APPLICATION NOTE 65609

A sensitive and robust analytical solution for pesticide residues analysis in apple using GC-(AEI)-MS/MS

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Goal

The objective of this study is to develop an analytical solution for trace-level quantitation of 211 pesticides in apple using gas chromatography coupled to triple quadrupole mass spectrometry. The optimized method was validated following EU SANTE/11813/2017 guidelines, and evaluated for maximum residue levels (MRLs) compliance with the Food Safety and Standards Authority of India (FSSAI) and the European Commission (EC).

Introduction

Apple is a popular edible fruit in which all parts, including the skin, are suitable for human consumption. Apples are a commodity in high demand in the global market, hence billions of tons are produced annually. India is the fifth-largest producer of apples in the world[1]. Cultivating apples in monocultures comes with risks as apple trees are susceptible to several fungal and bacterial diseases and insect pests. In order to reduce these risks, many commercial orchards use agrochemicals to maintain high fruit quality, tree health, and high yields. Currently, 288 chemicals are registered under the Central Insecticide Board and Registration Committee (CIBRC) of India[2].

The use of agrochemicals inevitably could result in the occurrence of pesticide residues in apples. Therefore, it is necessary to have robust methods that provide accurate and precise results to facilitate effective monitoring of pesticides residue in apples and to ensure compliance with legislative MRLs. The EC and FSSAI have set MRLs in apple; the lowest MRL is 0.01 mg/kg[3,4].

The aim of this work was to develop and validate a multi-residue analytical method for monitoring pesticides residue in apples by use of the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) sample preparation method followed by GC-MS analysis using the Thermo Scientific™ TSQ™ 9000 triple quadrupole GC-MS/MS system equipped with the advance electron ionization source (AEI)[5].
Data acquisition and processing were carried out using Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2. The optimized method was validated as single laboratory validation approach. These validation parameters have been verified as per SANTE/11813/2017 guidelines[6].

Experimental

Chemicals, apparatus, and consumables

- Acetonitrile, Optima™ LC/MS Grade, Fisher Scientific™ (P/N A955-4)
- Acetic acid glacial (certified ACS), Fisher Scientific™ (P/N A38S-500)
- GC-Multiresidue Pesticide Kit (Restek, Cat.# 32562)
- Analytical balance (ACZET, CY2202, San Diego, CA) and precision balance (ACZET, CY205C, San Diego, CA)
- Vortex mixer (Thermo Scientific™, P/N 88880017TS)
- Refrigerated centrifuge (Thermo Scientific™ Sorvall™ ST8 ventilated benchtop centrifuge)
- Variable volume micropipettes (Thermo Scientific)
- QuEChERS Salts (2007.01) Mylar Pouch 6 g Magnesium Sulfate (Anhydrous), 1.5 g sodium acetate (Thermo Scientific™, P/N 60105-341)
- 150 mg anhydrous magnesium sulfate, 50 mg primary secondary amine (Thermo Scientific™, P/N 60105-203)

GC-MS/MS analysis

A Thermo Scientific™ TRACE™ 1310 gas chromatograph was coupled to a TSQ 9000 triple quadrupole mass spectrometer configured with advanced electron ionization (AEI) using electron ionization. The GC-MS/MS conditions used for pesticide residues analysis are given below in Table 1.

Table 1. GC-MS/MS instrument conditions

Gas chromatography	
Instrumentation	TRACE 1310 GC with Thermo Scientific™ TriPlus™ RSH autosampler
Column	Thermo Scientific™ TraceGOLD™ TG-5SIL MS W/5 m safeguard, 30 m x 0.25 mm ID x 0.25 µm (P/N 26096-1425)
Injector	Split/splitless (SSL)
Liner	SSL splitless liner, single taper, deactivated (P/N 453A1925UI)
Injector mode	Splitless
Splitless time	2 min
Injection volume	1.0 µL
Injector temp.	250 °C
Column flow	1.20 mL/min
Carrier gas and purity	Helium (99.999%)
Purge flow	5.00 mL/min
Split flow	50.00 mL/min Gas Saver Flow 10 mL/min after 10 min
Total run time	34.9 min
GC oven program	70 °C, 2 min, 25 °C/min to 90 °C, 1.5 min, 25 °C/min to 180 °C, 5 °C/min to 280 °C, 10 °C/min to 300 °C, 5 min.
Mass spectrometry	
Instrumentation	Triple quadrupole mass spectrometer (TSQ 9000)
Acquisition mode	Timed selected reaction monitoring (t-SRM mode)
MS transfer line temp.	250 °C
Ion source temp.	320 °C
Ion source	AEI (Advanced Electron Ionization)
Ionization	Electron Ionization (EI)
Collision gas and pressure (psi)	Argon at 70
Peak width (Da)	0.7 (both Q1 and Q3)

Sample preparation

Apples collected from the local market were coarsely cut, packed in zip lock pouch, and frozen overnight at -40 °C for nearly 12–16 hours in the deep freezer prior to analysis. The frozen samples were homogenized in dry ice to avoid losses of incurred residues. The homogenized samples were extracted using QuEChERS AOAC 2007.01 method as described below[5].

Sample extraction and clean-up

- Homogenized sample (15 g) was weighed into a 50 mL extraction tube.
- For recovery, blank samples (n=7 for each level) were spiked at 0.001 mg/kg, 0.005 mg/kg, and 0.010 mg/kg before addition of acetonitrile (extraction solvent). 75 µL of a 5 mg/kg dilution of triphenylphosphate was added as the internal standard.
- Acetonitrile (containing 1% acetic acid) (15 mL) was added to the tube.
- The tube was shaken vigorously for 1 minute on a vortex mixer at 2500 rpm.
- QuEChERS 2007.01 salts (6 g $MgSO_4$, 1.5 g sodium acetate) were added to the tube and it was mixed vigorously for 1 minute on a vortex mixer at 2500 rpm.
- The tube was centrifuged at 5000 rpm for 5 min.
- The supernatant (1 mL) was transferred into the 2 mL microcentrifuge tube containing 150 mg $MgSO_4$, 50 mg PSA.
- Samples were vortexed for 1 min at 2500 rpm and centrifuged at 10000 rpm for 5 min.
- After the dSPE clean-up step, the final blank extracts (1 g sample/mL of acetonitrile) were spiked with a mixture of 211 pesticides at nine concentrations in the range of 0.0001 to 0.050 mg/kg except for captan, captafol, THPI, and phthalimide that were spiked in the range of 0.001 to 0.5 mg/kg. The matrix-matched calibration by post-extraction spiking was done as shown in Table 2.

Table 2. Matrix-matched calibration standards preparation

Working standard (µg/mL)	Volume taken from working standard (µL)	Extracted matrix (µL)	Final concentration (mg/kg)	Total volume (µL)
1.000	50	950	0.050	1000
0.500	50	950	0.025	1000
0.200	50	950	0.01	1000
0.100	50	950	0.005	1000
0.050	50	950	0.0025	1000
0.020	50	950	0.001	1000
0.010	50	950	0.0005	1000
0.005	50	950	0.00025	1000
0.002	50	950	0.0001	1000

- Robustness of the method was tested using repeat injections of matrix spiked at the 0.010 mg/kg level.
- The supernatant was transferred into a GC autosampler vial for analysis.

Data acquisition and processing

The data acquisition and processing were carried out by using Chromeleon 7.2 CDS software, which allows instrument control, method development, quantitative/qualitative analysis, and customizable reporting all within one package. The data was acquired in t-SRM mode, which includes two or more transitions per analyte. The target list of analytes given in Appendix 1 includes quantitative and qualitative ion transitions, collision energies, and retention time (min). For data processing, the ion ratio (±30%), retention time (±0.1 min), linearity (>0.99 with residuals <±20), recovery (70–120%) and precision (±20%) were set as per the SANTE guidelines[6].

Results and discussion

Sample preparation

It was observed in trials that degradation of pesticides such as captan, captafol, and folpet was occurring very prominently when homogenization was done at ambient temperature. It is reported that loss of pesticides may occur through hydrolysis by free water, oxidation, enzymatic degradation following the release of enzymes when cells are ruptured, degradation due to pH, or the formation of insoluble complexes by interaction with matrix components[7,8]. Cryogenic milling steps minimized the degradation more than 70% for captan, captafol, folpet conversion to their degradation products.

Compliance with EU SANTE criteria

The method performance was tested in accordance to the SANTE/11813/2017 guidance document, which requires that the following criteria are satisfied for the identification of pesticide residues:

I. A minimum of two product ions are detected for each pesticide with peak S/N >3 (or, in case noise is absent, a signal should be present in at least five subsequent scans) and with the mass resolution for precursor-ion isolation equal to or better than unit mass resolution.

II. Retention time tolerance of ±0.1 minutes compared with standards in the same sequence.

III. Ion ratio within ±30% (relative) of the average of calibration standards from the same sequence.

GC-MS/MS analysis

A TSQ 9000 triple quadrupole GC-MS/MS system equipped with an AEI source and coupled with a TRACE 1310 GC system was used. The AEI source provides highly efficient electron ionization of analytes and a more focused ion beam that provides an unparalleled level of sensitivity and inherent robustness. The gas chromatographic analysis offered excellent separation for the target analytes and absence of an isobaric interference from the matrix. An extracted ion chromatogram (XIC) is shown in Figure 1 for 211 compounds at 0.01 mg/kg concentration, including the addition of triphenyl phosphate as an internal standard.

In this method, the automatically optimized dwell time for all target analytes ensured that at least 12 points per chromatographic peak were obtained, critical for accurate peak integration and compound quantification.

Identification and quantitation

User-defined parameters for data processing include a minimum of two SRM transitions per analyte, retention time, correlation coefficient, residuals, and ion ratios, which are set in the data processing method based upon the SANTE guidelines. An identification of ethion has been demonstrated by selecting two SRM transitions (230.9→128.9 and 230.9→174.9) at same RT 18.42 min. Further, the quantitation was performed by using linearity range of 0.0001-0.050 mg/kg with R^2>0.9986 and residuals values <20% (Figure 2).

