

Application News

SGLC-LC/MS-048EN

LCMS-8060NX

Analysis of 331 Pesticides and Their Metabolites in Garlic

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User Benefits

- ◆ Established an effective, fast and simple sample preparation method for analysis of pesticides in garlic.
- ◆ 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. Garlics, a widely consumed spice, are no exception. Pesticide residues in garlic 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 garlic 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 Scepter C18 column on Shimadzu LCMS-8060NX.

Table 1. LCMS conditions

UHPLC condition:

LC system:	Shimadzu Nexera™ LC-40B X3
Column:	Shim-pack Scepter C18, 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 0.01% formic acid
Mobile phase B:	2mM ammonium formate in methanol containing 0.01% 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: 227-31012-05

Experimental

Materials:

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

SHIMSEN QuEChERS dSPE tube (P/N: 380-00195)

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, 900 mg MgSO₄, P/N: 380-00195), 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.

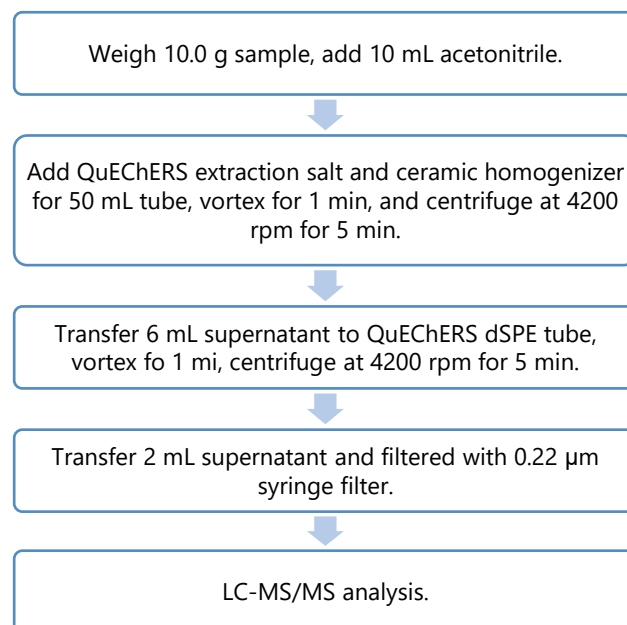


Figure 1. QuEChERS sample preparation workflow for garlic.

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	triflusulfuron-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 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.

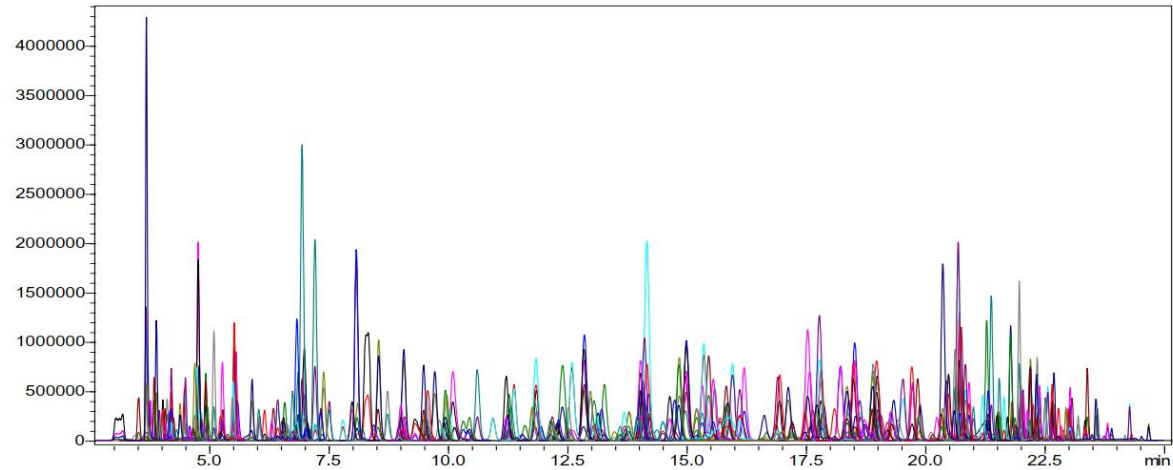


Figure 2. MRM chromatogram of 331 pesticides and their metabolites standards in garlic matrix (concentration: 10 ng/mL).

