



Gas Chromatography/ Mass Spectrometry

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Pesticide Residues Analysis by Clarus 690 Gas Chromatograph and SQ 8 Mass Spectrometer

Introduction

Pesticide residues are commonly found on many different food products and may have harmful effects

on humans, animals and the environment. Therefore, many countries have set limits on acceptable levels pesticide residues on foods and feed to prevent such harmful effects from occurring. Gas chromatography/mass spectrometry (GC/MS) methods are the traditional analytical method for pesticide residues and are widely used because of the sensitivity and selectivity offered. To determine low levels of pesticides, an inert injector is needed to offer lower reactivity to labile compounds to get excellent sensitivity and repeatability. A new capillary split/splitless injector for the PerkinElmer Clarus® 690 GC is designed with electro-polished inside surfaces, a gold seal and optimized internal geometry all of which reduce the chance of the analytes of interest interacting with reactive sites and decomposing.

In this study, various residual pesticides were analyzed by a PerkinElmer Clarus 690 GC combined with a PerkinElmer Clarus SQ 8 MS. The results of method detected limit (MDL) and repeatability are excellent. This system is highly sensitive and repeatable for the analysis of pesticide residues.

Experimental Details

A PerkinElmer Clarus 690 GC was connected to a PerkinElmer Clarus SQ 8 MS in electron ionization (EI) mode to perform these experiments with the conditions presented in Table 1, Table 2 and Table 3 for four groups of pesticide mixtures (Tables 4 to 7). An ultra deactivated single taper inlet liner with wool for split/splitless inlets (Part No. N6502035) combined with a pulse splitless injection function was used for low level of pesticide residues determination in this study.

A PerkinElmer Elite 5MS column (30 m x 0.25 mm x 0.25 μ m) and a PerkinElmer Elite 1701 column (30 m x 0.25 mm x 0.25 μ m) were used to separate the target compounds.

Group 1 and 4 calibration standards were purchased from ANPEL Laboratory Technologies (Shanghai) Inc. Group 2 and 3 calibration standards were provided by a private laboratory. Group 1 standards were diluted with n-hexane (HPLC grade, Honeywell), group 2 and 3 standards were diluted with n-hexane/acetone (1:1, V/V) and group 4 standards were diluted with acetone (HPLC grade, Merck) to produce the required concentration of the calibration solutions (shown in Tables 4 to 7).

Method precision was investigated with six injections of the level 1 standard. Method detection limits were determined by analyzing seven replicates of the level 2 standard.

Table 1. Analytical parameters for the group 1 pesticides.

GC Parameters			
Injector Type	Capillary injector with capillary split/splitless ultra deactivated single taper inlet liner with wool		
Analytical Column	Elite-5MS (30 m x 0.25 mm x 0.25 μ m)		
Inlet Temp	280 °C		
Injection Volume	1 μ L		
Initial Oven Temp	50 °C		
Oven Hold	1.0 min		
Ramp	20 °C/min		
2 nd Oven Temp	170 °C		
Oven Hold	0 min		
Ramp	6 °C/min		
3 rd Oven Temp	300 °C		
Oven Hold	1 min		
Instrument Time Event	Time	Event	Value
	-1.00 min	Car	4 ml/min
	-0.75 min	Spl	Off
	1.50 min	Spl	50 ml/min
	1.55 min	Car	1 ml/min
MS Parameters			
Mass Range (amu)	45 to 450		
GC Inlet Line Temp	290 °C		
Ion Source Temp	260 °C		
Function Type	Scan		
Ionization	EI		

Table 2. Analytical parameters for the group 2 and 3 pesticides.

