrenstorfer (Augsburg, Germany) or LGC Standards (Teddington, UK). Stock solutions were prepared in acetonitrile at a concentration of 100mg/L, stored at -20 °C and restored to room temperature and diluted to 100μg/L before detection. Standard working solutions were prepared by diluting the stock solution to 0.001, 0.005, 0.01, 0.02, 0.05, 0.1mg/L in solvent (acetonitrile) and stored at 4 °C. The samples of fruits and vegetables were purchased from markets in Dongcheng District, Beijing, China. The proportion of different species of vegetables and fruits is depicted in Fig.1. All the samples were crushed by a blender and stored in plastic bottles at 4 °C.

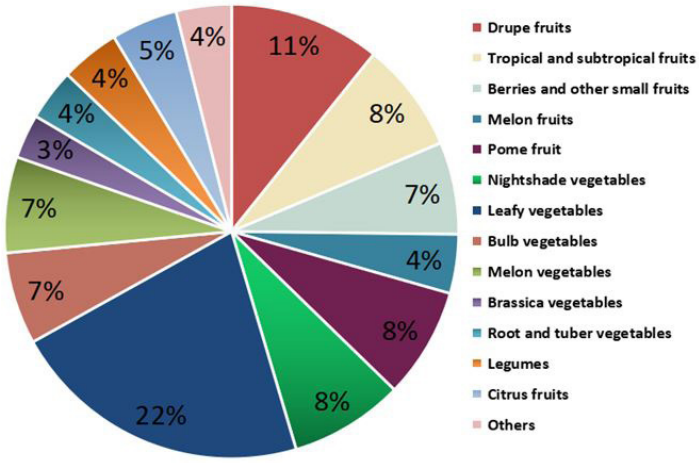

Figure 1: The proportion of different species of vegetables and fruits(N=381)

Sample preparation and extraction

An extraction method, based on QuEChERS methodology [19] was applied for pesticides from samples. 10 g crushed sample of each fruit or vegetable was precisely weighed with the accuracy to 0.001 g, then put in 50 mL polytetrafluoroethylene (PTFE) centrifuge tube and added 10 mL acetonitrile, extracted in 1 min through high-speed homogenate, added 4g $MgSO_4$ and 0.5g NaCl, vortexed in 1 min, centrifuged in 5 min under 5000 rpm. Then 6 mL upper acetonitrile phase solution was put into 15 mL centrifuge tube containing 400 mg C18 + 400 mg PSA + 1200 mg MgSO4, vortexed in 1 min and centrifuged in 5 min under 5000 rpm; then the supernatant was filtrated with 0.22μm organic filter membrane for the following determination.

API-TOF/MS analysis

Vertical introduction atmospheric pressure ionization time-of-flight mass spectrometer (TAPI-TOF1000, Guangzhou HeXin Instrument) was used for mass spectrometry. The mass spectrometry parameters were as follows: ion mode, positive; capillary temperature, 90 °C; spectrum speed, 1 time/s; the discharge gas was helium, and the flow rate was 0.3L/min; the temperature of the loading platform was 180 °C. During the process, after the heating temperature of the loading platform, the low-temperature plasma jet and the temperature of ion transfer tube got stabilized, we needed to use a pipette to drop 10 μL sample onto the loading platform and keep the same injection position each time. The entire time of the detection process did not exceed 5 minutes. After acquisition, we had to input the collected characteristic mass spectrum information of pesticide standards into the database.

UPLC-Q-TOF/MS analysis

Ultra-high performance liquid chromatography–quadrupole-time-of-flight mass spectrometry (UPLC-Q-TOF/MS, Agilent1290-G6545, USA) equipped with Zorbax Eclipse Plus-C18 column(150mm(L)×3mm with 1.8μm of particle size, Agilent, USA) was used for chromatographic separation. 2mM of ammonium acetate and 0.05 % formic acid solution were used as mobile phrase A, and methanol aqueous solution which contained 0.05 % formic acid was used as mobile phrase B. The column was equilibrated with 90% of mobile phase A and 10% of mobile phase B for 30 minutes before injection. The amount of mobile phase A maintained unchanged at 90% from 0 to 0.5min. From 0.5 to 3 min, the amount of mobile phase A decreased from 90% to 50 %, from 3 to 20 min to 0 %, then maintained for 4 minutes and at last went back to 90% at 24.1 min. The temperatures of column oven and auto sampler were set at 40 °C and 4 °C, respectively. The flow rate was 0.4 mL/min and the injection volume was 2μL.

Mass spectrometry parameters: UPLC-Q-TOF/MS equipped with Dual AJS ESI source was operated in full-scan TOF mode. Mass spectrometry detection was carried out in positive electro spray ionization mode (ESI+). The following operating conditions were used: scan range, 50m/z-1200m/z; capillary voltage, 3500V; fragmentor voltage, 120V; skimmer voltage, 65V. The temperature of the drying gas and sheath gas were 250 °C and 325 °C, and the flow rates of the drying gas and sheath gas were set to 7 L/min and 12 L/min. The nebulizer pressure was 35 psi, and the nozzle voltage was 300V.

Method validation

The selectivity of the API-TOF/MS system was evaluated by comparing the chromatograms obtained by injections of blank and spiked samples(100μg/kg), to evaluate the influence of interferents from the matrix or analyses on the presence of signals of the monitored ions.

The method was validated according to the SANTE standard (SANTE/11813/2017) [20], which determined the linearity, repeatability, LOD and LOQ. Calibration curves were obtained by standard solutions, ranging from 1 to 100 μg/L. Recovery and precision were determined based on 4 different sorts of samples (including apple, tomato, grape and pakchoi) spiked at 5, 20 and 100 μg/kg. The estimated LODs and LOQs for all the pesticides were calculated by 3 and 10 times of the signal-to-noise ratio(S/N) of the quantitative ions, respectively, which was used as the spiked level to the blank matrix solutions.

Statistical analysis

A highly authoritative assessment mode-Kappa test [21] was applied to compare the consistency of the two methods API-TOF/MS and UPLC-Q-TOF/MS. The SPSS 16.0 statistical software was used to analyse the Kappa value between the two methods. The Kappa test formula is shown in formula (1),

$$\text{Kappa} = \frac{p_0 - p_e}{1 - p_e} \quad (1)$$

P_0--Number of consistent samples actually detected.

P_e--Total number of tested samples.

The general evaluation criteria is that: if the Kappa value<0.2, there is slight consistency between the two methods;if the Kappa value is between 0.2-0.4, there is fair consistency between the two methods; if the Kappa value is between 0.4-0.7, there is strong consistency between the two methods; if the Kappa value is between 0.7-1, there is substantial consistency between the two methods.

Results and Discussion

Method optimization and selectivity

The study took 100μg/L triazophos as an example to investigate the influence of the flow rate of helium and thermal desorption temperature on API-TOF/MS signal.

The flow rate of helium

The flow rate of helium directly affects the stability and ionization efficiency of the LTP jet. If the flow rate of helium is too low, the density of the formed LTP jet is low, which is not only susceptible to air fluctuations, but also lead to weak interaction between sample molecules and LTP jet. As a result, the ionization efficiency is poor. Conversely, when the flow rate of helium is too high, the plasma density is relatively high, then the collision between the plasma jet and the sample molecules intensifies, which could contribute to the increase of fragmentation degree of the sample molecules, so the signal of molecular ion peak weakens [22]. What's more, excessive flow rate may even cause the sample to be blown away directly when ionizing the sample, and the target cannot be detected. The study investigated the influence of helium gas flow rate in the range of 0.1 to 1 L/min on the sample signal. As is shown in Fig. 2A, it is found that when the helium gas flow rate is 0.3 L/min, the plasma jet is stable and the sample signal response is the best.

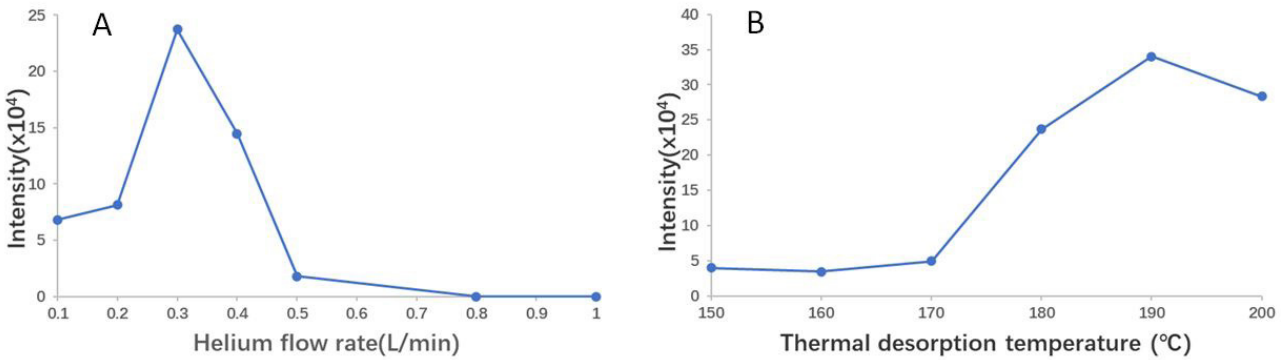

Figure 2: Optimization of different parameters for API; (A)effect of helium flow rate; (B) effect of thermal desorption temperature

Thermal desorption temperature

In the ionization source, the sample molecules are heated and desorbed to form gaseous molecules, which are then ionized by the LTP jet to form ions. When the flow rate of helium is constant, increasing the thermal desorption temperature within a certain range can raise the sample desorption rate and capacity, thereby enhancing the detection signal strength and reducing the limit of detection (LOD). Nevertheless, if the temperature is too high, the sample may desorb quickly or even decompose, causing a decrease of the sample concentration in the ionization source, which may result in weak detection signals [23]. Therefore, the sample signal intensity increases first and then decreases with the increase of the thermal desorption temperature, as is shown in Fig. 2B. In addition, high temperature promotes molecular thermal movement, considering this, the collision of high-speed sample ions with the wall of the ion transmission tube will also lead to losing ions, thereby weakening the detection signal. In this study, the best thermal desorption temperature of the samples was investigated between 150°C to 200°C. For pesticides which are difficult to volatile, such as phosmet and chlorpyrifos, a higher thermal desorption temperature is required to obtain higher sensitivity. It is finally determined that the thermal desorption temperature is 190 °C.

Selectivity

The absence of characteristic m/z signals in mass spectrum of the blank extract confirms the selectivity of the method. Figure 3 showed the selectivity of triazophos for API-TOF/MS. Besides, the selectivity was satisfactory for all the 128 pesticides evaluated.

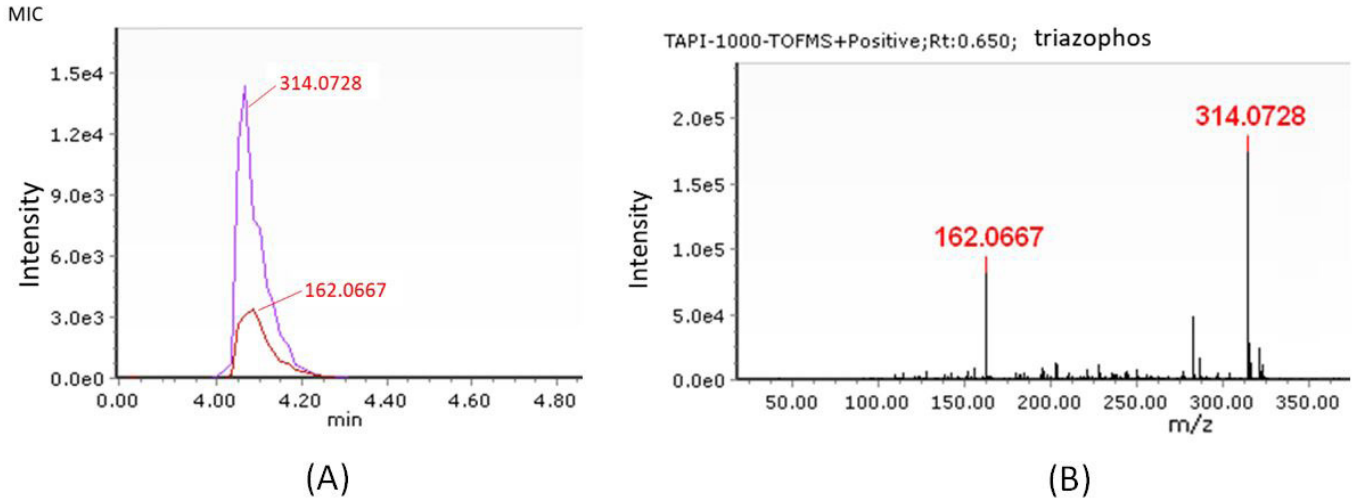

Figure 3: The mixed ion chromatography (MIC)(A) of triazophos and mass spectrum(B) of triazophos for API-TOF/MS

The Accurate Mass Database and Mass Spectrum Library Developed for Pesticides

A pesticide database was established based on TOF's accurate mass spectrometry data. We can obtain a complete mass spectrum under specific conditions to achieve the purpose of identifying target ions. If sample signal matches the database information, it can be analyzed immediately and output the results. In this study, we used 100 μg/L triazophos (precursor ion 314.0728, product ion 162.0667) for mass axis calibration to ensure the mass accuracy less than 100 ppm. The ion current diagrams of 128 pesticides were collected respectively, and the mass spectra were extracted. Then, a database containing the accurate mass and abundance ratios of 2-3 characteristic ions of 128 pesticides was established. The most abundant ions were regarded as quantitative ions, and all pesticide information is shown in Table 1. In some cases, we selected isotope peaks as characteristic ions and quantitative ions in order to distinguish from pesticides with similar mass numbers, such as deltamethrin, myclobutanil, triadimefon, clofentezine, prochloraz, chlorpyrifos, difenoconazole, bromopropylate and envalerate.

To perform quantitative analysis, we need to integrate the quantitative ion peaks and obtain regression equations. Maximum residue limits (MRL) for pesticides have been established in foods for quality control and protection of consumer health in many countries and regions, including China. The use of pesticides in foods is controlled by several regulations in China, including National food safety standard-Maximum residue limits for pesticides in food (GB2763-2019 [24]). According to the requirements of GB2763-2019, the MRL values of each fruit and vegetable are entered into the database. In the actual sample detection, after extracting the

sample mass spectrum and matching the characteristic peak of the database, if characteristic ion peaks of a certain pesticide appears in the mass spectrum of the sample solution with the S/N greater than 3, the consistency score is above 85 and the test concentration of this pesticide in the sample exceeds the MRL, then the sample could be defined as unqualified; if the consistency score is above 50 and the test concentration is lower than or close to the MRL, it could be defined as suspected failure; if the consistency score is less than 50 and the test concentration is much lower than the MRL, it is defined as qualified.

No.	Pesticide	Formula	Mass of neutral molecule (Da)	Cas No.	Chemical class	Confirmatory transition 1(m/z)	Confirmatory transition 2(m/z)
1	Acephate	$C_4H_{10}NO_3PS$	183.0119	30560-19-1	Organo phosphorus	184.0203*	142.9904
2	Acetamiprid	$C_{10}H_{11}ClN_4$	222.0672	135410-20-7	Nicotine	223.0688*	126.0106
3	Aldicarb	$C_7H_{14}N_2O_2S$	190.0776	116-06-3	Carbamate	89.0425*	-
4	Ametryn	$C_9H_{17}N_5S$	227.1205	834-12-8	Heterocycle	228.1292*	186.0819
5	Amitraz	$C_{19}H_{23}N_3$	293.1892	33089-61-1	Amidine	294.1894	163.1238*
6	Azoxystrobin	$C_{22}H_{17}N_3O_5$	403.1168	131860-33-8	Methoxy acrylate	404.1391*	-
7	Benomyl	$C_{14}H_{18}N_4O_3$	290.1379	17804-35-2	Carbamate	192.0728	160.0520*
8	Benzoximate	$C_{18}H_{18}ClNO_5$	363.0874	29104-30-1	Carbamate	364.0764*	199.0162
9	Bifenazate	$C_{17}H_{20}N_2O_3$	300.1474	149877-41-8	Amide	301.1569*	213.1054
10	Bifenthrin	$C_{23}H_{22}ClF_3O_2$	422.1260	82657-04-3	Pyrethroid	361.1919	181.1004*
11	Bitertanol	$C_{20}H_{23}N_3O_2$	337.1790	55179-31-2	Heterocycle	338.1669*	99.0748
12	Boscalid	$C_{18}H_{12}Cl_2N_2O$	342.0327	188425-85-6	Amide	343.0338	307.0630*
13	Bromopropylate	$C_{17}H_{16}Br_2O_3$	425.9466	18181-80-1	Others	410.9320*	408.9320
14	Buprofezin	$C_{16}H_{23}N_3OS$	305.1562	69327-76-0	Heterocycle	306.1518*	201.0995
15	Cadusafos	$C_{10}H_{23}O_2PS_2$	270.0877	95465-99-9	Organo phosphorus	271.0872*	212.9944
16	Carbaryl	$C_{12}H_{11}NO_2$	201.0790	63-25-2	Carbamate	202.0800	145.0652*
17	Carbendazim	$C_9H_9N_3O_2$	191.0695	10605-21-7	Carbamate	192.0756*	160.0518
18	Carbofuran	$C_{12}H_{15}NO_3$	221.1052	1563-66-2	Carbamate	222.1140	165.0901*
19	Carbosulfan	$C_{20}H_{32}N_2O_3S$	380.2134	55285-14-8	Carbamate	381.2265*	222.1140
20	Cartap	$C_7H_{15}N_3O_2S_2$	237.0606	15263-53-3	Amide	238.0600	195.0576*
21	Chlordimeform	$C_{10}H_{13}ClN_2$	196.0767	6164-98-3	Amidine	197.0832*	152.0202
22	Chlorfenapyr	$C_{15}H_{11}BrClF_3N_2O$	405.9695	122453-73-0	Heterocycle	406.9547*	-
23	Chlorfluazuron	$C_{20}H_9Cl_3F_5N_3O_3$	538.9630	71422-67-8	Benzoylurea	539.9633*	158.0387
24	Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	348.9263	2921-88-2	Organo phosphorus	349.9322*	197.9261/ 199.9166
25	Chlorpyri fosmethyl	$C_7H_7Cl_3NO_3PS$	320.8950	5598-13-0	Organo phosphorus	321.8727*	305.8903
26	Clofentezine	$C_{14}H_8Cl_2N_4$	302.0126	74115-24-5	Heterocycle	303.0117*	305.0109
27	Clothianidin	$C_6H_8ClN_5O_2S$	249.0087	210880-92-5	Nicotine	250.0195	131.9678*
28	Cyfluthrin	$C_{22}H_{18}Cl_2FNO_3$	433.0648	68359-37-5	Pyrethroid	434.0726*	191.0013
29	Cyhalothrin	$C_{23}H_{19}ClF_3NO_3$	449.1006	68085-85-8	Pyrethroid	450.0518	225.0034*
30	Cypermethrin	$C_{22}H_{19}Cl_2NO_3$	415.0742	71697-59-1	Pyrethroid	416.0889	191.0013*
31	Cyprodinil	$C_{14}H_{15}N_3$	225.1266	121552-61-2	Heterocycle	226.1415*	-
32	Cyromazine	$C_6H_{10}N_6$	166.0967	66215-27-8	Heterocycle	167.1021*	125.0786
33	Deltamethrin	$C_{22}H_{19}Br_2NO_3$	502.9732	52918-63-5	Pyrethroid	505.9811	278.8979*

