

Application News

No. SSK-GCMS-1903

GC-MS, LC-MS

Gas Chromatograph Mass Spectrometer
Liquid Chromatograph Mass Spectrometer

Analysis of Multi-Residual Pesticides Using GC-MS/MS and LC-MS/MS

식품의약품안전처 고시 제2019-65호 '식품의 기준 및 규격' 중 '7.1.2.2 다중농약다성분 분석법(제2법)' 1)이 개정됨에 따라 기존 GC-MS/MS 및 LC-MS/MS 분석 대상 성분이 395 종에서 473 종으로 확대되었다. GC-MS/MS의 경우에는 기존의 성분 281 종에서 메틸펜타클로로페닐 설파이드(Methyl pentachloro-rophenyl sulfide) 및 펜타클로로아닐린(Pentachloro-roaniline) 2 종이 제외되고, Phorate 대사체 등 총 60 종이 새로 추가되어 322종으로 확대되었으며, LC-MS/MS의 경우에는 기존의 성분 114종에서 아설람(Asulam) 등 10 여종이 제외되고 아바멕틴(Abamectin) 등 50 여종이 추가되어 151종으로 확대되었다. 이에 본 뉴스레터에서는 GC-MS/MS 및 LC-MS/MS를 이용하여 추가된 성분에 대한 MRM 분석조건을 최적화하고 전체 473 종에 대한 동시 분석방법을 확립하고자 하였다.

분석 조건은 아래 <표 1>, <표 3>에 나타내었으며, 분석 대상 성분은 <표 2>, <표 4>에 나타내었다.

GC-MS/MS 장비 구성 및 분석 조건

표 1. 분석조건

System	: GCMS-TQ8050
Column	: SH-Rxi-5Sil MS (30 m x 0.25 mm I.D x 0.25 µm)
GC	
Injection Temp.	: 280 °C
High Press. Inject.	: 250.0 kPa, 1.5 min
Oven Temp.	: 70 °C (3 min) - (20 °C/min) → 180 °C - (5 °C/min) → 330 °C (10 min)
Injection Mode	: Split (10:1)
Carrier Gas	: He
Flow rate	: 0.8 mL/min
Purge Flow	: 5.0 mL/min
MS	
Interface Temp.	: 300 °C
Ion Source Temp.	: 250 °C



그림 1. GC-MS/MS System

표 2. GC-MS/MS 분석 대상 성분 (322 종)

