Study on higher sensitivity for analysis of pesticide residues in foods by using GC-MS/MS (1)

Product used : Mass spectrometer (MS)

Introduction

The analysis of pesticide residues in foods requires the separation and detection of trace amounts of target pesticides present in complex matrices, and therefore, analytical instruments used for such measurements must have high performance. The GC-MS/MS method is effective for simultaneous analysis of multiple components in complex matrices, and is currently used by many analytical institutions as a general analytical method. Naturally, detection sensitivity can differ depending on the analytical instrument used, but various methods exist to increase the sensitivity of conventional analytical methods. For the purpose of increasing sensitivity, it can be effective to apply a sample injection method that is different from the normal hot splitless injection method generally used in GC, and among them, a relatively large number of examples exist using large volume injection (LVI) technology. The Multi Mode Injector (MMI manufactured by Agilent) used in this study allows the selection of various modes, such as cold splitless mode and solvent vent mode, in addition to the general hot splitless mode, depending on the purpose of measurement. However, there are relatively few examples for the application of cold splitless injection methods for the analysis of pesticide residues in food products. In this study, we compare the results of various cold splitless injection methods using MMI to improve GC-MS/MS detection sensitivity by suppressing adsorption and thermal decomposition of the target pesticides in the GC inlet.

Experimental

1. Sample Conditions

Standard Reagents : Pesticide Mixture Standard Solution PL-1,2,3,4,5,6,9,10,11,12,13 made by FUJIFILM Wako Pure Chemical Co.
Sample Concentration : Pesticide mixed standard solutions were prepared at 0.1, 0.5, 1, 2, 5, 10, and 20 ppb
Sample Volume : 2 µL (+ 0.2 µL co-injection of analyte protectants : SFA10mix made by Hayashi Pure Chemical Industry Co.)

2. GC Conditions

Gas chromatograph : 8890GC (Agilent Technologies, Inc.)
Inlet mode : Hot/cold splitless mode
Inlet temperature (hot splitless) : 250 ° C
Inlet temperature (cold splitless) : 60 ° C (0.01 min) → 320 ° C (200 ° C / min, 10 min) → 60 ° C (200 ° C / min, 0 min)
Column : VF-5MS (length : 30 m, inner diameter : 0.25 mm, film thickness : 0.25 µm)
Oven temperature : 50 ° C (1 min) → 125 ° C (25 ° C / min, 0 min) → 300 ° C (10 ° C / min, 10 min)
Flow rate : 1.0 mL/min (constant flow)

3. MS Conditions

Mass spectrometer : JMS-TQ4000GC (JEOL Ltd.)
Measurement mode : SRM
SRM mode : High-sensitivity mode
Ion source temperature : 280 ° C
Interface temperature : 300 ° C
Ionization current : 50 µA
Ionization voltage : 70 eV

JMS-TQ4000GC

Results

Of the 292 components selected for measurement, a total of 283 components were detectable at 0.1 ppb by using hot splitless mode. The following page lists the compound names and retention times of the 283 components that were detectable. Nine components that were not detected at 0.1 ppb using the conventional hot inlet method included: procymidone, acetamiprid, halfenprox, imibenconazole, bifenox, flumiclorac pentyl, azoxystrobin, propaquizafop, and thiacloprid. On the other hand, all target components were detectable at 0.1 ppb using the MMI with cold splitless mode. Fig. 1 shows an EIC comparison of imibenconazole, bifenox, and azoxystrobin at 0.1 ppb as an example for the components that were not detected with a hot splitless injector. To confirm the effect of the application of the cold splitless mode on sensitivity, peak area ratios (cold/hot splitless) were calculated for the 283 components for which detection of 0.1 ppb was possible in both modes, and a scatter plot of the ratios sorted by compound number (retention time) is shown in Fig. 2.

