

Application News

SGLC-LC/MS-051EN

LCMS-8060NX

Analysis of 331 Pesticides and Their Metabolites in rapeseed oil

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User Benefits

- ◆ Established an effective, fast and simple sample preparation method for analysis of pesticides in rapeseed oil.
- ◆ Realized simultaneous quantitative analysis of multi pesticides and metabolites, such as organophosphates, organochlorines, pyrethroids, triazole, amides, triazines and carbamate esters.
- ◆ SHIMSEN QuEChERS provides precise amounts salts in sachet packs and SPE sorbents in centrifuge tube for enhanced laboratory efficiency and throughput.

Introduction

Pesticides are essential tools in agriculture for protecting crops from pests and diseases, but their presence in food products must be carefully monitored to ensure consumer safety. rapeseed oil, a widely consumed cooking oil, are no exception. Pesticide residues in rapeseed oil can pose potential health risks and impact the quality of the final products. Therefore, rigorous analysis methods are crucial to determine the levels of pesticide residues in rapeseed oil and ensure compliance with regulatory standards. In this application, we present a complete workflow according to GB23200.121-2021, from sample preparation using SHIMSEN QuEChERS, to sample analysis using Shim-pack GIST C18-AQ column on Shimadzu LCMS-8060NX.

Table 1. LCMS conditions

UHPLC condition:

LC system:	Shimadzu Nexera™ LC-40B X3
Column:	Shim-pack GIST C18-AQ, 1.9 μ m, 100 $\times$ 2.1 mm *1
Column Temp.:	40 °C
Flow rate:	0.3 mL/min
Mobile phase A:	2mM ammonium formate in water containing 0.01% formic acid
Mobile phase B:	2mM ammonium formate in methanol containing 0.01% formic acid
Gradient program:	3% B (0 min) $\rightarrow$ 3%B (1 min) $\rightarrow$ 15% B (1.5 min) $\rightarrow$ 50% B (2.5 min) $\rightarrow$ 70% B (18 min) $\rightarrow$ 98% B (23 min) $\rightarrow$ 98% B (27 min) $\rightarrow$ 3% B (27.1 min) $\rightarrow$ 3% B (30 min)
Injection volume:	2 μ L (co-injection, 20 μ L water)

MS conditions:

Interface:	Heated ESI (Positive or Negative)
Interface temp:	300 °C
Collision gas:	Ar
Nebulizing gas:	N ₂ , 3 L/min
Heating gas flow:	Zero air, 10 L/min
DL temperature:	150 °C
Drying gas flow:	N ₂ , 10 L/min
Heat block temp:	400 °C
MS mode:	MRM

*1 P/N: 227-30807-02

Experimental

Materials:

SHIMSEN QuEChERS Extract Salt (P/N: 380-00149)

SHIMSEN QuEChERS II (P/N: 380-00990-16)

Filter and vial:

SHIMSEN Disc HPTFE syringe filter (P/N: 380-00341)

LabTotal Vial (P/N: 227-34001-01)

Sample Preparation:

2.0 g of homogenized sample in 50 mL centrifuge tube was added with 5 mL ultrapure water, 10 mL of acetonitrile followed by SHIMSEN QuEChERS extraction salt (4 g MgSO₄, 1 g NaCl, 0.5 g DHS, 1 g TSCD, P/N: 380-00149) and a single piece of ceramic homogenizer (P/N: 380-00171). The tube was shake vigorously for 1 min after which centrifuged for 5 minutes at 4200 rpm. 6 mL of the supernatant was transferred into SHIMSEN QuEChERS II (300mg C18, 30 mg PSA, 900 mg MgSO₄, P/N: 380-00990-16), vortex and mix for 1min, centrifuged at 4200 rpm for 5 min, and filtered 2 mL of the supernatant through a 0.22 μ m syringe filter for LC-MS/MS analysis. Figure shows the simplified sample preparation workflow.

Weigh 2.0 g sample, add 5 mL ultrapure water and 10 mL acetonitrile.

Add QuEChERS extraction salt and ceramic homogenizer for 50 mL tube, vortex for 1 min, and centrifuge at 4200 rpm for 5 min.

Transfer 6 mL supernatant to QuEChERS dSPE tube, vortex for 1 min, centrifuge at 4200 rpm for 5 min.

Transfer 2 mL supernatant and filtered with 0.22 μ m syringe filter.

LC-MS/MS analysis.

Figure 1. QuEChERS sample preparation workflow for rapeseed oil.

Table 2. List of MRM used for each pesticides.

No.	Compounds	Mode	Retention time (min)	Precursor ion	Quantifying ion	Q1 Pre Bias	CE	Q3 Pre Bias	Qualifying ion	Q1 Pre Bias	CE	Q3 Pre Bias
1	methamidophos	+	3.978	142.1	94	-16	-15	-17	125.1	-16	-16	-23
2	acephate	+	4.525	184.2	143	-20	-8	-15	95	-20	-23	-16
3	omethoate	+	4.708	214.1	183	-23	-10	-19	155	-23	-14	-28
4	oxamyl oxime	+	4.719	163	72.1	-11	-12	-16	90	-11	-18	-20
5	propamocarb	+	4.732	189.2	102.1	-30	-20	-23	144.1	-30	-12	-15
6	aldicarb sulfoxide	+	4.789	207	89	-13	-15	-19	132	-19	-10	-10
7	dinotefuran	+	4.817	203.1	129.1	-22	-12	-22	113.1	-22	-10	-12
8	aldicarb sulfone	+	4.917	240.1	148	-15	-12	-29	166	-13	-11	-20
9	oxamyl	+	4.996	237.1	72	-12	-10	-15	90.1	-12	-8	-20
10	nitenpyram	+	5.033	271.1	126	-14	-26	-20	189.1	-14	-13	-19
11	oxydemeton- methyl	+	5.071	247	169	-30	-24	-30	105.1	-30	-20	-30
12	demeton-S- methyl-sulfone	+	5.173	263	169	-30	-24	-30	125	-30	-30	-26
13	flonicamid	+	5.195	230.1	203.1	-25	-10	-25	174.2	-11	-25	-19
14	thiamethoxam	+	5.25	292	211.1	-30	-20	-22	181.1	-30	-30	-19
15	methomyl	+	5.262	163.1	88	-18	-8	-16	106.1	-18	-10	-19
16	monocrotophos	+	5.289	224.1	193	-15	-9	-22	127.1	-18	-20	-15
17	dicrotophos	+	5.435	238	112.1	-12	-12	-11	193	-12	-9	-20
18	phosfolan- methyl	+	5.453	228	168	-11	-25	-13	109	-11	-15	-22
19	chlordimeform	+	5.474	197.1	46.2	-21	-35	-19	117.3	-22	-40	-24
20	spirotetramat- enol-glucoside	+	5.521	464	302	-22	-16	-23	216	-22	-42	-16
21	imidacloprid	+	5.686	256.1	209.1	-29	-14	-22	175.1	-29	-17	-18
22	clothianidin	+	5.792	250	169.1	-29	-12	-17	132	-29	-14	-24
23	methiocarb sulfoxide	+	5.862	242.1	185.1	-30	-24	-19	122.1	-11	-40	-26
24	flumetsulam	+	5.858	326.1	129.1	-12	-15	-25	109	-12	-51	-23
25	imidaclothiz	+	5.921	262.1	181.1	-13	-25	-14	122	-10	-40	-15
26	vamidothion	+	5.932	287.8	118.1	-14	-35	-22	146.1	-14	-26	-16
27	mevinphos	+	5.976/6.729	225	127.1	-25	-17	-23	193	-25	-8	-20
28	3-hydroxy carbofuran	+	6.044	238.1	163.1	-27	-14	-17	181.2	-27	-10	-19
29	acetamiprid	+	6.071	223.1	126.1	-30	-22	-30	56.1	-30	-15	-23
30	trichlorfon diethyl	+	6.079	257	109	-10	-34	-22	220.8	-29	-11	-24
31	aminoethyl hexanoate	+	6.131	216.2	143.3	-24	-25	-10	100.3	-24	-25	-23
32	dimethoate	+	6.136	230	199	-26	-15	-21	125	-26	-30	-22
33	demeton-S- sulfoxide	+	6.16	275.1	197	-10	-17	-15	141	-10	-30	-28
34	carbendazim	+	6.14	192.1	160.1	-30	-39	-30	132.1	-30	-40	-24
35	metamitron	+	6.164	203.1	175	-10	-18	-20	104	-10	-23	-22
36	sulfoxaflor	+	6.172/6.280	278.1	174.2	-21	-11	-19	154.1	-20	-26	-25
37	methiocarb sulfone	+	6.31	258.1	122.1	-13	-23	-24	201.1	-29	-8	-14
38	demeton-S- sulfone	+	6.356	291	234.8	-14	-15	-18	263	-11	-11	-20
39	chloridazon	+	6.364	222	92.1	-25	-26	-16	77.1	-25	-36	-30
40	cymoxanil	+	6.498	199.1	128.1	-21	-8	-25	111.1	-21	-18	-21
41	thiacloprid	+	6.649	253	126.1	-28	-30	-22	99	-28	-43	-17
42	isoxaflutole- diketonitrile	-	6.811	358.1	79	12	23	26	64	12	50	11
43	pirimicarb- desmethyl	+	6.788	225	72.1	-30	-42	-30	180.1	-30	-15	-30
44	fensulfothion oxon	+	6.875	293.1	237	-11	-29	-18	265	-11	-23	-20
45	thiabendazole	+	7.151	202	175.1	-30	-35	-30	131.1	-30	-25	-24

Table 2 continue. List of MRM used for each pesticides.

