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Application News

LCMS™-8050 and GCMS-TQ™8040

Method for the determination of 431 Residual Pesticides in Honey using LCMS-8050 and GCMS-TQ8040 NX

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User Benefits

- The method involves study of LOQ on both LC-MS/MS and GC-MS/MS, based on validation parameters like linearity, recovery, repeatability and within-laboratory reproducibility.
- A simple liquid-liquid extraction procedure has been employed for quantifying pesticides at trace levels in complex matrix like honey using Ultra-fast technologies of LCMS-8050 and GCMS-TQ8040 NX.
- LCMS Method Package for Residual Pesticide Ver.3 and GCMS Smart Pesticides Database™ Ver.2 from Shimadzu Corporation enables ease of optimizing instrumental method.

1. Introduction

The use of honey (Fig. 1) has grown and has been adopted into consumption habits due to its high nutritional value, palatable flavor, and medicinal properties. Several reports indicate the presence of pesticide residues from different classes, mainly neonicotinoid insecticides, organophosphates and pyrethroids in honey.

Fig. 1 Honey

Therefore, to protect human health, the European Union has set maximum residue limits (MRLs) for the presence of insecticides in honey. Thus, increasing the importance of having analytical method for determination of a range of pesticides present in honey.

This study reports a validated method for the determination of 431 pesticides in honey using LCMS-8050 and GCMS-TQ8040 NX. The multi-residue extraction was performed using simple liquid-liquid extraction method for simultaneous quantification of 244 pesticides by LC-MS/MS and 214 pesticides by GC-MS/MS. Out of these, 27 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 pesticides regulated	No. of pesticides covered in this method
EU	409	182
EIC	22	19

2. Materials and Methods

The reference standards were procured from Restek Corporation having catalogue numbers:
LC multi residue pesticides kit – 31971
GC multi residue pesticides kit – 32562

Honey sample was procured from local market and used to prepare matrix-matched calibration standards and recovery samples.

The calibration standards were analyzed from 0.2 to 20 µg/L for LC-MS/MS and from 1 to 50 µg/L for GC-MS/MS. Linearity was plotted by external standard method and using weighted regression of $1/C^2$. For LC-MS/MS, sample was spiked with 4 levels i.e., 1, 5, 10 and 25 µg/kg. For GC-MS/MS, sample was spiked with 3 levels i.e., 5, 10 and 25 µg/kg. Recovery samples were prepared in six replicates at each level. The compounds marked with asterisk (*) in summary result Table 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-8050 with Nexera™ X2 (Fig. 2) and GCMS-TQ8040 NX (Fig. 3), manufactured by Shimadzu Corporation Japan, were used for quantitation. LabSolutions Insight™ was used for data processing, which helped in evaluating validation parameters with ease.

2.1. Sample preparation

This study uses single extraction procedure for GC-MS/MS and LC-MS/MS. For extraction, sodium sulphate (Na_2SO_4) salt was used in optimised proportion to maximize recoveries of pesticides. Ethyl acetate was used as extraction solvent. After extraction, the aliquot of ethyl acetate was divided in two parts.

For GC-MS/MS, clean up was performed using optimum combination of PSA (Primary secondary amine) and anhydrous $MgSO_4$ to minimise matrix interference. For LC-MS/MS, the aliquot was reconstituted using methanol : water (60:40 v/v).

Both final extracts were filtered through 0.22 µm nylon filter (P/N: 226-82113-22). The final reconstitution volume was adjusted such that recovery 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. 2 Shimadzu LCMS™-8050

Fig. 3 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-8050
Auto-sampler	: Nexera X2 SIL-30AC
Column	: Shim-pack XR-ODS (P/N: 228-41606-94) (100 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	: B Concentration →10% (0.0 min to 1.0 min) →60% (3.0 min) → 99% (12.0 - 16.0 min) →10% (16.20 to 20 min)
Run time	: 20 min
Injection volume	: 20 µL (Co-injection with water)
Column oven temp	: 40 °C

MS	
Ionization mode	: ESI
Nebulizing gas flow	: 3 L/min
Interface temp.	: 300 °C
Heating gas flow	: 10 L/min
Drying gas flow	: 10 L/min
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-Rxi-5Sil MS (30 m × 0.25 mm I.D., df = 0.25 µm)
Liner	: Topaz Liner, Splitless Single Taper w/Wool

GC	
Injector temp.	: 250 °C
Column oven temp	: 80 °C (2 min), 20 °C/min to 180 °C (0 min), 5 °C/min to 300 °C (3 min)
Run time	: 34 min
Injection mode	: Splitless (High pressure at 250 kPa)
Injection volume	: 1 µL
Carrier gas	: He
Linear Velocity	: 40.4 cm/sec (Constant mode)

MS	
Ionization mode	: EI
Ion source temp.	: 230 °C
Interface temp.	: 280 °C
Solvent cut time	: 5.0 min
Loop Time	: 0.3 sec

3. Result and Discussion

Validation parameters like specificity, linearity, recovery and precision were studied as per SANTE guidelines[1]. Results obtained on LC-MS/MS and GC-MS/MS are shown in Table 4 and 5, respectively.

3.1. Specificity

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 match calibration standards were used. Calibration curve ranged from 0.2 to 20 µg/L for LC-MS/MS and from 1 to 50 µg/L for GC-MS/MS. All calibration standards were found within 80 to 120% accuracy as per SANTE guidelines.

The compounds marked with asterisk (*) in summary result Table 4 and 5; were two times the concentration levels mentioned above.

The linearity graphs of some representative compounds are shown in Fig. 4 and 5.

3.3. Recovery study

Recovery was evaluated by analysing six replicates at each level. For LC-MS/MS and GC-MS/MS, spiking was done at 4 levels and 3 levels, respectively. (The spiking levels were two times for * marked compounds in Table 4 and 5). All recovery samples were analysed against matrix match 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. (Refer to Table 4 and 5)

3.4. Precision study

For single laboratory validation studies, six replicates of various concentration levels were studied for their precision

Repeatability (RSD_r):

Repeatability experiment was performed by injecting six replicates of 4 concentration levels for LC-MS/MS and 3 levels for GC-MS/MS. The % RSD for repeatability of six injections at their respective LOQ levels were found to be less than 20%. (Refer to Table 4 and 5)

Reproducibility (RSD_R):