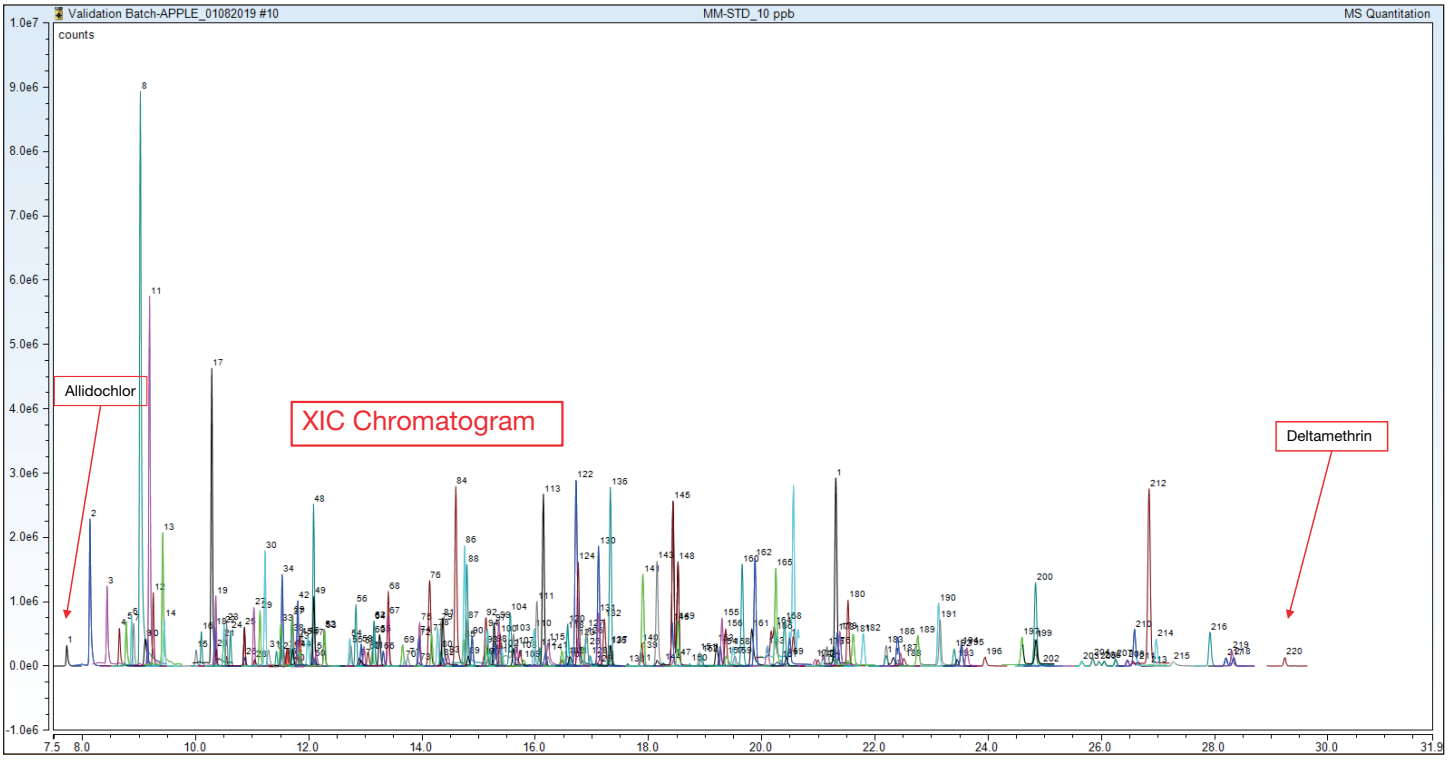
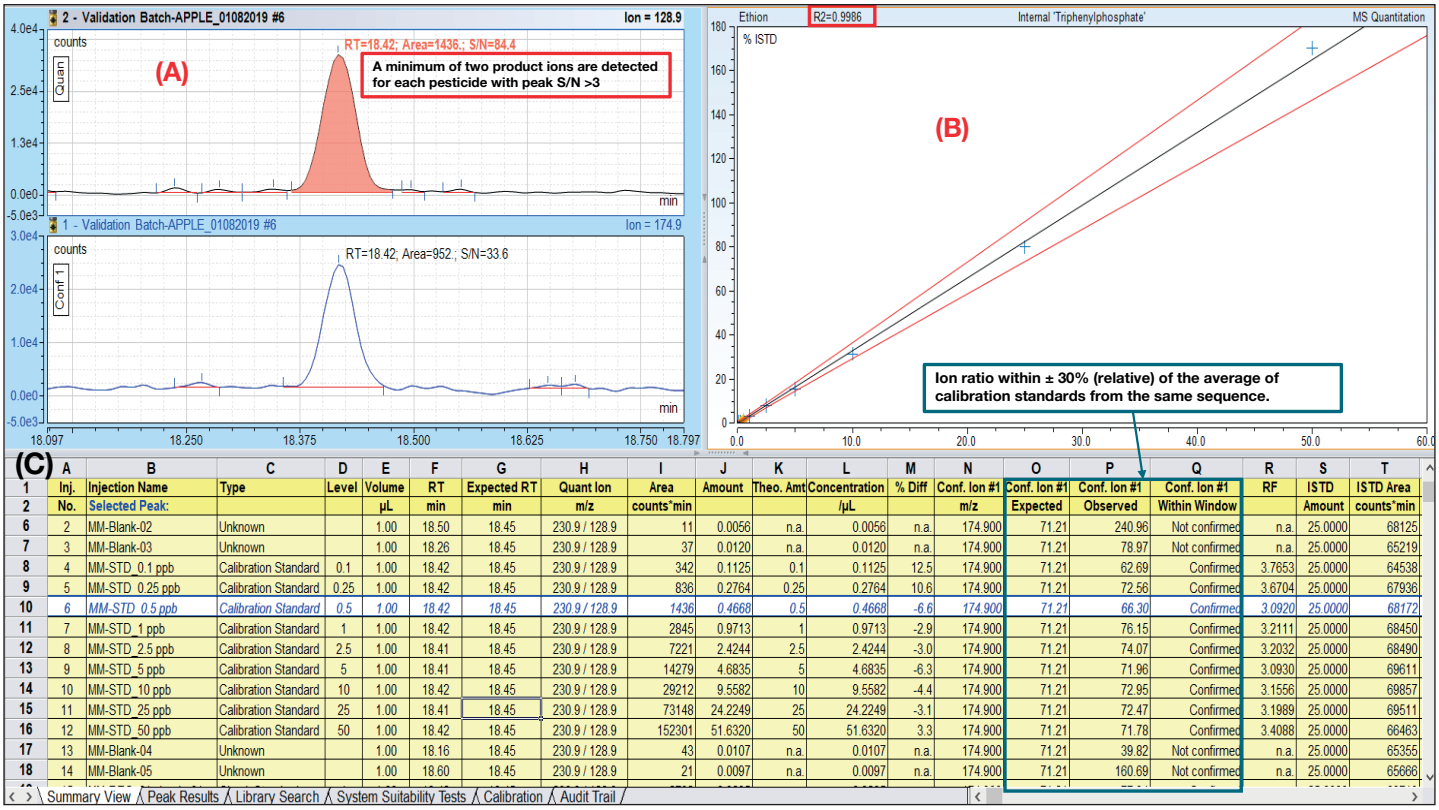


Figure 1. Extracted ion chromatogram (XIC), quantitative SRM transitions, for 211 pesticides extracted from a TIC chromatogram plot in apple matrix at 0.01 mg/kg. Details of compounds analyzed are given in Appendix 1.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
1	Inj.	Injection Name	Type	Level	Volume	RT	Expected RT	Quant Ion	Area	Amount	Theo. Amt	Concentration	% Diff	Conf. Ion #1	Conf. Ion #1	Conf. Ion #1	Conf. Ion #1	RF	ISTD	ISTD Area
2	No.	Selected Peak:			µL	min	min	m/z	counts*min			/µL		m/z	Expected	Observed	Within Window		Amount	counts*min
6	2	MM-Blank-02	Unknown		1.00	18.50	18.45	230.9 / 128.9	11	0.0056	n.a.	0.0056	n.a.	174.900	71.21	240.96	Not confirmed	n.a.	25.0000	68125
7	3	MM-Blank-03	Unknown		1.00	18.26	18.45	230.9 / 128.9	37	0.0120	n.a.	0.0120	n.a.	174.900	71.21	78.97	Not confirmed	n.a.	25.0000	65219
8	4	MM-STD_0.1 ppb	Calibration Standard	0.1	1.00	18.42	18.45	230.9 / 128.9	342	0.1125	0.1	0.1125	12.5	174.900	71.21	62.69	Confirmed	3.7653	25.0000	64538
9	5	MM-STD_0.25 ppb	Calibration Standard	0.25	1.00	18.42	18.45	230.9 / 128.9	836	0.2764	0.25	0.2764	10.6	174.900	71.21	72.56	Confirmed	3.6704	25.0000	67936
10	6	*MM-STD_0.5 ppb*	*Calibration Standard*	*0.5*	*1.00*	*18.42*	*18.45*	*230.9 / 128.9*	*1436*	*0.4668*	*0.5*	*0.4668*	*-6.6*	*174.900*	*71.21*	*66.30*	*Confirmed*	*3.0920*	*25.0000*	*68172*
11	7	MM-STD_1 ppb	Calibration Standard	1	1.00	18.42	18.45	230.9 / 128.9	2845	0.9713	1	0.9713	-2.9	174.900	71.21	76.15	Confirmed	3.2111	25.0000	68450
12	8	MM-STD_2.5 ppb	Calibration Standard	2.5	1.00	18.41	18.45	230.9 / 128.9	7221	2.4244	2.5	2.4244	-3.0	174.900	71.21	74.07	Confirmed	3.2032	25.0000	68490
13	9	MM-STD_5 ppb	Calibration Standard	5	1.00	18.41	18.45	230.9 / 128.9	14279	4.6835	5	4.6835	-6.3	174.900	71.21	71.96	Confirmed	3.0930	25.0000	69611
14	10	MM-STD_10 ppb	Calibration Standard	10	1.00	18.42	18.45	230.9 / 128.9	29212	9.5582	10	9.5582	-4.4	174.900	71.21	72.95	Confirmed	3.1556	25.0000	69857
15	11	MM-STD_25 ppb	Calibration Standard	25	1.00	18.41	18.45	230.9 / 128.9	73148	24.2249	25	24.2249	-3.1	174.900	71.21	72.47	Confirmed	3.1989	25.0000	69511
16	12	MM-STD_50 ppb	Calibration Standard	50	1.00	18.42	18.45	230.9 / 128.9	152301	51.6320	50	51.6320	3.3	174.900	71.21	71.78	Confirmed	3.4088	25.0000	66463
17	13	MM-Blank-04	Unknown		1.00	18.16	18.45	230.9 / 128.9	43	0.0107	n.a.	0.0107	n.a.	174.900	71.21	39.82	Not confirmed	n.a.	25.0000	65355
18	14	MM-Blank-05	Unknown		1.00	18.60	18.45	230.9 / 128.9	21	0.0097	n.a.	0.0097	n.a.	174.900	71.21	160.69	Not confirmed	n.a.	25.0000	65666

Summary View | Peak Results | Library Search | System Suitability Tests | Calibration | Audit Trail

Figure 2. Chromeleon results browser showing identification and quantitation of ethion with (A) SRM chromatogram of quantifier ion and confirmation ion; (B) calibration curve for matrix-matched standard with its acceptance tolerance window; (C) summary view table with complete batch result acceptance criteria meeting SANTE guidelines requirement for individual pesticide

Method performance

In this method, the linear response was assessed over a concentration range of 0.0001–0.050 mg/kg by applying a 1/x weighting factor. Matrix enhancement was observed >20% for most of the target analytes in apple; therefore, matrix-matched calibration standards were used for quantitation (Figure 3). The matrix-matched calibration standard range (0.0001–0.050 mg/kg) offered an excellent correlation coefficient (>0.99) with <20% residuals for all the target analytes (Appendix 2). In Figure 4, the ion ratios observed for ethion in matrix standard (76.1%) and spiked sample (78.0%) were within ±30% (49.8–92.6%) of standard which is an agreement with the EU SANTE guideline criteria. Also, the optimized method offered excellent area repeatability (%RSD ≤15%) for replicate injection (n=100) of for chloroneb, tolyfluanid, permethrin peak 1 and permethrin peak 2 spiked at 0.010 mg/kg and shown in Figure 5. The ion ratio and retention time repeatability for chloroneb, tolyfluanid, *cis*-permethrin, and *trans*-permethrin spiked at 0.010 mg/kg are presented in Figure 6 and Figure 7. The recoveries for >95% pesticides were observed in the range of 70–120% with <20% RSD for 0.001 (LOQ) (lowest spiked concentration 0.001 mg/kg (equivalent to 1 ng/mL concentration in the final vial), 0.005 (LOQx5), and 0.010 (LOQx10) mg/kg (Appendix 2), which were within acceptance criteria of the EU SANTE guidelines. In Figure 8 recovery and precision data for apple extractions (n=7) at a concentration of 0.005 mg/kg are represented. A few pesticides like captan, captafol, folpet, phosmet, fluoridone, prochloraz, azinophos methyl, and pyraclofos have recoveries in the range of 50–70% with <20% RSD at each recovery level, which was consistent at each level.

