

Application News

No. SSK-GCMS-2103

GC-MS & LC-MS
Gas Chromatograph Mass Spectrometer
Liquid Chromatograph Mass Spectrometer

식품의약품안전처 ‘식품의 기준 및 규격’에 따른 GC-MS/MS 및 LC-MS/MS를 이용한 잔류농약 다성분 분석

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

□ 연구 배경

식품의약품안전처 고시 제2021-54호 ‘식품의 기준 및 규격’ 중 ‘7.1.2.2 다성분 시험법-제2법’이 개정됨에 따라 규제 대상 농약 성분의 수가 473 종에서 511 종으로 확대되었다. GC-MS/MS 대상 성분은 기존 322 종 중, Phorate 대사체를 포함해 총 80 여종의 성분이 제외되고, 신규로 EMA((2-ethyl-6-methylaniline)를 포함한 41 종이 추가되어 총 273 종으로 축소되었으며, LC-MS/MS 대상 성분은 기존 151 종 중, 뷰프로페진(Buprofezin) 등 30 여종이 제외되고 신규로 알레트린(Allethrin) 등 150여 종이 추가되어 총 238 종으로 확대되었다. 이에 이 뉴스레터에서는 ‘식품의 기준 및 규격’의 규제 대상 성분 511 종에 대해 GC-MS/MS(그림 1)와 LC-MS/MS(그림 2)를 이용하여 분석 방법을 확립하고자 하였다. 분석 조건 및 대상 성분은 아래 <표 1> - <표 4>에 나타내었다.

□ GC-MS/MS 장비 구성 및 분석 조건



그림 1. GC-MS/MS System

표 1. GC-MS/MS 분석 조건

GC System	Nexis GC-2030
Analytical column	: SH-Rtx-5 (30 m x 0.25 mm, 0.25 µm)
Carrier gas	: He (99.999%)
Column Flow	: 1.2 mL/min
Injection temp.	: 280 °C
Carrier gas	: Splitless
Flow control	: Linear velocity (40.0 cm/sec)
	: 60 °C → 20 °C/min → 180 °C (4 min) → 5 °C /min → 300 °C → 5 °C/min → 310 °C (2 min)
Injection mode	: High pressure injection (250 kPa, 1.5 min)
Injection volume	: 1 µL
MS/MS system	GCMS-TQ8050
Ionization method	: EI
Interface Temp.	: 320 °C
Ion Source Temp.	: 230 °C
Acquisition Mode	: MRM

□ LC-MS/MS 장비 구성 및 분석 조건



그림 2. LC-MS/MS System

표 2. LC-MS/MS 분석 조건

UHPLC System	Nexera X3
Flow	: 0.2 mL/min
Mobile phase (A)	: Water with 5 mM ammonium acetate and 0.1 % formic acid
Mobile phase (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 (2.1x150 mm., 3 µm)
Column oven	: 40 °C
Injection volume	: 2 µL
MS/MS System	LCMS-8060NX
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
Desolvation Line temp.	: 250 °C
Heat block temp.	: 400 °C

표 3. GC-MS/MS 분석 대상 성분 (273종)