Reproducibility experiment was performed on six different recovery samples at concentration levels mentioned in section 3.3. The % RSD of six recovery samples at their respective LOQ levels were found to be less than 20%. (Refer to Table 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)	Precision % RSD_r (n=6)
1	Methamidophos	3.233	142.20>93.95	-15	0.9981	0.001	102.65	48.86	7.75	13.96
2	Acephate	3.753	184.00>143.00	-9	0.9997	0.005	101.83	60.04	4.21	4.61
3	Omethoate	4.040	214.10>125.00	-21	0.9991	0.001	101.10	57.92	18.62	15.06
4	Dinotefuran	4.247	203.15>114.15	-12	0.9976	0.005	96.97	83.34	7.39	6.39
5	Aminocarb	4.644	209.00>137.05	-23	0.9909	0.001	94.55	60.33	13.47	10.07
6	Butoxycarboxim	4.326	240.10>106.15	-14	0.9968	0.001	102.70	94.89	10.24	10.12
7	Aldicarb Sulfone	4.392	240.10>86.20	-23	0.9972	0.001	102.60	100.21	9.72	12.87
8	Oxamyl	4.447	237.10>72.10	-22	0.9989	0.001	100.70	107.15	7.59	10.91
9	Methomyl	4.724	163.00>87.90	-10	0.9993	0.001	98.65	127.06	4.42	4.21
10	Thiamethoxam	4.902	292.00>181.10	-23	0.9940	0.001	104.70	106.38	15.89	8.77
11	Dimethachlor	4.964	256.10>224.00	-5	0.9943	0.005	104.47	84.02	15.90	10.70
12	Monocrotophos	4.963	240.90>127.10	-21	0.9957	0.005	93.67	84.42	9.75	9.25
13	Dicrotophos	5.132	237.90>72.00	-26	0.9958	0.001	98.70	93.67	18.36	17.18
14	Carbendazim	5.465	192.10>160.15	-18	0.9927	0.001	104.15	86.74	13.81	15.75
15	Imidacloprid	5.360	256.10>209.00	-18	0.9972	0.005	98.64	72.58	11.21	9.71
16	Clothianidin	5.447	249.80>132.05	-16	0.9972	0.005	90.67	87.95	9.09	14.99
17	Vamidothion	5.560	288.10>146.05	-13	0.9988	0.001	101.45	115.96	3.27	6.72
18	Carbofuran-3-hydroxy	5.607	255.00>220.05	-9	0.9872	0.005	88.73	89.29	9.00	6.87
19	Mevinphos*	5.612	225.10>127.00	-18	0.9969	0.01	93.92	81.56	4.21	4.19
20	Acetamiprid	5.636	223.10>126.10	-22	0.9968	0.001	103.95	97.18	5.32	6.73
21	Fenuron	5.663	165.00>72.15	-17	0.9950	0.001	96.85	120.97	4.03	9.13
22	Dioxacarb	5.668	224.10>167.00	-11	0.9920	0.01	106.49	55.98	20.00	19.36
23	Dimethoate	5.693	230.00>125.00	-20	0.9985	0.005	106.10	94.82	3.43	5.35
24	Trichlorfon	5.721	257.00>109.00	-17	0.9922	0.005	92.52	96.39	7.88	15.15
25	Thiabendazole	5.934	201.80>175.00	-26	0.9812	0.005	110.92	94.55	8.95	17.14
26	Thiacloprid	5.886	253.00>90.10	-39	0.9984	0.005	98.54	102.03	20.07	8.79
27	Fuberidazole	6.081	184.90>157.15	-24	0.9904	0.005	101.36	92.26	5.51	12.61
28	Tricyclazole*	6.137	190.00>136.00	-30	0.9984	0.002	98.95	105.33	11.06	9.76
29	Oxadixyl	6.287	296.20>219.05	-16	0.9982	0.005	101.98	107.46	10.61	3.70
30	Triasulfuron	6.455	401.90>141.00	-23	0.9928	0.01	91.74	125.62	19.78	5.25
31	Allidochlor	6.472	174.10>98.05	-14	0.9944	0.001	103.45	96.36	12.58	10.78
32	Carbetamide	6.509	236.90>192.10	-9	0.9973	0.001	103.10	126.80	10.36	9.79
33	Metsulfuron-Methyl	6.564	381.90>167.10	-16	0.9887	0.001	107.80	101.41	10.62	15.27
34	Bendiocarb	6.802	224.10>109.00	-19	0.9987	0.001	101.30	126.22	15.43	9.19
35	Propoxur	6.808	209.90>93.10	-26	0.9948	0.001	95.65	110.53	14.46	16.23
36	Thidiazuron	6.838	221.00>102.00	-17	0.9902	0.005	101.56	89.49	12.24	8.59
37	Carbofuran	6.849	222.10>123.15	-23	0.9999	0.001	100.30	119.32	5.27	7.43
38	Dimethirimol	7.134	210.20>140.10	-22	0.9946	0.005	98.73	75.53	9.14	6.96
39	Ethirimol	7.135	210.20>140.20	-22	0.9927	0.001	96.65	66.78	9.48	9.50
40	Simazine	6.950	202.00>131.90	-21	0.9906	0.005	100.37	92.53	14.39	7.04
41	Hexazinone	6.955	253.20>71.05	-22	0.9990	0.005	96.48	91.63	6.41	9.31
42	Penoxsulam	6.970	483.90>195.00	-29	0.9975	0.001	101.85	111.89	15.90	18.15
43	Metribuzin	6.986	215.10>187.10	-19	0.9894	0.005	91.60	52.61	3.66	5.62
44	Pyracarbolid	7.024	218.10>125.10	-8	0.9870	0.005	110.95	84.77	14.07	9.99
45	Tebuthiuron	7.048	229.10>116.00	-27	0.9916	0.005	94.22	93.36	6.34	2.68
46	Imazalil	7.270	297.10>159.05	-12	0.9896	0.01	98.54	108.74	14.36	12.48
47	Thiodicarb	7.095	354.90>88.00	-18	0.9962	0.001	104.45	61.61	11.96	9.93
48	Carbaryl	7.113	202.10>145.10	-11	0.9995	0.001	100.40	115.98	18.70	14.87
49	Pirimicarb	7.374	239.20>182.05	-16	0.9943	0.001	103.35	128.11	7.10	7.51
50	Monolinuron	7.382	215.10>99.10	-36	0.9896	0.001	96.45	121.13	17.59	8.93

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)	Precision % RSD_r (n=6)
51	Flumeturon	7.412	233.00>72.15	-22	0.9991	0.001	100.60	102.50	9.01	16.03
52	Diuron	7.413	233.00>72.10	-21	0.9990	0.001	100.90	111.64	8.52	15.49
53	Thiofanox	7.488	241.20>184.00	-12	0.9966	0.001	98.30	113.11	17.67	16.47
54	Simetryn	7.603	214.10>96.00	-27	0.9931	0.001	98.75	92.77	18.65	10.91
55	Chlorotoluron	7.592	213.10>72.15	-23	0.9978	0.001	98.90	111.02	4.88	11.26
56	Azimsulfuron	7.553	425.10>182.10	-18	0.9961	0.001	102.15	117.88	4.70	11.11
57	Flutriafol*	7.590	302.10>70.05	-21	0.9957	0.002	99.55	117.04	6.02	10.67
58	Metobromuron	7.690	259.00>148.10	-16	0.9925	0.005	98.40	86.87	7.34	6.84
59	Isoprocarb	7.703	194.10>95.00	-16	0.9992	0.001	101.00	80.11	10.24	6.29
60	Metazachlor	7.701	277.90>134.10	-11	0.9996	0.001	99.75	93.97	8.40	8.42
61	Tembotrione	7.569	457.90>262.10	-34	0.9830	0.005	110.97	92.61	7.57	12.71
62	Spiroxamine	7.841	298.20>144.20	-20	0.9967	0.001	98.40	95.97	16.75	6.27
63	Metalaxyl*	7.800	280.10>220.00	-15	0.9994	0.002	99.60	117.74	3.93	5.21
64	Atrazine	7.813	216.10>174.10	-13	0.9954	0.001	98.45	111.91	10.41	17.80
65	Propachlor	7.849	212.10>170.10	-6	0.9974	0.001	98.75	117.81	10.87	13.00
66	Methabenzthiazuron	7.829	222.10>150.10	-30	0.9859	0.001	93.50	121.04	16.34	7.70
67	Lenacil	7.856	234.90>153.15	-6	0.9895	0.005	105.61	110.37	10.69	10.21
68	Isoproturon	7.880	207.20>72.15	-21	0.9989	0.001	101.50	92.70	12.25	9.06
69	Iodosulfuron methyl Sodium	7.839	529.80>389.80	-17	0.9947	0.005	98.60	92.63	12.96	15.32
70	Forchlorfenuron	7.906	248.10>93.15	-35	0.9929	0.001	96.95	119.62	17.92	17.40
71	Norflurazon	7.954	304.10>283.95	-18	0.9960	0.001	96.90	119.66	13.91	13.76
72	Prometon	8.113	226.20>142.00	-24	0.9981	0.001	98.50	118.49	6.45	7.82
73	Secbumeton	8.113	226.20>142.10	-22	0.9995	0.001	100.05	114.01	7.32	8.75
74	Mexacarbate	8.319	223.10>151.15	-11	0.9968	0.005	97.59	99.23	4.87	5.68
75	Chlorantraniliprole	8.046	483.90>285.90	-14	0.9988	0.001	98.90	105.30	18.83	14.08
76	Desmedipham	8.049	318.00>136.10	-26	0.9997	0.001	99.05	91.41	3.74	8.97
77	Phenmedipham	8.050	318.10>136.10	-26	0.9979	0.001	97.30	116.80	6.39	11.44
78	Diphenamid	8.087	239.90>134.15	-6	0.9991	0.001	100.00	93.57	13.80	18.43
79	Fenpropimorph	8.335	304.20>147.10	-27	0.9950	0.001	102.50	109.01	15.68	10.64
80	Cycluron	8.120	199.20>88.95	-15	0.9940	0.001	96.40	113.42	13.67	7.81
81	Monuron	8.121	199.10>46.10	-17	0.9965	0.001	98.40	108.72	13.80	9.36
82	Sulfosulfuron	8.081	471.00>211.00	-10	0.9907	0.001	102.50	112.81	17.28	14.44
83	Fluridone	8.166	330.10>309.00	-31	0.9952	0.001	95.60	102.42	7.08	9.33
84	Terbumeton	8.322	226.00>170.10	-18	0.9975	0.001	100.45	98.95	5.26	3.51
85	Azoxystrobin	8.240	404.00>371.95	-5	0.9997	0.001	100.85	95.82	6.65	14.84
86	Clomazone	8.369	239.90>125.00	-11	0.9955	0.001	98.55	101.05	6.97	15.96
87	Furalaxyl	8.403	302.10>95.00	-26	0.9995	0.001	99.95	115.30	2.71	5.97
88	Methoprotryne	8.444	272.20>197.95	-23	0.9987	0.001	98.75	105.89	12.35	9.92
89	Ametryn	8.515	228.10>186.00	-21	0.9986	0.001	99.10	137.65	6.88	6.88
90	Diethofencarb	8.487	268.20>226.05	-10	0.9983	0.001	99.30	80.80	12.82	7.51
91	Fenobucarb	8.510	208.10>95.00	-15	0.9971	0.001	100.95	78.27	16.49	15.68
92	Ethofumesate	8.520	304.10>287.00	-10	0.9891	0.005	101.80	77.36	10.69	7.23
93	Fenamidone	8.618	312.10>236.00	-16	0.9956	0.001	96.95	107.14	10.66	15.43
94	Ethiprole	8.636	397.00>350.90	-21	0.9796	0.005	112.55	106.56	9.86	10.15
95	Mandipropamid	8.650	412.10>327.90	-11	0.9951	0.001	96.85	116.41	8.96	12.75
96	Siduron	8.645	233.20>137.10	-16	0.9960	0.005	101.98	98.22	10.95	4.65
97	Linuron*	8.678	248.80>160.00	-21	0.9982	0.002	98.40	95.90	18.90	13.72
98	Methiocarb	8.739	226.10>121.10	-19	0.9980	0.001	100.65	119.71	2.15	8.15
99	Pyrimethanil*	8.779	200.10>107.00	-15	0.9905	0.01	86.52	87.43	16.48	19.10
100	Boscalid	8.759	343.00>270.95	-35	0.9975	0.005	95.59	103.72	12.93	9.84

