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GC-MS/MS와 LC-MS/MS를 이용한 생약재 중 261종 농약의 동시분석

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Development of Multi-residue Analytical Method for 261 Pesticides in Herbal Medicines using GC-MS/MS and LC-MS/MS

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Abstract

BACKGROUND: A new analytical method has been developed to determine 261 pesticide residues in herbal medicines.

METHODS AND RESULTS: The extraction of pesticides was carried out by modified method of the Korea Food Standards Codex sample extraction and determination was performed using GC-MS/MS and LC-MS/MS. During the pre-treatment process of the test method, Solid-liquid separation was changed to centrifugation. The method was validated by the precision and accuracy results. 261 pesticides spiked at three level 20, 50, 100 ug/kg in herbal medicines. The limit of quantification of method were 4-40 ug/kg for GC-MS/MS and 2-45 ug/kg for LC-MS/MS, respectively. Among the pesticides analysed by GC-MS/MS and LC-MS/MS, 244 pesticides (94% of total number) in chinese matrimony vine and 224 pesticides (86% of total number) in korean angelica root and 231 pesticides (89% of total number) in jujube and 214 (82% of total number) in cnidium showed recoveries in the range of 70-120% with RSD ≤ 20%.

CONCLUSION: These results indicated that GC-MS/MS and LC-MS/MS analysis with the sample extraction in this study can be applied to multi-residue analysis of pesticides in herbal medicines.

Key words: GC-MS/MS, Herbal Medicine, LC-MS/MS, MRL, Pesticide

서론

생약재는 약용식물의 특정 부위 또는 전체를 건조한 것으로 예로부터 동양의학과 함께 질병의 예방이나 상처의 치료에 많이 사용되어 왔다. 하지만, 생약재 재배시에 발생하는 병해충 및 잡초의 효율적인 방제를 위해 유기합성농약을 사용하게 되는데 사용된 농약은 수확 후 건조된 생약재에까지 잔류할 가능성이 있다. 뿐만 아니라, 외국으로부터 수입되는 생약재에는 각 나라별로 사용하는 농약의 종류가 달라 우리나라에 등록되어 있지 않은 농약이 검출되는 문제점도 있기 때문에 생약재로부터 잔류농약을 분석하여 관리하는 것은 매우 중요한 일이라고 할 수 있다[1-5].

서울시 보건환경연구원에서 2003-2015년까지 매년 약령시장에서 유통되는 국산 및 수입 생약재의 잔류농약 오염실태를 모니터링한 보고서에 의하면 생약재 중 잔류농약 모니터링 검사 건수 대비 검출율은 진피, 구기자, 대추, 인삼, 천궁 순으로 나타났다. 또한 천궁의 경우 매년 부적합이 8% 이

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상으로 endosulfan이 MRL의 약 25배까지 검출되거나 천궁에 등록되지 않은 농약성분인 hexaconazole, pendimethalin, triadimefon이 검출되는 등 품목별로 미등록된 농약들이 사용되고 있음을 알 수 있었다(서울시 보건환경연구원 2003-2015). 따라서 생약재는 잔류농약에 대한 안전성이 매우 취약한 농산물로 효율적인 안전관리를 위해서 잔류농약에 대한 지속적인 연구와 모니터링이 필요하다.

농산물에 있어 잔류농약 분석은 극미량의 잔류농약을 측정하는 기술로 전처리법과 기기분석으로 이루어진다. 잔류농약 분석은 1960년도 미국 FDA에서 잔류농약분석법의 기초를 처음 마련하였으며, 현재까지 수많은 농약 물질의 분석 전처리법과 분석장비가 등장하고 있다[6]. 미국 AOAC (Association of Analytical Communities)에서는 2007년 1월부터, 유럽 표준위원회에서는 2007년 10월부터 QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe)법을 유럽 품질표준규격 (European Standard: EN 15662)로 인정하였다[7]. QuEChERS 법이 등장한 이래로 세계적으로 이 전처리법을 이용하여 농산물별, 농약 종류별, 분석장비별로 최적의 방법을 찾으려는 많은 검증이 이루어지고 있다[8]. 현재 국내에서도 다중농약다성분 분석법들이 많이 개발되어 사용되고 있으며, 대표적으로 식품공전 중 다중농약다성분 분석법-제2법(MFDS, 2017)과 농산물품질관리원의 농산물 등의 유해물질 분석법 (MOLEG, 2020) 등이 있다. 식품공전 중 다중농약다성분 분석법-제2법 및 농산물품질관리원의 농산물 등의 유해물질 분석법은 acetonitrile 추출법으로 전처리한 후 GC-MS/MS, LC-MS/MS를 활용하여 기기분석하는 방법으로 유사성을 갖고 있다.

생약재 중 잔류농약 분석법의 연구는 매우 적다. 이로 인해 생약재 중 잔류농약 분석은 다양하게 연구되어진 농산물이나 식품 중의 잔류농약 분석법을 주로 응용하고 있는 실정이다. 생약재에는 일반적인 농산물에 비해 다양한 화학 성분들이 함유되어 있어 잔류농약 분석시 농약 성분의 추출 및 분리가 어렵기 때문에 시료의 전처리에서부터 분석법 그리고 결과의 해석까지 매우 세심한 주의가 필요하다. 현재 식품의약품안전처에서는 생약재 중 잔류농약의 분석을 위하여 '생약 등의 잔류·오염물질 기준 및 시험방법'을 고시하고 있다. 생약재 시료를 acetone으로 추출하여 여과한 다음 dichloromethane을 이용하여 액/액 분배(liquid-liquid extraction)를 하고 고상추출법(solid phase extraction)으로 정제과정을 거친 후 기기분석하는 방법이다. 하지만 이러한 방법을 생약재에 적용하여 실험할 경우 생약재의 종류에 따라 추출, 분배, 정제 및 기기분석 등 복잡한 일련의 과정을 거치기 때문에 많은 시간과 경비가 소모되고 오차의 발생요인이 커져서 이 방법으로는 모든 생약과 농약을 적용하는데 어느 정도 한계가 있는 것으로 나타났다. 실제로 2009-2012년도 식품의약품안전처 보고서에 의하면 기존에 고시된 생약재 중의 다중농약다성분 분석법은 액/액 분배시 층분리가 잘 되지 않아 농약의 분리가 용이하지 않았으며, 기기분석 상에서 간섭피크가 많이 발생하여 회수율 및 재현성이 떨어지는 것으로 나타나 좀 더 정밀하고 정확한 분석법의 개선이 필요하다고 서술하였다. 이

를 개선하고자 다중농약다성분 분석 성분 중 적용하기 어려운 성분들을 대상으로 물리화학적 특성을 조사하였고 생약재의 종류별 특성을 고려해 생약재 품목별로 특화된 단성분 분석법을 제시하였다(MFDS, 2009-2012).

따라서 본 연구는 생약재 품목 중 약용부위별 잔류농약 검출 빈도가 비교적 높은 당귀(當歸, *Angelica gigas Nakai*), 천궁(川芎, *Cnidii Rhizoma*), 구기자(枸杞子, *Lycii Fructus*), 대추(待秋, *Zizyphi Fructus*)를 대상으로 식품공전 중 다중농약다성분 분석법-제2법의 전처리 방법을 일부 변형하여 전처리한 후 GC-MS/MS와 LC-MS/MS를 이용하여 각각의 기기분석 조건을 확립한 후 분석하여 다중농약다성분 분석법의 생약재 중 적용가능성을 검증하고자 하였다.

재료 및 방법

다성분 분석대상 농약 및 시약

시험대상 농약은 생약재 중 잔류허용기준이 설정된 성분을 포함 비교적 검출이력이 높은 fungicide 70성분, herbicide 56성분, insecticide 129성분, insect growth regulator 2성분, plant growth regulator 2성분, nematocidal 1성분, acaricide 1성분 등 총 261성분이었다. 분석에 사용한 표준품은 Dr. Ehrenstorfer (Germany), Sigma-Aldrich (USA), Wako (Japan), AccuStandard® (USA)에서 구입하여 사용하였다. 각각의 농약 표준품은 용매에 따른 용해도를 고려하여 acetone과 methanol으로 1,000 mg/L의 stock solution을 제조하였다. 각각의 stock solution은 일정량을 취한 후 acetone과 methanol로 표선하여 10 mg/L 혼합 working solution을 제조하였다. 시험에 사용한 acetone, acetonitrile, dichloromethane, methanol, hexane은 Merck (Germany)사의 잔류분석용 시약을 구입하여 사용하였으며, 3차 증류수는 Milipore사의 Mili-Q Direct8 system (USA)을 사용하였다. Sodium chloride 및 magnesium sulfate는 Merck (Germany)사의 제품을 구입하여 사용하였다.

시료전처리 방법

생약재 중 잔류농약을 분석하기 위한 전처리방법은 적은 양의 시료를 짧은 시간동안 진탕추출하기 때문에 균질화된 시료의 확보가 무엇보다 중요하다. 따라서 균질화 측면에서 전처리 시험방법은 식품공전 중 다중농약다성분 분석법-제2법을 변형하여 사용하였다(MFDS, 2017). 식품공전 시험법 중 추출 후 감압여과 대신 원심분리를 통한 전처리방법을 적용하였다. 시험에 사용된 생약재 시료는 분쇄기를 이용하여 균질화한 후 blank 시료 및 회수율 시험에 사용하였다. 균질화된 당귀, 천궁, 구기자, 대추 각각의 시료 10 g을 200 mL centrifuge용 bottle에 넣고 증류수 40 mL를 첨가하여 1시간 동안 습윤 시킨 후 acetonitrile 50 mL 넣고 NaCl 1 g 및 MgSO₄ 4 g을 첨가하여 10분간 진탕 추출하였다. 각 추출 물을 원심분리기(Avanti J-15R, Beckman coulter, USA)로 3,000 rpm에서 5분간 원심분리하였다. 이 후 상층액 20 mL

를 50 mL 시험관에 분취하여 40°C 이하 수욕조에서 감압농축 후 농축잔류물을 dichloromethane:methanol=95:5(v/v) 2 mL로 재용해하였다. NH₂ SPE cartridge (1 g/6 mL, Waters, USA)에 dichloromethane 5 mL로 pre-washing 한 후 상기 시료 2 mL를 loading하고 dichloromethane:methanol=90:10(v/v) 10 mL를 용출시켜 40°C 이하 수욕조에서 감압 농축하였다. 농축잔류물은 GC-MS/MS 분석대상 농약의 경우 acetone: hexane=20:80(v/v) 2 mL에 재용해 하였으며, LC-MS/MS 분석대상 농약의 경우 methanol 2 mL에 재용해한 후 0.2 µm syringe (PTFE) filter (Whatman®, USA)로 여과한 후 분석시료로 사용하였다. 농약성분의 정량 분석을 위한 검량선은 각각의 표준품을 각각의 용매에 녹여 1,000 mg/L의 stock solution을 조제한 후 무처리 시료 추출액과 혼합하여 10, 20, 50, 100, 200 및 500 µg/L 농도로 matrix matched calibration을 작성하였다.

기기분석 조건 확립

GC-MS/MS 분석은 SCION-TQ (Bruker, USA) 기기를 사용하였고, 데이터 처리는 MS Work Station 8을 사용하였다. 컬럼은 DB-5MS (30 m × 0.25 mm × 250 µm, Agilent,

USA)을 사용하였고 oven 온도를 70°C에서 시작하여 승온 프로그램을 설정하여 300°C까지 올려 34.5분 이내에 모든 농약성분이 분리되도록 하였다. 시료 주입량은 1 µL로 하였다. LC-MS/MS 분석은 XEVO-TQD (Waters, USA) 기기를 사용하였고, 데이터 처리는 massHunter quantitative analysis 소프트웨어를 사용하였다. 컬럼은 역상 칼럼인 BEH-C18 (2.5 mm I.D × 100 mm L, 1.7 µm, waters, USA)을 사용하였고 0.1% formic acid가 함유된 acetonitrile과 0.1% formic acid가 함유된 증류수를 사용하여 최적화된 기울기 용리방식으로 12분 이내에 모든 농약 성분이 분리되도록 하였다. 유속은 0.4 mL/min, 주입량은 2 µL로 하였다. 간섭물질의 방해를 배제하고 정량적인 분석이 가능한 multiple reaction monitoring (MRM) 조건을 설정하고자 261성분의 각각의 농약을 acetone 과 methanol을 사용하여 100 µg/L 수준으로 희석하였고 full scan mode에서 각 물질의 모분자(precursor ion)의 질량스펙트럼을 확인한 후 최적의 충돌에너지(collision energy)를 선택하여 생성된 조각이온(daughter ion) 중 최적의 이온을 선택하였다. GC-MS/MS 분석대상 농약 102종과 LC-MS/MS 분석대상 농약 159종에 대한 MRM조건은 각각 Table 1과 2에 나타내었다.