No.	Compounds	Mode	Retention time (min)	Precursor ion	Quantifying ion	Q1 Pre Bias	CE	Q3 Pre Bias	Qualifying ion	Q1 Pre Bias	CE	Q3 Pre Bias
46	fensulfothion oxon sulfone	+	7.153	309.1	175	-18	-20	-20	253	-15	-25	-20
47	florasulam	+	7.168	360.1	129.1	-24	-23	-23	109.1	-24	-54	-18
48	phosfolan	+	7.203	256	228	-13	-12	-25	140	-13	-15	-26
49	tricyclazole	+	7.266	190	163	-21	-21	-30	136	-21	-26	-24
50	aldicarb	+	7.29	207.9	116	-14	-6	-12	89	-15	-15	-18
51	oxadixyl	+	7.651	279.1	219.1	-30	-18	-23	133.1	-30	-30	-24
52	phosmet oxon	+	7.706	302	160	-11	-40	-19	133	-11	-25	-16
53	phosphamidon	+	7.601/7.776	300	174.1	-15	-22	-17	127	-15	-40	-22
54	formothion	+	7.701	258	199	-23	-8	-16	125	-10	-23	-25
55	metolcarb	+	7.983	166.1	109.1	-18	-20	-20	107.1	-18	-15	-19
56	cinosulfuron	+	8.089	414.1	183.1	-20	-30	-19	157.1	-20	-15	-16
57	triflumizole metabolite FM-6- 1	+	8.188	295	43.1	-10	-23	-18	73	-10	-18	-15
58	cyanazine	+	8.229	241.1	104	-30	-31	-19	68.1	-30	-39	-27
59	thifensulfuron- methyl	+	8.338	388.1	167.1	-19	-16	-18	141.1	-19	-22	-27
60	spirotetramat- mono-hydroxy	+	8.471	304.1	254.1	-11	-18	-29	211	-15	-19	-16
61	phenamacril	+	8.498	217.1	104	-11	-40	-20	189.1	-11	-17	-22
62	dichlorvos	+	8.493	238	109.1	-12	-21	-20	220.9	-12	-11	-15
63	probenazole	+	8.517	224	41	-16	-42	-18	39	-11	-55	-17
64	triasulfuron	+	8.613	402.1	167.1	-20	-18	-30	141.1	-20	-20	-26
65	metsulfuron- methyl	+	8.653	382.1	167.1	-14	-12	-13	199	-13	-20	-15
66	propoxur	+	8.681	210.1	111.1	-23	-13	-20	168.1	-23	-7	-18
67	thidiazuron	+	8.773	221.2	102	-15	-16	-18	128	-15	-17	-23
68	pirimicarb- desmethyl- formamido	+	8.794	253.1	72	-20	-25	-20	225	-17	-10	-18
69	fenamiphos sulfoxide	+	8.814	319.8	233	-30	-23	-26	292.1	-30	-16	-21
70	thiophanate- methyl	+	8.806	343	151	-12	-19	-29	311	-12	-10	-17
71	metribuzin	+	8.846	215.1	187.1	-25	-18	-18	84.1	-25	-21	-30
72	bendiocarb	+	8.876	224.1	167.1	-25	-15	-18	109.1	-25	-30	-20
73	carbofuran	+	8.888	222.1	123.1	-25	-30	-22	165.1	-25	-20	-17
74	hexazinone	+	8.927	253.2	171.1	-30	-20	-18	85.1	-30	-31	-15
75	demeton-S- methyl	+	8.995	231	89	-21	-24	-19	61	-10	-21	-23
76	malaoxon	+	9.019	314.9	127	-15	-20	-23	99	-15	-45	-19
77	tebuthiuron	+	9.141	229.1	172.1	-30	-20	-30	116.1	-30	-25	-23
78	amidosulfuron	+	9.189	370.2	261.1	-13	-14	-27	218.1	-13	-23	-22
79	simazine	+	9.258	202.1	132	-30	-19	-25	124.1	-30	-17	-23
80	fenamiphos sulfone	+	9.29	335.9	266	-16	-14	-29	188.1	-16	-35	-21
81	chlorsulfuron	+	9.286	358.1	141.1	-18	-17	-15	167	-17	-18	-30
82	ethirimol	+	9.307	210.2	140.1	-13	-22	-25	98.1	-13	-26	-16
83	sulfentrazone	-	9.452	385	307.1	18	23	21	199	18	35	20
84	fenthion sulfoxide	+	9.684	295	280	-11	-25	-10	109	-11	-25	-20

Table 2 continue. List of MRM used for each pesticides.

No.	Compounds	Mode	Retention time (min)	Precursor ion	Quantifying ion	Q1 Pre Bias	CE	Q3 Pre Bias	Qualifying ion	Q1 Pre Bias	CE	Q3 Pre Bias
85	carbaryl	+	9.89	202.1	145.1	-22	-9	-26	127.1	-22	-27	-22
86	carboxin	+	10.142	236.1	143	-10	-22	-16	87	-10	-23	-19
87	pirimicarb	+	10.17	239.2	72.1	-30	-40	-30	182.2	-30	-19	-30
88	fenthion sulfone	+	10.459	311	125	-11	-18	-15	233.1	-14	-23	-24
89	penoxsulam	+	10.486	484.1	195	-11	-27	-15	444	-18	-25	-18
90	fosthiazate	+	10.545	284.1	104.1	-30	-21	-19	228	-30	-15	-24
91	cyantraniliprole	+	10.553	475	286	-11	-19	-22	444	-17	-19	-24
92	spirotetramat- enol	+	10.788	302.1	216	-15	-27	-17	270	-11	-20	-15
93	phorate sulfoxide	+	10.835	277	199	-10	-10	-15	96.9	-10	-34	-19
94	disulfoton sulfoxide	+	10.855	291	185	-30	-20	-19	213	-30	-16	-23
95	chlortoluron	+	10.898	213.1	72	-10	-40	-16	46.1	-13	-25	-19
96	isoprocarb	+	11.269	194.1	95	-21	-30	-17	137.1	-22	-15	-14
97	disulfoton sulfone	+	11.344	306.8	96.9	-15	-20	-18	125	-15	-25	-23
98	simetryn	+	11.361	214.2	96.2	-25	-24	-21	68.2	-24	-30	-27
99	phorate sulfone	+	11.422	293	171.1	-22	-9	-19	115	-22	-24	-20
100	tritosulfuron	+	11.45	446	195	-16	-20	-23	221	-21	-19	-12
101	imazalil	+	11.428	297	159	-15	-24	-15	201	-15	-18	-21
102	flutriafol	+	11.494	302.1	123	-15	-28	-22	109	-15	-31	-19
103	methacrifos	+	11.514/13.7 81	240.8	209	-12	-10	-23	125	-12	-20	-24
104	metazachlor	+	11.752	278.1	210.1	-30	-14	-22	134.1	-30	-35	-24
105	mesosulfuron- methyl	+	11.785	504.1	182.1	-34	-25	-18	139	-34	-52	-26
106	isoproturon	+	11.795	207.1	72	-23	-40	-28	165.1	-23	-20	-17
107	atrazine	+	11.872	216.1	174.1	-30	-17	-18	96.1	-30	-25	-17
108	chlorpropham	+	11.895	214	172	-10	-10	-18	154	-18	-16	-14
109	propachlor	+	11.895	212.1	170	-30	-22	-18	94.1	-30	-20	-18
110	metalaxyl	+	11.969	280.1	220.2	-30	-10	-24	192.2	-30	-25	-20
111	fensulfothion	+	12.304	309	281	-11	-15	-30	253	-11	-18	-26
112	diuron	+	12.293	233	72	-14	-21	-15	46	-12	-16	-19
113	heptenophos	+	12.339	251	127	-28	-11	-25	109	-28	-29	-20
114	forchlorfenuron	+	12.343	248.1	129.1	-30	-17	-23	93.1	-30	-34	-17
115	tribenuron- methyl	+	12.374	396.1	155	-19	-30	-30	181	-19	-30	-28
116	isoxaflutole	+	12.373	360.1	251	-20	-19	-27	144	-23	-50	-30
117	orthosulfamuron	+	12.435	425	199.1	-30	-13	-21	227	-30	-15	-24
118	spirotetramat- keto-hydroxy	+	12.451	318	300	-12	-13	-23	214	-12	-25	-16
119	isocarbophos	+	12.484	231	121	-16	-19	-23	109	-11	-24	-13
120	iodosulfuron- methyl-sodium	+	12.622	507.9	167	-20	-19	-19	83	-26	-53	-15
121	fenpropidin	+	12.775	274.1	147.1	-30	-35	-30	117.2	-14	-53	-21
122	clethodim sulfone	+	12.777	392.1	300	-11	-14	-22	164	-11	-26	-19
123	fensulfothion sulfone	+	13.04	325	191	-12	-23	-11	173	-21	-24	-19

