

Analysis of 331 Pesticides and Their Metabolites in Grapes

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User Benefits

- ◆ Established an effective, fast and simple sample preparation method for analysis of pesticides in grapes.
- ◆ 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. Grapes, a widely consumed fruit, are no exception. Pesticide residues in grapes 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 grapes 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 C-18-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 μm, 100 × 2.1 mm *1
Column Temp.:	40 °C
Flow rate:	0.3 mL/min
Mobile phase A:	2mM ammonium formate in water containing 0.1% formic acid
Mobile phase B:	2mM ammonium formate in methanol containing 0.1% formic acid
Gradient program:	3% B (0 min) → 3%B (1 min) → 15% B (1.5 min) → 50% B (2.5 min) → 70% B (18 min) → 98% B (23 min) → 98% B (27 min) → 3% B (27.1 min) → 3% B (30 min)
Injection volume:	2 μL (co-injection, 20 μL 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 dSPE tube (P/N: 380-00196-01)
Filter and vial:
SHIMSEN Disc HPTFE syringe filter (P/N: 380-00341);
LabTotal Vial (P/N: 227-34001-01)

Sample Preparation:

10 g of homogenized sample in 50 mL centrifuge tube was added with 10 mL of acetonitrile followed by SHIMSEN QuEChERS extraction salt (4 g MgSO₄, 1g 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 dSPE tube (30 mg PSA, 15 mg GCB, 900 mg MgSO₄, P/N: 380-00196-01), vortex and mix for 1 min, centrifuged at 4200 rpm for 5 min, and filtered 2 mL of the supernatant through a 0.22 μm syringe filter for LC-MS/MS analysis. Figure shows the simplified sample preparation workflow.

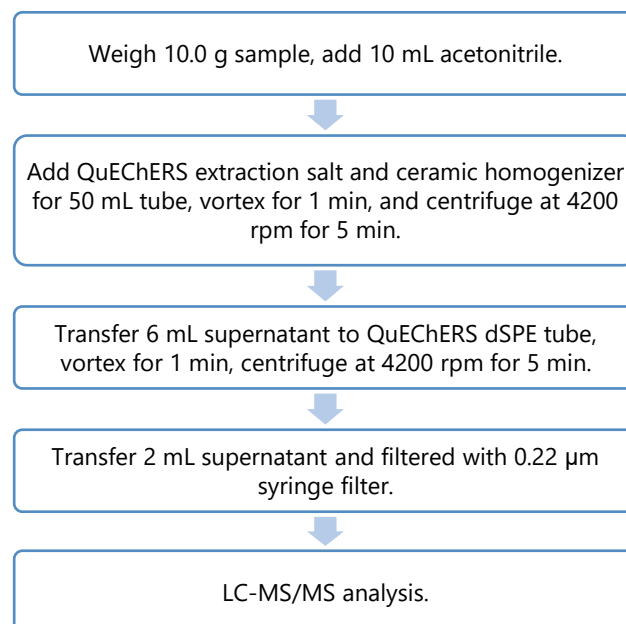


Figure 1. QuEChERS sample preparation workflow for grape.

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	imidaclathiz	+	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-diketetonitrile	-	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	+	11.514/13.781	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	fensulfthion	+	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	fensulfthion 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	+	12.986/13.156	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	+	13.315/14.119	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	chlorantraniliprole	+	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	azinthos-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	+	15.430/16.601	289.1	151.1	-11	-14	-18	120	-11	-20	-14
153	terbutylazine	+	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 metabolite CCIM	-	16.919	216	179.1	10	31	16	180.2	15	25	17
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	methoxyfenozid e	+	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	+	17.238/20.148	377.9	158.9	-19	-28	-30	70	-19	-23	-30
218	fenoxanil	+	19.862/20.212	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
245	prochloraz metabolite	+	21.461	353	308	-12	-14	-17	310	-12	-14	-17
246	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
250	prochloraz metabolite	+	21.584	325	282.1	-11	-15	-21	284.1	-11	-15	-21
251	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	+	21.709/22.38	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	+	22.760/22.837	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	+	22.724/23.025	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	pro sulfocarb	+	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
			24.515									
			24.541									
			24.592									
			24.678									
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 chromatographic peaks, which are either its cis-trans isomers or non-enantiomeric isomers. The sum of the peak areas need to be used for quantification.