Table 1. Parameters for 102 pesticides residue analysis by GC-MS/MS

No.	Compound	Retention time (min)	Parent ion (m/z)	Quantitative ion (m/z)	Collision energy (V)	Quantitative ion (m/z)	Collision energy (V)
1	Alachlor	14.8	188	131	15	160	15
2	Aldrin	16.1	263	193	30	226	20
3	BHC-α	12.4	181	145	15	109	15
4	BHC-β	13.0	181	109	15	145	15
5	BHC-δ	13.2	181	145	25	109	25
6	BHC-γ	13.2	181	145	10	109	10
7	Bifenthrin	22.4	181	166	20	167	20
8	Bromobutide	14.6	119	91	10	65	30
9	Bromopropylate	23.5	341	183	15	185	15
10	Butachlor	17.2	176	147	15	134	15
11	Cadusafos	12.1	159	131	15	97	15
12	Captan	17.6	149	70	20	79	20
13	Chlorfenapyr	19.2	59	31	10	41	10
14	Chlorobenzilate	20.2	251	139	30	251	30
15	Chlorothalonil	13.6	266	133	30	170	30
16	Chlorpyrifos	15.9	314	258	15	285	15
17	Chlorpyrifos-methyl	14.6	286	93	20	271	20
18	Cyfluthrin-1	27.2	163	91	15	127	10
	Cyfluthrin-2	28.0	163	91	15	127	10
	Cyfluthrin-3	28.2	163	91	15	127	10
	Cyfluthrin-4	28.3	163	91	15	127	10
19	Cyhalothrin-1	25.0	181	152	15	127	15
	Cyhalothrin-2	25.1	181	152	15	127	15
20	Cypermethrin-1	28.4	163	127	10	91	15
	Cypermethrin-2	28.6	163	127	10	91	15
	Cypermethrin-3	28.8	163	127	10	91	15
	Cypermethrin-4	28.9	163	127	10	91	15

No.	Compound	Retention time (min)	Parent ion (m/z)	Quantitative ion (m/z)	Collision energy (V)	Quantitative ion (m/z)	Collision energy (V)
21	Deltamethrin	31.7	253	93	15	172	15
22	Diazinon	13.3	304	179	15	137	15
23	Dichlofluanid	15.7	224	123	15	77	15
24	Diclofop-methyl	22.2	340	253	15	281	15
25	Dicloran	12.6	206	176	10	206	10
26	Dicofol	16.5	139	75	15	111	15
27	Dieldrin	19.2	263	193	20	191	20
28	Dimethenamid	14.4	230	154	25	137	25
29	Diphenamid	16.6	167	152	25	165	25
30	Diphenylamine	11.5	169	168	15	167	15
31	Dithiopyr	15.7	354	286	15	306	15
32	Endosulfan- α	18.2	241	206	15	205	15
33	Endosulfan- β	20.4	241	170	10	206	10
34	Endosulfan-sulfate	21.7	387	289	10	206	10
35	Endrin	19.9	263	193	10	228	10
36	EPN	23.5	157	77	15	110	15
37	Esprocarb	15.7	222	91	15	162	10
38	Ethalfuralin	11.5	276	248	10	202	10
39	Etoxazole	23.8	141	113	15	112	20
40	Etridiazole	7.5	211	183	10	140	20
41	Fenamiphos	18.5	303	195	10	288	10
42	Fenazaquin	23.8	160	117	20	145	20
43	Fenitrothion	15.5	277	260	15	109	15
44	Fenoxanil	19.3	189	125	15	154	15
45	Fenthion	16.2	278	109	30	125	30
46	Fipronil	17.1	367	213	10	120	10
47	Fluacrypyrim	20.8	204	189	5	145	5
48	Fthalide	16.6	243	179	15	215	15
49	Furathiocarb	24.2	163	107	15	135	15
50	Heptachlor	15.1	272	237	30	235	30
51	Heptachlor-epoxide	17.3	353	263	15	282	15
52	Indoxacarb	30.0	150	123	35	114	35
53	Isofenphos	17.2	213	121	20	185	10
54	Malathion	15.7	173	99	15	127	15
55	Mecarbam	17.3	131	86	25	85	25
56	Mepronil	20.9	119	91	10	65	15
57	Methiocarb	10.6	168	153	15	109	20
58	Methoxychlor	23.6	227	169	15	212	15
59	Metolachlor	15.9	162	133	10	134	10
60	Metolcarb	6.5	108	107	10	79	15
61	Nuarimol	21.7	235	139	30	123	30
62	o,p'-DDT	20.6	235	165	10	199	10
63	Ofurace	21.0	232	186	10	158	20
64	Oxadiazon	18.6	175	112	30	140	30
65	p,p'-DDD	20.6	235	165	10	199	10
66	p,p'-DDE	18.9	246	176	25	211	25
67	p,p'-DDT	20.6	235	165	30	199	30
68	Paclobutrazol	18.2	236	125	10	167	10
69	Parathion-ethyl	16.2	291	109	15	70	10
70	Parathion-methyl	14.8	263	127	15	109	15
71	PCTA	15.7	296	263	10	246	35
72	Pentachloroaniline	14.3	265	194	10	203	10
73	Pentoxazone	24.5	285	70	5	285	5

No.	Compound	Retention time (min)	Parent ion (m/z)	Quantitative ion (m/z)	Collision energy (V)	Quantitative ion (m/z)	Collision energy (V)
74	Permethrin	26.9	183	182	10	154	10
75	Phenthoate:PAP	17.4	274	121	25	246	25
76	Phorate	12.2	260	75	10	231	10
77	Phosphamidone	14.3	127	109	25	95	25
78	Pirimiphos-ethyl	16.6	333	180	20	163	20
79	Procymidone	17.6	283	96	10	283	10
80	Propanil	14.5	161	99	15	126	15
81	Propoxur-1	7.5	110	63	15	64	15
	Propoxur-2	10.7	110	63	15	64	15
82	Prothiofos	18.5	309	239	20	281	10
83	Pyrazophos	25.4	221	193	20	149	20
84	Pyrimidifen	29.0	184	169	20	184	20
85	Pyriminobac-methyl	21.1	302	256	15	230	15
86	Pyriproxyfen	24.7	136	96	10	78	10
87	Pyroquilon	13.4	173	130	15	144	15
88	Quinoclamine	15.9	172	128	10	89	25
89	Quintozene	13.0	237	143	20	119	20
90	Simazine	12.7	201	173	10	186	10
91	Simeconazole	14.8	121	101	20	91	20
92	Tefluthrin	13.6	177	127	15	157	15
93	Terbuthylazine	13.2	214	132	20	119	20
94	Tetradifon	24.4	356	159	15	229	15
95	Thiazopyr	15.7	327	277	15	252	15
96	Thifluzamide	19.1	194	125	20	166	20
97	Thiobencarb	16.0	100	72	25	71	25
98	Tolclofos-methyl	14.8	265	250	10	93	10
99	Tolyfluanid	17.2	238	91	15	137	15
100	Tralomethrin	31.5	253	93	20	172	20
101	Trifluralin	11.7	306	206	15	264	15
102	Vinclozolin	14.7	285	213	15	186	15

Table 2. Parameters for 159 pesticides residue analysis by LC-MS/MS

No.	Compound	Retrntion time (min)	Parent (m/z)	Quantitative ion (m/z)	Collision energy (V)	Quantitative ion (m/z)	Collision energy (V)	Cone (V)
1	Acetamiprid	1.48	223	126	20	56	20	28
2	Aldicarb	1.76	213	89	16	116	16	24
3	Amisulbrom	5.20	468	229	15	148	15	21
4	Amitraz	5.00	294	163	18	122	18	31
5	Azimsulfuron	2.95	425	139	46	182	46	20
6	Azinphos-methyl	3.17	318	261	8	160	8	14
7	Azoxystrobin	3.19	404	372	15	329	15	22
8	Bendiocarb	2.08	224	109	18	167	18	20
9	Benthiavalicarb-Isopropyl	2.87	382	180	31	116	31	30
10	Benzoximate	4.98	364	199	8	105	8	18
11	Bifenox	3.89	341	189	22	310	22	16
12	Bitertanol	3.70	338	99	16	70	16	15
13	Boscalid	3.34	342	307	20	140	20	35
14	Buprofezin	3.88	306	201	12	57	12	25
15	Carbaryl	2.22	202	117	28	145	28	22
16	Carbendazim	0.79	192	160	18	132	18	27

No.	Compound	Retrntion time (min)	Parent (m/z)	Quantitative ion (m/z)	Collision energy (V)	Quantitative ion (m/z)	Collision energy (V)	Cone (V)
17	Carbofuran	2.12	222	165	16	123	16	28
18	Carbosulfan	8.02	381	118	22	76	22	34
19	Carfentrazone-ethyl	9.02	412	277	30	346	30	24
20	Chlorantraniliprole	2.69	484	453	17	286	17	21
21	Chlorfluazuron	6.22	539	158	20	383	20	42
22	Chlorpropham	3.47	214	154	18	172	18	12
23	Chromafenozide	3.69	395	175	22	339	22	16
24	Clofentezine	4.63	303	138	22	102	22	28
25	Clomazone	3.50	239	89	44	125	44	22
26	Clothianidin	1.33	250	132	18	169	18	18
27	Cyazofamid	4.14	325	108	20	261	20	20
28	Cyclosulfamuron	5.02	422	139	44	261	44	20
29	Cyflufenamid	5.25	413	295	15	203	15	36
30	Cyhalofop-butyl	1.62	358	120	27	256	27	18
31	Cymoxanil	2.98	199	111	18	128	18	17
32	Cyproconazole	2.66	292	125	24	70	24	30
33	Cyprodinil	6.32	226	93	33	108	33	50
34	Daimuron	7.23	269	91	36	151	36	18
35	Dichlorvos	4.35	220	79	26	109	26	22
36	Diethofencarb	3.01	268	124	40	226	40	22
37	Difenoconazole	4.26	406	251	25	111	25	40
38	Diflubenzuron	3.58	311	269	8	227	8	26
39	Dimepiperate	4.99	264	119	16	146	16	8
40	Dimethoate	1.46	230	125	20	199	20	24
41	Dimethomorph(E)	2.70	388	165	30	301	30	35
	Dimethomorph(Z)	2.84	388	165	30	301	30	35
42	Dimethylvinphos	3.22	331	170	35	127	35	21
43	Diniconazole	3.88	326	159	34	70	34	40
44	Dinotefuran	0.81	203	157	7	129	7	18
45	Dithianon	2.35	295	238	26	268	26	45
46	Diuron	5.3	233	72	18	46	18	28
47	Edifenphos	3.98	311	109	32	111	32	26
48	Emamectin benzoate (B1a)	4.13	887	158	32	82	32	45
	Emamectin benzoate(B1b)	3.78	887	158	32	82	32	45
49	Ethaboxam	1.99	321	200	26	183	26	36
50	Ethiofencarb	2.33	226	107	17	164	17	25
51	Ethoprophos	3.4	243	173	14	131	14	18
52	Etofenprox	7.54	394	177	15	107	15	26
53	Etrimfos	3.3	331	81	34	268	34	40
54	Fenamidone	3.25	312	92	25	236	25	31
55	Fenarimol	5.9	331	81	34	268	34	40
56	Fenbuconazole	3.11	337	125	36	70	36	32
57	Fenhexamid	3.61	302	97	22	55	22	35
58	Fenobucarb	3.39	208	95	14	152	14	16
59	Fenothiocarb	2.94	254	160	9	72	9	21
60	Fenoxaprop-P-ethyl	3.6	361	91	36	288	36	26
61	Fenoxycarb	3.66	302	88	18	116	18	16
62	Fenpropathrin	3.82	350	125	14	97	14	24
63	Fenpyroximat	6.01	422	366	15	138	15	26
64	Ferimzone	1.62	255	132	20	91	20	46
65	Flonicamid	3.2	230	174	18	203	18	26
66	Fluazifop-P-butyl	5.7	384	282	22	328	22	38

No.	Compound	Retrntion time (min)	Parent (m/z)	Quantitative ion (m/z)	Collision energy (V)	Quantitative ion (m/z)	Collision energy (V)	Cone (V)
67	Fluazinam	5.6	465	373	26	338	26	32
68	Flubendiamide	4.12	683	274	33	408	33	15
69	Fludioxonil	3.01	247	180	28	126	28	45
70	Flufenoxuron	5.9	489	141	46	158	46	34
71	Flumioxazin	2.95	355	298	28	326	28	46
72	Fluopicolide	3.46	383	145	48	173	48	35
73	Fluquinconazole	3.36	376	307	30	349	30	46
74	Flusilazole	3.5	316	165	28	247	28	30
75	Flutolanil	3.7	324	65	40	262	40	28
76	Forchlorfenuron	2.18	248	129	15	93	15	36
77	Fosthiazate	2.25	284	104	22	228	22	22
78	Hexaconazole	3.69	314	70	22	159	22	34
79	Hexaflumuron	4.73	459	175	39	276	39	22
80	Hexazinone	5.88	253	71	30	171	30	6
81	Hexythiazox	3.6	353	168	26	228	26	24
82	Imazalil	1.9	297	159	22	69	22	40
83	Imazosulfuron	9.8	413	153	14	156	14	18
84	Imibenconazole	5.1	413	125	29	171	29	36
85	Imidacloprid	1.4	256	175	20	209	20	28
86	Indanofan	4.04	341	175	14	187	14	21
87	Iprobenphos	3.66	289	91	20	205	20	12
88	Iprodione	3.7	330	245	16	288	16	21
89	Iprovalicarb	3.12	321	119	16	203	16	22
90	Isoprocarb	2.49	194	95	14	137	14	18
91	Isoprothiolane	3.66	291	189	22	231	22	26
92	Kresoxim-methyl	4.19	314	206	7	116	7	18
93	Linuron	3.01	249	160	18	181	18	31
94	Lufenuron	5.47	511	141	41	158	41	33
95	Mandipropamid	3.27	412	328	16	356	16	16
96	Mefenacet	6.7	299	120	22	148	22	18
97	Mepanipyrim	3.43	224	77	40	106	40	40
98	Metalaxyl	2.35	280	192	17	220	17	20
99	Metamifop	4.98	441	123	29	288	29	39
100	Metconazole	3.75	320	70	22	125	22	32
101	Methabenzthiazuron	2.12	222	150	32	165	32	24
102	Methidathion	2.95	303	145	10	85	10	12
103	Methomyl	1.08	163	106	10	88	10	20
104	Metobromuron	2.49	259	170	20	148	20	25
105	Metrafenone	7.52	409	209	14	227	14	16
106	Metribuzin	1.99	215	89	20	131	20	35
107	Monocrotophos	2.32	224	127	14	193	14	12
108	Myclobutanil	3.23	289	125	32	70	32	28
109	Napropamide	3.47	272	171	18	129	18	24
110	Novaluron	4.12	493	158	19	141	19	36
111	Oxamyl	0.97	237	72	10	90	10	15
112	Oxaziclomefon	5.57	376	161	30	190	30	36
113	Penconazole	4.74	284	70	16	159	16	34
114	Pencycuron	3.69	329	125	40	125	40	34
115	Pendimethalin	1.32	282	212	10	194	10	15
116	Phosalone	5.87	368	182	14	111	14	16
117	Phoxim	4.82	299	77	28	129	28	12
118	Piperophos	4.96	354	171	22	143	22	31
119	Pirimicarb	1.23	239	72	18	182	18	34
120	Pirimiphos-methyl	4.36	306	108	32	164	32	30