Table 2 continue. List of MRM used for each pesticides.

No.	Compounds	Mode	Retention time (min)	Precursor ion	Quantifying ion	Q1 Pre Bias	CE	Q3 Pre Bias	Qualifying ion	Q1 Pre Bias	CE	Q3 Pre Bias
124	clethodim sulfoxide	+	12.986/13.1 56	376.1	206	-18	-14	-16	164.1	-18	-23	-13
125	flumorph	+	13.373	372.1	285.1	-17	-15	-29	165.2	-17	-23	-28
126	metazosulfuron	+	13.374	476.1	182	-17	-21	-21	295	-17	-16	-23
127	methidathion	+	13.577	303	145	-21	-8	-15	85.1	-21	-22	-30
128	demeton	+	13.783	259	89	-13	-9	-18	61	-10	-32	-13
129	clomazone	+	13.842	240.1	125	-27	-10	-22	89.1	-27	-35	-16
130	fenobucarb	+	14.103	208.1	95	-10	-30	-20	152	-18	-15	-12
131	phenmedipham	+	14.113	318.1	168	-11	-20	-19	136	-11	-35	-16
132	flucetosulfuron	+	13.315/14.1 19	488	156	-25	-21	-28	273	-25	-26	-28
133	bensulfuron- methyl	+	14.148	411.1	149.2	-20	-14	-28	182.2	-20	-35	-19
134	chlorantranilipro le	+	14.222	484	452.9	-24	-19	-30	285.9	-24	-16	-30
135	saflufenacil	+	14.274	501.1	349	-20	-28	-23	459	-40	-15	-21
136	azinphos-methyl	+	14.457	318.1	132.1	-15	-14	-23	261	-15	-7	-28
137	ametryn	+	14.521	228.1	186.1	-30	-25	-19	68.1	-30	-30	-27
138	terbufos sulfoxide	+	14.56	305	186.9	-30	-20	-30	97	-30	-52	-10
139	propanil	+	14.676	218	162	-24	-15	-17	127	-24	-26	-23
140	phosmet	+	14.686	318	160	-16	-30	-17	133.2	-16	-35	-25
141	terbufos sulfone	+	14.748	321	171	-22	-12	-17	115	-22	-26	-24
142	albendazole	+	14.806	266	234	-12	-30	-23	191	-12	-25	-30
143	diethofencarb	+	14.821	268.1	226.1	-30	-15	-24	180.1	-30	-25	-19
144	pyrifthalid	+	14.838	319	139	-22	-27	-25	179	-22	-31	-29
145	linuron	+	14.829	249	160.1	-27	-17	-17	182.1	-28	-14	-19
146	benazolin-ethyl	+	14.937	272	198	-13	-15	-25	170	-18	-25	-19
147	ethofumesate	+	14.951	304.1	241.1	-20	-13	-13	259	-22	-16	-29
148	pyrimethanil	+	14.96	200.1	107	-30	-25	-19	168.1	-30	-29	-30
149	methiocarb	+	15.179	226.1	169.1	-25	-19	-18	121.1	-25	-25	-23
150	dimethenamid	+	15.201	276.1	244.1	-14	-23	-25	168.1	-14	-30	-17
151	ethiprole	+	15.259	397	255	-20	-45	-26	351	-20	-15	-24
152	pyrisoxazole	+	15.430/16.6 01	289.1	151.1	-11	-14	-18	120	-11	-20	-14
153	terbuthylazine	+	15.712	230.1	174.1	-10	-25	-20	104.1	-15	-25	-22
154	flurtamone	+	15.783	334.1	247.1	-12	-35	-19	303	-12	-20	-23
155	promecarb	+	15.866	208.2	109.1	-22	-10	-19	151.1	-22	-15	-16
156	paclobutrazol	+	16.078	294.1	70.1	-15	-21	-28	125.1	-15	-40	-22
157	fenpropimorph	+	16.045	304.2	147.2	-30	-24	-27	119.1	-30	-30	-22
158	fenamidone	+	16.128	312.1	236.1	-11	-15	-24	92.1	-11	-24	-16
159	halosulfuron- methyl	+	16.11	435	182	-16	-21	-21	139	-10	-40	-16
160	fludioxonil	+	16.144	266.1	229	-10	-14	-18	158	-10	-46	-19
161	azoxystrobin	+	16.199	404.1	372.1	-30	-25	-26	329	-30	-28	-23
162	boscalid	+	16.185	343	307.1	-12	-18	-30	271.1	-12	-30	-26
163	molinate	+	16.363	188.1	126.1	-21	-13	-13	98.1	-20	-20	-18
164	propyzamide	+	16.365	256.1	190	-28	-13	-20	173	-28	-20	-18
165	cyproconazole	+	16.463	292.1	70.1	-30	-20	-27	125.1	-30	-30	-22
166	ethoxysulfuron	+	16.786	399.1	261	-20	-15	-29	218	-20	-26	-23

Table 2 continue. List of MRM used for each pesticides.

No.	Compounds	Mode	Retention time (min)	Precursor ion	Quantifying ion	Q1 Pre Bias	CE	Q3 Pre Bias	Qualifying ion	Q1 Pre Bias	CE	Q3 Pre Bias
167	triadimefon	+	16.839	294.1	69.2	-21	-22	-26	197.1	-21	-15	-21
168	fluxapyroxad	+	16.831	382	362.1	-11	-14	-25	342.1	-11	-21	-22
169	flutolanil	+	16.864	324.1	262.1	-16	-25	-27	242	-16	-20	-25
170	myclobutanil	+	16.874	289.1	70.1	-30	-21	-28	125.1	-30	-30	-22
171	chlorimuron-ethyl	+	16.876	415.1	186	-20	-20	-19	83.1	-20	-43	-15
172	fluopicolide	+	16.892	382.9	173	-17	-22	-30	145	-17	-47	-24
173	dimethomorph	+	16.915	388.1	301	-19	-30	-21	165.1	-19	-25	-30
174	cyazofamid	-	16.919	216	179.1	10	31	16	180.2	15	25	17
175	metabolite CCIM											
175	mepronil	+	17.058	270.2	119.1	-30	-25	-30	228.1	-30	-18	-30
176	malathion	+	17.1	331	127.1	-17	-12	-13	125	-12	-26	-25
177	triflusalufuron-methyl	+	17.208	493.1	264.1	-18	-15	-29	96.1	-18	-54	-18
178	mandipropamid	+	17.24	412.1	328.1	-11	-10	-22	125	-11	-25	-20
179	isoprothiolane	+	17.296	291.1	231.1	-14	-20	-25	189.1	-14	-30	-20
180	triadimenol	+	17.325	296.1	70.1	-10	-21	-15	99.2	-14	-16	-20
181	propyrisulfuron	+	17.356	456	261	-17	-16	-28	196	-17	-15	-20
182	uniconazole	+	17.439	292.1	70.1	-21	-24	-27	125	-21	-28	-23
183	sedaxane	+	17.629/19.2 10	332	159	-13	-38	-28	292	-12	-15	-20
184	pyrazosulfuron-ethyl	+	17.831	415.1	182.1	-21	-18	-19	139.1	-21	-42	-24
185	pyridaphenthion	+	17.957	341.1	189.1	-17	-15	-20	205.1	-23	-15	-22
186	prometryn	+	17.947	242.2	158.1	-30	-15	-29	200.2	-30	-12	-22
187	methoxyfenozide	+	18.053	369.2	149.1	-18	-16	-16	313.1	-18	-8	-22
188	fluopyram	+	18.059	397	173	-28	-20	-18	207.9	-28	-15	-22
189	fenpyrazamine	+	18.065	332	304	-16	-13	-17	272	-12	-13	-21
190	mefenacet	+	18.13	299.1	148.1	-15	-21	-15	120.1	-15	-40	-21
191	fenhexamid	+	18.16	301.9	97.1	-15	-23	-19	55.1	-15	-40	-22
192	isazofos	+	18.246	316	164	-11	-16	-19	122	-11	-26	-10
193	triticonazole	+	18.304	318.1	70.1	-11	-21	-15	125.1	-11	-26	-25
194	procymidone	+	18.43	284	256	-23	-18	-27	67	-19	-44	-28
195	ethoprophos	+	18.453	243.1	131	-26	-20	-23	97	-27	-32	-17
196	iprovalicarb	+	18.269/18.5 44	321.2	119.1	-30	-19	-22	203.1	-30	-8	-22
197	triazophos	+	18.583	314.1	162.2	-23	-35	-17	119.2	-23	-25	-21
198	flufenacet	+	18.628	364	152.1	-19	-30	-15	194.1	-19	-16	-20
199	tetraconazole	+	18.679	372	159.1	-27	-31	-29	70.2	-27	-24	-27
200	acetochlor	+	18.826	270.1	224.1	-10	-8	-17	148.2	-16	-19	-18
201	fenarimol	+	18.875	331	268.1	-16	-22	-28	259.1	-17	-26	-26
202	spirotetramat	+	19.028	374	302	-14	-17	-23	330	-14	-15	-25
203	napropamide	+	19.078	272.2	129.2	-30	-16	-23	171.1	-30	-17	-18
204	alachlor	+	19.064	270.1	238.1	-30	-10	-26	162.2	-30	-19	-30
205	epoxiconazole	+	19.162	330.1	121.2	-12	-20	-26	101	-12	-43	-21
206	cyclosulfamuron	+	19.201	422.2	261	-30	-17	-27	218.1	-30	-28	-22
207	metolachlor	+	19.227	284.1	252.1	-30	-25	-27	176.2	-30	-20	-19
208	chromafenozide	+	19.444	395.3	175.1	-14	-40	-20	339.2	-15	-7	-19
209	iprodione	+	19.526	330.1	245	-13	-16	-25	288	-25	-14	-20