No.	Name	No.	Name	No.	Name	No.	Name
1	2,6-DIPN, 2,6-Diisopropyl-naphthalene	67-3	o,p'-DDT	134-1	Flucythrinate, Iso. 1**	203	Phosalone
2-1	Acetochlor	67-4	p,p'-DDT	134-2	Flucythrinate, Iso. 2**	204	Phosmet
2-2	EMA2-ethyl-6-methylaniline	68-1	Deltamethrin	135	Fluensulfone	205	Phthalide, Fthalide
2-3	HEMA2-1-hydroxyl-ethyl-6-methyl-aniline	68-2	Tralomethrin	136	Flufenpyr-ethyl	206	Picoxystrobin
3	Acrinathrin	69	Desmetryn	137	Flumetralin	207	Piperonyl butoxide
4	Alachlor	70	Dialifor	138	Flumioxazin	208	Pirimicarb
5-1	Aldrin	71	Diallate	139	Fuopyram	209	Pirimiphos-ethyl
5-2	Dieldrin	72	Diazinon	140	Fluorochloridone	210	Pirimiphos-methyl
6	Allidochlor	73	Dichlobenil	141	Fluquinconazole	211	Pretilachlor
7	Ametryn	74	Dichlofenthion	142	Flusilazole	212-1	Prochloraz
8	Anilofos	75	Dichlofluamid	143	Flutianil	212-2	2,4,6-trichlorophenol
9	Aramite	76	Dichlormid	144-1	Fluvalinate, Iso. 1	213	Procymidone
10	Aspon	77	Diclobutrazol	144-2	Fluvalinate, Iso. 2	214	Prodiamine
11	Atrazine	78	Diclofop-methyl	145	Fluxapyroxad	215	Profenofos
12	Azaconazole	79	Dicloran**	146	Fonofos	216	Profluralin
13	Benfluralin	80	Dicofol	147	Formothion	217	Prohydrojasmon
14	Benfuresate	81	Dicrotophos	148	Halfenprox	218	Prometon
15	Benodanil	82	Diethatyl-ethyl	149-1	Heptachlor	219	Prometryn
16	Benzoylprop-ethyl	83	Diethofencarb	149-2	Heptachlor epoxide	220	Propachlor
17-1	α-BHC	84	Difenoconazole	150	Heptenophos	221	Propanil
17-2	β-BHC	85	Diflufenican	151	Hexythiazox	223	Propetamphos
17-3	δ-BHC	86	Dimepiperate	152	Indanofan	222	Propazine
18	Lindane, γ-BHC	87	Dimethachlor	153	Indoxacarb**	223	Propetamphos
19	Bifenox	88	Dimethametryn	154	Ipconazole	224	Propham
20	Bifenthrin	89	Dimethenamid	155	Iprobenfos	225-1	Propiconazole, Iso. 1
21	Boscalid	90	Dimethipin*	156	Iprodione*	225-2	Propiconazole, Iso. 2
22	Bromobutide	91-1	Dimethomorph E*	157	Isazofos	226	Propisochlor
23	Bromophos-methyl	91-2	Dimethomorph Z*	158	Isofenphos	227	Propyzamide
24	Bromophos-ethyl	92-1	Dimethylvinphos E	159	Isofenphos-methyl	228	Prothiofos
25	Bromopropylate	92-2	Dimethylvinphos Z	160	Isoprocarb	229	Pyracarbolid
26	Bupirimate	93	Diniconazole	161	Isopropalin	230	Pyraclufos
27	Buprofezin	94	Dinitramine	162	Isoprothiolane	231	Pyraflufen-ethyl
28	Butachlor	95	Dioxathion	163	Isopyrazam	232	Pyrazophos
29	Butafenacil	96	Diphenamid	164	Isotianil	233	Pyridalyl
30	Butralin	97	Diphenylamine	165	Isoxadifen-ethyl	234	Pyrifenox
31	Butylate	98	Dithiopyr	166	Kresoxim-methyl	235	Pyritalid
32	Cadusafos	99	Edifenphos*	167	Leptophos	236	Pyrimethanil
