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Application News

LCMS™-8045 and GCMS-TQ™8040

Method for the determination of 326 Residual Pesticides in Rice using LCMS-8045 and GCMS-TQ8040 NX

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User Benefits

- A modified QuEChERS extraction procedure has been employed for quantifying the pesticides at the desirable concentration levels by using Ultra-fast technologies of LCMS™-8045 and GCMS-TQ™8040 NX.
- Shorter run time of analysis increases the productivity and throughput of the LC-MS/MS and GC-MS/MS system.
- Method employs lower injection volume and lesser flow rate, enhancing column life and stability of assay over longer durations of analysis.

1. Introduction

Rice is the most widely consumed staple food for a large part of the world's human population, especially in Asia. It is the agricultural commodity with the third-highest worldwide production. To meet the continuous demand of consumption and to increase the yield rate, several pesticides and chemicals are used during the entire life cycle of rice crop. Therefore, Maximum Residual Limits (MRL) are listed by various international regulatory bodies for wide variety of pesticides. Thus, increasing the importance of analytical method for determination of a range of pesticides present in rice.

Based on these requirements, Shimadzu Application Development Center (ADC) has developed and validated a simple, sensitive and high throughput multiclass, multiresidue method for the determination of 326 pesticides in rice by using LCMS-8045 and GCMS-TQ8040 NX. The multi-residue extraction was performed with modified QuEChERS[1] method for simultaneous quantification of 220 pesticides by LC-MS/MS and 158 pesticides by GC-MS/MS. Out of these, 52 pesticides were common and analyzed by both the techniques. Regulation wise coverage of number of pesticides is shown in Table 1.

Table 1 Coverage of pesticides as per regulations

Compliance / Regulation	No. of compounds regulated	No. of compounds covered in this method
FSSAI	105	62
EU	475	243
JAPAN	310	130
APEDA	275	127

2. Materials and Methods

The reference standards were procured from Restek with below catalogue numbers:
LC multi residue pesticides kit – 31971
GC multi residue pesticides kit – 32562
Rice sample procured from local market, was used to prepare matrix-matched calibration standards and fortified samples. The calibration standards were analyzed in the range of 2 to 20 µg/L. Calibration curves were generated by external standard method and using weighted regression of $1/C^2$. Fortified samples were prepared in six replicates of each 10 and 20 µg/kg. The compounds marked with asterisk (*) in summary result tables 4 and 5; were present in both LCMS and GCMS standard mixture. Hence their calibration curve range and spiking levels were two times the concentration levels mentioned above.

Shimadzu LCMS-8045 with Nexera X2 (Fig. 1) and GCMS-TQ8040 NX (Fig. 2), manufactured by Shimadzu Corporation Japan, were used to quantify residual pesticides in rice sample.

Shimadzu's Method Package Ver.3 for LC-MS/MS and Smart Pesticides Database Ver.2 for GC-MS/MS enabled quick instrumental method optimization for higher throughput. For most of the compounds, 1 target and 2 reference MRM transitions were included in the method.

Shimadzu's data processing software LabSolutions Insight™ was used for data processing, which helped in evaluating validation parameters with ease.

2.1. Sample preparation

In this study, single extraction approach was used for LC-MS/MS and GC-MS/MS. The procedure involved modified QuEChERS method. Acidified ethyl acetate and anhydrous sodium sulphate were used in optimised proportion to get maximum recoveries of pesticides.

After extraction, the aliquot was divided in two parts. For LC-MS/MS, clean up was performed using C-18 and PSA (Primary secondary amine). For GC-MS/MS, clean up was performed using C-18, PSA and anhydrous $MgSO_4$. The clean up was optimized to minimise matrix interference, reduce instrument contamination and achieve lower LOQs.

After clean up, supernatant was evaporated and reconstituted in mobile phase and ethyl acetate for LC-MS/MS and GC-MS/MS, respectively. The final reconstitution volume was adjusted such that fortified samples concentration is diluted by four times in LC-MS/MS and two times in GC-MS/MS.

All samples were analysed as per conditions shown in Table 2 and 3 for LC-MS/MS and GC-MS/MS, respectively.

Fig. 1 Shimadzu LCMS™-8045

Fig. 2 Shimadzu GCMS-TQ™8040 NX

2.2. Analytical Conditions

Table 2 Instrument configuration and Analytical Conditions: LC-MS/MS

System Configuration	
LC-MS/MS	: LCMS-8045
Auto-sampler	: Nexera X2 SIL-30AC
Column	: Shim-pack™ XR-ODS II, (150 mm × 3.0 mmI.D., 2.2 µm)

LC	
Flow rate	: 0.4 mL/min
Mobile phase A	: 2 mM Ammonium formate in water + 0.02% Formic acid
Mobile phase B	: 2 mM Ammonium formate in methanol + 0.02% Formic acid
Gradient program	: 90-10%B (1.0 min to 4.5 min) → 45-50%B (4.5 min to 15.75 min) → 0-100%B (15.75 min to 18.0 min) → 97-3%B (18.0 min to 21.0 min)
Run time	: 21 min
Injection volume	: 10 µL (Co-injection with water)
Column oven temp	: 40 °C

MS	
Ionization	: ESI
Nebulizing gas flow	: 3 L/min
Heating gas flow	: 10 L/min
Drying gas flow	: 10 L/min
Interface temp.	: 300 °C
DL temp.	: 250 °C
Heating block temp.	: 400 °C

Table 3 Instrument configuration and Analytical Conditions: GC-MS/MS

System Configuration	
GC-MS/MS	: GCMS-TQ8040 NX
Auto-injector	: AOC™-20i + s
Column	: SH-I-5Sil MS (30 m × 0.25 mm I.D., df = 0.25 µm)
Liner	: Topaz Liner, Splitless Single Taper w/Wool

GC	
Injector temp.	: 280 °C
Column oven temp	: 60 °C (1 min), 40 °C/min to 170 °C (0 min), 10 °C/min to 310 °C (7.25 min)
Run time	: 25 min
Injection mode	: Splitless (High pressure at 250 kPa)
Injection volume	: 1 µL
Carrier gas	: He
Linear Velocity	: 36.5 cm/sec (Constant mode)

MS	
Ionization mode	: EI
Interface temp.	: 300 °C
Ion source temp.	: 230 °C
Solvent cut time	: 3.5 min
Loop Time	: 0.5 sec

3. Result and Discussion

Validation parameters like specificity, linearity, recovery and precision were studied as per SANTE guidelines[2]. Results obtained on LC-MS/MS and GC-MS/MS are shown in Table 4 and 5, respectively.

3.1. System precision and specificity

System precision was evaluated by calculating variation of the peak area and retention time of six injections of 10 µg/L pesticide mixture. The %RSD of peak area for 207 compounds on LC-MS/MS and 149 compounds on GC-MS/MS was found to be less than 20%. The retention times' %RSD was within 1 for 218 and 159 compounds on LC-MS/MS and GC-MS/MS, respectively. Specificity of the method was determined by comparing the response of blank sample (reagent and matrix) against reporting level. Response in reagent/matrix blank sample was well within 30% of the reporting limit and met the acceptance criteria.

3.2. Linearity study

For linearity study, matrix-matched calibration standards were used. Calibration curve ranged from 2 to 20 µg/L (4 to 40 µg/L for compounds marked with * in summary results tables 4 and 5). All calibration standards were found within 80 to 120% accuracy as per SANTE guidelines. The linearity graphs of some representative compounds are shown in Figure 3 and 4.

3.3. Recovery study

Recovery was evaluated by analysing fortified samples at 10 and 20 µg/kg (20 and 40 µg/kg for * marked compounds in summary result tables 4 and 5) (six replicates at each level) against matrix-matched calibration curve. Mean recoveries for most of the compounds were found within 70-120%. As per SANTE guidelines, all the compounds were found to be reproducible with 20 %RSD at their LOQ levels.

3.4. Precision study

For precision, repeatability and within-laboratory reproducibility studies were carried out. Concentrations of fortified samples were back calculated against matrix matched linearity.