Table 2 continue. List of MRM used for each pesticides.

No.	Compounds	Mode	Retention time (min)	Precursor ion	Quantifying ion	Q1 Pre Bias	CE	Q3 Pre Bias	Qualifying ion	Q1 Pre Bias	CE	Q3 Pre Bias
210	fipronil	-	19.623	387	351	14	17	23	282	14	32	17
	desulfinyl											
211	cyazofamid	+	19.682	325	108.1	-11	-12	-21	261.1	-24	-11	-30
212	fenbuconazole	+	19.71	336.9	125.1	-26	-27	-25	70	-26	-20	-28
213	thifluzamide	+	19.783	528.8	148	-26	-38	-26	488.9	-34	-24	-21
214	fenamiphos	+	20.025	304.1	217.1	-15	-15	-23	202	-15	-45	-21
215	diflubenzuron	+	20.012	311	158	-11	-15	-30	141.2	-11	-24	-11
216	flusilazole	+	20.055	316.1	247.1	-30	-18	-27	165.1	-30	-29	-30
217	bromuconazole	+	17.238/20.1 48	377.9	158.9	-19	-28	-30	70	-19	-23	-30
218	fenoxanil	+	19.862/20.2 12	329.1	302.1	-17	-12	-30	86.1	-17	-22	-15
219	bupirimate	+	20.293	317.1	108	-30	-26	-19	210.2	-30	-23	-22
220	fipronil	-	20.28	435	330	10	16	21	250	10	28	24
221	silthiofam	+	20.464	268.1	252	-10	-8	-26	73.1	-10	-27	-30
222	diclobutrazol	+	20.642	328	70	-12	-21	-15	70	-12	-22	-15
223	fenothiocarb	+	20.65	254.1	72.1	-13	-10	-28	160.1	-13	-14	-16
224	penconazole	+	20.678	284.1	70	-14	-17	-27	159	-14	-27	-30
225	iprobenfos	+	20.751	289.1	91.1	-30	-21	-16	205	-30	-10	-22
226	penflufen	+	20.838	318	141	-12	-20	-16	234	-12	-28	-18
227	fenoxycarb	+	20.852	302.1	88.1	-15	-21	-16	116.1	-15	-10	-12
228	tebufenozide	+	20.892	353.2	133.1	-18	-20	-24	297.1	-18	-8	-15
229	parathion	+	20.873	292	236.2	-11	-15	-23	264	-11	-10	-26
230	dimoxystrobin	+	20.938	327	205.1	-30	-15	-30	116	-30	-35	-30
231	tebuconazole	+	20.988	308.1	70.1	-11	-23	-15	125	-11	-31	-25
232	rotenone	+	21.079	395.1	213.1	-14	-22	-23	192.1	-14	-22	-18
233	chlorbenzuron	+	21.134	309	156	-21	-17	-18	111	-10	-45	-23
234	fipronil sulfide	-	21.164	419	262	16	29	16	383	12	13	17
235	cyprodinil	+	21.191	226.1	93.1	-30	-34	-16	108.1	-30	-27	-19
236	carfentrazone-ethyl	+	21.224	429.1	412	-11	-11	-17	346	-15	-26	-29
237	penthiopyrad	+	21.237	360	276	-18	-11	-28	177	-27	-34	-17
238	pyrametostrobin	+	21.26	382.1	194.1	-14	-18	-15	163	-14	-15	-19
239	propisochlor	+	21.308	284.1	224.1	-20	-9	-24	73.1	-20	-12	-29
240	picoxystrobin	+	21.323	368.1	205.1	-10	-13	-16	145	-18	-35	-29
241	quinalphos	+	21.335	299	163.1	-15	-20	-30	147.1	-15	-21	-27
242	isofenphos-methyl	+	21.416	332.1	231	-23	-14	-25	121.1	-23	-33	-22
243	phenthoate	+	21.425	321	247	-23	-11	-17	79.1	-23	-41	-30
244	kresoxim-methyl	+	21.434	314.1	222.2	-16	-13	-24	235.1	-16	-15	-25
	prochloraz											
245	metabolite	+	21.461	353	308	-12	-14	-17	310	-12	-14	-17
	BTS44596											
246	flubendiamide	-	21.498	681	254.1	32	26	27	273.8	32	15	28
247	fluthiacet-methyl	+	21.533	404	274.1	-29	-30	-20	344.1	-29	-23	-26
248	propiconazole	+	21.451	342.1	159.1	-12	-25	-19	161	-12	-31	-19
249	sulfotep	+	21.547	323	115	-16	-31	-20	171.1	-16	-15	-18
	prochloraz											
250	metabolite	+	21.584	325	282.1	-11	-15	-21	284.1	-11	-15	-21
	BTS44595											
251	zoxamide	+	21.602	335.8	187	-16	-24	-20	159	-16	-41	-30
252	edifenphos	+	21.63	311	283	-24	-20	-30	111.1	-24	-35	-21

Table 2 continue. List of MRM used for each pesticides.

