

「Application Note」

Multi-residue Analysis of 207 Pesticides by ChroZen TQ LC/MS

- TQ LC/MS Application



Abstract

As the need of food growing worldwide, agricultural demand for pesticide gets highly increased and also the related government departments strongly restrict the use of pesticides. This leads the need for determination of numerous pesticides in trace level with fast and accurate method to assure the safety of agricultural food.

There are hundreds of pesticides to be determined in agricultural products and some have structural similarity of co-eluting compounds which are hard to be separated in a single chromatograph.

In this study, 207 kinds of pesticides were analyzed by ChroZen Triple Quadrupole LC/MS according to the regulation listed in PLS (Positive List System) which facilitates safety managements for pesticides in Korea, which is specified by National Agricultural Products Quality Management Service (NAQS).

Instruments and Software

Item	Description	Part No.
ChroZen TQ LC/MS System	ChroZen LC-TQ	CRZLCTQAY60
	1) Heater Electrospray (H-ESI) Source	
	2) Atmospheric Pressure Chemical Ionization (APCI) Source	
	3) Foreline Pump x 2set	
	4) PC, 24-inch Monitor	
ChroZen UHPLC System	5) Workstation Software	
	UHPLC Solvent Tray	5451011010
	ChroZen UHPLC Pump	9431011010
	ChroZen UHPLC Column Compartment	5431011010
ACC	ChroZen UHPLC Autosampler (Cooling)	9451011011
	UHPLC Performance Kit	9361011150
	ESI Needle	3944450A
	APCI Needle	3944365
	Hamilton 500ul	81265
	ChroZen TQ Installation Kit	394440790
	Programmable Syringe Pumps for MS Infusion	NE-1000
	Autosampler vial 100/pk	5182-0715
Autosampler cap, Septa 100/pk	5182-0717	

Table 1. ChroZen TQ LC/MS system

Reagents and Standards

LC-MSMS Mix-a (10 µg/mL) and
Carbendazim solution (100 µg/mL)



Fig 1. ChroZen TQ LC/MS

MRM Conditions & Retention Time

Compound	RT	MRM Conditions (Precursor / Product / CE)	Compound	RT	MRM Conditions (Precursor / Product / CE)
Abamectin B1	11.5	(+) 890.5 > 567.3 [12.0V]	Diethofencarb	5.1	(+) 268.0 > 226.0 [9.0V]
Acephate	1.9	(+) 184.0 > 143.0 [13.0V]	Diflubenzuron	6.6	(+) 311.0 > 158.0 [8.0V]
Acetamiprid	2.9	(+) 223.0 > 99.0 [38.0V]	Dimepiperate	8.4	(+) 264.0 > 119.0 [11.0V]
Aldicarb	3.3	(+) 191.0 > 89.0 [10.0V]	Dimethametryn	6.5	(+) 256.0 > 186.0 [29.0V]
Amisulbrom	8.7	(+) 466.0 > 227.0 [14.0V]	Dimethenamide	5.3	(+) 276.0 > 244.0 [19.0V]
Azimsulfuron	4.3	(+) 425.0 > 182.0 [20.0V]	Dimethomorph (E)	5.1	(+) 388.0 > 301.0 [17.5V]
Azinphos-methyl	4.9	(+) 318.0 > 132.0 [11.0V]	Dimethomorph (Z)	5.5	(+) 388.0 > 301.0 [17.5V]
Azoxystrobin	4.9	(+) 404.0 > 372.0 [10.0V]	Diniconazole	7.8	(+) 326.0 > 70.0 [16.5V]
Bendiocarb	3.6	(+) 224.0 > 109.0 [14.0V]	Dinotefuran	2.5	(+) 203.0 > 129.0 [11.0V]
Bensulfuron-Methyl	4.7	(+) 411.0 > 119.0 [33.0V]	Diphenamid	4.6	(+) 240.0 > 165.0 [55.0V]
Benthiavalicarb-isopropyl	5.6	(+) 382.0 > 180.0 [35.0V]	Dithiopyr	8.7	(+) 402.0 > 354.0 [20.0V]
Benzobicyclon	5.5	(+) 447.0 > 257.0 [23.0V]	Diuron	4.5	(+) 233.0 > 72.0 [35.0V]
Benzoximate	8.0	(+) 364.0 > 199.0 [17.0V]	Dymron	5.7	(+) 269.0 > 151.0 [19.0V]
Bitertanol	7.7	(+) 338.0 > 99.0 [12.0V]	Edifenphos	7.1	(+) 311.0 > 109.0 [41.0V]
Boscalid	5.3	(+) 343.0 > 307.0 [12.5V]	Esprocarb	9.3	(+) 266.0 > 91.0 [33.0V]
Bromacil	3.7	(+) 261.0 > 205.0 [15.0V]	Ethaboxam	4.0	(+) 320.0 > 183.0 [35.0V]
Buprofezin	9.2	(+) 306.0 > 201.0 [8.0V]	Ethiofencarb	4.0	(+) 226.0 > 107.0 [11.0V]
Cadusafos	8.1	(+) 271.0 > 159.0 [19.0V]	Ethofenprox	12.7	(+) 394.0 > 177.0 [21.0V]
Cafenstrole	5.8	(+) 351.0 > 100.0 [15.0V]	Ethoprophos	6.3	(+) 243.0 > 131.0 [27.0V]
Carbaryl	3.8	(+) 202.0 > 145.0 [7.0V]	Ethoxysulfuron	5.6	(+) 399.0 > 217.0 [33.0V]
Carbendazim	2.8	(+) 192.0 > 160.0 [13.0V]	Etoxazole	10.2	(+) 360.0 > 141.0 [23.5V]