Repeatability (RSD_r):

Repeatability experiment was performed by injecting six replicates at 10 µg/kg and 20 µg/kg concentration levels. The %RSD for repeatability of six injections at their respective LOQ levels were found to be less than 20%. (Refer to Tables 4 and 5)

Reproducibility (RSD_R):

Reproducibility experiment for recoveries was performed on six different fortified samples at 10 µg/kg and 20 µg/kg concentration levels. The %RSD for recovery of six fortified samples at their respective LOQ levels were found to be less than 20%, except 17 compounds in GC-MS/MS in Table 5. (Refer to Tables 4 and 5)

Table 4 Summary results of LC-MS/MS analysis

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision	
									% RSD_R (n=6)	% RSD_r (n=6)
1	Methamidophos	2.65	142.20>93.95	-15	0.997	0.01	104.48	54.20	4.61	2.91
2	Acephate	3.12	184.00>143.00	-10	0.998	0.01	107.94	61.82	2.10	2.38
3	Omethoate	3.67	214.10>183.00	-11	0.999	0.01	106.13	65.25	2.86	2.18
4	Aldicarb-sulfoxide	3.98	207.10>89.10	-14	0.998	0.01	107.26	70.42	6.57	5.44
5	Dinotefuran	4.07	203.15>114.15	-13	0.999	0.01	107.9	72.75	2.61	4.30
6	Butocarboxim-sulfone	4.22	240.10>222.95	-4	0.998	0.01	106.65	89.61	4.55	5.94
7	Aldicarb-sulfone (Aldoxycarb)	4.38	240.10>86.20	-21	0.996	0.01	101.82	98.32	4.67	2.19
8	Oxamyl	4.51	237.10>72.10	-22	0.992	0.01	104.33	92.01	3.85	0.41
9	Aminocarb	4.59	209.00>152.05	-5	0.997	0.01	104.98	93.64	7.83	4.46
10	Nitenpyram	4.59	271.10>225.00	-12	0.998	0.01	100.14	60.07	12.27	10.58
11	Methomyl	4.98	163.00>87.90	-10	0.997	0.01	103.81	101.73	4.26	5.60
12	Thiamethoxam	5.1	292.00>211.10	-13	0.973	0.01	105.82	90.75	5.04	6.88
13	Flonicamid	5.11	230.10>203.00	-16	0.998	0.02	109.64	100.85	14.66	7.78
14	Monocrotophos	5.15	240.90>127.10	-21	0.996	0.01	110.45	101.75	10.46	7.64
15	Dicrotophos	5.45	237.90>72.00	-26	0.986	0.01	100.84	100.39	8.31	3.30
16	Imidacloprid	5.73	256.10>209.00	-17	0.999	0.01	104.86	100.69	7.30	5.49
17	Carbendazim	5.77	192.10>160.15	-6	0.996	0.01	105.11	95.05	7.46	4.21
18	Clothianidin	5.84	250.00>169.10	-13	0.984	0.01	115.53	103.08	5.42	4.60
19	Vamidothion	6	288.10>146.05	-6	0.998	0.01	108.69	95.49	6.08	1.41
21	Mevinphos*	6.05	225.10>127.00	-17	0.997	0.02	105.46	98.38	3.61	2.41
20	3-Hydroxycarbofuran	6.05	255.00>163.15	-19	0.990	0.01	117.67	104.16	4.54	5.27
22	Acetamiprid	6.09	223.10>126.10	-11	0.993	0.01	102.31	96.29	4.85	1.45
23	3,4,5-Trimethacarb	6.14	194.10>137.10	-2	0.997	0.01	98.83	83.58	12.33	4.73
24	Dioxacarb	6.14	224.10>123.00	-16	0.998	0.01	108.42	76.38	15.11	5.96
25	Dimethoate	6.17	230.00>198.90	-4	0.999	0.01	101.38	99.55	6.90	4.20
26	Fenuron	6.17	165.00>46.10	-14	0.998	0.01	103.96	96.85	5.93	2.56
27	Trichlorfon	6.2	257.00>109.00	-17	0.998	0.01	114.44	107.14	9.58	5.48
28	Thiacloprid	6.42	253.00>126.05	-11	0.994	0.01	107.92	100.94	4.65	4.08
29	Thiabendazole	6.43	202.00>131.15	-27	0.998	0.01	94.36	90.05	12.50	6.10
30	Cymoxanil	6.46	199.10>128.15	-9	0.995	0.01	95.81	101.49	11.90	8.76
31	Fuberidazole	6.61	184.90>156.15	-17	0.995	0.01	99.09	85.20	7.35	5.84
32	Tricyclazole*	6.78	190.10>136.00	-24	0.997	0.02	105.97	103.98	16.44	3.37
33	Oxadixyl	6.89	296.20>279.05	-8	0.994	0.01	108.24	100.89	7.07	9.55
34	Metalaxyl-M (Mefenoxam)	6.9	280.20>220.00	-6	0.996	0.01	100.91	115.98	11.36	7.41
35	Allidochlor	7.17	174.10>98.05	-14	0.983	0.01	113.34	83.37	13.00	5.61
36	Carbetamide	7.19	237.10>192.10	-5	0.994	0.01	110.8	89.37	5.98	6.22
37	N-(2,4-Dimethylphenyl)formamide	7.32	150.10>107.10	-21	0.991	0.01	118.45	102.14	12.00	9.81
38	Thiophanate-methyl	7.36	343.00>311.00	-11	0.992	0.01	107.55	94.74	22.16	5.10
39	Fenamiphos-sulfoxide	7.37	320.10>171.00	-24	0.999	0.01	117.37	114.11	14.71	14.97
40	Propoxur	7.52	209.90>168.15	-9	0.999	0.01	109	95.83	9.43	7.05
41	Thidiazuron	7.56	221.00>102.00	-16	0.993	0.01	115.42	85.56	14.55	3.35
42	Carbofuran	7.58	222.10>165.00	-6	0.996	0.01	105.59	98.87	7.24	5.25
43	Dimethirimol	7.8	210.20>140.10	-22	0.975	0.01	101.27	83.06	6.16	4.98
44	Ethirimol	7.8	210.20>140.20	-16	0.997	0.01	107.72	80.99	12.73	6.46
45	Tebuthiuron	7.82	229.10>116.00	-27	0.987	0.01	101.27	95.15	8.87	8.67
46	Hexazinone	7.84	253.20>171.15	-6	0.984	0.01	99.52	91.79	5.29	3.04
47	Carbaryl (NAC)	7.87	202.10>145.10	-12	0.995	0.01	101.18	101.99	4.21	5.54
48	Metribuzin	7.87	215.10>187.10	-18	0.999	0.01	110.89	92.81	9.39	9.79
49	Carboxin	7.92	236.10>143.10	-5	0.990	0.01	103.11	86.28	5.20	3.96
50	Pyracarbolid	7.92	218.10>125.10	-8	0.994	0.01	106.74	94.01	9.09	8.54
51	Ethiofencarb	8.12	226.10>107.00	-21	0.999	0.01	104.7	97.49	3.54	3.06
52	Spiroxamine	8.13	298.20>144.20	-10	0.997	0.02	102.15	52.45	14.16	10.34
53	Diuron (DCMU)	8.15	233.00>46.15	-17	0.998	0.01	104.77	104.46	11.74	9.22
54	Pirimicarb	8.15	239.20>72.00	-13	0.999	0.01	94.26	94.56	6.24	6.13
55	Fluometuron	8.17	233.10>46.20	-18	0.988	0.01	104.75	87.94	13.22	9.62
56	Monolinuron	8.19	215.10>148.00	-15	0.999	0.01	105.38	89.10	9.16	8.24

Table 4 Summary results of LC-MS/MS analysis (Contd.)

