

Simultaneous analysis of pesticide residues by GC-MS/MS method using Hydrogen carrier gas

Product used : Mass spectrometer (MS)

Introduction

In the field of mass spectrometry, helium has primarily been used as the carrier gas for gas chromatography. However, due to the ongoing global supply chain disruptions, reduced production caused by issues at supply plants, and political and economic factors, there has been a long-term shortage of helium, leading to continuous price increases. To continue performing mass spectrometry, it is becoming essential to select alternative carrier gases to helium. Nitrogen or hydrogen are generally considered as alternative carrier gases, but it is desirable to understand the characteristics of each gas type for proper operation. When using hydrogen as an alternative carrier, it is important to note that it is a highly reactive gas, and safety measures such as the installation of hydrogen sensors must be thoroughly considered. Due to its high reactivity, reduction reactions may occur within the ion source depending on the target compound, potentially altering the detected mass spectrum patterns. However, hydrogen also has advantages as an alternative carrier gas, such as a wide range of average linear velocities that provide good separation efficiency under various analytical conditions, less sensitivity loss compared to nitrogen carriers, and stable supply through the use of hydrogen generators. Switching to an alternative carrier gas requires a review of the previously used measurement conditions. This report introduces an example of using hydrogen as a carrier gas for the simultaneous analysis of pesticide residues in food by GC-MS/MS method.

Experimental

1. Sample Conditions

Standard Reagents : Pesticides standard solution 48, 63, 70, 73, 77, 79, Pesticide-Mix 1598 made by KANTO CHEMICAL CO.,INC.

Sample Concentration : Pesticide mixed standard solutions were prepared at 5, 10, 20, 50, and 100ppb

Sample Volume : 2μL (+ 0.3μL co-injection of analyte protectants : SFA10mix made by Hayashi Pure Chemical Industry Co.)

2. GC Conditions

Gas chromatograph : 8890GC (Agilent Technologies, Inc.)

Column : DB-5MS (Agilent Technologies, Inc., length : 20m, inner diameter : 0.18mm, film thickness : 0.36μm)

Oven temperature : 50°C (1min) – 125°C (25°C/min, 0min) – 300°C (10°C/min, 10min)

Inlet temperature : 250°C

Inlet mode : Pulsed splitless mode (70kPa, 1min)

Flow rate : 0.5mL/min (constant flow)

Carrier gas : Hydrogen

3. MS Conditions

Mass spectrometer : JMS-TQ4000GC (JEOL Ltd.)

Measurement mode : SRM

SRM mode : Variable speed (5 or 10ms)

Ion source temperature : 280°C

Interface temperature : 300°C

Ionization current : 50μA

Ionization voltage : 70V



JMS-TQ4000GC

Results

Single SCAN measurements were conducted for all 336 components set as measurement targets, and changes in the spectral patterns when using a hydrogen carrier were confirmed. Significant changes in the spectral patterns were observed for 14 components: Cyanazine, Fipronil, TCMTB, Cyhalothrin, Fenarimol, Cyfluthrin, Cypermethrin, Bupirimate, Benfuracarb, Methyl parathion, Parathion, Fenitrothion, Acrinathrin, and Fenvalerate. Therefore, automatic optimization of SRM transitions using product ion scan measurements was performed. Using the optimized SRM transitions, SRM measurements for all 336 components were conducted. As a result, detection at 5 ppb was sufficiently possible, and the linearity of the calibration curves was judged to be good for a total of 329 components. For six components "Oryzalin, Flutriafol, Isoxathion oxon, Thiacloprid, Propiconazole, and Captan" detection at 5 ppb was possible, but improvements were deemed necessary for some items such as the linearity of the calibration curves, area reproducibility, or chromatogram shape. In this study, the only component for which detection at 5 ppb was difficult was Captafol.

As an example from the 329 components judged to be measurable, the EIC and calibration curves for three components "Cyanazine, Cyfluthrin, and p,p'-DDD" are shown on the next page (Fig. 1-3).

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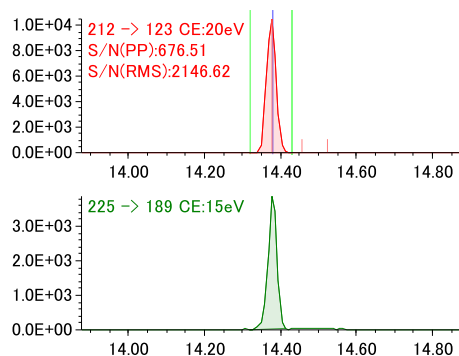


Fig. 1 EICs at 5ppb and calibration curve of Cyanazine

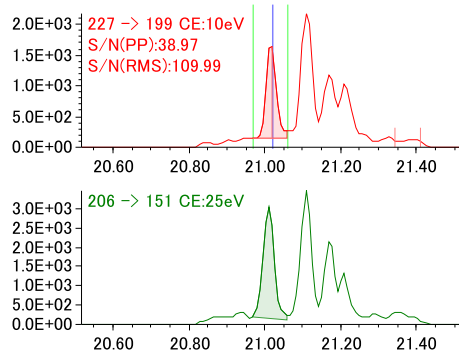


Fig. 2 EICs at 5ppb and calibration curve of Cyfluthrin

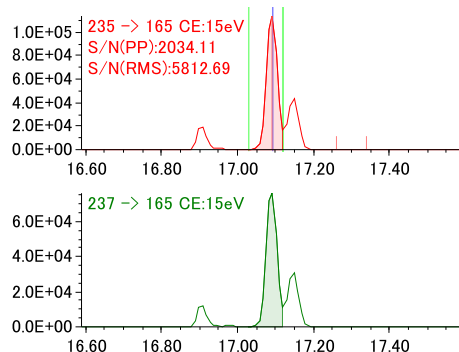


Fig. 3 EICs at 5ppb and calibration curve of p,p'-DDD

Fig. 4 shows the 5 ppb area reproducibility (n=3) and the correlation coefficient of the calibration curves for all 329 components measured. Among the 329 components, 308 components showed good reproducibility with a CV of 20% or less. Additionally, 249 components showed a correlation coefficient of $r=0.999$ or higher for the calibration curves, confirming no issues with linearity. The component with the worst linearity, acetamidrid, had a correlation coefficient of $r=0.994$, which is still acceptable.