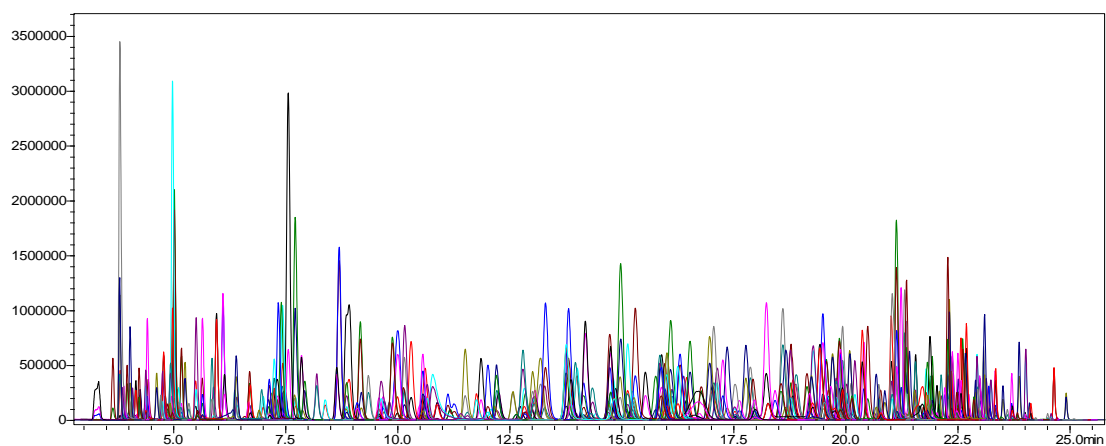


Figure 2. MRM chromatogram of 331 pesticides and their metabolites standards in grape matrix (concentration: 10 ng/mL).

