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Original article

Rapid analytical method for the determination of 220 pesticide with their isomers by GCMS-TIC

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ABSTRACT

This paper presents a cost-effective and validated multi residue modified and miniaturized method for the determination of 220 chemically different groups of pesticides and their isomers. This determination method is performed with single Quaid Gas Chromatography Mass Spectrometry -Total Ion Chromatogram GCMS-TIC. Two methods was experimented and modified with different GCMS parameters to analyses most common used pesticide and their residues in the standers solution and can be applied for real environmental samples. The results showed by single Quaid GCMS-TIC it can analyze 220 pesticides including their isomers within 49.6 min and low detection limit by using modified method 2 as described in this research. Limit of detection (LOD) was ranged from 0.78 to 14.74 ng/ml (ppb) with good separation and resolution. Limit of quantification (LOQ) was ranged between 2.34 and 44.22 ng/ml (ppb). Method 2 was more accurate, shorter, and clear separation rather than method 1. This method can be successfully applied in real environmental samples proven to be a good option for routine analysis of pesticide within the maximum residue limits (MRL) referenced to European commission especially with the most common GCMS-TIC which exists in most of labs and low income countries.

1. Introduction

Hundreds of pesticides are used worldwide for pest control during most of agriculture production, that is why it is necessary to develop and employ multiclass methods for pesticide residue determination. In this study the recovery was from 70 to 120% and relative standard deviation (RSD) < 20% for 60 pesticides and limits of quantification of 5 μg kg − 1 for almost all studied pesticides and this method was successfully applied in real samples proven to be a good option for routine analysis (Estéfani et al., 2019). Amulti-residue method of 107 pesticide residues in wolfberry has been developed and validated using QuEChERS Nano Column Purification Coupled with Ultra Performance Liquid Chromatography Tandem Mass Spectrometry. Similar pretreatment approaches were compared, and the linearity, matrix, analysis limits, precision, stability, and accuracy were validated, which verifies the satisfactory performance of this new method. The LODs and LOQs were in the range of 0.14–1.91 μg/kg and 0.46–6.37 μg/kg, respectively. The recovery of analyses at three fortification levels (10 μg/kg, 50 μg/kg, 100 μg/kg) ranged from 63.3 to 123.0%, 72.0–118.6% and 67.0–118.3%, respectively, with relative standard deviations (RSDs) below 15.0% (Jia-Nan et al., 2019).

A fast analytical method was developed for the determination of 133 pesticide residues using gas chromatography-tandem mass spectrometry (GC–MS/MS). All pesticides showed good linearity in the respective range, both with values of r^2 > 0.99. The average recoveries of the pesticides spiked samples ranged from 70.0% to 112.2% with the RSDs of 0.2%–14.4% (Shuang, et al., 2020). Meanwhile, (Rutkowska, et al., 2018) determined 235 pesticides in challenging, dry, complex herb matrices and the results showed most recoveries ranged from 70 to 120% (RSD < 18%), reaching the quantification limit of 0.001 to 0.002 mg kg − 1. With excellent linearity within the range from 0.001 to 2.00 μg mL − 1, and a correlation coefficient higher than 0.999 was obtained

The Quantitative estimation of pesticide residues in tea samples was established by employing Liquid Chromatography with tan-

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dem mass spectrometer using electron spray ionization (LC-ESI-MS/MS) in multiple reaction modes (MRM). Recoveries were between 70 and 120% with the acceptable relative standard deviation (RSD). The limits of detection ranged from 0.03 to 1.4 ng/mL^{-1} and limit of quantifications from 0.1 to 2.6 ng.mL-1 for all the samples under investigation (Reddy, et al. 2018). The sensitive and rapid liquid chromatography-tandem mass spectrometry (LC-MS/MS) method is developed for simultaneous determination of 187 pesticide residues in edible fungi. At low and high fortification levels, recoveries ranged from 70 to 118%. The relative standard deviation (RSD) was always below 30% and was below 25% for 169 pesticides, accounting for 90%. The limit of detection (LOD) was 0.01– 85 μg kg-1, 165 pesticides had LOD #10 mg kg-1, accounting for 88%. The proposed method is suitable for determination of 187 pesticide residues in shiitake, black fungus, nameko and enoki mushroom (Chang, et al., 2014).

The mluti-residues Analysis of pesticide residues using GCMS in leafy vegetables was provided by (Selim et al., 2011) to determine 86 pesticides residue with highly recovery % and acceptable LOD and LOQ. Furthermore, (EL-Saeid et al., 2012) the same methodology was applied using GCMS for the determination of 86 pesticide residues in non-leafy vegetables with highly recovery % and acceptable LOD and LOQ. Conversely, (Acosta-Dacal, et al., 2021) it was reported that the 218 analytes are extracted using a single step, without clean-up, with matrixmatched calibration, and two complementary techniques: liquid and gas chromatography tandem triple quad mass spectrometry (LC-MS/MS and GC–MS/MS). The used method was fully validated on a representative agricultural soil sample with limits of detection (LOD) ranged between 0.024 and 6.25 ng g^{-1}. (Shen, et al., 2009) reported the determination of 107 pesticide residues using off-line dispersive solid-phase extraction and gas chromatography-tandem mass spectrometry in some Chinese vegetables, Also, (Ishaqa and Nawazb, 2018) Analyze the organochlorine (OCPs) pesticide residues in contaminated milk using gas chromatography.

2. Materials and methods

2.1. Chemicals and standard solutions

Certified reference standards of the tested pesticides were GC Multiresidue Pesticide Kit with a Cataloged number. 32,562 and purchased from Restek Corporation, U.S. which contain 9 ampules. Comprehensive 220 compound kit covers food safety lists by the FDA, USDA, and other global governmental agencies. Each ampule standard includes different 5 pesticide groups (Organophosphorus (group 1), Organochlorine (group 2), Organonitrogen (group 3), Synthetic Pyrethroid (group 4), and Herbicide (group 5) Methyl Esters) with concentration 100 μg/mL = ppm each and dissolved in toluene. Acetonitrile reagents used was of LC–MS grade and acetone of pesticide grade.

Stock solutions, 2 μg/mL, of mixture pesticide standards were prepared by dissolving 100 μL of the pesticide group in mixture of acetonitrile: Acetone 80:20, the volume of which was calculated in order to prepare 2 mg/mL solutions. The solvents used were acetonitrile and acetone were chosen in accordance with the solubility of the analyte. The stock solutions were stored at low temperature (−20 °C) in containers that prevent any loss of solvent and entry of water.

The working standards used for quantitative were prepared in acetonitrile for the GC–MS analysis system. Intermediate stock standard mixtures of 10 μg/mL in acetonitrile were prepared by diluting 500 μL of the stock solutions in class A volumetric flasks of 1 mL. By diluting the intermediate stock standard mixtures, the intermediate working standards of 1, 0.1, 0.01 and 0.001 μg/mL = ppm were prepared in solvent.