No.	Compounds	Mode	Retention time (min)	Precursor ion	Quantifying ion	Q1 Pre Bias	CE	Q3 Pre Bias	Qualifying ion	Q1 Pre Bias	CE	Q3 Pre Bias
253	etrimfos	+	21.632	293	265	-15	-16	-28	125	-15	-24	-23
254	anilofos	+	21.638	368	199	-18	-20	-21	125	-18	-22	-22
255	hexaconazole	+	21.676	314.1	70.2	-15	-21	-28	159.2	-15	-29	-30
256	benalaxyl	+	21.695	326.2	148.2	-16	-13	-15	294.1	-16	-15	-20
257	benzovindiflupyr	+	21.691	398	342	-15	-18	-23	378	-15	-14	-26
258	chlorfenvinphos	+	21.709/22.3 8	358.9	155.1	-18	-12	-30	99	-18	-33	-18
259	fonofos	+	21.732	247.1	109	-27	-19	-19	137.1	-26	-10	-14
260	fenthion	+	21.782	279.2	169.1	-30	-17	-18	247.1	-30	-12	-18
261	fipronil sulfone	-	21.784	451	415	17	17	19	282	17	27	18
262	pyrimorph	+	21.853	385.2	242.1	-14	-27	-18	272.1	-14	-33	-21
263	metconazole	+	21.853	320	70.1	-23	-22	-15	125.1	-11	-40	-25
264	diazinon	+	21.976	305	169.1	-30	-15	-18	153.1	-30	-20	-16
265	pyraflufen-ethyl	+	21.977	413	339	-20	-19	-19	253	-15	-34	-30
266	prochloraz	+	22.044	376	308	-19	-11	-21	266	-19	-17	-29
267	coumaphos	+	22.175	363	227	-18	-26	-23	307.1	-18	-18	-21
268	triflumuron	+	22.269	359.1	156	-17	-16	-30	139	-17	-33	-26
269	phorate	+	22.291	261	75	-29	-10	-30	47	-17	-55	-11
270	oxadiargyl	+	22.311	340.9	150.9	-13	-27	-27	223	-13	-15	-24
271	famoxadone	+	22.318	392	331	-11	-12	-25	238	-13	-20	-10
272	bitertanol	+	22.352	338.2	269.2	-17	-9	-29	99.1	-17	-15	-18
273	diniconazole	+	22.368	326.1	70	-12	-24	-15	159	-12	-27	-18
274	phosalone	+	22.416	368	182.1	-30	-14	-19	111	-30	-39	-20
275	spinosad A	+	22.547	732.4	142	-20	-27	-17	98.1	-20	-55	-21
276	pirimiphos- methyl	+	22.549	306.1	108.1	-30	-31	-19	95	-30	-29	-17
277	cadusafos	+	22.567	271.1	159	-30	-20	-29	97	-30	-25	-18
278	pyraclostrobin	+	22.58	388.1	194.1	-19	-20	-21	163.1	-19	-35	-30
279	ametoctradin	+	22.589	276.2	176.1	-10	-35	-20	149	-10	-35	-17
280	cyflufenamid	+	22.598	413.2	295.1	-20	-10	-30	203	-20	-30	-20
281	tolclofos-methyl	+	22.611	301.1	125.2	-14	-16	-16	175.1	-20	-23	-20
282	phoxim	+	22.638	299	77.1	-30	-20	-30	129.1	-30	-25	-13
283	disulfoton	+	22.633	275.2	89.1	-12	-15	-20	60.8	-10	-32	-12
284	pencycuron	+	22.721	329.1	125.1	-17	-15	-22	218.1	-17	-15	-23
285	pyraoxystrobin	+	22.733	413.1	205.1	-15	-18	-16	145	-15	-10	-17
286	metrafenone	+	22.769	409	209.1	-15	-17	-16	227.1	-20	-22	-18
287	isopyrazam	+	22.781	360.1	244	-11	-24	-25	320.1	-11	-21	-22
288	difenoconazole	+	22.760/22.8 37	406.1	251	-30	-25	-27	337.1	-30	-17	-24
289	chlorpyrifos- methyl	+	22.838	321.9	125.1	-22	-23	-23	125.1	-28	-15	-24
290	bifenox	+	22.845	359	310	-12	-15	-17	342	-10	-7	-27
291	clofentezine	+	22.932	303	138.1	-21	-14	-26	102.1	-21	-34	-19
292	benzoximate	+	22.972	364.1	199	-13	-12	-23	105	-27	-26	-21
293	dimepiperate	+	23.008	264.1	146.1	-29	-7	-15	91.1	-29	-36	-16
294	ipconazole	+	22.724/23.0 25	334.2	70.1	-22	-26	-21	125.1	-13	-43	-13
295	triflumizole	+	23.056	346.1	73.1	-17	-25	-30	278	-17	-22	-30
296	indoxacarb	+	23.122	528.1	293	-26	-15	-21	249.1	-26	-17	-27
297	diflufenican	+	23.191	395.1	266	-14	-35	-21	246	-14	-34	-19
298	spinosad D	+	23.228	746.4	142	-28	-30	-17	98	-22	-55	-12

Table 2 continue. List of MRM used for each pesticides.

No.	Compounds	Mode	Retention time (min)	Precursor ion	Quantifying ion	Q1 Pre Bias	CE	Q3 Pre Bias	Qualifying ion	Q1 Pre Bias	CE	Q3 Pre Bias
299	pretilachlor	+	23.202	312.2	252.2	-15	-29	-28	176.2	-15	-35	-18
300	EPN	+	23.224	324	156.9	-12	-20	-18	296.1	-11	-13	-16
301	cycloxydim	+	23.249	326.2	280.2	-12	-12	-21	180.2	-12	-20	-14
302	spinetoram J	+	23.302	748.5	142.1	-40	-33	-14	98.2	-30	-55	-21
303	pyrethrin II	+	23.294	373.2	161.1	-11	-11	-19	133.1	-13	-20	-28
304	fluoroglycofen-ethyl	+	23.302	465.1	344	-17	-15	-26	223	-17	-33	-17
305	trifloxystrobin	+	23.311	409.1	186.1	-20	-40	-20	145	-20	-20	-26
306	clethodim	+	23.33	360.2	164.1	-18	-19	-17	268.1	-18	-11	-30
307	hexaflumuron	-	23.349	459	438.9	16	12	29	175.1	16	36	29
308	prosulfocarb	+	23.367	252	91	-12	-45	-19	128	-12	-15	-15
309	novaluron	+	23.399	493	158	-15	-18	-28	141.1	-15	-40	-27
310	amisulbrom	+	23.423	466	227	-10	-19	-13	148	-10	-47	-29
311	profenofos	+	23.486	372.9	302.8	-18	-25	-30	345	-18	-20	-24
312	fenoxaprop-ethyl	+	23.514	362.1	288	-28	-26	-20	121.1	-28	-30	-23
313	quizalofop-ethyl	+	23.585	373	299	-13	-28	-20	270.9	-11	-26	-28
314	cyflumetofen	+	23.616	465.2	173	-14	-24	-18	145	-14	-55	-28
315	fenaminstrobin	+	23.649	434.1	171	-21	-40	-20	212	-12	-14	-25
316	fluazifop-butyl	+	23.658	384	328	-14	-11	-16	282	-14	-10	-30
317	oxaziclomefone	+	23.666	376.1	190.1	-19	-34	-20	161.1	-19	-40	-28
318	metamifop	+	23.696	441.1	288	-16	-24	-16	180	-21	-19	-21
319	oxyfluorfen	+	23.512	362	316	-18	-19	-25	140	-27	-52	-27
320	furathiocarb	+	23.769	383.2	252.1	-27	-13	-27	195	-27	-10	-21
321	emamectin benzoate	+	23.856	886.5	158.1	-40	-25	-17	82.1	-40	-55	-15
322	terbufos	+	23.819	289	103.2	-14	-9	-18	57.1	-14	-24	-24
323	sethoxydim	+	23.821	328.1	178.1	-12	-19	-21	282.2	-12	-12	-22
324	metaflumizone	-	23.825	505.1	302	24	21	30	285	24	48	28
325	spinetoram L	+	23.865	760.7	142.2	-22	-32	-25	98.2	-28	-55	-18
326	diclofop-methyl	+	23.85	358	281	-25	-15	-22	120.2	-18	-27	-26
327	lactofen	+	23.861	479.2	344	-18	-25	-25	223.1	-18	-25	-25
328	buprofezin	+	23.865	306.1	116.1	-30	-23	-12	201.1	-30	-20	-22
329	teflubenzuron	-	23.865	379	339	13	11	22	359	13	6	24
330	fluazinam	-	23.887	463	416	22	20	13	398	13	17	17
331	propaquizafop	+	23.931	444.1	100.1	-23	-19	-19	371	-23	-16	-18
332	imibenconazole	+	23.932	411	125.1	-20	-31	-22	171	-20	-20	-18
333	enestroburin	+	23.942	400.1	178	-19	-25	-14	137	-15	-15	-16
334	picolinafen	+	23.975	377.1	238.1	-19	-40	-24	359.1	-19	-25	-17
335	oxadiazon	+	24.004	345	303	-16	-13	-13	220	-24	-18	-23
336	butachlor	+	24.004	312.2	238.1	-23	-11	-28	162	-16	-22	-13
337	tolfenpyrad	+	24.08	384.1	197.1	-10	-35	-12	154.1	-10	-35	-29
338	piperonyl butoxide	+	24.085	356.3	177.1	-24	-31	-19	119	-24	-22	-22
339	lufenuron	-	24.152	509	326	36	17	21	339	36	11	22
340	pyribenzoxim	+	24.232	610.1	413.1	-22	-25	-30	180.1	-22	-20	-19
341	coumoxystrobin	+	24.258	437.1	205.1	-12	-10	-16	145.1	-12	-35	-17
342	ethion	+	24.291	385	199	-19	-15	-22	143	-19	-20	-25
343	hexythiazox	+	24.352	353.1	228	-18	-20	-24	168.1	-18	-30	-30
344	triallate	+	24.355	304	143	-15	-27	-25	86	-15	-17	-16
345	fenpropathrin	+	24.365	350.3	97.2	-12	-45	-19	125.2	-10	-23	-28

Table 2 continue. List of MRM used for each pesticides.