Carbofuran	3.6	(+) 222.0 > 165.0 [9.5V]	Etrifos	7.4	(+) 293.0 > 125.0 [33.0V]
Carboxin	3.9	(+) 236.0 > 143.0 [11.0V]	Famoxadone	7.4	(+) 392.0 > 331.0 [15.0V]
Carfentrazone-ethyl	7.0	(+) 412.0 > 346.0 [27.0V]	Fenamiphos	6.6	(+) 304.0 > 217.0 [20.0V]
Carpropamide	7.2	(+) 334.0 > 139.0 [25.0V]	Fenarimol	6.1	(+) 331.0 > 268.0 [18.0V]
Chlorpyrifos	10.0	(+) 351.7 > 200.0 [18.0V]	Fenazaquin	11.1	(+) 307.0 > 161.0 [19.0V]
Chlorsulfuron	3.7	(+) 358.0 > 141.0 [23.0V]	Fenbuconazol	6.3	(+) 337.0 > 70.0 [12.5V]
Chromafenozide	6.0	(+) 395.0 > 339.0 [7.0V]	Fenhexamid	6.0	(+) 302.2 > 55.0 [59.0V]
Clethodim	8.7	(+) 360.0 > 164.0 [17.5V]	Fenobucarb	5.0	(+) 208.0 > 95.0 [19.0V]
Clofentezine	8.2	(+) 303.0 > 138.0 [11.5V]	Fenoxaprop-ethyl	8.9	(+) 362.0 > 288.0 [37.0V]
Clomazone	4.9	(+) 240.0 > 125.0 [20.0V]	Fenoxycarb	6.7	(+) 302.0 > 116.0 [8.0V]
Clothianidin	2.9	(+) 250.0 > 169.0 [15.0V]	Fenpyroximate	10.6	(+) 422.0 > 366.0 [15.5V]
Cyazofamid	6.3	(+) 325.0 > 108.0 [9.5V]	Fentrazamide	7.2	(+) 350.0 > 197.0 [5.0V]
Cyclosulfamurum	5.9	(+) 422.0 > 261.0 [23.0V]	Ferimzone(E)	5.0	(+) 255.0 > 124.0 [25.0V]
Cyflufenamid	7.8	(+) 413.0 > 295.0 [12.0V]	Ferimzone(Z)	5.0	(+) 255.0 > 124.0 [25.0V]
Cyhalofop_butyl	8.4	(+) 358.0 > 256.0 [10.0V]	Flonicamid	2.7	(+) 230.0 > 203.0 [23.0V]
Cymoxanil	3.1	(+) 199.0 > 128.0 [7.0V]	Fluacrypyrim	8.2	(+) 427.0 > 145.0 [33.0V]
Cyproconazole_1	5.6	(+) 292.0 > 70.0 [12.0V]	Flubendiamide	6.8	(-) 681.0 > 254.0 [25.0V]
Cyproconazole_2	5.9	(+) 292.0 > 70.0 [30.0V]	Flucetosulfuron	4.9	(+) 488.0 > 273.0 [35.0V]
Demeton-S-methyl	3.7	(+) 231.0 > 89.0 [10.0V]	Fludioxonil	5.2	(+) 266.0 > 229.0 [21.0V]
Diazinon	7.5	(+) 305.0 > 169.0 [27.0V]	Flufenacet	6.2	(+) 364.0 > 152.0 [25.0V]
Dichlofos(DDVP)	3.6	(+) 221.0 > 109.0 [23.0V]	Flufenoxuron	10.2	(+) 489.0 > 158.0 [27.0V]
Fluopicolide	5.6	(+) 383.0 > 173.0 [32.0V]	Phenthoate	7.0	(+) 321.0 > 79.0 [50.0V]
Fluquinconazole	6.0	(+) 376.0 > 349.0 [18.0V]	Phosphamidone	3.3	(+) 300.0 > 127.0 [22.0V]
Flusilazole	6.5	(+) 316.0 > 247.0 [16.5V]	Phoxim	7.8	(+) 299.0 > 77.0 [40.0V]
Flutolanil	5.4	(+) 324.0 > 242.0 [18.5V]	Piperophos	8.2	(+) 354.0 > 171.0 [25.0V]
Fluxapyroxad	5.5	(+) 382.1 > 362.1 [21.0V]	Pirimicarb	3.8	(+) 239.0 > 72.0 [18.0V]
Forchlorfenuron	4.3	(+) 248.0 > 129.0 [19.0V]	Pirimiphos-methyl	7.9	(+) 306.0 > 108.0 [35.0V]
Fosthiazate	4.0	(+) 284.0 > 104.0 [25.0V]	Probenazole	3.4	(+) 224.0 > 41.2 [10.0V]
Furathiocarb	9.1	(+) 383.0 > 167.0 [23.5V]	Profenofos	8.8	(+) 372.7 > 303.0 [16.0V]
Gibberellic acid	2.9	(-) 345.0 > 239.0 [10.0V]	Propamocarb	2.3	(+) 189.0 > 102.0 [13.0V]
Halosulfuron-methyl	6.1	(+) 435.0 > 182.0 [16.0V]	Propanil	5.2	(+) 218.0 > 127.0 [33.0V]
Haloxyfop	8.9	(+) 362.0 > 316.0 [16.0V]	Propaquizafop	9.2	(+) 444.0 > 100.0 [14.0V]
Hexaconazol	7.5	(+) 314.0 > 70.0 [12.5V]	Propoxur	3.6	(+) 210.0 > 111.0 [12.0V]