No.	Compound	Retrntion time (min)	Parent (m/z)	Quantitative ion (m/z)	Collision energy (V)	Quantitative ion (m/z)	Collision energy (V)	Cone (V)
121	Pretilachlor	4.65	312	176	28	252	28	18
122	Probenazole	2.12	224	41	8	196	8	20
123	Prochloraz	2.95	376	70	34	307	34	16
124	Profenofos	5.06	373	128	40	303	40	30
125	Propamocarb	0.58	189	144	12	102	12	25
126	Pyraclufos	0.56	361	257	23	111	23	36
127	Pyraclostrobin	5.9	388	163	25	194	25	25
128	Pyributicarb	6.65	333	108	29	181	29	27
129	Pyridaben	3.37	365	147	24	309	24	22
130	Pyridaphenthion	2.1	341	189	22	92	22	40
131	Pyrifitalid	4.36	319	139	30	179	30	32
132	Pyrimethanil	4.56	200	107	24	82	24	45
133	Quinzafofop-ethyl	5.36	373	91	30	299	30	24
134	Sethoxydim	5.52	328	178	22	282	22	28
135	Silafluofen	4.56	410	216	16	379	16	24
136	Simetryn	6.82	214	124	20	96	20	41
137	Spirodiclofen	6.67	411	71	13	313	13	31
138	Spiromesifen	1.56	371	273	10	255	10	16
139	Tebuconazole	3.49	308	70	22	125	22	34
140	Tebufenozide	4.02	353	133	20	297	20	13
141	Tebufenpyrad	5.17	334	117	34	145	34	46
142	Tebupirimfos	5.8	319	153	29	277	29	23
143	Teflubenzuron	4.87	379	339	15	196	15	18
144	Terbufos	5.68	289	103	9	233	9	12
145	Tetraconazole	3.41	372	159	30	70	30	35
146	Thiabendazole	0.84	202	175	25	131	25	51
147	Thiacloprid	1.68	253	126	20	90	20	35
148	Thiamethoxam	1.17	292	132	22	211	22	22
149	Thiodicarb	1.68	355	88	16	108	16	20
150	Tiadinil	3.17	268	101	19	45	19	39
151	Triadimefon	3.3	294	197	15	69	15	25
152	Triadimenol	2.82	296	70	10	99	10	21
153	Triazophos	3.69	314	119	35	162	35	25
154	Trichlorfon	1.27	257	109	18	221	18	20
155	Tricyclazole	1.49	190	136	27	163	27	35
156	Trifloxystrobin	5.11	409	145	40	186	40	28
157	Triflumizole	3.67	346	278	10	60	10	16
158	Triflumuron	4.24	359	156	16	139	16	31
159	Vamidotion	4.68	288	118	24	146	24	14

회수율, 검출한계 및 정량한계 측정

잔류분석법의 효율성과 신뢰성을 검증하기 위하여 회수율 시험을 진행하였으며, 각 농약에 대한 회수율 시험은 20, 50, 100 ug/kg 수준에서 5반복 결과를 확인하였다. 검출한계(limits of detection, LOD)와 정량한계(limits of quantification, LOQ)는 MS/MS상에서 측정 가능한 최소 검출량을 이용하여 아래 식에 따라 산출하였으며, LOD는 S/N ratio 3 이상, LOQ는 S/N ratio 10 이상을 기준으로 측정하였다.

$$\text{LOD (mg/kg)} = (\text{기기상의 최소검출량(ng)} / \text{시료주입량 (uL)}) \times (\text{최종부피(mL)} / \text{시료량(g)})$$

Matrix effect 조사

잔류농약 분석 시 matrix effect (suppression 혹은 enhancement)의 원인은 서로 다른 반응과 현상에 의해 결정 되는데, 수많은 시료와 농약성분의 반응을 명확히 규명하는 것은 매우 어렵기 때문에 본 연구의 matrix effect 검증은 변동 폭에 따른 간섭 정도에 초점을 두어 표준농약성분의 chromatogram상 피크 면적의 수치를 기준으로 측정하였다. 생약재 4품목 각각의 무처리 농산물 시료 추출용액을 이용하여 검량선 작성시 만든 matrix matched standard를 비교하여 matrix effect를 조사하였다. Matrix effect의 산출은 solvent standard의 피크 면적과 matrix matched standard의 피크 면적의 비로 판단하며, 다음과 같은 식으로 산출하여 백분

율로 나타내었다[9, 10].

$$\%ME = (\text{Peak area of matrix matched standard} - \text{peak area of solvent standard}) / (\text{Peak area of solvent standard}) \times 100$$

결과 및 고찰

검출한계 및 정량한계

각 농약별 LOD는 GC-MS/MS 분석에서 2-10 ug/kg,

LC-MS/MS에서 1-8 ug/kg 수준이었으며, LOQ는 GC-MS/MS 분석에서 4-40 ug/kg, LC-MS/MS에서 2-45 ug/kg 범위를 나타내었다(Table 3, 4). 이는 시료 중 함유된 ug/kg 수준의 미량의 잔류농약의 검출이 가능할 것으로 판단되었다. 각각의 표준용액으로부터 acetone과 methanol로 희석하여 6단계의 농도별 분석용 작업표준용액을 제조하였으며, 이를 이용하여 GC-MS/MS와 LC-MS/MS에 주입하여 얻은 chromatogram의 피크면적을 이용하여 검량선을 작성하였다. 이를 통해 얻은 검량선의 직선성은 양호하였으며, 각각의 상관계수(r^2)는 모두 0.99 이상의 결과를 나타내었다.

Table 3. Average recovery and RSD of 261 pesticides spiked in korean angelica root and chinese matrimony vine different concentrations with GC-MS/MS and LC-MS/MS (n=5)

No.	Compound	LOQ (ug/kg)	Recovery,% (RSD,%) <i>Lycii Fructus</i>			Recovery,% (RSD,%) <i>Angelica gigas Nakai</i>		
			20 ug/kg	50 ug/kg	100 ug/kg	20 ug/kg	50 ug/kg	100 ug/kg
			1	Acetamidiprid	4.5	98.3(9.6)	98.7(4.2)	107.0(4.7)
2	Alachlor	5	90.2(4.7)	83.7(2.8)	86.2(3.4)	68.5(5.2)	67.5(2.2)	68.5(5.4)
3	Aldicarb	10	50.2(4.1)	101.0(1.2)	70.2(5.2)	42.5(5.2)	48.2(2.1)	52.5(5.2)
4	Aldrin	20	96.7(4.9)	89.8(1.9)	91.3(2.7)	75.0(9.2)	77.5(5.5)	84.5(2.2)
5	Amisulbrom	8	68.8(4.1)	69.2(5.2)	78.2(5.4)	162.5(6.4)	159.0(5.4)	144.5(9.2)
6	Amitraz	8	92.0(5.2)	115.0(9.1)	108.0(5.1)	56.2(10.2)	46.2(5.2)	66.2(8.2)
7	Azimsulfuron	4.5	75.0(4.1)	80.2(10.5)	106.5(5.9)	101.0(4.1)	106.0(2.5)	104.0(6.3)
8	Azinphos-methyl	4.5	102.5(2.1)	93.3(1.0)	102.0(9.5)	97.5(9.2)	114.0(7.0)	71.5(7.3)
9	Azoxystrobin	4.5	100.2(5.4)	112.0(4.5)	117.5(5.2)	52.5(6.7)	54.7(10.6)	63.0(1.6)
10	Bendiocarb	16	115.0(7.5)	115.3(3.6)	119.3(4.2)	197.5(1.2)	146.0(5.9)	133.7(2.8)
11	Benthiavalicarb-isopropyl	4.5	110.5(5.2)	118.0(7.6)	109.5(4.1)	111.0(4.1)	118.3(2.4)	115.0(5.2)
12	Benzoximate	4.5	87.5(8.3)	107.3(8.8)	110.0(4.1)	72.5(5.2)	76.0(3.5)	78.0(7.1)
13	BHC- α	5	98.4(4.1)	87.5(1.6)	89.2(2.3)	76.7(3.3)	74.9(5.9)	99.6(1.6)
14	BHC- β	4	76.0(5.4)	79.3(2.0)	70.2(2.6)	81.5(7.2)	106.7(8.4)	109.9(4.7)
15	BHC- δ	4	95.4(3.3)	81.1(0.7)	83.5(2.6)	76.7(5.8)	94.2(5.6)	103.0(5.2)
16	BHC- γ	4	74.0(9.5)	79.3(1.6)	79.2(4.6)	76.9(3.3)	76.6(9.6)	101.4(2.6)
17	Bifenox	4.5	115.0(8.1)	109.0(3.2)	106.3(6.8)	71.2(7.5)	72.2(5.4)	78.0(7.8)
18	Bifenthrin	5	107.4(1.3)	112.2(1.7)	101.9(2.2)	78.8(9.6)	94.3(2.9)	108.4(1.9)
19	Bitertanol	9	67.5(8.9)	89.0(3.4)	91.7(9.8)	108.3(8.1)	137.3(1.6)	145.3(1.2)
20	Boscalid	4.5	110.0(9.8)	108.7(5.8)	115.0(6.8)	72.5(4.5)	97.0(5.1)	113.0(1.8)
21	Bromobutide	4	80.2(0.2)	85.2(2.2)	87.2(1.3)	86.1(2.4)	87.0(2.7)	82.0(2.1)
22	Bromopropylate	20	108.0(3.7)	98.8(1.6)	100.1(2.4)	24.0(7.5)	57.9(5.7)	75.9(2.7)
23	Buprofezin	4.5	116.7(6.5)	107.3(1.8)	111.7(3.3)	141.7(5.4)	116.0(1.6)	119.7(1.1)
24	Butachlor	20	86.0(4.6)	70.3(5.6)	85.0(6.6)	84.8(10.3)	80.0(10.6)	106.5(6.5)
25	Cadusafos	20	97.8(3.7)	82.1(2.1)	80.7(8.7)	82.8(6.3)	87.6(4.2)	86.2(0.3)
26	Captan	4	162.5(2.9)	166.4(8.3)	125.5(6.4)	179.6(2.3)	172.1(2.1)	221.3(1.9)
27	Carbaryl	4.5	118.3(1.6)	108.7(7.3)	107.7(7.5)	137.5(7.7)	98.0(1.4)	51.0(8.3)
28	Carbendazim	4.5	98.5(3.5)	106.0(8.7)	108.4(8.5)	73.2(9.5)	74.0(2.3)	78.5(4.2)
29	Carbofuran	4.5	98.3(5.5)	124.7(3.3)	102.0(2.0)	165.0(5.2)	143.3(5.8)	151.3(3.1)
30	Carbosulfan	3	60.4(2.5)	64.2(0.2)	72.4(10.4)	72.5(4.3)	71.0(7.6)	79.0(8.2)
31	Carfentrazone-ethyl	4.5	91.7(0.2)	94.0(3.2)	113.3(8.9)	170.0(4.2)	111.3(1.3)	101.5(7.8)
32	Chlorantraniliprole	4.5	52.2(5.2)	74.0(2.2)	71.5(2.9)	126.7(7.8)	143.3(1.3)	133.3(4.3)
33	Chlorfenapyr	4	81.9(1.8)	110.9(2.3)	93.0(2.4)	115.2(5.2)	95.2(9.2)	92.2(4.2)
34	Chlorfluzaron	5	78.3(1.2)	96.0(2.4)	118.0(3.8)	70.2(2.5)	76.0(1.9)	86.5(9.3)
35	Chlorobenzilate	9	110.4(3.5)	97.5(2.1)	99.7(2.0)	43.2(9.2)	67.2(5.5)	83.0(6.7)