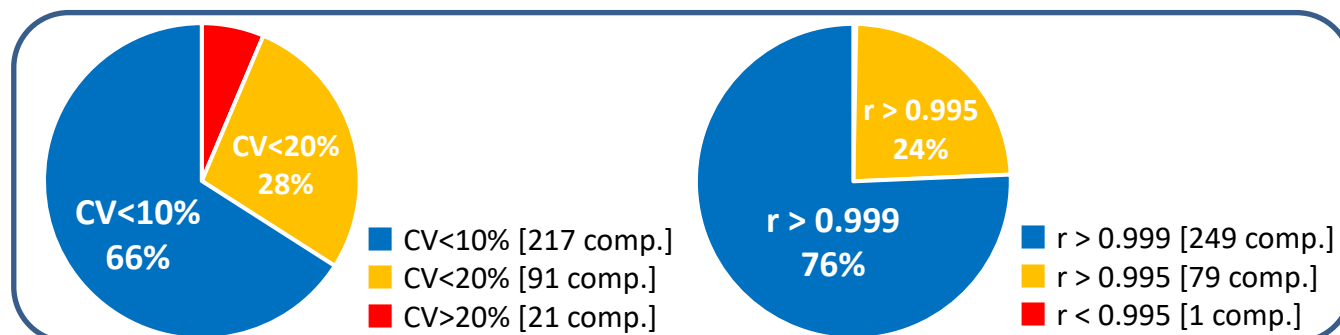


Fig. 4 Coefficient of variation of area and correlation coefficient of the calibration curve

Conclusion

As an application example of simultaneous analysis of pesticide residues in food using GC-MS/MS with hydrogen carrier gas, measurement conditions were optimized, and a calibration curve was created in the range of 5 ppb to 100 ppb by measuring a mixed pesticide standard solution. Out of the 336 pesticide components set as measurement targets, 329 components could be detected without any issues down to 5 ppb. This resulted in a favorable outcome, indicating that 98% of the pesticide compounds examined could be quantified using hydrogen carrier gas.

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Target pesticides (No.1~170)