Hexaflumuron	8.5	(-) 459.0 > 439.0 [10.0V]	Pyraclufos	7.7	(+) 361.0 > 138.0 [50.0V]
Hexazinone	3.7	(+) 253.0 > 171.0 [14.0V]	Pyraclostrobin	7.6	(+) 388.0 > 194.0 [7.5V]
Hexythiazox	9.8	(+) 353.0 > 228.0 [14.5V]	Pyrazolate	7.9	(+) 439.0 > 91.0 [52.0V]
Imazalil	3.8	(+) 297.0 > 159.0 [16.5V]	Pyrazophos	7.9	(+) 374.0 > 222.0 [18.0V]
Imazosulfuron	5.4	(+) 413.0 > 153.0 [17.0V]	Pyribenzoxim	9.3	(+) 610.0 > 180.0 [34.0V]
Imicyafos	3.3	(+) 305.0 > 201.0 [19.0V]	Pyributicarb	9.8	(+) 331.0 > 181.0 [17.0V]
Imidacloprid	2.8	(+) 256.0 > 209.0 [13.5V]	Pyridaben	11.1	(+) 365.0 > 147.0 [25.0V]
Inabenfide	5.1	(+) 339.0 > 321.0 [14.0V]	Pyridaphenthion	5.7	(+) 341.0 > 189.0 [30.0V]
Iprobenfos	6.9	(+) 289.0 > 91.0 [25.0V]	Pyrifluquinazon	5.7	(+) 465.0 > 423.0 [19.0V]
Iprovalicarb	6.0	(+) 321.0 > 119.0 [14.0V]	Pyrifthalid	4.9	(+) 319.0 > 139.0 [25.0V]
Isoprocarb	4.3	(+) 194.0 > 95.0 [19.0V]	Pyrimethanil	5.2	(+) 200.0 > 107.0 [19.5V]
Isoprothiolane	5.6	(+) 291.0 > 231.0 [14.0V]	Pyrimidifen	9.2	(+) 378.0 > 184.0 [22.0V]
Isopyrazam	8.1	(+) 360.2 > 244.0 [20.0V]	Pyriminobac-methyl(E)	4.9	(+) 362.0 > 330.0 [16.0V]
Kresoxim-methyl	7.1	(+) 314.0 > 116.0 [17.0V]	Pyriminobac-methyl(Z)	5.5	(+) 362.0 > 330.0 [19.0V]
Linuron	5.2	(+) 249.0 > 160.0 [16.0V]	Pyrimisulfan	4.5	(+) 420.1 > 370.0 [23.0V]
Lufenuron	9.5	(-) 509.0 > 326.0 [10.0V]	Pyriproxyfen	9.9	(+) 322.0 > 96.0 [14.0V]
Malathion	5.6	(+) 331.0 > 99.0 [18.0V]	Pyroquilon	3.6	(+) 174.0 > 132.0 [25.0V]
Mandipropamid	5.3	(+) 429.0 > 328.0 [29.0V]	Quinalphos	7.1	(+) 299.0 > 271.0 [11.0V]
Mefenacet	5.9	(+) 299.0 > 148.0 [17.0V]	Quinmerac	3.1	(+) 222.0 > 204.0 [13.0V]
Mepanipyrim	6.3	(+) 224.0 > 106.0 [20.0V]	Quinoclamine	3.5	(+) 208.0 > 105.0 [21.0V]
Mepronil	5.6	(+) 270.0 > 119.0 [27.0V]	Quizalofop-ethyl	8.9	(+) 373.0 > 91.0 [23.5V]
Metalaxyl	4.4	(+) 280.2 > 220.0 [17.0V]	Saflufenacil	4.8	(+) 501.0 > 349.0 [28.0V]
Metamifop	8.9	(+) 441.0 > 288.0 [20.0V]	Sethoxydim	9.3	(+) 328.0 > 283.0 [7.0V]
Metazosulfuron	5.2	(+) 476.0 > 182.0 [28.0V]	Spinetoram(J)	7.8	(+) 748.5 > 142.0 [40.0V]
Metconazole	7.5	(+) 320.0 > 70.0 [20.0V]	Spinetoram(L)	8.6	(+) 760.0 > 142.0 [40.0V]
Methabenzthiazuron	4.4	(+) 222.0 > 165.0 [14.0V]	Spirodiclofen	10.6	(+) 412.0 > 71.6 [14.0V]
Methiocarb	5.2	(+) 226.0 > 169.2 [13.0V]	Spirotetramat	6.0	(+) 374.1 > 216.1 [45.0V]
Methomyl	2.7	(+) 163.0 > 88.0 [8.0V]	Sulfoxaflor	3.0	(+) 278.0 > 174.0 [14.0V]
Methoxyfenozide	5.6	(+) 369.0 > 149.0 [11.5V]	Tebuconazole	7.0	(+) 308.0 > 70.0 [13.0V]
Metobromuron	4.3	(+) 259.0 > 148.0 [13.0V]	Tebufenozide	6.6	(+) 353.0 > 133.0 [17.0V]
Metolcarb	3.5	(+) 166.0 > 109.0 [10.0V]	Tebufenpyrad	9.1	(+) 334.0 > 145.0 [24.0V]
Metrafenone	8.0	(+) 409.0 > 209.0 [20.0V]	Teflubenzuron	9.4	(-) 379.0 > 339.0 [9.0V]
Mevinphos	2.9	(+) 225.0 > 127.0 [23.0V]	Terbuthylazin	5.4	(+) 230.0 > 174.0 [13.0V]