2.2. Pesticide analysis by gas chromatography–mass spectrometry (GC–MS-TIC)

Analyte separation, detection, and identification were performed by gas chromatography–mass spectrometry (GC–MS) on an Agilent (Palo Alto, CA) 6890 N gas chromatograph equipped with an Agilent DB-5MS column (30 m × 0.25 mm × 0.25μmfilm thickness) and 5973 N mass selective detector Table 1.

2.3. Quality Control/Assurance

Solvents was used in this study were 99.99% pure and residue analytical grade. By using pesticide standard mixture, the recoveries of pesticides were detected in three replicates. The analysis was done to keep reproducibility and repeatability under acceptable range. Acetonitrile solvent and different pesticides concentration limits was used as blank samples for limit of detection (LOD).

3. Results

In this research, several experiments were conducted to separate the largest number of different groups of pesticides in the same run and also in the shortest possible separation time using several variables parameters by GCMS-TIC.

The results indicate that two methods have been reached to separate 220 pesticides belonging to different chemical groups, such as Organophosphorus OPPs, Organochlorines OCPs, Organonitrogens ONPs, Synthetic Pyrethroids, and Herbicides Methyl Esters and its isomers, as well as in terms of application and use such as Insecticides, Herbicides, Fungicides, and Nematocides.

Furthermore, the results indicated as in Table 2 and Fig. 2 that the second method was better in terms of separating the number of 220 pesticides and its isomers within a retention time

Table 1
Gas Chromatography Mass Spectrometry -Total Ion Chromatogram (GCMS-TIC) Parameters for Pesticides Analysis Methods.

Parameter	Method 1	Method 2
Carrier gas	Helium	Helium
Inlet temp.	250C	250 °C
Mode	Splitless	Splitless
Pressure	9.954 psi	9.954 psi
Injection Source	GC ALS	GC ALS
Total Flow	64 mL/min	65 mL/min
Thermal Aux Temp.	280 °C	281 °C
Injection Volume	1 μL	1 μL
Coulmn	Agilent DB-5 ms 350 °C:	30 m × 250 μm × 0.25 μm
Agilent DB-5 ms 350 °C:		30 m × 250 μm × 0.25 μm
Pressure	9.954 psi	9.954 psi
Flow	1 mL/min	2 mL/min
Average Velocity	37.132 cm/sec	37.132 cm/sec
Holdup Time	1.3466 min	1.3466 min
Flow Program	1 mL/min	1 mL/min
Oven Program:	Initial temperature 90 °C hold for 2 min then 6 °C/min to 200 °C for 5 min then 7 °C/min to 290 °C for 7 min	Initial temp. 90 °C for 2 min then 6 °C/min to 150 °C for 5 min then 5 °C/min to 220 °C for 5 min then 6 °C/min to 290 °C for 2 min
Run Time	45.19 min	49.667 min
Solvent Delay	3.00 min	3.00 min
EMV Mode	Relative	Relative
EM Voltage	1482	1482
MS Source	230 °C	230 °C
MS Quad	150 °C	155 °C
Actual EMV	1482.35	1482.35
GAIN FACTOR	0.46	0.46

Table 2
Pesticides Groups, RT and Target and Qualified ions, Limit of Detection (LOD) and Limit of quantification (LOQ) using GCMS-TIC method 2.

No	Component Name	RT	Groups	Q. ions			LOD ng/ml	LOQng/ml
				1	2	3		
1	Allidochlor	5.77	3	138	56	70	7.44	22.32
2	Biphenyl	8.637	3	154	152	153	6.98	20.94
3	Dichloroaniline	9.375	3	161	99	163	8.64	25.92
4	Mevinphos	9.827	1	127	192	109	2.82	8.46
5	Etridazole	10.531	3	211	213	183	1.76	5.28
6	Pebulate	11.567	3	128	57	72	5.73	17.19
7	Methacrifos	11.67	1	240	208	180	10.51	31.53
8	Chloroneb	12.099	2	191	193	206	10.03	30.09
9	2-Phenylphenol	12.219	5	170	169	141	4.21	12.63
10	Pentachlorobenzene	12.597	2	250	252	248	2.37	7.11
11	Tecnazene	13.278	3	203	261	215	6.21	18.63
12	Propachlor	13.369	3	120	196	93	1.44	4.32
13	Diphenylamine	13.406	3	169	168	167	2.14	6.42
14	Cycloate	13.575	3	83	154	55	8.57	25.71
15	Sulfotep	15.408	1	322	202	266	4.11	12.33
16	Chlorpropham	15.967	5	213	127	129	1.30	3.9
17	Ethalfluralin	16.305	3	316	55	276	3.72	11.16
18	Trifluralin	16.478	3	306	264	335	5.28	15.84
19	Benfluralin	16.579	3	292	264	276	12.71	38.13
20	Phorate	16.639	1	75	260	97	0.88	2.64
21	BHC, alpha-	17.039	2	217	219	183	1.93	5.79
22	Hexachlorobenzene	17.088	2	284	286	282	1.96	5.88
23	Pentachloroanisole	17.177	2	280	265	237	3.06	9.18
24	BHC, beta-	17.832	2	219	181	109	1.76	5.28
25	Atrazine	18.126	3	200	173	215	2.77	8.31
26	Clomazone	18.206	3	204	125	127	5.81	17.43
27	BHC, delta-	18.224	2	219	109	183	2.33	6.99
28	Quintozene	18.361	5	249	295	237	1.25	3.75
29	Pentachlorobenzonitrile	19.686	3	275	277	273	5.63	16.89
30	Terbufos	20.169	1	231	57	97	2.64	7.92
31	Terbutylazine	20.312	3	214	229	173	10.58	31.74
32	Fonofos	20.57	1	109	137	246	3.55	10.65
33	Propisochlor	20.753	3	174	146	222	1.89	5.67
34	Propyzamide	20.93	3	255	175	173	3.72	11.16
35	Profluralin	21.193	3	55	330	318	10.28	30.84
36	Pyrimethanil	21.525	3	198	199	200	3.90	11.7
37	Diazinon	21.6	1	179	137	152	4.75	14.25
38	Disulfoton	21.714	3	88	60	97	2.99	8.97
39	Fluchloralin	21.766	3	326	306	264	2.10	6.3
40	Terbacil	22	3	161	117	160	2.47	7.41
41	Chlorothalonil	22.2	3	266	264	268	2.10	6.3
42	Triallate	22.733	3	86	268	143	1.58	4.74
43	Isazophos	22.744	1	119	257	161	1.53	4.59
44	Tefluthrin	22.778	4	177	197	178	2.76	8.28
45	Endosulfan ether	22.916	2	69	241	239	3.30	9.9
46	Pentachloroaniline	23.099	3	263	267	265	3.12	9.36
47	Propanil	23.156	3	161	163	217	0.94	2.82
48	Dimethachlor	23.219	3	134	197	132	2.45	7.35
49	Acetochlor	23.219	3	146	162	59	9.88	29.64
50	Chlorpyrifos-methyl	23.27	1	286	288	125	5.29	15.87
51	Tolclofos-methyl	23.322	1	265	267	125	0.78	2.34
52	Transfluthrin	23.333	4	163	127	165	1.64	4.92
53	Alachlor	23.408	3	188	160	146	1.54	4.62
54	Fenchlorphos	23.421	1	285	287	109	2.14	6.42
55	Fenitrothion	23.711	1	277	260	125	1.39	4.17
56	Pentachlorothioanisole	23.762	2	296	298	294	2.89	8.67
57	Pirimiphos-methyl	23.848	1	290	276	305	2.29	6.87
58	Prodiamine	23.888	3	321	279	333	2.12	6.36
59	Dichlofluanid	23.946	3	226	123	224	2.09	6.27
60	Anthraquinone	24.06	4	208	180	152	2.91	8.73
61	Aldrin	24.123	2	66	293	263	0.86	2.58
62	Malathion	24.129	1	93	173	125	2.99	8.97
63	Metolachlor	24.335	3	238	162	240	2.45	7.35
64	Fenthion	24.472	1	278	169	109	3.13	9.39
65	Chlorpyrifos	24.855	1	314	197	199	2.59	7.77
66	Dichlorobenzophenone	24.895	5	139	250	111	3.29	9.87
67	Parathion	25.136	1	291	97	109	2.15	6.45
68	Triadimefon	25.176	3	57	85	208	1.13	3.39
69	Chlorthal-dimethyl	25.307	3	301	299	303	2.68	8.04
70	Fenson	25.428	2	268	141	77	1.82	5.46
71	Bromophos-methyl	25.439	1	331	329	125	7.35	22.05