GC Parameters			
Injector Type	Capillary injector with capillary split/splitless ultra deactivated single taper inlet liner with wool		
Analytical Column	Elite-5MS (30 m x 0.25 mm x 0.25 μ m)		
Inlet Temp	290 °C		
Injection Volume	1 μ L		
Initial Oven Temp	50 °C		
Oven Hold	1.5 min		
Ramp	25 °C/min		
2 nd Oven Temp	190 °C		
Oven Hold	0 min		
Ramp	10 °C/min		
3 rd Oven Temp	300 °C		
Oven Hold	5 min		
Instrument Time Event	Time	Event	Value
	-1.00 min	Car	4 ml/min
	-0.75 min	Spl	Off
	1.50 min	Spl	50 ml/min
	1.55 min	Car	1 ml/min
MS Parameters			
Mass Range (amu)	45 to 450		
GC Inlet Line Temp	290 °C		
Ion Source Temp	260 °C		
Function Type	Scan		
Ionization	EI		

Table 3. Analytical parameters for the group 4 pesticides.

GC Parameters			
Injector Type	Capillary injector with capillary split/splitless ultra deactivated single taper inlet liner with wool		
Analytical Column	Elite-1701 (30 m x 0.25 mm x 0.25 μ m)		
Inlet Temp	280 °C		
Injection Volume	1 μ L		
Initial Oven Temp	50 °C		
Oven Hold	1.0 min		
Ramp	20 °C/min		
2 nd Oven Temp	120 °C		
Oven Hold	0 min		
Ramp	8 °C/min		
3 rd Oven Temp	260 °C		
Oven Hold	5 min		
Instrument Time Event	Time	Event	Value
	-1.00 min	Car	80 cm/s
	-0.75 min	Spl	Off
	1.50 min	Spl	50 ml/min
	1.55 min	Car	60 cm/s
MS Parameters			
Mass Range (amu)	45 to 450		
GC Inlet Line Temp	260 °C		
Ion Source Temp	260 °C		
Function Type	Scan		
Ionization	EI		

Table 4. The group 1 pesticides mixture.

No.	Compound Name	CAS	Quantitative Ion	Qualitative Ion		Level 1/ppb	Level 2/ppb
1	Bifenthrin	82657-04-3	181	166	165	200	50
2	Fenpropathrin	64257-84-7	97	181	125	200	50
3	Lambda Cyhalothrin	91465-08-6	181	197	208	200	50
4	Baythriod	68359-37-5	163	206	165	200	50
5	Cypermethrin	52315-07-8	163	181	165	200	50
6	Fenvalerate	51630-58-1	125	167	181	200	50
7	Deltamethrin	52918-63-5	181	253	251	200	50

Table 5. The group 2 pesticides mixture.

No.	Compound Name	CAS	Quantitative Ion	Qualitative Ion		Level 1/ppb	Level 2/ppb
1	Phorate	298-02-2	260	121	231	25	25
2	Metalaxyl	57837-19-1	206	249	234	75	7.5
3	Chlorpyrifos	2921-88-2	314	258	286	25	25
4	TriadilMefon	43121-43-3	208	210	181	50	50
5	Pendimethalin	40487-42-1	252	220	162	100	10
6	Fipronil	120068-37-3	367	369	351	125	125
7	Profenofos	41198-08-7	339	374	297	150	150
8	Fenvalerate	51630-58-1	125	167	181	100	100
9	Deltamethrin	119446-68-3	323	325	265	150	150

Table 6. The group 3 pesticides mixture.

No.	Compound Name	CAS	Quantitative Ion	Qualitative Ion		Level 1/ppb	Level 2/ppb
1	Dichlorvos	62-73-7	109	185	79	60	6
2	Chlorpyrifos	2921-88-2	314	258	286	20	20
3	Isocarbophos	24353-61-5	136	230	289	50	5
4	Fipronil	120068-37-3	367	369	351	100	100
5	Machette	23184-66-9	176	160	188	25	2.5
6	Triazophos	24017-47-8	161	172	257	75	75
7	Difenoconazole	119446-68-3	323	325	265	150	150

Table 7. The group 4 pesticides mixture.