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision	
									% RSD_R (n=6)	% RSD_r (n=6)
57	Phorate-sulfone	8.2	293.00>96.90	-34	0.977	0.01	102.56	91.29	17.73	9.08
58	Disulfoton-sulfoxide	8.23	290.80>97.00	-34	0.996	0.01	110.98	109.84	4.39	5.76
59	Phorate-sulfoxide	8.24	277.00>198.90	-10	0.997	0.01	118.78	79.75	17.41	11.88
60	Flutriafol*	8.33	302.10>70.05	-22	0.998	0.02	97.44	101.26	8.94	4.80
61	Chlorotoluron	8.37	213.10>46.10	-10	0.999	0.01	87.78	100.92	11.97	9.60
62	Simetryn	8.4	214.10>96.00	-20	0.985	0.01	113.49	88.39	19.91	14.23
63	Isoprocarb	8.46	194.10>95.00	-11	0.997	0.01	110.02	100.20	6.83	7.10
64	Propham	8.48	180.10>138.00	-12	0.999	0.02	107.18	91.86	12.86	5.67
65	Metazachlor	8.5	277.90>210.05	-6	0.996	0.01	106.28	101.46	6.36	5.53
66	Metobromuron	8.5	259.00>170.00	-19	0.990	0.01	97.23	104.32	16.35	8.30
67	Metalaxyl*	8.6	280.10>220.00	-6	0.994	0.02	117	90.92	5.68	5.78
68	Desmedipham	8.62	318.00>182.00	-6	0.976	0.02	103.6	100.13	11.22	13.03
69	Atrazine	8.63	216.10>174.10	-13	0.998	0.01	104.57	97.31	10.18	8.00
70	Propachlor	8.64	212.10>170.10	-6	0.998	0.02	101.47	97.59	8.59	4.29
71	Isoproturon	8.66	207.20>46.10	-12	0.993	0.01	95.64	97.36	5.22	6.20
72	Forchlorfenuron	8.67	248.10>129.15	-17	0.976	0.01	103.51	90.14	7.00	7.88
73	Lenacil	8.68	234.90>153.15	-6	0.998	0.01	100.87	90.44	12.07	16.67
74	Methabenzthiazuron	8.69	222.10>150.10	-32	0.958	0.01	94.42	84.04	15.57	9.83
75	Norflurazon	8.69	304.10>283.95	-18	0.975	0.01	119.06	90.08	14.54	13.64
76	Phenmedipham	8.77	318.10>168.10	-14	0.970	0.01	120	93.50	4.43	6.35
77	Chlorantraniliprole	8.79	483.90>452.90	-19	0.962	0.01	110.56	88.59	14.12	7.14
78	Diphenamid	8.87	239.90>134.15	-6	0.999	0.02	97.71	94.57	14.72	15.09
79	Fluridone	8.87	330.10>309.00	-31	0.996	0.01	108.47	92.42	7.83	14.16
80	Secbumeton	8.87	226.20>142.10	-12	0.984	0.02	100.6	90.19	8.74	5.85
81	Prometon	8.88	226.20>142.00	-12	0.986	0.01	101.64	104.78	23.55	15.12
82	Cycluron	8.92	199.20>88.95	-10	0.994	0.01	99	99.58	10.64	6.81
83	Monuron	9.06	199.10>46.10	-17	0.970	0.01	96.41	97.05	12.43	6.80
84	Azoxystrobin	9.07	404.00>371.95	-5	0.987	0.01	110.09	95.76	6.56	11.60
85	Dimethachlor	9.08	256.10>224.00	-5	0.986	0.01	97.15	95.47	11.55	4.67
86	Azinphos-methyl	9.1	318.00>160.15	-7	0.996	0.01	107.95	82.92	12.83	7.67
87	Phosmet	9.18	318.00>77.00	-47	0.999	0.01	107.84	94.96	5.90	6.17
88	Mexacarbate	9.19	223.10>151.15	-14	0.999	0.01	110.9	103.97	10.63	4.78
89	Terbumeton	9.2	225.90>170.00	-6	0.997	0.01	108.68	84.33	6.18	12.64
90	Furalaxyl	9.26	302.10>95.00	-17	0.994	0.01	98.6	80.20	17.72	12.41
91	Clomazone	9.3	239.90>125.00	-11	0.996	0.01	119.82	77.88	13.79	4.76
92	Methoprotryne	9.35	272.20>240.00	-13	0.994	0.02	92.47	77.38	18.43	7.65
93	Ametryn	9.41	228.10>186.00	-9	0.993	0.01	114.99	85.69	14.13	5.23
94	Fludioxonil*	9.48	247.00>180.15	28	0.990	0.02	112.19	100.62	8.82	11.13
95	Boscalid	9.59	343.00>306.95	-11	0.994	0.01	101.12	107.95	16.85	10.65
96	Flutolanil*	9.61	324.10>242.00	-20	0.979	0.02	106.82	98.00	13.07	5.70
97	Methiocarb	9.62	226.10>121.10	-19	0.983	0.01	100.85	79.23	11.63	7.72
98	Methoxyfenozide	9.71	369.20>149.15	-8	0.977	0.02	104.8	91.01	14.21	11.06
99	Sebuthylazine	9.73	230.10>174.05	-8	0.998	0.01	109.79	73.61	12.69	16.08
100	Terbuthylazine	9.74	230.10>174.05	-7	0.993	0.01	107.5	75.36	27.06	10.12
103	Paclobutrazol*	9.75	294.10>70.10	-22	0.998	0.02	97.72	91.40	11.77	4.71
101	Benzthiazuron	9.75	208.10>151.10	-6	0.992	0.01	103.02	85.70	13.91	6.49
102	Dimethomorph (E, Z)	9.75	388.10>165.10	-34	0.999	0.01	92.37	105.49	6.67	11.08
104	Malathion	9.76	348.10>127.05	-17	0.988	0.02	111.46	97.95	6.72	12.36
105	Pyrimethanil*	9.77	200.10>107.00	-24	0.984	0.02	103.63	71	7.73	5.76
106	Promecarb	9.78	208.10>109.10	-10	0.996	0.01	105.17	89.00	17.44	7.02
107	Mepronil	9.83	270.20>119.05	-13	0.997	0.01	107.77	81.35	8.76	8.22
108	Pyridaphenthion	9.88	341.10>188.95	-12	0.988	0.01	106.64	73.79	11.80	9.67
109	Myclobutanil*	9.89	289.10>70.05	-22	0.994	0.02	106.12	75.45	15.27	9.42
110	Triadimefon*	9.91	294.10>69.00	-22	0.995	0.02	101.77	73.01	17.15	8.41
111	Bifenazate	9.95	301.10>170.00	-14	0.942	0.02	96.36	35.86	13.63	7.02
112	Butafenacil	9.98	492.10>330.85	-14	0.998	0.01	112.02	94.03	16.90	5.76

Table 4 Summary results of LC-MS/MS analysis (Contd.)