33	Carbophenothion	100-1	α-Endosulfan	168	Mefenpyr-diethyl	237-1	Pyriminobac-methyl E
34	Carboxin	100-2	β-Endosulfan	169	Mepanipyrim	237-2	Pyriminobac-methyl Z
35	Carfentrazone-ethyl	100-3	Endosulfan sulfate	170	Mepronil	238	Quinalphos
36	Chinomethionat	101-1	Endrin	171	Metalaxyl	239	Quinoxifen
37	Chlorbenside	101-2	δ-keto-Endrin	172	Methidathion	240	Quintozene
38	Chlorbufam	102	EPN	173	Methoprotryn	241	Quizalofop-ethyl
39-1	Chlordane-cis	103	Epoxiconazole	174	Methoxychlor	242	Silafluofen
39-2	Chlordane-trans	104	EPTC	175	Methyl trithion	243	Simeconazole
40	Chlorethoxyfos	105	Etaconazole	176	Metolachlor	244	Simetryn
41	Chlorfenapyr	106	Ethalfuralin	177	Metribuzin	245	Spiromesifen
42	Chlorfenson	107	Ethion	178	MGK-264	246	Spiroxamine
43	Chlorflurenol-methyl	108	Ethofumesate	179	Molinate*	247	Sulfotep
44	Chlornitrofen	109	Ethoprophos	180	Monolinuron	248	Tebuconazole
45	Chlorobenzilate	110	Ethychozate	181	Myclobutanil	249	Tebufenpyrad
46	Chloropropylate	111	Etoxazole	182	Nitrapyrin	250	Tebupirifos
47	Chloroneb	112	Etridiazole	183	Nitrothal-isopropyl	251	Tecnazene
48	Chlorothalonil	113	Fenamidone	184-1	Nonachlor-cis	252	Tefluthrin
49	Chlorpropham	114	Fenarimol	184-2	Nonachlor-trans	253	Terbacil
50	Chlorpyrifos	115	Fenbuconazole	185	Nuarimol	254	Terbutometon
51	Chlorpyrifos-methyl	116	Fenchlorphos	186	Ortho-phenyl phenol	255	Terbutryn
52	Chlorthal-dimethyl	117	Fenclorim**	187	Oxadiazon	256	Tetrachlorvinphos
53	Chlorthion	118	Fenfuram	188	Oxadixyl	257	Tetraconazole
54	Chlorthiophos	119	Fenitrothion	189	Oxyfluorfen	258	Tetradifon
55	Chlozolinate	120	Fenobucarb	190	Paclobutrazol	259	Tetramethrin
56	Cinmethylin	121	Fenothiocarb	191	Parathion	260	Thifluzamide
57	Clomazone	122	Fenoxanil**	192	Parathion-methyl	261	Thiometon
58	Coumaphos	123	Fenpropathrin***	193	Penconazole	262	Thionazin
59	Cyanophos	124	Fenpropimorph	194	Pendimethalin	263	Tolclofos-methyl
60	Cyflufenamid	125	Fenpyrazamine	195	Penflufen	264	Triadimefon
61	Cyfluthrin	126	Fenson	196	Pentachlorobenzonitrile	265	Triadimenol
62	Cyhalofop-butyl	127	Fenthion	197	Penthiopyrad	266	Tri-allate
63-1	γ-Cyhalothrin	128-1	Fenvalerate, Iso. 1*	198	Pentoxazone	267	Triazophos
63-2	λ-Cyhalothrin	128-2	Fenvalerate, Iso. 2*	199-1	Permethrin-cis	268	Tridiphane
64	Cypermethrin	129	Fipronil	199-2	Permethrin-trans	269	Trifloxystrobin
65	Cyprazine	130	Flamprop-isopropyl	200	Perthane	270	Triflumizole
66	Cyprodinil	131	Fluacrypyrim	201	Phenthoate	271	Trifluralin
67-1	p,p'-DDD	132	Fluazifop-butyl	202-1	Phosphamidon E	272	Vinclozolin
67-2	p,p'-DDE	133	Fluchloralin	202-2	Phosphamidon Z	273	Zoxamide