No.	Pesticide	Formula	Mass of neutral molecule (Da)	Cas No.	Chemical class	Confirmatory transition 1(m/z)	Confirmatory transition 2(m/z)
34	Demeton	$C_8H_{19}O_3PS_2$	258.0513	8065-48-3	Organo phosphorus	259.0679*	89.0476
35	Diazinon	$C_{12}H_{21}N_2O_3PS$	304.1010	333-41-5	Organo phosphorus	305.1172*	-
36	Dichlorvos	$C_4H_7Cl_2O_4P$	219.9459	62-73-7	Organo phosphorus	220.9455*	127.0097
37	Diethofencarb	$C_{14}H_{21}NO_4$	267.1471	87130-20-9	Carbamate	268.1472*	226.1017
38	Difenoconazole	$C_{19}H_{17}Cl_2N_3O_3$	405.0647	119446-68-3	Heterocycle	406.0742*	408.0674
39	Diflubenzuron	$C_{14}H_9ClF_2N_2O_2$	310.0321	35367-38-5	Benzoylurea	311.0323*	158.0387
40	Dimethoate	$C_5H_{12}NO_3PS_2$	228.9996	60-51-5	Organo phosphorus	230.0045*	198.9699
41	Dimethomorph	$C_{21}H_{22}ClNO_4$	387.1237	110488-70-5	Heterocycle	388.1222*	-
42	Diniconazole	$C_{15}H_{17}Cl_2N_3O$	325.0749	83657-24-3	Heterocycle	326.0813*	-
43	Dinotefuran	$C_7H_{14}N_4O_3$	202.1066	165252-70-0	Nicotine	203.1095*	-
44	Enestroburin	$C_{22}H_{22}ClNO_4$	399.1237	238410-11-2	Methoxy acrylate	400.1239*	178.0391
45	Epoxiconazole	$C_{17}H_{13}ClFN_3O$	329.0731	133855-98-8	Heterocycle	330.0740	121.0507*
46	Ethoprophos	$C_8H_{19}O_2PS_2$	242.0564	13194-48-4	Organo phosphorus	243.0534*	197.0089
47	Etofenprox	$C_{25}H_{28}O_3$	376.2038	80844-07-1	Pyrethroid	377.2117*	163.1127
48	Etoxazole	$C_{21}H_{23}F_2NO_2$	359.1697	153233-91-1	Heterocycle	360.1659*	141.0162
49	Fenarimol	$C_{17}H_{12}Cl_2N_2O$	330.0327	60168-88-9	Heterocycle	331.0361*	333.0290
50	Fenbuconazole	$C_{19}H_{17}ClN_4$	336.1142	114369-43-6	Heterocycle	337.1135*	_
51	Fenitrothion	$C_9H_{12}NO_5PS$	277.0174	122-14-5	Organo phosphorus	278.0148	262.0436*
52	Fenpropathrin	$C_{22}H_{23}NO_3$	349.1678	39515-41-8	Nicotine	350.1797	125.0885*
53	Fenpyroximate	$C_{24}H_{27}N_3O_4$	421.2002	134098-61-6	Heterocycle	422.1823*	366.1324
54	Fenthion	$C_{10}H_{15}O_3PS_2$	278.0200	55-38-9	Organo phosphorus	279.0305*	247.0022
55	Fenvalerate	$C_{25}H_{22}ClNO_3$	419.1288	51630-58-1	Pyrethroid	420.1366*	422.1347
56	Fipronil	$C_{12}H_4Cl_2F_6N_4OS$	435.9387	120068-37-3	Organo chlorine	436.9335*	367.9404
57	Flucythrinate	$C_{26}H_{23}F_2NO_4$	451.1595	70124-77-5	Pyrethroid	452.1673*	199.0943
58	Flufenoxuron	$C_{21}H_{11}ClF_6N_2O_3$	488.0362	101463-69-8	Benzoylurea	489.0251*	158.0498
59	Flusilazole	$C_{16}H_{15}F_2N_3Si$	315.1003	85509-19-9	Heterocycle	316.1082*	_
60	Flutolanil	$C_{17}H_{16}F_3NO_2$	323.1133	66332-96-5	Amide	324.1251*	282.0740
61	Flutriafol	$C_{16}H_{13}F_2N_3O$	301.1027	76674-21-0	Heterocycle	302.1209*	233.0781
62	Forchlor fenuron	$C_{12}H_{10}ClN_3O$	247.0512	68157-60-8	Benzoylurea	248.0623*	129.0284
63	Haloxy fopmethyl	$C_{16}H_{13}ClF_3NO_4$	375.0485	69806-40-2	Heterocycle	376.0545*	-
64	Hexaconazole	$C_{14}H_{17}Cl_2N_3O$	313.0749	79983-71-4	Heterocycle	314.0884*	_
65	Hexythiazox	$C_{17}H_{21}ClN_2O_2S$	352.1012	78587-05-0	Heterocycle	353.1003*	228.0296
66	Imazalil	$C_{14}H_{14}Cl_2N_2O$	296.0483	35554-44-0	Heterocycle	297.0675*	255.0094
67	Imidacloprid	$C_9H_{10}ClN_5O_2$	255.0523	138261-41-3	Nicotine	256.0576	209.0563*
68	Isazophos	$C_9H_{17}ClN_3O_3PS$	313.0417	42509-80-8	Organo phosphorus	314.0572	162.0442*

No.	Pesticide	Formula	Mass of neutral molecule (Da)	Cas No.	Chemical class	Confirmatory transition 1(m/z)	Confirmatory transition 2(m/z)
69	Isocarbophos	$C_{11}H_{16}NO_4PS$	289.0538	24353-61-5	Organo phosphorus	272.0030	230.9821*
70	Isofen phosmethyl	$C_{14}H_{22}NO_4PS$	331.1007	99675-03-3	Organo phosphorus	272.0175*	230.9821
71	Isoprocarb	$C_{11}H_{15}NO_2$	193.1103	2631-40-5	Carbamate	194.1195	137.0953*
72	Kresoxim methyl	$C_{18}H_{19}NO_4$	313.1314	143390-89-0	Methoxy acrylate	314.1353	267.0977*
73	Malathion	$C_{10}H_{19}O_6PS_2$	330.0361	121-75-5	Organo phosphorus	331.0377	284.9999*
74	Mercapto dimethur	$C_{11}H_{15}NO_2S$	225.0823	2032-65-7	Carbamate	226.0823	169.0685*
75	Metalaxyl	$C_{15}H_{21}NO_4$	279.1471	57837-19-1	Amide	280.1514*	220.1334
76	Methami dophos	$C_2H_8NO_2PS$	141.0013	10265-92-6	Organo phosphorus	141.9919*	111.9983
77	Methidathion	$C_6H_{11}N_2O_4PS_3$	301.9619	950-37-8	Organo phosphorus	302.9503	145.0029*
78	Methiocarb-sulfoxide	$C_{11}H_{15}NO_3S$	241.0773	2635-10-1	Carbamate	242.0780*	185.0628
79	Methiocarb-sulfone	$C_{kj}H_{15}NO_4S$	257.0722	2179-25-1	Carbamate	258.0751*	201.0531
80	Methomyl	$C_5H_{10}N_2O_2S$	162.0463	16752-77-5	Carbamate	163.0452	106.0227*
81	Monocro tophos	$C_7H_{14}NO_5P$	223.0610	2157-98-4	Organo phosphorus	224.0638*	127.0196
82	Myclobutanil	$C_{15}H_{17}ClN_4$	288.1142	88671-89-0	Heterocycle	289.1118*	291.1097
83	Novaluron	$C_{17}H_9ClF_8N_2O_4$	492.0123	116714-46-6	Benzoylurea	493.0120*	158.0387
84	Omethoate	$C_5H_{12}NO_4PS$	213.0225	1113-02-6	Organo phosphorus	214.0255*	182.9808
85	Oxamyl	$C_7H_{13}N_3O_3S$	219.0678	23135-22-0	Carbamate	220.0756	90.0546*
86	Parathion	$C_{10}H_{14}NO_5PS$	291.0330	56-38-2	Organo phosphorus	292.0416*	276.0622
87	Parathion methyl	$C_8H_{10}NO_5PS$	263.0017	298-00-0	Organo phosphorus	264.0095	248.0430*
88	Penconazole	$C_{13}H_{15}Cl_2N_3$	283.0643	66246-88-6	Heterocycle	284.0774*	158.9712
89	Pendimethalin	$C_{13}H_{19}N_3O_4$	281.1376	40487-42-1	Others	282.1360	212.0638*
90	Permethrin	$C_{21}H_{20}Cl_2O_3$	390.0789	52645-53-1	Pyrethroid	391.0868	183.0762*
91	Phorate	$C7H_{17}O_2PS_3$	260.0128	298-02-2	Organo phosphorus	261.0206*	214.9788
92	Phosalone	$C_{12}H_{15}ClNO_4PS_2$	366.9869	2310-17-0	Organo phosphorus	367.9962	182.0037*
93	Phosfolan	$C_7H_{14}NO_3PS_2$	255.0153	947-02-4	Organo phosphorus	256.0294*	_
94	Phosfolan methyl	$C_5H_{10}NO_3PS_2$	226.9840	5120-23-0	Organo phosphorus	227.9630*	_
95	Phosmet	$C_{11}H_{12}NO_4PS_2$	316.9945	732-11-6	Organo phosphorus	317.9929*	160.0406
96	Phoxim	$C_{12}H_{15}N_2O_3PS$	298.0541	14816-18-3	Organo phosphorus	299.0624	129.0457*

No.	Pesticide	Formula	Mass of neutral molecule (Da)	Cas No.	Chemical class	Confirmatory transition 1(m/z)	Confirmatory transition 2(m/z)
97	Picoxystrobin	$C_{18}H_{16}F_3NO_4$	367.1031	117428-22-5	Methoxy acrylate	368.1146*	145.0652
98	Pirimicarb	$C_{11}H_{18}N_4O_2$	238.1430	23103-98-2	Carbamate	239.1500*	182.1346
99	Prochloraz	$C_{15}H_{16}Cl_3N_3O_2$	375.0308	67747-09-5	Heterocycle	376.0374	307.9910*/ 309.9910
100	Procymidone	$C_{13}H_{11}Cl_2NO_2$	283.0167	32809-16-8	Organo chlorine	284.0206*	256.0294
101	Profenofos	$C_{11}H_{15}BrClO_3PS$	371.9351	41198-08-7	Organo phosphorus	372.9365*	-
102	Propamocarb	$C_9H_{20}N_2O_2$	188.1525	24579-73-5	Carbamate	189.1529*	102.0507
103	Propiconazole	$C_{15}H_{17}Cl_2N_3O_2$	341.0698	60207-90-1	Heterocycle	342.0707*	158.9826
104	Pymetrozine	$C_{10}H_{11}N_5O$	217.0964	123312-89-0	Heterocycle	218.1043*	105.044
105	Pyraclostrobin	$C_{19}H_{18}ClN_3O_4$	387.0986	175013-18-0	Methoxy acrylate	388.1117	194.0733*
106	Pyridaben	$C_{19}H_{25}ClN_2OS$	364.1376	96489-71-3	Heterocycle	365.1206*	309.0599
107	Pyrimethanil	$C_{12}H_{13}N_3$	199.1109	53112-28-0	Heterocycle	200.1162*	-
108	Spinosad	$C_{41}H_{65}NO_{10}$	731.4608	131929-60-7	Others	732.4609*	190.0369
109	Spirodiclofen	$C_{21}H_{24}Cl_2O_4$	410.1052	148477-71-8	Heterocycle	411.0929*	313.042
110	Sulfotep	C8H20O5P2S2	322.0227	3689-24-5	Organo phosphorus	323.0303*	295.0035
111	Taufluvalinate	$C_{26}H_{22}ClF_3N_2O_3$	502.1271	102851-06-9	Pyrethroid	503.1479*	250.0614
112	Tebuconazole	$C_{16}H_{22}ClN_3O$	307.1451	107534-96-3	Heterocycle	308.1458*	310.1463
113	Tebufenozide	$C_{22}H_{28}N_2O_2$	352.2151	112410-23-8	Amide	353.2234	133.0543*
114	Teflubenzuron	$C_{14}H_6Cl_2F_4N_2O_2$	379.9742	83121-18-0	Benzoylurea	380.9854	158.0495*
115	Thiabendazole	C10H7N3S	201.0361	148-79-8	Heterocycle	202.0439*	-
116	Thiacloprid	$C_{10}H_9ClN_4S$	252.0236	111988-49-9	Nicotine	253.0323*	126.0106
117	Thiamethoxam	$C_8H_{10}ClN_5O^3S$	291.0193	153719-23-4	Nicotine	292.0002	211.0586*
118	Thiophanate methyl	$C_{12}H_{14}N_4O_4S_2$	342.0456	23564-05-8	Carbamate	343.0338*	192.0728
119	Tolfenpyrad	$C_{21}H_{22}ClN_3O_2$	383.1401	129558-76-5	Amide	384.1426*	197.0832
120	Tolylfluanid	$C_{10}H_{13}Cl_2FN_2O_2S_2$	345.9780	731-27-1	Organosulfur	346.9849*	215.0849
121	Tralkoxydim	$C_{20}H_{27}NO_3$	329.1991	1869922-68-8	Others	330.2022*	-
122	Triadimefon	$C_{14}H_{16}ClN_3O_2$	293.0931	43121-43-3	Heterocycle	294.0969*	197.0799/ 199.0660
123	Triadimenol	$C_{14}H_{18}ClN_3O_2$	295.1088	55219-65-3	Heterocycle	296.1120*	-
124	Triazophos	$C_{12}H_{16}N_3O_3PS$	313.0650	24017-47-8	Organo phosphorus	314.0728*	162.0667
125	Trichlorfon	$C_4H_8Cl_3O_4P$	255.9226	52-68-6	Organo phosphorus	256.9334*	220.953
126	Tricyclazole	$C_9H_7N_3S$	189.0361	41814-78-2	Heterocycle	190.0369*	163.0338
127	Trifloxystrobin	$C_{20}H_{19}F_3N_2O_4$	408.1297	141517-21-7	Methoxy acrylate	409.1372	186.0480*
128	Zoxamide	$C_{14}H_{16}Cl_3NO_2$	335.0247	156052-68-5	Amide	336.0294*	186.9733

* Quantification transition (m/z).

Table 1: Basic information of 128 pesticides used in API-TOF/MS

Linearity, LOQ and LOD

Calibration curves were obtained by standard solutions at six different concentration levels (1, 5, 10, 20, 50, 100μg/L). As was shown in Table 2, most pesticides detected by API-TOF/MS had a good linear relationship between 2~100μg/L with the correlation coefficient (R^2)>0.99. Besides, the LODs were between 0.9~5μg/L, most of which were lower than or close to MRL.