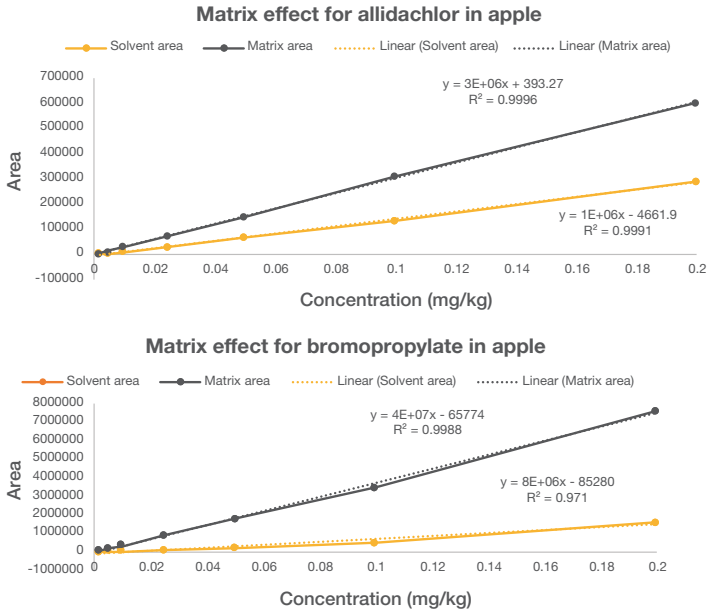


Figure 3. Matrix effect for allidochlor and bromopropylate in apple

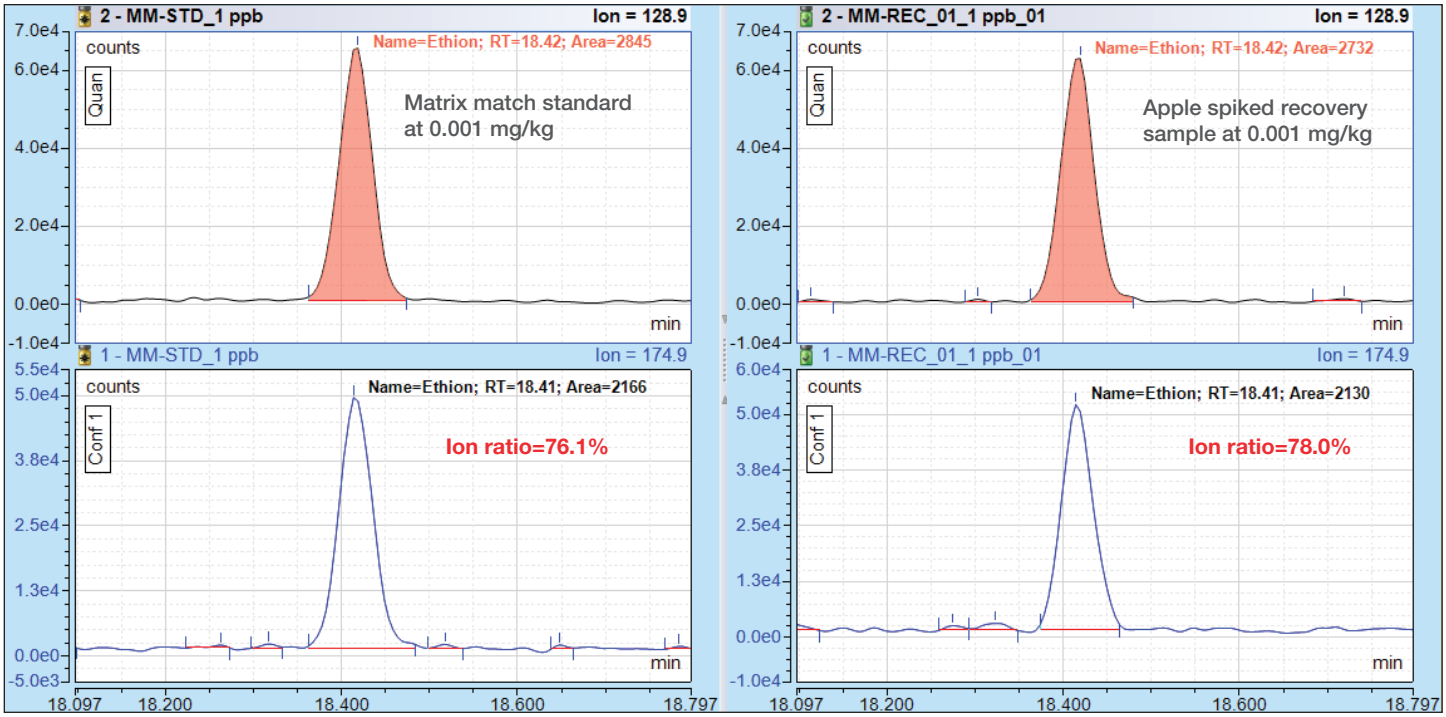


Figure 4. Comparison of ion ratios for ethion in matrix-matched standard (MMS at 0.001 mg/kg) as well as spiked apple sample at 0.001 mg/kg

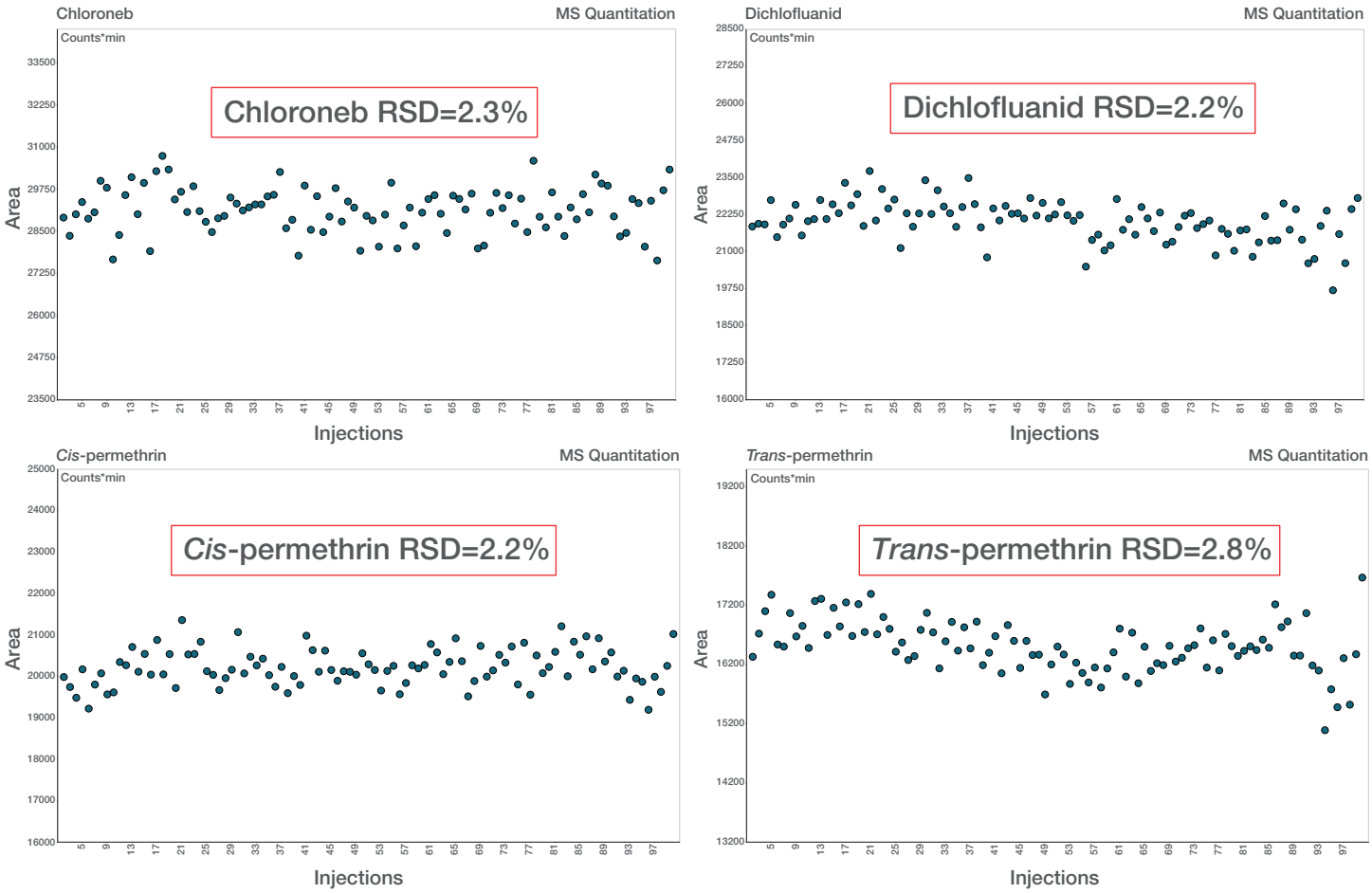


Figure 5. Area repeatability for chloroneb, dichlofluanid, *cis*-permethrin, and *trans*-permethrin (n=100) at 0.010 mg/kg