No.	Compound Name	CAS	Quantitative Ion	Qualitative Ion		Level 1/ppb	Level 2/ppb
1	Dichlorvos	62-73-7	109	185	79	1.00	20
2	Methamidophos	10265-92-6	94	95	141	0.50	1
3	Mevinphos	7786-34-7	192	127	164	0.50	50
4	Ethoprophos	13194-48-4	158	97	200	0.50	50
5	Phorate	298-02-2	260	121	231	1.00	20
6	Disulfoton	298-04-4	88	274	186	0.50	50
7	Isazophos	42509-80-8	161	97	119	0.50	50
8	Monocrotophos	6923-22-4	127	67	-	1.00	100
9	Dimethoate	60-51-5	87	93	125	0.50	50
10	Chlorpyrifos	2921-88-2	199	197	97	0.50	50
11	Methyl Parathion	298-00-0	263	125	109	1.00	100
12	Malathion	121-75-5	173	125	158	0.50	50
13	Fenitrothion	122-14-5	277	125	109	0.50	50
14	Parathion	56-38-2	291	97	109	1.00	100
15	Isofenphos-methyl	99675-03-3	199	58	121	0.50	50
16	Isocarbophos	24353-61-5	120	121	136	0.50	50
17	Methidathion	950-37-8	145	85	157	1.00	100
18	Ethion	563-12-2	231	384	199	0.50	50
19	Triazophos	24017-47-8	161	172	257	1.00	100

Results and Discussion

The total ion chromatograms of the level 1 calibration standards are shown in Figures 1 through 4. All target compounds were quantified using selected ion scanning mode. Tables 8 to 11 summarizes the results for retention time, quantitative and qualitative ion, precision, method detection limits (MDLs) and

quantitation limits (MQLs). The precision data (RSD %) are in the range of 0.44 – 3.64% for the replicates of the level 1 standard sample; the MDLs per sample were calculated for most target compounds to be in the range of 0.08 – 10.73 ng/mL because of their different chemical properties.

Table 8. Results for retention time, precision, MDL and MQL for the group 1 pesticides mixture.

No.	Compound Name	RT	RSD%	MDL/ppb	MQL/ppb
1	Bifenthrin	20.79	0.87	3.40	13.60
2	Fenpropathrin	21.07	1.89	4.40	17.60
3	Lambda Cyhalothrin	22.36	1.17	4.19	16.76
4	Baythriod	24.24, 24.64, 24.74, 24.81	2.92	9.62	38.48
5	Cypermethrin	25.00, 25.16, 25.25, 25.32	2.34	9.81	39.24
6	Fenvalerate	26.41, 26.73	2.75	4.02	16.08
7	Deltamethrin	29.06	2.91	3.23	12.92

Table 9. Results for retention time, precision, MDL and MQL for the group 2 pesticides mixture.

No.	Compound Name	RT	RSD%	MDL/ppb	MQL/ppb
1	Phorate	9.07	2.11	1.69	6.76
2	Metalaxyl	10.58	2.25	1.03	4.12
3	Chlorpyrifos	11.09	2.09	1.22	4.88
4	TriadiMefon	11.26	2.09	1.21	4.84
5	Pendimethalin	11.62	0.83	1.88	7.52
6	Fipronil	11.68	2.27	10.60	42.40
7	Profenofos	12.66	2.05	10.41	41.64
8	Fenvalerate	18.26, 18.47	2.77	4.12	16.48
9	Difenoconazole	18.74, 18.81	0.75	3.52	14.08

Table 10. Results for retention time, precision, MDL and MQL for the group 3 pesticides mixture.

No.	Compound Name	RT	RSD%	MDL/ppb	MQL/ppb
1	Dichlorvos	6.39	0.44	0.08	0.32
2	Chlorpyrifos	11.1	2.01	1.29	5.16
3	Isocarbophos	11.28	3.23	0.54	2.16
4	Fipronil	11.68	3.42	10.73	42.92
5	Machette	12.25	3.19	0.4	1.6
6	Triazophos	13.66	3.64	8.42	33.68
7	Difenoconazole	18.74, 18.81	0.74	3.49	13.96

Table 11. Results for retention time, precision, MDL and MQL for the group 4 pesticides mixture.