Pesticide	API-TOF/MS				UPLC-Q-TOF/MS			
	Linear regression equation	Correlation coefficient R^2	LOD μg/L	LOQ μg/L	Linear regression equation	Correlation coefficient R^2	LOD μg/L	LOQ μg/L
Acephate	y=11329.621x +5666.314	0.9998	1	3	y=3651.286x -10400.059	0.9987	0.3	1
Acetamiprid	y=966408.206x -66151.432	0.9999	3	6	y=28219.991x -23285.911	0.9955	0.1	0.3
Aldicarb	y=174335.710x -46546.316	0.9976	3	7	y=259.836x +1989.494	0.9927	1	4
Ametryn	y=177591.494x +148606	0.9892	1	3	y=116721.282x -182111.436	0.9941	0.3	1.2
Amitraz	y=461563.505x +116233.160	0.9974	2	7	y=17504.118x +26679.82	0.9921	0.8	2.7
Azoxystrobin	y=76208.515x +6570.254	0.9998	1	3	y=45536.124x +203208.339	0.9978	0.7	2.3
Benomyl	y=284419.672x +35650.424	0.9967	3	5	y=2652.954x +22632.112	0.9974	1.5	5
Benzoximate	y=2204.489x -153.362	0.9999	3	7	y=57.281x -208.833	0.9979	1.3	4
Bifenazate	y=101115.377x +14803.798	0.9984	2	5	y=6274.606x -2627.721	0.9965	0.7	2.4
Bifenthrin	y=75043.820x +34471.375	0.9959	1	3.5	y=42.84x +503.825	0.9997	0.8	2
Bitertanol	y=136733.953x -35380.112	0.9983	1	4	y=2179.007x -17664.925	0.9989	0.6	1.5
Boscalid	y=735103.150x -117938.748	0.9994	1	3	y=8046.930x -10708.910	0.9998	0.3	1
Bromopropylate	y=49218.367x +4235.544	0.9997	3	9	y=25467.6x +75431.5	0.9980	1.3	4
Buprofezin	y=35413.215x +22706.850	0.9916	1	4.5	y=42491.358x +138985.495	0.9978	0.8	3
Cadusafos	y=53387.510x +5155.940	0.9961	1	4	y=24829.98x +7715.455	0.9975	0.4	1.2
Carbaryl	y=249634.639x +19934.148	0.9808	3	8	y=14348.239x -95392.49	0.9906	1	2
Carbendazim	y=91289.124x +27986.164	0.9974	2	5	y=28088.595x +64843.755	0.9970	1.3	4.5
Carbofuran	y=39478.696x +78507.792	0.9684	2	6	y=28373.881x -110380.214	0.9950	0.3	1.2
Carbosulfan	y=1333388.177x +65834.289	0.9930	1	4	y=13380.08x -4800.629	0.9986	0.7	2.6
Cartap	y=37494.132x +8130.000	0.9967	3	10	y=1883.041x +9036.537	0.9910	2	7
Chlordimeform	y=206543.425x -65026.924	0.9971	1	3	y=30030.170x +884.836	0.9978	0.6	2.6

Pesticide	API-TOF/MS				UPLC-Q-TOF/MS			
	Linear regression equation	Correlation coefficient R^2	LOD μg/L	LOQ μg/L	Linear regression equation	Correlation coefficient R^2	LOD μg/L	LOQ μg/L
Chlorfluazuron	y=88380.714x -5630.179	1.0000	3	15	y=1532.045x +9931.952	0.9907	2.2	7.2
Chlorpyrifos	y=28619.395x +130.249	0.9999	2	5	y=1904.364x -5234.632	0.9935	0.5	1.8
Chlorpyrifos methyl	y=3730.934x +650.139	0.9996	3	10	y=135.50x -379.880	0.9969	1.5	5
Clofentezine	y=62708.888x +1172.604	0.9999	2	5	y=1657.524x +11418.718	0.9999	0.6	2
Clothianidin	y=5047.258x +432.504	0.9975	2	7	y=2811.697x -8059.273	0.9917	0.9	2.8
Cyfluthrin	y=20505.740 -9670.512	0.9946	1	4	y=401.018x -1816.312	0.9926	0.3	1
Cyhalothrin	y=13999.608x -3877.597	0.9983	3	10	y=62.157x -23.13	0.9959	1	4
Cypermethrin	y=14338.722x +1954.437	0.9950	2	8	y=128.373x +1463.651	0.9983	0.7	2.5
Cyprodinil	y=44360.163x +9242.223	0.9930	1	4	y=124246.637x -236214.58	0.9964	0.7	2.5
Cyromazine	y=69372.631x +57123.392	0.9871	2	4	y=8449.106x +13850.159	0.9986	0.1	0.5
Deltamethrin	y=107836.280x -1569.321	0.9999	3	10	y=4.753x -25.466	0.9915	0.3	1.2
Demeton	y=7289.709x +138.338	0.9977	2	7	y=452.953x -932.044	0.9961	0.6	2
Diazinon	y=66803.190x -4566.362	0.9999	2	5	y=59152.62x -44812.352	0.9926	0.6	1.9
Dichlorvos	y=9714.333x +999.946	0.9990	1	3	y=1158.70x -10124.785	0.9968	0.8	3
Diethofencarb	y=26980.940x +17800.336	0.9940	2	7	y=9956.182x -41918.895	0.9949	0.5	2
Difenoconazole	y=430857.462x +167568.518	0.9957	1	3	y=4698.756x -28601.275	0.9980	0.2	0.7
Diflubenzuron	y=2382005.844 -757016.304	0.9969	1	3	y=1620.488x -5401.28	0.9970	0.3	1
Dimethoate	y=78524.973x +903.468	0.9999	2	5	y=13950.191x -11029.711	0.9960	0.5	1.8
Dimethomorph	y=1072459.272x +41299.001	0.9999	1	4	y=5165.791x +47647.979	0.9975	0.4	1.4
Diniconazole	y=33921.873x +8569.227	0.9977	1	3	y=4594.274x -14694.09	0.9971	0.4	1.2
Dinotefuran	y=139.949x +302.977	0.9981	1	3	y=17428.857x +36814.347	0.9972	0.6	2
Enestroburin	y=13744.531x -1116.937	0.9999	3	7	y=33747.731x +262332.548	0.9974	0.7	2.2
Epoxiconazole	y=371554.631x +3239.017	0.9994	1	3	y=8072.807x +15130.244	0.9994	0.8	2.3
Ethoprophos	y=10784.106x +10457.624	0.9928	2	7	y=24795.954x -64765.26	0.9953	0.4	1.2

Pesticide	API-TOF/MS				UPLC-Q-TOF/MS			
	Linear regression equation	Correlation coefficient R^2	LOD μg/L	LOQ μg/L	Linear regression equation	Correlation coefficient R^2	LOD μg/L	LOQ μg/L
Etoxazole	y=490774.030x +134568.128	0.9958	1	3.5	y=63599.903x +28024.261	0.9974	0.7	2.3
Fenarimol	y=609164.719x +100065.570	0.9946	1	3	y=4870.56x -25361.083	0.9982	0.5	1.8
Fenbuconazole	y=667246.294x -150694.998	0.9990	2	7	y=5039.280x -6743.460	0.9998	0.7	2.5
Fenitrothion	y=43264.834x -22488.896	0.9935	3	8	y=1118.08x +1151.041	0.9937	0.7	2.4
Fenpropathrin	y=315670.492x +13535.562	0.9907	3	10	y=23.723x +1250.955	0.9999	0.7	2.5
Fenpyroximate	y=422858.355x +59300.160	0.9967	1	3	y=24576.340x +76091.458	0.9980	0.3	1
Fenthion	y=33307.280x +14625.074	0.9925	2	5	y=241.888x +1716.168	0.9928	0.6	2
Fenvalerate	y=2252.253x +353.617	0.9989	5	15	y=533.456x -1418.105	0.9981	2	5
Fipronil	y=41594.141x -10591.230	0.9982	1	4	y=5095.9037x -727.60	0.9999	0.3	1.2
Flucythrinate	y=20185.196x -8572.810	0.9948	3	10	y=13.805x +12.649	0.9997	1.2	4
Flufenoxuron	y=201686.616x +31614.112	0.9994	3	6	y=1587.805x -6037.487	0.9962	1	2.8
Flusilazole	y=451555.916x +5070.836	0.9997	1	4	y=24566.857x -42764.702	0.9953	0.7	2
Flutolanil	y=24222.379x -760.359	1.0000	3	8	y=31772.825x -56004.366	0.9950	0.7	2
Flutriafol	y=222561.320x +126341.720	0.9944	2	7	y=11855.254x -69562.457	0.9949	0.6	1.5
Forchlorfenuron	y=351761.084x +42152.982	0.9957	1	2.6	y=5709.202x +117514.853	0.9963	0.9	3
Haloxyfopmethyl	y=27338.114x +8796.838	0.9976	3	8	y=18874.567x +146735.090	0.9986	0.3	1.1
Hexaconazole	y=213139.778x +14838.407	0.9841	1	2	y=4322.76x +1974.981	0.9913	0.5	2
Hexythiazox	y=280699.683x +70217.623	0.9984	2	7	y=8348.887x +84894.762	0.9987	0.6	2
Imazalil	y=1342773.629x -446849.687	0.9973	1	5	y=34150.149x -120152.239	0.9970	0.1	0.5
Imidacloprid	y=43281.456x -4338.585	0.9996	3	7	y=8431.408x -23381.241	0.9941	0.1	0.5
Isazophos	y=57568.749x +26106.665	0.9719	2	7	y=67076.589x -433735.260	0.9944	0.2	0.7
Isocarbophos	y=24346.740x +9809.087	0.9941	2	5	y=11.931x +144.136	0.9944	1.5	5
Isofenphosmethyl	y=174417.223x +5935.767	0.9990	3	12	y=476.065x +6099.753	0.9978	0.9	2.8
Isoprocarb	y=7017980x +4193763	0.9961	3	9	y=16770.518x -107934.494	0.9903	0.5	2

Pesticide	API-TOF/MS				UPLC-Q-TOF/MS			
	Linear regression equation	Correlation coefficient R^2	LOD μg/L	LOQ μg/L	Linear regression equation	Correlation coefficient R^2	LOD μg/L	LOQ μg/L
Malathion	y=4655.306x +1849.503	0.9956	2	7	y=5748.370x -16957.745	0.9938	1	5
Mercaptodimethur	y=7937.191x -2470.018	0.9981	3	8	y=12007.810x -52508.416	0.9954	1.4	5
Metalaxyl	y=223723.202x +7214.266	0.9972	1	3	y=36834.587x +70851.474	0.9988	0.4	1.5
Methamidophos	y=6286.149x +1189.439	0.9989	2	4	y=4653.242x -13327.963	0.9984	1.2	4
Methidathion	y=39054.896x +9138.922	0.9993	1	3.5	y=10945.920x -82624.803	0.9923	0.5	2.5
Methiocarb-sulfone	y=44552.298x -8462.112	0.9996	3	10	y=5559.017x -25031.294	0.9925	1.7	5
Methiocarb-sulfoxide	y=154402.685x +60527.451	0.9950	3	6	y=32966.082x -57687.208	0.9969	2.4	8.1
Methomyl	y=74434.486x -3156.287	0.9955	2	5	y=2898.084x -156.579	0.9992	0.4	1.1
Monocrotophos	y=64668.371x -2366.364	0.9951	2	5	y=18779.822x -169.674	0.9930	0.8	2.5
Myclobutanil	y=369430.916x -1332.435	0.9999	1.5	5	y=6212.792x +173.792	0.9991	0.6	2
Novaluron	y=275291.300x +116561.333	0.9957	1	4	y=54.770x +25.245	0.9751	0.4	1.6
Omethoate	y=50096.238x +83099.711	0.9942	1	5	y=12307.385x -17531.825	0.9992	0.3	1
Oxamyl	y=3886.118x -213.163	0.9995	2	4	y=562.7x +130.561	0.9938	0.6	1.6
Parathion	y=900.539x -302.040	0.9970	3	8	y=6321.065x -15419.655	0.9990	0.8	2.5
Parathionmethyl	y=3069.905x -1192.440	0.9959	3	10	y=75.996x +449.937	0.9975	1	3.2
Penconazole	y=66352.345x +65980.455	0.9815	1	3.3	y=7198.167x -9774.024	0.9943	0.8	2.6
Pendimethalin	y=53431.649x +28053.631	0.9932	2	5	y=1544.916x +2846.833	0.9903	0.6	2
Permethrin	y=283552.355x -2142.597	0.9980	3	9	y=696.281x -555.611	0.9920	1	3
Phorate	y=7322.371x -1867.257	0.9986	1	3	y=224.67x -1170.272	0.9955	0.3	1
Phosalone	y=151100.885x +44707.491	0.9976	3	8	y=3757.8x +29566.998	0.9980	0.4	1.3
Phosfolan	y=174341.723x -46535.688	0.9976	2	5	y=32889.187x +51882.871	0.9954	0.8	2.5
Phosfolanmethyl	y=85643.343x +8771.484	0.9995	2	6	y=26898.118x -64502.985	0.9958	0.4	1.2
Phosmet	y=14272.392 -4218.511	0.9980	1	3	y=6574.317x +49450.734	0.9990	0.3	1
Phoxim	y=63378.707x +5174.645	0.9996	2	6	y=4970.485x +64952.990	0.9952	0.6	2.5

Pesticide	API-TOF/MS				UPLC-Q-TOF/MS			
	Linear regression equation	Correlation coefficient R^2	LOD μg/L	LOQ μg/L	Linear regression equation	Correlation coefficient R^2	LOD μg/L	LOQ μg/L
Pirimicarb	y=39007.626x +67251.252	0.9624	1	4	y=55561.257x +130311.284	0.9980	1	4
Prochloraz	y=9323.448x -2059.821	0.9993	2	5	y=8540.118x +5232.260	0.9981	0.2	0.6
Procymidone	y=103393.789x -35417.782	0.9974	3	7	y=91.268x +1073.578	0.9929	0.7	2
Profenofos	y=39635.044x +7872.969	0.9978	2	5	y=3823.239x +22213.893	0.9994	0.2	0.6
Propamocarb	y=387552.025x +7925.024	0.9905	3	8	y=25985.616x -81927.1	0.9992	1	4
Propiconazole	y=144561.183x +75945.257	0.9966	1	3	y=3399.140x -14456.542	0.9969	0.8	2.5
Pymetrozine	y=552404.015x +55511.903	0.9996	1	5	y=6246.094x -3521.826	0.9961	0.9	3
Pyraclostrobin	y=109533.998x -43263.953	0.9962	1	3	y=31027.04x -16311.820	0.9932	0.1	0.4
Pyridaben	y=171487.361x +70.512	1.0000	3	9	y=4843.902x +11844.118	0.9984	0.8	2.5
Pyrimethanil	y=4958.423x +18003.066	0.9999	2	6	y=58668.991x -232751.556	0.9976	0.8	2.5
Spinosad	y=9576.476x +6989.599	0.9995	2	5	y=29059.971x -71867.796	0.9961	1.2	4
Spirodiclofen	y=140695.382x -4068.396	0.9965	1	4	y=5304.188x +45450.031	0.9976	0.6	2
Sulfotep	y=7389.972x -364.552	0.9973	1	4	y=17101.083x +178135.151	0.9958	0.6	2
Taufluvalinate	y=74033.777x +31945.915	0.9933	1	4	y=76.116x +629.016	0.9976	0.5	1.7
Tebuconazole	y=565616.405x +31653.387	0.9916	1	4	y=10527.725x -32025.769	0.9966	0.5	2
Tebufenozide	y=321723.267x +215695.927	0.9953	2	5	y=6225.2x -10566.923	0.9960	0.7	2.4
Teflubenzuron	y=109825.311x -8941.458	0.9995	1	4	y=6.280x +281.105	0.9997	0.4	1.5
Thiabendazole	y=284520.675x +34540.454	0.9967	3	10	y=162.927x +6016.735	0.9929	1.2	4
Thiacloprid	y=418129.478x -74327.009	0.9988	1	2	y=23325.110x -28958.169	0.9924	0.2	0.6
Thiamethoxam	y=56122.072x +8529.918	0.9993	1	3.5	y=6319.91x -15289.50	0.9990	0.4	1.3
Thiophanatemethyl	y=104699.539x -43687.557	0.9934	1	3	y=16990.504x -158198.9	0.9955	0.4	1.2
Tolfenpyrad	y=614192.319x -3438.679	1.0000	2	5	y=9250.232x -10855.531	0.9934	0.6	2
Tolylfluanid	y=772.046x +1065.665	0.9970	3	8	y=7386.506x +102064.906	0.9958	1.1	3.2
Tralkoxydim	y=256342.054x -5559.011	0.9998	2.5	5	y=22215.007x -11668.446	0.9930	0.9	3

Pesticide	API-TOF/MS				UPLC-Q-TOF/MS			
	Linear regression equation	Correlation coefficient R^2	LOD μg/L	LOQ μg/L	Linear regression equation	Correlation coefficient R^2	LOD μg/L	LOQ μg/L
Triadimenol	y=19903.606x +4394.353	1.0000	2	5	y=1566.464x -9122.156	0.9980	0.4	1.5
Triazophos	y=95742.115x -7327.331	0.9998	0.9	3	y=66900.577x -437575.866	0.9948	0.5	2
Trichlorfon	y=65681.616x +14775.175	0.9940	1	4	y=2296.061x +6440.623	0.9911	0.5	1.7
Tricyclazole	y=1047886.516x +48043.513	0.9946	1	4	y=65286.050x -22254.962	0.9904	0.4	1.4
Trifloxystrobin	y=188553.911x +20840.061	0.9944	2	6	y=44505.361x +226919.816	0.9984	0.3	0.8
Zoxamide	y=171937.757x +170933.674	0.9966	2	7	y=7393.506x +101943.910	0.9958	0.3	0.8

Table 2: Parameters of the analytical curves to API-TOF/MS and UPLC-Q-TOF/MS methods

Accuracy and precision

The accuracy and precision were tested via the recovery and reproducibility experiments respectively, which were carried out on four kinds of blank samples (including apple, tomato, grape and pakchoi) with three spiked levels at 5 μg/kg, 20 μg/kg, 100 μg/kg. The relative standard deviations (RSDs) which represented the precision of this method were evaluated from the recovery test of six replicates for individual. The results in Table 3 showed that, for API-TOF/MS, the recoveries of pesticides were in the range of 70%-120% with RSDs<20% and could meet the requirement of SANTE/11813/2017 guideline, in which the acceptable mean recoveries were those within the range 70%-120%, with an associated repeatability RSDs≤20%, indicating that this method may meet the daily monitoring requirements.