MilbemectinA3	11.3	(+) 511.3 > 183.0 [14.0V]	Tetraconazole	6.1	(+) 372.0 > 70.0 [13.5V]
MilbemectinA4	12.0	(+) 525.0 > 197.0 [17.0V]	Thenylchlor	6.2	(+) 324.0 > 127.0 [21.0V]
Molinate	6.0	(+) 188.0 > 126.0 [17.0V]	Thiabendazol	3.0	(+) 202.0 > 175.0 [19.5V]
Monocrotophos	2.7	(+) 224.0 > 193.0 [7.5V]	Thiacloprid	3.0	(+) 253.0 > 126.0 [17.0V]
Myclobutanil	5.6	(+) 289.0 > 70.0 [16.0V]	Thiamethoxam	2.7	(+) 292.0 > 211.0 [11.5V]
Napropamid	6.3	(+) 272.0 > 171.0 [18.0V]	Thiazopyr	7.1	(+) 397.0 > 377.0 [23.0V]
Nicosulfuron	3.4	(+) 411.0 > 182.0 [18.0V]	Thidiazuron	3.6	(+) 221.0 > 102.0 [14.0V]
Novaluron	8.6	(+) 493.0 > 141.0 [35.0V]	Thifensulfuron-methyl	3.4	(+) 388.0 > 167.0 [14.0V]
Nuarimol	5.1	(+) 315.0 > 252.0 [27.0V]	Thiobencarb	8.0	(+) 258.0 > 125.0 [23.0V]
Ofurace	3.6	(+) 282.0 > 160.0 [27.0V]	Thiodicarb	3.8	(+) 355.0 > 88.0 [8.5V]
Omethoate	2.3	(+) 214.0 > 125.0 [20.0V]	Tiadinil	5.9	(-) 266.0 > 71.0 [30.0V]
Oxadiazon	9.5	(+) 362.0 > 220.0 [45.0V]	Triadimefon	5.6	(+) 294.0 > 197.0 [14.0V]
Oxadixyl	3.3	(+) 279.0 > 219.0 [8.0V]	Triazophos	5.9	(+) 314.0 > 162.0 [17.0V]
Oxamyl	2.6	(+) 237.0 > 72.0 [9.5V]	Tricyclazol	3.2	(+) 190.0 > 136.0 [25.5V]
Oxaziclomefon	8.9	(+) 376.0 > 190.0 [21.0V]	Trifloxystrobin	8.4	(+) 409.0 > 186.0 [11.0V]
Paclobutrazol	5.4	(+) 294.0 > 70.0 [15.0V]	Triflumizole	8.3	(+) 346.0 > 278.0 [9.0V]
Penconazol	6.9	(+) 284.0 > 70.0 [10.5V]	Triflumuron	7.6	(+) 359.0 > 156.0 [19.0V]
Pencycuron	7.9	(+) 329.0 > 125.0 [20.0V]	Uniconazole	6.5	(+) 292.0 > 70.0 [35.0V]
Penoxsulam	3.7	(+) 484.1 > 195.0 [30.0V]	Vamidothion	2.9	(+) 288.0 > 146.0 [8.5V]
Pentoxazone	6.7	(+) 354.0 > 133.0 [21.0V]			