No.	Compounds	Mode	Retention time (min)	Precursor ion	Quantifying ion	Q1 Pre Bias	CE	Q3 Pre Bias	Qualifying ion	Q1 Pre Bias	CE	Q3 Pre Bias
346	chlorpyrifos	+	24.366	351.9	199.9	-27	-18	-21	97	-27	-25	-18
347	pyriproxyfen	+	24.44	322.1	96.1	-30	-10	-10	185.1	-30	-20	-20
348	tralkoxydim	+	24.45	330.2	284.2	-16	-10	-30	138.1	-16	-25	-25
349	pendimethalin	+	24.481	282.2	212.1	-30	-10	-23	194	-30	-18	-20
350	spiromesifen	+	24.499	388	273.1	-14	-15	-21	255.2	-14	-27	-19
351	dinocap	-	23.525/ 23.750/ 24.441/ 24.505/ 25.012/ 25.161	295.1	209	11	32	22	134.1	21	51	25
352	flufenoxuron	+	24.515	489	158.1	-11	-20	-12	141.2	-11	-39	-17
353	flucythrinate	+	24.541	469	412	-23	-14	-22	181	-30	-36	-10
354	propargite	+	24.592	368.2	231.2	-26	-17	-25	175.2	-26	-10	-19
355	etoxazole	+	24.678	360.1	141.1	-30	-13	-26	113.1	-30	-35	-21
356	butralin	+	24.702	296.2	240.1	-14	-12	-25	222.1	-14	-21	-24
357	pyrethrin I	+	24.717	329.2	161.1	-11	-10	-19	133	-11	-19	-25
358	spirodiclofen	+	24.869	411.1	71.2	-21	-16	-28	313.1	-21	-11	-22
359	chlorfluazuron	+	24.931	540	382.9	-26	-21	-27	158	-26	-20	-30
360	fenpyroximate	+	25.008	422.2	366.1	-30	-30	-26	138.1	-30	-25	-26
361	flumetralin	+	25.008	422.1	107.1	-22	-54	-22	143	-15	-47	-27
362	proquinazid	+	25.049	373	331	-18	-23	-18	289	-14	-40	-22
363	pyridaben	+	25.2	365.1	147.1	-18	-42	-27	309	-18	-23	-22
364	fenvalerate	+	25.221	437	167.1	-17	-15	-26	125	-16	-40	-24
365	deltamethrin	+	25.176	523	281	-36	-16	-22	506	-38	-11	-28
366	fenazaquin	+	25.291	307	161.1	-15	-10	-30	131	-15	-46	-24
367	tau-fluvalinate	+	25.364	503.1	208	-40	-13	-22	181	-40	-30	-18
368	abamectin	+	25.409	890.5	305.2	-34	-25	-22	567.3	-34	-14	-30
369	bioresmethrin	+	25.474	339.2	171.1	-24	-25	-18	128.1	-24	-25	-23
370	methoprene	+	25.49	279.2	191.2	-10	-9	-15	237.2	-10	-9	-28
371	permethrin	+	25.625 /25.931	408.2	183.1	-14	-14	-20	355.2	-21	-8	-27
372	bifenthrin	+	26.039	440.3	181.1	-16	-21	-18	166.2	-16	-43	-18
373	etofenprox	+	26.104	394	177.1	-19	-26	-20	107	-19	-33	-19
374	ivermectin	+	26.251	892.5	569.2	-26	-16	-40	307.1	-26	-28	-20
375	pyridalyl	+	26.437	491.9	110.9	-18	-27	-19	108.9	-18	-28	-20

^a Pesticide contains two chromatograpeseedhic peaks, which are either its cis-trans isomers or non-enantiomeric isomers. The sum of the peak areas need to be used for quantification.

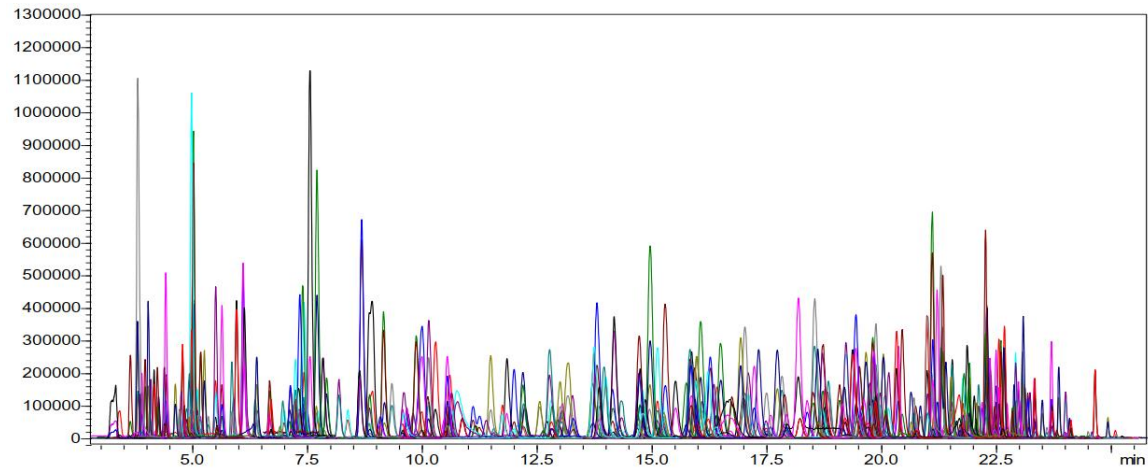


Figure 2. MRM chromatogram of 331 pesticides and their metabolites standards in rapeseed oil matrix (concentration: 4 ng/mL).

Table 3. List of recovery and %RSD for each pesticides.