Pakchoi													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Acephate	114.35	3.22	92.02	9.23	85.41	2.73	74.75	4.86	74.09	14.42	96.03	13.92	1
Acetamiprid	74.65	0.68	83.08	0.91	114.95	0.67	98.26	11.83	93.35	16.68	104.60	9.57	1
Aldicarb	78.79	3.44	73.90	10.31	90.50	3.11	85.13	7.52	74.60	5.12	80.05	9.41	0.03
Ametryn	116.66	0.42	94.35	0.53	89.26	0.67	94.88	13.20	70.01	17.02	93.80	6.54	/
Amitraz	83.40	5.58	71.06	1.53	105.15	2.54	106.61	9.14	96.16	14.89	106.31	7.06	/
Azoxystrobin	86.31	4.15	94.23	0.13	109.20	0.84	78.63	11.13	95.22	16.20	110.13	3.84	/
Benomyl	91.33	3.01	93.35	0.37	94.07	1.02	76.43	2.52	99.24	17.51	115.15	7.27	/
Benzoximate	76.13	7.20	89.91	2.67	70.02	3.22	73.73	4.06	92.03	17.57	101.82	10.26	/
Bifenazate	98.33	4.77	112.64	1.66	113.53	0.73	93.60	3.61	71.38	17.80	75.60	14.48	/
Bifenthrin	108.55	5.92	85.48	12.51	84.25	3.94	107.27	13.97	87.59	15.37	107.16	8.68	/
Bitertanol	94.19	6.13	98.74	1.60	93.92	7.09	84.40	11.63	108.77	11.36	97.85	5.45	/
Boscalid	110.50	1.07	106.63	0.68	101.79	0.62	78.57	7.51	107.54	18.20	82.37	10.63	/
Bromo propylate	93.01	15.20	105.26	9.51	95.16	4.16	88.68	9.50	74.49	4.22	94.32	12.13	/
Buprofezin	84.01	9.74	95.97	0.81	111.44	0.88	73.46	2.72	74.14	6.39	112.81	17.99	/
Cadusafos	89.26	2.44	105.56	1.25	108.15	1.15	85.86	18.71	78.31	10.85	72.22	17.25	0.02

Pakchoi													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Carbaryl	114.19	0.92	84.36	0.94	113.64	1.34	114.89	8.22	102.40	2.64	113.48	8.45	5
Carbendazim	93.71	1.37	84.18	0.81	102.61	0.83	109.14	17.01	90.34	17.76	100.42	12.15	/
Carbofuran	92.12	0.37	99.62	0.43	108.48	1.19	76.35	2.72	94.79	12.23	112.99	8.46	0.02
Carbosulfan	116.00	13.92	100.25	2.83	103.64	1.19	82.42	16.89	98.03	3.15	118.68	19.93	0.05
Cartap	90.24	5.97	104.29	5.29	105.26	5.16	108.16	9.19	80.37	13.18	104.53	4.33	/
Chlordimeform	77.97	2.31	85.15	3.56	85.78	0.89	116.79	10.17	85.19	15.17	97.00	18.46	0.01
Chlorfenapyr	104.95	6.28	83.40	6.52	108.69	0.85	119.60	7.29	97.03	15.71	72.08	10.66	10
Chlorfluazuron	105.24	5.02	91.85	3.97	113.39	1.53	95.24	9.88	77.19	8.91	95.74	18.43	7
Chlorpyrifos	112.90	3.28	101.57	3.04	90.93	2.32	80.60	3.49	104.62	14.82	82.34	5.12	0.1
Chlorpyrifos methyl	95.60	5.22	86.59	4.32	113.24	6.57	83.07	19.25	110.81	8.94	72.20	5.33	/
Clofentezine	104.29	9.42	100.85	2.69	70.75	1.67	110.28	4.36	88.94	16.67	102.35	6.32	/
Clothianidin	81.48	1.37	79.74	1.15	105.27	0.88	86.21	16.65	106.43	16.28	114.91	4.74	2
Cyfluthrin	99.89	2.73	94.46	1.53	86.26	6.55	113.99	7.00	75.18	14.98	76.66	6.75	0.5
Cyhalothrin	93.63	10.93	71.15	3.63	93.30	18.16	107.50	6.57	88.98	10.43	87.35	12.04	2
Cypermethrin	105.20	10.52	76.67	12.54	105.12	3.07	118.45	11.73	111.56	15.17	86.11	10.16	2
Cyprodinil	89.44	0.64	71.73	1.16	75.42	0.87	107.26	15.49	90.11	18.23	95.30	8.03	/
Cyromazine	82.58	0.42	74.13	0.60	106.77	0.52	105.17	8.33	78.70	7.42	72.62	7.57	/
Deltamethrin	85.56	13.47	74.33	5.24	94.39	5.57	112.94	2.84	80.14	9.16	88.50	11.19	0.5
Demeton	105.84	5.09	97.80	4.35	98.43	2.12	77.35	9.76	97.56	4.33	106.44	10.25	0.02
Diazinon	115.71	1.35	104.41	0.92	104.65	0.67	81.36	9.55	80.46	11.89	81.27	18.11	0.2
Dichlorvos	79.72	1.77	93.89	3.09	108.76	4.03	113.38	13.65	116.91	17.54	98.49	14.17	0.1
Diethofencarb	106.49	4.46	84.06	4.30	113.44	1.01	82.46	6.65	95.35	14.94	105.25	2.11	/
Difenoconazole	103.33	1.68	110.19	1.32	88.18	1.04	111.35	7.16	71.42	14.64	97.57	11.76	/
Diflubenzuron	117.64	2.02	72.09	0.72	86.18	1.78	84.62	16.39	110.96	16.11	74.30	10.69	1
Dimethoate	106.40	1.50	117.42	1.38	109.19	0.59	93.77	14.19	82.36	15.25	109.20	14.83	1
Dimethomorph	101.34	0.56	104.46	0.89	116.24	0.85	96.95	11.35	116.71	6.66	119.85	19.43	/
Diniconazole	109.41	2.47	83.97	1.72	76.18	1.36	87.33	17.31	92.91	19.58	89.74	14.47	/
Dinotefuran	92.89	0.61	75.07	0.57	74.41	0.49	74.81	10.74	71.78	11.32	115.79	16.45	6
Enestroburin	95.10	15.52	74.15	1.01	110.89	0.95	84.73	7.32	82.95	13.02	86.62	3.87	/
Epoxiconazole	86.95	9.73	80.43	2.68	93.80	0.98	86.68	19.25	101.89	10.09	81.37	9.23	/
Ethoprophos	92.75	1.34	119.41	0.43	107.90	0.83	84.17	5.88	73.24	12.87	105.37	14.39	0.02
Etofenprox	77.60	2.96	81.01	3.36	97.82	1.41	95.03	2.69	103.58	16.13	110.83	4.02	1
Etoxazole	77.70	1.24	87.33	0.77	92.14	0.44	102.88	19.18	81.10	9.87	86.10	7.46	/
Fenarimol	115.16	2.41	90.58	5.37	75.71	0.97	77.62	14.07	72.67	8.88	102.88	11.25	/
Fenbuconazole	92.06	5.92	86.32	12.09	99.12	1.84	103.32	16.05	104.20	12.02	83.07	12.03	/
Fenitrothion	97.85	1.44	71.80	2.90	76.39	1.41	108.69	9.64	102.50	10.17	91.48	11.55	0.05
Fenpropathrin	108.00	9.14	86.23	3.63	74.13	5.14	90.79	16.32	76.99	9.70	111.17	12.51	1
Fenpyroximate	72.74	7.00	81.28	0.77	94.46	0.93	84.05	4.77	95.65	11.84	93.86	9.63	/
Fenthion	107.36	12.34	86.29	3.24	83.15	4.63	98.53	14.16	103.90	4.19	110.92	4.04	0.05
Fenvalerate	96.20	6.10	73.68	4.40	83.37	3.42	90.15	10.15	109.98	5.12	96.01	8.29	1
Fipronil	95.19	7.93	95.01	5.20	96.77	1.02	106.13	3.19	85.31	3.18	89.22	6.27	0.02

Pakchoi													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Flucythrinate	81.63	7.03	86.30	8.79	91.77	7.74	100.51	18.94	74.29	11.17	77.04	4.28	/
Flufenoxuron	112.80	2.39	108.88	2.95	110.99	1.03	118.41	14.53	107.55	12.79	72.94	10.79	/
Flusilazole	118.83	0.95	98.42	0.72	87.89	0.79	100.38	7.98	90.13	18.73	92.84	13.40	/
Flutolanil	115.46	7.89	110.89	0.65	105.78	0.64	88.28	7.26	92.44	16.86	84.89	6.71	/
Flutriafol	103.14	0.72	109.23	0.89	104.38	0.78	93.83	18.99	91.18	12.57	108.11	7.48	/
Forchlor fenuron	94.15	8.32	76.26	4.24	105.22	0.93	118.69	6.26	84.46	9.83	110.74	3.42	/
Haloxyfop methyl	94.50	14.02	88.58	0.62	114.25	0.99	74.13	15.60	92.88	18.36	102.79	7.18	/
Hexaco nazole	99.30	13.21	103.01	1.81	102.75	0.89	86.65	13.39	75.43	11.58	91.21	12.03	/
Hexythiazox	106.20	13.96	70.37	2.13	111.61	0.86	81.93	14.66	91.24	16.28	82.88	13.57	/
Imazalil	75.32	1.02	105.21	0.42	91.97	0.35	88.24	16.88	94.62	17.81	98.62	10.60	/
Imidacloprid	97.49	0.56	103.73	0.90	91.20	0.69	89.50	18.61	102.99	7.15	110.11	16.16	0.5
Isazophos	108.74	0.44	91.07	0.44	80.61	15.38	103.59	15.42	73.48	12.35	94.13	9.98	0.01
Isocarbophos	71.32	2.68	89.60	5.66	71.95	4.32	107.94	11.90	83.54	13.14	96.73	15.98	0.05
Isofenphos methyl	90.63	9.24	84.15	9.05	97.02	2.53	110.23	11.26	81.14	7.72	85.13	16.70	0.01
Isoprocarb	114.89	1.14	91.31	0.55	103.89	0.50	93.05	9.67	93.34	18.03	107.47	9.04	/
Kresoxim methyl	103.98	4.10	72.09	1.39	107.17	0.71	112.80	4.32	80.52	13.65	78.49	2.44	/
Malathion	92.54	1.45	119.67	1.67	113.36	0.97	118.42	12.13	86.04	4.24	82.64	15.85	8
Mercaptodi methur	91.59	1.04	110.94	1.10	102.76	1.15	89.66	15.30	77.10	13.04	116.09	8.86	/
Metalaxyl	108.87	1.75	103.78	0.62	95.15	1.02	104.46	0.47	83.16	9.50	108.57	9.78	/
Methami dophos	116.83	8.33	95.62	10.47	88.85	18.24	86.98	19.23	75.76	16.38	107.84	12.31	0.05
Methidathion	95.25	0.89	106.21	0.48	102.47	1.12	76.85	6.92	89.22	9.25	113.66	10.00	0.05
Methiocarb-													
sulfoxide	93.01	1.83	111.57	0.88	97.72	5.18	90.47	5.35	79.03	4.33	83.25	9.83	/
Methiocarb-													
sulfone	88.65	4.67	116.27	5.61	73.96	8.55	109.05	5.74	96.21	3.56	89.92	19.20	/
Methomyl	92.04	10.19	92.65	3.24	95.07	0.92	82.36	9.58	71.33	19.39	96.92	19.81	0.2
Monocro tophos	101.52	2.05	105.65	0.49	100.71	0.60	113.34	18.36	107.81	9.47	102.34	9.52	0.03
Myclobutanil	101.34	13.99	98.32	2.22	102.45	1.31	71.42	10.92	90.37	6.78	118.60	9.55	0.05
Novaluron	98.36	5.95	71.33	19.08	89.57	16.88	109.60	6.24	110.24	12.83	71.63	8.53	/
Omethoate	110.67	5.93	94.87	3.72	91.75	2.71	70.23	12.23	75.91	6.92	76.61	11.03	0.02
Oxamyl	88.85	5.41	108.70	9.26	81.84	9.96	93.66	4.13	96.23	4.44	100.48	4.31	/
Parathion	95.52	0.67	87.70	0.22	100.50	0.79	102.46	13.86	103.03	9.04	78.62	12.46	0.01
Parathion methyl	88.01	7.62	108.59	14.10	109.14	8.40	114.49	10.91	109.23	2.90	85.13	8.66	0.02
Penconazole	114.89	3.38	108.60	0.60	102.49	0.99	88.57	16.21	81.23	5.17	110.36	13.71	/
Pendim ethalin	103.02	9.11	111.58	2.92	110.65	1.76	77.76	16.82	97.13	10.80	119.89	11.30	0.2

Pakchoi													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Permethrin	93.42	13.50	76.63	11.17	114.17	6.04	103.16	8.09	110.10	17.92	72.36	13.33	1
Phorate	89.82	8.68	81.91	3.10	95.45	1.51	90.26	3.10	77.32	7.66	110.31	2.75	0.01
Phosalone	76.55	12.52	108.19	0.72	80.00	1.27	82.81	5.97	86.25	10.39	90.61	13.67	1
Phosfolan	74.13	2.00	97.91	0.68	99.79	0.58	90.66	15.53	108.36	14.84	98.78	9.59	0.03
Phosfolan methyl	78.90	0.57	112.73	0.58	104.43	0.77	83.01	4.56	96.33	7.11	100.21	11.88	0.03
Phosmet	92.24	9.47	76.12	0.56	81.95	1.18	72.99	6.44	93.32	3.34	91.24	4.41	/
Phoxim	82.84	15.24	95.78	1.56	108.87	1.12	85.46	3.23	94.05	17.29	72.48	8.73	0.1
Picoxystrobin	92.46	1.96	107.55	0.67	107.04	1.00	86.88	8.74	108.17	16.23	103.95	10.90	/
Pirimicarb	106.67	4.88	89.49	1.24	103.38	0.85	94.72	15.55	94.10	15.62	76.39	11.23	5
Prochloraz	92.41	2.33	102.22	0.74	101.86	0.98	91.88	13.79	76.68	17.25	89.11	8.44	/
Procymidone	105.58	10.62	98.52	15.14	104.25	7.21	79.31	13.15	81.49	7.41	80.73	12.92	/
Profenofos	104.50	14.86	92.78	1.88	117.10	1.50	99.56	19.23	82.36	2.58	80.38	14.12	5
Propamocarb	83.49	1.45	108.13	1.38	98.24	0.83	72.24	13.03	84.16	14.24	91.97	12.04	/
Propiconazole	109.77	1.94	93.44	1.91	89.92	1.66	73.47	12.77	91.46	4.40	104.27	7.78	/
Pymetrozine	103.60	5.61	116.28	1.29	106.34	0.67	110.88	17.96	76.89	13.59	115.55	9.38	/
Pyraclostrobin	116.22	1.27	111.74	0.60	105.86	0.79	96.18	13.92	75.08	15.84	101.63	11.86	/
Pyridaben	74.15	0.63	104.23	0.98	109.16	1.14	106.21	8.32	99.59	14.77	108.71	14.99	/
Pyrimethanil	112.87	0.47	77.79	0.49	81.28	1.12	109.77	11.37	96.14	3.93	94.53	14.53	/
Spinosad	104.26	0.77	72.73	1.00	74.49	1.17	71.29	9.42	86.38	9.46	80.76	7.20	/
Spirodiclofen	106.90	10.63	78.12	1.94	104.86	2.28	96.96	13.01	110.70	12.07	77.84	15.33	/
Sulfotep	104.95	4.29	92.00	1.91	115.76	1.22	73.74	11.84	91.12	4.01	115.89	4.04	0.01
Taufluvalinate	112.07	7.83	77.55	5.80	98.12	6.22	91.58	9.06	100.64	5.27	86.16	2.36	0.5
Tebuconazole	94.09	1.74	104.98	0.62	94.23	1.00	82.58	6.56	84.37	17.92	93.73	3.30	/
Tebufenozide	110.47	9.45	106.62	1.56	109.13	0.72	96.52	9.22	101.08	16.66	102.32	7.45	10
Teflubenzuron	92.73	11.08	92.57	6.05	77.67	9.29	93.51	3.72	110.15	9.40	77.71	7.39	0.5
Thiabendazole	89.69	4.18	107.96	12.62	76.61	12.93	80.43	3.84	115.77	14.04	87.59	5.75	/
Thiacloprid	82.81	1.16	72.01	16.75	90.12	7.61	83.31	2.94	76.26	10.11	104.62	13.73	/
Thiamethoxam	94.49	0.78	77.23	0.16	110.02	0.71	94.58	8.29	104.74	6.79	99.30	18.74	3
Thiophanat emethyl	87.84	1.25	106.67	1.12	117.82	1.89	83.57	7.51	71.54	18.20	82.37	10.63	/
Tolfenpyrad	76.92	2.98	104.40	0.81	84.99	1.44	91.91	12.01	95.09	14.36	82.60	9.54	/
Tolylfluanid	109.24	10.26	95.14	5.09	82.35	2.10	104.34	7.10	106.88	8.81	102.34	4.17	/
Tralkoxydim	108.67	1.08	111.19	1.15	103.67	0.90	113.15	6.04	96.32	15.97	98.28	7.00	/
Triadimefon	82.34	1.19	114.74	1.10	102.51	0.86	84.46	7.47	80.40	8.83	108.07	2.41	/
Triadimenol	105.12	3.50	106.47	1.74	104.52	1.56	111.89	6.86	71.56	15.86	113.62	8.52	/
Triazophos	102.22	0.49	111.87	0.69	80.84	15.28	88.84	15.57	73.83	11.45	95.36	10.03	/
Trichlorfon	112.99	4.35	109.92	1.71	108.84	6.39	70.19	5.10	111.81	6.13	83.30	2.83	0.1
Tricyclazole	86.51	0.45	79.16	0.72	73.28	0.59	71.29	11.23	95.81	9.46	80.76	7.20	/
Trifloxystrobin	96.21	2.53	85.26	1.99	108.56	0.87	83.12	4.92	97.24	4.46	73.98	16.83	/
Zoxamide	104.99	4.25	96.19	1.60	114.23	0.74	106.40	3.43	91.25	14.18	77.59	11.64	/