No.	Compound	LOQ (ug/kg)	Recovery,% (RSD,%) <i>Lycii Fructus</i>			Recovery,% (RSD,%) <i>Angelica gigas Nakai</i>		
			20 ug/kg	50 ug/kg	100 ug/kg	20 ug/kg	50 ug/kg	100 ug/kg
			36	Chlorothalonil	4	103.0(5.3)	91.1(7.9)	94.9(4.9)
37	Chlorpropham	5	125.0(5.7)	105.0(9.4)	102.5(7.2)	82.5(9.7)	93.1(8.9)	94.7(5.4)
38	Chlorpyrifos	16	104.8(2.9)	90.9(1.9)	94.5(2.5)	41.2(2.4)	66.6(5.5)	99.0(3.2)
39	Chlorpyrifos -methyl	9	101.0(2.6)	93.4(3.0)	95.7(3.2)	72.5(1.1)	79.6(6.6)	75.4(9.7)
40	Chromafenozide	4.5	116.7(5.1)	112.7(2.0)	104.5(3.8)	117.5(9.0)	55.3(5.5)	86.6(10.9)
41	Clofentezine	9	81.7(5.4)	109.0(3.2)	99.3(1.5)	73.3(7.6)	74.0(7.0)	99.3(1.7)
42	Clomazone	4.5	106.7(5.4)	97.3(1.3)	111.7(0.3)	90.0(3.6)	97.3(7.8)	89.7(6.1)
43	Clothianidin	9	71.1(3.3)	68.7(7.6)	87.7(3.6)	77.0(9.5)	81.0(5.8)	89.0(2.7)
44	Cyazofamid	5	98.3(6.5)	88.7(4.9)	111.3(4.9)	72.2(10.1)	72.1(4.4)	80.9(1.5)
45	Cyclosulfamuron	4.5	60.5(5.7)	71.4(7.8)	75.2(4.2)	95.7(4.5)	76.0(2.4)	112.2(1.2)
46	Cyflufenamid	4.5	110.0(5.2)	105.0(4.6)	95.0(8.5)	107.5(6.9)	110.0(4.4)	115.4(6.1)
47	Cyfluthrin	10	118.3(8.7)	86.4(8.4)	87.8(2.9)	133.7(1.1)	167.4(2.3)	94.3(1.0)
48	Cyhalofop-butyl	9	93.3(9.2)	108.0(1.9)	112.0(6.1)	75.0(8.9)	77.0(1.8)	71.0(6.7)
49	Cyhalothrin	4	115.0(5.8)	111.9(1.2)	123.5(3.9)	147.3(2.8)	97.5(6.7)	95.5(5.2)
50	Cymoxanil	8	96.7(2.0)	83.0(4.5)	105.0(6.3)	112.5(8.9)	116.0(1.8)	108.5(1.0)
51	Cypermethrin	4	110.1(6.7)	100.2(6.6)	88.2(3.0)	90.0(9.0)	79.0(5.3)	95.0(1.5)
52	Cyproconazole	4.5	108.3(7.5)	112.7(5.7)	112.7(3.4)	97.5(10.9)	90.7(10.2)	95.7(7.1)
53	Cyprodinil	45	106.7(9.8)	119.3(5.1)	105.2(4.3)	170.0(5.1)	148.7(1.6)	145.7(6.5)
54	Daimuron	9	110.0(0.1)	114.7(4.1)	105.3(3.8)	75.0(5.7)	78.0(7.4)	72.7(1.7)
55	Deltamethrin	4	83.9(5.0)	66.4(4.7)	65.9(4.2)	96.7(5.3)	82.5(1.0)	119.8(1.7)
56	Diazinon	10	106.7(7.9)	100.8(3.2)	102.5(2.2)	93.6(6.3)	103.2(1.9)	110.0(8.0)
57	Dichlofluanid	10	62.6(8.5)	63.7(4.0)	67.7(7.2)	53.1(6.8)	57.6(7.9)	84.4(1.0)
58	Dichlorvos	8	58.3(7.8)	60.0(3.3)	69.7(2.0)	60.0(10.6)	41.0(1.2)	72.5(3.2)
59	Diclofop-methyl	4	105.8(3.4)	98.1(1.9)	100.9(3.1)	71.1(10.2)	67.1(4.2)	82.5(2.2)
60	Dicloran	10	104.4(3.9)	90.5(1.4)	93.8(2.8)	83.2(6.2)	87.5(4.6)	93.1(2.6)
61	Dicofol	4	98.3(3.7)	91.7(2.3)	94.7(2.8)	87.2(4.3)	97.8(4.5)	106.9(2.3)
62	Dieldrin	4	106.7(3.1)	96.1(3.8)	98.1(2.8)	72.2(10.7)	83.7(6.4)	97.0(3.8)
63	Diethofencarb	4.5	98.3(7.9)	118.0(2.9)	123.7(5.2)	195.0(6.3)	156.7(4.8)	116.7(1.8)
64	Difenoconazole	4.5	108.3(3.6)	91.3(5.8)	92.7(4.9)	101.7(1.4)	90.7(7.1)	87.7(3.7)
65	Diflubenzuron	4.5	97.5(0.9)	126.0(1.1)	129.0(9.7)	152.5(6.5)	79.0(5.6)	78.0(1.1)
66	Dimepiperate	4.5	106.7(8.4)	100.0(4.9)	117.0(5.1)	119.2(5.9)	110.0(8.8)	105.5(8.0)
67	Dimethenamid	4	106.5(3.3)	96.8(1.1)	98.9(2.9)	79.5(6.1)	75.9(8.0)	89.3(3.4)
68	Dimethoate	4.5	118.3(1.4)	103.3(1.5)	116.3(1.1)	103.5(2.5)	114.7(1.1)	115.3(3.3)
69	Dimethomorph	4.5	98.3(1.5)	103.3(1.7)	116.7(6.3)	103.3(5.6)	114.0(1.8)	114.7(4.0)
70	Dimethylvinphos	4.5	125.0(1.2)	118.0(2.6)	102.7(6.6)	94.0(5.3)	152.0(9.5)	151.0(9.3)
71	Diniconazole	9	88.3(1.6)	100.0(2.9)	112.0(3.2)	102.5(5.3)	114.0(8.5)	90.3(7.0)
72	Dinotefuran	4	81.7(1.4)	101.3(8.3)	116.0(7.1)	117.2(3.2)	115.3(1.5)	114.5(1.0)
73	Diphenamid	4	99.0(4.9)	91.0(1.6)	93.6(2.3)	79.3(10.5)	102.6(4.5)	110.2(2.5)
74	Diphenylamine	4.5	88.3(3.7)	85.1(2.4)	91.0(2.6)	74.9(2.3)	87.9(5.7)	96.9(2.0)
75	Dithianon	6	121.7(1.6)	114.0(4.1)	96.0(4.2)	97.7(4.8)	81.0(1.4)	72.0(8.6)
76	Dithiopyr	3	104.9(2.9)	98.2(1.5)	100.2(3.4)	26.2(3.7)	55.9(6.1)	71.4(3.3)
77	Diuron	4.5	119.2(6.7)	124.0(3.2)	108.3(3.7)	117.5(3.1)	146.0(1.2)	149.7(1.0)
78	Edifenphos	4.5	98.3(6.3)	113.3(8.1)	114.3(3.4)	95.0(3.9)	138.0(1.4)	97.5(1.1)
79	Emamectin benzoate	8	113.3(1.1)	106.7(1.1)	109.3(1.4)	170.5(8.2)	135.2(8.5)	153.2(1.5)
80	Endosulfan- α	4	123.1(7.3)	100.7(2.7)	97.8(1.7)	71.3(4.3)	86.4(9.2)	85.0(5.0)
81	Endosulfan- β	4	83.5(8.5)	119.6(2.4)	99.1(4.1)	119.3(4.3)	89.9(3.7)	98.4(9.4)
82	Endosulfan-sulfate	4	106.2(2.9)	117.0(2.3)	116.3(2.3)	118.5(8.3)	97.8(6.7)	97.6(6.7)
83	Endrin	4	105.4(4.2)	89.7(2.2)	93.6(3.2)	76.2(2.9)	96.2(1.2)	92.9(2.9)
84	EPN	4	85.8(7.0)	74.3(3.3)	110.3(2.3)	94.9(2.2)	109.2(7.5)	95.7(5.7)
85	Esprocarb	4.5	105.5(3.9)	98.0(2.1)	101.8(2.0)	88.2(2.3)	96.8(9.8)	91.8(1.8)
86	Ethaboxam	9	100.5(3.9)	100.2(5.2)	97.5(4.1)	71.5(5.2)	82.5(1.3)	85.2(5.2)

No.	Compound	LOQ (ug/kg)	Recovery,% (RSD,%) <i>Lycii Fructus</i>			Recovery,% (RSD,%) <i>Angelica gigas Nakai</i>		
			20 ug/kg	50 ug/kg	100 ug/kg	20 ug/kg	50 ug/kg	100 ug/kg
			87	Ethalfuralin	6	107.0(3.3)	94.9(3.0)	102.6(3.9)
88	Ethiofencarb	4.5	100.0(1.1)	100.0(5.3)	91.5(9.3)	112.5(5.7)	95.4(9.0)	108.9(1.9)
89	Ethoprophos	2	118.3(7.0)	89.0(5.3)	118.0(7.2)	95.0(5.2)	89.3(1.3)	84.2(4.2)
90	Etofenprox	7	85.0(6.3)	75.0(4.3)	92.0(4.3)	80.0(9.2)	82.2(1.0)	109.6(1.6)
91	Etoxazole	4	118.0(3.7)	101.1(4.1)	80.0(1.0)	85.0(8.3)	88.5(8.2)	82.5(6.3)
92	Etridiazole	4	113.5(8.5)	93.2(9.9)	80.6(8.8)	82.7(2.8)	115.2(5.0)	88.5(8.5)
93	Etrimfos	4.5	124.0(0.8)	143.1(4.1)	127.2(5.4)	53.5(9.4)	52.6(1.5)	55.2(5.7)
94	Fenamidone	7	118.3(5.8)	92.0(9.0)	102.3(4.9)	110.2(8.2)	97.5(1.3)	97.9(7.9)
95	Fenamiphos	9	114.2(3.5)	104.8(2.5)	109.1(2.7)	71.2(4.6)	70.5(3.2)	71.7(1.7)
96	Fenarimol	4	72.2(8.6)	104.0(2.7)	124.0(1.6)	135.0(9.8)	103.3(7.3)	106.0(1.0)
97	Fenazaquin	4.5	91.5(6.8)	101.0(6.4)	85.4(5.5)	67.3(6.7)	103.7(1.6)	91.6(1.6)
98	Fenbuconazole	9	75.0(4.8)	94.0(4.3)	82.0(5.0)	116.7(2.9)	98.0(1.3)	101.5(1.5)
99	Fenhexamid	6	54.2(5.2)	62.2(5.4)	72.4(4.6)	65.0(6.1)	62.0(6.1)	60.5(0.5)
100	Fenitrothion	4.5	114.6(4.3)	98.7(2.0)	104.5(2.9)	72.1(2.3)	86.0(1.0)	93.6(3.6)
101	Fenobucarb	9	116.7(6.5)	116.7(6.9)	112.0(3.9)	110.0(5.6)	102.3(3.2)	106.5(6.5)
102	Fenothiocarb	8	75.0(6.6)	54.0(6.2)	103.5(8.4)	127.5(4.1)	161.5(4.2)	114.4(1.4)
103	Fenoxanil	9	104.9(3.2)	97.2(2.1)	100.4(3.6)	88.8(3.8)	94.4(6.7)	92.2(2.2)
104	Fenoxaprop-P-ethyl	4.5	100.0(4.2)	111.2(1.5)	109.7(6.6)	72.5(7.4)	98.7(2.5)	89.1(9.1)
105	Fenoxycarb	4.5	95.0(8.2)	114.7(2.0)	112.3(7.7)	193.3(1.5)	137.5(1.5)	144.5(3.7)
106	Fenpropathrin	4.5	95.0(9.8)	111.3(3.7)	114.0(1.3)	102.5(1.7)	89.0(1.5)	84.6(4.6)
107	Fenpyroximat	4	89.7(6.6)	101.1(8.7)	108.3(2.2)	85.0(1.8)	82.3(3.5)	91.9(1.9)
108	Fenthion	4.5	112.9(3.4)	103.0(1.5)	107.1(2.6)	71.0(9.9)	68.3(4.6)	86.4(4.7)
109	Ferimzone	18	100.0(5.2)	107.3(2.8)	110.7(4.6)	106.7(3.8)	97.3(1.0)	92.9(2.9)
110	Fipronil	9	116.9(3.3)	100.4(1.8)	104.7(3.4)	75.5(7.1)	90.9(6.2)	83.5(3.5)
111	Flonicamid	4	110.0(6.4)	111.3(6.3)	107.0(3.8)	95.0(8.9)	76.7(8.3)	98.6(8.6)
112	Fluacrypyrim	4.5	119.2(2.9)	107.4(1.7)	109.3(1.9)	78.5(3.5)	78.9(3.9)	75.4(5.6)
113	Fluazifop-P-butyl	4.5	90.0(3.8)	83.0(3.1)	107.0(1.4)	90.0(3.9)	106.0(1.6)	101.6(1.6)
114	Fluazinam	4.5	113.7(7.3)	115.2(5.4)	110.5(3.5)	116.2(5.1)	111.2(2.2)	100.4(1.4)
115	Flubendiamide	4.5	75.2(0.2)	90.0(4.1)	102.0(2.0)	90.0(5.1)	96.0(6.3)	88.3(8.3)
116	Fludioxonil	9	70.0(1.0)	77.3(7.6)	85.0(4.9)	76.7(8.2)	88.0(3.5)	86.2(6.2)
117	Flufenoxuron	9	125.0(3.2)	94.0(9.9)	118.0(5.5)	115.0(5.5)	101.3(6.3)	87.1(7.1)
118	Flumioxazin	4.5	125.0(5.4)	74.0(7.3)	100.0(5.2)	245.0(9.1)	136.0(5.7)	121.8(1.8)
119	Fluopicolide	9	105.0(6.9)	82.0(7.2)	92.3(6.2)	115.0(8.4)	107.2(7.0)	95.5(5.5)
120	Fluquinconazole	4.5	77.0(5.6)	105.3(5.8)	115.0(3.6)	98.3(5.9)	88.7(1.0)	103.5(1.5)
121	Flusilazole	4.5	90.0(4.1)	94.0(9.3)	106.3(2.0)	93.3(4.7)	90.3(1.5)	99.7(9.7)
122	Flutolanil	4.5	65.0(0.9)	144.7(5.6)	116.0(9.0)	57.5(10.2)	52.0(6.3)	63.6(3.6)
123	Forchlorfenuron	4.5	77.5(2.3)	82.7(5.0)	88.3(7.3)	117.5(4.4)	96.0(3.7)	99.6(9.6)
124	Fosthiazate	4	108.3(3.7)	88.0(6.8)	88.3(2.6)	83.3(9.8)	81.7(3.9)	104.1(4.1)
125	Fthalide	4	97.2(4.1)	89.2(2.4)	92.3(3.0)	86.5(2.3)	94.6(2.4)	83.3(3.3)
126	Furathiocarb	6	101.8(7.0)	85.4(8.4)	76.1(4.9)	43.2(2.5)	98.3(1.2)	92.2(2.2)
127	Heptachlor	10	88.6(5.1)	71.9(4.7)	71.0(5.1)	79.2(2.0)	92.0(9.2)	84.5(4.5)
128	Heptachlor-epoxide	4.5	102.4(5.6)	109.0(2.0)	116.7(3.8)	53.6(4.8)	80.2(3.5)	94.3(4.3)
129	Hexaconazole	4.5	98.3(9.3)	84.7(7.0)	87.7(6.1)	112.5(2.3)	92.0(1.5)	103.3(2.9)
130	Hexaflumuron	4	86.0(9.2)	117.3(2.8)	110.3(5.7)	92.5(5.1)	78.5(1.5)	87.0(7.4)
131	Hexazinone	9	123.3(6.9)	115.3(2.4)	102.0(5.7)	93.3(8.2)	81.0(1.3)	94.8(4.8)
132	Hexythiazox	2	103.3(0.8)	88.7(6.0)	86.7(5.7)	98.3(6.2)	119.3(1.5)	83.7(3.7)
133	Imazalil	9	107.5(9.9)	121.3(2.1)	118.7(4.2)	93.3(8.2)	101.0(1.4)	111.4(1.2)
134	Imazosulfuron	4	52.4(5.2)	55.4(1.2)	65.2(8.9)	77.5(4.1)	73.0(3.2)	70.2(10.2)
135	Imibenconazole	9	91.7(8.3)	114.7(2.8)	95.7(6.1)	106.7(2.3)	92.0(2.3)	91.4(1.4)
136	Imidacloprid	9	70.0(0.2)	90.0(8.2)	93.0(10.6)	72.5(8.3)	72.3(3.5)	79.3(9.3)
137	Indanofan	10	117.5(1.2)	88.0(6.3)	103.7(3.5)	110.0(6.0)	105.5(3.4)	93.8(1.2)
138	Indoxacarb	4.5	88.5(7.5)	107.7(3.1)	97.0(3.6)	71.3(5.7)	105.8(9.6)	115.6(8.6)
139	Iprobenphos	4	117.5(1.1)	90.7(8.6)	92.0(6.1)	85.2(8.5)	82.0(10.2)	87.5(9.4)