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

No.	Compounds	Spiked amount (0.01 mg/kg, n=3)		No.	Compounds	Spiked amount (0.01 mg/kg, n=3)	
		Avg recovery	%RSD			Avg recovery	%RSD
1	methamidophos	91.77%	2.32%	78	fenamiphos sulfone	108.72%	2.65%
2	acephate	97.96%	1.68%	79	tebuthiuron	106.70%	3.12%
3	omethoate	99.53%	3.39%	80	Sulfentrazone	98.63%	4.70%
4	oxamyl oxime	105.99%	1.61%	81	carbaryl	109.33%	2.34%
5	dinotefuran	102.01%	1.50%	82	carboxin	104.15%	2.74%
6	propamocarb	89.25%	2.53%	83	ethirimol	95.82%	2.39%
7	aldicarb sulfoxide	101.72%	2.95%	84	fenthion sulfone	107.32%	0.52%
8	aldicarb sulfone	105.41%	0.99%	85	penoxsulam	94.47%	0.86%
9	oxamyl	105.67%	1.81%	86	cyantranilprole	105.22%	2.27%
10	nitenpyram	95.95%	1.96%	87	pirimicarb	103.53%	2.34%
11	oxydemeton-methyl	100.62%	2.38%	88	fosthiazate	103.08%	1.02%
12	demeton-S-methyl-sulfone	105.89%	2.04%	89	spirotetramat-enol	90.98%	3.43%
13	methomyl	105.99%	2.96%	90	disulfoton sulfoxide	104.12%	3.22%
14	monocrotophos	110.69%	4.72%	91	chlortoluron	106.22%	3.49%
15	thiamethoxam	100.13%	3.03%	92	phorate sulfoxide	108.05%	2.29%
16	flonicamid	102.08%	3.77%	93	simetryn	103.21%	2.03%
17	chlordimeform	95.45%	2.58%	94	mesosulfuron-methyl	95.57%	4.37%
18	phosfolan-methyl	100.69%	1.78%	95	methacrifos*	107.04%	3.06%
19	spirotetramat-enol-glucoside	87.94%	1.92%	96	disulfoton sulfone	107.86%	3.37%
20	dicrotophos	101.92%	1.58%	97	tritosulfuron	97.41%	3.36%
21	imidacloprid	97.44%	1.86%	98	phorate sulfone	105.64%	2.31%
22	flumetsulam	93.19%	3.59%	99	isoprocarb	108.54%	2.03%
23	clothianidin	100.46%	1.34%	100	flutriafol	101.74%	2.03%
24	methiocarb sulfoxide	100.55%	2.43%	101	tribenuron-methyl	97.05%	4.10%
25	imidaclothiz	82.23%	3.68%	102	atrazine	105.19%	1.51%
26	vamidotion	105.54%	3.29%	103	imazalil	101.97%	2.79%
27	3-hydroxy carbofuran	93.80%	0.36%	104	isoproturon	103.79%	2.61%
28	acetamiprid	102.09%	1.04%	105	metazachlor	103.80%	1.69%
29	mevinphos*	94.67%	2.39%	106	fensulfothion	105.82%	2.23%
30	methiocarb sulfone	109.19%	0.56%	107	propachlor	105.12%	1.48%
31	carbendazim	103.80%	3.82%	108	chlorpropham	106.98%	1.48%
32	dimethoate	103.56%	2.46%	109	orthosulfamuron	98.39%	0.99%
33	trichlorfon	96.66%	0.32%	110	iodosulfuron-methyl-sodium	96.96%	3.55%
34	demeton-S-sulfoxide	101.92%	1.86%	111	diuron	107.31%	2.07%
35	metamitron	105.84%	2.38%	112	forchlorfenuron	91.80%	4.82%
36	diethyl aminoethyl hexanoate	95.65%	3.99%	113	isoxaflutole	107.91%	5.25%
37	sulfoxaflor*	99.37%	3.09%	114	metalaxyl	105.72%	1.87%
38	chloridazon	96.80%	0.45%	115	heptenophos	105.56%	1.55%