Apple													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Acephate	118.37	16.72	104.46	2.15	91.70	2.48	71.79	7.68	72.31	10.18	84.26	12.80	0.5
Acetamiprid	70.23	16.41	114.23	1.90	102.40	1.67	112.74	9.92	80.63	16.41	109.06	9.16	0.8
Aldicarb	70.27	18.19	99.07	15.30	99.80	2.87	82.52	5.82	106.05	8.38	112.47	6.93	0.02
Ametryn	79.61	1.16	108.05	1.52	101.51	1.45	89.32	15.39	72.83	15.24	75.82	8.62	/
Amitraz	97.76	6.00	79.50	2.13	91.12	1.20	112.44	5.40	90.71	7.93	103.48	19.21	0.5
Azoxystrobin	86.13	4.28	88.37	2.21	100.24	1.97	82.69	13.24	103.20	8.01	93.54	14.88	/
Benomyl	76.50	13.03	97.27	1.73	99.51	2.22	90.83	3.31	77.37	14.27	107.57	15.54	/
Benzoximate	113.44	7.31	94.69	12.58	93.61	5.35	89.45	1.14	109.58	5.32	95.56	3.92	/
Bifenazate	80.69	5.38	109.71	2.45	112.58	2.98	89.24	15.57	91.19	15.21	73.59	12.18	0.2
Bifenthrin	110.78	7.75	106.22	6.09	108.43	14.33	81.23	12.59	94.14	12.80	97.09	18.96	/
Bitertanol	104.36	11.71	102.49	3.13	92.79	4.14	85.48	6.72	88.51	12.10	115.40	14.48	2
Boscalid	91.26	0.97	112.58	0.82	101.06	2.45	78.67	13.81	96.28	10.85	110.22	18.14	2
Bromo propylate	90.83	4.84	85.90	4.04	103.89	6.94	97.65	7.54	85.42	12.95	100.58	3.54	2
Buprofezin	84.39	7.94	85.40	2.58	98.08	1.45	105.17	5.68	81.28	9.37	95.08	5.01	3
Cadusafos	89.03	4.67	101.83	1.89	101.16	2.03	73.12	17.03	73.50	19.15	104.42	16.08	0.02
Carbaryl	108.83	1.07	118.94	2.59	104.22	1.54	94.29	3.35	95.38	15.95	74.40	10.58	/
Carbendazim	119.50	4.39	107.51	1.93	99.44	1.02	109.89	7.56	91.27	12.38	85.82	5.23	5
Carbofuran	90.75	0.77	106.16	1.37	101.35	1.48	116.76	11.89	93.45	6.81	92.42	3.84	0.02
Carbosulfan	119.00	13.31	95.29	1.78	93.42	1.41	75.92	15.86	82.46	17.99	107.85	18.88	0.2
Cartap	100.43	10.37	98.82	5.39	104.82	9.28	86.07	12.65	75.49	12.21	103.32	17.35	/
Chlordimeform	77.51	13.97	106.21	10.24	99.08	1.97	80.45	7.88	95.40	17.95	119.69	2.85	0.01
Chlorfenapyr	100.23	3.90	97.42	13.91	99.79	3.36	83.66	13.88	84.67	3.01	93.26	4.87	/
Chlorfluazuron	105.39	10.58	98.82	6.65	91.00	2.40	97.19	4.23	102.05	9.15	98.57	12.54	/
Chlorpyrifos	98.45	6.26	115.66	3.61	107.07	4.17	90.60	3.54	96.53	5.28	83.14	8.73	1
Chlorpyrifos methyl	111.84	19.55	114.56	7.60	110.53	7.90	109.33	5.71	83.22	3.46	93.07	16.38	/
Clofentezine	89.34	8.21	91.46	11.30	75.57	2.19	82.17	19.72	106.70	17.32	104.10	6.73	0.5
Clothianidin	101.81	3.86	75.37	1.86	113.37	2.05	90.70	4.83	72.73	7.45	106.27	15.07	0.4
Cyfluthrin	114.33	5.96	94.92	3.50	83.07	6.43	114.46	13.33	95.58	4.93	117.45	2.46	0.5
Cyhalothrin	115.59	8.91	87.31	5.17	98.48	10.03	75.42	7.21	72.86	8.83	86.63	5.95	0.2
Cypermethrin	105.83	5.27	97.20	13.69	99.30	5.84	98.35	12.04	101.77	12.76	77.74	4.64	2
Cyprodinil	110.28	0.68	103.67	1.65	97.51	1.55	76.45	10.54	90.43	16.47	90.62	7.81	2
Cyromazine	71.63	5.27	84.10	3.70	93.81	1.11	81.42	18.52	84.26	6.80	98.21	18.67	/
Deltamethrin	95.51	17.69	77.37	3.80	105.51	5.80	85.86	16.36	71.97	3.51	90.44	12.13	0.1
Demeton	93.42	10.78	119.85	6.91	101.29	1.83	93.02	15.96	103.16	9.36	102.54	5.25	0.02
Diazinon	115.82	0.65	104.51	1.86	101.22	1.59	106.73	12.30	114.04	18.21	107.91	17.05	0.3
Dichlorvos	103.08	3.36	103.77	1.81	105.50	2.86	77.43	9.07	94.14	19.33	106.24	3.45	0.1
Diethofencarb	97.91	1.82	78.38	1.06	101.71	2.01	95.29	7.13	77.31	18.06	98.48	3.79	/
Difenoconazole	115.72	11.39	106.28	1.80	102.03	3.58	102.01	11.62	86.51	5.57	103.51	8.41	0.5
Diflubenzuron	82.92	3.52	112.32	6.18	99.00	3.35	76.72	6.49	70.67	4.99	106.19	18.07	5
Dimethoate	115.72	1.27	116.55	2.13	103.74	1.46	96.83	15.52	110.92	12.68	110.34	4.62	1
Dimethomorph	99.47	13.96	76.33	5.89	94.71	2.00	111.76	14.43	96.55	14.17	89.70	7.80	/

Apple													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Diniconazole	109.07	3.89	112.51	2.32	99.81	1.49	90.56	10.53	105.47	15.17	75.01	12.88	0.2
Dinotefuran	70.31	3.38	102.35	1.91	98.71	1.53	79.45	13.45	106.95	11.99	100.18	9.44	/
Enestroburin	102.46	5.38	70.41	1.50	102.26	2.53	92.43	17.20	91.17	9.53	86.42	5.99	/
Epoxiconazole	93.28	1.74	91.64	1.55	97.17	0.85	88.16	16.04	76.54	7.98	93.55	10.87	0.5
Ethoprophos	73.85	0.75	114.99	2.59	93.34	1.23	95.42	4.04	84.37	12.06	114.53	6.32	0.02
Etofenprox	94.66	5.24	73.52	4.66	79.91	1.89	102.31	16.46	105.76	5.25	85.52	3.12	0.6
Etoxazole	87.97	0.75	98.87	1.84	100.89	1.88	93.02	12.04	100.51	14.45	95.69	16.56	0.1
Fenarimol	89.25	0.66	115.93	2.14	97.75	3.03	94.55	18.69	101.18	14.70	106.73	12.46	0.3
Fenbuconazole	118.84	15.85	83.92	11.49	104.64	4.78	93.51	7.78	118.02	15.33	91.31	11.31	0.1
Fenitrothion	74.93	9.79	80.71	3.09	89.76	4.15	96.23	14.79	82.52	14.79	86.95	3.84	0.5
Fenpropathrin	80.36	9.30	93.40	7.36	104.10	5.39	82.96	17.42	100.43	6.95	107.79	12.81	5
Fenpyroximate	92.04	6.54	82.33	2.24	95.10	2.57	104.99	17.83	88.53	12.59	90.49	4.20	0.3
Fenthion	91.91	17.98	109.26	10.42	84.40	10.24	85.79	4.67	90.73	15.08	89.55	3.19	0.05
Fenvalerate	77.03	14.65	114.67	9.88	102.18	8.30	104.83	18.32	87.78	17.41	94.35	14.68	/
Fipronil	118.26	0.00	104.35	8.26	90.71	10.34	96.25	17.56	92.73	5.01	101.63	9.10	0.02
Flucythrinate	95.22	16.90	116.43	7.66	103.24	5.84	81.75	10.13	103.34	4.19	86.41	6.25	0.5
Flufenoxuron	98.14	5.47	111.77	3.21	107.53	3.10	75.45	11.44	93.43	13.47	80.56	3.95	1
Flusilazole	106.19	1.56	111.59	2.91	100.38	2.45	90.51	5.27	85.44	13.91	104.80	11.41	0.2
Flutolanil	118.75	1.24	104.05	2.71	93.94	2.37	117.80	13.71	105.53	11.41	118.45	2.65	/
Flutriafol	98.22	1.25	92.14	2.23	101.14	1.91	95.21	14.24	110.95	18.20	105.13	12.09	0.3
Forchlor fenuron	90.62	3.58	71.65	6.85	100.93	1.58	79.48	16.45	93.27	2.56	77.51	13.63	/
Haloxyfop methyl	106.47	7.45	77.97	2.97	100.67	1.97	100.49	3.25	91.44	15.95	109.02	9.41	0.02
Hexaconazole	93.52	7.25	104.81	3.46	103.67	2.59	93.59	14.41	109.30	18.88	102.73	16.87	0.5
Hexythiazox	105.43	5.39	82.14	3.24	94.19	2.79	83.39	18.36	75.33	7.04	93.58	11.90	0.5
Imazalil	80.11	0.41	113.48	1.01	98.39	1.53	105.47	10.49	82.98	15.09	107.67	5.08	5
Imidacloprid	91.78	2.39	77.29	1.77	113.45	2.59	114.62	19.95	104.80	19.78	70.38	7.35	0.5
Isazophos	92.08	1.16	102.91	1.43	104.92	2.06	83.61	17.82	89.56	16.75	90.34	19.47	0.01
Isocarbophos	78.28	11.30	109.95	11.57	109.25	9.34	98.96	8.31	94.14	14.70	83.09	15.92	0.01
Isofenphos methyl	117.19	11.98	97.28	8.07	110.72	2.25	88.73	6.95	71.25	16.35	104.78	2.55	0.01
Isoprocarb	106.30	1.00	103.05	2.98	103.53	1.93	84.69	19.32	93.92	4.60	91.69	16.58	/
Kresoxim methyl	92.83	8.25	78.64	4.04	99.32	2.34	92.95	10.60	88.41	13.57	74.64	2.70	0.2
Malathion	86.05	1.96	107.24	1.46	97.42	2.24	72.46	11.16	87.20	4.70	94.32	19.78	2
Mercaptodi methur	101.42	3.09	119.87	1.80	101.42	2.48	98.75	10.94	92.28	8.58	107.42	10.55	/
Metalaxyl	70.09	3.21	93.28	2.34	98.80	1.60	112.35	8.61	101.25	9.79	103.00	12.96	1
Methami dophos	115.84	7.32	109.78	6.53	87.60	12.67	74.03	9.82	116.56	8.57	94.22	16.38	0.05
Methidathion	108.67	0.97	99.03	1.68	104.63	2.53	104.73	5.10	98.76	16.80	116.70	9.45	0.05
Methiocarb-sulfoxide	77.76	0.88	110.70	1.99	100.48	1.78	96.21	4.56	110.34	12.55	85.64	17.95	/

Apple													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Methiocarb-sulfone	92.40	3.07	103.86	2.60	91.65	3.81	79.27	7.66	72.85	5.01	75.65	15.32	/
Methomyl	78.14	17.46	96.73	4.32	98.08	2.14	105.52	12.65	91.60	8.49	103.25	6.76	0.2
Monocro tophos	109.31	3.09	110.77	2.32	101.47	2.31	115.83	17.70	84.95	8.31	97.58	19.35	0.03
Myclobutanil	91.52	10.34	93.97	3.44	97.39	1.71	97.73	16.74	119.76	14.95	112.92	17.34	0.5
Novaluron	112.04	2.38	96.20	2.03	95.72	6.46	84.20	5.06	110.05	12.04	91.15	13.21	3
Omethoate	115.16	18.80	100.80	3.17	93.80	3.19	72.81	10.25	102.88	13.33	105.82	3.04	0.02
Oxamyl	82.05	5.28	84.44	4.04	99.43	7.42	109.33	10.44	84.86	8.08	97.53	6.99	/
Parathion	119.76	1.49	109.04	1.84	99.75	1.02	86.47	19.50	74.17	9.35	106.43	11.91	0.01
Parathion methyl	82.98	10.13	82.25	8.95	100.43	9.79	79.58	5.04	107.28	11.24	87.64	4.84	0.01
Penconazole	101.29	3.65	107.99	2.99	100.28	2.05	108.78	13.58	89.79	16.41	90.35	13.92	0.2
Pendimethalin	75.57	14.29	97.47	8.75	99.01	1.47	105.33	13.48	105.95	17.41	117.50	15.35	/
Permethrin	94.57	11.40	72.97	9.34	91.39	13.26	86.32	18.00	104.38	14.87	94.52	6.16	2
Phorate	98.84	8.78	102.11	9.07	89.95	6.74	84.10	4.56	78.86	4.93	79.62	5.68	0.01
Phosalone	90.90	2.78	82.11	4.24	110.62	3.31	82.67	4.15	115.34	16.02	86.26	19.37	2
Phosfolan	74.99	2.52	98.29	1.73	99.62	1.67	94.68	17.94	84.21	12.22	105.84	16.67	0.03
Phosfolan methyl	74.21	1.31	110.69	1.23	100.13	1.51	97.17	8.39	104.82	2.39	83.13	5.06	0.03
Phosmet	105.89	5.92	71.77	5.00	102.11	2.32	85.00	9.42	89.39	4.14	110.33	5.14	3
Phoxim	99.34	5.89	74.18	7.13	102.86	6.03	86.23	18.29	108.54	2.10	82.94	6.40	0.3
Picoxystrobin	93.56	2.00	106.45	1.97	101.88	1.76	91.08	15.06	106.67	14.32	105.89	15.91	/
Pirimicarb	76.85	15.20	82.11	1.59	95.79	1.98	95.39	18.42	105.34	11.26	87.16	6.79	1
Prochloraz	89.85	2.60	101.01	2.15	98.87	1.91	97.91	11.35	79.11	13.88	109.02	19.75	2
Procymidone	109.37	3.02	79.23	8.98	104.36	6.38	110.61	4.77	76.76	5.02	117.19	14.14	/
Profenofos	89.35	4.29	77.17	5.53	101.11	2.01	71.60	12.88	83.29	18.50	84.16	7.41	0.05
Propamocarb	112.08	0.87	105.45	2.04	92.56	1.66	115.54	16.49	92.49	7.77	99.75	12.69	/
Propiconazole	106.63	1.81	100.86	2.49	100.28	2.95	89.52	8.40	93.48	16.75	107.64	4.44	0.1
Pymetrozine	104.90	9.41	107.08	1.65	100.06	0.87	105.45	7.14	91.35	14.01	98.34	17.64	/
Pyraclostrobin	115.75	1.97	107.88	2.21	99.75	1.52	114.25	15.01	111.22	16.11	101.01	17.74	0.5
Pyridaben	96.91	9.77	71.46	3.12	89.13	3.19	74.83	7.04	102.32	14.02	94.41	17.54	2
Pyrimethanil	89.46	0.61	114.19	1.82	98.33	1.90	101.76	4.23	93.24	17.74	81.29	8.23	7
Spinosad	108.87	1.19	108.63	1.94	97.54	1.53	103.50	11.38	108.61	7.07	104.30	12.03	/
Spirodiclofen	104.28	5.80	77.82	7.28	102.00	1.95	78.69	15.15	72.75	14.55	84.75	15.30	0.5
Sulfotep	94.90	13.02	71.10	4.21	102.33	1.34	80.58	3.21	88.36	17.22	87.43	7.25	0.01
Taufluvalinate	98.51	12.69	94.25	6.97	89.47	10.80	90.66	14.58	108.41	6.89	75.54	13.10	/
Tebuconazole	77.85	2.31	108.93	1.09	99.82	2.21	73.63	4.01	110.13	7.39	86.26	11.03	0.3
Tebufenozide	97.98	7.93	101.29	2.61	103.52	2.05	103.22	14.93	73.66	17.06	84.97	13.80	3
Teflubenzuron	113.56	8.80	93.57	5.76	98.46	11.93	90.40	10.10	99.57	11.45	82.55	12.48	1
Thiabendazole	83.70	3.18	97.61	1.58	114.20	2.93	101.61	9.39	91.29	5.07	106.23	5.32	3
Thiacloprid	111.73	5.80	73.25	8.64	100.78	6.01	107.20	3.88	84.62	5.70	114.90	10.63	0.7
Thiamethoxam	79.31	1.43	98.96	1.84	99.74	1.01	112.38	6.89	111.93	11.53	87.82	11.37	0.3