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)	Precision % RSD_r (n=6)
101	Flutolanil*	8.829	324.10>261.90	-17	0.9862	0.01	98.82	128.30	3.81	2.87
102	Sebuthylazine	8.838	230.10>96.15	-26	0.9920	0.005	104.66	121.36	10.82	2.47
103	Terbuthylazine	8.837	230.10>104.00	-33	0.9907	0.005	106.13	117.05	6.55	10.05
104	Methoxyfenozide	8.907	369.20>312.95	-7	0.9909	0.005	106.93	114.45	18.83	11.22
105	Paclobutrazol*	8.917	294.00>125.05	-37	0.9865	0.01	82.52	122.71	12.50	12.86
106	Dimethomorph	8.936	388.10>301.00	-21	0.9903	0.001	105.10	137.91	13.30	11.60
107	Permethrin	8.904	391.00>241.05	-17	0.9981	0.005	106.09	139.81	7.93	7.71
108	Malathion	8.920	348.10>127.05	-17	0.9906	0.005	84.63	107.22	7.31	5.52
109	Ethoxysulfuron	8.914	398.90>261.00	-16	0.9911	0.005	95.71	121.67	17.79	14.86
110	Benzthiazuron	8.934	208.10>151.10	-6	0.9896	0.001	104.00	126.17	4.86	8.21
111	Promecarb	8.932	208.00>109.10	-16	0.9945	0.001	100.90	106.69	8.48	10.78
112	Fluopicolide	8.957	383.00>144.95	-50	0.9900	0.005	118.52	115.37	4.29	8.56
113	Mepronil	9.003	270.20>119.05	-26	0.9959	0.001	100.55	127.55	7.42	7.91
114	Triadimefon*	9.092	294.10>69.00	-19	0.9923	0.002	102.05	125.33	14.43	4.89
115	Myclobutanil*	9.112	289.10>70.05	-28	0.9939	0.01	91.89	111.38	10.10	7.01
116	Propetamphos	9.131	282.10>138.00	-17	0.9824	0.01	108.28	103.12	16.29	14.62
117	Propyzamide	9.148	256.00>190.00	-14	0.9847	0.001	91.05	97.41	12.74	13.99
118	Isoxathion	9.231	314.00>97.05	-40	0.9953	0.001	99.65	118.80	7.66	12.26
119	Bifenazate	9.198	301.10>170.00	-17	0.9885	0.001	93.90	133.05	11.46	14.65
120	Triazophos	9.195	314.10>162.05	-9	0.9969	0.001	101.25	105.67	14.43	13.67
121	Mefenacet	9.206	299.00>148.15	-19	0.9980	0.001	96.75	118.22	6.44	13.61
122	Butafenacil	9.219	492.10>330.85	-25	0.9897	0.001	97.25	109.51	11.16	7.82
123	Isazofos	9.193	314.10>162.05	-12	0.9969	0.001	97.95	108.23	3.44	5.42
124	Spirotetramat	9.305	374.10>216.00	-39	0.9920	0.001	95.70	136.09	9.94	12.07
125	Pyrazosulfuron ethyl	9.245	414.90>182.10	-21	0.9902	0.001	93.80	102.49	14.12	9.00
126	Bromuconazole	9.316	377.90>159.05	-21	0.9767	0.005	90.93	102.58	16.61	11.78
127	Iprovalicarb	9.324	321.20>91.00	-52	0.9922	0.005	86.96	100.99	7.35	3.13
128	Chloroxuron	9.327	291.10>72.15	-33	0.9925	0.01	99.88	71.98	15.28	8.06
129	Triadimenol*	9.333	298.10>70.05	-22	0.9980	0.01	105.65	101.73	7.95	7.69
130	Terbutryn	9.408	242.10>157.95	-15	0.9986	0.001	99.35	121.84	11.98	8.76
131	Prometryne	9.406	242.10>158.00	-29	0.9975	0.001	98.60	137.03	6.15	11.37
132	Prometryn	9.405	242.10>158.00	-12	0.9993	0.005	100.84	83.26	2.90	7.05
133	Cyproconazole	9.409	292.10>125.05	-35	0.9851	0.005	114.10	112.16	9.12	13.50
134	Fluquinconazole*	9.398	376.00>349.00	-21	0.9919	0.002	97.60	129.83	18.13	14.78
135	Fenhexamid	9.456	302.10>97.10	-24	0.9940	0.005	99.80	99.06	8.77	8.70
136	Flufenacet	9.464	364.10>152.05	-24	0.9977	0.001	99.50	118.67	10.48	6.23
137	Naled (Dibrom)	9.433	395.80>127.15	-21	0.9936	0.01	109.43	123.51	14.55	12.68
138	Tetraconazole	9.465	372.00>159.00	-37	0.9807	0.005	103.90	100.34	16.13	3.92
139	Mepanipyrim	9.495	224.10>77.00	-41	0.9959	0.005	108.33	98.41	6.31	4.89
140	Fenarimol*	9.515	331.00>139.10	-39	0.9924	0.01	108.44	119.25	15.61	19.19
141	Dodine	9.684	228.10>60.10	-25	0.9841	0.005	95.22	88.24	10.07	6.33
142	Tridemorph	9.778	298.10>57.10	-34	0.9943	0.005	106.76	85.51	9.59	8.81
143	Epoxiconazole	9.624	330.00>121.10	-25	0.9841	0.005	80.65	121.50	5.69	5.95
144	Fenbuconazole	9.710	337.10>125.05	-28	0.9878	0.005	98.44	118.71	19.54	5.01
145	Spinosad A	9.844	732.30>142.10	-33	0.9951	0.001	103.55	75.73	10.79	15.84
146	Picoxystrobin	9.810	368.00>205.10	-11	0.9948	0.005	91.29	86.56	8.82	4.59
147	Bupirimate*	9.813	317.20>166.00	-21	0.9990	0.002	100.20	106.70	4.05	15.12
148	Metolachlor	9.795	284.10>176.10	-26	0.9961	0.001	98.65	105.04	9.70	17.09
149	Tebufenozide	9.826	353.20>133.10	-16	0.9900	0.005	104.17	92.40	9.95	11.07