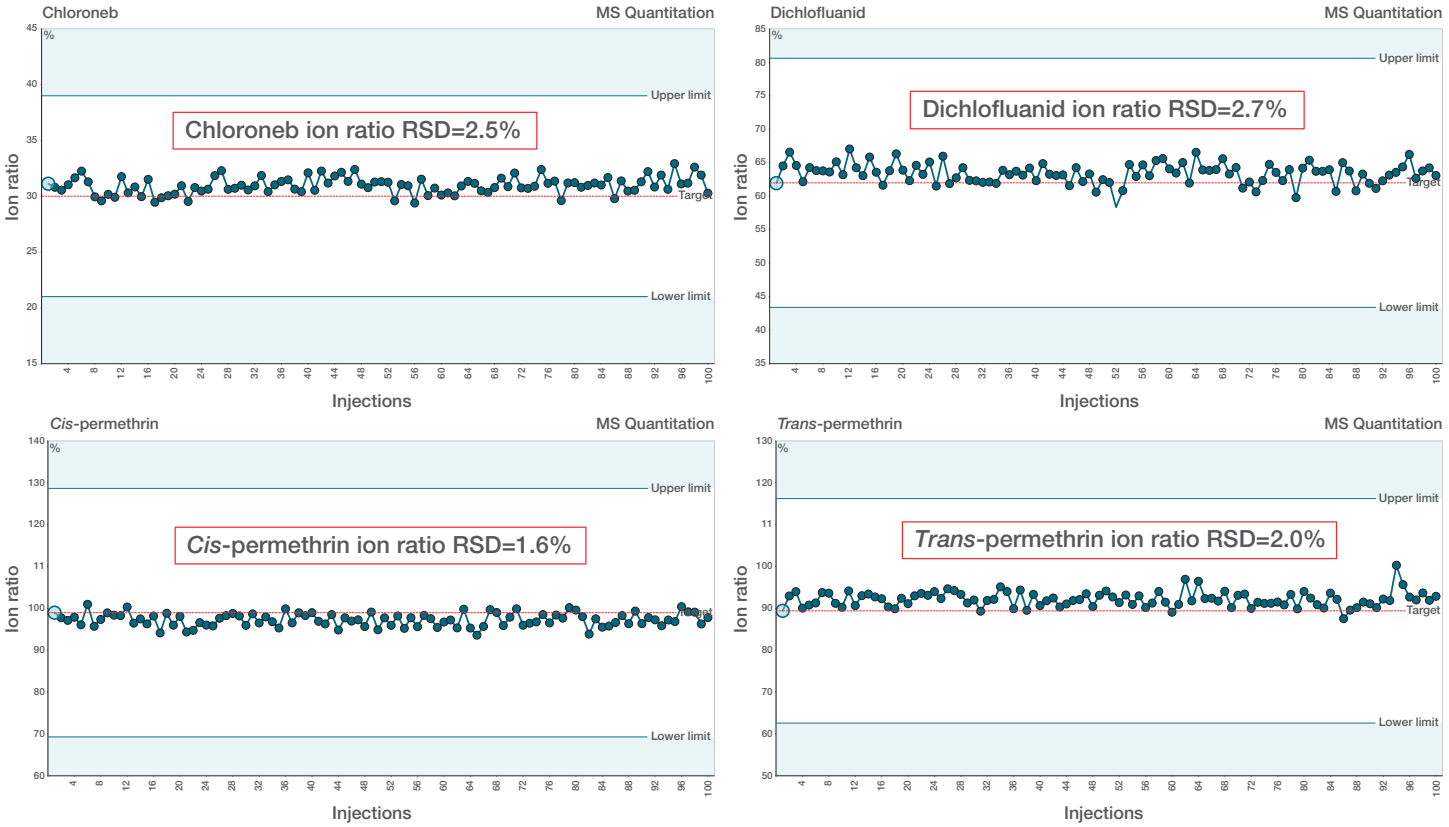


Figure 6. Ion ratio repeatability of chloroneb, dichlofluanid, *cis*-permethrin, and *trans*-permethrin (n=100) at 0.010 mg/kg. Data was acquired continuously for 3 days without any system maintenance or tuning.

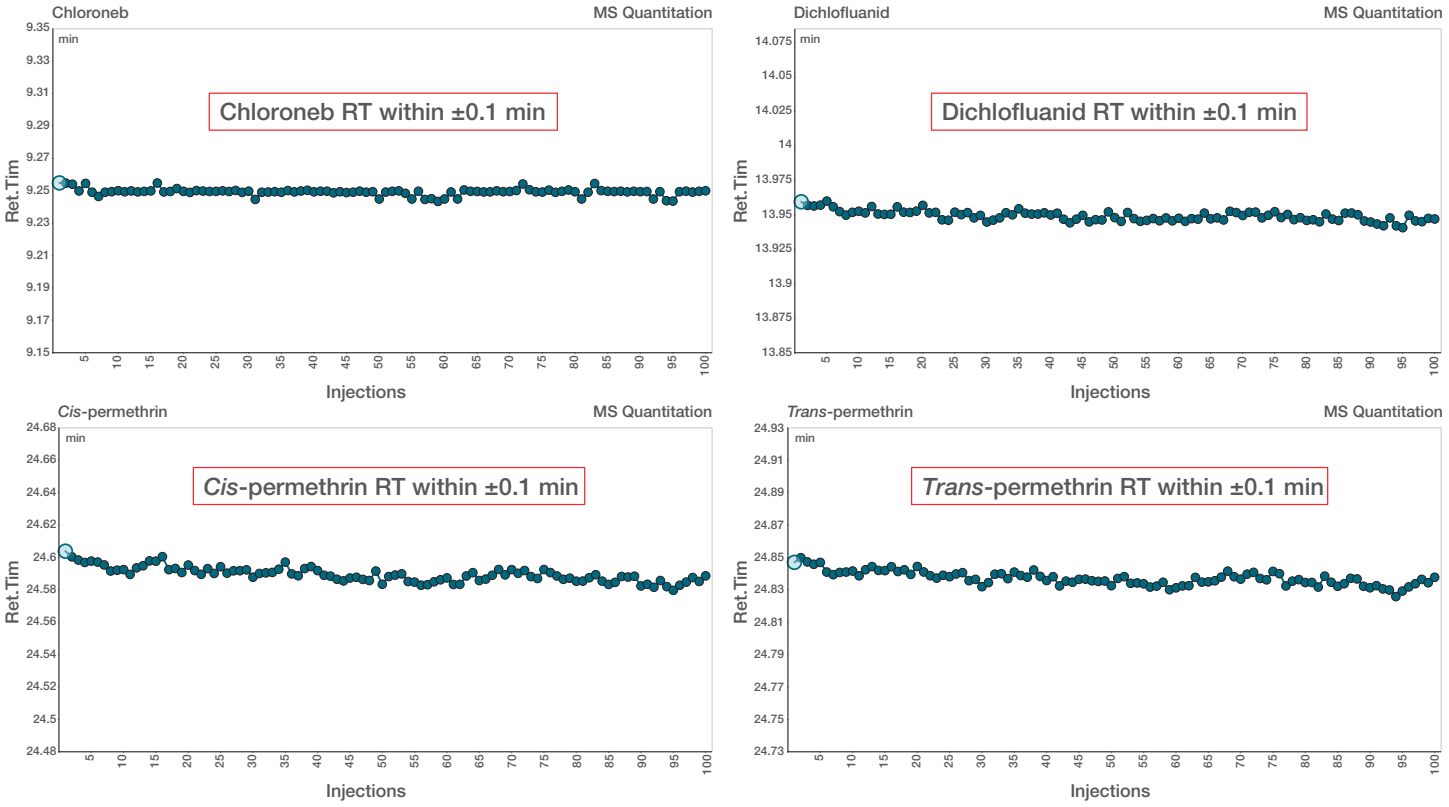


Figure 7. Retention time repeatability of chloroneb, dichlofluanid, *cis*-permethrin, and *trans*-permethrin (n=100) at 0.010 mg/kg

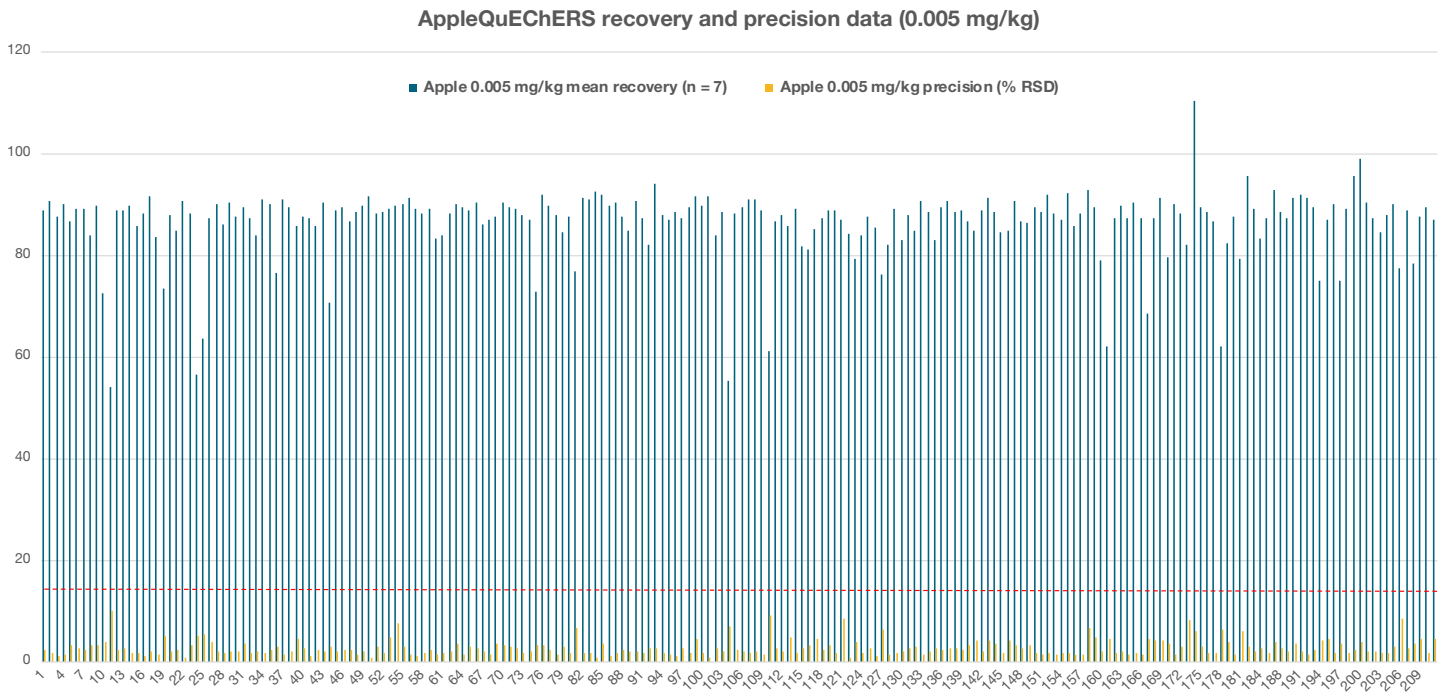


Figure 8. Recovery and precision data for apple extractions (n=7) at a concentration of 0.005 mg/kg

Conclusion

- A cryo-milling followed by QuEChERS 2017.01 extraction and GC-AEI-MSMS analysis offered a trace level quantitation of more than 200 pesticides.
- Optimized method offered excellent sensitivity (LOQ=0.001 mg/kg) for more than 95% of compounds, significantly below the current regulatory requirement (0.01 mg/kg).
- The linearity range (0.0001–0.050 mg/kg) offered excellent R^2 (>0.99) with <20% residuals, ion ratio within ±30%, recoveries within 70–120%, and precision (<20% RSD).
- Difficult analytes like captan and captafol with their metabolites offered excellent recovery even at 0.01 mg/kg.
- The use of the QuEChERS method for extraction and cleanup followed by analysis using GC-MS/MS can increase productivity for commercial food testing laboratories.
- At least 40 injections (standards, samples, blank) could be completed in a day (24 h cycle) providing <10% variation in the area.
- TSQ 9000 triple quadrupole GC-MS/MS system, in combination with Chromeleon CDS software and HyperSep dSPE products, is the ideal solution for the routine analysis of pesticides in apple, providing extraordinary sensitivity, robustness, ease of use, cost effectiveness, and reliability.
- The method validation data were within the acceptance criteria of the SANTE guidelines and comply with the EU and FSSAI MRLs requirements by achieving excellent lower limits of quantitation (LOQ).