No.	Compound	LOQ (ug/kg)	Recovery,% (RSD,%) <i>Lycii Fructus</i>			Recovery,% (RSD,%) <i>Angelica gigas Nakai</i>		
			20 ug/kg	50 ug/kg	100 ug/kg	20 ug/kg	50 ug/kg	100 ug/kg
			140	Iprodione	4.5	97.5(6.1)	104.0(1.0)	92.3(6.5)
141	Iprovalicarb	4	91.7(6.9)	98.0(5.8)	110.7(4.2)	82.5(6.7)	80.7(1.9)	86.0(8.6)
142	Isofenphos	4.5	112.1(3.6)	102.0(2.0)	104.4(3.2)	136.4(2.3)	145.6(4.1)	119.8(5.9)
143	Isoprocarb	4.5	106.7(5.1)	113.3(2.0)	108.0(5.8)	196.7(7.3)	154.0(2.2)	152.3(4.7)
144	Isoprothiolane	9	118.3(4.5)	92.7(6.7)	117.5(4.7)	106.7(8.4)	119.0(3.6)	92.0(5.2)
145	Kresoxim-methyl	9	91.7(1.6)	115.3(7.4)	119.7(7.3)	85.0(1.8)	84.0(3.3)	109.0(4.5)
146	Linuron	9	95.0(3.7)	122.7(6.2)	102.3(7.4)	85.0(9.2)	98.5(5.2)	101.2(7.2)
147	Lufenuron	4	125.0(8.2)	86.0(2.7)	118.7(3.4)	70.0(3.0)	92.0(1.9)	105.7(3.5)
148	Malathion	3	108.1(3.2)	99.2(2.6)	103.4(2.0)	77.0(7.7)	92.2(7.4)	116.8(1.6)
149	Mandipropamid	10	97.5(5.6)	105.3(7.9)	113.7(1.2)	90.0(8.9)	80.7(7.7)	111.0(4.2)
150	Mecarbam	4.5	98.1(4.0)	89.2(3.4)	88.0(6.9)	77.0(0.6)	99.0(3.9)	111.4(2.8)
151	Mefenacet	4.5	90.0(5.7)	122.0(5.9)	118.7(4.2)	52.5(5.1)	86.7(3.9)	94.3(5.2)
152	Mepanipyrim	7	106.7(8.8)	110.7(4.3)	96.3(2.1)	85.0(9.7)	83.3(1.8)	102.3(4.7)
153	Mepronil	4.5	106.5(3.9)	92.7(7.8)	111.6(7.4)	71.4(8.0)	99.3(2.6)	104.1(1.9)
154	Metalaxyl	4.5	91.7(7.1)	105.3(8.1)	89.0(5.8)	71.2(7.1)	76.7(7.5)	73.3(4.0)
155	Metamifop	4.5	125.0(2.6)	98.0(5.6)	102.0(6.7)	98.3(5.5)	84.0(3.9)	104.3(6.2)
156	Metconazole	4.5	108.3(4.5)	117.0(5.6)	99.0(4.0)	111.3(1.2)	116.0(1.6)	104.0(2.3)
157	Methabenzthiazuron	4.5	111.7(9.3)	133.3(3.1)	116.9(5.0)	93.3(8.2)	86.7(6.7)	82.7(6.2)
158	Methidathion	9	80.0(8.8)	118.0(6.8)	88.0(3.7)	102.2(8.6)	92.0(4.4)	98.0(0.8)
159	Methiocarb	4.5	78.2(5.6)	109.7(2.8)	98.9(3.0)	95.4(4.4)	86.5(4.0)	92.8(3.8)
160	Methomyl	4	110.0(5.6)	92.7(2.0)	97.7(0.9)	72.5(7.0)	72.7(2.9)	74.0(8.3)
161	Methoxychlor	4.5	80.2(2.7)	82.3(2.6)	85.6(4.1)	88.9(7.8)	77.3(7.5)	89.9(7.7)
162	Metobromuron	3	118.2(2.2)	98.0(5.4)	105.0(2.5)	152.5(4.8)	146.7(8.2)	144.7(7.4)
163	Metolachlor	5	103.2(3.3)	89.6(2.3)	90.7(2.4)	142.7(2.4)	146.6(10.5)	127.5(1.2)
164	Metolcarb	10	78.0(2.3)	78.3(5.8)	78.5(4.3)	80.3(1.5)	88.5(1.7)	89.5(5.9)
165	Metrafenone	4.5	83.3(9.4)	94.0(7.5)	92.7(3.0)	106.7(8.4)	108.0(10.5)	102.3(5.7)
166	Metribuzin	4	103.3(2.2)	105.3(5.5)	114.0(3.2)	110.2(4.5)	117.3(6.5)	112.0(1.3)
167	Monocrotophos	4.5	87.5(4.0)	116.7(5.2)	113.0(1.9)	101.2(4.2)	97.0(10.4)	93.0(4.5)
168	Myclobutanil	4.5	86.7(1.2)	118.0(2.9)	128.3(8.4)	141.7(6.7)	143.3(8.6)	149.7(1.3)
169	Napropamide	5	107.5(3.3)	99.0(6.8)	60.3(5.1)	168.3(2.0)	144.0(8.4)	146.0(8.3)
170	Novaluron	8	118.3(2.2)	108.7(5.1)	111.3(1.1)	167.5(4.3)	101.3(10.9)	99.0(3.9)
171	Nuarimol	4	108.6(2.4)	119.1(1.8)	93.4(2.9)	82.6(2.4)	77.3(3.7)	78.2(2.2)
172	o,p'-DDT	4	119.2(3.5)	105.5(1.2)	109.5(3.0)	85.5(8.6)	96.8(0.8)	106.1(7.7)
173	Ofurace	4	105.4(3.8)	94.8(2.0)	96.9(3.9)	79.2(6.2)	94.5(2.0)	105.7(2.4)
174	Oxadiazon	4.5	102.2(4.0)	94.1(2.1)	96.5(2.7)	44.0(8.4)	79.0(3.3)	95.8(1.7)
175	Oxamyl	4.5	90.0(2.1)	95.3(9.7)	82.0(3.9)	37.5(10.3)	42.0(5.4)	89.3(2.3)
176	Oxaziclomefon	4	115.0(2.8)	87.3(3.7)	84.3(4.3)	106.7(4.8)	107.3(1.1)	92.0(3.8)
177	p,p'-DDD	4	119.2(3.5)	105.5(1.2)	109.5(3.0)	115.5(8.6)	96.8(0.8)	106.1(7.7)
178	p,p'-DDE	4	106.4(4.1)	95.3(1.8)	97.3(2.2)	72.7(8.9)	73.5(4.7)	86.5(1.0)
179	p,p'-DDT	8	109.7(4.3)	110.2(5.1)	99.7(7.2)	118.7(4.3)	99.1(7.7)	98.5(8.7)
180	Paclobutrazol	9	95.6(4.3)	88.3(1.8)	90.9(1.8)	72.9(10.4)	69.7(8.3)	82.0(2.3)
181	Parathion-ethyl	6	127.9(4.6)	93.0(2.0)	90.9(3.8)	94.6(9.4)	85.9(4.2)	92.6(2.8)
182	Parathion-methyl	5	95.9(4.6)	83.0(2.0)	80.9(3.8)	80.2(5.6)	80.2(0.6)	90.7(2.1)
183	PCTA	4.5	96.1(4.7)	87.8(2.9)	89.0(3.2)	31.7(8.9)	58.0(4.8)	75.3(1.5)
184	Penconazole	4.5	97.5(4.4)	94.0(3.9)	112.0(6.6)	105.0(6.8)	98.7(8.6)	93.7(7.0)
185	Pencycuron	9	108.3(4.1)	116.7(4.0)	106.7(2.2)	118.3(7.9)	101.3(1.8)	112.3(5.1)
186	Pendimethalin	8	91.0(5.2)	88.7(9.2)	101.7(4.0)	73.5(5.2)	98.2(5.4)	95.0(4.6)
187	Pentachloroaniline	4	102.7(4.1)	93.8(2.8)	97.2(3.2)	72.1(10.6)	72.0(6.0)	83.0(2.3)
188	Pentoxazone	4	108.7(4.2)	98.9(2.0)	99.6(2.1)	123.0(4.3)	51.4(5.4)	68.6(2.9)
189	Permethrin	8	99.6(4.1)	93.5(2.0)	96.2(2.7)	80.8(2.2)	97.7(9.4)	119.3(2.2)
190	Phenthoate:PAP	9	108.9(4.2)	96.5(5.7)	104.2(3.2)	66.1(8.3)	94.6(4.7)	116.0(5.8)
191	Phorate	9	109.3(2.4)	98.8(3.1)	102.9(3.9)	37.4(6.0)	59.8(6.4)	76.3(2.0)
192	Phosalone	4	106.7(8.6)	114.7(9.4)	96.7(5.5)	118.9(3.4)	83.0(6.2)	99.7(2.6)