(*continued on next page*)

Table 2 (*continued*)

No	Component Name	RT	Groups	Q. ions			LOD ng/ml	LOQng/ml
				1	2	3		
72	Isodrin	25.634	2	193	195	263	0.94	2.82
73	Diphenamid	26.091	3	167	72	165	2.25	6.75
74	Cyprodinil	26.126	3	224	225	226	2.00	6
75	Pirimiphos-ethyl	26.206	1	304	333	318	6.40	19.2
76	Isopropalin	26.257	3	280	238	264	1.89	5.67
77	Heptachlor epoxide	26.314	2	353	355	81	8.42	25.26
78	Metazachlor	26.417	3	133	209	132	2.77	8.31
79	Pendimethalin	26.435	3	252	281	162	1.68	5.04
80	Penconazole	26.498	3	159	248	161	1.51	4.53
81	Tolylfluanid	26.602	3	137	240	238	1.55	4.65
82	Chlozolinate	26.715	5	259	188	331	1.33	3.99
83	Bromfenvinphos-methyl	26.784	1	295	297	109	2.32	6.96
84	Chlorfenvinphos 2	26.795	1	323	267	269	1.72	5.16
85	Chlorfenvinphos 1	26.807	1	267	323	269	1.82	5.46
86	Fipronil	26.881	3	367	369	213	5.83	17.49
87	Quinalphos	26.927	1	146	157	156	4.88	14.64
88	Chlorbenside	27.081	2	125	127	268	1.41	4.23
89	Procymidone	27.299	3	283	96	285	4.85	14.55
90	Chlordane, cis-	27.339	2	375	373	377	1.07	3.21
91	Bromophos-ethyl	27.35	1	359	242	97	5.48	16.44
92	DDE, o,p'-	27.562	2	246	318	248	3.51	10.53
93	Paclobutrazol	27.562	3	236	238	82	2.32	6.96
94	Endosulfan I	27.596	2	241	239	195	0.94	2.82
95	Endosulfan II	27.734	2	241	195	339	2.27	6.81
96	Chlordane, trans-	27.734	2	375	373	377	3.88	11.64
97	Nonachlor, cis-	27.814	2	409	407	411	7.16	21.48
98	Chlorfenson	27.825	2	111	175	302	8.47	25.41
99	Fenamiphos	27.968	1	303	154	217	5.22	15.66
100	Bromfenvinphos	27.991	1	267	323	269	13.41	40.23
101	Iodofenfos	28.065	1	377	379	93	6.38	19.14
102	Flutolanil	28.117	3	173	281	145	2.50	7.5
103	Prothiofos	28.123	1	309	113	267	2.18	6.54
104	Profenofos	28.191	1	337	374	208	7.65	22.95
105	DDE, p,p'-	28.191	2	318	216	246	4.94	14.82
106	Pretilachlor	28.34	3	262	238	162	2.03	6.09
107	DDT, o,p'-	28.352	2	235	237	165	7.21	21.63
108	Oxadiazon	28.495	3	344	258	175	2.33	6.99
109	DDD, o,p'-	28.683	2	235	237	165	9.03	27.09
110	DDD, p,p'-	28.695	2	235	237	165	9.15	27.45
111	DDT, p,p'-	28.735	2	235	237	165	6.46	19.38
112	Flusilazole	28.861	3	233	206	234	11.94	35.82
113	Oxyfluorfen	28.861	3	361	300	252	2.80	8.4
114	Bupirimate	28.964	3	273	208	316	9.82	29.46
115	Nitrofen	29.129	3	283	202	285	6.03	18.09
116	Ethylan	29.216	2	223	224	179	2.84	8.52
117	Fluazifop-P-butyl	29.324	5	282	383	254	1.02	3.06
118	Chlorobenzilate	29.359	5	251	253	139	4.27	12.81
119	Chlorthiophos 3	29.364	1	325	269	360	3.24	9.72
120	Nonachlor, trans-	29.467	2	409	407	411	3.19	9.57
121	Ethion	29.49	1	384	231	153	4.61	13.83
122	Endrin aldehyde	29.593	2	345	67	250	1.14	3.42
123	Chlorthiophos 2	29.685	1	360	362	97	6.21	18.63
124	Chlorthiophos 1	29.708	1	325	269	360	8.41	25.23
125	Sulprofos	29.836	1	322	156	140	7.91	23.73
126	Triazophos	29.896	1	161	313	162	6.51	19.53
127	Carbophenothion	29.936	1	344	157	342	5.31	15.93
128	4,4′-Methoxychlor olefin	29.936	2	308	310	238	10.75	32.25
129	Carfentrazone ethyl	29.936	5	330	290	340	13.75	41.25
130	Endosulfan sulfate	30.062	2	242	239	237	4.08	12.24
131	Lenacil	30.074	3	153	154	152	4.84	14.52
132	Norflurazon	30.177	3	303	145	102	1.51	4.53
133	Hexazinone	30.314	3	171	128	83	10.82	32.46
134	Tebuconazole	30.486	3	250	125	252	4.05	12.15
135	Propargite	30.549	3	135	350	81	9.33	27.99
136	Resmethrin 1	30.692	4	143	123	171	10.52	31.56
137	Piperonyl butoxide	30.869	1	176	149	177	12.54	37.62
138	Resmethrin 2	31.041	4	143	123	171	10.25	30.75
139	Nitralin	31.167	3	316	274	300	14.74	44.22
140	Endrin	31.207	2	263	281	261	3.72	11.16
141	Endrin ketone	31.258	2	317	315	67	11.44	34.32
142	Iprodione	31.264	3	314	187	316	5.73	17.19
143	Pyridaphenthion	31.487	1	188	340	97	2.64	7.92
144	Phosmet	31.556	1	160	317	161	2.99	8.97
145	Bromopropylate	31.756	5	341	339	343	8.64	25.92