Table 2. MRM conditions and retention time

LC Conditions and MS Conditions

LC conditions																															
Mobile Phase	A: 5mM AF + 0.1% FA in Water B: 5mM AF + 0.1% FA in MeOH																														
Flow Rate	0.3ml/min																														
Injection Vol.	5.0 μ L																														
Column	2.1mm I.D. x 100mm, 2.7 μ m																														
Column Temperature	40°C																														
Pump Gradient	<table border="1"> <thead> <tr> <th>Time(min)</th> <th>A(%)</th> <th>B(%)</th> </tr> </thead> <tbody> <tr> <td>0</td> <td>85</td> <td>15</td> </tr> <tr> <td>1</td> <td>85</td> <td>15</td> </tr> <tr> <td>1.5</td> <td>40</td> <td>60</td> </tr> <tr> <td>10</td> <td>10</td> <td>90</td> </tr> <tr> <td>12</td> <td>10</td> <td>90</td> </tr> <tr> <td>12.1</td> <td>2</td> <td>98</td> </tr> <tr> <td>16</td> <td>2</td> <td>98</td> </tr> <tr> <td>16.1</td> <td>85</td> <td>15</td> </tr> <tr> <td>21</td> <td>85</td> <td>15</td> </tr> </tbody> </table>	Time(min)	A(%)	B(%)	0	85	15	1	85	15	1.5	40	60	10	10	90	12	10	90	12.1	2	98	16	2	98	16.1	85	15	21	85	15
Time(min)	A(%)	B(%)																													
0	85	15																													
1	85	15																													
1.5	40	60																													
10	10	90																													
12	10	90																													
12.1	2	98																													
16	2	98																													
16.1	85	15																													
21	85	15																													
MS conditions																															
Source Type	HESI																														
Spray Voltage	4500V (Positive) / 4000V (Negative)																														
Cone Temperature	200°C																														
Cone Gas Flow	20																														
Heated Probe Temperature	300°C																														
Probe Gas Flow	45																														
Nebulizer Gas Flow	50																														
Active Exhaust	On																														