Calibration curve : Linear
S/N(PP) : STD 5ppb

No.	Compound Name	RT [min]	Quantifier Ion Q1->Q3	Qualifier Ion Q1->Q3	Correlation coefficient (r)	S/N(PP)
1	Methamidophos	6.63	141->95 CE:5	95->80 CE:10	0.9984	720.6
2	Dichlorvos	6.77	185->93 CE:10	109->79 CE:5	0.9994	1323.5
3	EPTC	8.25	189->128 CE:5	128->86 CE:5	0.9991	2921.5
4	Mevinphos	8.93	192->127 CE:10	127->109 CE:10	0.9994	797.1
5	Acephate	9.07	136->94 CE:15	94->64 CE:5	0.9980	69.1
6	Butylate	8.72	156->57 CE:5	146->90 CE:5	0.9998	2073.1
7	Nitrapyrin	9.35	194->133 CE:15	196->135 CE:15	0.9992	209.3
8	Etridiazole	9.35	211->183 CE:10	213->185 CE:15	0.9993	159.2
9	Methacrifos	9.78	208->180 CE:5	208->165 CE:15	0.9992	692.0
10	Chloroneb	9.95	191->141 CE:10	206->191 CE:15	0.9993	3926.8
11	Tebuthiuron	10.15	171->156 CE:15	171->129 CE:10	0.9985	17.0
12	Isoprocarb	10.27	136->121 CE:10	121->103 CE:10	0.9994	618.7
13	XMC	10.55	122->107 CE:10	107->77 CE:10	0.9985	156.4
14	Omethoate	10.91	156->110 CE:10	156->141 CE:5	0.9959	126.5
15	Tecnazene	10.99	261->203 CE:15	215->179 CE:15	0.9988	490.6
16	Fenobucarb	11.03	150->121 CE:10	121->103 CE:10	0.9993	723.2
17	Propoxur	11.06	152->110 CE:10	110->92 CE:10	0.9993	869.6
18	Propachlor	11.11	120->77 CE:15	120->92 CE:10	0.9992	37.4
19	Chlorethoxyfos	11.15	153->97 CE:10	153->125 CE:5	0.9989	326.2
20	Demeton-S-methyl	10.92	88->60 CE:5	109->79 CE:5	0.9985	58.9
21	Diphenylamine	11.35	167->139 CE:20	167->140 CE:15	0.9991	93.0
22	Ethiophosphos	11.37	200->158 CE:5	158->114 CE:5	0.9991	178.2
23	Ethalfuralin	11.41	276->202 CE:15	316->276 CE:10	0.9985	537.4
24	Chlorpropham	11.60	213->127 CE:15	171->127 CE:10	0.9992	1555.4
25	Trifluralin	11.57	306->264 CE:10	264->206 CE:10	0.9993	735.4
26	Dicrotophos	11.64	193->127 CE:10	127->109 CE:10	0.9993	320.4
27	Benfluralin	11.63	292->264 CE:10	292->206 CE:15	0.9989	762.6
28	Bendiocarb	11.73	166->151 CE:15	126->108 CE:10	0.9995	1830.6
29	Monocrotophos	11.81	192->127 CE:10	127->109 CE:10	0.9985	85.7
30	Cadusafos	11.91	159->131 CE:10	158->114 CE:5	0.9993	45.7
31	Diallate 1	11.66	234->150 CE:20	234->192 CE:10	0.9991	2343.3
32	Phorate	12.02	121->65 CE:10	231->175 CE:15	0.9996	218.1
33	α-HCH	11.87	217->181 CE:10	219->183 CE:10	0.9986	2240.2
34	Diallate 2	11.86	234->150 CE:20	234->192 CE:10	0.9991	818.5
35	Hexachlorobenzene	12.30	284->249 CE:25	286->251 CE:25	0.9988	3788.0
36	Thiometon	11.97	88->60 CE:5	125->79 CE:5	0.9994	262.3
37	Dimethoate	12.42	93->63 CE:5	125->79 CE:5	0.9986	111.7
38	Dicloran	12.48	206->176 CE:15	176->148 CE:15	0.9990	523.3
39	Carbofuran	12.48	164->149 CE:15	164->131 CE:15	0.9994	443.4
40	Simazine	12.53	201->138 CE:10	201->173 CE:5	0.9994	593.4
41	Chlorbufam	12.27	223->127 CE:15	153->125 CE:15	0.9971	222.5
42	Atrazine	12.61	215->200 CE:10	200->122 CE:10	0.9975	338.8
43	Dimethipin	12.37	118 -> 58 CE:10	124 -> 76 CE:5	0.9957	162.1
44	β-HCH	12.38	217->181 CE:10	219->183 CE:10	0.9986	3827.5
45	Clomazone	12.71	204->107 CE:20	125->89 CE:10	0.9981	2520.1
46	Quintozene	12.80	249->214 CE:15	295->237 CE:20	0.9983	1288.1
47	Propazine	12.66	214->172 CE:10	229->214 CE:10	0.9970	483.0
48	γ-HCH	12.57	217->181 CE:10	219->183 CE:10	0.9991	4092.5
49	Propetamphos	12.80	138->110 CE:10	194->166 CE:10	0.9994	26.0
50	Terbufos	12.88	231->175 CE:15	231->129 CE:20	0.9992	1199.6
51	Cyanophos	12.92	243->109 CE:15	243->116 CE:5	0.9988	1848.3
52	Propyzamide	12.95	173->145 CE:15	175->147 CE:15	0.9993	151.9
53	Diazinon	12.95	304->179 CE:10	179->137 CE:15	0.9996	392.4
54	Phosphamidon 1	13.01	264->127 CE:20	127->109 CE:10	0.9991	121.5
55	Pyroquilon	13.13	173->130 CE:15	173->144 CE:20	0.9997	1041.5
56	Pyrimethanil	13.14	198->183 CE:20	198->156 CE:20	0.9991	126.7
57	Prohydrojasmon 1	13.19	184->83 CE:10	153->97 CE:5	0.9989	517.9
58	Terbacil	13.29	142->109 CE:5	88->60 CE:5	0.9986	139.6
59	Tefluthrine	13.17	161->144 CE:15	160->117 CE:10	0.9996	1061.3
60	Isazofos	13.22	177->127 CE:15	197->141 CE:10	0.9997	2085.1
61	Disulfoton	13.24	257->162 CE:10	161->119 CE:10	0.9993	229.8
62	δ-HCH	13.47	181->145 CE:15	217->181 CE:10	0.9994	2073.0
63	Triallate	13.39	268->184 CE:20	268->226 CE:10	0.9991	1544.0
64	Phosphamidon 2	13.48	238->166 CE:10	166->137 CE:10	0.9997	2129.6
65	Prohydrojasmon 2	13.51	184->83 CE:10	153->97 CE:5	0.9989	62.7
66	Iprobenfos	13.53	204->91 CE:15	204->171 CE:5	0.9991	775.3
67	Oxabetrinil	13.57	103->76 CE:10	73->45 CE:5	0.9985	19.7
68	Benoxacor	13.68	259->120 CE:20	259->176 CE:10	0.9993	1380.2
69	Formothion	13.69	170->93 CE:5	125->79 CE:5	0.9980	135.8
70	Ethiofencarb	13.37	168->107 CE:10	107->77 CE:10	0.9994	664.7
71	Phosphamidon 2	13.77	264->127 CE:20	127->109 CE:10	0.9991	123.6
72	Benfluresate	13.85	256->163 CE:10	163->121 CE:10	0.9999	2905.6
73	Dichlofenthion	13.84	279->223 CE:15	223->205 CE:20	0.9995	2080.3
74	Dimethenamid	13.89	230->154 CE:10	154->137 CE:10	0.9993	2373.5
75	Propanil	13.92	217->161 CE:10	161->126 CE:15	0.9995	532.3
76	Acetochlor	13.94	223->132 CE:20	146->131 CE:15	0.9991	576.5
77	Chloropyrifos-methyl	14.00	286->241 CE:25	286->271 CE:15	0.9980	818.4
78	Bromobutide	13.99	198->151 CE:10	198->153 CE:10	0.9977	128.4
79	Metribuzin	14.02	232->176 CE:10	119->91 CE:10	0.9977	412.1
80	Vinclozoline	14.05	198->145 CE:15	285->212 CE:15	0.9992	467.4
81	Carbofuran-3-hydroxy	14.07	180->137 CE:10	137->81 CE:15	0.9979	180.0
82	Spiroxamine 1	14.05	198->126 CE:5	100->58 CE:10	0.9978	241.7
83	Parathion methyl	14.14	263->109 CE:15	263->246 CE:5	0.9993	244.8
84	Alachlor	14.13	188->160 CE:10	188->132 CE:15	0.9988	164.0
85	Tolclofos-methyl	14.15	265->250 CE:15	265->220 CE:25	0.9994	658.5