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision	
									% RSD_R (n=6)	% RSD_r (n=6)
113	Propyzamide	9.98	256.00>190.00	-14	0.991	0.01	109.05	98.41	19.02	7.24
114	Triazophos	9.98	314.10>162.05	-9	0.994	0.01	106.74	85.74	10.65	5.54
115	Fluoxastrobin	10	458.80>427.00	-7	0.997	0.01	111.16	72.76	11.92	11.75
116	Isoxathion	10.01	314.00>105.15	-5	0.983	0.01	102.41	97.23	1.44	3.41
117	Spinosyn A	10.03	732.60>142.20	-29	0.996	0.01	98.26	84.32	8.52	7.80
118	Mefenacet	10.04	299.00>148.15	-6	0.994	0.01	94.72	101.13	9.80	5.32
119	Spirotetramat	10.07	374.10>216.00	-23	0.998	0.01	118.58	94.34	8.80	10.77
120	Isazofos	10.09	314.10>120.00	-18	0.997	0.01	104.68	97.19	17.34	15.16
121	Chloroxuron	10.1	291.10>72.15	-8	0.994	0.02	90.06	70.51	12.82	8.49
122	Triadimenol*	10.11	296.10>70.05	-22	0.997	0.04	104.58	88.52	10.36	7.47
123	Bromuconazole	10.13	377.90>159.05	-26	0.988	0.02	87.71	89.36	19.68	10.36
124	Iprovalicarb	10.14	321.20>119.15	-6	0.999	0.01	109.21	95.79	10.96	9.50
125	Tetraconazole	10.16	372.00>159.00	-30	0.995	0.01	95.61	98.11	11.74	7.94
126	Fluquinconazole*	10.18	376.00>349.00	-20	0.997	0.02	110.04	99.05	6.29	14.86
127	Cyproconazole	10.2	292.10>70.05	-22	0.979	0.01	86.85	75.50	13.21	13.40
128	Fenhexamid	10.22	302.10>97.10	-24	0.981	0.02	113.23	84.05	15.95	6.48
129	Flufenacet	10.22	364.10>152.05	-9	0.988	0.01	94.4	88.45	8.48	5.63
130	Prometryn	10.23	242.10>158.00	-12	0.988	0.01	95.69	82.49	13.29	10.68
131	Terbutryn	10.24	242.10>157.95	-10	0.999	0.01	108.64	79.91	10.02	8.47
133	Fenarimol*	10.3	331.00>268.00	-23	0.994	0.02	116.43	100.81	17.81	16.78
132	Azinphos-ethyl	10.3	346.00>97.00	-33	0.998	0.01	91.92	74.02	14.30	11.60
134	Fipronil*	10.32	435.00>330.00	16	0.999	0.02	113.15	88.00	8.12	2.39
135	Triticonazole	10.34	318.10>70.15	-22	0.991	0.01	114.16	100.15	9.88	5.69
136	Cyazofamid	10.36	325.00>108.10	-15	0.998	0.01	110.8	91.93	17.37	5.35
137	Mepanipyrim	10.39	224.10>77.00	-41	0.993	0.01	113.69	80.51	10.61	8.35
138	Epoxiconazole	10.4	330.00>121.10	-11	0.977	0.01	109.2	96.69	19.63	12.12
139	Fenbuconazole	10.4	337.10>125.05	-29	0.992	0.01	85.56	78.81	14.28	15.12
140	Etaconazole	10.47	328.10>159.00	-28	0.980	0.02	84.46	85.52	17.3	15.31
141	Spinosyn D	10.49	746.60>142.10	-30	0.986	0.01	90.34	78.65	13.88	12.76
142	Picoxystrobin	10.5	368.00>145.10	-12	0.999	0.01	117.71	94.55	19.53	10.46
143	Tebufenozide	10.51	353.20>133.10	-11	0.998	0.01	110.06	80.71	17.29	19.72
144	Flusilazole*	10.53	316.10>247.00	-13	0.994	0.04	99.94	83.25	11.37	4.07
145	Spinetoram J	10.53	748.50>142.15	-26	0.990	0.01	106.51	61.35	7.93	5.42
146	Fenamiphos	10.55	304.10>216.95	-13	0.997	0.01	109.69	92.04	13.07	17.01
147	Rotenone	10.57	395.10>213.00	-23	0.997	0.02	101.01	86.73	10.34	10.12
148	Diflubenzuron	10.58	311.00>158.10	-16	0.998	0.01	118.13	79.78	8.68	10.94
150	Bupirimate*	10.59	317.20>166.00	-19	0.999	0.02	112.74	90.94	7.52	4.45
149	Alachlor	10.59	270.10>238.00	-11	0.958	0.01	106.25	86.15	10.19	5.73
151	Metolachlor	10.62	284.10>252.05	-6	0.996	0.01	110.35	91.77	8.15	10.34
152	Fenoxycarb	10.65	302.10>88.00	-12	0.987	0.01	108.69	86.22	10.72	7.20
153	Tetrachlorvinphos	10.75	366.90>127.15	-16	0.959	0.02	96.53	90.81	12.59	7.5
154	Dimoxystrobin	10.76	327.10>116.10	-12	0.981	0.01	106.32	86.44	8.59	6.53
155	Neburon	10.79	274.80>87.95	-17	0.995	0.01	101.98	99.13	11.22	5.76
156	Sulfotep	10.87	323.00>97.00	-27	0.984	0.01	106.42	89.83	8.61	7.34
157	Kresoxim-methyl	10.92	314.10>267.00	-8	0.992	0.01	111.63	86.54	9.52	11.18
158	Famoxadone	10.95	391.90>331.25	-10	0.999	0.02	111.05	70.45	19.02	10.65
159	Quinalphos	10.95	299.10>147.05	-17	0.997	0.01	89.75	86.18	10.16	7.06
160	Edifenphos	10.96	311.00>109.00	-17	0.998	0.01	93.89	86.55	11.28	11.81
161	Tebuconazole*	10.98	308.20>70.05	-22	0.999	0.02	98.99	76.90	12.88	7.48
162	Spinetoram L	11.02	760.60>142.10	-31	0.982	0.01	82.44	70.01	7.21	7.83
164	Penconazole*	11.03	284.10>70.05	-17	0.996	0.02	110.27	86.86	5.57	3.60
163	Emamectin B1a	11.03	886.40>158.20	-31	0.992	0.01	95.48	56.12	11.80	9.22
165	Chlorfenvinphos (E, Z)	11.09	359.00>169.95	-39	0.992	0.01	112.67	102.56	12.52	6.39
166	Coumaphos	11.09	363.00>227.00	-16	0.975	0.01	113	85.10	7.55	17.57
167	Benalaxyl	11.1	326.20>148.10	-11	0.995	0.01	115.43	100.49	12.36	8.54
168	Triflumuron	11.19	359.00>156.05	-17	0.994	0.02	110.93	70.02	10.74	6.78

Table 4 Summary results of LC-MS/MS analysis (Contd.)