Apple													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Thiophanate methyl	112.45	1.09	105.48	1.23	105.01	1.65	77.28	12.54	96.62	10.47	110.22	18.14	5
Tolfenpyrad	111.34	4.03	96.50	1.80	96.45	2.04	77.04	16.25	115.54	14.86	105.09	5.99	/
Tolylfluanid	90.23	8.02	94.02	3.78	94.03	4.83	74.63	16.45	96.51	3.08	74.27	9.12	5
Tralkoxydim	97.78	0.76	101.31	1.97	97.80	2.34	91.85	13.80	99.04	18.31	118.85	16.72	/
Triadimefon	80.10	1.93	109.31	2.78	96.81	1.71	70.66	13.01	71.39	14.48	99.52	7.95	1
Triadimenol	101.86	7.69	117.21	1.31	99.44	0.91	95.42	7.56	108.32	17.34	112.52	14.99	1
Triazophos	91.53	1.26	102.83	1.56	104.67	2.08	86.67	18.30	118.75	15.49	90.35	19.43	0.2
Trichlorfon	70.68	9.20	107.85	4.59	112.14	4.03	77.21	8.03	77.87	14.03	91.78	9.50	0.2
Tricyclazole	102.94	1.06	105.37	1.23	112.73	1.72	102.49	10.20	108.07	6.45	105.00	14.17	/
Trifloxystrobin	96.14	1.28	108.75	0.96	108.13	2.17	93.20	6.32	83.21	11.57	84.27	17.37	0.7
Zoxamide	102.78	4.21	73.79	4.61	104.91	2.48	114.42	10.01	88.61	11.95	95.24	10.95	/

Grape													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Acephate	97.46	12.57	101.92	1.92	91.84	2.93	110.42	5.67	82.39	7.21	79.95	9.47	0.5
Acetamiprid	106.59	0.69	85.16	0.93	110.70	0.76	90.81	13.50	101.08	10.68	117.10	6.74	2
Aldicarb	95.17	4.52	107.87	9.61	105.18	2.11	88.09	8.35	88.28	3.02	103.83	10.81	0.02
Ametryn	103.29	0.48	108.74	0.83	105.27	0.79	103.92	18.50	74.97	12.83	74.14	15.42	/
Amitraz	80.58	4.63	75.18	1.54	92.04	2.79	88.22	7.44	75.08	2.59	92.37	17.91	/
Azoxystrobin	73.12	6.20	85.08	1.56	104.91	0.50	75.21	15.23	118.63	5.61	100.23	4.59	5
Benomyl	83.71	2.12	116.16	0.74	107.91	1.14	107.65	5.68	76.48	12.46	83.44	6.61	/
Benzoximate	77.57	4.45	84.71	4.71	90.36	6.46	71.20	6.10	78.19	4.64	96.32	10.50	/
Bifenazate	83.82	2.23	113.27	2.25	118.23	1.16	98.68	15.94	82.75	8.81	115.25	13.51	0.7
Bifenthrin	98.36	6.48	117.89	6.87	108.34	5.02	88.64	9.12	113.33	12.11	71.28	10.98	/
Bitertanol	103.91	5.44	100.20	5.42	91.57	3.94	82.54	4.75	85.24	5.85	94.80	7.27	/
Boscalid	107.51	2.02	97.79	1.10	109.69	1.33	118.22	4.34	92.36	6.04	73.88	6.31	5
Bromo propylate	94.80	3.28	103.25	5.58	89.34	2.11	84.24	5.06	94.20	3.07	98.62	13.06	2
Buprofezin	87.58	7.94	85.29	0.71	103.58	1.22	101.83	6.98	92.79	5.23	104.94	13.64	1
Cadusafos	91.66	4.63	103.13	1.71	105.73	1.22	104.27	16.82	78.49	17.01	116.09	18.02	0.02
Carbaryl	94.54	1.40	90.97	0.79	107.54	0.77	100.68	12.57	84.12	18.01	76.52	5.21	/
Carbendazim	77.15	1.99	97.11	1.26	99.38	0.34	107.75	19.52	107.63	11.52	111.82	17.42	3
Carbofuran	93.67	0.64	96.69	0.98	105.69	0.62	110.45	9.20	94.38	15.57	92.56	19.02	0.02
Carbosulfan	115.20	13.33	95.84	3.51	98.18	1.36	106.96	18.93	88.75	7.58	96.02	13.60	/
Cartap	84.21	3.90	99.21	17.34	89.35	6.03	97.52	8.60	96.15	7.07	86.83	6.83	/
Chlordimeform	116.20	4.30	101.08	1.65	99.82	1.26	109.75	13.97	103.75	12.16	111.10	18.73	0.01
Chlorfenapyr	104.32	7.44	110.90	13.83	110.89	2.65	86.27	6.42	110.40	10.95	76.32	4.32	/

Grape													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Chlorfluazuron	99.43	2.77	95.80	7.56	98.74	2.40	75.34	8.85	106.94	4.95	81.96	9.07	/
Chlorpyrifos	86.98	4.30	102.26	2.60	112.87	2.16	106.10	4.33	95.71	3.31	94.54	7.39	0.5
Chlorpyrifos methyl	82.93	14.79	118.26	11.39	113.34	6.04	95.65	5.82	87.72	7.10	85.12	5.47	/
Clofentezine	93.32	4.31	90.59	9.85	71.02	1.81	109.04	13.25	86.10	5.01	71.21	15.37	2
Clothianidin	103.36	2.89	105.52	2.37	115.95	1.94	85.37	3.88	91.63	3.90	97.72	3.22	0.7
Cyfluthrin	112.28	4.26	115.90	3.39	105.72	0.27	94.90	14.37	103.52	2.58	96.42	5.76	/
Cyhalothrin	115.73	2.67	89.49	7.09	75.30	10.65	112.61	1.35	84.61	3.88	72.46	9.56	0.2
Cypermethrin	92.00	3.96	104.32	18.49	101.90	5.36	93.61	2.67	80.65	3.63	113.85	16.08	0.2
Cyprodinil	81.34	0.65	106.10	0.45	102.61	0.85	88.25	10.78	108.95	1.59	118.71	12.78	20
Cyromazine	97.95	4.42	81.73	2.52	83.48	1.87	106.30	11.80	86.44	17.45	103.82	9.64	/
Deltamethrin	100.46	11.13	79.64	3.98	93.13	5.09	110.39	4.35	103.20	4.52	98.62	5.06	0.2
Demeton	90.67	18.13	111.06	8.27	100.52	2.62	93.51	5.67	87.19	9.05	112.45	4.26	0.02
Diazinon	116.78	1.20	106.01	1.23	106.28	1.50	74.81	0.10	103.81	15.68	119.42	17.14	/
Dichlorvos	92.76	2.04	98.49	3.89	100.22	2.88	91.04	12.84	86.37	15.75	89.55	2.11	0.2
Diethofencarb	98.16	1.24	99.74	3.01	105.71	1.28	107.09	8.61	116.50	8.99	102.66	4.64	/
Difenoconazole	75.61	0.82	106.93	1.60	115.54	1.24	97.59	15.77	94.24	4.83	75.52	17.45	0.5
Diflubenzuron	92.87	6.64	113.27	1.97	108.90	2.14	112.89	5.35	98.26	5.94	104.03	4.27	/
Dimethoate	115.00	2.29	114.96	1.47	105.98	0.63	97.58	6.26	93.41	1.95	92.34	13.68	0.02
Dimethomorph	89.33	5.30	76.16	4.15	98.99	1.16	90.72	5.82	110.82	7.22	110.63	10.35	5
Diniconazole	75.18	3.52	111.33	0.95	104.30	1.55	115.02	5.32	97.54	4.35	72.47	6.67	0.2
Dinotefuran	89.75	3.24	103.86	2.46	100.92	0.81	87.86	14.60	105.39	14.96	97.83	3.23	0.9
Enestroburin	105.33	4.89	88.89	1.41	105.92	0.45	101.83	8.06	109.37	7.65	108.34	6.05	/
Epoxiconazole	76.38	5.96	92.35	2.55	98.17	1.69	74.14	16.04	113.57	14.22	108.20	12.95	0.5
Ethoprophos	104.30	1.99	115.28	1.07	104.09	1.54	88.71	9.58	77.63	5.99	112.76	9.45	0.02
Etofenprox	110.35	4.98	86.85	2.85	83.13	1.42	119.01	2.84	104.36	7.04	88.72	8.48	4
Etoxazole	92.56	1.16	101.37	1.13	105.88	0.83	118.59	18.86	93.23	9.07	103.08	11.62	0.5
Fenarimol	99.60	2.11	102.53	1.05	104.17	1.25	109.70	8.88	74.60	16.81	92.94	15.78	0.3
Fenbuconazole	75.02	2.23	94.20	14.29	78.32	10.66	81.48	5.21	108.78	9.20	93.84	3.58	1
Fenitrothion	90.54	15.73	77.64	3.81	91.03	0.35	86.37	4.39	86.27	7.54	106.67	6.25	0.5
Fenpropathrin	94.68	4.70	116.90	11.13	79.70	9.18	99.72	18.06	89.50	12.02	116.42	16.37	5
Fenpyroximate	100.12	7.94	80.43	2.04	97.08	1.60	92.68	5.23	99.21	9.62	75.17	95.26	0.1
Fenthion	88.62	10.37	113.00	9.16	102.98	4.84	90.68	5.01	92.86	5.63	94.52	7.73	0.05
Fenvalerate	84.13	7.34	113.79	8.17	79.19	2.48	114.65	6.04	84.53	15.87	83.47	6.08	/
Fipronil	101.66	5.90	76.39	3.56	94.22	10.53	103.64	6.32	89.46	4.68	90.65	10.81	0.02
Flucythrinate	70.28	4.36	75.73	6.33	76.74	8.13	97.23	11.35	80.44	9.59	70.36	5.87	/
Flufenoxuron	80.62	2.69	112.13	1.30	114.33	1.18	99.25	5.72	102.46	4.80	96.33	10.42	/
Flusilazole	96.59	1.21	113.02	0.76	103.37	0.98	100.05	9.26	80.21	6.64	83.32	11.35	0.5
Flutolanil	79.57	4.91	93.41	1.75	93.70	1.27	94.47	3.89	104.39	3.81	99.74	15.13	/
Flutriafol	100.48	1.45	101.87	1.37	106.04	1.01	97.25	12.97	93.86	18.70	81.22	11.73	0.8
Forchlor fenuron	103.56	3.24	99.03	11.10	104.56	0.97	86.46	3.30	106.26	2.37	79.49	9.50	0.05
Haloxyfop methyl	90.33	4.75	81.09	2.78	108.31	1.33	81.60	5.07	94.42	4.91	112.77	17.04	0.02

Grape													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Hexaconazole	94.12	6.28	104.85	1.59	107.83	0.61	82.85	13.46	72.42	16.33	113.85	12.72	0.1
Hexythiazox	100.66	3.25	77.17	5.32	99.96	1.44	113.05	5.44	104.21	3.76	96.03	8.36	1
Imazalil	102.21	1.03	114.41	0.56	101.28	3.40	98.84	7.29	77.46	3.89	103.74	14.79	5
Imidacloprid	98.97	2.44	104.35	1.74	110.78	1.15	82.14	7.63	84.55	12.75	98.60	10.42	1
Isazophos	112.89	4.98	117.55	1.12	108.85	1.51	85.34	3.86	74.56	11.31	72.90	13.49	0.01
Isocarbophos	97.34	9.76	116.65	5.35	93.64	5.57	107.80	6.41	110.74	3.25	95.58	11.85	0.05
Isofenphos methyl	103.03	5.24	113.57	4.61	113.90	2.41	82.14	5.25	89.28	3.06	104.29	15.90	0.01
Isoprocarb	91.85	1.18	95.69	0.95	110.49	1.45	90.40	18.39	90.51	10.63	73.59	2.52	/
Kresoxim methyl	90.77	9.90	78.34	4.26	103.68	1.60	103.62	5.56	79.71	12.67	100.44	8.43	1
Malathion	113.31	2.29	106.98	1.67	103.13	1.02	82.48	8.38	92.57	4.97	92.11	110.44	8
Mercapto dimethur	86.57	1.03	105.06	1.26	107.89	0.61	106.60	4.11	112.88	15.65	82.49	2.04	/
Metalaxyl	81.54	1.54	94.36	0.89	101.62	0.48	106.36	9.69	89.43	2.54	96.61	11.93	1
Methami dophos	107.95	4.20	109.64	5.91	103.45	2.09	102.35	8.63	103.22	4.68	83.13	7.70	0.05
Methidathion	114.46	7.79	93.09	0.50	110.57	1.00	96.25	5.97	76.42	14.22	103.58	14.50	0.05
Methiocarb-													
sulfoxide	101.65	1.01	112.46	1.34	104.52	1.02	94.49	4.71	87.45	4.76	84.25	9.74	/
Methiocarb-													
sulfone	96.94	2.68	103.33	1.13	104.10	0.87	84.62	6.00	95.14	2.66	92.20	7.51	/
Methomyl	102.86	9.78	96.70	3.34	97.77	2.37	101.54	9.95	101.67	11.43	104.66	15.56	0.2
Monocro tophos	112.46	1.56	109.31	1.28	104.07	0.76	108.54	17.56	109.96	13.42	116.25	19.79	0.03
Myclobutanil	97.67	5.20	96.57	2.32	103.37	1.53	106.49	18.13	118.16	19.11	110.58	15.38	1
Novaluron	100.33	1.09	76.24	3.94	96.40	3.53	96.14	4.56	78.21	1.26	110.17	4.61	/
Omethoate	81.44	11.40	99.63	5.28	97.28	3.53	77.89	15.96	73.56	3.60	97.64	16.69	0.02
Oxamyl	91.94	8.00	101.67	8.41	114.88	7.22	108.93	14.24	77.84	4.38	110.98	10.59	/
Parathion	93.40	1.70	74.84	1.70	108.97	0.86	94.22	5.44	95.52	14.06	94.57	17.92	0.01
Parathion methyl	92.42	5.70	92.47	2.31	108.57	2.10	77.20	6.74	103.53	4.35	116.84	7.38	0.02
Penconazole	107.24	2.75	104.66	3.03	103.71	0.92	91.97	13.83	113.14	6.83	103.58	10.78	0.2
Pendimethalin	100.00	17.51	94.65	5.18	106.56	2.28	91.51	11.36	113.05	18.67	108.25	17.25	/
Permethrin	93.42	5.09	97.60	5.65	117.14	16.30	99.02	13.15	93.54	10.96	76.81	5.93	2
Phorate	91.12	19.43	113.69	5.39	101.28	5.17	92.79	5.08	104.12	7.29	96.73	8.58	0.01
Phosalone	87.99	3.24	83.47	5.55	116.78	3.89	104.55	13.69	104.82	10.59	108.57	3.15	/
Phosfolan	77.27	1.90	97.57	1.87	102.79	1.21	76.56	16.33	86.57	10.37	85.70	15.26	0.03
Phosfola methyl	109.80	1.21	112.22	1.37	103.63	0.65	103.71	4.60	107.56	3.94	99.14	4.41	0.03
Phosmet	95.88	3.21	81.00	3.72	110.98	2.85	119.61	8.97	86.22	5.24	72.41	2.25	10
Phoxim	88.34	4.35	74.90	6.14	114.74	1.81	86.75	13.77	75.70	11.95	74.26	14.66	0.05
Picoxystrobin	96.30	0.81	106.39	1.04	106.57	1.01	100.10	19.49	110.44	13.04	89.18	4.34	1
Pirimicarb	104.41	4.43	87.88	1.40	101.05	0.95	90.24	4.38	89.41	2.29	112.74	11.12	1