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)	Precision % RSD_r (n=6)
150	Flusilazole*	9.838	316.10>247.00	-16	0.9913	0.002	96.50	117.77	15.53	10.95
151	Diflubenzuron	9.890	311.00>158.10	-12	0.9831	0.005	112.33	103.85	3.72	6.91
152	Hydramethylnon	9.978	495.10>151.00	-54	0.9932	0.001	105.60	72.06	14.05	15.73
153	Fenoxycarb	9.918	302.10>116.15	-12	0.9938	0.001	97.05	105.06	8.37	11.29
154	Phenthoate	9.990	320.90>247.00	-11	0.9945	0.001	101.45	71.63	9.30	12.23
155	Iprobenfos	10.025	288.90>205.00	-11	0.9927	0.001	103.70	76.76	10.15	7.56
156	Clodinafop-Propargyl	10.028	349.90>237.90	-26	0.9843	0.005	113.97	65.78	18.56	15.50
157	Dimoxystrobin	10.051	327.10>116.10	-25	0.9959	0.001	96.35	113.30	9.10	11.00
158	Neburon	10.065	274.80>87.95	-17	0.9854	0.005	108.73	93.52	13.59	6.07
159	Sulfotep	10.118	323.00>97.00	-27	0.9919	0.005	100.92	44.64	8.94	4.36
160	Dichlobutrazol	10.136	328.00>70.10	-22	0.9825	0.001	91.15	111.79	19.24	15.03
161	Kresoxim methyl	10.129	314.10>235.00	-19	0.9892	0.005	110.18	86.89	18.48	15.60
162	Tolylfluanid	10.362	364.00>227.85	-25	0.9887	0.005	108.44	94.40	5.49	9.64
163	Anilofos	10.203	367.90>125.00	-34	0.9978	0.001	97.90	107.37	11.92	7.76
164	Edifenphos	10.216	311.00>111.05	-17	0.9947	0.001	102.45	107.43	8.29	18.21
165	Spinosad D	10.364	746.40>142.10	-31	0.9851	0.001	104.40	81.39	16.54	8.45
166	Penconazole*	10.279	284.10>70.05	-26	0.9912	0.002	101.15	109.76	6.21	8.63
167	Tebuconazole*	10.296	308.00>70.05	-23	0.9952	0.01	105.94	104.23	9.30	5.60
168	Spinetoram A	10.421	748.50>142.20	-31	0.9886	0.001	102.45	96.58	13.39	11.47
169	Benalaxyl	10.330	326.20>91.05	-45	0.9898	0.001	104.65	126.06	17.87	15.81
170	Cyprodinil*	10.351	226.10>93.00	-33	0.9939	0.002	103.60	112.50	14.69	8.94
171	Chlorfenvinphos (E, Z)	10.395	359.00>169.95	-39	0.9900	0.001	99.35	128.97	12.59	7.71
172	Diazinon	10.445	305.10>169.10	-12	0.9984	0.001	100.25	102.99	8.14	12.96
173	Propiconazole	10.458	342.00>158.90	-28	0.9978	0.005	98.47	111.51	3.97	15.80
174	Fonofos	10.483	247.00>109.10	-21	0.9928	0.005	94.96	47.48	14.22	7.73
175	Pyraclostrobin	10.514	388.00>194.10	-15	0.9990	0.001	101.50	111.57	15.69	7.70
176	Zoxamide	10.525	336.00>159.00	-18	0.9964	0.001	99.80	133.64	6.25	7.52
177	Fluoxastrobin	10.560	458.80>427.00	-6	0.9891	0.005	108.17	97.55	19.86	15.29
178	Triflumuron	10.570	359.00>156.05	-20	0.9938	0.005	102.37	112.45	14.19	5.34
179	Bromfenvinfos	10.556	404.90>155.10	-13	0.9986	0.001	98.15	120.80	10.29	20.12
180	Pyraclofos	10.629	361.10>256.90	-22	0.9956	0.001	98.95	126.75	8.85	9.98
181	Hexaconazole	10.643	314.10>70.00	-35	0.9956	0.005	109.24	104.33	13.57	7.94
182	Baycor (Bitertanol)	10.670	338.00>269.05	-11	0.9871	0.005	106.61	107.48	16.51	7.23
183	Phosalone	10.677	368.00>182.00	-17	0.9949	0.001	98.35	91.99	19.47	12.57
184	Metconazole	10.673	320.10>70.15	-23	0.9921	0.001	99.65	135.92	17.64	17.99
185	Prochloraz*	10.679	376.00>307.95	-8	0.9949	0.002	104.00	106.79	4.21	7.28
186	Pirimiphos-methyl	10.784	306.10>164.10	-18	0.9991	0.001	99.80	94.32	9.73	8.42
187	Metrafenone	10.803	409.00>209.10	-6	0.9959	0.005	90.36	96.18	7.40	5.31
188	Phorate	10.792	261.00>75.15	-11	0.9898	0.025	99.12	45.87	15.14	12.06
189	Tolclofos-methyl	10.805	301.00>174.90	-26	0.9930	0.005	93.79	73.45	17.89	17.11
190	Clofentezine	10.810	303.00>138.15	-15	0.9934	0.001	100.95	89.88	17.55	9.51
191	Spinetoram B	10.949	760.60>142.10	-31	0.9907	0.005	111.85	58.81	15.15	10.96
192	Pencycuron	10.826	329.10>125.00	-10	0.9903	0.005	82.10	100.07	13.34	12.38
193	Indoxacarb	10.899	527.70>218.00	-24	0.9901	0.005	104.11	84.83	10.14	11.99
194	Thiobencarb	10.893	258.10>125.10	-17	0.9989	0.001	99.35	86.17	11.37	9.26
195	Orbencarb	10.893	258.10>125.10	-11	0.9986	0.001	97.40	99.58	15.72	8.32
196	Diniconazole	10.954	326.10>70.05	-42	0.9965	0.005	93.49	102.24	18.52	9.83
197	Emamectin Benzoate B1a	11.049	886.40>158.10	-41	0.9937	0.001	104.75	71.37	11.16	19.66

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)	Precision % RSD_r (n=6)
198	Difenoconazole	10.970	406.10>250.90	-40	0.9937	0.001	94.75	138.40	12.55	17.61
199	Trifloxystrobin	11.006	409.10>145.10	-29	0.9956	0.001	102.55	102.96	10.14	6.50
200	Pyrethrin-II	11.042	373.00>161.00	-12	0.9836	0.005	92.40	108.84	16.23	8.79
201	Novaluron	11.106	493.00>158.00	-14	0.9846	0.01	96.02	118.93	12.82	11.32
202	Triflumizole*	11.240	345.90>278.10	-11	0.9952	0.002	103.75	95.50	10.74	9.63
203	Ipconazole	11.268	334.10>70.10	-43	0.9975	0.005	102.63	109.67	7.76	3.30
204	Pretilachlor	11.304	312.20>252.05	-7	0.9983	0.005	99.54	105.23	5.09	8.34
205	Fenoxaprop-Ethyl	11.492	361.90>119.10	-29	0.9886	0.01	87.53	63.45	8.90	9.92
206	Profenofos	11.525	375.00>304.70	-19	0.9981	0.001	100.75	97.66	12.97	4.10
207	Furathiocarb	11.559	383.20>195.00	-44	0.9962	0.005	110.65	85.24	8.56	13.61
208	Tetramethrin	11.621	332.20>164.10	-24	0.9969	0.005	94.56	89.64	7.81	5.92
209	Temephos	11.663	466.90>125.10	-33	0.9896	0.001	106.75	110.55	16.65	13.84
210	Tebufenpyrad*	11.677	334.20>117.00	-53	0.9921	0.002	105.25	105.35	13.51	12.35
211	Buprofezin	11.751	306.20>201.05	-16	0.9974	0.001	103.30	130.09	8.49	4.93
212	Tolfenpyrad	11.794	384.00>197.10	-26	0.9983	0.001	102.55	107.66	10.06	13.70
213	Pirimiphos-ethyl	11.820	334.10>198.15	-12	0.9969	0.001	99.05	111.66	10.12	8.87
214	Chlorpyrifos-oxon	11.820	334.00>197.85	-30	0.9986	0.001	98.60	121.88	5.10	6.82
215	Alachlor	11.914	270.10>238.00	-11	0.9877	0.001	93.85	76.74	15.31	4.49
216	Piperonyl butoxide*	11.912	356.20>177.00	-26	0.9991	0.002	100.70	98.10	5.06	2.36
217	Pyriproxyfen*	12.044	322.10>78.05	-54	0.9926	0.002	103.80	127.19	3.03	11.28
218	Hexythiazox	12.148	353.10>228.00	-20	0.9971	0.001	101.00	93.52	4.27	11.68
219	Chlorpyrifos	12.187	350.00>197.95	-21	0.9926	0.005	100.85	69.60	5.33	7.40
220	Flufenoxuron	12.252	489.00>158.10	-21	0.9850	0.001	107.45	91.09	18.20	10.56
221	Quinoxyfen	12.262	308.00>197.00	-31	0.9991	0.001	101.05	127.33	13.43	8.52
222	Etoxazole	12.317	360.10>141.10	-17	0.9957	0.001	103.00	90.41	11.70	8.67
223	Propargite*	12.334	368.20>231.10	-6	0.9933	0.002	104.25	95.48	8.55	10.36
224	Tri-allate	12.346	304.00>143.00	-27	0.9876	0.005	82.49	49.91	19.17	15.84
225	Pyrethrin-I	12.480	329.00>161.10	-11	0.9885	0.001	105.80	100.73	17.05	17.42
226	Spirodiclofen	12.580	411.10>71.10	-35	0.9977	0.01	92.44	102.73	16.96	5.27
227	Fenpyroximate	12.589	422.10>215.10	-34	0.9833	0.005	99.46	97.91	10.15	7.79
228	Flumetralin	12.592	422.10>117.10	-53	0.9972	0.01	96.02	93.25	12.00	5.68
229	Chlorfluazuron	12.616	539.90>158.00	-35	0.9938	0.001	100.20	99.78	15.87	19.71
230	Pyridaben*	12.998	365.20>147.10	-35	0.9961	0.002	103.75	96.50	3.93	5.45
231	Fenazaquin	13.178	307.20>57.00	-15	0.9982	0.001	100.75	103.13	9.86	4.48
232	Moxidectin	13.640	640.40>622.20	-15	0.9974	0.01	98.13	65.58	17.35	10.98
233	Etofenprox	13.711	394.00>135.10	-27	0.9800	0.005	106.94	110.50	3.71	1.02
234	Flonicamid	4.899	227.95>81.00	10	0.9939	0.005	100.66	87.41	17.05	14.08
235	MCPA	8.004	199.00>141.00	14	0.9964	0.001	96.80	119.54	11.82	19.95
236	Fludioxonil*	8.745	247.00>126.15	35	0.9900	0.01	85.26	104.19	19.11	9.56
237	Fipronil*	9.804	435.00>330.00	16	0.9969	0.002	98.45	109.43	10.34	5.27
238	Flubendiamide	9.836	680.90>254.10	27	0.9970	0.001	102.20	86.83	6.60	10.87
239	Fenoxaprop-P	10.076	332.00>152.00	22	0.9966	0.01	100.15	73.75	17.70	11.88
240	Hexaflumuron	11.057	458.80>175.10	45	0.9811	0.025	105.59	107.22	8.08	15.43
241	Novaluron	11.107	491.00>470.90	13	0.9925	0.001	94.15	130.81	19.51	19.41
242	Lufenuron	11.743	508.90>339.00	25	0.9817	0.005	117.70	96.71	9.37	12.02
243	Fluazinam	11.755	463.00>397.95	14	0.9764	0.005	90.62	85.80	16.10	7.26
244	Teflubenzuron	11.917	379.00>338.90	12	0.9939	0.005	96.64	85.86	9.89	7.27