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Appendix

Appendix 1. List of pesticides with their SRM transitions, collision energies (V), and retention time (min)

Sr. No.	Compound	RT	Quantifier ion			Qualifier ion 1		
			Q1	Q3	CE (V)	Q1	Q3	CE (V)
1	2,3,5,6-Tetrachloroaniline	10.352	230.8	157.9	18	230.8	159.8	18
2	4,4'-Methoxychlor olefin	19.328	308	238.2	12	238.1	152.1	34
3	Acetochlor	12.947	223.1	132	20	146.1	130	24
4	Acrinathrin	23.567	208.1	180.9	8	289	93.1	8
5	Alachlor	13.173	188.1	160.1	8	188.1	130	32
6	Aldrin	14.361	262.7	192.9	32	254.9	219.9	20
7	Allidochlor	7.73	132	56.1	8	132	49	26
8	Anthraquinone	14.386	180.1	152	12	208.1	152	22
9	Atrazine	11.447	215.1	58.1	10	200.1	122	8
10	Azinphos-ethyl	23.66	132	77	12	132	51	26
11	Azinphos-methyl	22.546	132	77	12	160	77	16
12	Benfluralin	10.564	292	264	8	292	160	20
13	BHC, Alpha	11.046	180.9	144.9	14	216.9	181	8
14	BHC, Beta	11.523	180.9	145	14	216.9	180.9	8
15	BHC, delta	12.293	180.9	144.9	14	182.9	147	14
16	BHC, gamma	11.718	180.9	144.9	12	216.9	180.9	8
17	Bifenthrin	21.347	181	165.9	10	181	179	12
18	Bromfenvinphos	16.604	266.9	159	14	268.9	161.1	14
19	Bromfenvinphos-methyl	15.433	294.9	109	16	294.9	79.1	30
20	Bromophos-ethyl	16.007	358.8	302.8	14	302.8	284.8	14
21	Bromophos-methyl (Bromophos)	14.811	330.8	315.8	14	328.9	313.8	14
22	Bromopropylate	21.367	340.8	185	14	184.9	156.9	12
23	Bupirimate	17.362	273.1	193.2	8	273.1	108	14
24	Captafol	20.376	183.1	79.1	8	150.1	79	6
25	Captan	15.641	117	82	30	149	70	20
26	Carbophenothion	19.298	157	45	12	342	157	10
27	Carfentrazon-ethyl	19.237	340.1	312.1	10	290	99.9	36
28	Chlorbenside	16.048	125	89	16	268	125	10
29	Chlordane alpha-*cis*	16.499	372.8	265.9	14	271.8	236.8	12
30	Chlordane gamma-*trans*	16.1	372.8	265.9	20	271.9	236.9	14
31	Chlorfenapyr	17.663	327.9	246.9	14	248.9	137.1	18
32	Chlorfenson	16.785	175	111	10	111	75	14
33	Chlorfenvinphos	15.408	266.9	159	16	268.9	161	14
32	Chlorobenzilate	18.181	139	111	12	251	111	34
35	Chloroneb	9.264	190.9	113	14	193	53.1	32
36	Chlorothalonil	12.075	263.9	132.9	40	265.9	170	24
37	Chlorpropham	10.518	127	65	20	171	127	8
38	Chlorpyrifos-ethyl	14.193	313.9	257.9	12	196.9	168.9	12
39	Chlorpyrifos-methyl	12.997	285.9	92.9	20	287.9	92.9	20
40	Chlorthal-dimethyl (Dacthal)	14.356	300.9	222.9	22	300.9	272.9	12
41	Chlorthiophos	18.553	324.9	268.9	12	268.9	205	14
42	Chlozolinate	15.318	186	145	14	188	147	14
43	Clomazone	11.552	125	89	16	204	107	18
44	Coumaphos	24.829	226	163	18	209.9	182	10
45	Cycloate	10.371	154.1	83.1	8	154.1	55.1	18
46	Cyfluthrin peak 1	25.658	163	127.1	6	206	151.1	18

Sr. No.	Compound	RT	Quantifier ion			Qualifier ion 1		
			Q1	Q3	CE (V)	Q1	Q3	CE (V)
47	Cyfluthrin peak 2	25.889	163	127	6	206	151.1	18
48	Cyfluthrin peak 3	25.958	163	127	6	226	206.1	12
49	Cyfluthrin peak 4	26.048	163	127	6	226	206.1	10
50	Cyhalothrin I (lambda)	23.188	180.9	152	22	197.1	141.1	10
51	Cypermethrin peak 1	26.29	163	127.1	6	180.9	151.9	18
52	Cypermethrin peak 2	26.496	163	127	6	180.9	151.9	18
53	Cypermethrin peak 3	26.567	163	127	6	163	91	12
54	Cypermethrin peak 4	26.63	163	127.1	6	180.9	152.2	20
55	Cyprodinil	15.152	224.1	208.1	18	224.1	197.1	20
56	DDD p,p	18.436	235	165	20	235	199	14
57	DDD, o,p	17.352	235	165	20	235	199	14
58	DDE o,p	16.149	246	176.1	28	248	176.1	30
59	DDE p,p	17.143	246	176.1	28	317.9	248	18
60	DDT o,p	18.548	235	165.1	22	235	199.1	10
61	DDT p,p	19.684	235	165.1	22	236.8	165	22
62	Deltamethrin	29.279	252.8	92.9	16	252.8	172	8
63	Diallate-*cis*	11.065	234.1	150	18	235.8	152	18
64	Diallate-*trans*	10.88	234.1	150	18	235.8	152	18
65	Diazinon	11.829	137.1	84.1	12	137.1	54.1	20
66	Dichlobenil	8.14	170.9	99.9	24	170.9	136	12
67	Dichlofluanid	13.978	224	123	10	226	123	10
68	Dichlorobenzophenone, 4, 4	14.618	139	111	12	139	74.9	26
69	Dicloran (Bortran)	11.301	206	176	10	160	124.1	8
70	Dieldrin	17.322	276.9	240.8	6	262.9	190.9	30
71	Dimethachlor	12.852	197.1	148	10	134	77	24
72	Diphenamid	14.816	167.1	165.1	20	167.1	152.1	16
73	Diphenylamine	10.3	168.1	167.1	14	169.1	167.1	24
74	Disulfoton	12.111	88	59.8	6	142	81	10
75	Edifenphos	19.394	172.9	109	8	310	109	26
76	Endosulfan ether	12.767	238.9	204	12	240.9	206	14
77	Endosulfan peak 1	16.498	194.9	160	8	240.8	205.8	14
78	Endosulfan peak 2	18.296	194.9	159	8	158.9	123	12
79	Endosulfan sulfate	19.53	271.7	236.8	12	238.7	203.9	12
80	Endrin	17.965	280.8	244.9	8	244.9	173	22
81	Endrin Aldehyde	18.759	249.8	214.9	24	173	138.1	16
82	Endrin-Ketone	21.06	316.8	281	10	316.8	208.9	28
83	EPN	21.311	169	77	22	169	141	8
84	Esfenvalerate	28.353	167	125	10	125	89	18
85	Ethalfluralin	10.381	276	202	14	315.9	276.1	8
86	Ethion	18.447	230.9	128.9	22	230.9	174.9	12
87	Etofenprox	26.88	163.1	107.1	16	163.1	135.1	10
88	Etridiazole (Terrazole)	8.882	182.8	139.9	14	211	139.9	18
89	Fenamiphos	16.644	154	139	10	303.1	195	8
90	Fenarimol	23.44	139	74.9	26	139	111	14
91	Fenchlorfos	13.426	284.9	269.9	14	286.9	271.9	14
92	Fenitrothion	13.767	277	260	6	277	109	16

Sr. No.	Compound	RT	Quantifier ion			Qualifier ion 1		
			Q1	Q3	CE (V)	Q1	Q3	CE (V)
93	Fenpropathrin	21.649	181	151.9	22	181	126.8	28
94	Fenson	14.776	141	77	8	141	50.9	30
95	Fenthion	14.295	278	109	18	278	125	14
96	Fenvalerate	27.964	167	125	10	125	89	18
97	Fipronil	15.257	366.9	212.9	28	368.9	214.9	30
98	Fluazifop-P-butyl	17.91	282.1	91.1	18	282.1	238.1	16
99	Fluchloralin	11.865	306	264	8	326	63	12
100	Flucythrinate peak 1	26.586	157	107.1	12	199.1	107.1	22
101	Flucythrinate peak 2	26.977	157	107	12	199	107	22
102	Fludioxonil	16.92	248	127	26	248	182	10
103	Fluquinconazole	24.861	340	298	16	340	108.1	36
104	Fluridone	27.298	328.1	189.1	38	328.1	258.8	24
105	Flusilazole	17.336	233.1	164.9	16	233.1	151.9	14
106	Flutolanil	16.749	173	145	14	173	95	28
107	Flutriafol	16.594	123	75	24	219.1	123	12
108	Fluvalinate peak 1	28.198	250	55.1	16	250	199.9	18
109	Fluvalinate peak 2	28.347	250	55.1	16	250	200	16
110	Folpet	15.822	259.9	130	14	261.9	130	14
111	Fonofos	11.865	109	62.9	10	246	109	14
112	Heptachlor	13.42	271.8	236.8	12	273.8	238.8	14
113	Heptachlor epoxide	15.41	352.8	262.9	16	354.7	264.9	12
114	Hexachlorobenzene	11.156	281.8	211.8	28	283.8	213.8	30
115	Hexazinone	19.857	171.1	71.1	14	171.1	85.1	12
116	Iodofenfos	16.78	376.8	361.8	16	378.8	363.8	14
117	Iprodione	21.025	314	245	10	315.7	247	10
118	Isazophos	12.116	256.9	161.9	4	118.9	76	18
119	Isodrin	15.157	192.9	123	28	192.9	157	20
120	Isopropalin	14.911	280.1	238.2	8	280.1	180.2	10
121	Lenacil	19.56	153	82.1	16	153	110	14
122	Leptophos	22.485	171	124.3	10	171	51	38
123	Linuron	13.958	187	124	20	248	61.1	8
124	Malathion	13.973	158	125	6	173.1	99	12
125	Metalaxyl	13.34	234.1	146.1	20	249.1	190.1	6
126	Metazachlor	15.177	209	132.1	16	133.1	132.1	12
127	Methacrifos	9.163	124.9	47.1	12	207.9	180.1	6
128	Methoxychlor	21.523	227.1	141.1	32	227.1	169.1	22
129	Metolachlor	14.158	238.1	162.1	10	162.1	133.1	14
130	Mevinphos	8.665	192	127	10	127	95	14
131	MGK-264 A	14.841	164.1	98.1	10	164.1	80.1	24
132	MGK-264 B	15.192	164.1	98.1	12	164.1	67.1	6
133	Mirex	23.163	272	236.8	14	273.8	238.8	14
134	Myclobutanil	17.251	179	125	14	150	123	14
135	N-(2,4-Dimethylphenyl) formamide	9.118	149.1	120.1	14	149.1	106.1	16
136	Nitralin	20.45	316.2	274	8	274	169	12
137	Nitrofen	17.89	202	139	24	283	162	20
138	Nonachlor-*cis*	18.478	408.8	299.9	18	406.8	299.9	14