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision	
									% RSD_R (n=6)	% RSD_r (n=6)
169	Cyprodinil*	11.2	226.10>93.00	-37	0.950	0.02	108.07	43.87	12.94	8.09
170	Pyraclostrobin	11.21	388.00>163.10	-14	0.998	0.01	102.1	92.16	7.26	3.99
171	Diazinon	11.22	305.10>169.10	-12	0.982	0.01	94.24	79.21	10.25	8.17
172	Bromfenvinphos	11.25	404.90>155.10	-13	0.959	0.01	105.55	92.75	7.54	9.01
173	Prothioconazole	11.25	344.00>154.00	-45	0.993	0.02	103.94	81.83	14.93	17.55
174	Zoxamide	11.25	336.00>186.95	-18	0.997	0.01	109.88	86.31	9.42	8.45
175	Hexaconazole	11.33	314.10>70.00	-22	0.981	0.01	96.81	65.35	17.71	12.64
176	Pyraclofos	11.33	361.10>256.90	-22	0.991	0.01	105.73	66.25	12.04	5.50
178	Prochloraz*	11.37	376.00>307.95	-8	0.990	0.02	114.74	75.58	13.24	6.33
177	Metconazole	11.37	320.10>70.15	-23	0.997	0.01	104.88	79.16	14.12	7.33
179	Phosalone	11.38	368.00>182.00	-17	0.998	0.01	107.52	71.42	9.51	5.85
180	Indoxacarb	11.48	528.10>203.00	-37	0.995	0.01	91.6	79.25	15.82	13.50
181	Pyrazophos	11.48	374.10>222.05	-12	0.998	0.01	98.34	90.35	12.22	9.01
182	Pencycuron	11.49	329.10>125.00	-10	0.998	0.01	96.28	82.91	13.26	3.52
183	Novaluron	11.57	493.00>158.00	-18	0.993	0.01	115.48	62.64	10.15	13.14
184	Pirimiphos-methyl	11.58	306.10>164.10	-18	0.985	0.01	117.34	86.88	13.83	7.60
185	Clofentezine	11.59	303.00>102.10	-37	0.983	0.01	102.46	62.95	15.64	7.27
186	Trifloxystrobin	11.63	409.10>186.10	-6	0.993	0.01	103.08	79.35	6.28	6.21
187	Difenoconazole (isomer)	11.64	406.10>250.90	-20	0.997	0.01	105.5	80.62	12.28	4.85
188	Orbencarb	11.69	258.10>125.10	-11	0.995	0.01	98.89	65.42	8.44	8.44
189	Thiobencarb	11.69	257.80>125.10	-11	0.995	0.01	103.12	68.19	15.20	6.88
190	Triflumizole*	11.89	346.00>278.00	-6	0.979	0.02	101.1	61.70	7.78	7.27
191	Ipconazole	11.93	334.10>70.10	-17	0.990	0.01	98.85	47.85	19.17	4.39
192	Pretilachlor	12	312.20>252.05	-7	0.993	0.01	110.97	64.69	16.39	7.11
193	Clethodim (isomer)	12.05	360.10>164.15	-21	0.997	0.01	115.54	68.87	4.86	9.09
194	Cycloate	12.09	216.10>83.00	-17	0.993	0.01	119.67	65.63	18.53	12.93
195	Fluazifop-butyl	12.09	384.20>281.90	-7	0.996	0.02	112.96	62.81	11.56	6.47
196	Fluazifop-P-butyl	12.09	384.10>282.00	-6	0.992	0.02	110.35	59.22	15.3	12.29
197	Lufenuron	12.19	508.90>339.00	12	0.995	0.02	83.04	49.99	19.71	5.16
198	Profenofos	12.25	375.00>304.70	-19	0.998	0.01	104.87	68.21	11.46	3.47
199	Temephos	12.25	467.00>125.00	-38	0.993	0.02	108.69	50.46	16.78	4.12
200	Furathiocarb	12.27	383.20>195.00	-10	0.997	0.01	100.43	77.68	10.52	8.17
201	Tetramethrin	12.36	332.20>164.10	-24	0.987	0.01	100.3	63.41	19.16	10.20
202	Tebufenpyrad*	12.41	334.20>117.00	-25	0.997	0.02	106.5	74.50	13.07	4.28
203	Buprofezin	12.47	306.20>201.05	-6	0.998	0.02	93.17	73.51	9.95	6.23
204	Tolfenpyrad	12.49	384.00>197.10	-26	0.997	0.01	107.19	53.84	17.31	5.40
205	Ethion	12.58	385.00>143.00	-25	0.998	0.01	106.95	55.82	9.52	5.22
206	Pirimiphos-ethyl	12.6	334.10>198.15	-12	0.998	0.01	103.73	73.24	4.17	6.53
207	Chlorpyrifos-oxon	12.63	334.00>277.80	-13	0.998	0.01	99.2	66.29	4.40	5.61
208	Piperonyl butoxide*	12.69	356.20>177.00	-3	0.997	0.02	102.62	54.85	10.67	2.62
209	Flufenoxuron	12.82	489.00>158.10	-21	0.992	0.01	106.79	39.01	16.94	5.50
210	Pyriproxyfen*	12.84	322.10>96.05	-6	0.969	0.02	106.2	56.06	5.96	3.67
211	Hexythiazox	12.9	353.10>228.00	-11	0.984	0.01	105.04	51.55	10.12	11.64
212	Chlorpyrifos	13	350.00>197.95	-21	0.997	0.01	113.68	73.96	12.98	6.30
213	Etoxazole	13.04	360.10>141.10	-15	0.997	0.01	99.59	53.19	10.63	7.98
214	Propargite*	13.06	368.20>231.10	-6	0.994	0.02	109.87	50.21	8.31	6.04
215	Quinoxyfen	13.13	308.00>197.00	-31	0.995	0.01	107.42	37.24	14.56	4.79
216	Pendimethalin	13.15	282.20>212.00	-11	0.995	0.01	106.23	45.80	11.35	5.66
217	Carbophenothion	13.22	343.00>157.05	-13	0.990	0.01	117.71	41.94	9.43	8.92
218	Chlorfluazuron	13.23	539.90>382.85	-20	0.999	0.01	118.5	38.92	12.11	13.38
219	Fenpyroximate	13.36	422.10>366.00	-4	0.992	0.01	115.08	45.17	11.93	4.35
220	Spirodiclofen	13.37	411.10>313.05	-14	0.997	0.01	110.02	43.81	13.97	7.03

Table 5 Summary results of GC-MS/MS analysis

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision	
									% RSD_R (n=6)	% RSD_r (n=6)
1	Allidochlor	4.731	132.10>56.00	8	0.997	0.01	104.00	114.60	15.78	10.29
2	Dichlobenil	5.067	170.90>136.00	14	1.000	0.01	99.00	80.34	22.39	9.13
3	Mevinphos-2*	5.431	127.00>95.00	18	0.995	0.02	109.50	102.94	8.04	6.53
4	Mevinphos-1*	5.432	192.00>127.00	12	0.999	0.02	101.50	107.26	9.72	8.38
5	Etridiazole	5.573	210.90>139.90	22	0.999	0.01	98.50	106.66	10.45	3.53
6	3,4-Dichloroaniline	5.575	161.00>99.00	22	0.996	0.01	99.00	101.03	11.84	9.04
7	Pebulate	5.582	161.10>128.10	6	0.999	0.01	100.50	99.76	6.13	2.41
8	Methacrifos	5.776	240.00>208.00	4	0.993	0.01	101.00	112.74	17.10	7.86
9	Chloroneb	5.886	193.00>113.00	18	0.999	0.01	99.00	92.17	12.09	4.34
10	THPI (Tetrahydrophthalimide)	5.934	151.10>79.00	18	0.995	0.02	90.60	92.02	9.34	4.08
11	2-Phenylphenol	6.071	170.10>141.10	24	0.999	0.01	95.00	96.43	12.42	7.30
12	Pentachlorobenzene	6.082	251.90>214.90	22	0.995	0.01	97.00	127.30	14.06	7.99
13	Tecnazene	6.539	260.90>202.90	14	0.999	0.01	103.00	109.93	18.21	11.19
14	Propachlor	6.600	120.00>77.00	20	0.998	0.01	99.00	113.63	12.65	13.93
15	Ethalfluralin	6.755	276.00>202.00	18	0.992	0.01	94.50	90.76	17.96	14.46
16	Diphenylamine	6.774	169.10>66.00	24	0.999	0.01	99.00	126.83	14.85	11.73
17	2,3,5,6-Tetrachloroaniline	6.821	230.90>158.00	22	1.000	0.01	99.50	91.76	3.86	3.01
18	Trifluralin	6.855	264.10>206.10	8	0.994	0.01	99.50	117.23	18.70	16.00
19	Benfluralin	6.895	292.10>160.00	22	0.997	0.01	96.00	81.33	15.25	6.77
20	Chlorpropham	6.931	127.10>92.00	18	0.993	0.01	102.00	88.59	15.47	5.28
21	Sulfotep	6.965	266.00>146.00	18	0.992	0.01	99.00	101.91	6.41	5.80
22	Di-allate-1	7.180	234.10>192.10	14	0.998	0.01	101.50	78.00	18.61	13.21
23	alpha-BHC	7.355	180.90>144.90	16	0.999	0.01	100.50	86.44	13.91	5.64
24	Hexachlorobenzene	7.438	283.80>213.80	28	0.996	0.01	98.50	106.07	16.58	11.65
25	Pentachloroanisole	7.493	264.80>236.80	16	0.995	0.01	102.00	103.50	16.59	10.73
26	Atrazine	7.661	215.10>58.00	14	0.991	0.01	100.00	87.93	13.47	7.74
27	Profluralin	7.691	318.10>199.10	16	0.997	0.02	100.80	100.75	10.33	5.97
28	Clomazone	7.722	204.10>107.00	20	0.997	0.01	100.50	103.46	10.82	4.94
29	beta-BHC	7.798	180.90>144.90	16	0.995	0.01	100.50	89.83	8.60	9.16
30	Quintozene	7.803	294.80>236.80	16	0.991	0.01	98.50	104.89	9.13	9.85
31	Disulfoton	7.833	186.00>97.00	16	0.994	0.02	89.60	98.43	6.18	6.72
32	Phorate	7.833	231.00>129.00	24	0.999	0.01	100.00	99.76	6.13	2.39
33	Terbufos	7.833	231.00>128.90	26	0.992	0.01	84.00	89.90	11.71	12.11
34	Terbuthylazine	7.859	229.10>173.10	6	0.999	0.01	105.50	116.64	17.52	8.49
35	gamma-BHC (Lindane)	7.869	180.90>144.90	16	0.995	0.01	90.50	88.23	18.77	10.40
36	Diazinon	7.870	179.10>122.10	24	0.996	0.01	92.00	98.70	13.90	8.27
37	Pentachlorobenzonitrile	7.898	274.80>239.80	18	0.994	0.01	101.50	111.39	9.26	7.54
38	Fluchloralin	7.900	326.00>63.00	16	0.997	0.01	99.00	113.11	11.98	11.97
39	Propyzamide	7.919	172.90>144.90	16	0.998	0.01	97.50	93.64	8.38	7.88
40	Fonofos	7.947	137.10>109.10	8	0.979	0.01	100.00	84.31	12.30	8.45
41	Tefluthrin	8.057	177.00>127.10	16	0.999	0.01	92.50	91.17	12.39	9.37
42	Pyrimethanil*	8.073	198.10>158.10	18	0.999	0.02	98.50	95.99	22.72	12.59
43	Isazofos	8.098	257.00>119.00	18	0.997	0.01	99.00	101.64	8.21	7.56
44	Chlorothalonil	8.236	263.90>168.00	24	0.957	0.01	86.00	105.30	11.35	11.66
45	Tri-allate	8.239	268.10>184.00	20	0.992	0.01	96.50	108.00	4.32	6.61
46	Terbacil	8.253	161.00>144.00	14	0.985	0.01	115.00	89.20	6.81	6.70
47	delta-BHC	8.362	180.90>144.90	16	0.993	0.01	109.00	97.94	34.50	17.26
48	Endosulfan ether	8.612	240.90>203.90	18	0.986	0.02	104.40	104.43	6.87	3.21
49	Pentachloroaniline	8.620	262.90>191.90	22	0.997	0.01	99.50	96.20	12.80	3.93
50	Acetochlor	8.694	174.10>146.10	12	0.997	0.02	96.00	96.90	7.49	3.11
51	Chlorpyrifos-methyl	8.745	285.90>93.00	22	0.999	0.01	99.00	108.06	12.95	9.23
52	Vinclozolin	8.790	285.00>212.00	12	0.987	0.02	108.40	98.89	10.22	2.60
53	Tolclofos-methyl	8.871	264.90>93.00	24	0.998	0.02	100.40	100.32	2.80	1.66