No.	Compound Name	RT	RSD%	MDL/ppb	MQL/ppb
1	Dichlorvos	7.65	1.12	0.71	2.84
2	Methamidophos	8.88	1.90	0.28	1.12
3	Mevinphos	10.45	1.41	4.02	16.08
4	Ethoprophos	12.52	1.91	4.25	17.00
5	Phorate	13.23	2.19	2.81	11.24
6	Disulfoton	14.77	0.73	2.04	8.16
7	Isazophos	15.48	1.54	7.21	28.84
8	Monocrotophos	15.67	1.05	10.52	42.08
9	Dimethoate	15.81	2.79	6.34	25.36
10	Chlorpyrifos	16.77	2.81	5.05	20.20
11	Methyl Parathion	16.93	3.29	4.73	18.92
12	Malathion	17.31	2.45	4.88	19.52
13	Fenitrothion	17.44	2.63	4.90	19.60
14	Parathion	17.87	3.79	6.04	24.16
15	Isofenphos-methyl	17.98	2.37	2.13	8.52
16	Isocarbophos	18.28	2.10	3.40	13.60
17	Methidathion	19.2	0.58	5.03	20.12
18	Ethion	20.57	1.84	4.72	18.88
19	Triazophos	21.65	2.02	9.90	39.60

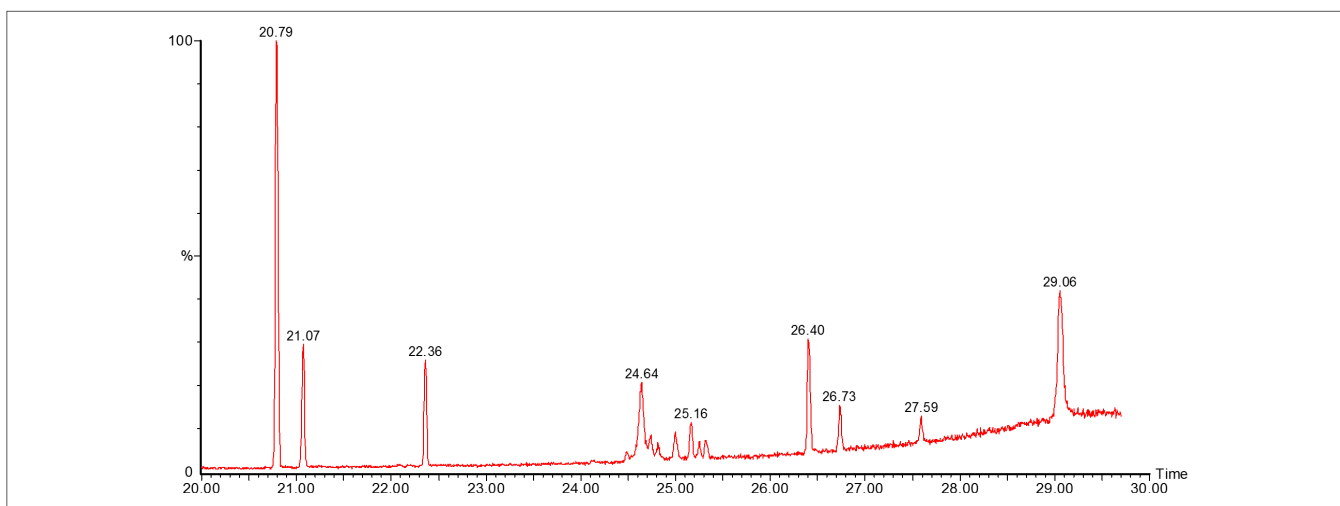


Figure 1. Total ion chromatogram of the level 1 calibration standard for the group 1 pesticides mixture.