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	78.06%	3.87%	78	fenamiphos sulfone	103.06%	2.65%
2	acephate	85.62%	3.41%	79	tebuthiuron	100.18%	2.21%
3	omethoate	86.29%	4.28%	80	Sulfentrazone	81.07%	8.22%
4	oxamyl oxime	91.04%	3.66%	81	carbaryl	96.97%	3.04%
5	dinotefuran	98.07%	2.50%	82	carboxin	76.75%	7.14%
6	propamocarb	72.50%	4.99%	83	ethirimol	84.04%	7.23%
7	aldicarb sulfoxide	89.57%	2.58%	84	fenthion sulfone	101.07%	3.37%
8	aldicarb sulfone	99.93%	2.16%	85	penoxsulam	89.36%	5.37%
9	oxamyl	98.22%	1.94%	86	cyantraniliprole	90.23%	5.31%
10	nitenpyram	79.53%	4.30%	87	pirimicarb	94.85%	4.26%
11	oxydemeton-methyl	90.18%	3.00%	88	fosthiazate	87.82%	6.51%
12	demeton-S-methyl-sulfone	93.21%	5.06%	89	spirotetramat-enol	88.20%	3.94%
13	methomyl	94.02%	2.70%	90	disulfoton sulfoxide	95.91%	4.18%
14	monocrotophos	106.57%	1.40%	91	chlortoluron	94.54%	4.63%
15	thiamethoxam	84.42%	4.58%	92	phorate sulfoxide	102.22%	1.84%
16	flonicamid	101.23%	2.40%	93	simetryn	97.35%	3.26%
17	chlormimeform	102.66%	1.51%	94	mesosulfuron-methyl	88.12%	3.70%
18	phosfolan-methyl	89.31%	5.16%	95	methacrifos*	84.33%	4.99%
19	spirotetramat-enol-glucoside	82.06%	2.13%	96	disulfoton sulfone	99.31%	5.23%
20	dicrotophos	103.10%	2.66%	97	tritosulfuron	93.26%	4.58%
21	imidacloprid	99.85%	2.91%	98	phorate sulfone	97.99%	3.98%
22	flumetsulam	85.43%	6.87%	99	isoprocarb	99.05%	2.20%
23	clothianidin	114.28%	3.00%	100	flutriafol	97.27%	3.65%
24	methiocarb sulfoxide	101.73%	4.75%	101	tribenuron-methyl	82.30%	5.68%
25	imidaclothiz	85.36%	5.67%	102	atrazine	98.60%	2.84%
26	vamidothion	93.81%	1.07%	103	imazalil	94.44%	3.07%
27	3-hydroxy carbofuran	94.31%	2.15%	104	isoproturon	90.77%	5.11%
28	acetamiprid	92.60%	7.12%	105	metazachlor	75.31%	10.27%
29	mevinphos*	96.48%	2.36%	106	fensulfothion	101.76%	2.75%
30	methiocarb sulfone	116.85%	2.38%	107	propachlor	95.06%	3.81%
31	carbendazim	96.08%	4.04%	108	chlorpropham	90.90%	4.09%
32	dimethoate	96.84%	2.87%	109	orthosulfamuron	85.31%	3.03%
33	trichlorfon	94.37%	6.74%	110	iodosulfuron-methyl-sodium	78.57%	3.30%
34	demeton-S-sulfoxide	86.36%	6.03%	111	diuron	97.96%	3.33%
35	metamitron	95.59%	3.98%	112	forchlorfenuron	92.69%	6.06%
36	diethyl aminoethyl hexanoate	99.62%	1.38%	113	isoxaflutole	101.85%	1.73%
37	sulfoxaflor*	96.67%	4.69%	114	metalaxyl	91.51%	5.44%
38	chloridazon	95.15%	3.63%	115	heptenophos	101.01%	2.45%
39	demeton-S-sulfone	94.13%	2.11%	116	fensulfothion sulfone	99.70%	2.42%