Grape													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Prochloraz	90.54	2.88	101.16	1.28	103.50	0.71	96.69	15.13	115.82	13.71	117.60	8.55	2
Procymidone	101.45	7.23	89.98	2.44	106.98	5.05	88.28	5.49	72.13	14.14	112.23	14.25	5
Profenofos	81.37	13.39	84.80	1.80	107.79	1.13	73.11	9.04	113.33	4.76	111.37	13.91	/
Propamocarb	97.32	1.22	105.89	2.00	95.03	0.98	112.78	15.09	108.58	15.72	109.26	2.39	2
Propiconazole	84.57	12.27	119.65	2.46	105.52	1.93	81.93	9.69	94.75	4.37	108.14	9.52	/
Pymetrozine	83.23	4.45	107.43	1.98	103.68	1.59	98.43	6.58	96.36	2.51	95.48	4.29	/
Pyraclostrobin	99.67	0.77	112.21	1.30	117.78	0.92	108.70	14.26	114.62	3.82	81.91	3.25	2
Pyridaben	100.06	7.15	73.88	6.53	91.83	2.01	74.82	4.82	87.58	5.79	76.27	5.14	/
Pyrimethanil	84.89	6.69	115.89	0.79	101.61	0.75	98.13	18.99	92.31	3.77	98.76	8.59	4
Spinosad	91.79	1.47	108.73	1.01	101.95	0.84	81.54	9.09	100.06	12.74	110.28	5.94	/
Spirodiclofen	89.22	4.44	97.67	3.53	106.26	2.44	107.17	4.34	92.23	3.86	104.17	9.26	0.2
Sulfotep	110.33	3.25	74.51	3.85	110.74	1.68	75.16	8.50	83.28	6.81	112.63	11.31	0.01
Taufluvalinate	90.17	7.76	71.44	9.04	102.38	7.48	88.27	11.73	102.30	4.15	90.18	4.78	/
Tebuconazole	91.40	2.12	89.34	0.44	107.84	1.01	93.11	5.47	76.12	5.88	98.71	6.27	2
Tebufenozide	99.16	8.79	103.04	2.47	105.19	1.11	113.35	13.88	109.44	18.62	109.70	18.82	2
Teflubenzuron	103.43	4.80	79.94	3.87	90.22	8.20	72.15	12.68	88.50	11.31	92.14	14.34	/
Thiabendazole	104.89	4.38	76.20	7.28	92.35	4.49	93.55	8.07	103.75	11.23	89.18	5.37	5
Thiacloprid	85.30	5.07	98.60	5.76	77.29	4.77	84.24	4.85	86.61	18.42	77.49	4.89	1
Thiamethoxam	92.04	1.71	74.70	1.64	108.90	0.81	110.24	5.60	82.48	8.63	103.66	14.57	/
Thiophanate methyl	79.68	0.90	108.59	1.62	111.21	1.81	95.47	14.38	84.60	12.33	96.63	4.60	3
Tolfenpyrad	110.32	2.51	95.69	1.01	99.51	0.79	75.49	15.99	94.78	7.10	75.36	9.04	/
Tolylfluanid	90.34	6.67	90.33	4.99	104.66	1.25	89.54	7.99	95.90	5.73	96.40	6.96	3
Tralkoxydim	99.31	1.82	100.13	1.26	101.28	1.08	106.41	18.97	103.18	19.52	119.66	10.03	/
Triadimefon	95.73	1.74	107.01	2.26	99.81	0.66	105.32	5.66	110.10	12.75	113.33	12.89	0.3
Triadimenol	108.98	7.37	113.06	2.31	105.00	2.65	80.62	5.08	93.30	13.29	89.99	3.57	0.3
Triazophos	103.57	3.68	113.05	0.90	108.84	1.50	98.17	14.85	76.29	19.17	112.57	13.48	/
Trichlorfon	79.51	7.81	118.91	3.88	103.23	1.90	118.74	7.03	92.56	12.11	96.03	5.16	0.2
Tricyclazole	108.31	0.85	96.80	1.02	116.94	0.61	75.39	17.45	98.43	15.38	108.12	7.87	/
Trifloxystrobin	110.98	10.16	82.58	1.01	104.94	0.98	70.88	9.94	93.64	18.30	90.40	8.06	3
Zoxamide	95.34	3.21	73.77	3.64	110.15	1.23	111.37	3.56	93.11	9.24	71.20	15.65	5

Tomato													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Acephate	112.19	2.12	102.77	4.70	92.94	1.95	91.57	17.97	93.22	15.86	93.60	17.00	1
Acetamiprid	96.56	5.37	100.69	2.72	107.37	1.24	92.74	19.65	75.11	14.44	98.62	6.54	1
Aldicarb	94.74	2.01	112.68	7.77	103.02	3.04	85.04	7.40	86.41	12.94	91.24	5.67	0.03
Ametryn	97.01	0.79	100.39	11.32	89.80	1.77	109.52	12.66	92.76	5.59	84.89	6.54	/

Tomato													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Amitraz	88.75	4.93	74.87	4.29	109.04	1.06	99.77	7.70	117.89	7.89	105.31	13.93	0.5
Azoxystrobin	97.57	10.23	85.49	6.61	109.51	1.23	92.23	6.55	105.34	5.64	110.42	14.69	3
Benomyl	104.34	4.15	98.73	7.32	92.25	0.50	109.75	10.45	106.31	13.52	86.41	14.42	/
Benzoximate	71.35	14.31	109.91	4.52	113.89	3.61	73.52	7.69	79.89	4.58	74.51	7.47	/
Bifenazate	90.85	6.46	112.71	17.86	115.97	1.17	117.19	18.42	86.47	13.59	115.16	18.33	0.5
Bifenthrin	92.13	7.04	95.05	10.27	88.75	9.36	75.67	19.24	105.44	9.72	94.64	12.53	/
Bitertanol	112.28	10.96	107.12	2.41	88.19	1.87	104.39	10.35	103.14	14.46	84.35	11.58	3
Boscalid	74.40	2.18	104.95	14.70	102.05	1.40	84.21	13.32	71.62	9.65	93.14	4.71	2
Bromopropylate	103.08	8.58	104.92	9.42	95.26	2.48	92.63	12.18	92.52	10.89	82.37	4.81	/
Buprofezin	102.44	5.06	93.11	5.37	111.93	1.36	95.62	6.45	98.08	6.65	109.59	19.48	2
Cadusafos	92.19	4.50	100.10	9.76	108.49	0.88	99.96	18.76	87.59	9.60	70.43	17.25	0.02
Carbaryl	118.21	1.59	119.51	8.54	116.36	0.61	92.55	19.48	94.47	11.23	79.63	8.37	1
Carbendazim	70.97	3.40	84.65	3.20	101.29	1.97	85.56	10.11	112.49	14.58	81.06	18.43	3
Carbofuran	90.75	1.43	110.91	2.98	112.95	0.97	92.53	14.25	84.81	4.95	110.94	16.61	0.02
Carbosulfan	116.70	11.58	96.74	10.13	103.45	1.51	96.30	13.08	76.18	12.27	108.57	4.66	0.1
Cartap	90.22	12.40	105.98	9.57	90.24	5.92	86.06	16.01	82.23	6.14	100.88	9.45	/
Chlordimeform	110.17	5.03	104.45	17.04	87.36	1.45	115.81	18.44	117.07	8.20	104.38	13.41	0.01
Chlorfenapyr	108.24	4.72	108.74	7.53	110.55	1.64	82.15	13.47	79.25	9.31	70.67	16.24	/
Chlorfluazuron	90.21	3.20	99.86	5.62	107.99	2.40	102.62	4.71	106.57	13.09	81.61	6.01	/
Chlorpyrifos	89.81	4.96	83.14	1.54	83.33	1.13	83.64	18.78	84.53	8.47	103.33	6.29	0.5
Chlorpyrifos methyl	109.24	10.29	105.89	12.87	118.00	3.05	75.18	3.66	96.23	8.62	102.53	5.22	/
Clofentezine	89.21	3.09	86.30	2.34	90.16	1.40	99.74	8.97	112.55	4.46	73.31	9.06	0.5
Clothianidin	114.10	1.91	82.04	3.06	116.39	1.99	87.38	5.26	110.16	6.94	97.46	16.70	1
Cyfluthrin	107.20	4.29	90.12	9.45	93.89	3.16	73.62	6.83	98.52	14.28	93.52	13.21	0.2
Cyhalothrin	74.71	5.13	114.28	8.76	83.09	5.62	97.25	8.44	82.75	6.74	109.52	9.07	0.2
Cypermethrin	110.42	4.90	93.53	6.14	111.41	5.22	82.06	5.24	73.10	14.38	76.50	10.91	0.5
Cyprodinil	118.80	0.75	88.16	13.75	88.61	1.30	72.14	11.83	99.53	7.76	93.23	5.75	0.5
Cyromazine	71.91	6.73	71.29	14.40	80.83	1.86	88.20	11.72	75.04	4.86	105.11	18.22	/
Deltamethrin	83.52	4.95	79.03	7.12	85.68	4.42	76.61	6.09	93.64	19.93	92.41	12.22	0.2
Demeton	110.98	17.07	98.31	18.21	103.35	2.53	83.28	4.62	104.26	2.89	105.16	5.28	0.02
Diazinon	112.87	2.53	101.14	10.75	105.27	1.37	94.23	9.15	75.14	4.01	99.42	4.00	0.5
Dichlorvos	104.37	3.23	100.16	2.40	110.89	2.89	94.64	2.95	96.53	12.22	117.38	16.39	0.2
Diethofencarb	80.66	1.19	84.44	7.70	117.05	1.17	85.05	17.76	97.61	7.94	108.59	13.08	1
Difenoconazole	112.76	11.28	72.36	10.90	89.41	1.21	105.42	7.04	91.42	16.96	112.53	13.51	0.5
Diflubenzuron	95.20	13.27	112.01	7.98	111.06	1.85	75.21	14.24	86.25	13.94	94.27	14.59	/
Dimethoate	110.25	3.46	101.63	4.31	113.77	1.64	88.49	16.20	83.22	4.40	113.34	11.21	0.5
Dimethomorph	78.12	5.33	109.32	15.16	91.56	1.75	90.13	17.09	93.84	19.63	107.81	14.60	1
Diniconazole	83.70	5.52	105.80	15.27	76.12	1.37	110.48	12.28	96.60	8.05	101.30	10.40	/
Dinotefuran	70.04	5.19	95.33	18.65	111.26	1.55	86.77	12.70	115.48	12.14	113.93	19.59	0.5
Enestroburin	99.21	3.52	77.39	10.39	113.13	1.60	108.07	2.49	74.56	12.31	102.45	8.28	/
Epoxiconazole	96.28	4.63	81.24	13.79	88.39	1.27	97.45	12.60	72.16	15.88	119.24	12.88	/

Tomato													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Ethoprophos	78.50	1.41	94.13	5.24	104.35	0.81	74.44	14.54	77.64	12.63	95.83	5.38	0.02
Etofenprox	82.67	8.23	72.46	3.82	97.00	2.15	85.73	4.21	94.78	5.22	75.37	8.72	/
Etoxazole	95.92	2.97	86.37	3.54	92.05	1.08	73.21	8.36	89.49	8.82	118.30	14.98	/
Fenarimol	104.61	1.68	110.36	12.09	75.82	1.16	76.57	16.73	74.88	7.41	110.07	9.27	/
Fenbuconazole	103.95	8.21	92.87	13.83	107.37	6.41	86.52	11.03	75.35	10.72	71.40	7.83	/
Fenitrothion	72.57	8.91	71.42	2.76	86.90	2.19	95.15	18.43	89.24	19.10	105.72	4.82	0.5
Fenpropathrin	85.77	9.19	95.03	7.35	74.52	6.59	102.98	8.06	105.61	13.75	82.64	12.47	1
Fenpyroximate	88.57	3.31	90.03	2.54	95.15	1.10	101.24	8.81	96.44	14.02	92.50	11.32	0.2
Fenthion	105.70	5.60	72.80	8.58	96.81	5.47	75.30	10.48	88.41	18.35	94.39	2.03	0.05
Fenvalerate	102.02	3.63	105.51	8.45	78.15	7.98	78.47	13.50	112.78	8.61	94.18	8.19	0.2
Fipronil	95.04	15.13	94.01	4.21	96.25	6.37	99.05	15.54	95.36	8.98	72.53	3.04	0.02
Flucythrinate	86.35	5.72	96.23	6.91	74.86	4.25	92.92	18.05	96.73	15.28	108.04	18.71	0.2
Flufenoxuron	99.82	2.54	113.46	4.03	70.87	2.06	71.65	15.02	105.29	8.42	92.63	9.84	/
Flusilazole	72.64	2.70	105.87	9.04	88.36	1.15	84.35	16.92	76.69	3.76	117.19	8.40	0.2
Flutolanil	94.45	4.40	95.66	18.35	104.44	1.60	80.17	12.36	75.40	18.15	77.55	2.87	/
Flutriafol	107.39	1.26	118.60	11.02	108.15	1.14	75.86	13.12	91.75	6.36	108.94	13.24	/
Forchlor fenuron	100.94	2.40	90.03	6.07	111.77	1.55	95.32	9.89	95.17	6.55	84.45	5.52	/
Haloxyfop methyl	100.31	3.09	81.27	11.77	115.16	1.59	73.21	14.92	80.42	14.03	99.30	15.09	/
Hexaconazole	104.34	7.30	104.27	8.79	102.02	1.42	74.60	19.50	85.29	16.27	118.36	10.15	0.5
Hexythiazox	104.21	4.70	88.57	5.35	111.19	1.13	87.60	18.45	107.17	7.71	90.51	6.23	0.1
Imazalil	75.33	1.03	107.64	11.35	93.59	1.43	100.21	17.16	77.52	10.39	104.29	15.01	0.5
Imidacloprid	111.89	1.98	110.83	3.85	111.78	1.72	109.77	8.21	93.36	4.52	94.04	5.38	1
Isazophos	104.46	1.51	91.13	12.40	75.58	1.51	86.68	18.56	72.27	7.80	107.20	8.62	0.01
Isocarbophos	106.22	4.50	105.43	15.05	88.91	10.59	83.32	19.17	105.41	5.47	116.36	7.40	0.05
Isofenphos methyl	79.58	3.72	93.79	9.31	100.23	2.05	94.30	17.68	85.46	10.95	79.40	4.31	0.01
Isoprocarb	108.79	0.93	108.45	15.35	115.42	0.88	82.91	8.25	93.28	4.45	97.39	9.98	/
Kresoxim methyl	102.66	1.02	98.50	8.44	109.55	1.70	76.87	5.17	91.00	12.64	85.24	3.56	1
Malathion	82.42	2.47	116.29	10.87	116.66	1.72	71.76	4.89	101.27	13.05	71.46	6.26	0.5
Mercaptodi methur	94.68	1.10	111.44	10.99	101.90	1.29	102.30	6.70	119.66	1.32	77.71	9.00	/
Metalaxyl	76.09	2.32	91.22	9.81	94.51	2.10	75.31	6.65	79.54	8.08	94.61	9.82	0.5
Methami dophos	109.01	16.81	111.45	6.40	91.46	11.52	80.76	3.97	72.17	4.29	96.32	10.72	0.05
Methidathion	101.67	1.13	74.53	14.73	103.85	0.99	117.58	12.50	110.43	12.83	112.30	8.25	0.05
Methiocarb-sulfoxide	76.85	1.01	90.29	3.99	97.09	1.37	71.81	12.96	86.21	18.62	81.14	6.38	/
Methiocarb-sulfone	92.70	5.59	91.94	3.15	73.12	11.13	112.35	10.55	94.67	7.00	96.53	10.44	/
Methomyl	75.38	4.18	97.56	5.50	99.75	2.16	102.24	13.60	96.60	15.06	110.27	5.25	0.2
Monocro ophos	114.10	0.89	99.76	2.43	107.83	1.65	98.32	6.68	91.42	15.70	75.39	10.09	0.03