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Target Pesticides (No.1～150)

No.	Compound name	RT	No.	Compound name	RT	No.	Compound name	RT
1	Aldoxycarb (decomposed)	5.73	51	δ-BHC	13.16	101	Aldrin	14.79
2	EPTC	7.98	52	Pirimicarb	13.20	102	Tetraconazole	14.80
3	Mevinphos 1+2	8.70	53	Prohydrojasmon 2	13.22	103	Triadimefon	14.83
4	Acephate	8.81	54	Iprobenfos	13.23	104	Nitrothal isopropyl	14.85
5	Nitrapyrin	9.05	55	Oxabetrinil	13.26	105	Dicofol (decomposed)	14.97
6	Etridiazole	9.06	56	Benoxacor	13.38	106	Fthalide	15.07
7	Methacrifos	9.50	57	Formothion	13.40	107	Bromophos	15.08
8	Chloroneb	9.66	58	Phosphamidon 2	13.48	108	Diphenamid	15.08
9	Isoprocarb	9.98	59	Benfuresate	13.54	109	Fosthiazate 1	15.11
10	XMC	10.26	60	Dichlofenthion	13.55	110	Fosthiazate 2	15.15
11	Omethoate	10.63	61	Dimethenamid	13.59	111	trans-Chlorfenvinphos	15.23
12	Tecnazene	10.68	62	Propanil	13.62	112	Pendimethalin	15.26
13	Fenobucarb	10.74	63	Acetochlor	13.64	113	Fipronil	15.28
14	Propoxur	10.77	64	Bromobutide	13.68	114	Dimethametryn	15.36
15	Propachlor	10.80	65	Chloropyriphos-methyl	13.70	115	Isophenphos	15.39
16	Chlorethoxyphos	10.86	66	Metribuzin	13.71	116	Penconazole	15.43
17	Diphenylamine	11.05	67	Spiroxamine 1	13.76	117	cis-Chlorfenvinphos	15.45
18	Ethoprophos	11.07	68	Vinclozoline	13.77	118	Allethrin 3+4	15.46
19	Ethalfluralin	11.14	69	Alachlor	13.84	119	Mecarbam	15.47
20	Trifluralin	11.30	70	Parathion methyl	13.84	120	Pyrifenox 2	15.53
21	Chlorpropham	11.31	71	Tolclofos-methyl	13.85	121	Heptachlor Epoxide (isomer A)	15.53
22	Benfluralin	11.36	72	Simetryn	13.92	122	Oxychlordane	15.55
23	Dicrotophos	11.36	73	Mefenoxam	13.95	123	Phenthoate	15.56
24	Bendiocarb	11.45	74	Ametryn	13.98	124	Diclocymet 1	15.57
25	Monocrotophos	11.53	75	Carbaril	13.98	125	Quinalphos	15.59
26	Cadusafos	11.60	76	Prometryn	14.02	126	Heptachlor Epoxide (isomer B)	15.63
27	Phorate	11.71	77	Fenchlorphos	14.04	127	Methoprene	15.65
28	Hexachlorobenzene	11.98	78	Heptachlor	14.06	128	Triadimenol 1	15.67
29	Dimethoate	12.11	79	Pirimiphos methyl	14.21	129	Dimepiperate	15.70
30	Dicloran	12.15	80	Spiroxamine 2	14.28	130	Triflumizole	15.70
31	Carbofuran	12.19	81	Terbutryn	14.28	131	Thiabendazole	15.72
32	Simazine	12.23	82	Fenitrothion	14.31	132	Zoxamide (decomposed)	15.76
33	Atrazine	12.33	83	Ethofumesate	14.32	133	Triadimenol 2	15.81
34	Propazine	12.41	84	1-Naphthylacetamide	14.34	134	Bromophos ethyl	15.86
35	Clomazone	12.41	85	Bromacil	14.38	135	Propaphos	15.88
36	Quintozene	12.48	86	Malathion	14.43	136	Diclocymet 2	15.89
37	Propetamphos	12.51	87	Esprocarb	14.47	137	Methidathion	15.90
38	Terbufos	12.58	88	Metolachlor	14.59	138	Tetrachlorvinphos	15.97
39	Cyanophos	12.61	89	Diethofencarb	14.59	139	Chlorbenside	15.97
40	Propyzamide	12.66	90	Chlorpyrifos	14.61	140	trans-Chlordane	15.99
41	Diazinone	12.67	91	Quinoclamine	14.62	141	Butachlor	16.00
42	Phosphamidon 1	12.72	92	(Z)-Dimethylvinphos	14.66	142	Pyrifenox 1	16.02
43	Pyroquilon	12.83	93	Benthiocarb	14.67	143	Paclobutrazol	16.05
44	Pyrimethanil	12.85	94	Cyanazine	14.69	144	Fenothiocarb	16.06
45	Tefluthrine	12.90	95	Fenpropimorph	14.70	145	Butamifos	16.17
46	Prohydrojasmon 1	12.90	96	Fenthion	14.70	146	Fenamiphos	16.23
47	Disulfoton	12.94	97	Flufenacet	14.71	147	Imazamethabenz methyl 1	16.24
48	Isazophos	12.94	98	Chlorthal dimethyl	14.72	148	cis-Chlordane	16.24
49	Terbacil	12.98	99	Isofenphos oxon	14.75	149	Imazamethabenz methyl 2	16.26
50	Triallate	13.10	100	Parathion	14.78	150	Flutriafol	16.28