No.	Compounds	Spiked amount (0.02 mg/kg, n=3)		No.	Compounds	Spiked amount (0.02 mg/kg, n=3)	
		Avg recovery	%RSD			Avg recovery	%RSD
1	methamidophos	86.99%	2.29%	78	fenamiphos sulfone	99.49%	4.73%
2	acephate	95.19%	1.74%	79	tebuthiuron	91.13%	1.69%
3	omethoate	96.02%	1.97%	80	Sulfentrazone	97.50%	2.42%
4	oxamyl oxime	92.78%	2.66%	81	carbaryl	90.06%	0.44%
5	dinotefuran	96.06%	1.81%	82	carboxin	89.25%	2.21%
6	propamocarb	43.25%	8.14%	83	ethirimol	80.91%	1.71%
7	aldicarb sulfoxide	93.88%	2.22%	84	fenthion sulfone	95.66%	1.05%
8	aldicarb sulfone	99.65%	1.50%	85	penoxsulam	82.28%	4.12%
9	oxamyl	99.40%	1.19%	86	cyantraniliprole	98.45%	3.70%
10	nitenpyram	91.57%	1.20%	87	pirimicarb	92.69%	1.36%
11	oxydemeton-methyl	89.83%	2.32%	88	fosthiazate	94.68%	3.19%
12	demeton-S-methyl-sulfone	93.82%	1.81%	89	spirotetramat-enol	76.66%	1.13%
13	methomyl	93.55%	3.83%	90	disulfoton sulfoxide	95.19%	2.09%
14	monocrotophos	97.85%	5.30%	91	chlortoluron	92.38%	0.70%
15	thiamethoxam	97.94%	2.05%	92	phorate sulfoxide	96.24%	1.24%
16	flonicamid	94.61%	4.28%	93	simetryn	87.56%	1.10%
17	chlordimeform	91.29%	1.50%	94	mesosulfuron-methyl	79.13%	3.51%
18	phosfolan-methyl	93.65%	1.17%	95	methacrifos*	93.31%	4.57%
19	spirotetramat-enol-glucoside	87.29%	4.46%	96	disulfoton sulfone	96.67%	1.15%
20	dicrotophos	95.49%	2.79%	97	tritosulfuron	92.84%	3.65%
21	imidacloprid	95.38%	3.32%	98	phorate sulfone	96.15%	1.42%
22	flumetsulam	70.18%	3.84%	99	isoprocarb	90.54%	3.25%
23	clothianidin	103.40%	2.48%	100	flutriafol	93.97%	2.55%
24	methiocarb sulfoxide	95.37%	2.92%	101	tribenuron-methyl	84.24%	2.15%
25	imidaclothiz	96.59%	8.91%	102	atrazine	86.66%	1.26%
26	vamidothion	100.41%	4.22%	103	imazalil	78.90%	1.85%
27	3-hydroxy carbofuran	94.85%	0.94%	104	isoproturon	91.47%	1.03%
28	acetamiprid	98.24%	1.63%	105	metazachlor	94.60%	0.88%
29	mevinphos*	91.61%	1.75%	106	fensulfothion	93.61%	0.91%
30	methiocarb sulfone	91.70%	6.07%	107	propachlor	88.10%	0.14%
31	carbendazim	94.74%	1.39%	108	chlorpropham	89.18%	2.10%
32	dimethoate	98.82%	1.77%	109	orthosulfamuron	79.64%	2.02%
33	trichlorfon	88.87%	2.67%	110	iodosulfuron-methyl-sodium	81.10%	1.15%
34	demeton-S-sulfoxide	90.82%	1.97%	111	diuron	92.66%	2.73%
35	metamitron	97.00%	5.45%	112	forchlorfenuron	95.86%	1.66%
36	diethyl aminoethyl hexanoate	71.02%	4.49%	113	isoxaflutole	91.97%	3.07%
37	sulfoxaflor*	103.18%	0.91%	114	metalaxyl	93.66%	1.63%
38	chloridazon	99.41%	1.58%	115	heptenophos	89.69%	2.13%
39	demeton-S-sulfone	99.07%	0.47%	116	fensulfothion sulfone	98.98%	0.55%
40	thiacloprid	101.55%	2.87%	117	clethodim sulfone	86.15%	3.34%
41	cymoxanil	100.70%	2.03%	118	metazosulfuron	79.89%	4.39%
42	florasulam	81.06%	1.43%	119	spirotetramat-keto-hydroxy	88.87%	3.18%
43	fensulfothion oxon	89.73%	1.72%	120	methidathion	91.91%	3.02%
44	pirimicarb-desmethyl	95.58%	0.76%	121	flumorph	96.14%	0.98%
45	thiabendazole	94.05%	1.40%	122	fenpropidin	70.10%	0.70%
46	tricyclazole	92.94%	0.31%	123	clethodim sulfoxide*	72.97%	1.53%
47	fensulfothion oxon sulfone	102.75%	3.29%	124	azinphos-methyl	95.78%	3.12%
48	phosfolan	96.83%	0.54%	125	phenmedipham	90.29%	2.74%
49	aldicarb	95.70%	6.23%	126	clomazone	89.78%	2.25%
50	phosmet oxon	96.24%	2.41%	127	phosmet	94.56%	1.28%
51	oxadixyl	98.84%	2.68%	128	chlorantraniliprole	96.13%	2.75%
52	formothion	91.96%	1.17%	129	bensulfuron-methyl	89.48%	2.80%
53	cinosulfuron	82.92%	1.91%	130	demeton	90.15%	2.27%
54	metolcarb	94.10%	2.57%	131	pyriftalid	94.19%	1.21%
55	thifensulfuron-methyl	77.92%	2.55%	132	ametryn	84.06%	4.13%
56	probenazole	92.46%	2.52%	133	flucetosulfuron*	81.87%	4.51%
57	phosphamidon*	75.24%	1.94%	134	fenobucarb	91.33%	0.05%
58	cyanazine	93.60%	1.61%	135	linuron	87.60%	3.30%
59	triasulfuron	80.66%	3.07%	136	saflufenacil	85.88%	1.86%
60	phenamacril	98.13%	2.51%	137	pyrimethanil	78.90%	1.27%
61	metsulfuron-methyl	80.93%	1.16%	138	propanil	84.86%	1.38%
62	dichlorvos	86.93%	1.73%	139	albendazole	90.33%	3.53%
63	thiophanate-methyl	92.92%	2.23%	140	terbufos sulfone	95.13%	1.71%
64	thidiazuron	92.48%	3.19%	141	terbufos sulfoxide	94.52%	3.93%
65	bendiocarb	97.01%	1.93%	142	ethofumesate	97.87%	2.98%
66	spirotetramat-mono-hydroxy	94.68%	2.80%	143	methiocarb	90.39%	2.90%
67	propoxur	96.02%	1.98%	144	diethofencarb	93.53%	0.92%
68	chlorsulfuron	74.23%	3.01%	145	flurtamone	97.75%	0.84%
69	carbofuran	95.43%	0.66%	146	azoxystrobin	94.23%	2.44%
70	fenamiphos sulfoxide	90.70%	0.59%	147	fludioxonil	93.95%	4.51%
71	metribuzin	94.48%	3.77%	148	fenamidone	91.79%	1.45%
72	simazine	91.00%	2.54%	149	halosulfuron-methyl	93.37%	1.34%
73	hexazinone	92.64%	2.01%	150	pyrisoxazole*	83.78%	1.67%
74	malaixon	95.63%	0.72%	151	terbuthylazine	82.21%	3.84%
75	Amidosulfuron	85.17%	1.47%	152	dimethenamid	88.91%	0.13%
76	demeton-S-methyl	91.79%	0.65%	153	promecarb	91.94%	1.49%
77	fenthion sulfoxide	94.05%	2.52%	154	ethiprole	93.28%	2.20%
				155	boscalid	98.07%	0.94%
				156	chlorimuron-ethyl	80.81%	1.48%