39	demeton-S-sulfone	101.54%	1.48%	116	fensulfothion sulfone	104.75%	2.65%
40	thiacloprid	103.11%	3.42%	117	clethodim sulfone	96.16%	2.20%
41	cymoxanil	104.80%	1.23%	118	metazosulfuron	92.55%	1.54%
42	florasulam	93.14%	4.38%	119	spirotetramat-keto-hydroxy	101.11%	2.81%
43	fensulfothion oxon	101.54%	2.16%	120	methidathion	106.03%	1.75%
44	pirimicarb-desmethyl	97.33%	2.35%	121	flumorph	103.19%	1.49%
45	thiabendazole	138.08%	3.07%	122	fenpropidin	103.84%	3.02%
46	tricyclazole	99.96%	2.82%	123	clethodim sulfoxide*	91.85%	3.04%
47	fensulfothion oxon sulfone	105.66%	2.25%	124	azinphos-methyl	101.32%	12.90%
48	phosfolan	104.69%	1.25%	125	phenmedipham	105.34%	4.05%
49	aldicarb	98.02%	2.42%	126	clomazone	106.81%	2.84%
50	phosmet oxon	105.98%	2.71%	127	phosmet	105.27%	3.55%
51	oxadixyl	102.35%	4.48%	128	chlorantranilprole	103.14%	4.68%
52	formothion	103.23%	3.46%	129	bensulfuron-methyl	96.23%	1.23%
53	cinosulfuron	92.93%	2.62%	130	demeton	105.58%	1.98%
54	metolcarb	105.30%	1.54%	131	pyrifthalid	100.74%	2.63%
55	thifensulfuron-methyl	92.91%	4.21%	132	ametryn	104.24%	0.98%
56	probenazole	103.39%	1.86%	133	flucetosulfuron*	97.29%	2.58%
57	phosphamidon*	100.09%	3.93%	134	fenobucarb	103.53%	1.35%
58	cyanazine	101.71%	2.62%	135	linuron	106.01%	1.72%
59	triasulfuron	92.55%	3.13%	136	saflufenacil	96.86%	4.97%
60	phenamacril	104.78%	2.11%	137	pyrimethanil	102.13%	1.23%
61	metsulfuron-methyl	95.33%	2.05%	138	propanil	103.24%	1.50%
62	dichlorvos	106.05%	1.81%	139	alabendazole	104.43%	4.77%
63	thiophanate-methyl	102.78%	0.77%	140	terbufos sulfone	106.09%	1.45%
64	thidiazuron	93.42%	5.11%	141	terbufos sulfoxide	105.41%	2.95%
65	bendiocarb	106.06%	1.19%	142	ethofumesate	106.00%	1.14%
66	spirotetramat-mono-hydroxy	101.47%	1.08%	143	methiocarb	103.54%	1.88%
67	propoxur	108.28%	1.36%	144	diethofencarb	100.78%	1.62%
68	chlorsulfuron	93.81%	4.12%	145	flurtamone	105.57%	1.71%
69	carbofuran	105.08%	1.96%	146	azoxystrobin	104.79%	1.89%
70	fenamiphos sulfoxide	102.52%	2.93%	147	fludioxonil	105.82%	3.54%
71	metribuzin	101.76%	3.65%	148	fenamidone	106.00%	1.45%
72	simazine	106.88%	1.11%	149	halosulfuron-methyl	97.88%	2.10%
73	hexazinone	102.61%	1.72%	150	pyrisoxazole*	102.63%	2.00%
74	malaoxon	109.07%	4.06%	151	terbutylazine	104.41%	1.73%
75	Amidosulfuron	97.33%	3.63%	152	dimethenamid	106.30%	1.21%
76	demeton-S-methyl	102.17%	11.89%	153	promecarb	107.62%	2.08%
77	fenthion sulfoxide	103.78%	2.31%	154	ethiprole	106.14%	1.19%
				155	boscalid	103.56%	2.48%
				156	chlorimuron-ethyl	93.98%	3.01%