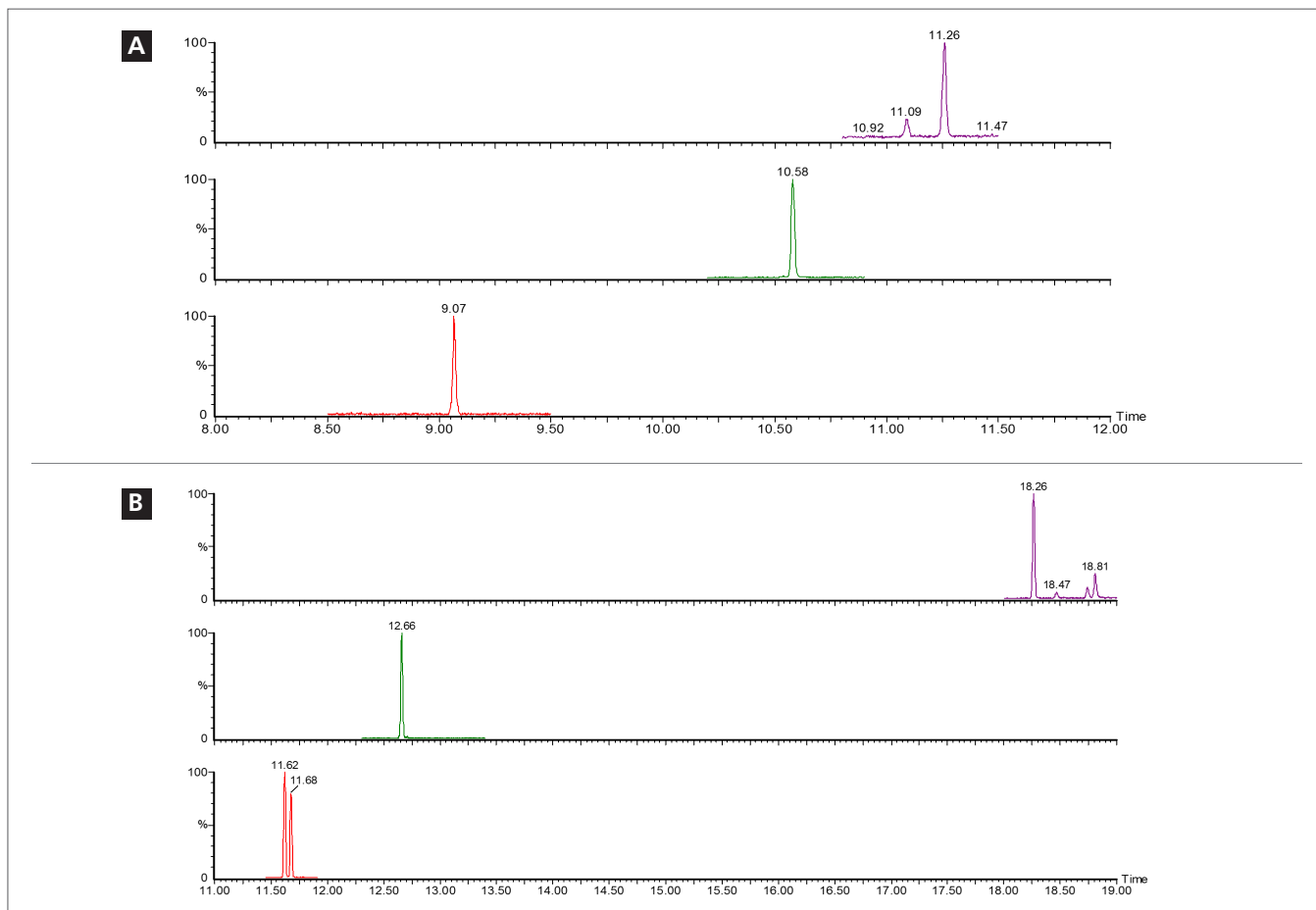


Figure 2. Total ion chromatogram of the level 1 calibration standard for the group 2 pesticides mixture, (A) Components eluting before 11.5 minutes; (B) Components eluting after 11.5 minutes.