번호	성분명	번호	성분명	번호	성분명	번호	성분명
1	2,6-Diisopropyl-naphthalene	70	Cydoate	141	Fenoxycarb	213	Myclobutanil
2	Acetochlor	71	Cyflufenamid	142	Fenpropathrin	214	Napropamide
3	Acibenzolar-S-methyl	72	Cyfluthrin*	143	Fenson	215	Nitrapyrin
4	Acrinathrin*	73	Cyhalofop butyl	144	Fenthion	216	Nitrothal-isopropyl
5	Alachlor	74	Cyhalothrin*	145	Fenvalerate*	217	trans_Nonachlor
	Aldrin	75	Crotoxyphos	146	Fipronil		cis_Nonachlor
6	Dieldrin	76	Cypermethrin*	147	Flamprop-isopropyl	218	Norflurazon
7	Allethrin*	77	Cyprazine	148	Fonicamid	219	Nuarimol
8	Allidochlor	78	Cyproconazole	149	Fluazifop-butyl	220	Ofurace
9	Ametryn	79	Cyprodinil	150	Fluchloralin	221	Oxadiazon
10	Anilofos	80	Deltamethrin(Tralomethrin)*	151	Flucythrinate*	222	Oxadixyl
11	Aramite*	81	Demeton_S	152	Fludioxonil	223	Oxydemeton-metyl
12	Aspon	82	Demeton_S_methyl_sulfone	153	Flufenpyr_ethyl	224	Oxyfluorfen
13	Atrazine	83	Demeton-O	154	Flumetralin	225	Paclobotrazole
14	Azaconazole	84	Desmetryn	155	Flumidorac_pentyl	226	Parathion-ethyl
15	Azinphos-ethyl	85	Dialifos	156	Flumioxazine	227	Parathion-methyl
16	Azinphos-methyl	86	Diallate*	157	Fluopyram	228	Pebulate
17	a_BHC	87	Diazinon	158	Fluorodifen	229	Penconazole
	b_BHC	88	Dichlobutrazol	159	Flurochloridone	230	Pendimethalin
	r_BHC	89	Dichlofenthion	160	Flurtamone	231	Penflufen
18	d_BHC	90	Dichlofluanid	161	Flusilazole	232	Pentachlorobenzonitrile
19	Benalaxyl	91	Dichlormid	162	Fluthiacet_methyl	233	Penthiopyrad
20	Benodanil	92	Dichlorvos	163	Flutianil	234	Permethrin*
21	Benoxacor	93	Diclofop-methyl	164	Flutolanil	235	Perthane
22	Benzoylprop_ethyl	94	Dicloran	165	Flutriafol	236	Phenothrin*
23	Bifenox	95	Dicofol	166	Fluvalinate*	237	Phenthoate
24	Bifenthrin	96	Diethatyl-ethyl	167	Folpet	238	Phentoxazone
25	Binapacryl	97	Diethofencarb	168	Fonofos	239	Phorate
26	Bromacil	98	Difenoconazole*	169	Fomothion		Phorate oxon
27	Bromobutide	99	Diflufenican	170	Fosthiazate*		Phorate oxon sulfone
28	Bromophos-ethyl	100	Dimepiperate	171	Fthalide		Phorate oxon sulfoxide
29	Bromophos-methyl	101	Dimethachlor	172	Furathiocarb		Phorate sulfone
30	Bromopropylate	102	Dimethametryn	173	Halfenprox		Phorate sulfoxide
31	Bupirimate	103	Dimethenamid	174	Heptachlor	240	Phosalone
32	Butachlor	104	Dimethoate		Heptachlor-epoxide	241	Phosmet(PMP)
33	Butafenacil	105	Dimethylvinphos-(Z)	175	Heptenophos	242	Phosphamidone*
34	Butralin	106	Diniconazole	176	Hexachlorbenzene	243	Picolinafen
35	Butylate	107	Dinitramine	177	Hexaconazole	244	Picoxystrobin
36	Cadusafos	108	Dioxathion	178	Imazalil	245	Piperonyl bitoxide
37	Captafol	109	Diphenamid	179	Indanofan	246	Piperophos
38	Captan	110	Diphenylamine	180	Indoxacarb	247	Pirimicarb
39	Carbophenothion	111	Dithiopyr	181	Iprobenfos	248	Pirimiphos-ethyl
40	Chinomethionat	112	Edifenphos	182	Iprodione	249	Pirimiphos-methyl
41	Chlorbenside	113	a_Endosulfan	183	Iprovalicarb*	250	pp_DDD
42	Chlorobenzilate		b_Endosulfan	184	Isazofos		pp_DDE
43	Chlorbufam		Endosulfan_sulfate	185	Isofenphos		pp_DDT
	Chlordane trans	114	Endrin	186	Isofenphos-methyl		op_DDT
44	Chlordane*	115	EPN	187	Isopropalin	251	Pretilachlor
45	Chlorethoxyfos	116	Epoxiconazole	188	Isoprothiolane	252	Probenazole
46	Chlorfenapyr	117	EPTC	189	Isotianil	253	Prochloraz
47	Chlorfenson	118	Esprocarb	190	Isoxadifen-ethyl	254	Procymidone
48	Chlorfluazuron	119	Etaconazole*	191	Isoxanthion	255	Profenofos
49	Chlorflurenol_methyl	120	Ethalfuralin	192	Kresoxim-methyl	256	Profluralin
50	Chloridazon	121	Ethion	193	Lactofen	257	Prometon
51	Chlornitrofen	122	Ethofumesate	194	Leptophos	258	Prometryn
52	Chloroneb	123	Ethoprophos	195	Malathion	259	Pronamide
53	Chloropropylate	124	Ethychlorate	196	Mecarbam	260	Propachlor
54	Chlorothalonil	125	Etofenprox	197	Mefenacet	261	Propanil
55	Chloroxuron	126	Etoxazole	198	Mefenpyr-diethyl	262	Propazine
56	Chlorpropham	127	Etridiazole	199	Mepronil	263	Propetamphos
57	Chlorpyrifos	128	Etrimfos	200	Metazachlor	264	Propham
58	Chlorpyrifos-methyl	129	Fenamidone	201	Metconazole	265	Propiconazole*
59	Chlorthal-dimethyl	130	Fenamiphos	202	Methidathion	266	Propisochlor
60	Chlorthion	131	Fenarimol	203	Methoprotryne	267	Prothiophos
61	Chlorthiophos*	132	Fenazaquin	204	Methoxychlor	268	Pyracarbolid
62	Chlozolinat	133	Fenbuconazole	205	Methyltrithion	269	Pyraclafos
63	Cinidon-ethyl	134	Fenchlorphos	206	Metolachlor	270	Pyrazophos
64	Cinmethylin	135	Fenclorim	207	Metrafenone	271	Pyridaben
65	Clomazone	136	Fenfuram	208	Metribuzin	272	Pyridalyl
66	Clomeprop	137	Fenitrothion	209	MGK-264*	273	Pyridaphenthion
67	Coumaphos	138	Fenobucarb	210	Mirex	274	Pyrifenox*
68	Cyanazine	139	Fenothiocarb	211	Molinate	275	Pyrimidifen
69	Cyanophos	140	Fenoxanil	212	Monolinuron	276	Pyriminobac-methyl(E)