Tomato													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Myclobutanil	101.05	4.73	96.09	3.35	103.06	1.40	75.88	17.52	82.40	10.98	73.64	18.60	1
Novaluron	115.25	3.68	106.05	17.07	98.27	5.17	96.59	9.24	81.71	12.28	82.27	10.48	0.02
Omethoate	103.07	11.84	95.94	11.71	99.53	2.11	110.20	11.12	95.04	9.43	90.27	15.36	0.02
Oxamyl	102.22	8.78	94.47	4.83	105.21	7.13	83.62	9.78	81.65	3.67	88.69	9.00	2
Parathion	102.60	1.70	78.99	11.94	110.66	0.86	86.15	13.97	82.50	13.61	96.63	5.51	0.01
Parathion methyl	90.34	10.59	89.76	4.69	102.84	5.36	108.07	16.33	73.17	8.28	91.34	13.06	0.02
Penconazole	113.92	4.63	104.81	3.94	102.20	0.93	73.73	16.31	83.70	13.32	112.27	10.25	0.2
Pendimethalin	89.21	10.76	112.74	8.89	109.98	1.25	74.94	3.05	110.21	12.85	87.33	4.23	/
Permethrin	84.34	1.47	72.62	14.06	79.34	19.83	89.73	19.72	110.44	8.74	93.46	9.45	1
Phorate	97.32	9.53	83.86	9.83	111.40	3.08	97.56	14.98	119.40	13.10	82.14	9.11	0.01
Phosalone	87.35	2.23	109.25	18.16	110.37	1.35	84.73	19.80	107.43	5.41	92.16	10.52	/
Phosfolan	79.70	2.44	91.29	2.49	102.47	0.94	94.45	15.32	93.63	13.96	88.92	18.59	0.03
Phosfolan methyl	72.42	0.93	102.32	9.33	106.95	1.37	98.41	9.52	109.28	9.43	102.70	4.87	0.03
Phosmet	104.20	4.09	97.67	3.56	78.53	0.38	106.56	12.45	85.60	4.52	85.71	9.86	/
Phoxim	71.42	2.23	104.41	4.11	106.89	1.67	76.32	16.71	95.90	10.55	84.25	7.17	0.05
Picoxystrobin	99.73	3.83	104.31	9.55	109.88	0.84	111.86	19.48	118.55	11.23	78.41	9.70	1
Pirimicarb	98.86	4.48	81.07	6.74	105.34	1.05	94.23	15.26	79.53	3.40	90.05	8.81	0.5
Prochloraz	98.40	4.88	98.90	5.85	103.47	1.22	104.40	18.70	91.92	18.96	72.06	12.52	/
Procymidone	103.84	4.77	77.41	16.20	104.25	5.27	89.23	7.66	99.32	9.65	99.76	7.25	2
Profenofos	81.46	7.11	110.79	13.97	117.79	1.75	88.42	10.78	84.23	12.67	81.10	8.10	10
Propamocarb	88.58	1.24	102.63	16.14	99.85	2.12	79.34	12.10	93.43	3.84	112.81	3.49	2
Propiconazole	105.07	14.99	116.79	10.59	85.15	1.14	114.39	13.39	71.37	10.03	78.00	10.66	3
Pymetrozine	105.09	10.52	105.33	12.95	109.24	2.24	85.02	10.34	86.60	12.23	93.10	12.50	/
Pyraclostrobin	119.56	2.52	106.85	8.20	107.10	1.42	95.17	6.73	70.01	17.81	96.87	5.84	1
Pyridaben	88.07	11.63	81.47	7.77	101.87	1.45	73.32	6.45	95.46	8.24	94.30	6.84	/
Pyrimethanil	97.21	0.82	93.86	5.63	71.49	1.15	90.43	17.39	100.11	6.93	88.24	8.15	1
Spinosad	74.87	1.70	94.08	17.86	75.51	1.39	85.71	7.65	93.55	14.68	100.61	14.32	/
Spirodiclofen	103.79	3.54	88.69	4.58	111.81	1.89	80.62	8.73	98.54	18.17	80.11	7.24	0.5
Sulfotep	90.32	9.21	75.82	2.38	116.62	1.15	87.57	15.76	90.40	7.33	100.50	15.23	0.01
Taufluvalinate	109.66	2.66	112.47	8.12	82.44	4.00	92.35	10.78	102.67	6.04	103.79	3.72	/
Tebuconazole	82.56	2.16	110.99	6.23	93.04	0.57	102.31	2.48	70.03	6.68	98.19	10.84	2
Tebufenozide	108.48	10.75	105.44	2.49	110.40	1.05	99.05	11.54	99.74	7.17	118.35	11.44	1
Teflubenzuron	75.73	6.06	83.49	6.29	114.18	10.98	92.20	11.44	90.31	12.04	94.55	19.70	/
Thiabendazole	90.22	9.11	83.91	6.04	90.24	7.25	72.52	9.67	99.14	7.05	107.62	10.28	/
Thiacloprid	90.49	2.85	70.97	18.52	80.37	3.97	73.89	7.34	105.14	8.08	73.23	5.04	0.5
Thiamethoxam	104.15	1.64	116.88	2.56	110.65	0.86	102.50	4.61	84.28	7.28	85.78	15.56	1
Thiophanate methyl	113.24	1.25	113.04	10.42	114.43	1.30	82.41	3.32	87.26	9.65	77.46	3.56	3
Tolfenpyrad	116.28	2.12	94.16	3.32	85.11	0.80	88.63	14.62	85.28	17.12	87.46	2.29	/
Tolylfluanid	90.22	3.01	103.50	2.94	90.15	8.26	112.85	19.88	113.32	8.23	103.19	4.29	3
Tralkoxydim	104.75	2.09	111.07	4.87	102.81	0.99	73.67	10.45	85.51	3.05	113.63	2.83	/

Tomato													
Pesticide	UPLC-Q-TOF/MS						UPLC-Q-TOF/MS						MRL (mg/kg)
	Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		Spiked concentration =5μg/kg		Spiked concentration =20μg/kg		Spiked concentration =100μg/kg		
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Triadimefon	99.66	3.08	107.84	8.37	102.02	1.16	89.57	9.08	114.99	7.33	80.31	10.10	1
Triadimenol	112.61	5.79	98.39	6.74	105.46	2.31	71.10	14.90	90.41	18.71	107.81	3.38	1
Triazophos	106.21	1.46	90.50	12.84	75.75	1.49	71.66	19.86	71.22	7.90	118.34	8.88	/
Trichlorfon	98.08	4.56	110.22	7.88	110.71	2.90	92.05	11.09	103.44	14.86	87.67	3.67	0.2
Tricyclazole	113.15	1.21	101.05	10.17	74.91	0.91	85.71	7.65	93.55	14.68	100.53	14.25	/
Trifloxystrobin	82.47	5.96	84.34	15.87	108.84	0.89	89.29	14.08	94.62	7.73	81.66	12.20	0.7
Zoxamide	100.20	2.30	73.91	3.44	116.77	0.84	95.55	15.52	87.64	16.47	103.34	8.11	2

Table 3: Results of the accuracy and precision (n =6) of two different methods obtained by the API-TOF/MS and UPLC-Q-TOF/MS for pakchoi, apple, grape and tomato

Comparison between API-TOF/MS and UPLC-Q-TOF/MS

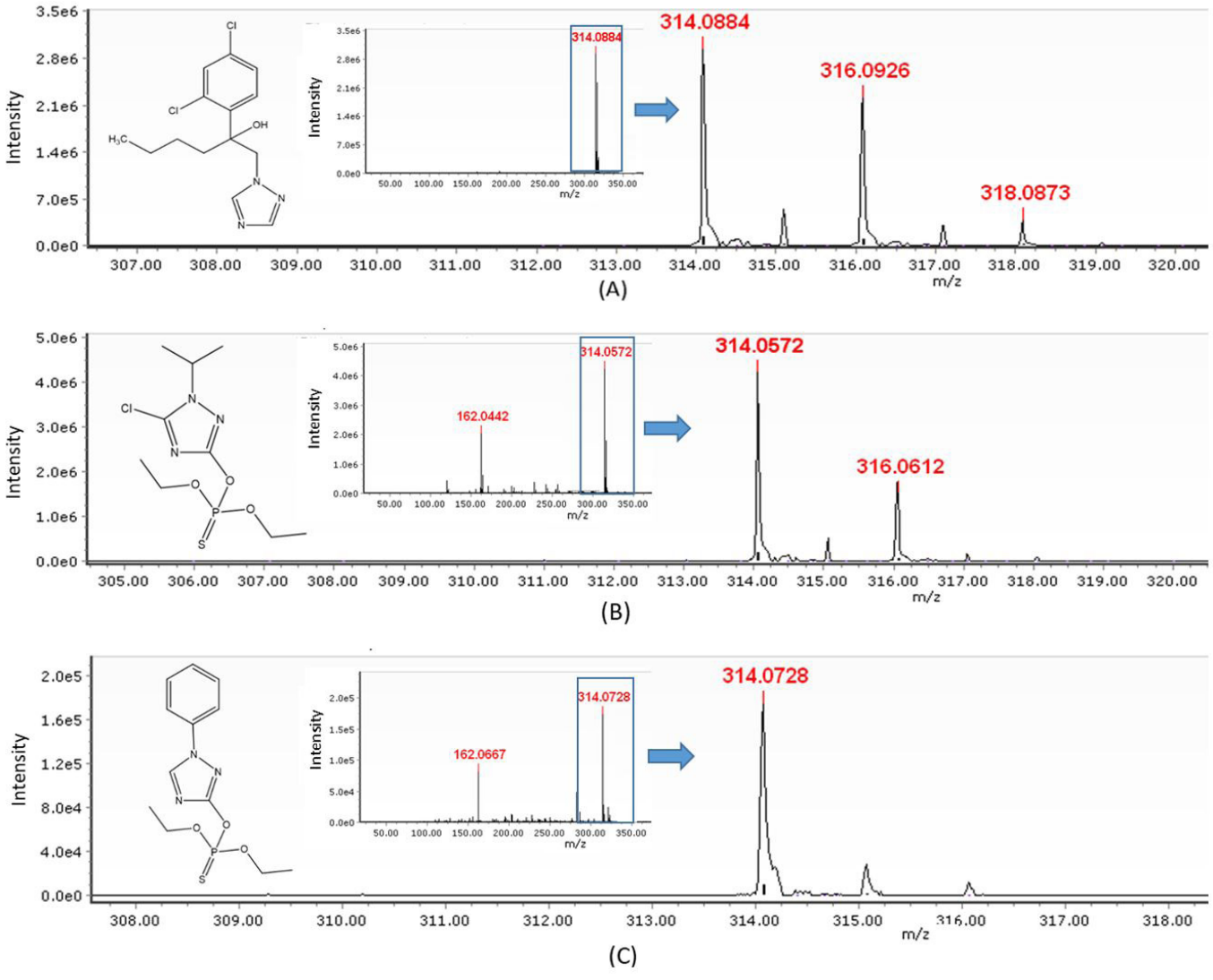

Figure 4: Mass spectrums of hexaconazole(A), isazophos(B) and triazophos(C) conducted by API-TOF/MS

It is impossible to ignore that high false positive rate always happening with rapid detection technology. Especially for direct ionization technology, lack of liquid-phase separation would make more troubles for molecular qualitative analysis. For example, it is difficult to identify pesticides with similar molecular mass. However, the characteristic peak area ratio and isotopic peaks may be considerable ways to distinguish them. Take the mass spectrums of triazophos, isazophos and hexaconazole for instance: the characteristic peaks of triazophos are 314.0728 and 162.0667; the characteristic peak of hexaconazole is 314.0884 without fragment ion peak; the characteristic peaks of isazophos are 314.0572 and 162.0442. Obviously, false positive results are likely to occur if they are used as quantitative ions. We get the information that triazophos has no Cl atom, isazophos contains one Cl atom, and hexaconazole contains two Cl atoms according to their structural formulas. Thus, the three pesticides can be distinguished according to the ratio of chlorine isotope peak height (35Cl: 37Cl= 3:1, n=1) [25]. In the actual sample detection, if there is a mass spectrum with m/z314, m/z316 and m/z318 ion peak height ratio of 9:6:1, it may be proved to be hexaconazole; the height ratio between m/z314 and m/z316 of 3:1 is isazophos, and the one without the m/z316 isotope peak is triazophos (Fig.4). However, for pesticides which couldn't be distinguished by isotopic peaks such as isocarbophos and isofenphosmethyl, the false positive results may be disappointing. While the same case could be avoided by the different chromatographic retention time for pesticides with similar molecular mass in UPLC-Q-TOF/MS (Figure 5).

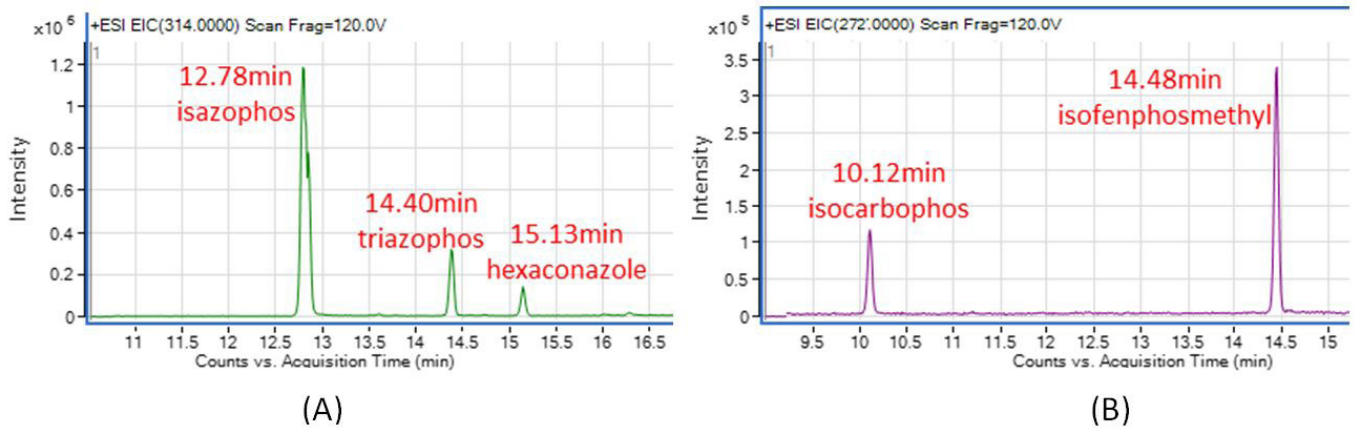

Figure 5: Extracted ion chromatograms (EIC) of isazophos, triazophos and hexaconazole (A) and isocarbophos and isofenphosmethyl (B) conducted by UPLC-Q-TOF/MS

Pesticides types	API-TOF/MS		UPLC-Q-TOF/MS	
	Number of pesticides detected vs total (proportion%)	Number of detected sample batches (proportion%)	Number of pesticides detected vs total (proportion%)	Number of detection sample batches (proportion%)
Carbamate	8/17(47.06)	26(22.03)	4/17(23.53)	47(30.32)
Heterocycle	8/34(23.53)	21(17.80)	15/34(44.12)	27(17.42)
Methoxy acrylate	1/6(16.67)	1(0.85)	3/6(50.00)	17(10.97)
Pyrethroid	4/11(36.36)	18(15.25)	0/11(0)	0(0)
Organophosphorus	5/31(16.13)	9(7.63)	3/31(9.68)	9(5.81)
Amide	2/8(25.00)	4(3.39)	2/8(25.00)	10(6.45)
Nicotine	5/6(83.33)	37(31.36)	5/6(83.33)	45(29.03)
Organochlorine	2/2(100.00)	2(1.69)	0/2(0)	0(0)
Benzoylurea	0/6(0)	0(0)	0/6(0)	0(0)
Amidine	0/2(0)	0(0)	0/2(0)	0(0)
Organosulfur	0/1(0)	0(0)	0/1(0)	0(0)
Others	0/4(0)	0(0)	0/4(0)	0(0)
Total	35/128(27.43)	118(100)	32/128(25.00)	155(100)

Table 4: Detection rate of different types of pesticides for API-TOF/MS and UPLC-Q-TOF/MS

Comparing with the occurrence of false positive rate, high false negative rate is unexpected evermore. Therefore, it is the most important to evaluate the detection rate between established new method and conventional method. A promising result demonstrated in 381 batches of testing samples (fruits and vegetables), the pesticide residue detection rates of API-TOF/MS and UPLC-Q-TOF/MS were 37.11% (118 batches detected) and 40.68% (155 batches detected), respectively. The detection rates of different types of pesticides were shown in Table 4. The results of Kappa test showed that the Kappa value was 0.569 with significance $p<0.05$, which indicated that the consistency was strong (Table 5). In addition, we found that the detection rate of methoxy acrylate pesticides by API-TOF/MS was lower than that of UPLC-Q-TOF/MS on the grounds that compared to ESI, API is suitable for the detection of medium-polarity, volatile small molecule compounds. While for the pyrethroid pesticides, the false positive results were higher API-TOF/MS mainly due to its thermal instability. Most of the quantification transition for the pyrethroid pesticides were fragment ions, which may be confusing by some pesticides with low molecular weight. Results in Table 2 showed that the LODs (0.9μg/L~5μg/L) and LOQs (2.6μg/L~15μg/L) of the API-TOF/MS method were relatively higher, resulting in a lower detection rate of pesticide residues than the UPLC-Q-TOF/MS method which had higher detection sensitivity (LODs, 0.1μg/L~2.4μg/L; LOQs, 0.3μg/L~8.1μg/L). Usually, the average time spent to finish the entire off-line UPLC-Q-TOF/MS process was more than 30 minutes. It only took 3–5 min to complete the same detection by using API-TOF/MS.

UPLC-Q-TOF/MS * API-TOF/MS Crosstabulation					
			API-TOF/MS		Total
			Unqualified number	Qualified number	
UPLC-Q-TOF/MS	Unqualified number	Count	10	7	17
		% within UPLC-Q-TOF/MS	58.82	41.18	100
		% within API-TOF/MS	58.82	1.92	4.50
	Qualified number	Count	7	357	364
		% within UPLC-Q-TOF/MS	1.92	98.08	100
		% within API-TOF/MS	41.18	98.08	95.50
Total		Count	17	364	381
		% within UPLC-Q-TOF/MS	4.46	95.54	100
		% within API-TOF/MS	100	100	100
Symmetric Measures					
		Value	Asymp. Std. Error[a]	Approx. T[b]	Approx. Siq.
Measure of Agreement	Kappa	**0.569004525**	0.103616528	11.10652524	0.000
N of Valid Cases		**381**			

[a].Not assuming the null hypothesis. b. Using the asymptotic standard error assuming the null hypothesis.

Table 5: The Kappa test results of API-TOF/MS and UPLC-Q-TOF/MS

Conclusions

API-MS based on LTP is rapidly developing into a popular technology for on-site sample analysis. In this study, a rapid and sensitive API-TOF/MS method was developed to analyze pesticide residues in fruits and vegetables. Initially instrumental parameters were optimized, and the linearity, sensitivity, accuracy and precision of the method were investigated. The proposed method was found to be simple with reduced analysis time, cost and suitability for pesticide monitoring. Further, the applicability of this method was demonstrated through detection of fruits and vegetables from the market. In terms of detection sensitivity, API-TOF/MS was slightly inferior compared to UPLC-Q-TOF/MS due to its higher LODs. What's more, considering the identification of pesticides with similar molecular mass, the establishment of a characteristic fragment database of pesticides to avoid the false positive results may be the developing direction.

Declaration of Competing Interest

The authors have declared no conflict of interest.

Acknowledgements

This work was supported by the National Science and Technology Major Projects of Food Safety Key Technology "Research and development of intelligent on-site rapid detection technology and related products for chemical pollutants in food" (Project No. 2018YFC1602800). We are sincerely grateful to Guangzhou Hexin Instrument Co., Ltd for their new product TAPI-TOF 1000.

Author Contributions

Xuemei Wang carried out the the experiment and wrote the manuscript. Shanshan Sun contributed to the research ideas and the article edition,funding acquisition. Jin Cao contributed to the article review and supervision. Above authors discussed results and approved the final manuscript. JiaoYi Luo and Yi Hong gave comprehensive equipment technique support and guidance.

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