40	thiacloprid	93.42%	3.94%	117	clethodim sulfone	88.41%	4.21%
41	cymoxanil	96.66%	6.04%	118	metazosulfuron	88.13%	2.88%
42	florasulam	91.63%	3.81%	119	spirotetramat-keto-hydroxy	91.16%	3.51%
43	fensulfothion oxon	84.67%	6.99%	120	methidathion	92.90%	5.56%
44	pirimicarb-desmethyl	85.62%	5.09%	121	flumorph	90.58%	3.88%
45	thiabendazole	79.11%	1.47%	122	fenpropidin	93.29%	3.69%
46	tricyclazole	90.96%	2.80%	123	clethodim sulfoxide*	84.21%	2.35%
47	fensulfothion oxon sulfone	93.50%	2.67%	124	azinphos-methyl	94.80%	3.85%
48	phosfolan	94.23%	3.78%	125	phenmedipham	100.10%	2.53%
49	aldicarb	88.41%	7.76%	126	clomazone	101.30%	0.99%
50	phosmet oxon	94.63%	4.25%	127	phosmet	96.74%	3.21%
51	oxadixyl	93.16%	9.22%	128	chlorantraniliprole	90.75%	4.15%
52	formothion	91.82%	5.43%	129	bensulfuron-methyl	93.40%	2.87%
53	cinosulfuron	77.31%	7.62%	130	demeton	97.13%	2.83%
54	metolcarb	97.36%	4.83%	131	pyrifthalid	97.93%	3.12%
55	thifensulfuron-methyl	85.32%	1.60%	132	ametryn	102.61%	1.86%
56	probenazole	95.26%	5.42%	133	flucetosulfuron*	84.01%	3.71%
57	phosphamidon*	82.30%	11.13%	134	fenobucarb	97.46%	2.40%
58	cyanazine	114.52%	4.49%	135	linuron	95.45%	3.43%
59	triasulfuron	85.85%	6.10%	136	saflufenacil	92.80%	1.85%
60	phenamacril	80.75%	10.83%	137	pyrimethanil	99.83%	2.51%
61	metsulfuron-methyl	82.84%	5.10%	138	propanil	94.30%	3.53%
62	dichlorvos	80.90%	9.60%	139	albendazole	85.27%	4.24%
63	thiophanate-methyl	80.66%	8.00%	140	terbufos sulfone	98.36%	3.92%
64	thidiazuron	86.87%	10.59%	141	terbufos sulfoxide	93.78%	2.59%
65	bendiocarb	89.22%	6.28%	142	ethofumesate	95.79%	3.96%
66	spirotetramat-mono-hydroxy	93.71%	2.82%	143	methiocarb	91.83%	5.58%
67	propoxur	82.03%	8.10%	144	diethofencarb	93.18%	5.68%
68	chlorsulfuron	79.51%	7.12%	145	flurtamone	94.23%	3.80%
69	carbofuran	94.41%	4.54%	146	azoxystrobin	91.67%	4.72%
70	fenamiphos sulfoxide	80.53%	10.28%	147	fludioxonil	96.84%	4.02%
71	metribuzin	88.67%	3.44%	148	fenamidone	101.11%	2.10%
72	simazine	93.06%	7.68%	149	halosulfuron-methyl	88.40%	4.40%
73	hexazinone	96.76%	3.95%	150	pyrisoxazole*	94.82%	2.20%
74	malaonoxon	91.38%	5.77%	151	terbutylazine	95.02%	2.06%
75	Amidosulfuron	83.12%	3.95%	152	dimethenamid	91.52%	5.92%
76	demeton-S-methyl	79.55%	10.67%	153	promecarb	95.11%	4.02%
77	fenthion sulfoxide	96.13%	4.15%	154	ethiprole	92.62%	5.32%
				155	boscalid	96.51%	2.75%
				156	chlorimuron-ethyl	91.65%	2.29%