Sr. No.	Compound	RT	Quantifier ion			Qualifier ion 1		
			Q1	Q3	CE (V)	Q1	Q3	CE (V)
139	Nonachlor-*trans*	16.594	406.8	299.8	14	408.8	299.8	18
140	Norflurazon	19.399	303	145	20	145	95	16
141	Ortho-phenylphenol	9.433	170.1	115	34	170.1	141.1	22
142	Oxadiazon	17.146	175	112	12	258	175	6
143	Oxyfluorfen	17.321	252	146	30	300	223	14
144	Paclobutrazol	16.248	236	125	12	138	103.1	14
145	Parathion (ethyl)	14.391	138.9	109	6	291	109	12
146	Parathion-methyl	13.1	263	109	12	263	79	30
147	Pebulate	8.917	128.1	57.1	8	128	72	6
148	Penconazole	15.297	248.1	157	22	159	123	20
149	Pendimethalin	15.117	252.1	162.1	8	252.1	161.1	14
150	Pentachloroaniline	12.747	262.9	191.9	20	264.9	193.6	18
151	Pentachloroanisole	11.246	264.8	236.9	10	279.9	236.8	22
152	Pentachlorobenzene	9.461	247.9	212.9	18	248	142	42
153	Pentachlorobenzonitrile	11.718	272.9	237.9	16	274.8	204.9	28
154	Pentachlorothioanisole	13.95	295.7	262.9	12	295.7	245.9	30
155	*Cis*-permethrin	24.6	183.1	153	12	183.1	168	12
156	*Trans*-permethrin	24.882	183	168.1	10	183	165.1	10
157	Perthane (Ethylan)	17.925	223.1	167	12	223.1	193	28
158	Phenothrin	22.33	123.1	41.1	24	123.1	81.1	8
159	Phorate	10.885	260	75	8	121	65	10
160	Phosalone	22.435	182	111	14	182	74.8	30
161	Phosmet	21.186	160	133	10	160	50.9	38
162	Phthalimide	9.041	147	76	25	103.7	76	10
163	Piperonyl butoxide	20.436	176.1	103.1	22	176.1	131.1	12
164	Pirimiphos-ethyl	14.761	304.1	168.1	12	318.1	166.1	12
165	Pirimiphos-methyl	13.676	290.1	125	20	290.1	233	8
166	Pretilachlor	16.935	162	132.1	20	262.1	202.1	6
167	Prochloraz	24.983	180	69	14	180.1	138.1	12
168	Procymidone	15.697	283	96.1	8	285	96.1	10
169	Prodiamine	13.721	321.1	279.1	6	275.1	255.1	8
170	Profenofos	17.001	336.9	266.9	12	338.9	268.9	14
171	Profluralin	11.597	318.1	199.1	12	347.1	330.1	6
172	Propachlor	10.119	176.1	57.1	8	120	77	16
173	Propanil	12.907	161	90	24	161	99	24
174	Propargite	20.251	135.1	107.1	12	135.1	77.1	26
175	Propisochlor	13.255	162.1	120.1	12	162.1	144.1	8
176	Propyzamide	11.824	172.9	109	24	172.9	145	14
177	Prothiofos	16.87	309	238.9	14	266.9	220.9	18
178	Pyraclofos	23.981	194	138	18	360	194.1	12
179	Pyrazophos	23.485	221	148.7	14	231.9	204.1	10
180	Pyridaben	24.876	147.1	117.1	20	147.1	132.1	12
181	Pyridaphenthion	20.98	340	199.1	8	199	92.1	14
182	Pyrimethanil	12.00	198.1	118	32	198.1	158.1	18
183	Pyriproxyfen	22.792	136.1	96	10	136.1	78	20
184	Quinalphos	15.581	146	118.1	10	157.1	102	22
185	Quintozene	11.638	294.8	236.9	14	213.8	178.9	14

Sr. No.	Compound	RT	Quantifier ion			Qualifier ion 1		
			Q1	Q3	CE (V)	Q1	Q3	CE (V)
186	Resmethrin peak 1	20.306	123.1	81.1	8	143	128.1	10
187	Resmethrin peak 2	20.527	171	127.9	14	143	128	10
188	Sulfotep	10.634	322	145.9	22	237.9	145.9	12
189	Sulprofos	18.966	156	108	30	322	156.1	10
190	Tebuconazole	20.13	250	125	20	125	89	16
191	Tebufenpyrad	21.802	276.1	171	10	318.1	131.1	14
192	Tecnazene	10.023	258.9	201	12	214.8	178.9	8
193	Tefluthrin	12.106	177	127	14	177	137	16
194	Terbacil	12.151	161	144	12	160	76	12
195	Terbufos	11.733	231	128.9	20	231	175	10
196	Terbuthylazine	11.738	214.1	104.1	16	214.1	132.1	10
197	Tetrachlorvinphos	16.208	328.9	109	18	330.9	109	18
198	Tetradifon	22.233	159	111	20	159	74.8	32
199	Tetrahydrophthalimide (THPI)	9.2	151	77.1	32	151	79.9	6
200	Tetramethrin peak 1	21.125	164	107.1	12	164	77.1	24
201	Tetramethrin peak 2	21.412	164	77.1	22	164	107.1	12
202	Tolclofos-methyl	13.173	265	219.9	20	265	250	12
203	Tolylfluanid	15.366	238	137	10	240	137	14
204	Transfluthrin	13.173	163	143	14	163	91.1	12
205	Triadimefon	14.482	208	126.7	12	208	111	20
206	Triadimenol	15.692	128	65	18	168.1	70	10
207	Triallate	12.297	268	183.9	18	268	226	12
208	Triazophos	18.936	161.1	134.1	8	257	162.1	6
209	Triflumizole	15.752	206	179	14	179	144	14
210	Trifluralin	10.513	306.1	264.1	8	264	160	14
211	Triphenylphosphate	20.286	215	168.1	16	326.1	169.1	28
212	Vinclozolin	13.068	197.9	145	14	212	172	14

Appendix 2. List of pesticides with validation data (ion ratio, linearity, recovery, and precision)

Sr. No.	Name of compound	Ion ratio (IR)		R^2	Range (mg/kg)	LOQ (mg/kg)	0.001 mg/k (n=7)		0.005 mg/kg (n=7)		0.010 mg/kg (n=7)	
		*IR range in MMS	#IR at 0.005 (mg/kg)				% Rec	% RSD	% Rec	% RSD	% Rec	% RSD
1	2,3,5,6-Tetrachloroaniline	66.43-123.37	98.3	0.9990	0.0001-0.05	0.001	91	3	89	2	86	6
2	4,4'-Methoxychlor olefin	88.83-164.97	130.4	0.9993	0.0001-0.05	0.001	92	1	91	2	88	5
3	Acetochlor	82.74-153.66	125.2	0.9993	0.0001-0.05	0.001	86	2	88	1	85	6
4	Acrinathrin	23.94-44.46	33.8	0.9995	0.00025-0.05	0.001	94	3	90	2	86	6
5	Alachlor	54.88-101.92	76.6	0.9979	0.00025-0.05	0.001	86	3	87	3	84	6
6	Aldrin	50.54-93.86	64.1	0.9995	0.00025-0.05	0.001	90	6	89	3	84	7
7	Allidochlor	13.58-25.22	19	0.9992	0.00025-0.05	0.001	90	3	89	2	86	6
8	Anthraquinone	65.52-121.68	93.9	0.9956	0.00025-0.05	0.001	90	3	84	3	82	5
9	Atrazine	64.61-119.99	94.9	0.9995	0.00025-0.05	0.001	89	7	90	3	85	5
10	Azinphos-ethyl	37.94-70.46	51.4	0.9995	0.0005-0.05	0.001	77	6	73	4	68	9
11	Azinphos-methyl	72.52-134.68	104.2	0.9993	0.0005-0.05	0.001	60	10	54	10	51	11
12	Benfluralin	32.69-60.71	48	0.9973	0.00025-0.05	0.001	93	4	89	2	86	7
13	BHC, Alpha	43.19-80.21	64.6	0.9987	0.0001-0.05	0.001	90	3	89	3	86	6
14	BHC, Beta	49.07-91.13	73.5	0.9991	0.0001-0.05	0.001	90	5	90	2	87	6

Sr. No.	Name of compound	Ion ratio (IR)		R^2	Range (mg/kg)	LOQ (mg/kg)	0.001 mg/k (n=7)		0.005 mg/kg (n=7)		0.010 mg/kg (n=7)	
		*IR range in MMS	#IR at 0.005 (mg/kg)				% Rec	% RSD	% Rec	% RSD	% Rec	% RSD
15	BHC, delta	46.41-86.19	64.7	0.9985	0.0001-0.05	0.001	86	3	86	2	82	5
16	BHC, gamma	42.56-79.04	59.1	0.9988	0.0001-0.05	0.001	91	6	88	1	85	7
17	Bifenthrin	6.58-12.22	8.1	0.9993	0.00025-0.05	0.001	92	3	92	2	89	6
18	Bromfenvinphos	44.17-82.03	62.6	0.9991	0.0001-0.05	0.001	88	2	84	2	82	7
19	Bromfenvinphos-methyl	14.14-26.26	18.1	0.9960	0.0005-0.05	0.001	86	11	73	5	70	8
20	Bromophos-ethyl	34.3-63.7	44.3	0.9993	0.0001-0.05	0.001	88	5	88	2	84	5
21	Bromophos-methyl (Bromophos)	47.95-89.05	66.5	0.9990	0.0001-0.05	0.001	86	3	85	2	80	7
22	Bromopropylate	111.3-206.7	169.1	0.9995	0.0001-0.05	0.001	92	2	91	1	88	5
23	Bupirimate	27.93-51.87	43.5	0.9978	0.00025-0.05	0.001	93	4	88	3	86	6
24	Captafol	73.99-137.41	116.8	0.9931	0.005-0.500	0.010	59	16	57	5	56	10
25	Captan	79.59-147.81	108.4	0.9883	0.0025-0.500	0.010	61	24	64	6	61	10
26	Carbophenothion	20.02-37.18	27.7	0.9978	0.00025-0.05	0.001	94	2	87	4	86	5
27	Carfentrazon-ethyl	14.77-27.43	19.2	0.9998	0.00025-0.05	0.001	92	4	90	2	86	6
28	Chlorbenside	24.08-44.72	34.5	0.9985	0.0001-0.05	0.001	89	4	86	2	85	5
29	Chlordane alpha-*cis*	84.07-156.13	126.4	0.9992	0.0001-0.05	0.001	90	2	90	2	86	6
30	Chlordane gamma-*trans*	52.57-97.63	72.3	0.9986	0.00025-0.05	0.001	91	5	88	2	85	6
31	Chlorfenapyr	45.57-84.63	64.6	0.9994	0.0005-0.05	0.001	90	5	89	4	87	5
32	Chlorfenson	32.9-61.1	49.8	0.9971	0.00025-0.05	0.001	89	2	87	2	85	5
33	Chlorfenvinphos	45.29-84.11	68.2	0.9976	0.00025-0.05	0.001	89	5	84	2	81	6
34	Chlorobenzilate	38.5-71.5	54.5	0.9994	0.0001-0.05	0.001	92	2	91	2	89	5
35	Chloroneb	21.28-39.52	31.2	0.9988	0.00025-0.05	0.001	90	4	90	2	87	5
36	Chlorothalonil	28.98-53.82	43.8	0.9985	0.00025-0.05	0.001	84	5	77	3	73	9
37	Chlorpropham	77.28-143.52	104.3	0.9985	0.00025-0.05	0.001	95	4	91	2	86	6
38	Chlorpyrifos-ethyl	95.06-176.54	131.9	0.9991	0.0001-0.05	0.001	91	3	89	2	86	6
39	Chlorpyrifos-methyl	45.22-83.98	63.8	0.9984	0.00025-0.05	0.001	85	6	86	5	82	6
40	Chlorthal-dimethyl (Dacthal)	55.79-103.61	78.6	0.9986	0.0001-0.05	0.001	88	3	88	3	85	5
41	Chlorthiophos	40.6-75.4	55.9	0.9982	0.0001-0.05	0.001	90	2	87	1	85	6
42	Chlozolinate	51.59-95.81	67.5	0.9981	0.00025-0.05	0.001	85	4	86	2	83	4
43	Clomazone	40.39-75.01	60	0.9989	0.0001-0.05	0.001	93	2	90	2	87	6
44	Coumaphos	111.44-206.96	168.8	0.9996	0.00025-0.05	0.001	78	11	71	3	65	9
45	Cycloate	49.98-92.82	69.2	0.9984	0.00025-0.05	0.001	88	3	89	2	87	6
46	Cyfluthrin peak 1	35.7-66.3	47.8	0.9999	0.0005-0.05	0.001	86	8	89	2	86	6
47	Cyfluthrin peak 2	28.7-53.3	42.3	0.9999	0.00025-0.05	0.001	88	3	87	2	83	8
48	Cyfluthrin peak 3	64.12-119.08	86.9	0.9999	0.00025-0.05	0.001	90	4	88	2	86	7
49	Cyfluthrin peak 4	46.9-87.1	66.2	0.9999	0.00025-0.05	0.001	94	4	90	2	87	6
50	Cyhalothrin I (lambda)	40.81-75.79	62	0.9996	0.0001-0.05	0.001	92	3	92	1	88	6
51	Cypermethrin peak 1	99.47-184.73	131.6	0.9998	0.0005-0.05	0.001	83	8	88	3	85	7
52	Cypermethrin peak 2	64.26-119.34	81.3	0.9997	0.0005-0.05	0.001	87	11	88	2	86	6
53	Cypermethrin peak 3	72.38-134.42	116.8	0.9999	0.001-0.05	0.005	<LOQ	<LOQ	89	5	87	7
54	Cypermethrin peak 4	65.45-121.55	89.7	0.9994	0.001-0.05	0.005	<LOQ	<LOQ	90	8	88	8
55	Cyprodinil	13.23-24.57	20.7	0.9989	0.00025-0.05	0.001	92	3	90	3	88	5
56	DDD p,p	15.82-29.38	23.1	0.9992	0.0001-0.05	0.001	92	2	91	1	88	6
57	DDD, o,p	20.51-38.09	30.6	0.9993	0.0001-0.05	0.001	91	2	89	1	87	6
58	DDE o,p	43.75-81.25	63.7	0.9995	0.0001-0.05	0.001	90	2	88	2	86	6
59	DDE p,p	25.62-47.58	38.2	0.9994	0.0001-0.05	0.001	91	3	89	2	86	5