No.	Compound Name	RT [min]	Quantifier Ion Q1-> Q3	Qualifier Ion Q1-> Q3	Correlation coefficient (r)	S/N(PP)
86	Simetryn	14.21	213->170 CE:10	213->152 CE:10	0.9995	626.1
87	Carbaryl	14.28	144->116 CE:10	144->115 CE:15	0.9996	159.3
88	Metalaxyl	14.25	206->132 CE:15	160->145 CE:10	0.9985	864.4
89	Ametryn	14.26	227->185 CE:5	227->212 CE:10	0.9991	447.0
90	Prometryn	14.30	226->184 CE:10	241->184 CE:10	0.9994	923.0
91	Fenchlorphos	14.34	285->240 CE:25	285->270 CE:15	0.9988	1219.6
92	Heptachlor	14.37	272->237 CE:20	274->239 CE:20	0.9993	3862.9
93	Pirimiphos methyl	14.49	276->244 CE:10	290->233 CE:10	0.9993	566.4
94	1-Naphthylacetamide	14.65	185->141 CE:20	141->115 CE:15	0.9992	1090.5
95	Terbutryn	14.57	185->170 CE:10	241->170 CE:15	0.9995	173.6
96	Fenitrothion	14.61	277->260 CE:5	277->109 CE:15	0.9978	245.4
97	Spiroxamine 2	14.56	198->126 CE:5	100->58 CE:10	0.9978	149.0
98	Methiocarb	14.32	168->153 CE:10	153->109 CE:10	0.9990	16.0
99	Ethofumesate	14.61	207->137 CE:10	207->161 CE:10	0.9995	845.7
100	Bromacil	14.68	205->188 CE:20	207->190 CE:20	0.9985	440.5
101	Dichlofluanid	14.43	224->123 CE:20	226->123 CE:20	0.9988	2137.1
102	Malathion	14.72	173->127 CE:5	127->99 CE:5	0.9982	546.0
103	Esprocarb	14.77	222->91 CE:15	222->162 CE:5	0.9991	1815.1
104	Quinoclamine	14.95	207->172 CE:15	172->128 CE:10	0.9976	477.5
105	Metolachlor	14.88	238->162 CE:10	162->133 CE:15	0.9991	2650.4
106	Chlorpyrifos	14.90	314->258 CE:20	197->169 CE:15	0.9984	1401.7
107	Dithiofencarb	14.86	267->225 CE:10	168->124 CE:5	0.9978	1227.0
108	(Z)-Dimethylvinphos	14.95	295->280 CE:15	109->79 CE:5	0.9961	74.1
109	Thiobencarb	14.96	100->72 CE:5	257->100 CE:5	0.9990	916.4
110	Cyanazine	14.98	212->123 CE:20	225->189 CE:15	0.9996	676.5
111	Chlorthal dimethyl	15.02	299->221 CE:20	301->273 CE:25	0.9987	3250.7
112	Fenthion	15.00	278->169 CE:15	278->245 CE:10	0.9976	660.1
113	Aldrin	15.10	263->228 CE:25	265->230 CE:20	0.9985	622.0
114	Flufenacet	15.00	151->136 CE:15	211->123 CE:10	0.9996	277.2
115	Fenpropimorph	14.98	128->110 CE:10	128->70 CE:5	0.9992	4501.8
116	Parathion	15.07	261->125 CE:15	291->109 CE:10	0.9967	750.9
117	Isafenphos oxon	15.02	229->201 CE:10	201->183 CE:15	0.9989	1639.1
118	Tetraconazole	15.06	171->136 CE:10	336->218 CE:15	0.9975	996.0
119	Triadimefon	15.11	208->127 CE:10	208->181 CE:10	0.9971	233.3
120	Nitrothal isopropyl	15.14	236->194 CE:10	194->148 CE:10	0.9983	2537.6
121	Dicofol (decomposed)	15.28	139->111 CE:10	250->139 CE:20	0.9995	636.8
122	Fthalide	15.39	243->215 CE:20	241->213 CE:20	0.9994	256.6
123	Bromophos-methyl	15.37	331->286 CE:30	329->284 CE:30	0.9994	1264.8
124	Diphenamid	15.37	167->152 CE:15	239->167 CE:10	0.9995	27.0
125	Fosthiazate 1	15.41	195->139 CE:5	195->104 CE:5	0.9973	31.0
126	Fosthiazate 2	15.45	195->139 CE:5	195->104 CE:5	0.9973	34.4
127	trans-Chlorfenvinphos	15.51	267->159 CE:10	323->267 CE:10	0.9978	244.0