표 4. LC-MS/MS 분석 대상 성분 (238종)

No.	Name	No.	Name	No.	Name	No.	Name
1-1	2,3,5-Trimethacarb	58	Demeton-S-methyl-sulfone	123	Mefenacet	181	Pyraclostrobin
1-2	3,4,5-Trimethacarb	59-1	Dichlorvos	124	Mefentrifluconazole	182	Pyraziflumid
2	Abamectin B1	59-2	Trichlorfon	125	Mephosfolan	183	Pyrazolate
3	Acephate	60	Diclosulam	126	Mesotrione	184	Pyrazoxyfen
4	Acetamiprid	61	Diflubenzuron	127-1	Metaflumizone (E)	185-1	Pyribencarb
5	Aldicarb	62	Dimethoate	127-2	Metaflumizone (Z)	185-2	KIE-9749
6	Allethrin	63	Dinotefuran	128	Metamifop	186	Pyribenzoxim
7	Ametoctradin	64	Diuron (DCMU)	129	Metamitron	187	Pyributicarb
8	Amisulbrom	65	Dodine	130	Metconazole	188	Pyridaben
9	Amitraz	66	Emamectin B1a	131	Methabenzthiazuron	189	Pyridaphenthion
10	Azamethiphos	67	Esprocarb	132	Methamidophos	190	Pyridate
11	Azinphos-methyl	68	Ethaboxam (EBX)	133	Methiocarb	191	Pyrifluquinazon
12	Azoxystrobin	69	Ethiofencarb	134	Methomyl	192	Pyrimidifen
13	Benalaxyl	70	Etofenprox	134	Thiodicarb	193	Pyrimisulfan
14	Bendiocarb	71	Etrimfos	135	Methoxyfenozide	194	Pyriofenone
15	Bensulide	72	Famoxadone	136	Metobromuron	195	Pyriproxyfen
16-1	Benthiavalicarb-isopropyl (R)	73-1	Fenamiphos	137	Metolcarb (MTMC)	196	Pyroquilon
16-2	Benthiavalicarb-isopropyl (S)	73-2	Fenamiphos-sulfone	138-1	Metominostrobin (E)	197	Quinoclamine
17	Benzobicyclon	73-3	Fenamiphos-sulfoxide	138-2	Metominostrobin (Z)	198	Saflufenacil
18	Benzoximate	74	Fenazaquin	139	Metrafenone	199	Secbumeton
19	6-Benzyl aminopurine	75	Fenhexamid	140	Mevinphos	200-1	Sedaxane-cis
20	Bioresmethrin	76	Fenoxaprop-P-ethyl	141	Monocrotophos	200-2	Sedaxane-trans
21	Bistrifluron	77	Fenoxycarb	142	Napropamide	201	Sethoxydim (isomer)
22	Bitertanol (diastereo isomers)	78	Fenpyroximate	143	Neburon	202	Simazine
23	Bixafen	79	Fensulfothion	144	Nitenpyram	203-1	Spinetoram J
24	Bromacil	80	Fentrazamide	145	Norflurazon	203-2	Spinetoram L
25	Butocarboxim	81-1	Ferimzone (E)	146	Noruron	204-1	Spinosyn A
26	Cafenstrole	81-2	Ferimzone (Z)	147	Novaluron	204-2	Spinosyn D
27	Carbaryl (NAC)	82	Fonicamid	148	Ofurace	205	Spirodiclofen
28	Carbendazim	83	Fluazinam	149	Omethoate	206	Spirotetramat
29	Carbetamide	84	Flubendiamide	150	Oryastrobin	206	Spirotetramat-enol
30	Carbofuran	85	Fludioxonil	151	Oryzalin	207	Sulfentrazone
30	3-Hydroxycarbofuran	86	Flufenacet	152	Oxadiazargyl	208	Sulfoxaflor
30	Furathiocarb	87	Flufenoxuron	153-1	Oxamyl	209	Sulprofos
31	Carpropamid	88	Fluometuron	153-2	Oxamyl oxime	210	Tebufenozide