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)	Precision % RSD_r (n=6)
1	Allidochlor	6.214	132.10>56.00	8	0.9995	0.005	97.18	92.42	2.33	1.90
2	Dichlobenil	6.695	170.90>136.00	14	0.9992	0.005	102.92	89.29	1.50	2.38
3	Biphenyl	7.041	154.10>128.10	22	0.9986	0.005	97.01	78.19	5.00	1.63
4	Mevinphos*	7.307	127.00>109.00	12	0.9989	0.01	99.12	96.92	6.12	4.31
5	3,4-Dichloroaniline	7.408	161.00>99.00	22	0.9948	0.005	89.75	71.26	5.43	3.47
6	Etridiazole	7.508	210.90>182.90	10	0.9993	0.005	96.97	84.31	3.46	4.07
7	Pebulate	7.563	161.10>128.10	6	0.9991	0.005	101.28	89.18	4.32	3.91
8	N-(2,4-dimethylphenyl) formamide	7.826	149.10>121.10	6	0.9846	0.005	92.88	88.42	11.64	7.14
9	Methacrifos	7.83	208.00>180.00	8	0.9993	0.005	103.32	91.66	1.48	0.97
10	THPI (Tetrahydrophthalimide)	7.875	151.10>79.00	18	0.9965	0.005	94.87	84.87	5.69	2.73
11	Chloroneb	7.933	206.00>141.00	20	0.9996	0.005	100.85	83.88	5.92	7.54
12	2-Phenylphenol	8.104	170.10>141.10	24	0.9993	0.005	98.95	89.98	1.50	2.13
13	Pentachlorobenzene	8.117	249.90>214.90	18	0.9981	0.005	105.79	80.58	6.05	4.19
14	Tecnazene	8.723	260.90>202.90	14	0.9991	0.005	104.62	82.89	7.86	5.71
15	Propachlor	8.835	120.00>77.00	20	0.9996	0.005	102.91	93.39	4.16	3.18
16	Diphenylamine	9.038	169.10>66.00	24	0.9992	0.005	102.53	96.09	3.89	10.25
17	2,3,5,6-Tetrachloroaniline	9.072	228.90>158.00	18	0.9998	0.005	102.38	84.24	2.79	2.96
18	Cycloate	9.113	154.20>72.00	6	1.0000	0.005	100.13	82.99	3.11	2.12
19	Ethalfluralin	9.141	276.00>202.00	18	0.9966	0.005	91.17	74.15	12.82	9.88
20	Chlorpropham	9.285	213.10>171.10	6	0.9998	0.005	99.41	89.48	4.08	5.89
21	Trifluralin	9.285	306.10>264.10	8	0.9970	0.005	91.85	79.30	6.54	7.27
22	Benfluralin	9.339	292.10>264.00	8	0.9972	0.005	96.75	89.01	6.77	5.52
23	Sulfotep	9.398	322.00>202.00	10	0.9948	0.005	109.89	81.43	5.83	6.86
24	Di-allate-1	9.653	234.10>150.00	20	0.9996	0.005	100.02	82.83	4.93	4.22
25	Phorate	9.662	260.00>75.00	8	0.9931	0.005	94.68	84.35	8.41	6.84
26	alpha-BHC	9.814	180.90>144.90	16	0.9993	0.005	101.42	85.04	3.44	4.63
27	Di-allate-2	9.847	234.10>150.00	20	0.9950	0.005	110.82	73.30	8.56	5.38
28	Hexachlorobenzene	9.91	283.80>248.80	24	0.9997	0.005	98.31	82.48	10.41	6.45
29	Pentachloroanisole	10.012	264.80>236.80	16	0.9987	0.005	102.63	80.09	4.18	2.88
30	Dicloran	10.093	206.00>176.00	10	0.9854	0.005	86.14	96.06	6.40	14.15
31	Atrazine	10.263	215.10>58.00	14	0.9956	0.005	105.06	87.03	5.32	9.79
32	beta-BHC	10.353	180.90>144.90	16	0.9999	0.005	99.79	88.56	2.82	4.70
33	Clomazone	10.358	204.10>107.00	20	0.9969	0.005	106.04	92.96	5.19	8.30
34	Quintozene	10.427	264.80>236.80	10	0.9933	0.005	107.48	96.18	12.28	9.91
35	Profluralin	10.432	318.10>199.10	16	0.9918	0.005	105.13	77.72	5.94	11.98
36	Pentachlorobenzonitrile	10.517	274.80>239.80	18	0.9978	0.005	93.02	87.04	5.76	8.34
37	gamma-BHC (Lindane)	10.525	180.90>144.90	16	0.9969	0.005	106.54	88.70	4.76	4.10
38	Terbuthylazine	10.561	229.10>173.10	6	0.9984	0.005	101.13	90.70	7.24	6.85
39	Terbufos	10.562	231.00>128.90	26	0.9975	0.005	99.07	82.77	3.85	5.67
40	Propyzamide	10.661	172.90>109.00	26	0.9911	0.005	93.55	87.95	3.92	3.19
41	Diazinon	10.67	304.10>179.10	10	0.9931	0.005	91.66	76.71	13.83	6.56
42	Fonofos	10.681	246.00>137.10	6	0.9948	0.005	93.42	84.43	6.40	5.79
43	Fluchloralin	10.712	306.00>264.00	8	0.9947	0.005	106.87	87.49	10.41	9.49