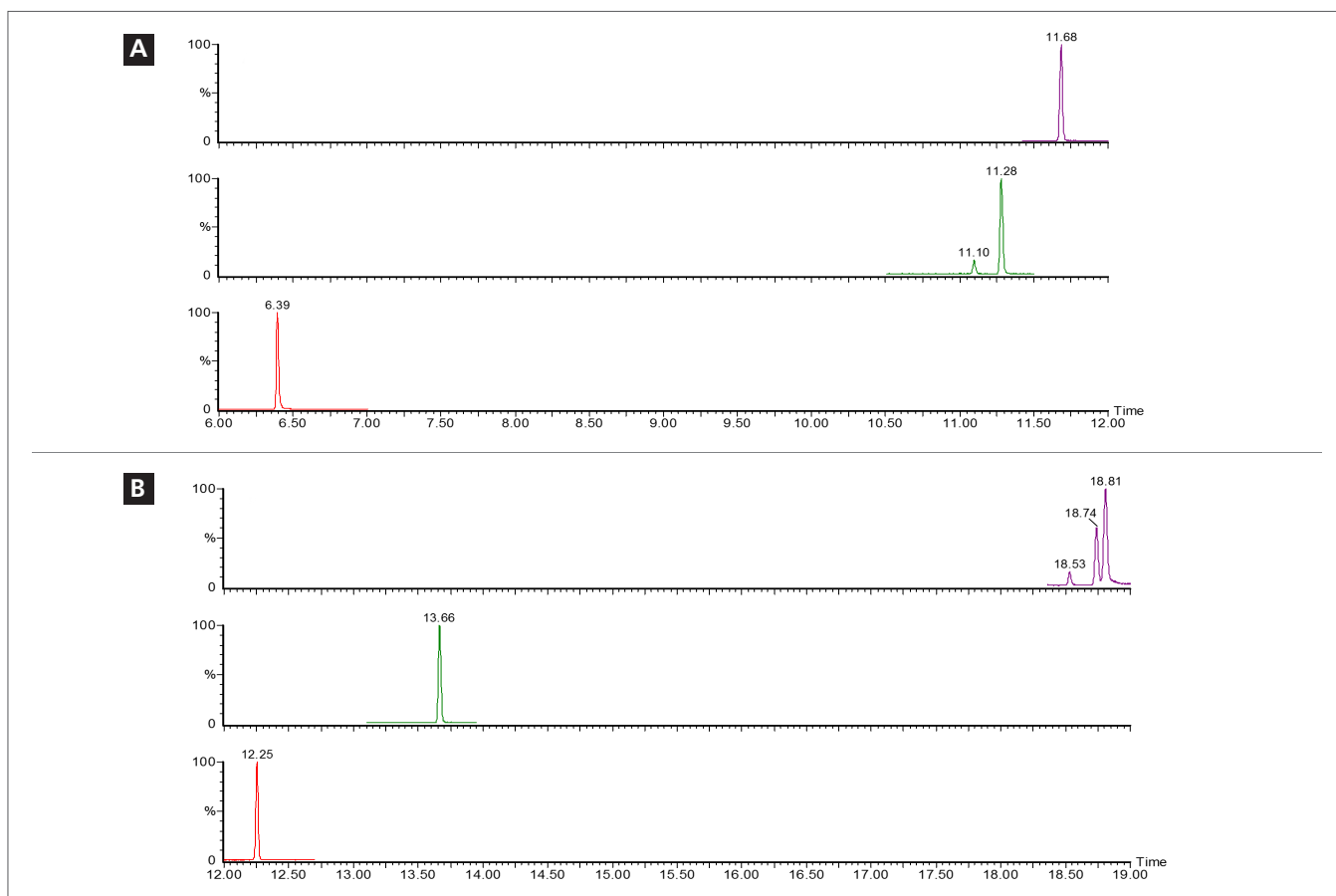


Figure 3. Total ion chromatogram of the level 1 calibration standard for the group 3 pesticides mixture, (A) Components eluting before 12 minutes; (B) Components eluting after 12 minutes.