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

No.	Compounds	Spiked amount (0.01 mg/kg, n=3)	
		Avg recovery	%RSD
157	propyzamide	91.02%	5.67%
158	paclobutrazol	100.51%	2.58%
159	dimethomorph	90.18%	5.61%
160	mandipropamid	95.57%	4.07%
161	isoprothiolane	94.48%	4.18%
162	flutolanil	93.88%	2.42%
163	molinate	100.34%	2.89%
164	fluxapyroxad	91.12%	3.11%
165	ethoxysulfuron	77.46%	6.89%
166	triflusaluron-methyl	90.23%	4.86%
167	fluopicolide	90.83%	3.36%
168	malathion	100.95%	2.45%
169	mepronil	100.16%	3.26%
170	myclobutanil	97.02%	2.04%
171	triadimefon	96.29%	4.39%
172	propyrisulfuron	87.47%	2.62%
173	fenpropimorph	92.74%	3.76%
174	pyrazosulfuron-ethyl	88.39%	4.22%
175	bromuconazole	95.82%	5.32%
176	mefenacet	94.28%	4.72%
177	sedaxane*	87.63%	3.14%
178	pyridaphenthion	96.67%	2.36%
179	methoxyfenozide	93.65%	3.62%
180	prometryn	97.80%	3.15%
181	triadimenol	95.50%	1.94%
182	cyproconazole	92.82%	5.65%
183	triazophos	96.91%	4.58%
184	fenpyrazamine	96.92%	3.96%
185	isazofos	101.31%	2.28%
186	procymidone	—	—
187	cyclosulfamuron	97.78%	1.37%
188	fenarimol	90.74%	4.61%
189	fluopyram	99.96%	3.28%
190	fenhexamid	91.20%	1.63%
191	iprovalicarb*	92.24%	3.47%
192	triticonazole	97.85%	3.45%
193	tetraconazole	92.69%	3.56%
194	ethoprophos	88.41%	7.47%
195	spirotetramat	84.54%	6.71%
196	flufenacet	93.70%	4.39%
197	napropamide	90.06%	5.83%
198	acetochlor	88.95%	5.43%
199	chromafenozide	101.33%	1.62%
200	alachlor	87.24%	7.20%
201	epoxiconazole	95.32%	4.85%
202	cyazofamid	90.28%	5.22%
203	metolachlor	95.23%	1.33%
204	uniconazole	94.37%	6.15%
205	fenbuconazole	98.13%	5.34%
206	diflubenzuron	99.19%	3.19%
207	iprodione	84.35%	6.38%
208	fipronil desulfinyl	104.67%	3.23%
209	thifluzamide	83.25%	6.46%
210	fenothiocarb	99.81%	3.23%
211	picoxystrobin	91.65%	5.92%
212	rotenone	99.17%	3.45%
213	bupirimate	91.00%	4.79%
214	flusilazole	92.68%	2.98%
215	fenoxycarb	99.59%	2.91%
216	fenamiphos	99.57%	3.25%
217	parathion	—	—
218	cyprodinil	101.39%	3.88%
219	fenoxanil*	92.59%	5.26%
220	quinalphos	96.17%	4.44%
221	dimoxystrobin	97.45%	3.71%
222	fipronil	92.35%	5.99%
223	tebufenozide	99.55%	4.16%
224	silthiofam	101.31%	3.41%
225	penconazole	96.05%	4.80%
226	penthiopyrad	94.46%	4.34%
227	chlorbenzuron	101.61%	3.99%
228	phenthoate	100.59%	4.15%
229	kresoxim-methyl	104.43%	3.06%
230	fluthiacet-methyl	99.13%	3.28%
231	diclobutrazol	99.31%	3.70%
232	pyrametostrobin	98.59%	3.15%
233	penflufen	99.21%	3.70%
234	iprobefos	99.31%	3.97%
235	fenthion	93.43%	5.24%
236	etrimfos	98.56%	2.58%