128	Pendimethalin	15.56	252->162 CE:10	252->208 CE:5	0.9985	431.0
129	Fipronil	15.55	367->255 CE:20	351->255 CE:20	0.9988	219.9
130	Dimethametryn	15.65	212->122 CE:10	212->94 CE:15	0.9995	1434.8
131	Chlzolinate	15.33	188->147 CE:15	188->153 CE:15	0.9990	367.1
132	Penconazole	15.69	248->157 CE:20	248->192 CE:15	0.9986	2284.6
133	Isafenphos	15.67	213->121 CE:10	213->185 CE:5	0.9992	891.9
134	Allethrin 1,2	15.65	123->81 CE:5	136->121 CE:10	0.9991	2.3
135	cis-Chlorfenvinphos	15.73	267->159 CE:10	323->267 CE:10	0.9978	1063.9
136	(Z)-Pyrifenox	15.75	262->227 CE:10	262->200 CE:15	0.9989	748.2
137	Mecarbam	15.75	159->131 CE:5	296->196 CE:10	0.9971	12.6
138	oxy-Chlordane	15.84	185->149 CE:5	185->121 CE:10	0.9986	92.2
139	Heptachlor Epoxide (isomer A)	15.85	353->263 CE:20	355->265 CE:20	0.9976	758.2
140	Allethrin 3,4	15.75	123->81 CE:5	136->121 CE:10	0.9991	2.7
141	Phenthoate	15.85	274->121 CE:20	274->246 CE:5	0.9990	712.7
142	Heptachlor Epoxide (isomer B)	15.93	183->155 CE:15	185->157 CE:15	0.9993	22.0
143	Diclocymet 1	15.86	277->221 CE:10	173->137 CE:10	0.9996	1032.1
144	Quinalphos	15.88	146->118 CE:10	157->129 CE:15	0.9996	191.4
145	Procyimidone	15.96	283->255 CE:10	96->67 CE:10	0.9983	278.9
146	Triadimenol 1	15.94	168->70 CE:10	128->100 CE:10	0.9986	287.6
147	Thiabendazole	16.02	201->174 CE:15	174->130 CE:10	0.9969	302.2
148	Triflumizole	15.92	206->179 CE:20	206->186 CE:15	0.9996	134.6
149	Captan	15.68	149->105 CE:5	149->107 CE:5	0.9940	4.8
150	Dimepiperate	16.00	145->112 CE:10	119->91 CE:10	0.9981	797.1
151	Zoxamide (decomposed)	15.39	187->159 CE:15	189->161 CE:15	0.9993	266.7
152	Methoprene	15.91	191->135 CE:10	191->121 CE:10	0.9950	42.8
153	Triadimenol 2	16.09	168->70 CE:10	128->100 CE:10	0.9986	78.9
154	Bromophos ethyl	16.14	359->285 CE:30	359->303 CE:15	0.9986	454.7
155	Methodathion	16.20	145->85 CE:5	85->58 CE:5	0.9968	531.7
156	Diclocymet 2	16.17	277->221 CE:10	173->137 CE:10	0.9996	1343.4
157	Propaphos	16.15	220->140 CE:10	304->220 CE:15	0.9995	2533.1
158	Chlorbenside	16.27	268->125 CE:15	125->89 CE:10	0.9987	1818.0
159	(E)-Pyrifenox	16.26	373->266 CE:20	375->266 CE:20	0.9979	1737.8
160	trans-Chlordane	16.30	262->227 CE:10	262->200 CE:15	0.9976	297.6
161	Tetrachlorvinphos	16.27	329->109 CE:15	109->79 CE:5	0.9978	337.1
162	Chinomethionate	16.02	206->148 CE:15	234->206 CE:10	0.9995	4047.3
163	Butachlor	16.29	176->147 CE:15	188->160 CE:10	0.9988	324.5
164	Paclobutrazol	16.33	236->125 CE:10	236->167 CE:10	0.9994	772.9
165	Disulfoton sulfone	16.01	213->97 CE:15	153->97 CE:15	0.9985	472.7
166	Fenothiocarb	16.35	160->72 CE:10	160->106 CE:10	0.9992	609.4
167	Butamifos	16.46	286->185 CE:25	286->202 CE:15	0.9968	84.8
168	cis-Chlordane	16.55	373->266 CE:20	375->266 CE:20	0.9992	1134.6
169	α -Endosulfan	16.22	241->206 CE:20	195->159 CE:10	0.9987	241.4
170	Namaphos	16.50	303->195 CE:10	154->139 CE:10	0.9979	246.0