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)	Precision % RSD_r (n=6)
44	Pyrimethanil*	10.833	198.10>183.10	14	0.9988	0.01	101.94	87.09	3.99	5.00
45	Chlorothalonil	10.915	263.90>168.00	24	0.9810	0.01	82.43	57.23	12.68	11.40
46	Disulfoton	10.957	186.00>153.00	6	0.9736	0.005	80.35	81.06	11.52	11.43
47	Isazofos	10.964	257.00>162.00	8	0.9957	0.005	99.14	86.04	7.95	6.59
48	Tefluthrin	10.977	177.00>127.10	16	0.9997	0.005	99.43	74.33	2.19	2.61
49	Terbacil	11.014	161.00>144.00	14	0.9973	0.005	99.3	93.56	10.42	8.52
50	Tri-allate	11.146	268.10>184.00	20	0.9999	0.005	99.21	84.05	3.34	4.15
51	delta-BHC	11.169	180.90>144.90	16	0.9994	0.005	97.06	88.92	5.88	8.24
52	Pentachloroaniline	11.579	262.90>191.90	22	0.9962	0.005	109.97	90.56	4.78	6.21
53	Endosulfan ether	11.607	240.90>205.90	16	0.9984	0.005	100.43	90.50	12.47	7.99
54	Dimethachlor	11.721	197.10>148.10	10	0.9966	0.005	92.22	93.98	3.20	6.24
55	Acetochlor	11.823	174.10>146.10	12	0.9992	0.005	103.83	89.46	6.21	5.13
56	Chlorpyrifos-methyl	11.866	285.90>93.00	22	0.9984	0.005	103.09	81.84	5.78	6.67
57	Propanil	11.872	160.90>99.00	24	0.9941	0.01	103.12	80.82	15.75	7.98
58	Vinclozolin	11.957	212.00>172.00	16	0.9945	0.005	88.67	80.07	5.16	8.19
59	Parathion-methyl	12.032	263.00>109.00	14	0.9934	0.005	90.62	87.41	8.65	7.00
60	Tolclofos-methyl	12.054	264.90>93.00	24	0.9983	0.005	94.52	82.54	8.06	4.19
61	Alachlor	12.054	188.10>160.10	10	0.9966	0.005	96.38	95.06	5.03	3.61
62	Transfluthrin	12.096	163.10>127.10	6	0.9994	0.005	101.83	79.95	7.06	2.46
63	Propisochlor	12.165	162.10>120.10	14	0.9946	0.005	92.1	109.95	5.54	7.62
64	Metalaxyl (Mefenoxam) *	12.241	249.20>190.10	8	0.9989	0.01	98.84	93.29	7.96	5.05
65	Heptachlor	12.29	271.80>236.90	20	0.9985	0.005	95.64	78.27	5.68	5.95
66	Fenchlorphos	12.313	286.90>271.90	18	0.9989	0.005	96.69	85.52	3.80	7.04
67	Pirimiphos-methyl	12.595	290.10>125.00	22	0.9947	0.005	89.31	85.52	5.21	4.30
68	Prodiamine	12.65	321.10>279.10	6	0.9933	0.005	104.23	98.85	12.74	15.34
69	Fenitrothion	12.685	277.00>260.00	6	0.9945	0.005	104.72	85.29	9.70	7.32
70	Pentachlorothioanisole	12.855	295.80>262.90	14	0.9999	0.005	98.83	74.03	4.03	4.82
71	Dichlofluanid	12.884	223.90>123.10	8	0.9978	0.005	100.58	83.68	2.48	5.54
72	Linuron*	12.89	248.00>61.00	16	0.9806	0.01	84.08	90.93	7.72	8.87
73	Malathion	12.91	173.10>99.00	14	0.9889	0.005	90.38	90.07	5.38	3.90
74	Metolachlor (S-Metolachlor)	13.073	162.10>133.10	16	0.9993	0.005	101.36	90.20	2.82	2.10
75	Chlorpyrifos	13.121	313.90>257.90	14	0.9975	0.005	101.64	78.83	3.28	3.49
76	Fenthion	13.237	278.00>109.00	20	0.9990	0.005	98.76	85.15	4.15	2.54
77	Aldrin	13.262	262.90>191.00	34	0.9894	0.005	110.75	72.90	11.56	9.15
78	Chlorthal-dimethyl	13.272	298.90>220.90	24	0.9973	0.005	103.44	78.15	7.82	3.94
79	Anthraquinone	13.326	180.10>152.10	14	0.9972	0.005	100.68	100.10	9.62	6.04
80	Parathion	13.342	291.10>109.00	14	0.9882	0.005	91.71	80.12	10.79	10.77
81	Triadimefon*	13.433	208.10>111.00	22	0.9967	0.01	92.47	87.33	5.39	3.60
82	4,4'-Dichlorobenzophenone	13.582	139.00>111.00	14	0.9993	0.005	96.82	82.83	2.52	4.19
83	Pirimiphos ethyl	13.729	304.10>168.10	12	0.9944	0.005	91.71	82.81	6.12	6.48
84	Fenson	13.73	141.00>77.00	16	0.9997	0.005	98.33	83.43	2.48	4.76
85	Bromophos	13.756	330.90>315.90	14	0.9967	0.005	92.88	84.20	9.88	5.53
86	Diphenamid	13.773	167.10>152.10	20	0.9991	0.005	96.97	89.52	3.20	4.23

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)	Precision % RSD_r (n=6)
87	MGK 264-1	13.809	164.10>93.00	10	0.9935	0.005	87.44	81.40	8.32	7.48
88	Isopropalin	13.886	280.10>238.10	8	0.9971	0.005	96.67	78.31	15.08	5.97
89	Pendimethalin	14.082	252.10>162.10	10	0.9798	0.005	95.43	87.91	12.49	9.95
90	Isodrin	14.088	192.90>157.00	20	0.9956	0.005	92.39	82.03	11.30	5.70
91	Cyprodinil*	14.12	224.10>208.10	16	0.9992	0.01	101.1	90.07	5.02	4.08
92	Metazachlor	14.141	209.10>132.10	18	0.9993	0.005	97.22	100.45	6.15	4.23
93	MGK 264-2	14.175	164.10>98.00	12	0.9975	0.005	102.21	86.03	8.50	8.20
94	Fipronil*	14.248	368.90>214.90	30	0.9942	0.01	88.65	89.97	8.96	9.21
95	Penconazole*	14.275	248.10>157.10	26	0.9864	0.01	89.81	88.00	5.83	2.43
96	Chlozolinate	14.308	330.90>258.90	6	0.9897	0.005	108.29	77.48	20.50	18.49
97	Tolylfluanid	14.35	238.00>137.10	14	0.9996	0.005	100.62	83.44	5.31	6.64
98	Heptachlor-exo-epoxide	14.368	352.80>262.90	14	0.9973	0.005	100.16	91.21	11.03	11.22
99	(Z)-Chlorfenvinphos	14.393	323.00>267.00	16	0.9949	0.005	96.9	84.79	9.45	8.08
100	Bromfenvinfos-methyl	14.413	294.90>266.90	6	0.9963	0.005	97.17	86.28	11.68	11.39
101	Allethrin-3,4 (Bioallethrin)	14.503	123.10>81.10	10	0.9993	0.005	99.56	111.39	20.27	13.86
102	Quinalphos	14.57	146.10>118.00	10	0.9908	0.005	90.7	84.32	6.68	5.37
103	Procymidone	14.681	283.00>96.00	10	0.9985	0.005	95.5	90.38	9.03	7.49
104	Triadimenol-1*	14.692	168.10>70.00	10	0.9982	0.01	97.57	94.74	5.56	6.06
105	Triflumizole*	14.759	206.10>179.10	14	0.9898	0.01	109.87	86.09	8.82	14.03
106	Folpet	14.809	259.90>130.00	14	0.9999	0.025	100.22	90.94	4.67	9.34
107	Bromophos-ethyl	14.997	358.90>302.90	16	0.9966	0.005	94.25	83.19	3.12	4.50
108	Chlorbenside	15.063	125.00>89.00	16	0.9941	0.005	91.64	82.17	9.18	8.05
109	trans-Chlordane	15.078	374.80>265.90	26	0.9969	0.005	93.56	78.98	7.90	9.49
110	o,p'-DDE	15.152	246.00>176.00	30	0.9995	0.005	99.21	80.96	3.68	4.21
111	Tetrachlorvinphos	15.211	328.90>109.00	20	0.9440	0.005	75.87	78.49	6.69	17.37
112	Paclobutrazol*	15.26	236.10>125.00	14	0.9946	0.01	92.29	91.99	4.58	2.00
113	cis-Chlordane	15.476	374.80>265.90	26	0.9932	0.005	89.07	80.18	14.14	3.08
114	alpha-Endosulfan	15.478	194.90>160.00	8	0.9961	0.005	97.71	83.81	13.47	12.90
115	trans-Nonachlor	15.576	406.80>299.90	24	0.9981	0.005	98.81	78.96	6.11	13.56
116	Flutriafol*	15.613	219.10>123.10	14	0.9954	0.01	95	88.71	4.82	2.94
117	Bromfenvinphos	15.621	266.90>159.00	14	0.9669	0.005	78.07	85.01	5.34	7.79
118	Fenamiphos	15.702	303.10>195.10	8	0.9651	0.01	108.18	107.72	4.65	11.25
119	Iodofenphos	15.788	376.90>361.80	22	0.9869	0.005	98.84	78.39	5.85	7.65
120	Flutolanil*	15.798	173.00>145.00	14	0.9895	0.01	88.66	85.29	3.00	1.85
121	Chlorfenson	15.825	175.00>111.00	12	0.9983	0.005	98.53	86.33	3.60	4.88
122	Prothiofos	15.897	309.00>238.90	14	0.9900	0.005	92.08	82.99	11.52	7.77
123	Pretilachlor	15.957	262.10>202.10	10	0.9973	0.005	96.44	89.42	9.66	8.41
124	Fludioxonil*	15.978	248.00>127.00	26	0.9820	0.01	80.73	82.55	8.15	7.08
125	Profenofos	16.041	338.90>268.90	18	0.9785	0.005	95.81	74.82	12.12	10.69
126	p,p'-DDE	16.172	246.00>176.00	30	0.9997	0.005	97.93	76.01	7.01	9.55
127	Oxadiazon	16.193	258.00>175.00	8	0.9988	0.005	102.31	82.13	5.09	4.64
128	Myclobutanil*	16.309	179.10>125.00	14	0.9906	0.01	91.93	90.81	5.70	1.46
129	Dieldrin	16.324	276.90>241.00	8	0.9947	0.01	105.95	63.68	9.67	16.79