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

No.	Compounds	Spiked amount (0.01 mg/kg, n=3)		No.	Compounds	Spiked amount (0.01 mg/kg, n=3)	
		Avg recovery	%RSD			Avg recovery	%RSD
157	propyzamide	106.03%	2.78%	237	carfentrazone-ethyl	99.95%	3.06%
158	paclobutrazol	105.98%	2.25%	238	tebuconazole	104.16%	1.25%
159	dimethomorph	103.07%	2.72%	239	fipronil sulfide	100.89%	3.36%
160	mandipropamid	102.60%	3.00%	240	fonofos	104.66%	1.98%
161	isoprothiolane	104.85%	2.74%	241	sulfotep	106.96%	0.87%
162	flutolanil	105.94%	1.73%	242	isofenphos-methyl	110.89%	1.96%
163	molinate	100.32%	4.25%	243	edifenphos	106.98%	1.06%
164	fluxapyroxad	103.07%	1.71%	244	propisochlor	103.81%	2.56%
165	ethoxysulfuron	97.18%	1.57%	245	benzovindiflupyr	107.26%	1.89%
166	triflusulfuron-methyl	98.15%	3.64%	246	zoxamide	105.39%	1.25%
167	fluopicolide	104.15%	1.74%	247	anilofos	107.11%	1.10%
168	malathion	105.98%	1.22%	248	propiconazole	100.70%	2.01%
169	mepronil	104.96%	1.81%	249	hexaconazole	107.90%	2.12%
170	myclobutanil	106.56%	1.23%	250	flubendiamide	106.44%	2.76%
171	triadimefon	106.06%	3.25%	251	diazinon	103.95%	2.19%
172	propyrisulfuron	92.35%	3.37%	252	pyraflufen-ethyl	102.15%	2.25%
173	fenpropimorph	101.99%	2.75%	253	coumaphos	101.89%	2.90%
174	pyrazosulfuron-ethyl	96.62%	2.93%	254	pyrimorph	104.70%	3.89%
175	bromuconazole	104.60%	1.60%	255	benalaxyl	108.18%	0.59%
176	mefenacet	105.37%	2.09%	256	chlorfenvinphos*	107.24%	2.74%
177	sedaxane*	104.46%	2.77%	257	metconazole	103.89%	2.48%
178	pyridaphenthion	103.82%	3.24%	258	phorate	106.21%	2.20%
179	methoxyfenozide	103.52%	3.36%	259	fipronil sulfone	103.02%	4.38%
180	prometryn	106.90%	0.53%	260	famoxadone	106.43%	3.94%
181	triadimenol	105.26%	2.17%	261	tolclofos-methyl	107.31%	1.34%
182	cyproconazole	103.17%	2.14%	262	clofentezine	102.87%	8.97%
183	triazophos	104.86%	3.48%	263	prochloraz	105.15%	0.80%
184	fenpyrazamine	103.88%	1.22%	264	phoxim	108.85%	3.37%
185	isazofos	107.90%	2.33%	265	oxadiargyl	1.071733	10.01%
186	procymidone	—	—	266	pyraclostrobin	103.51%	3.27%
187	cyclosulfamuron	98.67%	1.75%	267	bitertanol	109.08%	1.27%
188	fenarimol	104.22%	1.71%	268	pirimiphos-methyl	104.00%	1.18%
189	fluopyram	104.15%	2.78%	269	triflumuron	101.90%	5.42%
190	fenhexamid	99.30%	1.58%	270	phosalone	106.32%	1.50%
191	iprovalicarb*	105.90%	1.79%	271	diniconazole	103.49%	3.48%
192	triticonazole	105.86%	2.47%	272	benzoximate	104.95%	4.96%
193	tetraconazole	105.52%	1.24%	273	pyraoxystrobin	107.61%	2.90%
194	ethoprophos	104.42%	3.36%	274	disulfoton	110.81%	2.86%
195	spirotetramat	104.20%	1.97%	275	chlorpyrifos-methyl	97.14%	2.35%
196	flufenacet	105.63%	1.83%	276	bifenox	87.13%	19.42%
197	napropamide	105.93%	2.74%	277	metrafenone	114.75%	2.12%
198	acetochlor	105.00%	1.32%	278	pencycuron	108.25%	1.77%
199	chromafenozide	106.44%	1.98%	279	cyflufenamid	112.07%	3.33%
200	alachlor	106.43%	1.81%	280	ametoctradin	102.89%	0.82%
201	epoxiconazole	104.23%	2.13%	281	difenoconazole*	95.54%	0.68%
202	cyazofamid	105.47%	2.05%	282	EPN	117.75%	27.06%
203	metolachlor	106.37%	1.57%	283	cadusafos	107.57%	0.65%
204	uniconazole	101.53%	1.47%	284	isopyrazam*	105.79%	4.09%
205	fenbuconazole	105.38%	2.68%	285	dimepiperate	111.31%	2.55%
206	diflubenzuron	99.14%	4.31%	286	spinosad A	93.35%	5.66%
207	iprodione	102.19%	1.99%	287	diflufenican	99.96%	3.69%
208	fipronil desulfinyl	103.80%	1.33%	288	ipconazole*	109.61%	1.84%
209	thifluzamide	105.36%	3.67%	289	triflumizole	103.56%	0.73%
210	fenthiocarb	105.36%	2.28%	290	indoxacarb	111.37%	2.34%
211	picoxystrobin	105.23%	1.66%	291	trifloxystrobin	108.63%	4.16%
212	rotenone	106.07%	1.26%	292	prosulfofocarb	108.09%	1.50%
213	bupirimate	107.59%	2.77%	293	cycloxydim	104.01%	0.78%
214	flusilazole	105.97%	1.97%	294	amisulbrom	87.82%	15.03%
215	fenoxycarb	105.77%	1.80%	295	pretilachlor	102.96%	4.64%
216	fenamiphos	104.54%	1.87%	296	clethodim	97.80%	3.77%
217	parathion	—	—	297	hexaflumuron	113.42%	1.40%
218	cyprodinil	105.98%	1.36%	298	fenaminstrobin	108.65%	5.06%
219	fenoxanil*	104.06%	2.46%	299	fluoroglycofen-ethyl	101.96%	4.18%
220	quinalphos	105.07%	1.73%	300	profenofos	103.77%	2.64%
221	dimoxystrobin	103.97%	4.04%	301	quizalofop-ethyl	109.91%	0.43%
222	fipronil	102.73%	2.96%	302	fenoxaprop-ethyl	103.73%	7.12%
223	tebufenozide	109.87%	1.95%	303	oxyfluorfen	102.22%	4.93%
224	silthiofam	107.13%	1.34%	304	spinosad D	105.07%	2.55%
225	penconazole	103.70%	2.72%	305	oxaziclomefone	97.25%	7.17%
226	penthiopyrad	104.91%	1.18%	306	diclofop-methyl	111.20%	0.87%
227	chlorbenzuron	94.65%	0.89%	307	cyflumetofen	106.38%	3.52%
228	phenthoate	106.16%	1.01%	308	metamifop	101.91%	3.02%
229	kresoxim-methyl	108.93%	1.12%	309	terbufos	1.135767	7.94%
230	fluthiacet-methyl	105.69%	2.75%	310	enestroburin	109.83%	2.91%
231	diclobutrazol	104.27%	2.21%	311	teflubenzuron	104.75%	9.01%
232	pyrametostrobin	104.80%	2.84%	312	sethoxydim	99.48%	3.44%
233	penflufen	105.37%	1.24%	313	fluazifop-butyl	107.95%	4.47%
234	iprobefos	105.89%	0.69%	314	furathiocarb	106.28%	4.66%
235	fenthion	102.40%	2.60%	315	picolinafen	105.70%	6.68%
236	etrimfos	107.46%	1.57%	316	imibenconazole	108.53%	4.69%