No.	Compound	LOQ (ug/kg)	Recovery,% (RSD,%)			Recovery,% (RSD,%)		
			<i>Lycii Fructus</i>			<i>Angelica gigas Nakai</i>		
			20 ug/kg	50 ug/kg	100 ug/kg	20 ug/kg	50 ug/kg	100 ug/kg
193	Phosphamidone	4	92.4(4.8)	104.1(8.9)	107.3(1.8)	85.8(5.5)	82.6(9.8)	99.2(9.8)
194	Phoxim	4.5	115.0(1.5)	126.0(9.8)	125.7(5.3)	75.0(9.2)	77.0(7.7)	102.0(6.6)
195	Piperophos	4.5	111.7(0.2)	91.2(4.8)	102.7(2.0)	106.7(6.5)	105.3(4.8)	106.0(4.3)
196	Pirimicarb	7	95.0(5.2)	115.3(6.6)	113.7(6.7)	88.3(6.2)	84.0(1.3)	83.7(7.3)
197	Pirimiphos-ethyl	4.5	110.2(4.0)	97.0(1.8)	99.6(2.4)	52.2(3.7)	70.5(6.1)	86.2(1.9)
198	Pirimiphos-methyl	4.5	96.7(4.5)	94.0(0.6)	91.0(2.4)	93.3(4.8)	97.3(3.7)	98.3(3.9)
199	Pretilachlor	4	119.4(8.3)	125.3(7.5)	123.7(5.4)	102.5(3.1)	74.0(5.4)	71.7(1.9)
200	Probenazole	4.5	82.2(7.5)	80.2(3.4)	82.6(6.4)	75.2(6.5)	75.2(10.5)	79.2(1.2)
201	Prochloraz	4	93.0(3.9)	116.0(9.6)	110.3(8.8)	86.7(6.4)	83.2(7.4)	83.0(1.4)
202	Procymidone	9	119.6(3.6)	98.2(2.1)	96.4(2.3)	43.2(4.3)	64.2(8.0)	78.0(0.2)
203	Profenofos	4.5	83.3(4.3)	84.7(3.0)	82.3(1.9)	88.3(1.0)	117.3(2.8)	105.3(3.3)
204	Propamocarb	6	103.3(5.6)	108.7(8.5)	92.3(6.6)	77.5(4.2)	70.0(5.6)	72.0(5.1)
205	Propanil	4	100.8(3.1)	93.2(1.7)	97.5(3.4)	63.5(4.5)	87.8(4.2)	97.9(2.2)
206	Propoxur	4	75.8(5.0)	75.9(2.2)	72.3(3.4)	105.6(1.5)	110.7(7.1)	120.9(2.6)
207	Prothiofos	4.5	99.8(3.3)	94.9(1.0)	98.0(3.1)	75.4(7.8)	61.5(7.0)	79.4(2.3)
208	Pyraclofos	4.5	115.0(2.6)	73.0(2.2)	90.7(10.8)	77.2(10.2)	87.2(5.2)	107.5(1.5)
209	Pyraclostrobin	4	80.0(8.8)	113.3(1.3)	110.3(5.4)	116.7(2.1)	109.3(4.4)	118.3(9.2)
210	Pyrazophos	4.5	112.6(4.6)	105.0(2.6)	107.7(2.7)	76.0(1.4)	78.7(5.8)	97.5(2.5)
211	Pyributicarb	4.5	81.7(0.6)	73.3(6.9)	79.0(4.0)	110.5(6.2)	104.7(0.9)	94.7(3.5)
212	Pyridaben	4.5	118.3(7.2)	103.3(4.3)	117.0(4.4)	103.3(3.3)	109.2(1.3)	96.7(4.1)
213	Pyridaphenthion	4.5	105.0(6.9)	96.7(4.0)	106.5(3.9)	105.2(3.1)	110.7(7.2)	82.0(6.7)
214	Pyriftalid	4.5	87.5(4.0)	104.0(5.4)	105.7(8.9)	100.0(9.9)	94.7(6.8)	122.3(1.1)
215	Pyrimethanil	4	98.3(6.3)	114.0(1.8)	111.7(4.1)	104.3(9.1)	134.0(4.2)	146.0(7.9)
216	Pyrimidifen	4	102.1(3.6)	115.3(1.2)	113.3(3.8)	108.4(3.6)	99.2(5.4)	117.8(1.7)
217	Pyriminobac-methyl	4	94.3(3.5)	84.9(2.0)	88.1(2.8)	42.1(9.3)	66.0(5.8)	78.0(2.0)
218	Pyriproxyfen	9	103.9(2.8)	96.7(2.1)	98.8(3.2)	61.6(7.7)	87.2(2.6)	100.3(2.1)
219	Pyroquilon	10	113.0(7.0)	106.9(1.5)	112.0(2.9)	52.4(7.8)	81.7(7.9)	93.9(2.8)
220	Quinoclamine	4	114.1(3.4)	106.0(0.7)	114.2(3.0)	121.2(5.0)	118.4(1.7)	125.9(3.1)
221	Quintozene	4.5	101.5(5.3)	84.8(3.4)	87.8(1.9)	74.6(10.1)	94.8(8.2)	82.2(5.6)
222	Quinzalofop-ethyl	9	118.3(1.2)	107.3(7.3)	106.7(8.9)	116.7(8.0)	106.7(9.9)	107.0(9.8)
223	Sethoxydim	10	80.0(2.5)	85.3(3.6)	74.0(5.2)	177.5(2.0)	102.0(2.2)	118.5(1.6)
224	Silafluofen	4	90.0(3.5)	81.3(8.0)	102.7(2.2)	110.0(3.9)	77.0(1.3)	73.0(5.8)
225	Simazine	4	85.7(5.6)	83.6(0.8)	85.9(2.7)	64.0(1.4)	66.7(5.7)	90.7(4.6)
226	Simeconazole	5	107.4(3.1)	96.2(2.0)	99.7(2.8)	69.4(1.9)	91.7(4.8)	99.3(1.4)
227	Simetryn	6	86.7(4.5)	107.3(8.4)	98.2(6.3)	163.3(1.8)	150.7(4.3)	152.3(5.5)
228	Spirodiclofen	4.5	93.3(1.7)	119.2(4.4)	86.0(6.7)	84.1(2.0)	92.7(1.1)	92.0(5.9)
229	Spiromesifen	9	93.3(1.3)	98.0(8.9)	96.0(2.1)	96.7(6.1)	112.0(6.8)	88.5(2.4)
230	Tebuconazole	4.5	68.2(9.2)	98.0(8.7)	88.0(9.7)	92.5(9.6)	90.7(9.8)	89.7(9.8)
231	Tebufenozide	4.5	75.0(7.3)	77.2(7.2)	71.0(4.1)	74.0(6.1)	79.3(5.1)	78.3(2.3)
232	Tebufenpyrad	4.5	56.7(1.2)	101.3(5.1)	129.3(7.7)	171.7(8.9)	135.3(4.3)	144.7(3.8)
233	Tebupirimfos	4.5	116.7(4.9)	111.3(3.4)	98.3(0.4)	113.3(1.8)	109.3(1.7)	91.3(5.8)
234	Teflubenzuron	10	116.7(1.8)	114.0(3.0)	119.2(5.1)	205.0(4.2)	126.7(1.5)	152.0(6.6)
235	Tefluthrin	9	115.1(5.6)	101.3(0.8)	102.5(3.4)	72.8(3.1)	80.0(2.9)	95.9(2.4)
236	Terbufos	9	91.7(9.0)	98.7(8.9)	95.0(2.7)	105.0(4.4)	117.0(1.7)	81.5(4.9)
237	Terbuthylazine	4.5	103.2(3.7)	94.5(2.2)	98.0(2.1)	72.9(3.5)	91.6(6.0)	101.3(0.9)
238	Tetraconazole	7	103.3(6.8)	113.3(5.7)	103.7(0.4)	95.0(4.7)	92.0(3.2)	82.7(1.3)
239	Tetradifon	4.5	127.2(3.5)	91.4(5.7)	86.9(2.8)	75.2(9.6)	79.5(1.2)	87.2(5.3)
240	Thiabendazole	4.5	75.0(1.4)	85.3(3.6)	81.7(4.3)	75.0(5.7)	74.7(1.3)	75.0(2.4)
241	Thiacloprid	4.5	123.3(1.8)	105.3(6.1)	100.7(3.0)	108.3(5.3)	89.3(1.3)	89.0(3.0)
242	Thiamethoxam	10	127.5(3.9)	82.0(4.8)	86.7(8.0)	56.7(5.1)	79.0(4.9)	88.7(4.3)
243	Thiazopyr	9	96.1(3.1)	90.1(4.3)	95.3(3.8)	51.7(9.0)	75.8(5.6)	84.8(3.0)
244	Thifluzamide	10	57.0(8.0)	51.7(4.4)	61.1(10.6)	75.0(2.9)	80.0(1.5)	100.0(9.3)
245	Thiobencarb	4.5	125.0(6.0)	128.9(1.4)	74.2(6.6)	122.7(1.4)	95.4(7.6)	93.1(5.2)

No.	Compound	LOQ (ug/kg)	Recovery,% (RSD,%) <i>Lycii Fructus</i>			Recovery,% (RSD,%) <i>Angelica gigas Nakai</i>		
			20 ug/kg	50 ug/kg	100 ug/kg	20 ug/kg	50 ug/kg	100 ug/kg
			246	Thiodicarb	4.5	72.5(5.0)	79.0(7.5)	88.7(1.9)
247	Tiadinil	7	52.5(1.2)	55.0(4.1)	119.0(4.1)	72.5(4.5)	74.5(5.2)	114.5(5.2)
248	Tolclofos-methyl	7	99.1(4.2)	92.2(2.2)	94.3(2.6)	52.2(7.5)	76.5(5.4)	91.8(4.4)
249	Tolyfluamid	4	82.6(4.4)	72.7(3.7)	73.9(3.3)	40.3(9.1)	67.6(5.7)	91.0(5.6)
250	Tralomethrin	4.5	82.4(3.0)	65.8(4.1)	66.3(4.3)	93.6(3.6)	103.2(1.9)	110.0(8.0)
251	Triadimefon	4.5	102.5(3.1)	88.0(4.2)	97.0(4.8)	116.7(7.8)	118.7(1.8)	102.3(1.7)
252	Triadimenol	4.5	80.0(4.2)	82.4(1.3)	115.2(1.7)	95.0(3.9)	100.7(2.1)	92.0(10.7)
253	Triazophos	9	77.5(7.7)	82.0(8.2)	96.0(4.8)	82.5(4.4)	88.0(7.8)	101.5(3.6)
254	Trichlorfon	4.5	111.7(1.4)	104.0(2.6)	113.2(9.9)	97.0(10.8)	82.0(3.4)	118.3(1.7)
255	Tricyclazole	4.5	105.0(1.0)	114.0(5.3)	107.0(4.9)	98.3(1.7)	92.7(1.2)	83.3(3.9)
256	Trifloxystrobin	4.5	110.0(4.5)	128.7(1.8)	114.3(1.1)	152.5(1.6)	154.0(7.2)	154.0(1.7)
257	Triflumizole	4.5	116.7(2.0)	105.3(4.4)	108.0(1.9)	92.3(3.7)	118.7(1.6)	116.3(5.9)
258	Triflumuron	9	125.0(1.6)	118.0(7.4)	128.0(5.5)	212.5(5.0)	148.0(1.3)	168.3(6.0)
259	Trifluralin	4.5	102.4(2.7)	89.6(2.8)	96.0(2.9)	91.4(9.2)	73.8(3.9)	74.8(1.6)
260	Vamidotion	4	117.5(3.0)	112.0(4.0)	104.3(4.5)	70.0(3.5)	79.0(2.6)	72.0(3.7)
261	Vinclozolin	4	106.7(4.2)	96.9(3.5)	99.1(2.5)	73.8(8.9)	94.3(3.6)	103.3(1.9)

Table 4. Average recovery and RSD of 261 pesticides spiked in cnidium and jujube different concentrations with GC-MS/MS and LC-MS/MS (n=5)

No.	Compound	LOQ (ug/kg)	Recovery,% (RSD,%) <i>Zizyphi Fructus</i>			Recovery,% (RSD,%) <i>Cnidii Rhizoma</i>		
			20 ug/kg	50 ug/kg	100 ug/kg	20 ug/kg	50 ug/kg	100 ug/kg
			1	Acetamiprid	4.5	77.5(3.7)	123.3(4.5)	118.7(7.7)
2	Alachlor	5	80.4(2.5)	83.2(4.3)	85.9(3.6)	45.6(5.0)	49.2(2.5)	26.0(2.2)
3	Aldicarb	10	141.4(5.7)	216.0(4.1)	77.9(5.0)	157.5(0.8)	174.0(5.2)	93.0(2.2)
4	Aldrin	20	84.6(1.3)	76.7(3.7)	78.0(3.9)	105.0(2.0)	98.0(4.1)	71.0(8.9)
5	Amisulbrom	8	72.0(3.6)	73.0(1.3)	75.0(7.7)	190.7(4.1)	167.2(1.2)	152.5(4.2)
6	Amitraz	8	71.0(4.1)	79.0(4.1)	115.5(4.1)	165.2(0.4)	166.2(1.2)	155.5(1.2)
7	Azimsulfuron	4.5	105.2(0.4)	103.0(4.1)	104.5(4.9)	70.0(4.1)	107.0(1.9)	86.5(1.2)
8	Azinphos-methyl	4.5	77.5(4.1)	79.0(5.6)	82.5(4.3)	97.5(5.4)	114.0(4.2)	97.0(7.5)
9	Azoxystrobin	4.5	75.0(7.5)	75.2(2.8)	99.0(10.9)	142.5(1.1)	84.0(6.7)	119.2(1.3)
10	Bendiocarb	16	115.0(3.4)	116.7(1.4)	113.7(3.4)	116.7(3.9)	160.0(7.8)	152.3(2.1)
11	Benthiavalicarb-isopropyl	4.5	86.2(0.5)	85.0(2.9)	105.2(5.2)	107.5(4.1)	109.0(5.2)	112.5(1.1)
12	Benzoximate	4.5	90.0(5.5)	114.0(4.1)	114.0(5.4)	77.5(5.3)	74.0(11.0)	75.0(5.7)
13	BHC- α	5	77.5(1.9)	71.1(5.6)	72.9(5.5)	117.0(3.3)	111.0(3.7)	113.0(4.1)
14	BHC- β	4	85.4(3.1)	71.6(3.9)	70.0(4.4)	75.0(1.2)	73.0(7.2)	79.7(5.3)
15	BHC- δ	4	75.4(5.0)	70.6(6.0)	77.4(5.9)	75.0(1.2)	73.0(7.2)	79.5(5.4)
16	BHC- γ	4	81.6(8.4)	74.3(9.0)	72.8(1.6)	78.0(1.2)	73.0(1.2)	71.0(1.3)
17	Bifenox	4.5	102.5(4.1)	85.0(4.7)	77.5(4.6)	215.0(5.2)	178.7(5.3)	171.5(0.9)
18	Bifenthrin	5	91.5(4.3)	85.5(3.6)	86.9(2.9)	110.0(3.8)	107.0(4.8)	93.0(4.8)
19	Bitertanol	9	119.2(4.7)	114.0(2.4)	116.7(8.1)	108.3(1.0)	170.0(4.3)	179.7(9.2)
20	Boscalid	4.5	105.2(9.7)	117.3(5.7)	117.5(2.1)	96.7(6.1)	94.0(5.6)	101.2(2.5)
21	Bromobutide	4	79.6(7.2)	79.4(1.7)	89.6(1.4)	69.9(8.8)	87.7(9.7)	98.4(3.8)
22	Bromopropylate	20	87.3(2.1)	80.5(3.2)	81.7(3.3)	105.0(4.7)	98.0(2.3)	87.0(4.7)
23	Buprofezin	4.5	113.3(5.0)	112.0(5.1)	101.7(5.4)	108.3(7.1)	110.7(1.8)	103.7(3.7)
24	Butachlor	20	81.3(3.8)	79.3(6.1)	83.9(4.7)	113.0(7.9)	112.0(2.4)	114.0(8.2)
25	Cadusafos	20	80.2(2.3)	81.4(1.0)	89.0(3.8)	82.9(2.7)	88.2(1.6)	80.8(1.7)
26	Captan	4	179.8(2.8)	178.8(2.2)	158.4(9.1)	167.9(8.7)	210.5(4.8)	131.6(5.6)