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Target Pesticides (No.151～283)

No.	Compound name	RT
151	Flutolanil	16.29
152	Napropamide	16.31
153	Pretilachlor	16.42
154	Prothiofos	16.42
155	Hexaconazole	16.42
156	Chlorofenson	16.42
157	Isoprothiolane	16.44
158	Profenofos	16.50
159	Oxadiazon	16.52
160	Tribufos	16.59
161	Flamprop methyl	16.59
162	p,p'-DDE	16.60
163	Uniconazole P	16.61
164	Oxyfluorfen	16.62
165	Myclobutanil	16.65
166	Tricyclazole	16.65
167	Bupirimate	16.66
168	Kresoxim-methyl	16.67
169	Flusilazole	16.68
170	Buprofezin	16.70
171	Dieldrin	16.78
172	Imibenconazole debenzyl	16.80
173	Carboxin	16.80
174	Azaconazole	16.84
175	Chlorfenapyr	16.85
176	Isoxathion	16.92
177	Fenoxanil	17.01
178	Cyproconazole 1+2	17.05
179	1,1-Dichloro-2,2-bis (4-ethylphenyl) ethane	17.05
180	Flufenpyr ethyl	17.07
181	Pyriminobac methyl 1	17.12
182	Chlorobenzilate	17.20
183	Endrin	17.21
184	Fensulfothion	17.24
185	Ethion	17.33
186	Fluacrypyrim	17.37
187	Oxadixyl	17.37
188	p,p'-DDD	17.41
189	o,p'-DDT	17.46
190	Mepronil	17.61
191	Triazophos	17.64
192	Carfentrazone ethyl	17.73
193	Trifloxystrobin	17.79
194	Famphur	17.79
195	Azamethiphos	17.79
196	Benalaxyl	17.82
197	Norflurazon	17.91
198	Pyriminobac methyl 2	17.93
199	Pyraflufen-ethyl	17.95
200	Propiconazole 1	17.97

No.	Compound name	RT
201	Edifenphos	17.97
202	Quinoxyfen	18.01
203	Lenacil	18.06
204	Propiconazole 2	18.07
205	Endosulfan sulfate	18.11
206	p,p'-DDT	18.12
207	Hexazinone	18.21
208	Thenylchlor	18.29
209	Diflufenican	18.32
210	Diclofop methyl	18.33
211	Propargite 1+2	18.34
212	Resmethrin 1	18.34
213	Tebuconazole	18.36
214	Piperonyl butoxide	18.41
215	Resmethrin 2	18.45
216	Mefenpyr diethyl	18.58
217	Zoxamide	18.61
218	Epoxiconazole	18.62
219	Pyributicarb	18.65
220	Pyridafenthion	18.79
221	Iprodione	18.79
222	Bifenthrin	18.88
223	Phosmet	19.00
224	EPN	19.00
225	Picolinafen	19.00
226	Piperophos	19.01
227	Bromopropylate	19.02
228	Etoxazole	19.06
229	Fenpropathrin	19.10
230	Methoxychlor	19.12
231	Fenamidone	19.18
232	Tebufenpyrad	19.19
233	Anilofos	19.28
234	Furathiocarb	19.35
235	Phenothrin 1	19.36
236	Phenothrin 2	19.47
237	Tetradifon	19.56
238	Phosalone	19.63
239	Triticonazole	19.65
240	Cyhalothrin 1	19.67
241	Azinphos-methyl	19.75
242	Cyhalofop butyl	19.76
243	Pyriproxyfen	19.77
244	Cyhalothrin 2	19.84
245	Mefenacet	19.90
246	Acrinathrin	19.95
247	Pyrazophos	20.08
248	Fenarimol	20.22
249	Pyraclofos	20.41
250	Fenoxaprop ethyl	20.45