Table 2 (*continued*)

No	Component Name	RT	Groups	Q. ions			LOD ng/ml	LOQng/ml
				1	2	3		
146	Tetramethrin 1	31.865	4	164	123	81	2.33	6.99
147	Tetramethrin 2	31.928	4	164	123	81	5.81	17.43
148	Bifenthrin	31.928	4	181	165	166	1.30	3.9
149	Methoxychlor	31.979	3	227	228	346	3.55	10.65
150	Fenpropathrin	32.008	3	349	97	55	4.75	14.25
151	Tebufenpyrad	32.408	3	333	318	171	12.98	38.94
152	Tetradifon	32.494	2	356	159	111	8.57	25.71
153	Phenothrin 2	32.706	4	350	123	183	2.14	6.42
154	Phenothrin 1	32.752	4	123	183	81	4.21	12.63
155	Phosalone	32.849	1	182	121	367	2.77	8.31
156	Leptophos	32.923	1	171	375	377	3.72	11.16
157	Pyriproxyfen	33.118	3	136	226	96	1.76	5.28
158	Mirex	33.29	2	272	274	237	2.82	8.46
159	Cyhalothrin, lambda-	33.29	4	197	208	181	10.03	30.09
160	Fenarimol	33.347	3	219	330	139	1.44	4.32
161	Pyrazophos	33.484	1	232	221	373	3.90	11.7
162	Pyraclofos	33.507	1	360	194	138	4.11	12.33
163	Permethrin, cis-	33.616	4	183	165	163	10.51	31.53
164	Pyridaben	33.752	3	147	148	117	1.76	5.28
165	Permethrin, trans-	33.753	4	183	165	163	1.93	5.79
166	Fluquinconazole	33.776	3	340	342	341	10.58	31.74
167	Prochloraz	33.839	3	308	310	312	2.37	7.11
168	Cyfluthrin 1	33.948	4	206	165	163	0.88	2.64
169	Cyfluthrin 2	34.033	4	206	165	163	6.21	18.63
170	Cyfluthrin 3	34.382	4	206	165	163	5.28	15.84
171	Cyfluthrin 4	34.537	4	206	165	163	5.71	17.13
172	Cypermethrin 1	34.548	4	165	163	181	3.06	9.18
173	Cypermethrin 2	34.68	4	165	163	181	5.63	16.89
174	Cypermethrin 3	34.749	4	165	163	181	1.96	5.88
175	Cypermethrin 4	34.857	4	165	163	181	1.25	3.75
176	Flucythrinate 1	34.903	4	451	199	157	12.28	36.84
177	Etofenprox	35.401	3	163	135	376	1.89	5.67
178	Flucythrinate 2	35.47	4	451	199	157	12.28	36.84
179	Fluridone	35.739	3	328	329	330	0.88	2.64
180	Fludioxonil	35.91	3	248	249	247	8.57	25.71
181	Fenvalerate 1	36.522	4	125	167	225	2.99	8.97
182	Fenvalerate 2	36.683	4	125	167	225	3.55	10.65
183	tau-Fluvalinate 1	36.728	4	502	250	252	1.44	4.32
184	tau-Fluvalinate 2	36.831	4	502	250	252	2.82	8.46
185	Deltamethrin	36.934	4	255	253	181	5.73	17.19
186	2,4′-Methoxychlor	37.494	2	227	228	274	11.44	34.32
187	Acequinocyl	37.661	5	343	189	129	12.98	38.94
188	Acrinathrin	37.776	4	181	289	208	8.64	25.92
189	Azinphos-ethyl	37.839	1	160	132	125	2.14	6.42
190	Azinphos-methyl	37.993	1	160	161	132	4.21	12.63
191	BHC, gamma-	38.056	2	181	219	183	4.75	14.25
192	Bioallethrin	38.153	4	123	136	107	10.03	30.09
193	Captafol	38.288	3	313	311	349	3.90	11.7
194	Captan	38.354	3	264	265	266	6.21	18.63
195	Chlorfenapyr	38.445	3	247	137	59	5.81	17.43
196	Coumaphos	38.668	1	362	226	210	1.76	5.28
197	Diallate 1	38.966	3	234	236	86	1.30	3.9
198	Diallate 2	38.971	3	234	236	86	10.58	31.74
199	Diclobenil	39.446	3	171	173	136	1.93	5.79
200	Dicloran	39.773	3	206	176	124	2.33	6.99
201	Dieldrin	39.79	2	263	277	281	1.76	5.28
202	Edifenphos	39.893	1	310	173	109	2.64	7.92
203	EPN	40.619	1	157	169	185	10.51	31.53
204	Flutriafol	40.663	3	164	219	123	1.25	3.75
205	Folpet	40.858	3	260	262	264	2.37	7.11
206	Heptachlor	41.064	2	272	274	276	3.72	11.16
207	Linuron	41.258	3	61	248	160	5.63	16.89
208	Metalaxyl	41.487	5	206	132	249	3.06	9.18
209	Methyl parathion	42.111	1	263	109	125	1.96	5.88
210	MGK 264 1	42.374	3	164	210	111	5.71	17.13
211	MGK 264 2	42.517	3	164	210	111	5.28	15.84
212	Myclobutanil	42.671	3	179	181	152	3.72	11.16
213	N-(2;4-Dimethylphenyl)formamide	44.794	3	122	120	150	4.11	12.33
214	Tetrachloroaniline	44.886	3	231	229	233	1.89	5.67
215	Tetrachlorvinphos	45.189	1	331	329	333	2.77	8.31
216	Tetrahydrophthalimide	46.059	3	79	151	80	8.57	25.71
217	Triadimenol	46.511	3	168	128	112	11.44	34.32