No.	Compounds	Spiked amount (0.01 mg/kg, n=3)	
		Avg recovery	%RSD
237	carfentrazone-ethyl	92.95%	6.79%
238	tebuconazole	100.69%	3.94%
239	fipronil sulfide	94.24%	4.35%
240	fonofos	98.66%	2.97%
241	sulfotep	96.33%	2.94%
242	isofenphos-methyl	95.65%	5.32%
243	edifenphos	95.08%	2.47%
244	propisochochlor	101.52%	5.68%
245	benzovindiflupyr	100.13%	3.37%
246	zoxamide	103.65%	2.42%
247	anilofos	93.29%	3.91%
248	propiconazole	101.03%	2.78%
249	hexaconazole	93.53%	5.00%
250	flubendiamide	66.33%	7.24%
251	diazinon	95.50%	4.75%
252	pyraflufen-ethyl	87.65%	6.62%
253	coumaphos	93.56%	8.80%
254	pyrimorph	95.02%	5.06%
255	benalaxyl	102.29%	2.90%
256	chlorfenvinphos*	98.94%	3.36%
257	metconazole	92.09%	3.66%
258	phorate	96.12%	7.70%
259	fipronil sulfone	92.13%	6.09%
260	famoxadone	94.30%	8.02%
261	tolclofos-methyl	101.60%	6.86%
262	clofentezine	85.31%	6.42%
263	prochloraz	92.96%	7.06%
264	phoxim	94.57%	3.84%
265	oxadiargyl	112.65%	12.15%
266	pyraclostrobin	88.58%	4.60%
267	bitertanol	89.07%	8.66%
268	pirimiphos-methyl	101.48%	5.26%
269	triflumuron	100.43%	2.91%
270	phosalone	90.63%	5.27%
271	diniconazole	96.53%	3.73%
272	benzoximate	90.54%	7.26%
273	pyraoxystrobin	90.38%	5.62%
274	disulfoton	84.69%	3.75%
275	chlorpyrifos-methyl	95.43%	3.06%
276	bifenox	99.86%	8.78%
277	metrafenone	92.55%	6.13%
278	pencycuron	93.19%	4.58%
279	cyflufenamid	94.23%	5.13%
280	ametoctradin	94.87%	4.07%
281	difenoconazole*	92.48%	4.96%
282	EPN	254.12%	37.12%
283	cadusafos	94.67%	3.03%
284	isopyrazam*	95.72%	6.06%
285	dimepiperate	92.92%	3.23%
286	spinosad A	82.58%	4.89%
287	diflufenican	92.83%	6.64%
288	ipconazole*	91.60%	5.66%
289	triflumizole	92.53%	6.24%
290	indoxacarb	90.53%	10.89%
291	trifloxystrobin	86.66%	6.01%
292	prosulfocarb	93.82%	6.30%
293	cycloxydim	94.05%	3.78%
294	amisulbrom	112.40%	16.05%
295	pretilachlor	87.13%	4.17%
296	clethodim	91.12%	5.37%
297	hexaflumuron	86.03%	12.51%
298	fenaminstrobin	94.08%	6.58%
299	fluoroglycofen-ethyl	98.23%	6.87%
300	profenofos	99.10%	7.29%
301	quizalofop-ethyl	99.42%	6.83%
302	fenoxaprop-ethyl	94.03%	5.94%
303	oxyfluorfen	97.65%	20.09%
304	spinosad D	78.24%	5.79%
305	oxaziclomefone	93.53%	3.75%
306	diclofop-methyl	104.59%	8.11%
307	cyflumetofen	94.71%	6.25%
308	metamifop	102.13%	5.71%
309	terbufos	0.8384	21.25%
310	enestroburin	91.19%	6.45%
311	teflubenzuron	97.30%	11.62%
312	sethoxydim	101.98%	6.17%
313	fluazifop-butyl	103.65%	7.46%
314	furathiocarb	106.53%	5.22%
315	picolinafen	89.37%	9.90%
316	imibenconazole	90.77%	7.26%