No.	Compound	LOQ (ug/kg)	Recovery,% (RSD,%)			Recovery,% (RSD,%)		
			<i>Zizyphi Fructus</i>			<i>Cnidii Rhizoma</i>		
			20 ug/kg	50 ug/kg	100 ug/kg	20 ug/kg	50 ug/kg	100 ug/kg
27	Carbaryl	4.5	128.6(9.5)	140.0(5.9)	140.0(2.6)	85.0(11.8)	108.7(5.9)	110.0(4.2)
28	Carbendazim	4.5	102.5(3.5)	116.0(8.7)	98.4(8.5)	70.0(10.2)	75.3(1.6)	81.0(3.3)
29	Carbofuran	4.5	130.0(3.3)	142.0(9.4)	101.0(5.7)	151.7(9.5)	165.3(1.8)	171.0(2.0)
30	Carbosulfan	3	57.5(0.2)	58.7(7.6)	52.0(6.3)	53.3(1.5)	59.3(1.6)	58.7(1.9)
31	Carfentrazone -ethyl	4.5	111.7(9.9)	112.0(6.6)	115.3(1.3)	107.5(1.4)	100.0(9.8)	82.0(9.0)
32	Chlorantraniliprole	4.5	75.0(5.1)	85.0(1.7)	94.3(2.7)	107.5(2.3)	152.7(8.4)	103.3(3.0)
33	Chlorfenapyr	4	73.0(8.0)	72.0(8.8)	77.3(4.7)	83.3(5.1)	84.6(5.5)	88.5(2.5)
34	Chlorfluazuron	5	77.5(3.8)	115.0(3.8)	117.7(7.9)	90.0(7.7)	109.0(4.3)	110.5(1.6)
35	Chlorobenzilate	9	93.4(1.3)	82.3(3.9)	83.3(2.5)	105.0(4.0)	92.0(11.1)	90.0(4.2)
36	Chlorothalonil	4	150.2(4.9)	57.7(1.3)	52.3(6.0)	62.6(7.5)	56.1(3.8)	55.5(5.0)
37	Chlorpropham	5	115.0(8.9)	109.0(9.2)	101.5(0.6)	85.4(1.2)	82.2(10.2)	86.0(2.6)
38	Chlorpyrifos	16	83.3(4.2)	79.3(4.6)	82.0(3.2)	97.0(4.4)	85.0(1.9)	134.0(6.3)
39	Chlorpyriphos -methyl	9	75.9(2.5)	74.5(5.2)	77.4(3.5)	98.0(7.7)	111.4(1.6)	116.0(2.3)
40	Chromafenozide	4.5	111.7(1.0)	116.0(1.2)	96.0(1.5)	97.5(1.1)	92.0(2.6)	88.0(3.2)
41	Clofentezine	9	100.0(4.1)	107.0(1.3)	88.3(5.6)	116.7(3.8)	111.0(2.4)	119.2(8.3)
42	Clomazone	4.5	113.3(2.0)	113.3(9.6)	93.7(1.7)	91.7(3.1)	100.0(7.2)	105.0(1.0)
43	Clothianidin	9	111.7(5.3)	110.0(4.4)	119.3(7.0)	112.7(4.7)	102.7(1.3)	104.2(9.0)
44	Cyazofamid	5	115.0(7.4)	113.0(8.0)	116.0(2.6)	97.5(10.6)	103.3(1.9)	97.0(4.5)
45	Cyclosulfamuron	4.5	85.0(7.5)	85.9(9.9)	98.5(4.1)	71.7(9.1)	72.0(3.2)	73.0(2.5)
46	Cyflufenamid	4.5	87.5(2.5)	117.0(5.2)	102.3(1.7)	115.0(9.1)	112.0(8.6)	119.3(1.8)
47	Cyfluthrin	10	161.8(2.2)	131.4(9.2)	105.6(2.1)	96.7(1.3)	92.0(1.4)	76.6(10.3)
48	Cyhalofop-butyl	9	75.7(3.0)	77.0(1.7)	72.5(10.2)	107.5(1.2)	117.0(8.1)	98.0(5.6)
49	Cyhalothrin	4	123.6(2.9)	101.5(4.3)	102.3(4.2)	97.0(6.3)	103.0(6.4)	114.0(3.6)
50	Cymoxanil	8	100.0(5.5)	116.0(5.9)	111.3(9.2)	98.3(5.0)	110.7(3.6)	112.7(1.2)
51	Cypermethrin	4	115.4(8.8)	115.4(1.7)	125.3(2.8)	100.0(6.1)	95.0(2.5)	110.0(2.6)
52	Cyproconazole	4.5	125.0(6.9)	112.0(1.2)	118.3(5.0)	119.7(1.9)	116.7(9.7)	110.7(3.7)
53	Cyprodinil	45	111.7(3.7)	134.0(8.4)	132.3(6.1)	141.7(2.0)	156.7(6.3)	149.3(2.0)
54	Daimuron	9	88.3(3.4)	92.0(0.4)	101.2(1.1)	118.3(2.9)	87.3(1.7)	82.7(1.9)
55	Deltamethrin	4	110.6(1.6)	87.5(2.1)	88.1(1.2)	86.0(4.3)	102.0(3.5)	100.0(2.6)
56	Diazinon	10	79.1(3.0)	78.8(3.9)	77.3(8.1)	132.2(1.4)	162.3(4.5)	147.1(7.3)
57	Dichlofluanid	10	56.3(6.9)	36.8(1.1)	33.3(3.0)	164.4(7.2)	148.1(5.5)	142.5(8.8)
58	Dichlorvos	8	96.7(7.9)	95.0(10.4)	107.0(6.4)	107.5(1.9)	97.0(10.6)	85.0(2.4)
59	Diclofop-methyl	4	91.4(4.5)	81.7(3.4)	81.6(3.0)	108.0(3.8)	101.0(2.3)	91.0(3.8)
60	Dicloran	10	100.5(2.8)	80.4(3.2)	79.6(4.0)	174.5(1.2)	162.3(10.2)	166.2(5.2)
61	Dicofol	4	88.0(3.0)	83.2(4.0)	83.1(3.6)	110.0(3.3)	75.0(4.0)	71.0(4.2)
62	Dieldrin	4	93.9(2.9)	81.7(3.7)	81.8(3.1)	106.0(3.8)	77.0(4.2)	97.0(4.6)
63	Diethofencarb	4.5	110.0(5.0)	110.0(5.7)	101.0(5.4)	158.3(3.1)	148.7(4.1)	95.0(2.6)
64	Difenoconazole	4.5	113.3(3.5)	112.0(3.3)	110.7(8.4)	92.5(1.2)	104.0(10.9)	84.0(10.6)
65	Diffubenzuron	4.5	111.7(8.6)	98.0(4.3)	116.3(3.0)	137.5(3.3)	199.3(6.5)	170.7(3.8)
66	Dimepiperate	4.5	94.0(2.2)	106.0(2.9)	74.5(1.5)	78.3(9.0)	75.0(3.1)	75.0(1.4)
67	Dimethenamid	4	90.0(1.2)	85.6(3.8)	85.6(4.2)	103.0(3.2)	96.0(1.1)	87.0(4.0)
68	Dimethoate	4.5	108.3(9.1)	106.0(1.8)	109.0(7.6)	105.0(3.7)	119.3(0.7)	108.0(2.5)
69	Dimethomorph	4.5	125.0(1.2)	122.7(4.6)	131.0(9.4)	67.5(0.4)	84.0(7.7)	115.2(3.8)
70	Dimethylvinphos	4.5	107.5(1.8)	105.0(3.9)	101.7(7.6)	107.5(2.6)	143.3(5.7)	166.7(6.6)
71	Diniconazole	9	95.0(1.0)	107.0(1.0)	115.7(4.1)	105.0(6.1)	109.0(1.6)	116.0(4.0)
72	Dinotefuran	4	80.0(10.4)	122.0(1.2)	105.3(7.1)	115.0(4.9)	108.2(3.1)	104.7(4.7)
73	Diphenamid	4	95.6(2.0)	88.9(2.8)	87.9(3.6)	107.0(3.7)	95.0(2.0)	73.0(8.8)