No.	Compound name	RT
251	Spirodiclofen	20.63
252	Bitertanol 1	20.69
253	trans-Permethrin	20.71
254	Bitertanol 2	20.80
255	cis-Permethrin	20.83
256	Fluquinconazole	20.91
257	Pyridaben	20.91
258	Prochloraz	20.97
259	Cafenstrole	21.20
260	Cyfluthrin 1	21.23
261	Fenbuconazole	21.30
262	Cyfluthrin 2	21.32
263	Cyfluthrin 3+4	21.42
264	Cypermethrin 1	21.56
265	Cypermethrin 2	21.66
266	Flucythrinate 1	21.70
267	Boscalid	21.73
268	Cypermethrin 3+4	21.76
269	Flucythrinate 2	21.90
270	Etofenprox	21.90
271	Fluridone	22.19
272	Fenvalerate 1	22.56
273	Flumioxazin	22.60
274	Fluvalinate 1	22.63
275	Fluvalinate 2	22.72
276	Fenvalerate 2	22.81
277	Difenoconazole 1	23.19
278	Difenoconazole 2	23.26
279	Deltamethrin	23.53
280	Famoxadone	24.11
281	Tolfenpyrad	24.18
282	Cinidon ethyl	25.14
283	Fluthiacet methyl	25.60

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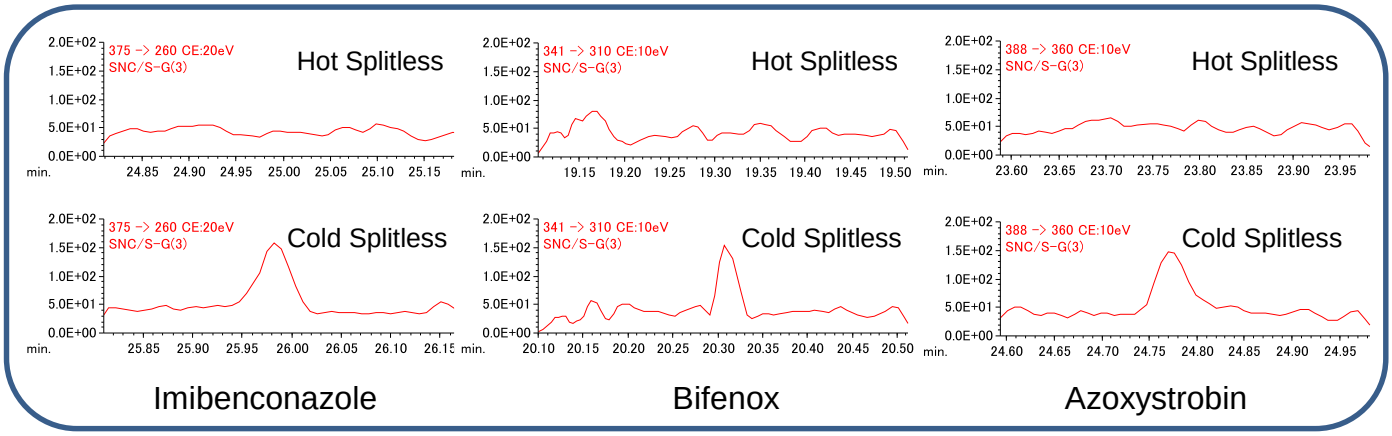

Fig.1 Comparison of EICs at 0.1 ppb (Hot / Cold Splitless)