Table 3. LC conditions and MS conditions

Result

1) Total Ion Chromatogram

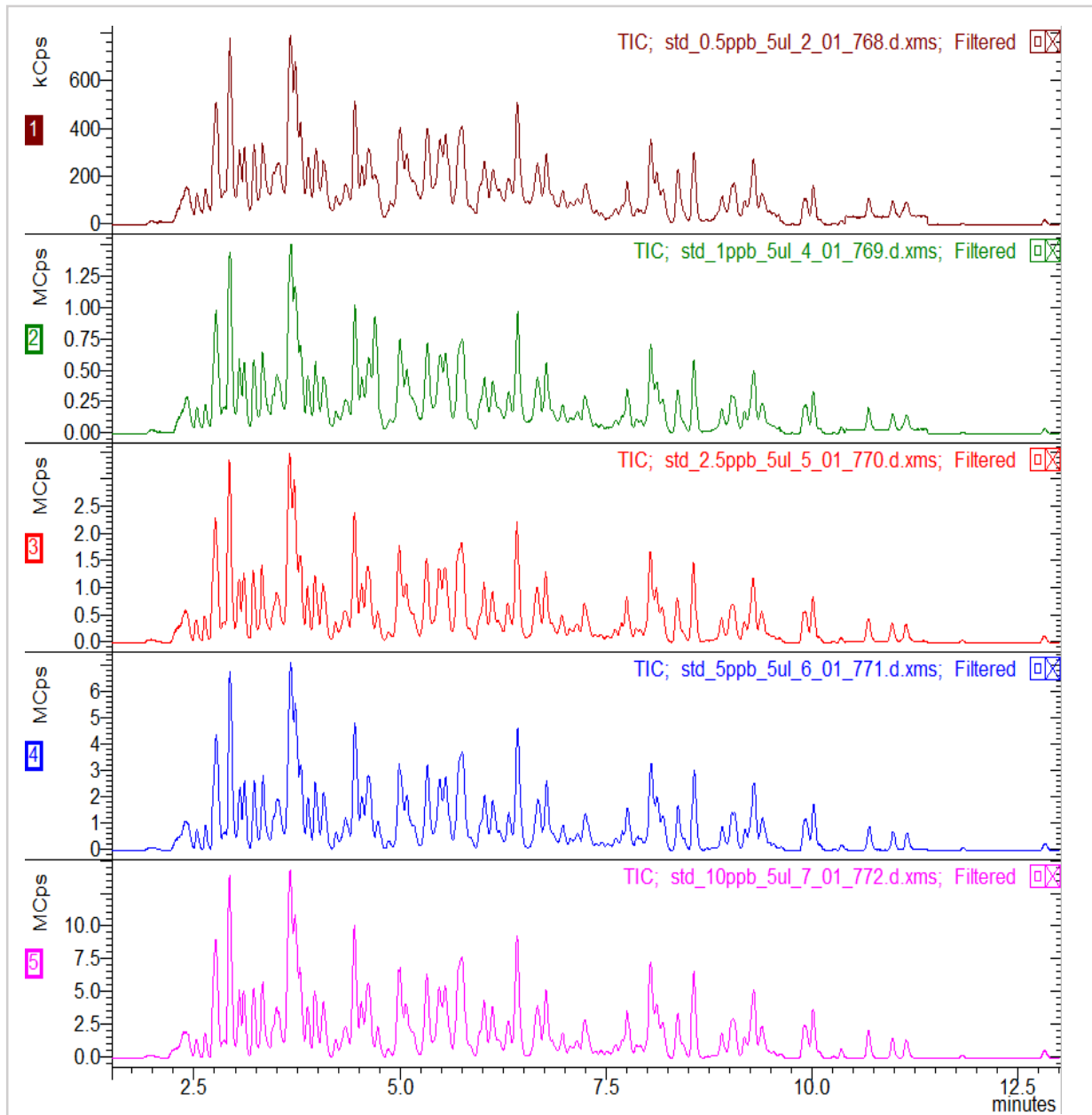


Fig 2. TIC chromatogram of 0.5, 1, 2.5, 5, 10ng/mL(ppb) standard

2) Total Ion Chromatogram(Overlay)