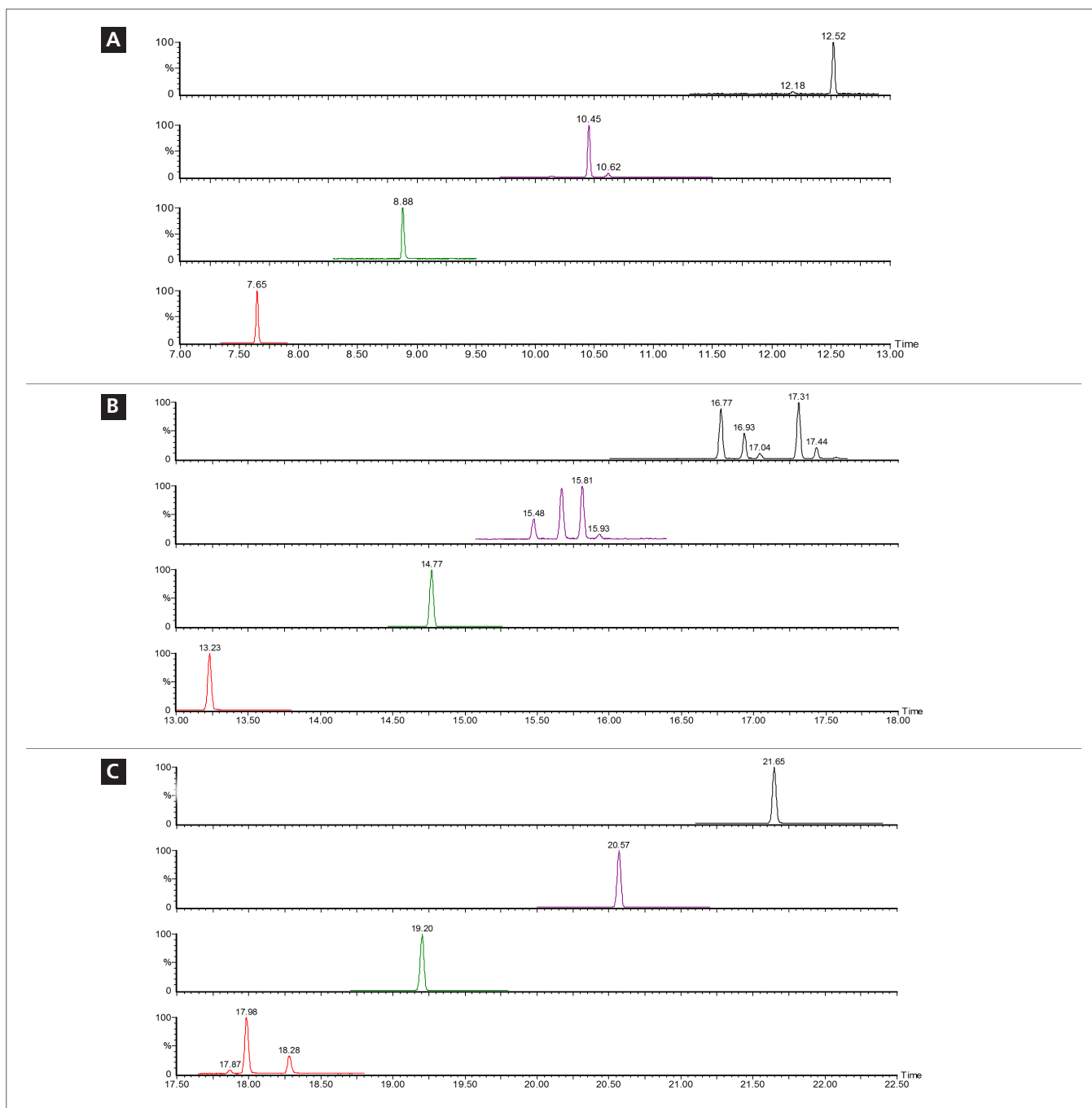


Figure 4. Total ion chromatogram of the level 1 calibration standard for the group 4 pesticides mixture, (A) Components eluting before 13 minutes; (B) Components eluting between 13 and 17.5 minutes; (C) Components eluting after 17.5 minutes.

Summary

In this study, the method detection limits (MDLs) and quantitation limits (MQLs) for various pesticide residues were determined using a PerkinElmer Clarus 690 GC combined with a PerkinElmer Clarus SQ 8 MS. The excellent sensitivity and repeatability for the pesticides demonstrates the new capillary split/splitless injector's good chemical inertness to labile compounds and satisfies the inertness required for pesticide residue determination.