Target pesticides (No.171～336)

Calibration curve : Linear
S/N(PP) : STD 5ppb

No.	Compound Name	RT [min]	Quantifier Ion Q1->Q3	Qualifier Ion Q1->Q3	Correlation coefficient (r)	S/N(PP)
171	Flutriafof	16.57	219->123 CE:10	123->95 CE:10	0.9987	1266.2
172	Imazamethabenz methyl 1+2	16.55	187->144 CE:10	256->187 CE:15	0.9974	381.7
173	Flutolanil	16.57	323->173 CE:15	173->145 CE:15	0.9993	3301.0
174	Napropamide	16.61	128->72 CE:5	271->128 CE:5	0.9985	1721.1
175	(E)-Metominostrobin	16.32	191->160 CE:10	238->210 CE:20	0.9990	1578.3
176	Fludioxonil	16.37	248->182 CE:15	248->154 CE:15	0.9992	2901.9
177	TCMTB	16.38	180->136 CE:15	180->109 CE:35	0.9983	164.4
178	Imazail	16.68	215->173 CE:10	215->159 CE:10	0.9983	995.7
179	Chlorfenson	16.71	175->111 CE:10	302->175 CE:10	0.9996	1383.7
180	Hexaconazole	16.71	214->172 CE:20	231->175 CE:10	0.9980	494.6
181	Tri thiophos	16.71	309->239 CE:15	267->239 CE:10	0.9993	1085.2
182	Pretilachlor	16.69	162->132 CE:15	162->147 CE:10	0.9994	920.2
183	Isoprothiolane	16.73	290->118 CE:10	189->145 CE:10	0.9986	773.0
184	Isoxathion oxon	16.74	161->105 CE:15	161->77 CE:25	0.9975	5.1
185	Profenofos	16.79	339->269 CE:15	337->267 CE:20	0.9984	268.9
186	Tricyclazole	16.95	189->162 CE:15	189->161 CE:20	0.9960	257.0
187	Zoxamide	18.88	189->161 CE:15	187->159 CE:15	0.9986	85.5
188	Thifluzamide	16.48	194->166 CE:15	166->125 CE:15	0.9989	36.9
189	Oxadiazon	16.79	175->112 CE:10	258->175 CE:10	0.9994	694.5
190	p,p'-DDE	16.90	246->176 CE:20	318->248 CE:20	0.9988	3032.1
191	Flamprop methyl	16.87	230->170 CE:15	105->77 CE:10	0.9991	1755.7
192	Barban	16.90	153->125 CE:15	153->90 CE:20	0.9980	25.8
193	Uniconazole P	16.90	234->165 CE:10	234->216 CE:10	0.9994	624.8
194	Triflurof (DEF)	16.87	202->147 CE:10	169->113 CE:5	0.9988	890.2
195	Myclobutanil	16.93	179->125 CE:10	181->127 CE:10	0.9989	1030.9
196	Oxyfluorfen	16.89	252->196 CE:20	252->224 CE:20	0.9951	230.4
197	Flusilazole	16.95	233->165 CE:15	233->152 CE:15	0.9990	670.0
198	Bupirimate	16.93	273->193 CE:10	316->208 CE:10	0.9990	1544.0
199	Kresoxim-methyl	16.95	206->116 CE:5	116->89 CE:10	0.9983	309.4
200	Buprofezin	16.99	175->132 CE:10	172->131 CE:5	0.9989	264.4
201	Dieldrin	17.10	277->241 CE:10	277->206 CE:20	0.9986	96.0
202	(Z)-Metominostrobin	16.70	191->160 CE:10	238->210 CE:20	0.9981	2042.8
203	Imibenconazole desbenzyl	17.08	235->166 CE:10	270->235 CE:5	0.9957	250.9
204	Carboxin	17.10	235->143 CE:10	235->218 CE:5	0.9987	1013.7
205	Azaconazole	17.13	217->173 CE:15	219->175 CE:15	0.9993	1800.8
206	Chlorfenapyr	17.12	247->227 CE:20	328->247 CE:20	0.9979	319.8
207	Isoxathion	17.20	177->130 CE:10	105->77 CE:10	0.9984	277.0
208	Cyproconazole 1+2	17.29	222->125 CE:20	139->111 CE:10	0.9989	1042.1
209	Fenoxanil	17.29	189->125 CE:10	189->154 CE:15	0.9992	394.2
210	Perthane	17.33	223->167 CE:15	223->165 CE:20	0.9993	1758.8
211	Flufenpyr ethyl	17.34	408->345 CE:10	373->345 CE:10	0.9964	263.3