Sr. No.	Name of compound	Ion ratio (IR)		R^2	Range (mg/kg)	LOQ (mg/kg)	0.001 mg/k (n=7)		0.005 mg/kg (n=7)		0.010 mg/kg (n=7)	
		*IR range in MMS	#IR at 0.005 (mg/kg)				% Rec	% RSD	% Rec	% RSD	% Rec	% RSD
60	DDT o,p	21.35-39.65	30.4	0.9981	0.0001-0.05	0.001	85	3	83	2	82	6
61	DDT p,p	44.45-82.55	60.8	0.9993	0.0001-0.05	0.001	85	3	84	2	81	6
62	Deltamethrin	52.36-97.24	78.2	0.9999	0.00025-0.05	0.001	88	3	88	2	82	8
63	Diallate-*cis*	27.16-50.44	37.4	0.9982	0.00025-0.05	0.001	87	10	90	4	88	7
64	Diallate-*trans*	23.8-44.2	32.2	0.9985	0.0001-0.05	0.001	89	2	89	1	87	7
65	Diazinon	38.22-70.98	53.8	0.9975	0.00025-0.05	0.001	86	8	89	3	86	6
66	Dichlobenil	50.96-94.64	73	0.9990	0.0001-0.05	0.001	90	3	90	3	87	7
67	Dichlofluanid	43.68-81.12	64.7	0.9987	0.0001-0.05	0.001	87	2	86	2	84	6
68	Dichlorobenzophenone, 4, 4	34.09-63.31	49.3	0.9978	0.0001-0.05	0.001	88	3	87	1	84	6
69	Dicloran (Bortran)	49.42-91.78	67	0.9987	0.00025-0.05	0.001	89	7	88	4	86	6
70	Dieldrin	82.32-152.88	109.9	0.9989	0.0005-0.05	0.001	93	8	90	3	89	7
71	Dimethachlor	82.39-153.01	115	0.9997	0.00025-0.05	0.001	90	2	89	3	87	6
72	Diphenamid	74.97-139.23	105.4	0.9967	0.00025-0.05	0.001	88	5	89	3	86	4
73	Diphenylamine	40.95-76.05	57.7	0.9978	0.0001-0.05	0.001	88	4	88	2	86	6
74	Disulfoton	13.23-24.57	16.9	0.9981	0.0005-0.05	0.001	91	3	87	2	84	7
75	Edifenphos	17.99-33.41	24.1	0.9988	0.00025-0.05	0.001	83	5	73	3	68	9
76	Endosulfan ether	74.48-138.32	110.9	0.9992	0.0001-0.05	0.001	91	4	92	3	89	6
77	Endosulfan peak 1	109.97-204.23	144	0.9991	0.00025-0.05	0.001	88	11	90	2	85	5
78	Endosulfan peak 2	57.12-106.08	103.2	0.9993	0.0005-0.05	0.001	90	11	88	1	84	4
79	Endosulfan sulfate	18.06-33.54	27.8	0.9995	0.00025-0.05	0.001	88	6	85	3	82	7
80	Endrin	96.32-178.88	122.7	0.9995	0.00025-0.05	0.001	92	10	88	2	86	7
81	Endrin Aldehyde	68.81-127.79	82.5	0.9972	0.00025-0.05	0.001	88	10	77	7	78	5
82	Endrin-Ketone	61.11-113.49	97.3	0.9989	0.0005-0.05	0.001	98	15	91	2	90	7
83	EPN	116.83-216.97	170.6	0.9991	0.0005-0.05	0.001	98	2	91	2	89	6
84	Esfenvalerate	28-52	37.6	0.9998	0.0005-0.05	0.001	88	3	93	1	89	6
85	Ethalfluralin	39.2-72.8	64.3	0.9977	0.0005-0.05	0.001	100	4	92	4	86	6
86	Ethion	49.84-92.56	76.4	0.9986	0.0001-0.05	0.001	90	2	90	1	87	6
87	Etofenprox	62.23-115.57	87.5	0.9999	0.0001-0.05	0.001	92	2	91	2	87	6
88	Etridiazole (Terrazole)	54.46-101.14	81.2	0.9990	0.0001-0.05	0.001	90	4	88	3	85	6
89	Fenamiphos	25.83-47.97	33.2	0.9992	0.0005-0.05	0.001	94	13	85	2	82	8
90	Fenarimol	124.39-231.01	174.5	0.9994	0.0001-0.05	0.001	92	2	91	2	89	5
91	Fenchlorfos	49.35-91.65	71	0.9989	0.0005-0.05	0.001	88	3	87	2	83	7
92	Fenitrothion	43.54-80.86	65.2	0.9968	0.0005-0.05	0.001	90	10	82	3	80	7
93	Fenpropathrin	12.95-24.05	19.2	0.9989	0.0005-0.05	0.001	97	5	94	3	90	6
94	Fenson	20.37-37.83	28.3	0.9990	0.0001-0.05	0.001	88	1	88	2	84	5
95	Fenthion	25.83-47.97	35.4	0.9990	0.00025-0.05	0.001	87	4	87	2	83	6
96	Fenvalerate	26.81-49.79	38.2	0.9998	0.0001-0.05	0.001	91	3	88	1	84	6
97	Fipronil	39.34-73.06	57.5	0.9973	0.0005-0.05	0.001	96	7	87	3	84	5
98	Fluazifop-P-butyl	68.74-127.66	99.7	0.9980	0.0001-0.05	0.001	91	1	90	2	88	5
99	Fluchloralin	55.51-103.09	67	0.9967	0.00025-0.05	0.001	96	6	92	5	88	7
100	Flucythrinate peak 1	47.53-88.27	64.8	0.9998	0.00025-0.05	0.001	91	3	90	2	86	6
101	Flucythrinate peak 2	47.81-88.79	70	0.9998	0.0001-0.05	0.001	94	4	92	1	88	6
102	Fludioxonil	34.79-64.61	46	0.9980	0.0001-0.05	0.001	92	6	84	3	83	6
103	Fluquinconazole	45.57-84.63	63.5	0.9995	0.0001-0.05	0.001	89	2	89	2	84	6
104	Fluridone	47.53-88.27	58	0.9975	0.001-0.05	0.005	<LOQ	<LOQ	55	7	51	8

Sr. No.	Name of compound	Ion ratio (IR)		R^2	Range (mg/kg)	LOQ (mg/kg)	0.001 mg/k (n=7)		0.005 mg/kg (n=7)		0.010 mg/kg (n=7)	
		*IR range in MMS	#IR at 0.005 (mg/kg)				% Rec	% RSD	% Rec	% RSD	% Rec	% RSD
105	Flusilazole	41.86-77.74	64	0.9983	0.00025-0.05	0.001	95	7	88	2	86	5
106	Flutolanil	18.48-34.32	26	0.9981	0.0001-0.05	0.001	92	2	89	2	87	5
107	Flutriafol	66.99-124.41	96.4	0.9983	0.0001-0.05	0.001	95	5	91	2	89	5
108	Fluvalinate peak 1	64.47-119.73	93.9	0.9998	0.00025-0.05	0.001	91	3	91	2	87	6
109	Fluvalinate peak 2	73.71-136.89	105.6	0.9998	0.0001-0.05	0.001	90	2	89	2	84	7
110	Folpet	47.81-88.79	73.7	0.9990	0.0005-0.05	0.001	65	15	61	9	59	9
111	Fonofos	92.61-171.99	126.6	0.9972	0.0001-0.05	0.001	86	5	87	3	84	8
112	Heptachlor	42.77-79.43	63.2	0.9984	0.0001-0.05	0.001	88	4	88	2	85	6
113	Heptachlor epoxide	47.6-88.4	70.9	0.9982	0.00025-0.05	0.001	87	9	86	5	83	5
114	Hexachlorobenzene	83.3-154.7	120.8	0.9994	0.0001-0.05	0.001	81	5	89	2	85	6
115	Hexazinone	29.68-55.12	42.2	0.9992	0.00025-0.05	0.001	93	5	82	3	80	5
116	Iodofenfos	29.12-54.08	38.6	0.9985	0.0001-0.05	0.001	88	4	81	3	78	7
117	Iprodione	33.32-61.88	49.8	0.9999	0.0005-0.05	0.001	87	7	85	5	80	7
118	Isazophos	73.29-136.11	110.1	0.9991	0.0005-0.05	0.001	93	5	87	2	86	8
119	Isodrin	45.36-84.24	62.8	0.9986	0.00025-0.05	0.001	88	7	89	3	86	6
120	Isopropalin	12.46-23.14	21.4	0.9961	0.0005-0.05	0.001	97	4	89	2	86	7
121	Lenacil	74.83-138.97	91.7	0.9990	0.0005-0.05	0.001	97	6	87	8	84	8
122	Leptophos	101.43-188.37	130.4	0.9987	0.0001-0.05	0.001	93	2	84	1	83	7
123	Linuron	31.71-58.89	49.2	0.9958	0.001-0.05	0.005	<LOQ	<LOQ	79	4	71	8
124	Malathion	71.54-132.86	105	0.9981	0.0001-0.05	0.001	87	3	84	2	81	6
125	Metalaxyl	37.03-68.77	45.6	0.9986	0.00025-0.05	0.001	92	6	88	3	88	7
126	Metazachlor	100.03-185.77	131.1	0.9974	0.00025-0.05	0.001	90	4	85	1	81	6
127	Methacrifos	186.06-345.54	269.1	0.9983	0.00025-0.05	0.001	78	3	76	6	80	7
128	Methoxychlor	66.5-123.5	96.1	0.9989	0.0001-0.05	0.001	84	3	82	2	79	7
129	Metolachlor	76.3-141.7	108.7	0.9993	0.0001-0.05	0.001	89	3	89	2	86	6
130	Mevinphos	36.4-67.6	52.4	0.9987	0.0001-0.05	0.001	88	2	83	2	80	7
131	MGK-264 A	74.62-138.58	105.4	0.9973	0.00025-0.05	0.001	87	8	88	3	85	6
132	MGK-264 B	85.89-159.51	121	0.9946	0.0001-0.05	0.001	89	6	85	3	84	7
133	Mirex	55.93-103.87	78.9	0.9992	0.0001-0.05	0.001	91	2	91	1	88	5
134	Myclobutanil	23.66-43.94	29.1	0.9986	0.00025-0.05	0.001	97	3	89	2	87	5
135	N-(2,4-Dimethylphenyl) formamide	75.18-139.62	86	0.9958	0.0005-0.05	0.001	98	7	83	3	83	4
136	Nitralin	13.65-25.35	20.8	0.9955	0.0005-0.05	0.001	101	5	90	2	91	5
137	Nitrofen	28.91-53.69	41.7	0.9990	0.00025-0.05	0.001	96	3	91	3	88	5
138	Nonachlor-*cis*	74.97-139.23	113	0.9986	0.00025-0.05	0.001	91	5	88	3	85	6
139	Nonachlor-*trans*	70-130	90.1	0.9994	0.0001-0.05	0.001	92	5	89	2	87	6
140	Norflurazon	47.95-89.05	77.6	0.9980	0.00025-0.05	0.001	95	4	87	3	83	7
141	Ortho-phenylphenol	69.79-129.61	101.2	0.9982	0.00025-0.05	0.001	77	8	85	4	83	6
142	Oxadiazon	32.76-60.84	44.4	0.9981	0.0001-0.05	0.001	88	4	89	2	86	5
143	Oxyfluorfen	55.09-102.31	78	0.9970	0.0005-0.05	0.001	104	5	91	4	90	4
144	Paclobutrazol	12.11-22.49	18.1	0.9986	0.00025-0.05	0.001	92	6	89	4	85	8
145	Parathion (ethyl)	60.55-112.45	79	0.9974	0.00025-0.05	0.001	87	4	85	2	84	6
146	Parathion-methyl	10.78-20.02	15.6	0.9971	0.001-0.05	0.005	<LOQ	<LOQ	85	4	80	7
147	Pebulate	32.27-59.93	41.6	0.9996	0.00025-0.05	0.001	87	4	91	3	87	6
148	Penconazole	41.58-77.22	60	0.9984	0.00025-0.05	0.001	89	3	87	3	85	5
149	Pendimethalin	46.9-87.1	68.6	0.9981	0.0001-0.05	0.001	93	6	86	3	86	6