■ LC-MS/MS 장비 구성 및 분석 조건

표 3. 분석조건

UHPLC System		Nexera X2
Flow	:	0.2 mL/min
Mobile phase	:	(A) Water with 5 mM ammonium acetate and 0.1 % formic acid (B) Methanol with 5 mM ammonium acetate and 0.1 % formic acid
Gradient	:	5 % B (0-1 min) – 60 % B (3 min) – 100 % B (13-18 min) – 5 % B (18.1-23 min)
Column	:	Shim-pack GIST-HP C18 (2.1 x 150 mm., 3 µm)
Column oven	:	40 °C
Injection volume	:	2 µL
MS/MS System		LCMS-8050
Ionization method	:	ESI
Data Acquisition	:	MRM
Nebulizer gas flow	:	3 L/min
Dry gas flow	:	10 L/min
Heating gas flow	:	10 L/min
Interface temp.	:	150 °C
DL temp.	:	250 °C
Heat block temp.	:	400 °C



그림 2. LC-MS/MS System

표 4. LC-MS/MS 분석 대상 성분 (151 종)

번호	성분명	번호	성분명	번호	성분명	번호	성분명
1	Abamectin B1	40	Dicrotophos	79	Isoxaben	116	Pyraclonil
2	Acephate	41	Diflubenzuron	80	Lenacil	117	Pyraclostrobin
3	Acetamiprid	42	Dimethomorph (E, Z)	81	Lufenuron	118	Pyraflufen-ethyl
4	Aldicarb	43	Dinotefuran	82	Malaoxon	119	Pyrazolate
5	Ametoctradin	44	Diuron (DCMU)	83	Mandipropamid	120	Pyribenzoxim
6	Amisulbrom	45	Ethaboxam (EBX)	84	Mepanipyrim	121	Pyributicarb
7	Azamesthiophos	46	Ethiofencarb	85	Mephosfolan	122	Pyridate
8	Azoxystrobin	47	Famoxadone	86	Metalaxyl	123	Pyrifthalid
9	Bendiocarb	48	Fenhexamid	87	Metamifop	124	Pyrimethanil
10	Bensulide	49	Fenoxaprop-P-ethyl	88	Metamitron	125	Pyriproxyfen
11	Benthiavalicarb-isopropyl	50	Fenpyroximate	89	Methabenzthiazuron	126	Pyroquilon
12	Benzobicyclon	51	Fentrazamide	90	Methiocarb	127	Quinoclamine
13	Benzoximate	52	Ferimzone	91	Methomyl	128	Quizalofop-ethyl
14	Bitertanol (diastereo isomers)	53	Fluacrypyrim		Thiodicarb	129	Simazine
15	Bixafen	54	Fluazinam	92	Methoxyfenozide	130	Spinetoram
16	Boscalid	55	Flubendiamide	93	Metolcarb (MTMC)	131	Spinosyn A
17	Buprofezin	56	Flufenacet	94	Metominostrobin (E, Z)		Spinosyn D
18	Butocarboxim	57	Flufenoxuron	95	Milbemectin A3	132	Spirodiclofen
19	Cafenstrole	58	Fluometuron		Milbemectin A4	133	Sulfentrazone
20	Carbaryl (NAC)	59	Fluopicolide	96	Monocrotophos	134	Sulfoxaflor
21	Carbendazim	60	Flupyradifurone	97	Neburon	135	Tebufenozide
22	Carbetamide	61	Fluquinconazole	98	Nitenpyram	136	Tebuthiuron
23	Carbofuran	62	Fluridone	99	Noruron	137	Teflubenzuron
24	Carboxin	63	Fluxapyroxad	100	Novaluron	138	Tepaloxymid (isomer)
25	Carfentrazone-ethyl	64	Forchlorfenuron	101	Omethoate	139	Thenylchlor
26	Carpropamid	65	Hexaflumuron	102	Oxamyl	140	Thiabendazole
27	Chlorantraniliprole	66	Hexazinone	103	Oxaziclomefone	141	Thiacloprid
28	Chlorfenvinphos (E, Z)	67	Hexythiazox	104	Pencycuron	142	Thiamethoxam
29	Chlorimuron-ethyl	68	Imazamox	105	Phenmedipham	143	Thiobencarb
30	Chlorobenzuron	69	Imazapic	106	Phosfolan	144	Tiadinil
31	Chlorotoluron	70	Imazaquin	107	Phoxim	145	Tricyclazole
32	Chromafenozide	71	Imazethapyr	108	Pinoxaden	146	Tridemorph (isomer)
33	Clofentezine	72	Imibenconazole	109	Promecarb	147	Trifloxystrobin
34	Clothianidin	73	Imicyafos	110	Propamocarb	148	2,3,5-Trimethacarb
35	Crufomate	74	Imidacloprid	111	Propaquizafop		3,4,5-Trimethacarb
36	Cyazofamid	75	Ipconazole	112	Propoxur	149	Triticonazole
37	Cycloprothrin	76	Isoprocarb	113	Proquinazid	150	Vamidothion
38	Cymoxanil	77	Isoproturon	114	Prosulfocarb	151	XMC
39	Daimuron	78	Isopyrazam	115	Prothioconazole		