(*continued on next page*)

Table 2 (*continued*)

No	Component Name	RT	Groups	Q. ions			LOD ng/ml	LOQng/ml
				1	2	3		
218	Tricyclazole	46.637	3	189	162	161	5.73	17.19
219	Triflumizole	47.432	3	278	206	287	1.44	4.32
220	Vinclozolin	47.483	3	285	212	287	0.88	2.64

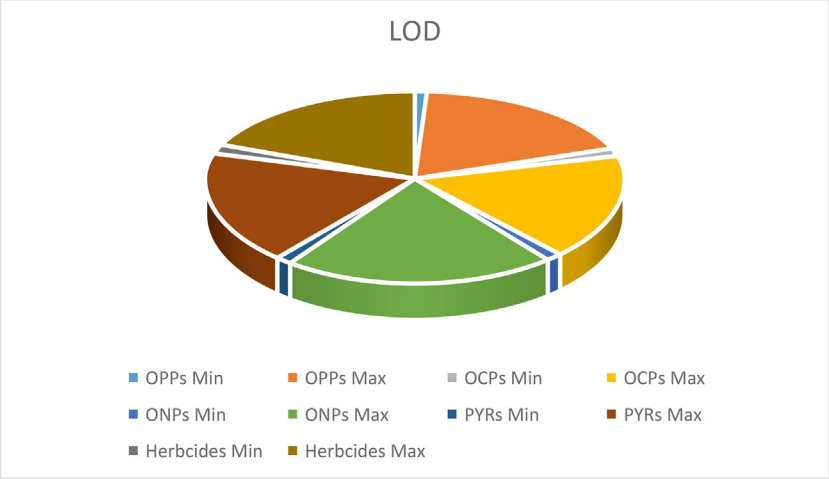

Fig. 1. Minimum and maximum LODs of the OPPs-, OCPs-, ONPs-, pyrethroids-, and herbicides-tested groups.

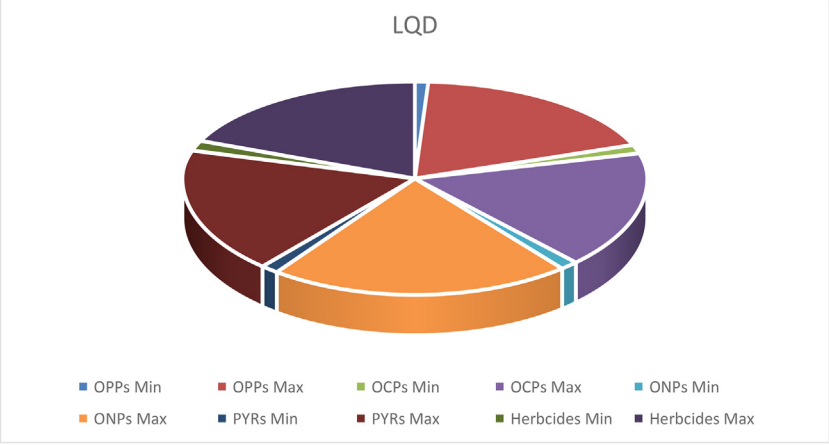

Fig. 2. Minimum and maximum LOQs of the OPPs-, OCPs-, ONPs-, pyrethroids-, and herbicides-tested groups.

49.6 min without any interference between the compounds, which could be relied upon in estimating this number of pesticides or their residues in the environmental samples. While the second method Fig. 1 is less efficient in the separation of the number of 220 pesticides with their isomers under this research and that the separation time is 45 min which is longer than method 1 and the presence of many overlaps between the separated pesticides is observed.

Limit of detection (LOD) and Limit of quantification (LOQ) of 220 tested and separated pesticides ranged from 0.78 to 14.74 and 2.34 to 44.22 ng/ml (ppb) as showed in Table 2 and Figs. 1 and 2 which is reflect the sensitivity of the GCMS-TIC and the accuracy of the tested parameters in method 2 (Table 1). As previously reported the LOD ranged from 0.03 to 1.4 ng/mL^{-1}, (Reddy, et al. 2018). 0.01– 85 μg kg-1, for 165 pesticides, (Chang, et al., 2014). Also LOD ranged between 0.024 and 6.25 ng g^{-1} as reported by (Acosta-Dacal, et al., 2021).

The LOD and LOQ of OPPs, OCPs, ONPs, Pyrethroids and Herbicides tested groups (Figs. 1 and 2) ranged from 0.78 to 2.34, 13.41 to 40.23; 0.86 to 2.58, 11.44 to 34.32; 0.88 to 2.64, 14.74to 44.22; 0.88 to 2.64, 12.28 to 36.84 and 1.02to 3.06, 13.75 to 41.25 ng/ml (ppb). respectively.

4. Discussion

Many studies was mentioned and discus the determination of different numbers of pesticides by different techniques. Estefani, et al 2019 develop a method and it was successfully applied in real samples proven to be a good option for routine analysis, also, reported multi-residue method of 107 pesticide residues has been

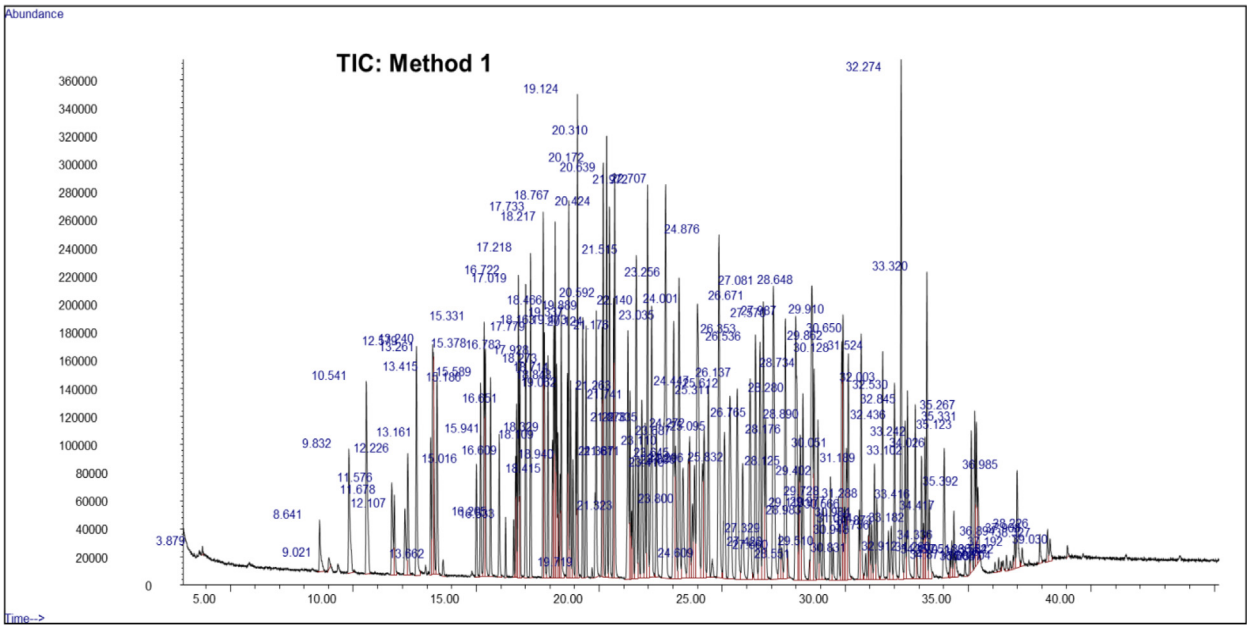

Fig. 3. GC–MS-TIC separation chromatogram of pesticide residues (220 Compound), method 1.