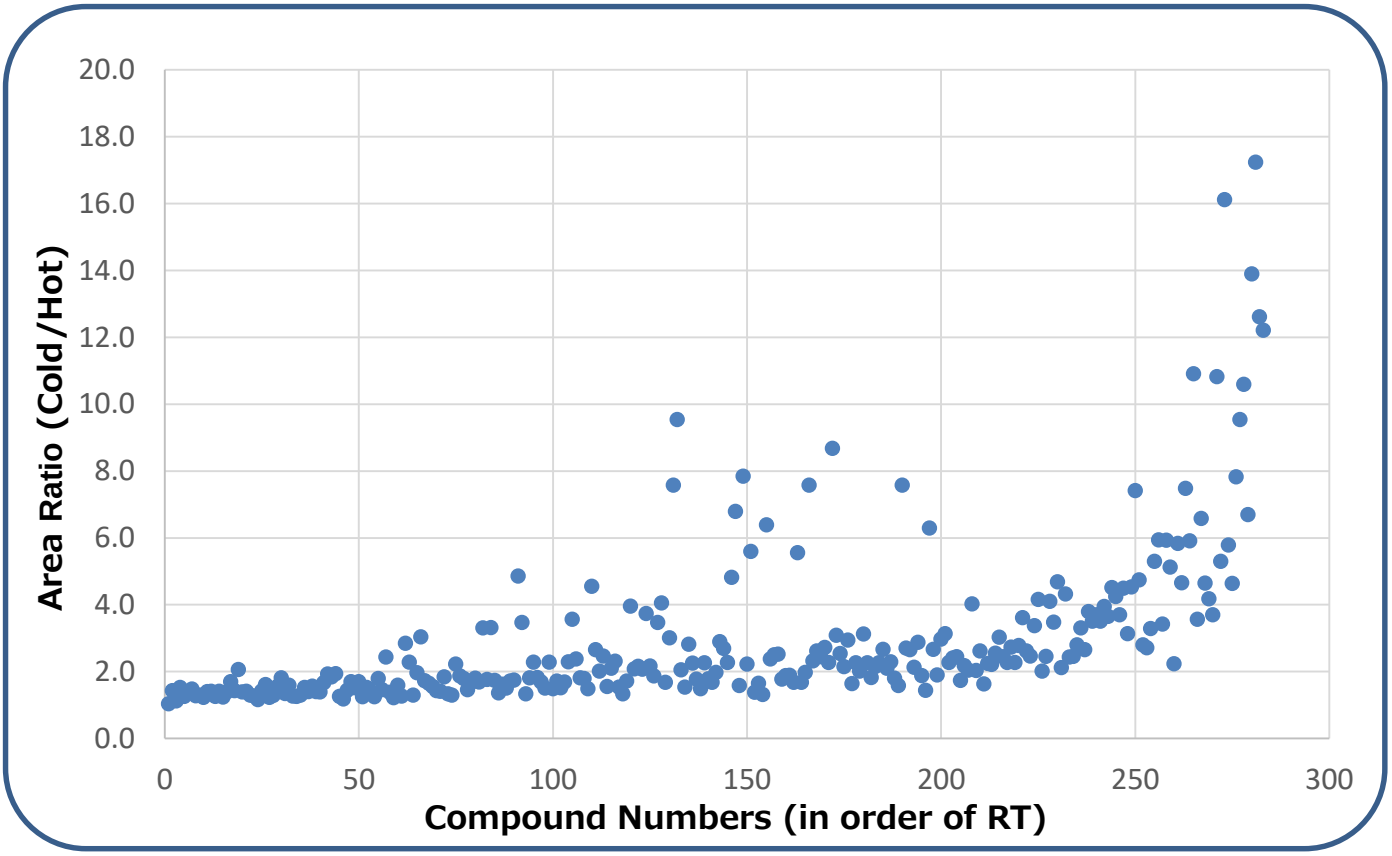

Fig.2 Scatter diagram of area ratios of measured pesticides (Cold / Hot)

By using the cold splitless method, the peak area ratio for the components in the first half of the retention time range increased by 1.5 to 2 times. Additionally, several components near the middle of the retention time range had area ratios that increased by approximately 5 to 10 times. These compounds are presumed to be components that experience a large suppression effect caused by compound decomposition in the GC injection port. Similarly, the higher the boiling point component (higher retention time range), the larger the area ratio increases (up to 17 times). These results are likely due to the combination of suppressing decomposition and suppressing adsorption inside the inlet while using cold splitless mode. In this study, there were no components whose sensitivity decreased (area ratio < 1) due to the application of cold splitless mode when compared to the conventional hot splitless mode.

Conclusion

This study showed that cold splitless injections using MMI improved the sensitivity of pesticides analysis by GC-MS/MS when compared to the more traditional hot splitless injection method. Furthermore, a number of components showed very large improvements in sensitivity in the middle to late retention times that were likely due to both suppression of thermal decomposition and minimization of adsorption in the inlet when using cold splitless methods. These results show that cold splitless injection methods using MMI can be effective for improving overall GC-MS/MS pesticide sensitivity.

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