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)	Precision % RSD_r (n=6)
130	o,p'-DDD	16.378	235.00>165.00	24	0.9991	0.005	97.53	76.15	2.68	5.05
131	Flusilazole*	16.379	233.10>165.10	14	0.9876	0.01	90.51	91.19	7.77	7.69
132	Oxyfluorfen	16.387	252.00>196.00	22	0.9777	0.025	102.58	75.12	11.94	12.13
133	Bupirimate*	16.401	273.10>108.10	16	0.9980	0.01	98.39	88.78	6.94	3.95
134	Chlorfenapyr	16.717	247.10>227.00	16	0.9873	0.025	91.64	68.26	7.73	7.50
135	Chlorthiophos-1	16.892	256.90>193.00	22	0.9671	0.025	97.01	69.59	19.71	16.28
136	Nitrofen	16.96	202.00>139.00	24	0.9839	0.005	84.83	78.81	13.51	12.47
137	Endrin	16.98	262.90>191.00	30	0.9885	0.005	82.75	70.61	15.50	18.31
138	1,1-Dichloro-2,2-bis(4-ethylphenyl)ethane	16.998	223.20>167.10	14	0.9980	0.005	100.74	76.92	3.98	3.63
139	Fluazifop-P-butyl	17.007	282.10>91.00	18	0.9936	0.005	94.36	76.12	3.95	5.10
140	Chlorthiophos-2	17.204	324.90>268.90	14	0.9850	0.005	83.75	76.53	9.55	19.09
141	Chlorobenzilate	17.243	139.00>111.00	16	0.9972	0.005	93.42	80.60	3.20	2.71
142	beta-Endosulfan	17.339	194.90>160.00	8	0.9991	0.005	96.58	76.72	6.95	10.72
143	cis-Nonachlor	17.506	406.80>299.90	24	0.9964	0.005	93.97	74.95	7.06	9.88
144	Ethion	17.527	230.90>129.00	24	0.9812	0.005	89.16	82.77	3.95	3.40
145	p,p'-DDD	17.531	235.00>165.00	24	0.9960	0.005	94.82	75.69	2.82	5.84
146	o,p'-DDT	17.596	235.00>165.00	24	0.9975	0.005	99.68	75.24	6.64	4.56
147	Chlorthiophos-3	17.623	324.90>268.90	14	0.9909	0.005	91.34	84.08	5.93	6.81
148	Triazophos	18.048	257.00>162.00	8	0.9865	0.01	92.4	91.98	5.33	4.17
149	Sulprofos	18.06	322.00>156.00	8	0.9820	0.005	87.5	71.34	9.51	11.31
150	Carfentrazone-ethyl*	18.342	340.10>312.10	14	0.9942	0.01	94.64	81.39	5.92	1.98
151	Carbophenothion	18.4	157.00>45.00	18	0.9764	0.005	84.69	76.56	4.20	5.36
152	4,4'-methoxychlor olefin	18.42	238.10>223.10	12	0.9989	0.005	105.24	79.55	3.28	3.88
153	Edifenphos	18.489	173.00>109.00	10	0.9402	0.005	87.4	84.48	5.44	6.47
154	Norflurazon	18.556	145.00>95.00	18	0.9820	0.01	84.79	93.34	9.51	4.09
155	Endosulfan sulfate	18.603	271.80>236.90	18	0.9966	0.005	95.18	83.35	0.98	2.89
156	Lenacil	18.677	153.10>136.10	14	0.9787	0.005	86.15	85.89	12.60	7.40
157	p,p'-DDT	18.778	235.00>165.00	24	0.9795	0.005	88.64	74.73	2.97	3.74
158	Hexazinone	18.999	171.10>71.00	16	0.9833	0.005	81.92	90.48	5.62	6.73
159	2,4'-Methoxychlor	19.005	227.10>121.10	16	0.9896	0.005	93.54	79.16	2.32	4.20
160	Tebuconazole*	19.254	250.10>125.10	22	0.9869	0.01	91.85	89.86	9.61	2.40
161	Propargite-1*	19.331	135.10>107.10	16	0.9939	0.01	92.04	81.58	4.72	5.95
162	Propargite-2*	19.382	135.10>107.10	16	0.9970	0.01	92.52	80.21	5.45	6.96
163	Resmethrin-1	19.444	143.10>128.10	10	0.9535	0.025	90.33	84.92	7.47	9.93
164	Piperonyl butoxide*	19.582	176.10>131.10	12	0.9947	0.01	94.55	82.89	4.74	4.04
165	Nitralin	19.6	316.10>274.00	8	0.9688	0.005	87.7	88.14	4.97	6.59
166	Resmethrin-2 (Bioresmethrin)	19.676	143.10>128.10	10	0.9953	0.005	94.56	78.93	8.69	7.37
167	Pyridaphenthion	20.127	340.00>199.10	8	0.9512	0.005	81.8	85.11	15.81	10.95
168	Endrin ketone	20.153	316.90>244.90	20	0.9943	0.01	97.51	91.88	5.10	14.38
169	Iprodione	20.204	314.00>245.00	12	0.9964	0.01	96.51	104.29	9.94	6.52
170	Tetramethrin-1	20.284	164.10>107.10	14	0.9984	0.005	97.26	81.31	6.03	8.55
171	Phosmet	20.332	160.00>105.00	18	0.9592	0.01	86.2	82.88	3.16	4.36
172	EPN	20.445	169.10>140.90	8	0.9877	0.005	91.45	86.43	6.61	8.28

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)	Precision % RSD_r (n=6)
173	Bifenthrin	20.496	181.10>166.10	12	0.9960	0.005	98.51	74.68	4.26	2.54
174	Bromopropylate	20.503	340.90>182.90	18	0.9929	0.005	94.78	84.84	3.52	5.52
175	Tetramethrin-2	20.588	164.10>107.10	14	0.9907	0.005	92.71	80.95	1.83	3.49
176	Methoxychlor	20.698	227.10>169.10	24	0.9869	0.005	96.75	79.21	4.82	3.49
177	Fenpropathrin	20.815	181.10>152.10	22	0.9835	0.005	98.6	75.29	12.70	5.86
178	Tebufenpyrad*	20.999	333.10>171.10	20	0.9909	0.01	89.83	75.79	5.20	2.46
179	Phenothrin-1	21.316	123.10>81.00	8	0.9952	0.01	104.37	70.59	8.39	15.08
180	Tetradifon	21.388	226.90>199.00	16	0.9990	0.005	96.58	76.22	9.21	8.18
181	Phenothrin-2	21.54	123.10>81.00	8	0.9955	0.005	102.01	78.52	7.19	5.86
182	Phosalone	21.61	182.00>111.00	14	0.9733	0.005	91.26	75.49	1.91	4.14
183	Leptophos	21.624	376.90>361.90	24	0.9814	0.005	89.52	71.33	3.19	6.27
184	Azinphos-methyl	21.729	160.10>77.00	20	0.9247	0.01	79.18	76.71	6.48	4.97
185	Pyriproxyfen*	21.979	136.10>78.00	20	0.9933	0.01	91.98	68.49	4.50	6.26
186	Mirex	22.286	271.80>236.80	18	0.9990	0.005	102.41	78.17	2.55	3.38
187	lambda-Cyhalothrin	22.38	181.10>152.10	24	0.9936	0.005	99.06	74.80	4.54	7.00
188	Fenarimol*	22.599	251.00>139.00	14	0.9904	0.01	90.94	88.38	3.78	2.47
189	Pyrazophos	22.675	221.10>193.10	12	0.9822	0.005	91.63	88.05	8.51	11.76
190	Acrinathrin-2	22.78	181.10>152.10	26	0.9896	0.005	91.16	81.57	9.22	10.52
191	Azinphos-ethyl	22.857	160.10>132.10	4	0.9499	0.005	87.3	85.28	5.43	4.90
192	Pyraclofos	23.223	194.00>138.00	22	0.9387	0.01	82.2	89.40	7.03	7.44
193	cis-Permethrine	23.848	183.10>153.10	14	0.9949	0.005	99.36	73.30	5.15	4.74
194	Coumaphos	24.05	362.00>109.00	16	0.9760	0.01	88.32	79.03	5.95	3.42
195	Fluquinconazole*	24.057	340.00>298.00	20	0.9903	0.01	91.66	84.83	2.88	3.24
196	Pyridaben*	24.096	147.10>117.10	22	0.9784	0.01	86.92	68.73	5.64	1.62
197	trans-Permethrine	24.107	183.10>153.10	14	0.9908	0.005	97.37	77.13	3.86	3.69
198	Prochloraz*	24.229	180.10>138.10	12	0.9732	0.02	106.27	104.34	4.99	2.15
199	Cyfluthrin-1	24.93	163.10>127.10	6	0.9938	0.01	97.72	80.04	5.99	4.33
200	Cyfluthrin-2	25.134	163.10>127.10	6	0.9717	0.01	82.4	83.54	5.64	5.12
201	Cyfluthrin-3	25.239	163.10>127.10	6	0.9702	0.01	93.03	75.66	6.07	2.30
202	Cyfluthrin-4	25.335	163.10>127.10	6	0.9730	0.01	92.6	74.57	4.76	4.07
203	Cypermethrin-1	25.539	163.10>127.10	6	0.9858	0.01	93.64	75.85	4.06	2.50
204	Cypermethrin-2	25.754	163.10>127.10	6	0.9840	0.01	86.18	80.82	5.62	3.99
205	Cypermethrin-3	25.847	163.10>127.10	6	0.9859	0.01	84.75	70.41	3.71	5.59
206	Flucythrinate-1	25.882	157.10>107.10	12	0.9881	0.005	93.79	75.00	3.79	3.06
207	Cypermethrin-4	25.942	163.10>127.10	6	0.9774	0.01	90.01	73.13	7.96	5.74
208	Etofenprox	26.142	163.10>135.10	10	0.9977	0.005	96.62	72.44	3.34	3.18
209	Flucythrinate-2	26.276	157.10>107.10	12	0.9865	0.005	86.13	77.55	4.10	3.72
210	Fenvalerate-1	27.235	225.10>147.10	10	0.9870	0.01	89.28	79.96	7.03	5.50
211	tau-Fluvalinate-1	27.522	250.10>55.00	18	0.9818	0.005	91.99	74.77	3.88	2.30
212	Fenvalerate-2 (Esfenvalerate)	27.644	225.10>119.10	20	0.9927	0.01	93.9	67.55	7.48	3.97
213	tau-Fluvalinate-2	27.671	250.10>55.00	18	0.9767	0.005	89.66	79.06	3.93	5.60
214	Deltamethrin-2 (Tralomethrin deg.-2)	28.681	252.90>93.00	20	0.9795	0.005	91.08	75.45	1.98	3.90