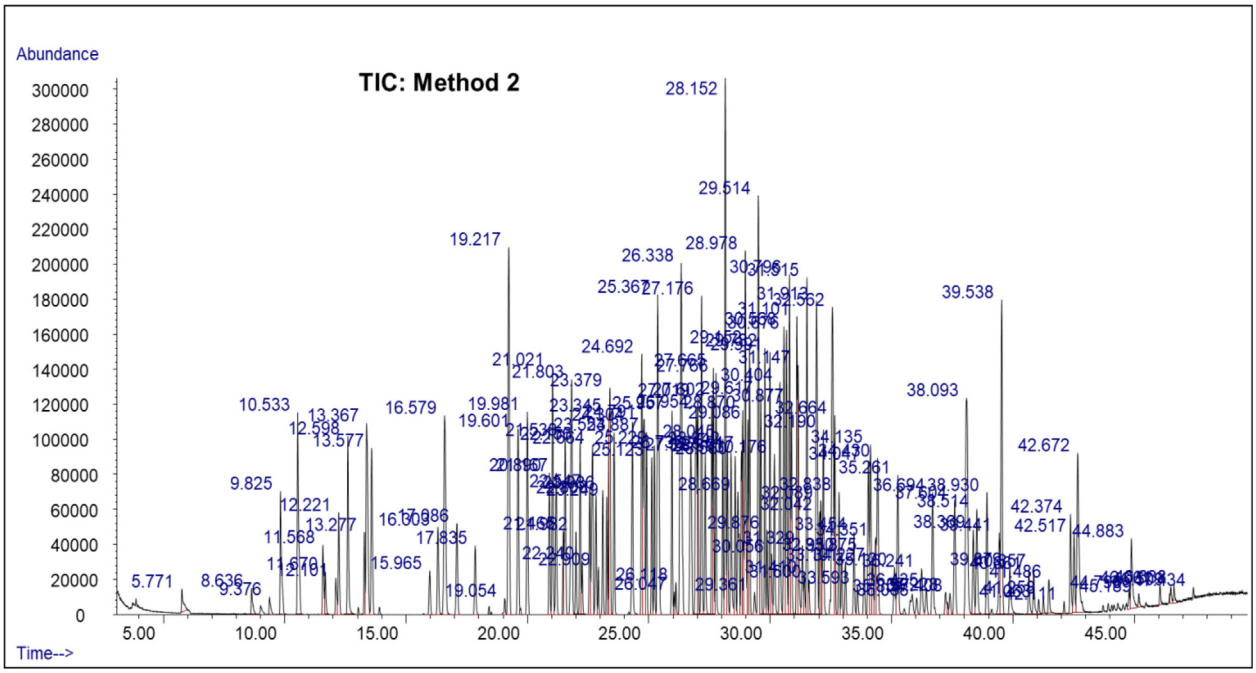

Fig. 4. GC–MS-TIC separation chromatogram of pesticide residues (220 Compound), method 2.

developed and validated using QuEChERS nano column purification coupled with Ultra Performance Liquid Chromatography Tandem Mass Spectrometry (UPLC-MSMS) (Jia-Nan et al., 2019). Meanwhile, a fast analytical method was developed for the determination of 133 pesticide residues using gas chromatography-tandem mass spectrometry GC–MS/MS (Shuang, et al., 2020). Additionally, a modified a multiresidue method using QuEChERS and GC–MS/MS to determine determined was reported. 235 pesticides (Rutkowska, et al., 2018). The use of Liquid Chromatography with tandem mass spectrometer using electron spray ionization (LC-ESI-MS/MS) was reported (Reddy, et al. 2018). for the quantitative estimation of pesticide residues. A sensitive and rapid liquid chromatography-tandem mass spectrometry (LC-MS/MS) method was developed for simultaneous determination of 187 pesticide residues (Chang, et al., 2014).

Most of the previous research has used sophisticated and expensive Chromatographic techniques that may not be available in most laboratories for many countries, while the method discussed in the current research has used a very common technique GCMS-TIC to separate 220 comprehensive pesticides and their isomers as showed in Table 2 and Figs. 3–9 which cover a food safety lists by the FDA, USDA, and other global governmental agencies