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	89.98%	6.32%
318	buprofezin	99.92%	5.11%
319	lactofen	82.29%	9.99%
320	tolfenpyrad	87.72%	7.07%
321	metaflumizone	92.04%	12.05%
322	oxadiazon	97.46%	6.67%
323	fluazinam	96.68%	5.82%
324	butachlor	94.15%	6.71%
325	pyriproxyfen	100.74%	2.37%
326	piperonyl butoxide	90.49%	6.82%
327	coumoxystrobin	104.79%	8.72%
328	ethion	87.04%	6.99%
329	pyribenzoxim	84.14%	6.96%
330	emamectin benzoate	74.99%	8.83%
331	spinetoram L	66.84%	15.23%
332	chlorpyrifos	100.31%	1.94%
333	spinetoram J	89.61%	5.36%
334	lufenuron	86.97%	7.85%
335	pendimethalin	94.88%	1.95%
336	hexythiazox	93.86%	3.58%
337	triallate	95.82%	3.15%
338	tralkoxydim	95.24%	5.63%
339	flucythrinate	75.78%	12.42%
340	flufenoxuron	90.15%	1.90%
341	propargite	88.30%	2.77%
342	dinocap*	106.48%	3.94%
343	etoxazole	96.61%	3.98%
344	butralin	92.08%	4.16%
345	fenpropathrin	70.91%	8.00%
346	fenpyroximate	87.26%	9.67%
347	proquinazid	90.65%	10.01%
348	flumetralin	102.26%	7.70%
349	chlorfluazuron	103.03%	4.16%
350	spirodiclofen	93.14%	4.87%
351	deltamethrin	115.48%	5.61%
352	fenazaquin	99.72%	18.35%
353	fenvalerate	—	—
354	pyridaben	98.85%	16.54%
355	bioresmethrin	93.95%	21.33%
356	tau-fluvalinate	90.36%	33.98%
357	methoprene	94.43%	4.42%
358	abamectin	101.56%	6.48%
359	permethrin*	91.05%	3.02%
360	etofenprox	107.48%	2.70%
361	bifenthrin	90.14%	6.41%
362	pyridalyl	92.43%	10.95%
363	ivermectin	130.07%	1.50%
364	benazolin-ethyl	88.94%	5.32%
365	pirimicarb-desmethyl- formamido	74.92%	12.47%
366	prochloraz metabolite BTS44595	96.40%	3.35%
367	prochloraz metabolite BTS44596	103.52%	2.97%
368	pyrethrin I	95.88%	5.38%
369	pyrethrin II	91.14%	14.50%
370	triflumizole metabolite FM- 6-1	97.46%	3.25%
371	isocarboxophos	100.68%	5.47%
372	cyazofamid metabolite CCIM	101.32%	2.04%
373	isoxaflutole-diketetonitrile	65.81%	8.59%
374	spiromesifen	98.98%	8.00%
375	novaluron	89.52%	7.77%

■ Results and Discussion

Garlic 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 garlic matrix. Three independent experiment was performed to determine average recovery and %RSD. Results shows majority of the compounds having a good recovery rate between 60%-130%, except EPN (254.12%). %RSD of all compound were below 30% except EPN (27.06%) and tau-fluvalinate (33.98%) . 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 garlic. Shimadzu SHIMSEN QuEChERS products were used for clean-up of the garlic, followed by analysis using Shim-pack Scepter C18 column on Shimadzu LCMS-8060NX. The recovery and reproducibility was determined using 10 µg/kg spiked garlic and garlic 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 garlic.

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