Table 5 Summary results of GC-MS/MS analysis (Contd.)

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision	
									% RSD_R (n=6)	% RSD_r (n=6)
54	Parathion-methyl	8.874	125.00>47.00	12	0.994	0.01	98.00	103.53	21.65	17.21
55	Propisochlor	8.910	162.10>120.10	14	0.996	0.01	101.50	98.77	43.21	8.79
56	Metalaxyl –M (Mefenoxam)	8.972	249.20>190.10	8	1.000	0.02	99.40	103.89	19.44	19.18
57	Fenchlorphos	9.030	284.90>239.90	26	0.991	0.01	105.50	94.17	15.34	11.94
58	Heptachlor	9.044	271.80>236.90	20	0.994	0.01	99.00	103.46	68.33	10.86
59	Pirimiphos-methyl	9.161	305.10>290.10	12	0.993	0.02	96.40	106.14	8.34	7.90
60	Prodiamine	9.179	321.10>279.10	6	0.999	0.01	99.00	84.13	7.75	4.29
61	Malathion	9.361	173.10>127.00	6	0.995	0.01	102.00	93.59	8.46	9.34
62	Metolachlor (S-Metolachlor)	9.506	238.10>162.10	12	0.999	0.01	100.00	108.56	17.40	12.87
63	Fenthion	9.604	278.00>109.00	20	0.995	0.01	83.00	88.71	14.78	10.01
64	Chlorthal-dimethyl	9.627	298.90>220.90	24	0.999	0.02	104.60	90.51	8.76	5.87
65	Parathion	9.674	291.10>137.00	6	0.949	0.02	106.20	103.70	2.81	2.89
66	Anthraquinone	9.806	208.10>152.10	22	0.997	0.01	115.50	101.11	17.40	3.57
67	Pirimiphos ethyl	9.839	304.10>168.10	12	0.992	0.01	101.50	96.06	17.96	12.67
68	4,4'-Dichlorobenzophenone	9.868	249.90>139.00	16	0.997	0.01	99.50	102.29	4.06	6.90
69	Diphenamid	9.958	239.10>167.10	8	0.999	0.02	101.00	101.36	6.92	4.03
70	Fenson	9.963	141.00>77.00	16	0.997	0.01	100.00	98.21	20.14	14.98
71	Pendimethalin	10.113	252.10>191.10	8	0.990	0.01	116.50	113.24	12.66	12.84
72	Cyprodinil*	10.177	224.10>197.10	22	0.996	0.04	101.20	86.21	9.62	5.42
73	Fipronil*	10.197	366.90>212.90	30	0.983	0.02	97.50	103.44	13.32	8.80
74	Chlozolinate	10.225	330.90>258.90	6	0.989	0.02	114.80	100.94	6.57	4.84
75	Penconazole*	10.268	248.10>157.10	26	0.989	0.02	81.00	117.97	19.03	16.19
76	(E)-Chlorfenvinphos	10.296	267.00>159.00	18	0.998	0.01	84.00	95.10	6.72	10.84
77	Bromfenvinfos-methyl	10.340	294.90>109.00	16	0.991	0.01	94.50	100.50	8.63	8.57
78	Quinalphos	10.414	146.10>118.00	10	0.999	0.01	99.50	72.71	27.47	10.19
79	Triadimenol*	10.503	168.10>70.00	10	0.986	0.04	98.40	104.42	3.63	7.99
80	Bromophos-ethyl	10.651	358.90>302.90	16	0.988	0.01	99.00	89.11	16.93	10.53
81	Chlorbenside	10.762	125.00>89.00	16	0.994	0.01	102.50	122.86	22.24	14.95
82	o,p'-DDE	10.769	248.00>176.00	28	0.995	0.01	99.50	95.26	4.97	7.57
83	p,p'-DDE	10.769	246.00>176.00	30	0.992	0.01	84.50	112.87	10.55	4.65
84	trans-Chlordane	10.772	374.80>265.90	26	0.998	0.02	98.60	92.02	9.34	4.08
85	Tetrachlorvinphos	10.786	330.90>109.00	22	0.997	0.02	102.80	117.21	16.76	7.35
86	Paclobutrazol*	10.863	236.10>125.00	14	0.990	0.02	81.00	92.37	11.69	6.80
87	Bromfenvinphos	11.017	266.90>159.00	14	0.995	0.01	110.00	104.90	8.20	10.72
88	trans-Nonachlor	11.047	406.80>299.90	24	0.950	0.02	105.60	103.79	3.19	1.46
89	Flutriafol*	11.068	219.10>123.10	14	0.998	0.02	99.00	78.16	6.69	11.92
90	Flutolanil*	11.099	281.10>173.00	12	0.998	0.02	98.50	96.19	10.09	6.21
91	Iodofenphos	11.145	376.90>361.80	22	0.997	0.01	102.50	79.81	28.07	12.96
92	Chlorfenson	11.188	175.00>111.00	12	1.000	0.01	99.50	105.13	15.39	7.75
93	Pretilachlor	11.190	238.10>146.10	10	0.993	0.01	103.00	95.16	27.08	14.97
94	Oxadiazon	11.297	258.00>175.00	8	0.995	0.02	113.60	98.99	5.36	4.00
95	Oxyfluorfen	11.403	361.00>300.00	14	1.000	0.01	100.00	98.29	9.24	6.16
96	Bupirimate*	11.456	273.10>108.10	16	0.996	0.02	103.50	92.37	6.61	3.04
97	Myclobutanil*	11.470	179.10>125.00	14	0.995	0.02	101.00	111.07	11.84	4.38
98	o,p'-DDD	11.489	235.00>165.00	24	0.998	0.01	81.00	99.97	12.78	8.83
99	Fluazifop-P-butyl	11.718	282.10>238.10	18	0.989	0.02	95.20	98.86	8.05	5.02
100	1,1-Dichloro-2,2-bis(4-ethylphenyl)ethane	11.789	223.20>167.10	14	0.981	0.01	95.50	97.23	3.59	4.74
101	Nitrofen	11.834	282.90>162.00	24	0.992	0.01	100.50	111.23	6.71	8.04
102	Chlorobenzilate	11.935	251.00>139.00	14	0.995	0.01	98.00	105.54	8.92	3.61
103	Ethion	12.062	230.90>129.00	24	0.994	0.01	106.00	107.33	27.25	19.44
104	Chlorthiophos-2	12.117	324.90>268.90	14	0.995	0.01	116.00	111.33	8.75	4.06
105	Chlorthiophos-3	12.117	324.90>268.90	14	0.995	0.01	116.00	104.53	11.04	9.24
106	o,p'-DDT	12.146	235.00>165.00	24	0.995	0.01	92.50	109.34	29.60	14.75