32	Chlorantraniliprole	89	Fluopicolide	154	Oxathiapiprolin	211-1	Tebufloquin
33-1	Chlorfenvinphos (E)	90	Flupoxam	155	Oxaziclomefone	211-2	Tebufloquin M1
33-2	Chlorfenvinphos (Z)	91	Flupyradifurone	156	Oxycarboxin	212	Tebuthiuron
34	Chlorfluazuron	92	Fluridone	157	Oxydemeton-methyl	213	Teflubenzuron
35	Chloridazone	93	Flusulfamide	158	Pebulate	214	Tepraloxydim (isomer)
36	Chlorobenzuron	94	Fluthiacet-methyl	159	Pencycuron	215-1	Terbufos
37	Chlorotoluron	95	Flutolanil	160	Penoxsulam	215-2	Terbufos oxon
38	Chloroxuron	96	Flutriafol (isomer)	161	Phenmedipham	215-3	Terbufos oxon sulfone
39	Chromafenozide	97	Fluxametamide	162-1	Phenothrin-cis	215-4	Terbufos oxon sulfoxide
40	Clofentezine	98	Fomesafen	162-2	Phenothrin-trans	215-5	Terbufos-sulfone
41	Clomeprop	99	Forchlorfenuron	163-1	Phorate	215-6	Terbufos-sulfoxide
42	Clothianidin	100	Fosthiazate (isomer)	163-2	Phorate oxon	216	Terbutylazine
43	Crotoxyphos	101	Hexaconazole	163-3	Phorate oxon sulfone	217	Tetraniliprole
44	Cruformate	102	Hexaflumuron	163-4	Phorate oxon sulfoxide	218	Thenylchlor
45	Cyanazine	103	Hexazinone	163-5	Phorate-sulfone	219	Thiabendazole
46	Cyantraniliprole	104	Imazalil	163-6	Phorate-sulfoxide	220	Thiacloprid
47	Cyazofamid	105	Imibenconazole	164	Phosfolan	221	Thiamethoxam
48-1	Cyclaniliprole	106	Imicyafos	165	Phoxim	222	Thiazopyr
48-2	NK-1375	107	Imidacloprid	166-1	Picarbutrazox	223	Thidiazuron
49	Cycloate	108	Inabentfide	166-2	TZ-1E	224	Thiobencarb
50	Cycloprothrin	109	Ipfencarbazone	167	Picolinafen	225	Tiadinil
51	Cyenopyrafen	110	Iprovalicarb	168	Piperophos	226	Tolfenpyrad
52	Cyflumetofen	111	Isoproturon	169	Probenazole	227	Triafamone
53	Cymoxanil	112	Isoxaben	170	Promecarb	228	Triazamate
54-1	Cyproconazole (I)	113	Isoxathion	171	Propamocarb	229	Tribufos
54-2	Cyproconazole (II)	114	Lenacil	172	Propaquizafop	230	Tricyclazole
55	Daimuron	115-1	Lepimectin A3	173	Propargite	231	Triflumuron
56-1	Demeton-O	115-2	Lepimectin A4	174	Propoxur	232	Triforine (isomer)
56-2	Demeton-S	116	Linuron	175	Proquinazid	233	Triticonazole
56-3	Demeton-S-sulfone	117	Lufenuron	176	Prosulfocarb	234	Uniconazole
56-4	Demeton-S-sulfoxide	118	Malaoxon	177	Pydiflumetofen	235	Valifenalate
56-5	Disulfoton	119	Malathion	178	Pyflubumide	236	Vamidothion
56-6	Disulfoton-sulfone	120	Mandestrobin	178	Pyflubumide-NH	237	Vernolate
56-7	Disulfoton-sulfoxide	121	Mandipropamid	179	Pymetrozine	238	XMC
57	Demeton-S-methyl	122	Mecarbam	180	Pyraclonil		