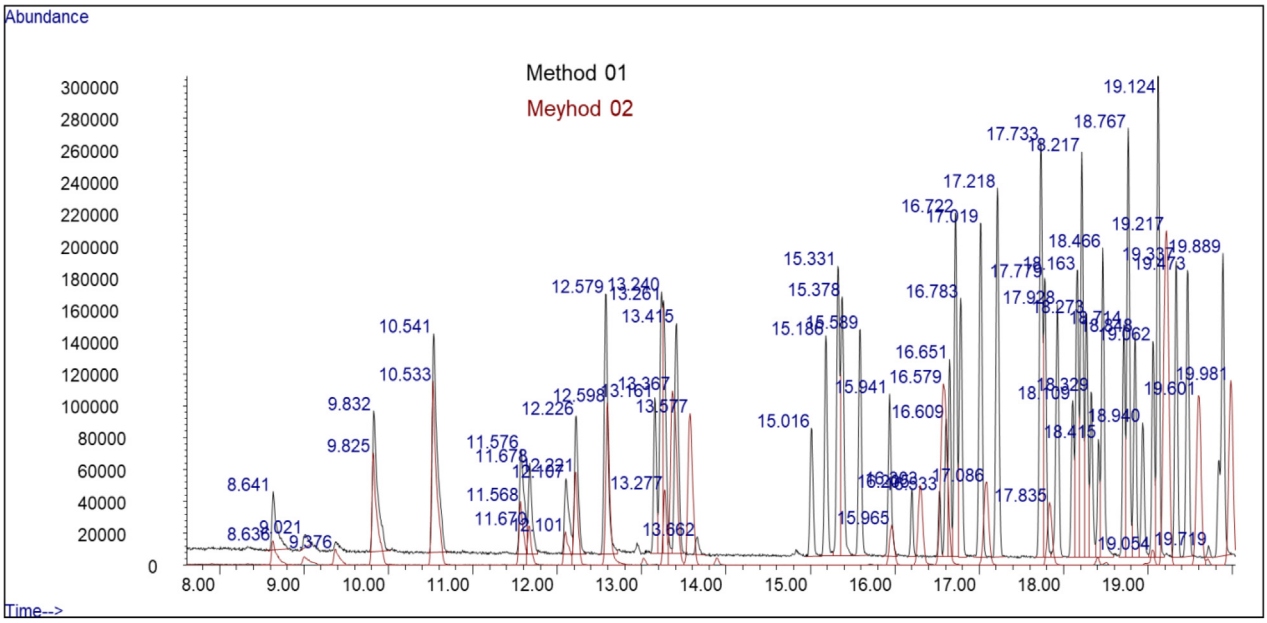

Fig. 5. GC–MS-TIC separation chromatogram of pesticide residues from RT 9– 20 min, methods 1 and 2.

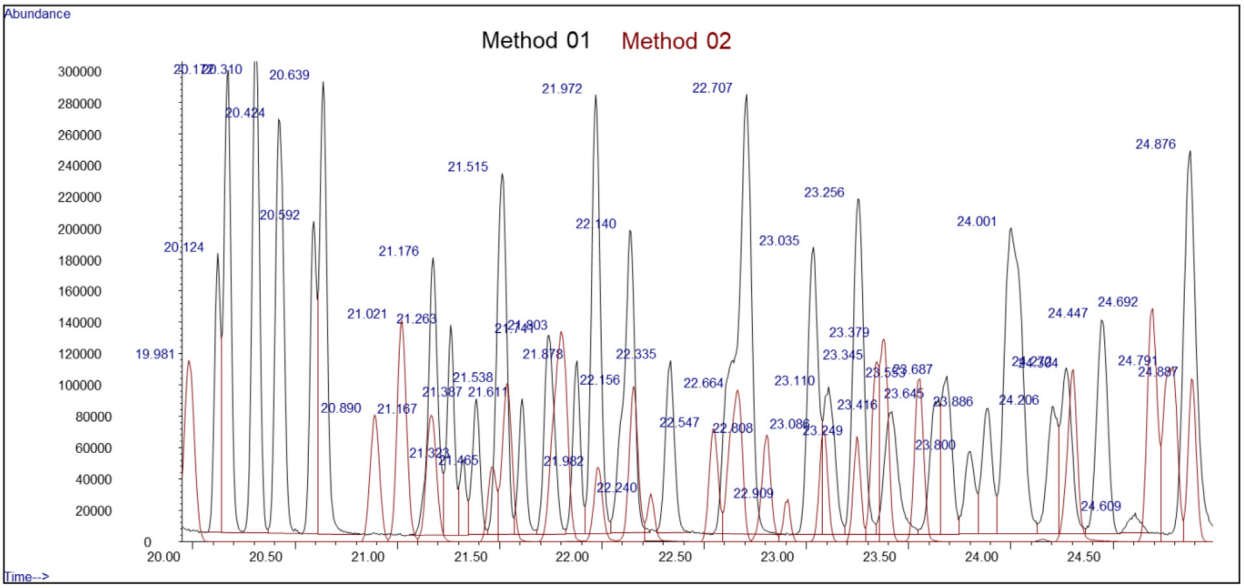

Fig. 6. GC–MS-TIC separation chromatogram of pesticide residues from RT 20–25 min, methods 1 and 2.

with highly accuracy with the possibility of applying in the future to estimating the pesticide residues with different environmental samples as mentioned in the previous researches.

Fourteen Isomers (Chlorfenvinphos 2, Chlorfenvinphos 1, Tetramethrin 1, etramethrin 2, Cyfluthrin 1, Cyfluthrin 2, Cyfluthrin 3, Cyfluthrin 4, Cypermethrin 1, Cypermethrin 2, Cypermethrin 3, Cypermethrin 4, tau-Fluvalinate 1 and tau-Fluvalinate 2.) was analyzed by current modified method which is more advantages for this method that we able to analyze the original compound and its related isomers such as Cyfluthrin and its 4 isomers (Cyfluthrin 1, Cyfluthrin 2, Cyfluthrin 3, Cyfluthrin 4. Also 4 isomers of Cypermethrin 1, Cypermethrin 2, Cypermethrin 3, Cypermethrin 4 and MGK 264–2) Was also analyzed by current instigated method using GCMS-TIC.

Using the modified method in present research it can be analyze 5 groups of pesticides in same mixture and GCMS-TIC run, 48 organophosphorus pesticides (OPPs) (group 1) compounds. Forty Organochlorine Pesticides Compounds (OCPs) (group 2) was separated and analyzed by the current investigated method as well as 87 Organonitrogen Fungicides Compounds (ONFs) (group 3), Meanwhile, Seventeen Synthetic Pyrethroid compound (group 5) was separated and analyzed Table 2.

5. Conclusions

This study demonstrated the possibility of estimating the different chemical groups of 220 pesticides and their isomers using the

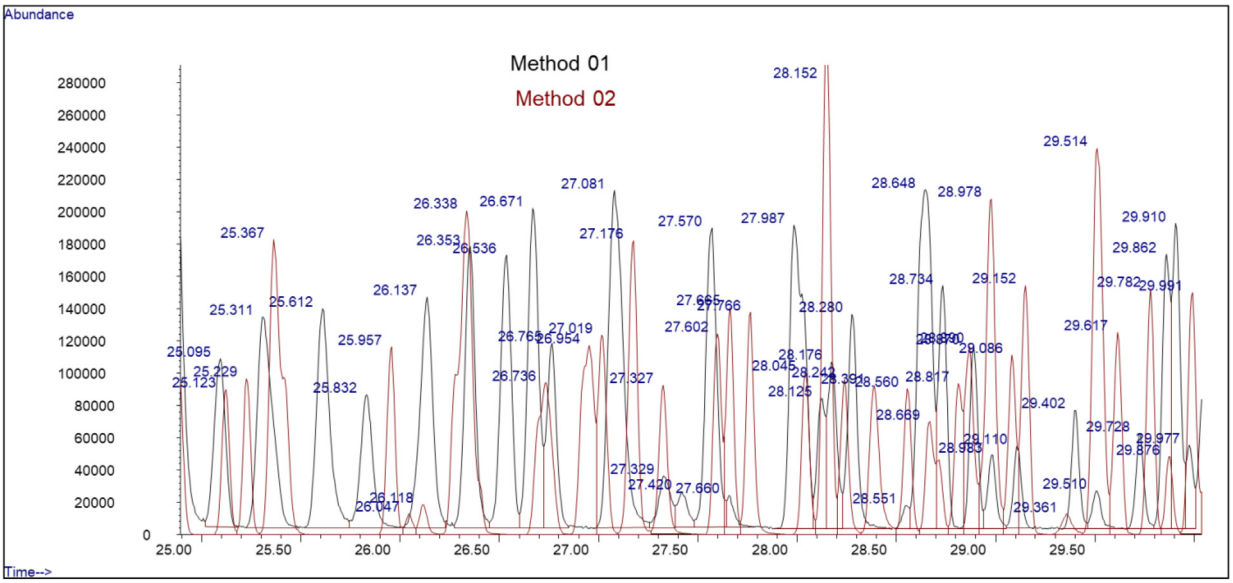

Fig. 7. GC–MS-TIC separation chromatogram of pesticide residues from RT 25–30 min, methods 1 and 2.