Table 3 continue. List of recovery and %RSD for each pesticides

No.	Compounds	Spiked amount (0.02 mg/kg, n=3)		No.	Compounds	Spiked amount (0.02 mg/kg, n=3)	
		Avg recovery	%RSD			Avg recovery	%RSD
157	propyzamide	92.27%	1.58%	237	carfentrazone-ethyl	85.45%	1.78%
158	paclobutrazol	90.12%	1.47%	238	tebuconazole	99.91%	3.30%
159	dimethomorph	92.25%	0.65%	239	fipronil sulfide	76.17%	2.44%
160	mandipropamid	101.13%	0.31%	240	fonofos	91.39%	3.47%
161	isoprothiolane	89.27%	0.86%	241	sulfotep	93.80%	2.45%
162	flutolanil	96.45%	1.67%	242	isofenphos-methyl	90.34%	3.46%
163	molinate	75.29%	3.49%	243	edifenphos	88.42%	2.77%
164	fluxapyroxad	98.24%	2.56%	244	propisochlor	94.32%	3.61%
165	ethoxysulfuron	76.40%	1.19%	245	benzovindiflupyr	88.57%	2.27%
166	triflusaluron-methyl	89.76%	2.58%	246	zoxamide	95.06%	2.76%
167	fluopicolide	91.73%	0.89%	247	anilofos	87.34%	0.92%
168	malathion	98.74%	0.88%	248	propiconazole	83.42%	2.62%
169	mepronil	92.89%	1.31%	249	hexaconazole	96.53%	6.44%
170	myclobutanil	89.06%	3.27%	250	flubendiamide	82.74%	2.02%
171	triadimefon	90.41%	2.78%	251	diazinon	91.49%	1.02%
172	propyrisulfuron	80.47%	5.05%	252	pyraflufen-ethyl	101.64%	0.88%
173	fenpropimorph	78.40%	1.73%	253	coumaphos	92.29%	1.56%
174	pyrazosulfuron-ethyl	87.08%	1.72%	254	pyrimorph	92.39%	2.16%
175	bromuconazole	89.04%	4.84%	255	benalaxyl	90.30%	1.59%
176	mefenacet	92.27%	0.17%	256	chlorfenvinphos*	82.85%	2.88%
177	sedaxane*	97.21%	1.12%	257	metconazole	85.47%	6.71%
178	pyridaphenthion	92.09%	2.52%	258	phorate	96.76%	5.49%
179	methoxyfenozide	95.98%	0.53%	259	fipronil sulfone	95.50%	5.68%
180	prometryn	81.11%	0.92%	260	famoxadone	87.09%	8.76%
181	triadimenol	86.16%	2.21%	261	tolclofos-methyl	74.40%	1.36%
182	cyproconazole	88.49%	0.67%	262	clofentezine	85.36%	1.48%
183	triazophos	92.75%	1.75%	263	prochloraz	94.36%	0.85%
184	fenpyrazamine	92.99%	0.78%	264	phoxim	88.06%	9.84%
185	isazofos	90.91%	1.12%	265	oxadiargyl	88.61%	2.01%
186	procymidone	—	—	266	pyraclostrobin	92.13%	5.82%
187	cyclosulfamuron	90.87%	4.51%	267	bitertanol	87.79%	4.32%
188	fenarimol	89.87%	0.37%	268	pirimiphos-methyl	96.31%	0.65%
189	fluopyram	94.33%	1.18%	269	triflumuron	92.29%	2.61%
190	fenhexamid	86.41%	1.77%	270	phosalone	85.84%	0.46%
191	iprovalicarb*	93.81%	2.81%	271	diniconazole	92.74%	2.97%
192	triticonazole	87.78%	1.38%	272	benzoximate	90.13%	1.68%
193	tetraconazole	91.69%	0.41%	273	pyraoxystrobin	90.86%	12.76%
194	ethoprophos	86.75%	0.61%	274	disulfoton	76.10%	8.10%
195	spirotetramat	94.23%	0.98%	275	chlorpyrifos-methyl	65.41%	26.05%
196	flufenacet	93.18%	3.57%	276	bifenox	86.04%	3.10%
197	napropamide	85.69%	2.92%	277	metrafenone	88.63%	2.34%
198	acetochlor	81.94%	2.29%	278	pencycuron	95.69%	3.07%
199	chromafenozide	96.42%	1.37%	279	cyflufenamid	67.85%	0.85%
200	alachlor	87.12%	1.37%	280	ametoctradin	85.45%	1.78%
201	epoxiconazole	92.85%	2.17%	281	difenoconazole*	87.76%	2.61%
202	cyazofamid	96.55%	3.16%	282	EPN	117.12%	32.35%
203	metolachlor	91.08%	2.23%	283	cadusafos	83.28%	1.94%
204	uniconazole	87.54%	1.27%	284	isopyrazam*	93.49%	0.78%
205	fenbuconazole	93.46%	1.71%	285	dimepiperate	74.38%	5.15%
206	diflubenzuron	86.30%	2.78%	286	spinosad A	48.14%	0.81%
207	iprodione	60.30%	54.08%	287	diflufenican	86.63%	3.67%
208	fipronil desulfinyl	95.47%	1.73%	288	ipconazole*	80.94%	3.48%
209	thifluzamide	90.56%	1.75%	289	triflumizole	85.62%	3.01%
210	fenothiocarb	84.40%	0.41%	290	indoxacarb	107.84%	6.04%
211	picoxystrobin	95.28%	1.82%	291	trifloxystrobin	95.65%	4.42%
212	rotenone	95.93%	3.98%	292	prosulfocarb	77.33%	1.15%
213	bupirimate	90.28%	2.00%	293	cycloxydim	68.18%	4.18%
214	flusilazole	87.34%	0.46%	294	amisulbrom	85.10%	8.61%
215	fenoxycarb	89.74%	5.46%	295	pretilachlor	80.90%	1.70%
216	fenamiphos	93.88%	1.46%	296	clethodim	83.57%	4.00%
217	parathion	—	—	297	hexaflumuron	99.00%	7.16%
218	cyprodinil	75.60%	2.01%	298	fenaminstrobin	93.07%	1.39%
219	fenoxanil*	91.10%	2.27%	299	fluoroglycofen-ethyl	93.19%	0.20%
220	quinalphos	84.75%	0.15%	300	profenofos	80.23%	7.12%
221	dimoxystrobin	91.65%	6.14%	301	quizalofop-ethyl	93.68%	10.41%
222	fipronil	95.18%	1.28%	302	fenoxaprop-ethyl	88.01%	1.48%
223	tebufenozide	92.37%	2.66%	303	oxyfluorfen	82.07%	19.20%
224	silthiofam	89.23%	0.56%	304	spinosad D	47.07%	8.36%
225	penconazole	76.01%	5.05%	305	oxaziclomefone	93.40%	1.74%
226	penthiopyrad	97.73%	1.92%	306	diclofop-methyl	78.06%	14.09%
227	chlorbenzuron	84.45%	0.19%	307	cyflumetofen	93.12%	1.23%
228	phenthoate	90.07%	1.01%	308	metamifop	98.19%	2.83%
229	kresoxim-methyl	87.71%	0.96%	309	terbufos	58.36%	15.58%
230	fluthiacet-methyl	85.34%	0.68%	310	enestroburin	87.87%	3.08%
231	diclobutrazol	86.30%	1.73%	311	teflubenzuron	88.68%	9.06%
232	pyrametostrobin	93.72%	4.60%	312	sethoxydim	71.75%	6.35%
233	penflufen	93.07%	3.54%	313	fluazifop-butyl	91.63%	2.11%
234	iprobefos	88.55%	1.51%	314	furathiocarb	95.12%	5.53%
235	fenthion	90.26%	0.63%	315	picolinafen	82.77%	3.69%
236	etrimfos	86.93%	2.83%	316	imibenconazole	77.83%	1.81%

Table 3 continue. List of recovery and %RSD for each pesticides.

No.	Compounds	Spiked amount (0.02 mg/kg, n=3)	
		Avg recovery	%RSD
317	propaquizafop	90.62%	1.56%
318	buprofezin	78.36%	7.67%
319	lactofen	90.58%	4.47%
320	tolfenpyrad	73.23%	8.93%
321	metaflumizone	93.48%	5.31%
322	oxadiazon	76.50%	15.71%
323	fluazinam	87.43%	2.27%
324	butachlor	85.13%	2.09%
325	pyriproxyfen	74.61%	3.45%
326	piperonyl butoxide	84.71%	3.68%
327	coumoxystrobin	94.88%	1.75%
328	ethion	85.66%	1.94%
329	pyribenzoxim	94.34%	6.27%
330	emamectin benzoate	49.27%	15.39%
331	spinetoram L	28.66%	12.45%
332	chlorpyrifos	76.99%	1.42%
333	spinetoram J	49.80%	14.60%
334	lufenuron	96.71%	7.64%
335	pendimethalin	71.73%	3.66%
336	hexythiazox	71.37%	3.74%
337	triallate	59.51%	2.17%
338	tralkoxydim	70.10%	2.89%
339	flucythrinate	62.41%	10.19%
340	flufenoxuron	96.47%	5.69%
341	propargite	85.80%	1.51%
342	dinocap*	81.12%	6.28%
343	etoxazole	79.41%	1.93%
344	butralin	74.88%	4.07%
345	fenpropathrin	81.50%	6.85%
346	fenpyroximate	79.35%	1.26%
347	proquinazid	50.32%	7.29%
348	flumetralin	74.48%	11.22%
349	chlorfluazuron	94.66%	4.09%
350	spirodiclofen	79.45%	2.13%
351	deltamethrin	81.52%	16.02%
352	fenazaquin	48.73%	3.71%
353	fenvalerate	—	—
354	pyridaben	70.66%	4.19%
355	bioresmethrin	67.75%	6.07%
356	tau-fluvalinate	83.57%	6.69%
357	methoprene	64.17%	3.01%
358	abamectin	94.85%	11.98%
359	permethrin*	56.28%	7.13%
360	etofenprox	49.25%	7.79%
361	bifenthrin	61.37%	15.50%
362	pyridalyl	48.91%	11.98%
363	ivermectin	72.23%	5.92%
364	benazolin-ethyl	90.06%	3.75%
365	pirimicarb-desmethyl- formamido	93.06%	0.37%
366	prochloraz metabolite BTS44595	78.58%	1.78%
367	prochloraz metabolite BTS44596	87.91%	2.01%
368	pyrethrin I	80.13%	2.04%
369	pyrethrin II	72.45%	13.17%
370	triflumizole metabolite FM- 6-1	93.82%	1.77%
371	isocarboxophos	94.69%	4.84%
372	cyazofamid metabolite CCIM	91.04%	4.23%
373	isoxaflutole-diketetonitrile	71.60%	5.52%
374	spiromesifen	86.35%	6.63%
375	novaluron	91.97%	12.05%

■ Results and Discussion

Rapeseed oil blank matrix was spiked with a standard solution of pesticides to a final concentration of 0.02 mg/kg. QuEChERS method sample preparation was performed according to Figure 1. Figure 2 shows the MRM chromatogram of the pesticide standards in rapeseed oil matrix. Three independent experiment was performed to determine average recovery and %RSD. Results show 353 compounds having a good recovery rate between 80%-120%. %RSD of all compound were below 20% except iprodione (54.08%) and EPN (32.35%). Recovery and %RSD for all the compounds are shown in Table 3.

■ Conclusion

This study presents a method for the determination of residues of 331 pesticides and their metabolites in rapeseed oil. Shimadzu SHIMSEN QuEChERS products were used for clean-up of the rapeseed oil, followed by analysis using Shim-pack GIST C18-AQ column on Shimadzu LCMS-8060NX. The recovery and reproducibility was determined using 20 µg/kg spiked rapeseed oil and rapeseed oil blank sample. The method has high recovery and good reproducibility, providing a reference for the determination of residues of 331 pesticides and their metabolites in rapeseed oil.

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