Table 5 Summary results of GC-MS/MS analysis (Contd.)

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	Determination Coefficient (R^2)	LOQ (mg/kg)	Accuracy at LOQ (%)	Recovery at LOQ (%)	Precision	
									% RSD_R (n=6)	% RSD_r (n=6)
107	p,p'-DDD	12.146	235.00>165.00	24	0.995	0.01	92.50	138.09	16.00	13.14
108	p,p'-DDT	12.146	235.00>165.00	24	0.995	0.01	92.50	92.37	11.69	6.80
109	cis-Nonachlor	12.160	406.80>299.90	24	0.973	0.02	109.00	91.09	6.24	4.12
110	Triazophos	12.378	257.00>162.00	8	0.987	0.01	109.00	89.39	10.95	9.21
111	Sulprofos	12.379	322.00>139.00	14	0.994	0.01	82.00	100.26	7.72	14.58
112	Carfentrazone-ethyl*	12.472	340.10>312.10	14	0.990	0.02	112.00	106.10	12.03	6.58
113	4,4'-methoxychlor olefin	12.562	308.00>238.10	16	0.997	0.01	101.00	104.34	6.38	5.67
114	Carbophenothion	12.587	341.90>157.00	14	0.999	0.01	101.00	87.41	12.72	8.24
115	Edifenphos	12.679	173.00>109.00	10	0.993	0.01	96.00	94.67	21.77	6.40
116	Norflurazon	12.724	303.00>145.00	22	0.995	0.01	100.50	123.06	17.87	17.25
117	2,4'-Methoxychlor	12.884	227.10>121.10	16	0.998	0.01	91.50	98.86	6.61	7.01
118	Hexazinone	12.976	171.10>71.00	16	0.981	0.02	115.60	107.71	9.30	9.10
119	Propargite*	13.037	173.10>135.10	16	0.998	0.01	101.00	98.84	8.30	7.08
120	Tebuconazole*	13.088	250.10>125.10	22	0.999	0.02	115.50	76.54	15.32	13.23
121	Piperonyl butoxide*	13.130	176.10>131.10	12	0.998	0.02	94.00	99.11	12.94	12.16
122	Nitralin	13.168	316.10>274.00	8	0.992	0.01	97.00	112.93	5.35	4.31
123	Pyridaphenthion	13.498	340.00>199.10	8	0.996	0.01	112.50	99.84	8.09	8.88
124	Bifenthrin	13.590	181.10>166.10	12	0.998	0.01	92.50	100.80	9.19	5.78
125	Tetramethrin-2	13.676	164.10>107.10	14	0.992	0.02	101.20	95.37	8.10	5.35
126	Phosmet	13.689	160.00>77.00	24	0.999	0.01	99.50	109.64	6.92	7.60
127	Bromopropylate	13.706	340.90>182.90	18	0.996	0.01	92.00	102.20	11.57	6.64
128	Methoxychlor	13.790	227.10>169.10	24	0.996	0.01	99.00	109.44	12.82	14.48
129	Fenpropathrin	13.797	265.10>210.10	12	0.992	0.01	100.00	93.37	22.13	9.75
130	Tebufenpyrad*	13.906	333.10>171.10	20	0.996	0.02	97.00	63.50	58.82	9.24
131	Tetradifon	14.224	355.90>159.00	18	0.971	0.02	90.80	117.21	16.76	7.35
132	Pyriproxyfen*	14.440	136.10>96.00	14	0.999	0.02	87.00	106.10	15.85	6.98
133	lambda-Cyhalothrin	14.569	197.00>141.00	12	0.998	0.02	94.00	113.21	13.14	9.30
134	Acrinathrin-2	14.699	289.10>93.00	14	0.993	0.01	98.00	95.51	21.72	13.82
135	Mirex	14.782	271.80>236.80	18	0.998	0.01	99.00	97.44	26.03	18.51
136	Pyrazophos	14.785	373.10>265.10	6	0.983	0.01	102.50	96.97	7.24	7.45
137	Fenarimol*	14.876	251.00>111.00	26	0.994	0.02	99.50	101.27	11.55	5.59
138	Azinphos-ethyl	14.991	160.10>132.10	4	0.986	0.01	107.50	103.43	10.70	11.54
139	Pyraclofos	15.111	360.10>194.00	14	0.991	0.01	104.50	101.21	16.04	6.97
140	cis-Permethrine	15.388	183.10>165.10	10	0.997	0.02	92.60	99.51	6.52	3.76
141	trans-Permethrine	15.516	183.10>153.10	14	0.995	0.01	104.50	102.57	4.47	5.94
142	Pyridaben*	15.583	364.10>147.10	22	0.997	0.02	98.00	97.16	7.52	15.89
143	Coumaphos	15.583	362.00>109.00	16	0.991	0.01	99.00	111.17	5.92	8.58
144	Fluquinconazole*	15.590	340.00>298.00	20	0.999	0.02	99.00	103.24	16.62	6.63
145	Cyfluthrin-1	15.922	163.10>127.10	6	0.993	0.01	94.50	106.41	15.20	12.23
146	Cyfluthrin-3	16.109	163.10>127.10	6	0.999	0.02	105.60	99.29	17.84	10.28
147	Cyfluthrin-4	16.109	163.10>127.10	6	0.999	0.02	105.60	105.50	3.08	5.53
148	Cypermethrin-1	16.249	163.10>127.10	6	0.998	0.01	84.50	107.37	11.61	13.72
149	Flucythrinate-1	16.409	157.10>107.10	12	0.999	0.01	96.50	89.74	20.17	13.26
150	Cypermethrin-3	16.423	163.10>127.10	6	0.997	0.02	101.00	92.02	16.43	15.57
151	Cypermethrin-4	16.423	163.10>127.10	6	0.997	0.02	101.00	99.45	12.51	13.71
152	Etofenprox	16.570	163.10>135.10	10	1.000	0.01	101.50	128.54	11.84	12.82
153	Flucythrinate-2	16.603	157.10>107.10	12	0.998	0.01	80.50	115.00	31.21	16.51
154	Fenvalerate-1	17.151	225.10>147.10	10	0.984	0.01	97.00	84.76	15.66	15.12
155	tau-Fluvalinate-1	17.245	250.10>55.00	18	0.991	0.01	89.50	97.03	6.34	10.73
156	tau-Fluvalinate-2	17.303	250.10>55.00	18	0.996	0.01	98.00	112.54	13.46	16.27
157	Fenvalerate-2 (Esfenvalerate)	17.354	225.10>119.10	20	0.979	0.01	117.00	77.40	34.77	6.60
158	Deltamethrin-2 (Tralomethrin deg.-2)	17.884	252.90>93.00	20	0.999	0.02	107.00	88.00	16.85	10.03