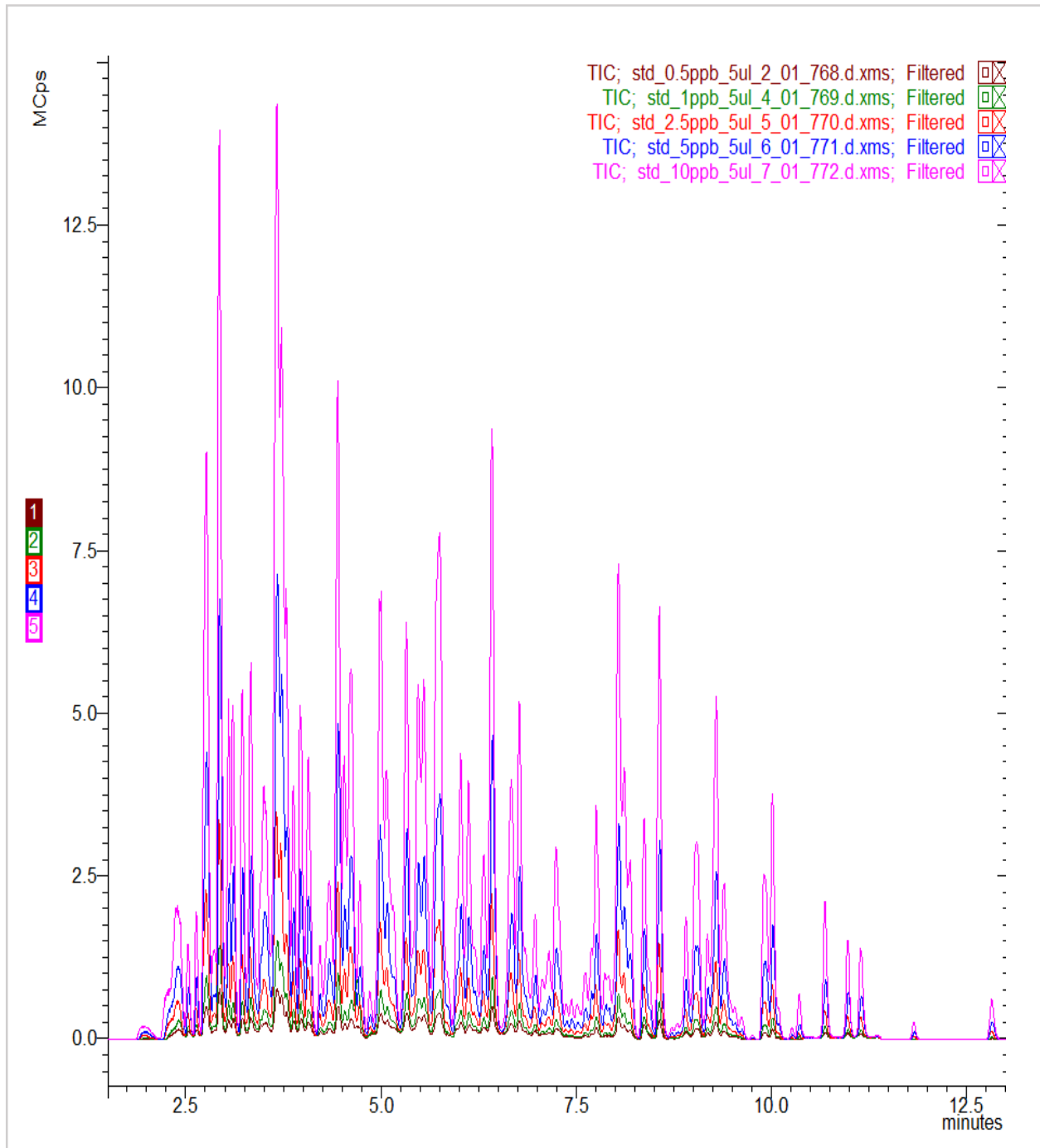


Fig 3. TIC chromatogram(overlay) of 0.5, 1, 2.5, 5, 10ng/mL(ppb) standard

3) EICs and Calibration Curves

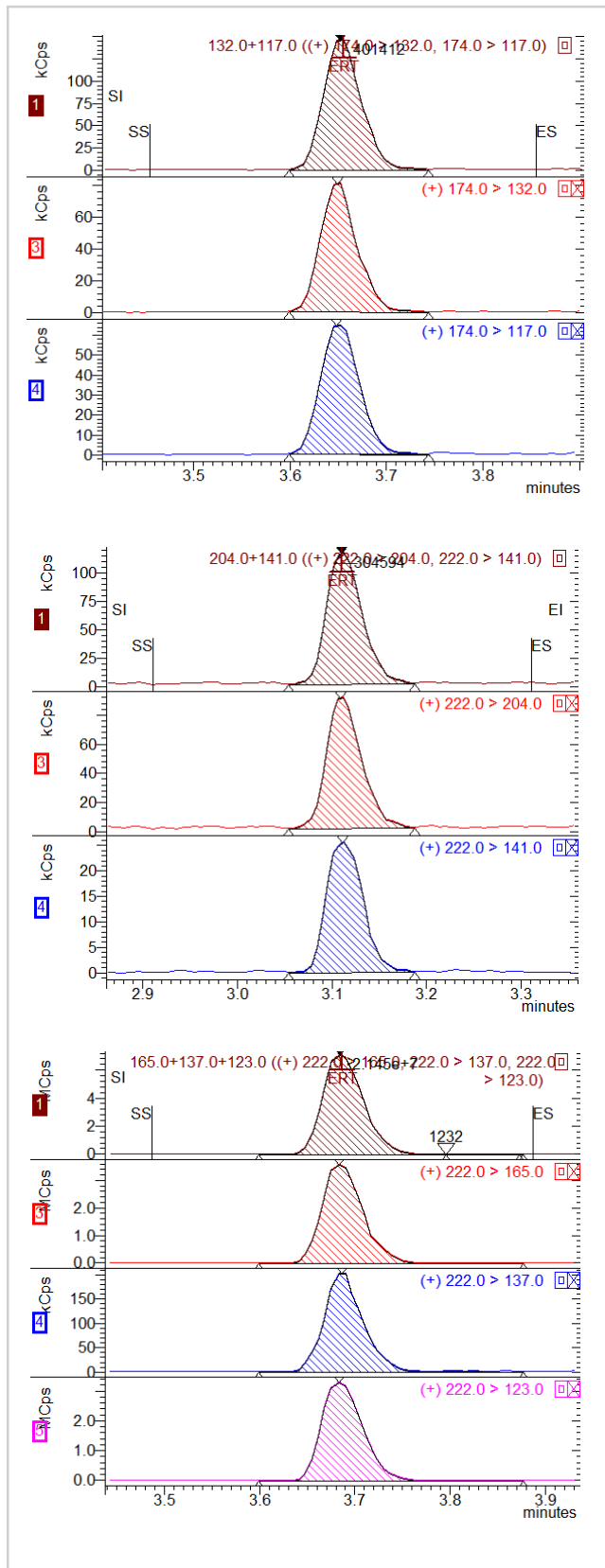


Fig 4. EICs of 0.5 ppb Qualitative/Quantitative Ion

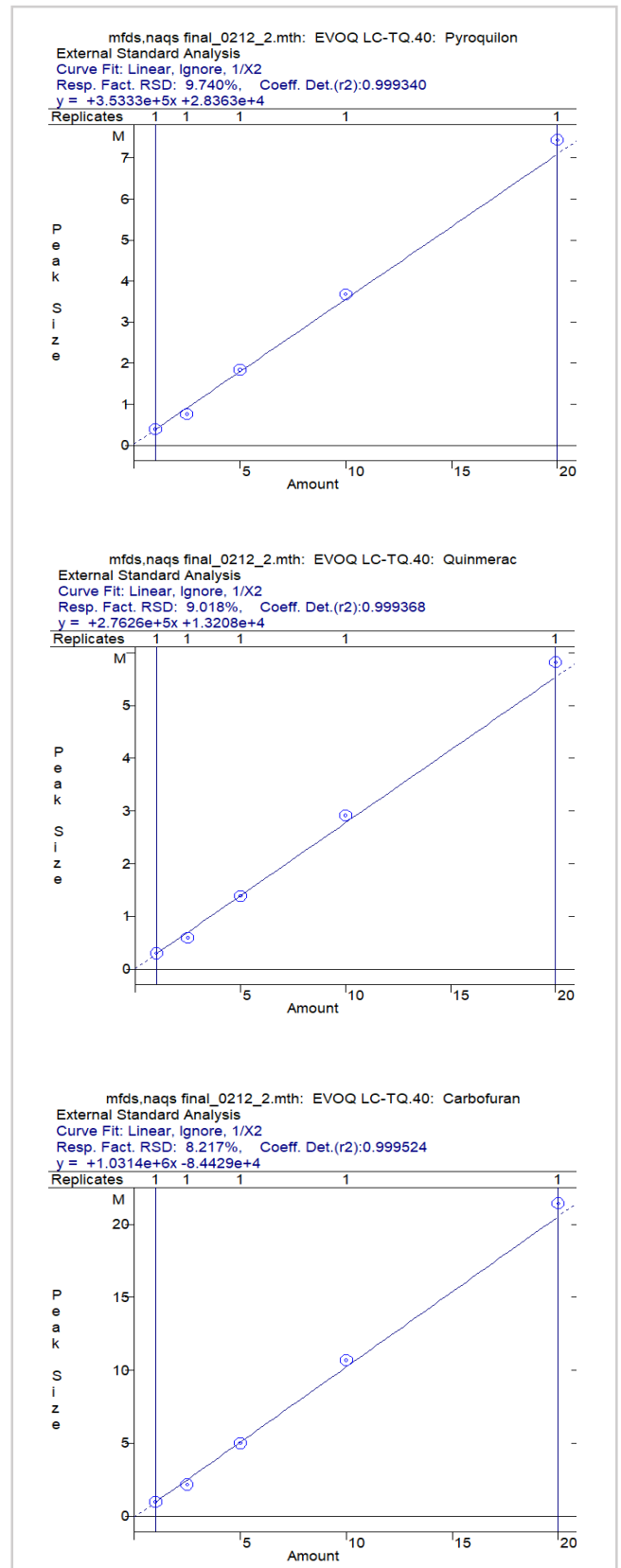


Fig 5. Calibration curves of 0.5, 1, 2.5, 5, 10 ng/mL(ppb)

Conclusion

In Korea, there are two standard methods for analyzing pesticide residues by following two government institutes.

National Agricultural Products Quality Management Service(NAQS)
- 207 pesticide residues

Ministry of Food and Drug Safety (MFDS)
-151 pesticide residues

ChroZen TQ LC/MS can perform the analysis of 207 pesticide residues and the result satisfies the regulations which require 1 ppb level detection for each compound. (Available even at 0.5 ppb in actual data)



60, Anyangcheondong-ro, Dongan-gu,
Anyang-si, Gyeonggi-do, 14042, Republic
of Korea

TEL: +82-31-428-8700

FAX: +82-31-428-8787

E-mail: export@youngincm.com

Homepage: www.youngincm.com