212	Endrin	17.51	279->243 CE:10	263->228 CE:20	0.9985	90.1
213	Pyriminobac methyl 1	17.39	302->256 CE:20	302->230 CE:20	0.9992	2088.3
214	Chlorobenzilate	17.49	251->139 CE:10	253->141 CE:10	0.9997	3656.3
215	Fensulfotrobin	17.53	292->264 CE:10	156->141 CE:15	0.9985	198.6
216	β-Endosulfan	17.37	241->206 CE:15	195->159 CE:10	0.9984	176.8
217	Oxadixyl	17.67	163->132 CE:10	132->117 CE:15	0.9994	1432.6
218	Ethion	17.61	231->175 CE:15	231->203 CE:5	0.9992	1338.9
219	p,p'-DDD	17.70	235->165 CE:15	237->165 CE:15	0.9995	2034.1
220	Fluacrypyrim	17.63	204->189 CE:10	145->115 CE:10	0.9987	134.2
221	o,p'-DDT	17.76	235->165 CE:15	237->165 CE:15	0.9993	774.9
222	Mepronil	17.89	269->119 CE:15	119->91 CE:10	0.9995	947.1
223	Triazophos	17.91	161->134 CE:10	162->119 CE:10	0.9991	397.7
224	Azamethiphos	18.07	215->171 CE:15	215->128 CE:20	0.9872	16.1
225	Carfentrazone ethyl	17.99	340->312 CE:10	330->310 CE:10	0.9980	367.2
226	Famphur	18.08	218->109 CE:20	218->186 CE:10	0.9992	463.3
227	Benalaxyl	18.10	266->148 CE:10	148->133 CE:15	0.9993	631.8
228	Trifloxystrobin	18.03	116->89 CE:10	222->162 CE:10	0.9991	15.7
229	Norflurazon	18.19	303->145 CE:25	173->145 CE:10	0.9988	476.0
230	Propiconazole 1	18.21	175->147 CE:15	173->145 CE:15	0.9992	16.5
231	Edifenphos	18.26	173->109 CE:5	310->173 CE:10	0.9981	369.2
232	Pyriminobac methyl 2	18.19	302->256 CE:20	302->230 CE:20	0.9992	1392.1
233	Quinoxifen	18.30	237->208 CE:25	307->237 CE:20	0.9995	2149.1
234	Pyraflufen-ethyl	18.21	412->349 CE:10	349->279 CE:25	0.9977	295.3
235	Lenacil	18.36	153->136 CE:15	153->135 CE:15	0.9991	833.6
236	Propiconazole 2	18.33	175->147 CE:15	173->145 CE:15	0.9992	65.9
237	Endosulfan sulphate	18.42	272->237 CE:20	272->235 CE:20	0.9991	2971.6
238	p,p'-DDT	18.41	235->165 CE:15	237->165 CE:15	0.9990	585.9
239	Hexazinone	18.49	171->85 CE:15	171->71 CE:10	0.9995	409.9
240	Thenylchlor	18.57	288->141 CE:10	288->174 CE:10	0.9992	507.2
241	Diclofop methyl	18.60	253->162 CE:15	340->253 CE:15	0.9993	2302.7
242	Diffufenican	18.57	266->238 CE:20	266->246 CE:20	0.9990	429.3
243	Tebuconazole	18.64	250->125 CE:20	250->153 CE:10	0.9989	739.4
244	Propargite 1+2	18.58	135->107 CE:10	173->130 CE:10	0.9997	15.8
245	Resmethrin 1	18.60	171->143 CE:5	171->128 CE:15	0.9963	2.4
246	Piperonyl butoxide	18.67	176->131 CE:10	176->145 CE:15	0.9992	417.7
247	Resmethrin 2	18.70	171->143 CE:5	171->128 CE:15	0.9963	46.5
248	Captafol	18.53	183->79 CE:10	183->150 CE:5	0.9673	3.5
249	Mefenpyr diethyl	18.84	253->189 CE:20	299->253 CE:10	0.9996	1688.5
250	Epoxiconazole	18.90	192->138 CE:10	165->138 CE:10	0.9991	548.7
251	Pyributicarb	18.92	165->108 CE:10	181->108 CE:5	0.9997	836.4
252	Carbosulfan	18.97	118->76 CE:10	163->135 CE:10	0.9990	176.9
253	Iprodione	19.05	314->245 CE:10	316->247 CE:10	0.9978	106.8
254	Pyridaphenthion	19.05	340->199 CE:10	340->204 CE:10	0.9992	406.9
255	Acetamiprid	19.18	152->116 CE:15	126->90 CE:5	0.9942	50.2