□ 잔류농약 511 종에 대한 크로마토그램

<그림 3>은 GC-MS/MS 분석 대상 성분 273종 (10 ng/mL)에 대한 크로마토그램이며, <그림 4>는 LC-MS/MS 분석 대상 성분 238종 (10 ng/mL)에 대한 크로마토그램으로 다성분 동시 분석시에도 우수한 감도와 분리능을 보여주는 것을 확인할 수 있다.

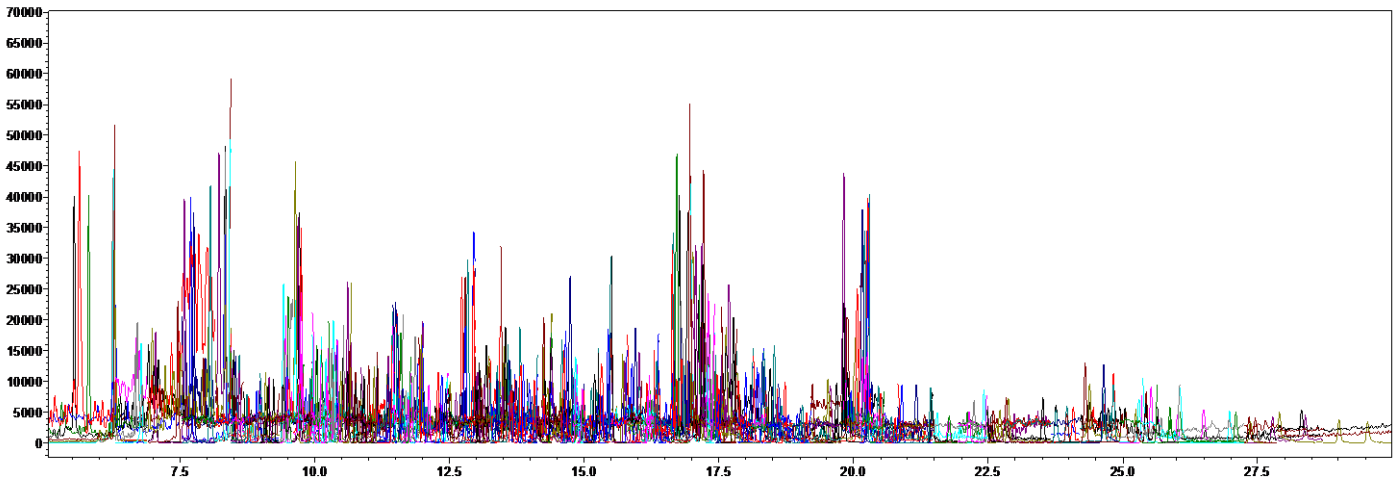


그림 3. GC-MS/MS 잔류농약 273 종 동시 분석 크로마토그램 (10 ng/mL)

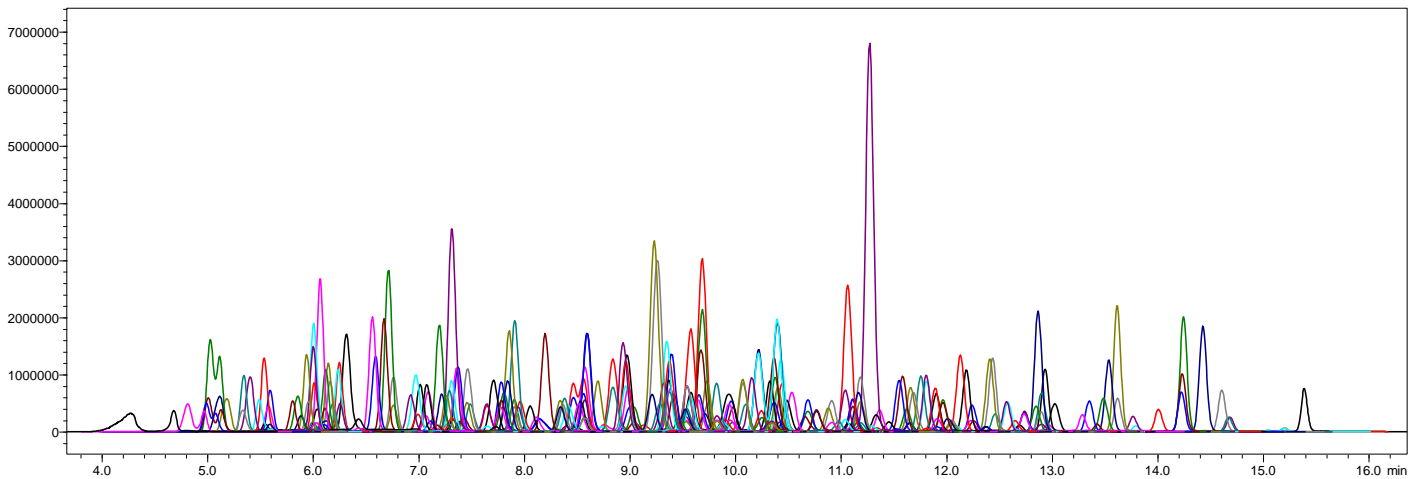


그림 4. LC-MS/MS 잔류농약 238 종 동시 분석 크로마토그램 (10 ng/mL)

□ 결론

Shimadzu GCMS-TQ8050의 Smart MRM Optimization 기능 및 Shimadzu LCMS-8060NX의 Scheduled MRM 기능을 활용하여 잔류농약 다성분 동시분석법을 최적화하였으며, 이를 이용하여 식품의약품안전처 고시 제 2021-54호 '식품의 기준 및 규격' 중 7.1.2.2 다성분 시험법-제2법 분석 대상 성분 511 종에 대한 동시 분석 방법을 확립하였다.

□ 참고문헌

- 1) 식품의약품안전처 고시 제 2021-54호 식품의 기준 및 규격 (21.6.29)



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