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

No.	Compounds	Spiked amount (0.01 mg/kg, n=3)	
		Avg recovery	%RSD
317	propaquizafop	108.77%	4.35%
318	buprofezin	112.50%	2.59%
319	lactofen	111.02%	4.45%
320	tolfenpyrad	109.18%	3.68%
321	metaflumizone	111.93%	1.82%
322	oxadiazon	119.02%	4.42%
323	fluazinam	102.41%	4.94%
324	butachlor	106.31%	1.38%
325	pyriproxyfen	112.69%	1.64%
326	piperonyl butoxide	108.12%	5.82%
327	coumoxystrobin	108.06%	4.05%
328	ethion	106.80%	3.22%
329	pyribenzoxim	109.86%	5.55%
330	emamectin benzoate	107.61%	3.85%
331	spinetoram L	91.41%	3.14%
332	chlorpyrifos	112.90%	2.18%
333	spinetoram J	95.48%	5.71%
334	lufenuron	105.89%	12.15%
335	pendimethalin	106.77%	3.59%
336	hexythiazox	112.48%	7.72%
337	triallate	112.52%	2.04%
338	tralkoxydim	102.82%	4.62%
339	flucythrinate	97.66%	18.84%
340	flufenoxuron	109.53%	7.32%
341	propargite	107.45%	4.62%
342	dinocap*	110.26%	5.60%
343	etoxazole	108.95%	0.79%
344	butralin	110.56%	3.19%
345	fenpropathrin	113.64%	7.60%
346	fenpyroximate	114.14%	8.19%
347	proquinazid	116.26%	6.24%
348	flumetralin	119.93%	7.51%
349	chlorfluazuron	103.79%	4.97%
350	spirodiclofen	103.41%	1.91%
351	deltamethrin	105.48%	4.87%
352	fenazaquin	105.27%	1.73%
353	fenvalerate	—	—
354	pyridaben	109.49%	2.31%
355	bioresmethrin	101.88%	11.26%
356	tau-fluvalinate	109.97%	1.85%
357	methoprene	108.90%	4.72%
358	abamectin	100.25%	7.25%
359	permethrin*	107.31%	8.81%
360	etofenprox	125.34%	3.34%
361	bifenthrin	118.40%	7.40%
362	pyridalyl	105.13%	5.94%
363	ivermectin	105.78%	5.26%
364	benazolin-ethyl	104.18%	2.19%
365	pirimicarb-desmethyl- formamido	107.54%	1.66%
366	prochloraz metabolite BTS44595	103.81%	2.52%
367	prochloraz metabolite BTS44596	105.55%	0.41%
368	pyrethrin I	114.38%	3.63%
369	pyrethrin II	111.59%	9.50%
370	triflumizole metabolite FM- 6-1	103.19%	1.01%
371	isocarboxiphos	103.64%	2.33%
372	cyazofamid metabolite CCIM	95.39%	2.71%
373	isoxaflutole-diketoneitrile	89.44%	7.11%
374	spiromesifen	106.34%	1.55%
375	novaluron	103.83%	1.13%

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■ Results and Discussion

Grape blank matrix was spiked with a standard solution of pesticides to a final concentration of 0.01 mg/kg. QuEChERS method sample preparation was performed according to Figure 1. Figure 2 shows the MRM chromatogram of the pesticide standards in grape matrix. Three independent experiment was performed to determine average recovery and %RSD. Results shows majority of the compounds having a good recovery rate between 80%-120%, except thiabendazole (138.08%) and etofenprox (125.34%). %RSD of all compound were below 20% except EPN (27.06%). Recovery and %RSD for all the compounds are shown in Table 3.

■ Conclusion

This study presents a method for the determination of 331 pesticides and their metabolite residues in grapes according to GB 23200.121-2021 method. Shimadzu SHIMSEN QuEChERS products were used for extraction and clean-up, followed analysis using Shim-pack GIST C18-AQ column on Shimadzu LCMS-8060NX. The recovery and reproducibility was determined using 0.01 mg/kg spiked grape blank sample. The results shows a high recovery rate of 82.23%-138.08%, and a good reproducibility, with %RSD of 0.32%-27.06%.



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