No.	Compound Name	RT [min]	Quantifier Ion Q1->Q3	Qualifier Ion Q1->Q3	Correlation coefficient (r)	S/N(PP)
256	Bifenthrin	19.13	181->166 CE:15	181->165 CE:20	0.9994	93.2
257	Phosmet	19.29	160->133 CE:15	160->105 CE:15	0.9990	491.5
258	EPN	19.29	157->110 CE:10	169->141 CE:10	0.9978	178.1
259	Picolinafen	19.26	376->239 CE:15	376->238 CE:20	0.9994	1247.7
260	Bromopropylate	19.30	185->157 CE:15	183->155 CE:15	0.9993	76.8
261	Piperophos	19.28	320->122 CE:5	140->98 CE:10	0.9988	430.7
262	Etoazazole	19.32	300->270 CE:25	204->176 CE:15	0.9991	514.4
263	Methoxychlor	19.39	227->169 CE:20	227->212 CE:20	0.9989	2223.9
264	Fenpropathrin	19.35	181->152 CE:20	265->210 CE:10	0.9995	15.0
265	Fenamidone	19.45	268->180 CE:15	238->194 CE:20	0.9986	344.5
266	Dicofol	19.60	139->111 CE:10	251->139 CE:10	0.9973	71.6
267	Tebufenpyrad	19.46	333->171 CE:15	333->276 CE:5	0.9993	2426.8
268	Anilofos	19.55	226->157 CE:15	226->184 CE:5	0.9992	447.6
269	Bifenox	19.57	311->189 CE:30	341->311 CE:10	0.9963	177.8
270	Furathiocarb	19.62	163->135 CE:5	163->107 CE:10	0.9993	148.2
271	Phenothrin 1	19.61	183->153 CE:15	123->81 CE:5	0.9979	4.8
272	Phenothrin 2	19.71	183->153 CE:15	123->81 CE:5	0.9979	16.1
273	Tetradifon	19.84	227->199 CE:15	159->131 CE:10	0.9996	190.6
274	Phosalone	19.91	182->111 CE:10	182->138 CE:10	0.9994	226.4
275	Triticonazole	19.93	235->217 CE:10	235->182 CE:15	0.9985	241.5
276	Azinphos-methyl	20.04	160->132 CE:5	160->104 CE:10	0.9988	53.7
277	Cyhalothrin 1	19.91	181->152 CE:30	197->141 CE:15	0.9998	37.4
278	Pyriproxyfen	20.02	136->96 CE:10	226->186 CE:15	0.9996	1317.3
279	Cyhalofop butyl	20.01	256->120 CE:5	357->256 CE:10	0.9993	622.7
280	Mefenacet	20.17	192->136 CE:10	192->109 CE:20	0.9992	671.7
281	Cyhalothrin 2	20.09	181->152 CE:30	197->141 CE:15	0.9998	14.0
282	Acrinathrin	20.17	208->181 CE:15	209->141 CE:20	0.9992	144.0
283	Pyrazophos	20.33	221->149 CE:15	221->193 CE:10	0.9994	435.4
284	Benfuracarb	20.50	190->102 CE:15	164->149 CE:15	0.9992	125.0
285	Fenarimol	20.49	251->139 CE:10	139->111 CE:10	0.9994	688.2
286	Pyralofos	20.66	194->138 CE:15	360->194 CE:10	0.9993	239.3
287	Oryzalol	20.42	317->275 CE:10	317->217 CE:10	0.9944	12.4
288	Fenoxacprop ethyl	20.70	361->288 CE:10	288->260 CE:10	0.9991	919.5
289	Spirdiclofen	20.88	312->259 CE:10	71->43 CE:5	0.9978	243.6
290	Bitertanol 1	20.94	170->141 CE:15	170->142 CE:15	0.9992	35.9
291	Permethrin 1	20.96	183->153 CE:15	183->168 CE:15	0.9995	12.0
292	Bitertanol 2	21.04	170->141 CE:15	170->142 CE:15	0.9992	7.9
293	Permethrin 2	21.08	183->153 CE:15	183->168 CE:15	0.9995	44.7
294	Fluquinconazole	21.18	340->298 CE:25	340->286 CE:30	0.9990	985.3
295	Dioxathion	20.82	125->97 CE:5	271->185 CE:5	0.9994	7.3
296	Prochloraz	21.22	180->138 CE:10	308->202 CE:10	0.9977	37.2
297	Pyridaben	21.17	147->119 CE:10	147->132 CE:15	0.9993	24.1
298	Cafenstrole	21.46	100->72 CE:5	188->119 CE:15	0.9992	153.8
299	Cyfluthrin 1	21.46	227->199 CE:10	206->151 CE:25	0.9998	39.0
300	Fenbuconazole	21.56	198->129 CE:10	129->102 CE:10	0.9988	860.1
301	Cyfluthrin 2	21.55	227->199 CE:10	206->151 CE:25	0.9998	54.2
302	Cyfluthrin 3	21.62	227->199 CE:10	206->151 CE:25	0.9998	28.1
303	Cyfluthrin 4	21.66	227->199 CE:10	206->151 CE:25	0.9998	24.9
304	Cypermethrin 1	21.80	163->127 CE:10	163->91 CE:15	0.9996	156.3
305	Boscalid	22.02	263->235 CE:10	265->237 CE:10	0.9994	68.5
306	Halfenprox	21.88	140->112 CE:10	342->140 CE:20	0.9992	645.0
307	Cypermethrin 2	21.91	163->127 CE:10	163->91 CE:15	0.9996	224.3
308	Cypermethrin 3	21.98	163->127 CE:10	163->91 CE:15	0.9996	157.6
309	Flucythrinate 1	21.95	157->107 CE:10	199->157 CE:10	0.9994	251.2
310	Cypermethrin 4	22.01	163->127 CE:10	163->91 CE:15	0.9996	201.9
311	Etofenprox	22.16	163->107 CE:15	163->135 CE:10	0.9994	387.4
312	Flucythrinate 2	22.16	157->107 CE:10	199->157 CE:10	0.9994	279.6
313	Silafluofen	21.93	179->151 CE:15	286->258 CE:10	0.9992	394.5
314	Fluridone	22.49	328->259 CE:25	328->288 CE:25	0.9974	281.8
315	Thiacloprid	22.82	251->224 CE:20	126->90 CE:5	0.9977	1.6
316	Pyrimidifos	22.23	184->169 CE:20	186->171 CE:20	0.9994	107.3
317	Flumioxazin	22.90	287->259 CE:15	345->326 CE:10	0.9987	32.8
318	Fenvalerate 1	22.85	167->125 CE:15	209->141 CE:20	0.9991	640.9
319	Pyraclostrobin	22.63	164->132 CE:10	132->104 CE:5	0.9987	447.3
320	Fluralinate 1	22.92	250->200 CE:15	250->208 CE:20	0.9992	218.4
321	Fluralinate 2	23.00	250->200 CE:15	250->208 CE:20	0.9992	265.2
322	Fenvalerate 2	23.11	167->125 CE:15	209->141 CE:20	0.9991	158.5
323	Difenoconazole 1	23.51	323->265 CE:20	265->202 CE:20	0.9993	130.7
324	Difenoconazole 2	23.60	323->265 CE:20	265->202 CE:20	0.9993	250.5
325	Deltamethrin 1	23.88	253->174 CE:10	181->152 CE:20	0.9990	2.5
326	Deltamethrin 2	24.10	253->174 CE:10	181->152 CE:20	0.9990	124.6
327	Flumiclorac pentyl	24.08	308->280 CE:10	308->252 CE:20	0.9983	52.8
328	Azoxystrobin	24.13	388->360 CE:10	388->300 CE:20	0.9972	16.3
329	Dimethomorph 1	23.88	301->165 CE:10	303->165 CE:10	0.9992	222.5
330	Famoxadone	24.48	224->196 CE:10	330->224 CE:10	0.9992	40.2
331	Tolfenpyrad	24.55	197->154 CE:15	197->169 CE:10	0.9995	49.5
332	Dimethomorph 2	24.35	301->165 CE:10	303->165 CE:10	0.9992	177.3
333	Imibenconazole	25.43	123->89 CE:10	376->260 CE:20	0.9991	10.2
334	Cinidon ethyl	25.58	358->330 CE:10	330->302 CE:15	0.9996	79.4
335	Fluthiacet methyl	26.13	232->188 CE:15	403->286 CE:10	0.9960	14.9
336	Propaquizafop	26.58	299->255 CE:20	299->271 CE:10	0.9986	1.7