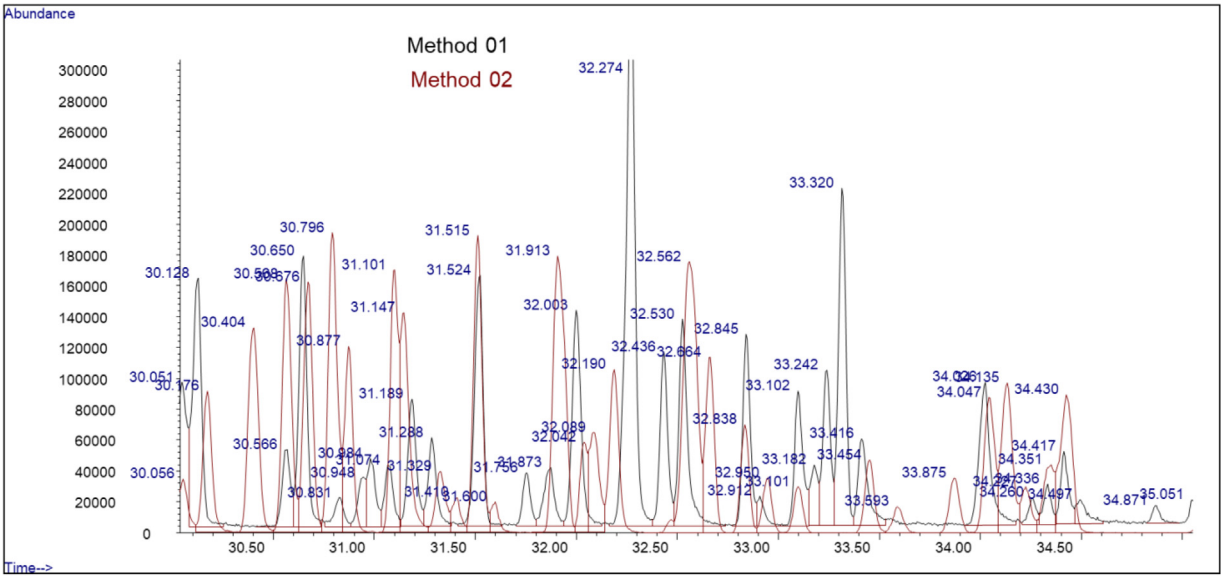

Fig. 8. GC–MS-TIC separation chromatogram of pesticide residues from RT 30–35 min, methods 1 and 2.

least expensive techniques of chromatographic devices, GC–MS-TIC, which may be found in most laboratories in most countries worldwide. These pesticides can be analyzed and separated within 49 min. The LODs and LOQs of the 220 tested and separated pesticides ranged from 0.78 to 14.74 and 2.34 to 44.22 ng mL − 1 (ppb), respectively. This encourages the application of this method to further research on estimating pesticide residues in different environmental samples, such as soil, water, and foods. There are two main strengths of this research: first, the number of pesticides with their isomers that can be separated in one injection and, second, the low cost of the analysis technique that uses a gas chromatography device with a single inexpensive mass spectrometer, which is available in most analysis laboratories, quarantine laboratories, and ports. Furthermore, although most researchers used the ethyl acetate solvent, the use of acetonitrile organic solvent in the GC–MS in this study encourages the future application of this method with extraction by QuEChERS method to estimate the pesticide residues in real environmental samples.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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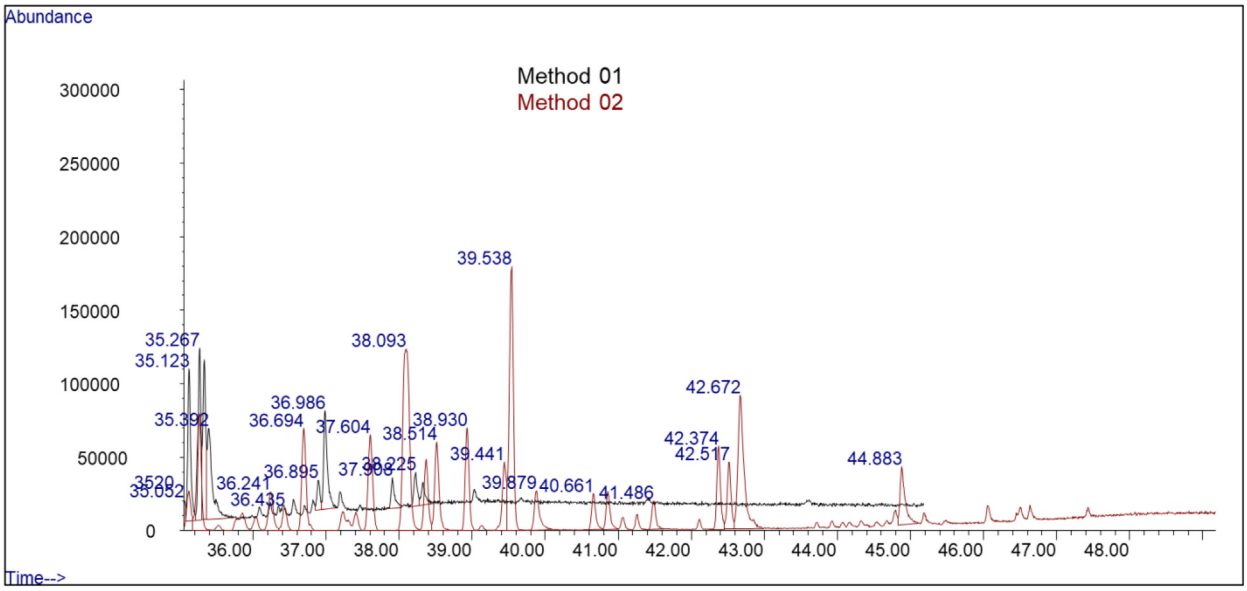

Fig. 9. GC–MS-TIC separation chromatogram of pesticide residues from RT 36–45 min; methods 1.

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