At LOQ level, out of total compounds, mean recoveries of 190 on LC-MS/MS and 207 on GC-MS/MS were found to be within 70-120 %. Whereas 17 compounds on LC-MS/MS and 7 compounds on GC-MS/MS showed recoveries less than 70 %. Only in LC-MS/MS 37 compounds 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 Table 4 and 5)

The method successfully achieved 1 µg/kg and 2 µg/kg LOQ on LC-MS/MS for 123 and 18 compounds, respectively. From remaining pesticides, 5 µg/kg LOQ was obtained on LC-MS/MS for 80 and on GC-MS/MS for 158 compounds. LOQ of 10 µg/kg could be achieved for 71 compounds (21 on LC-MS/MS and 50 on GC-MS/MS). Only 1 compound showed LOQ of 20 µg/kg on GC-MS/MS and 7 compounds showed LOQ of 25 µg/kg (2 on LC-MS/MS and 5 on GC-MS/MS). (Refer to Table 4 and 5). Representative chromatograms of a few compounds at their LOQ levels are shown in Fig. 4 and 5.

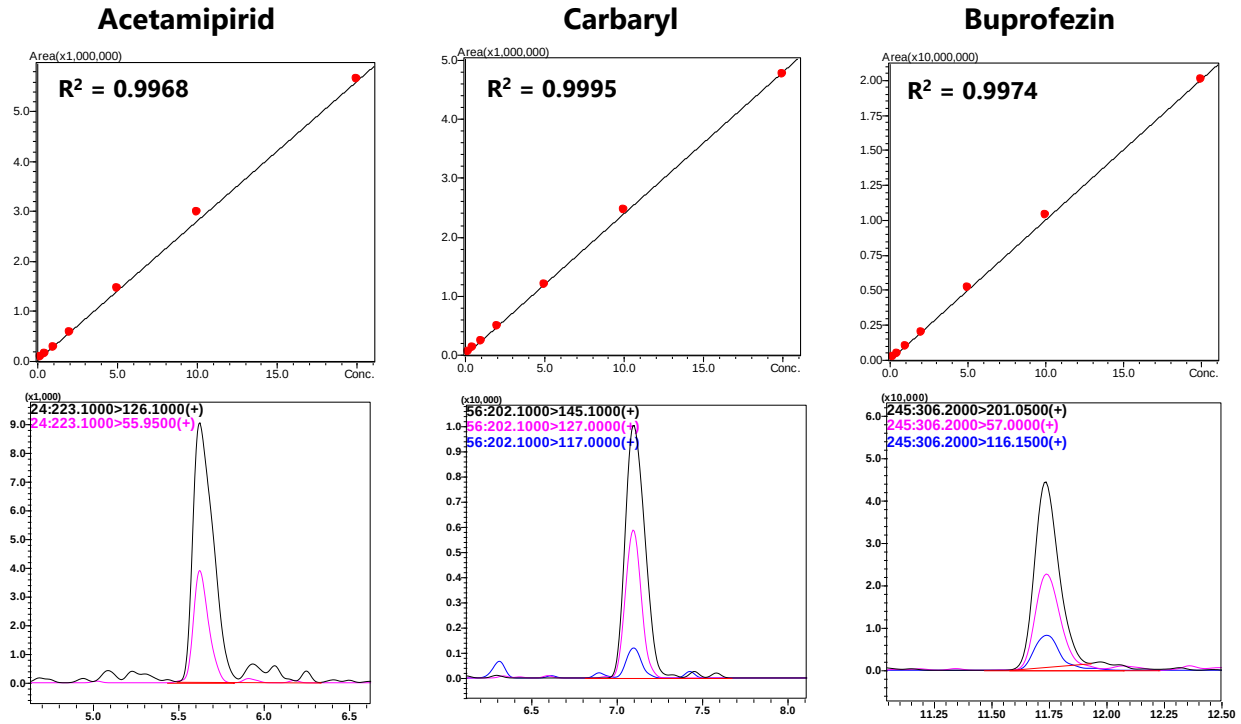

Fig. 4 Representative linearity graphs and chromatograms at LOQ level for LC-MS/MS compounds

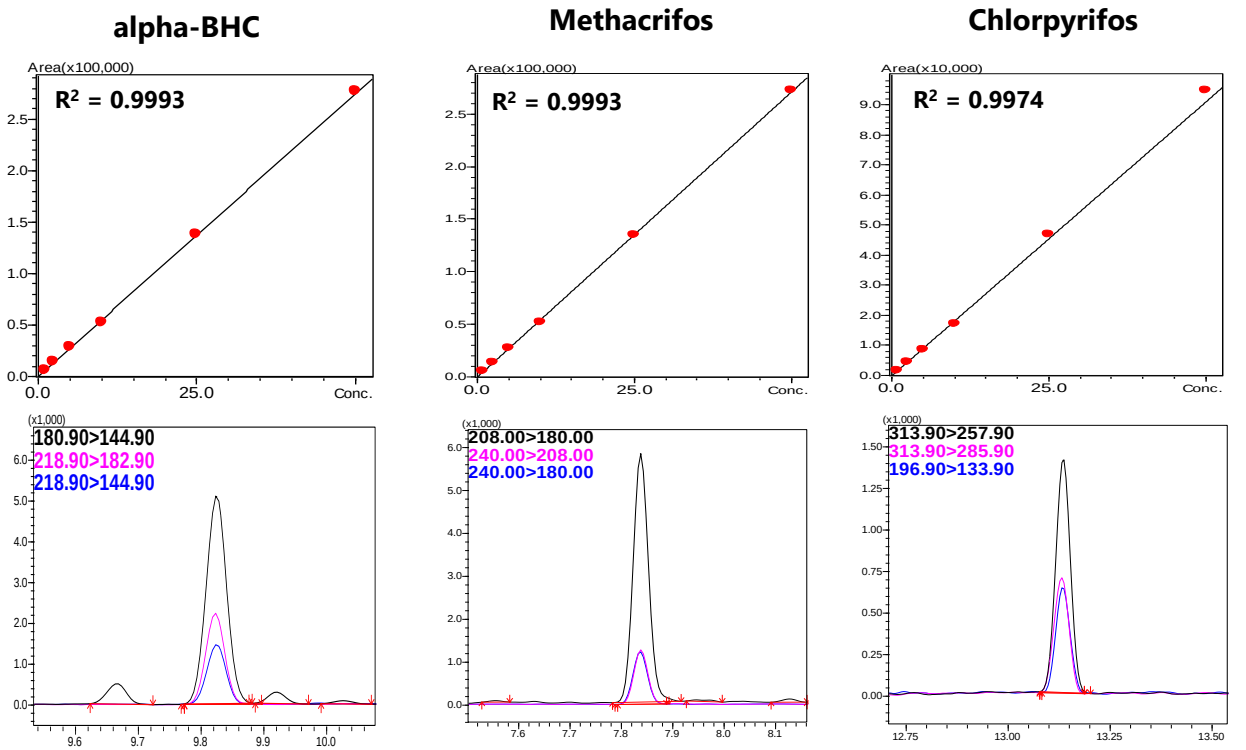

Fig. 5 Representative linearity graphs and chromatograms at LOQ level for GC-MS/MS compounds

4. Conclusion

A simple, sensitive and rapid method has been developed to quantify 431 pesticides by LC-MS/MS and GC-MS/MS in honey sample. Quantification of pesticides in honey is challenging due to the high sugar content. Highly sensitive Shimadzu LC-MS/MS and GC-MS/MS were able to achieve low LOQ levels even with simple liquid-liquid extraction and PSA clean-up.

The developed method is 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 honey samples.

5. References

1. Guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed. SANTE/11312/2021

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