Sr. No.	Name of compound	Ion ratio (IR)		R^2	Range (mg/kg)	LOQ (mg/kg)	0.001 mg/k (n=7)		0.005 mg/kg (n=7)		0.010 mg/kg (n=7)	
		*IR range in MMS	#IR at 0.005 (mg/kg)				% Rec	% RSD	% Rec	% RSD	% Rec	% RSD
150	Pentachloroaniline	55.09-102.31	77.2	0.9992	0.0001-0.05	0.001	91	3	89	2	87	5
151	Pentachloroanisole	36.89-68.51	58.4	0.9988	0.0001-0.05	0.001	90	2	89	1	86	6
152	Pentachlorobenzene	66.43-123.37	94	0.9991	0.0001-0.05	0.001	86	5	92	2	88	7
153	Pentachlorobenzonitrile	62.16-115.44	84.2	0.9984	0.0001-0.05	0.001	89	2	88	1	84	5
154	Pentachlorothioanisole	42.98-79.82	61.9	0.9992	0.00025-0.05	0.001	84	4	87	2	84	6
155	*Cis*-permethrin	61.25-113.75	92.9	0.9999	0.00025-0.05	0.001	98	3	92	2	89	4
156	*Trans*-permethrin	57.4-106.6	90.4	0.9990	0.00025-0.05	0.001	86	4	86	1	83	6
157	Perthane (Ethylan)	48.58-90.22	72.6	0.9994	0.0001-0.05	0.001	90	1	88	2	86	6
158	Phenothrin	277.34-515.06	464.1	0.9995	0.001-0.05	0.005	<LOQ	<LOQ	93	7	90	6
159	Phorate	318.71-591.89	445.8	0.9972	0.00025-0.05	0.001	98	8	89	5	85	5
160	Phosalone	39.34-73.06	55.1	0.9998	0.0001-0.05	0.001	83	3	79	2	74	7
161	Phosmet	47.74-88.66	72.5	0.9993	0.00025-0.05	0.001	71	7	62	5	57	9
162	Phthalimide	45.22-83.98	64.7	0.9976	0.005-0.500	0.010	98	10	87	2	84	5
163	Piperonyl butoxide	68.32-126.88	102	0.9987	0.0001-0.05	0.001	90	3	90	2	88	6
164	Pirimiphos-ethyl	35.42-65.78	50.8	0.9986	0.0001-0.05	0.001	91	6	87	1	85	5
165	Pirimiphos-methyl	62.51-116.09	84.4	0.9994	0.0001-0.05	0.001	90	3	90	2	87	5
166	Pretilachlor	35.35-65.65	50.5	0.9986	0.0001-0.05	0.001	87	5	87	2	83	5
167	Prochloraz	120.68-224.12	184.2	0.9996	0.001-0.05	0.005	<LOQ	<LOQ	68	4	64	9
168	Procymidone	39.27-72.93	54.7	0.9983	0.00025-0.05	0.001	88	5	87	4	85	5
169	Prodiamine	26.46-49.14	35.6	0.9966	0.0005-0.05	0.001	93	7	91	4	88	6
170	Profenofos	63-117	91.7	0.9976	0.00025-0.05	0.001	90	6	80	3	77	6
171	Profluralin	8.47-15.73	15	0.9958	0.0005-0.05	0.001	87	16	90	2	88	6
172	Propachlor	166.74-309.66	247.8	0.9988	0.0001-0.05	0.001	89	2	88	3	84	6
173	Propanil	115.64-214.76	169.6	0.9981	0.0005-0.05	0.001	95	9	82	8	80	6
174	Propargite	38.99-72.41	52.3	0.9963	0.001-0.05	0.005	<LOQ	<LOQ	110	6	94	6
175	Propisochlor	50.89-94.51	70	0.9982	0.0005-0.05	0.001	98	3	89	3	85	6
176	Propyzamide	121.03-224.77	171.9	0.9985	0.00025-0.05	0.001	89	4	88	2	86	6
177	Prothiofos	66.78-124.02	98.8	0.9989	0.00025-0.05	0.001	89	5	87	2	84	5
178	Pyraclofos	18.06-33.54	25.9	0.9992	0.0005-0.05	0.001	61	8	62	6	58	9
179	Pyrazophos	131.32-243.88	177.6	0.9999	0.00025-0.05	0.001	81	10	83	4	77	8
180	Pyridaben	33.53-62.27	47.9	0.9983	0.0001-0.05	0.001	90	3	87	2	84	6
181	Pyridaphenthion	21.28-39.52	32.5	0.9998	0.00025-0.05	0.001	94	10	79	6	76	7
182	Pyrimethanil	40.81-75.79	58.5	0.9993	0.0005-0.05	0.001	97	11	95	3	90	7
183	Pyriproxyfen	76.02-141.18	105.9	0.9990	0.0001-0.05	0.001	90	2	89	2	87	5
184	Quinalphos	15.96-29.64	23.6	0.9974	0.0005-0.05	0.001	87	8	83	3	83	6
185	Quintozene	59.01-109.59	86.6	0.9973	0.0001-0.05	0.001	92	6	87	2	84	6
186	Resmethrin peak 1	8.26-15.34	5.4	0.8109	0.005-0.05	-	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
187	Resmethrin peak 2	57.12-106.08	98.1	0.9989	0.001-0.05	0.005	<LOQ	<LOQ	93	4	89	6
188	Sulfotep	68.04-126.36	101.9	0.9980	0.0001-0.05	0.001	90	5	88	3	85	5
189	Sulprofos	82.04-152.36	111.4	0.9984	0.0001-0.05	0.001	92	3	87	2	86	5
190	Tebuconazole	60.9-113.1	85.8	0.9992	0.0001-0.05	0.001	93	3	91	4	88	5
191	Tebufenpyrad	35.63-66.17	49.3	0.9992	0.0001-0.05	0.001	92	2	92	2	90	5
192	Tecnazene	59.64-110.76	84.8	0.9991	0.0001-0.05	0.001	91	5	91	1	88	6
193	Tefluthrin	21.63-40.17	31.9	0.9982	0.0001-0.05	0.001	89	3	89	2	86	6
194	Terbacil	36.12-67.08	47.5	0.9987	0.0001-0.05	0.001	81	9	75	4	72	7
195	Terbufos	52.71-97.89	84.8	0.9970	0.0001-0.05	0.001	87	4	87	5	85	6

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Sr. No.	Name of compound	Ion ratio (IR)		R^2	Range (mg/kg)	LOQ (mg/kg)	0.001 mg/k (n=7)		0.005 mg/kg (n=7)		0.010 mg/kg (n=7)	
		*IR range in MMS	#IR at 0.005 (mg/kg)				% Rec	% RSD	% Rec	% RSD	% Rec	% RSD
196	Terbuthylazine	63.42-117.78	89.8	0.9995	0.00025-0.05	0.001	91	5	90	2	86	5
197	Tetrachlorvinphos	69.3-128.7	91.1	0.9989	0.0001-0.05	0.001	84	6	75	4	71	8
198	Tetradifon	66.92-124.28	91.5	0.9992	0.0005-0.05	0.001	85	5	89	2	87	6
199	Tetrahydrophthalimide (THPI)	98.49-182.91	141.3	0.9989	0.0025-0.500	0.010	113	5	95	2	90	6
200	Tetramethrin peak 1	101.01-187.59	130.3	0.9988	0.001-0.05	0.005	<LOQ	<LOQ	99	4	92	7
201	Tetramethrin peak 2	56.14-104.26	85.3	0.9980	0.00025-0.05	0.001	96	3	90	2	87	7
202	Tolclofos-methyl	183.12-340.08	261.1	0.9981	0.00025-0.05	0.001	91	3	87	2	84	6
203	Tolylfluanid	40.04-74.36	53.1	0.9986	0.0001-0.05	0.001	86	4	85	2	82	6
204	Transfluthrin	52.78-98.02	74.1	0.9979	0.00025-0.05	0.001	92	2	88	2	85	6
205	Triadimefon	74.9-139.1	117.6	0.9991	0.00025-0.05	0.001	92	4	90	3	87	5
206	Triadimenol	80.99-150.41	114.9	0.9994	0.0005-0.05	0.001	81	4	78	8	85	6
207	Triallate	37.24-69.16	56.4	0.9988	0.0005-0.05	0.001	90	3	89	3	86	6
208	Triazophos	60.9-113.1	84.6	0.9979	0.00025-0.05	0.001	85	5	78	4	75	7
209	Triflumizole	19.25-35.75	29.5	0.9966	0.0005-0.05	0.001	102	8	88	5	87	7
210	Trifluralin	40.6-75.4	58.3	0.9973	0.0005-0.05	0.001	90	5	90	2	87	5
211	Triphenylphosphate	30.59-56.81	44.3	-	ISTD	-	Internal standard					
212	Vinclozolin	53.55-99.45	64.8	0.9976	0.0001-0.05	0.001	90	3	87	4	86	7

* Ion ratio range in MMS (Matrix-Matched standard) calculated from average calibration points.
# Ion Ratio observed at 0.005 (mg/kg) concentration spiked in apple matrix.

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