At LOQ level, out of total compounds, mean recoveries of 179 on LC-MS/MS and 151 on GC-MS/MS were found to be within 70-120%. Whereas 41 compounds on LC-MS/MS and 1 compound on GC-MS/MS showed recoveries less than 70%. Only 6 compounds in GC-MS/MS displayed higher recoveries than 120%. As per SANTE guidelines, recoveries of all the compounds were found to be reproducible with less than 20 %RSD at their LOQ levels (Refer to Tables 4 and 5)

The method successfully achieved 10 µg /kg LOQ for 170 compounds on LC-MS/MS and 108 compounds on GC-MS/MS. 96 compounds showed LOQ of 20 µg/kg. Out of these, 48 were analyzed on each LC-MS/MS and GC-MS/MS. Remaining 4 compounds' LOQ was found to be 40 µg/kg (Refer to Tables 4 and 5). Representative chromatograms of few compounds at their LOQ levels are shown in figure 3 and 4.

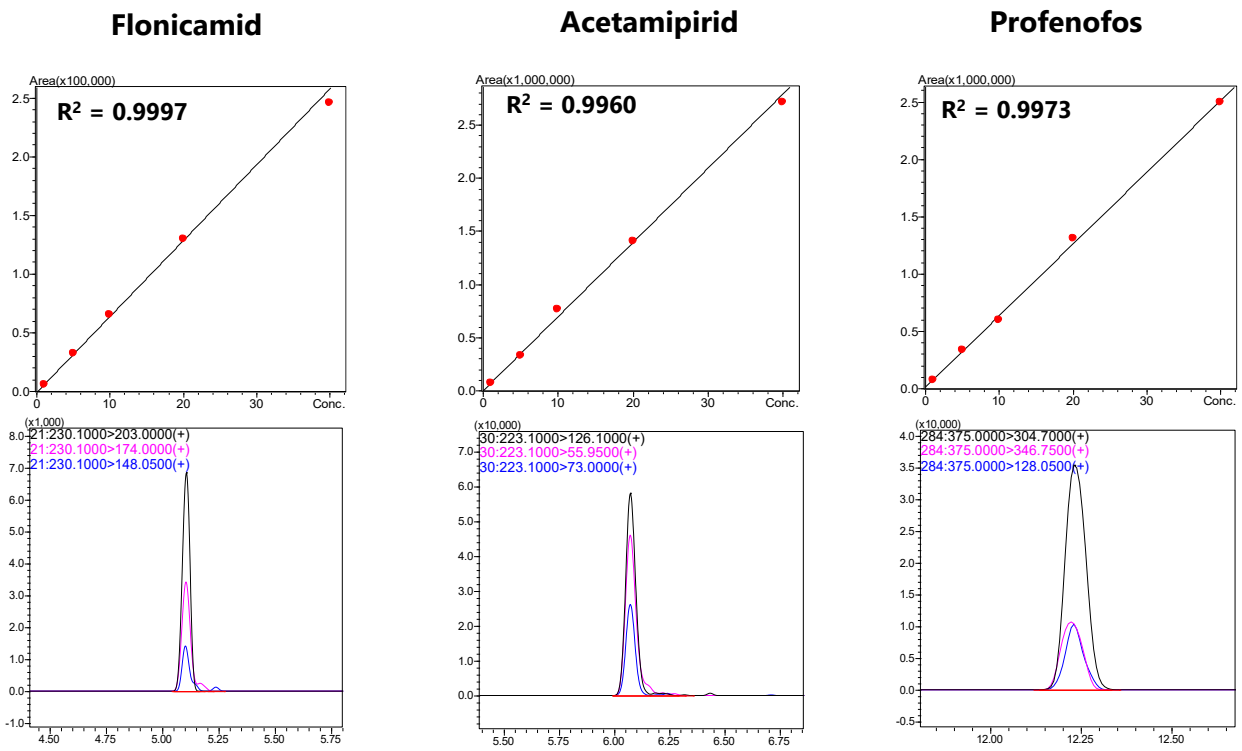

Fig. 3 Representative linearity graphs and chromatograms at LOQ level for LC-MS/MS compounds

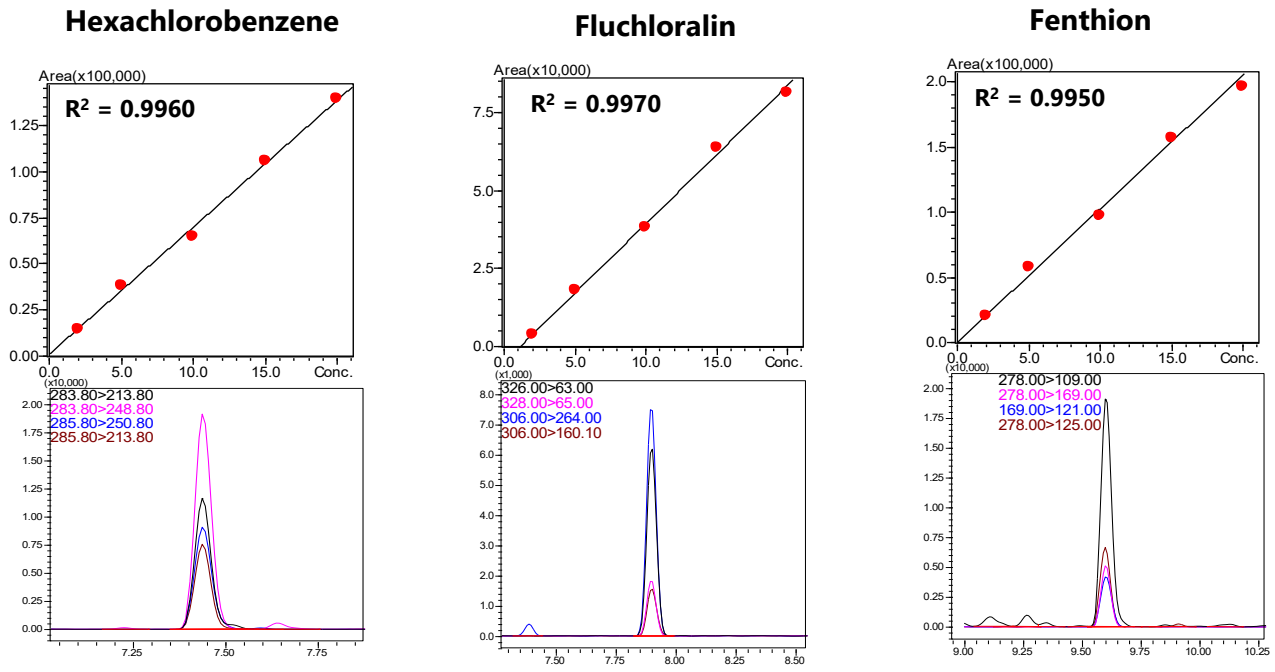

Fig. 4 Representative linearity graphs and chromatograms at LOQ level for GC-MS/MS compounds

4. Conclusion

A simple, sensitive and rapid method has been developed to quantify 326 pesticides by LC-MS/MS and GC-MS/MS in rice sample. A modified QuEChERS' extraction technique was used for sample preparation.

The method developed on Shimadzu LC-MS/MS and GC-MS/MS proved to be highly sensitive and reproducible as most of the compounds showed good RSD_r and RSD_R (as per SANTE guidelines) at trace levels.

This highlights the reliability of the method and enables its use in testing laboratories for multi-residue analysis of rice samples.

5. References

1. M. Anastassiades, S. J. Lehotay, D. Štajnbaher, F. J. Schenck, Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce, J. AOAC Int., 86, 412–431, (2003)
2. Guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed. SANTE/12682/2019

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