■ 잔류농약 473종에 대한 크로마토그램

〈그림 3〉은 GC-MS/MS 분석 대상 성분 322종 (10 ng/mL)에 대한 크로마토그램이며, 〈그림 4〉는 LC-MS/MS 분석 대상 성분 151종 (10 ng/mL)에 대한 크로마토그램으로 다성분 동시 분석시에도 우수한 감도와 분리능을 보여주는 것을 확인할 수 있다.

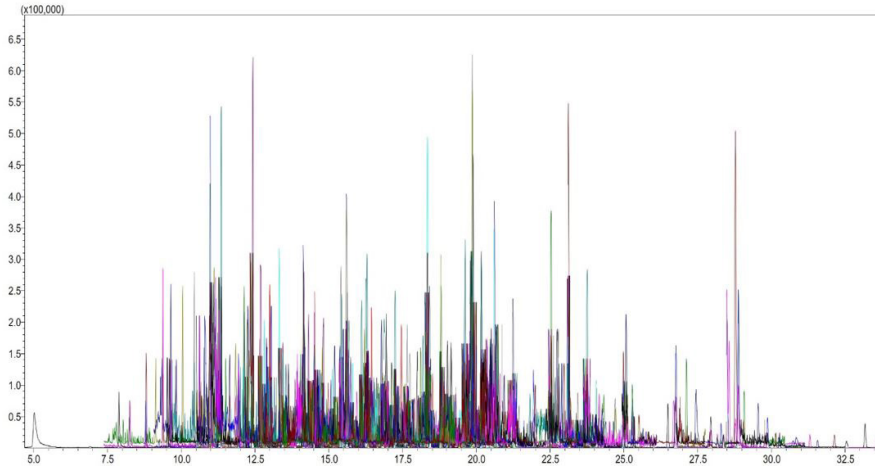


그림 3. GC-MS/MS 잔류농약 322종 동시 분석 크로마토그램 (10 ng/mL)

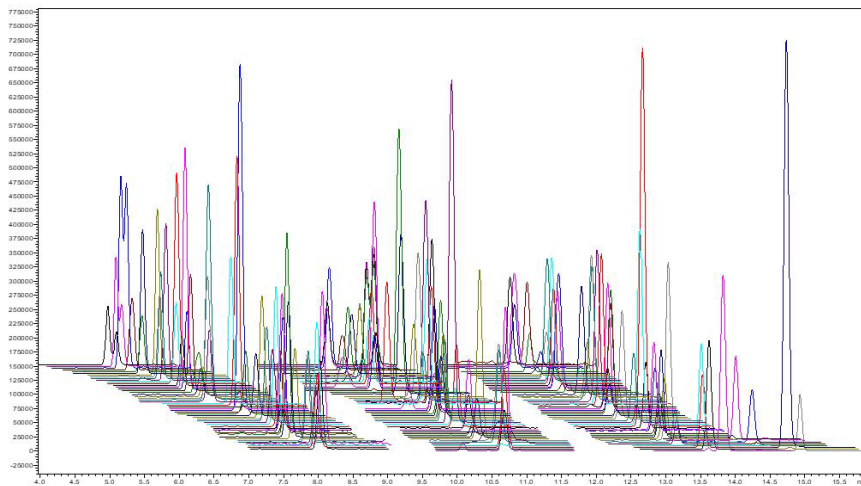


그림 4. LC-MS/MS 잔류농약 151종 동시 분석 크로마토그램 (10 ng/mL)

■ 결론

Shimadzu GCMS-TQ8050의 Smart MRM Optimization 기능과 Shimadzu LCMS-8050 triple quadrupole mass spectrometer의 scheduled MRM 기능을 이용하여 식품의약품안전처 고시 제2019-65호 '식품의 기준 및 규격' 중 7.1.2.2 다중농약다성분 분석법(제2법) 분석 대상 473 종에 대한 다성분 동시분석법을 확립하였다.

■ 참고문헌

- 1) 식품의약품안전처 고시 제2019-65호, 식품의 기준 및 규격 (2019. 7. 25)