No.	Compound	LOQ (ug/kg)	Recovery,% (RSD,%)			Recovery,% (RSD,%)		
			<i>Zizyphi Fructus</i>			<i>Cnidii Rhizoma</i>		
			20 ug/kg	50 ug/kg	100 ug/kg	20 ug/kg	50 ug/kg	100 ug/kg
74	Diphenylamine	4.5	79.0(5.9)	77.1(6.7)	79.4(4.8)	96.0(4.0)	80.0(3.8)	71.0(9.6)
75	Dithianon	6	85.0(6.8)	112.0(8.0)	80.5(8.3)	85.0(6.8)	112.0(8.0)	80.5(8.3)
76	Dithiopyr	3	80.3(2.8)	81.4(4.5)	83.2(4.1)	80.3(2.8)	81.4(4.5)	83.2(4.1)
77	Diuron	4.5	100.1(7.2)	110.7(5.9)	107.7(3.9)	140.0(9.4)	154.7(4.5)	157.3(4.2)
78	Edifenphos	4.5	118.3(5.5)	113.3(7.0)	103.7(1.6)	153.3(7.5)	146.7(3.5)	97.4(4.1)
79	Emamectin benzoate	8	115.0(6.1)	89.0(2.2)	92.0(8.4)	145.0(2.4)	144.7(5.6)	147.7(4.3)
80	Endosulfan- α	4	81.1(4.5)	79.2(5.5)	81.5(4.5)	107.0(4.2)	96.0(3.3)	76.0(5.1)
81	Endosulfan- β	4	92.0(1.8)	79.4(4.2)	79.1(4.2)	108.0(4.6)	98.0(2.1)	101.0(4.2)
82	Endosulfan-sulfate	4	83.1(3.7)	80.9(4.8)	84.5(3.8)	81.0(6.5)	83.0(2.5)	71.0(6.1)
83	Endrin	4	92.2(0.9)	74.2(5.1)	71.4(4.4)	110.8(3.6)	101.0(4.1)	89.0(6.0)
84	EPN	4	117.5(4.1)	83.2(4.0)	77.9(2.7)	102.0(4.9)	101.0(3.9)	101.0(4.5)
85	Esprocarb	4.5	84.0(1.8)	81.9(4.1)	83.3(3.5)	102.0(3.9)	97.0(2.0)	93.0(3.1)
86	Ethaboxam	9	82.5(4.1)	108.1(7.8)	82.0(1.1)	90.0(2.8)	119.0(1.2)	105.5(6.3)
87	Ethalfuralin	6	106.2(1.8)	75.3(4.6)	68.4(3.7)	100.0(4.3)	99.0(3.5)	106.0(2.6)
88	Ethiofencarb	4.5	71.0(10.3)	85.0(5.0)	87.3(6.9)	132.5(8.0)	114.0(3.0)	118.3(5.8)
89	Ethoprophos	2	90.0(1.4)	87.0(2.7)	114.0(0.9)	103.3(8.2)	116.7(2.8)	105.7(6.0)
90	Etofenprox	7	85.0(1.5)	104.0(1.1)	109.0(1.1)	70.5(2.2)	105.0(3.7)	102.7(1.2)
91	Etoxazole	4	95.9(9.2)	87.1(2.1)	87.0(3.1)	106.0(4.1)	78.0(3.0)	115.0(3.3)
92	Etridiazole	4	73.5(7.4)	72.8(10.1)	73.6(1.9)	75.0(2.9)	86.0(2.9)	71.0(3.4)
93	Etrimfos	4.5	115.0(4.1)	108.0(1.1)	82.5(5.7)	168.2(4.2)	169.0(2.1)	162.2(5.2)
94	Fenamidon	7	106.7(1.2)	98.0(3.9)	101.0(3.2)	116.7(1.4)	118.7(8.2)	118.7(3.5)
95	Fenamiphos	9	86.6(3.2)	80.2(6.6)	82.5(1.4)	115.0(5.4)	93.0(2.4)	99.0(1.4)
96	Fenarimol	4	116.7(6.0)	111.3(4.5)	119.7(3.9)	42.5(2.1)	96.0(2.9)	100.7(1.2)
97	Fenazaquin	4.5	81.0(2.0)	79.5(3.9)	80.2(2.6)	100.2(6.9)	105.1(2.4)	94.1(3.6)
98	Fenbuconazole	9	113.3(5.0)	108.0(6.1)	105.0(2.9)	91.7(1.6)	106.0(6.8)	111.0(4.1)
99	Fenhexamid	6	152.6(5.2)	155.0(5.2)	105.2(5.2)	55.0(1.1)	58.0(10.5)	51.5(4.5)
100	Fenitrothion	4.5	94.5(2.3)	76.1(3.4)	77.7(5.0)	52.1(2.3)	162.6(2.9)	150.6(5.9)
101	Fenobucarb	9	106.7(2.7)	102.0(2.9)	106.0(1.9)	95.0(9.1)	93.3(3.3)	98.0(1.8)
102	Fenothiocarb	8	100.0(4.1)	104.7(9.1)	113.7(6.3)	105.0(4.3)	108.7(10.6)	94.3(5.2)
103	Fenoxanil	9	85.3(2.6)	82.1(4.7)	82.4(4.0)	109.0(4.2)	101.0(2.8)	94.0(4.4)
104	Fenoxaprop-P-ethyl	4.5	105.0(7.6)	96.0(7.4)	104.7(9.8)	82.5(2.4)	116.7(2.9)	108.0(3.8)
105	Fenoxycarb	4.5	132.5(8.0)	119.0(1.2)	110.3(9.7)	171.7(4.4)	180.7(5.7)	145.0(5.8)
106	Fenpropathrin	4.5	105.0(9.0)	103.3(1.4)	96.5(0.7)	100.0(4.4)	112.0(10.2)	114.3(5.5)
107	Fenpyroximat	4	95.0(3.7)	109.0(7.7)	112.0(5.4)	113.3(8.0)	112.0(10.8)	108.3(8.4)
108	Fenthion	4.5	76.8(3.3)	78.0(4.1)	80.0(4.2)	107.0(4.2)	82.0(1.8)	90.0(3.6)
109	Ferimzone	18	106.7(7.2)	104.0(1.7)	115.3(5.1)	95.0(1.4)	116.7(3.0)	103.3(0.7)
110	Fipronil	9	109.5(2.8)	83.3(4.9)	81.2(3.7)	104.0(4.1)	98.0(2.1)	89.0(2.3)
111	Flonicamid	4	110.0(2.0)	112.0(2.9)	117.7(1.1)	131.7(1.9)	118.2(2.5)	109.3(6.6)
112	Fluacrypyrim	4.5	152.2(8.8)	109.1(2.3)	77.6(4.9)	105.0(4.1)	99.0(3.0)	93.0(2.1)
113	Fluazifop-P-butyl	4.5	113.3(4.0)	102.0(8.6)	111.7(6.1)	108.3(3.7)	104.7(2.1)	101.3(4.5)
114	Fluazinam	4.5	107.5(4.1)	111.1(5.2)	115.0(6.9)	95.5(1.1)	85.0(6.8)	105.2(3.0)
115	Flubendiamide	4.5	80.0(8.3)	102.0(8.6)	93.5(1.2)	80.7(7.1)	82.0(1.0)	90.0(6.1)
116	Fludioxonil	9	82.5(4.1)	92.0(5.8)	72.7(7.8)	115.0(1.2)	113.3(3.9)	119.5(6.5)
117	Flufenoxuron	9	140.0(3.6)	115.0(9.4)	104.7(9.6)	87.7(7.8)	90.0(7.0)	108.7(2.2)
118	Flumioxazin	4.5	95.0(7.4)	128.0(6.6)	146.5(2.7)	102.5(4.5)	152.0(5.6)	162.3(5.0)
119	Fluopicolide	9	110.0(0.3)	109.0(5.1)	109.7(6.3)	107.7(1.4)	109.3(1.7)	97.5(8.3)
120	Fluquinconazole	4.5	107.5(2.2)	111.0(2.5)	98.3(1.8)	90.0(5.7)	106.7(8.6)	88.0(7.0)
121	Flusilazole	4.5	94.0(1.9)	104.0(1.8)	112.0(3.6)	116.6(8.5)	100.0(3.5)	106.7(6.4)

No.	Compound	LOQ (ug/kg)	Recovery,% (RSD,%)			Recovery,% (RSD,%)		
			<i>Zizyphi Fructus</i>			<i>Cnidii Rhizoma</i>		
			20 ug/kg	50 ug/kg	100 ug/kg	20 ug/kg	50 ug/kg	100 ug/kg
122	Flutolanil	4.5	67.5(7.6)	139.0(9.2)	128.7(9.0)	165.0(8.9)	204.0(1.0)	95.0(6.0)
123	Forchlorfenuron	4.5	96.7(6.0)	94.0(2.3)	116.3(4.9)	83.3(8.2)	108.0(4.1)	105.7(1.7)
124	Fosthiazate	4	105.0(6.1)	102.0(1.9)	107.7(3.7)	96.7(4.6)	98.7(2.6)	95.7(1.6)
125	Fthalide	4	89.8(1.6)	83.4(4.0)	83.6(4.3)	108.0(4.3)	100.0(2.9)	87.0(4.4)
126	Furathiocarb	6	81.1(7.8)	76.0(5.3)	70.1(2.4)	104.0(4.3)	108.0(4.0)	85.0(3.0)
127	Heptachlor	10	83.9(2.6)	99.1(4.5)	92.6(6.4)	93.0(3.0)	95.0(6.3)	100.0(1.5)
128	Heptachlor-epoxide	4.5	95.7(3.5)	80.1(4.0)	79.5(2.8)	102.0(3.7)	96.0(1.6)	84.0(6.7)
129	Hexaconazole	4.5	90.0(5.7)	116.0(1.9)	111.0(4.0)	95.0(1.8)	77.0(1.8)	110.0(2.6)
130	Hexaflumuron	4	86.7(8.0)	103.0(8.0)	118.7(9.3)	87.5(6.6)	114.0(1.2)	108.7(3.7)
131	Hexazinone	9	81.7(9.9)	91.3(9.6)	92.7(5.5)	75.0(10.3)	74.0(2.1)	75.0(1.0)
132	Hexythiazox	2	103.3(2.2)	95.0(6.8)	99.7(4.7)	106.7(1.8)	114.0(5.7)	114.0(3.9)
133	Imazalil	9	67.5(5.7)	111.3(5.7)	123.3(9.1)	198.3(7.7)	162.7(3.8)	161.3(6.2)
134	Imazosulfuron	4	103.2(6.2)	102.3(2.2)	103.4(6.4)	72.5(6.2)	70.0(1.2)	70.5(5.2)
135	Imibenconazole	9	111.7(6.8)	111.0(9.4)	118.7(3.4)	91.7(8.3)	115.3(4.5)	95.0(2.2)
136	Imidacloprid	9	115.0(8.7)	101.0(1.2)	109.7(1.7)	101.1(4.7)	90.7(10.8)	93.3(8.9)
137	Indanofan	10	115.0(2.3)	106.0(1.3)	116.3(9.9)	72.5(1.2)	90.0(5.7)	80.0(3.3)
138	Indoxacarb	4.5	80.5(9.1)	76.1(9.0)	84.0(5.2)	95.0(3.2)	93.0(1.6)	87.0(3.2)
139	Iprobenphos	4	110.0(9.1)	105.0(1.6)	115.3(2.1)	102.5(3.4)	90.7(8.0)	89.5(4.2)
140	Iprodione	4.5	92.2(10.4)	109.0(5.1)	116.2(1.2)	115.0(1.9)	102.2(5.2)	94.2(0.3)
141	Iprovalicarb	4	106.7(7.4)	118.0(4.3)	105.3(1.6)	113.3(1.3)	92.0(1.6)	91.7(1.6)
142	Isofenphos	4.5	91.3(3.8)	83.1(3.4)	81.0(6.6)	106.0(3.7)	96.0(2.4)	80.0(3.5)
143	Isoprocarb	4.5	133.3(7.8)	123.3(1.9)	136.7(0.4)	152.2(3.3)	146.0(3.6)	95.7(3.1)
144	Isoprothiolane	9	110.1(5.0)	108.0(5.2)	119.3(1.3)	85.0(6.6)	102.7(1.1)	95.3(6.7)
145	Kresoxim-methyl	9	115.0(2.6)	76.0(2.3)	91.0(3.1)	80.0(4.2)	99.0(1.3)	103.0(1.8)
146	Linuron	9	130.0(5.4)	109.0(1.3)	124.0(7.9)	95.0(1.2)	88.5(5.2)	101.2(7.2)
147	Lufenuron	4	98.3(0.7)	80.0(2.9)	103.0(1.0)	112.5(5.2)	116.0(9.0)	97.5(8.8)
148	Malathion	3	90.1(2.1)	83.0(0.8)	83.9(3.0)	94.0(2.9)	88.0(2.0)	88.0(3.6)
149	Mandipropamid	10	117.5(4.8)	105.0(2.5)	112.5(3.5)	113.3(9.6)	103.0(5.3)	94.5(3.2)
150	Mecarbam	4.5	96.5(2.9)	83.2(4.0)	82.1(3.6)	115.0(3.8)	100.0(3.9)	82.0(3.6)
151	Mefenacet	4.5	165.0(6.1)	142.0(4.0)	134.0(4.7)	111.7(1.3)	163.3(3.9)	164.5(3.6)
152	Mepanipyrim	7	77.5(1.0)	104.0(6.3)	115.3(2.8)	77.5(1.2)	80.7(1.5)	103.7(5.4)
153	Mepronil	4.5	80.4(2.1)	85.7(5.3)	82.4(3.4)	101.0(1.6)	117.5(4.1)	95.5(1.1)
154	Metalaxyl	4.5	115.0(9.0)	90.0(1.5)	94.3(5.2)	112.5(1.0)	107.3(5.0)	103.0(5.7)
155	Metamifop	4.5	118.3(1.6)	97.0(8.7)	91.7(2.9)	138.3(9.1)	96.2(5.9)	92.3(9.1)
156	Metconazole	4.5	102.5(2.3)	109.0(2.5)	112.0(9.3)	111.7(4.0)	111.3(2.3)	114.0(3.6)
157	Methabenzthiazuron	4.5	131.7(7.9)	132.7(9.0)	142.7(2.5)	116.7(8.9)	109.3(3.9)	116.7(2.0)
158	Methidathion	9	91.1(1.6)	99.0(3.1)	106.5(6.5)	87.5(2.6)	94.7(1.4)	88.0(10.1)
159	Methiocarb	4.5	97.5(5.3)	101.2(3.2)	102.7(2.8)	106.0(8.0)	86.0(6.1)	115.0(0.5)
160	Methomyl	4	88.3(5.2)	86.7(1.1)	84.3(8.0)	85.0(11.6)	104.0(2.1)	110.7(2.0)
161	Methoxychlor	4.5	103.3(5.7)	91.2(3.9)	91.2(2.4)	110.0(3.4)	109.0(2.3)	99.0(3.8)
162	Metobromuron	3	170.0(9.6)	144.0(3.9)	148.0(4.2)	155.0(9.1)	156.0(10.5)	141.0(4.7)
163	Metolachlor	5	94.2(10.6)	88.1(3.1)	85.8(3.6)	93.0(4.4)	84.0(4.5)	112.0(3.1)
164	Metolcarb	10	70.0(5.3)	71.8(6.1)	76.2(3.2)	75.3(3.3)	74.1(1.2)	78.1(1.7)
165	Metrafenone	4.5	118.3(7.6)	114.0(1.6)	131.3(4.2)	108.3(1.5)	107.3(8.4)	110.3(3.9)
166	Metribuzin	4	118.3(8.8)	138.0(2.3)	137.3(3.4)	143.3(8.8)	144.7(2.1)	146.7(2.1)
167	Monocrotophos	4.5	116.7(6.2)	134.0(1.6)	119.7(7.3)	63.3(9.1)	111.3(5.8)	108.3(5.5)
168	Myclobutanil	4.5	132.5(4.1)	102.0(1.2)	55.5(1.1)	152.5(2.9)	92.7(4.8)	184.0(4.6)
169	Napropamide	5	107.5(1.3)	137.0(7.2)	138.0(7.6)	143.2(3.3)	144.0(8.3)	107.3(3.0)
170	Novaluron	8	141.7(2.0)	115.3(4.7)	132.7(4.5)	140.0(5.6)	145.3(8.8)	105.2(1.4)

No.	Compound	LOQ (ug/kg)	Recovery,% (RSD,%)			Recovery,% (RSD,%)		
			<i>Zizyphi Fructus</i>			<i>Cnidii Rhizoma</i>		
			20 ug/kg	50 ug/kg	100 ug/kg	20 ug/kg	50 ug/kg	100 ug/kg
171	Nuarimol	4	86.1(2.8)	81.5(3.7)	83.6(2.8)	112.0(3.2)	101.0(2.4)	88.0(3.4)
172	o,p'-DDT	4	96.0(2.4)	80.1(3.7)	80.4(2.4)	102.0(4.7)	99.0(2.5)	93.0(3.1)
173	Ofurace	4	89.3(3.4)	76.9(5.1)	78.3(4.7)	110.0(5.5)	104.0(3.7)	94.0(4.3)
174	Oxadiazon	4.5	79.0(3.1)	80.5(4.6)	83.0(3.7)	114.0(3.6)	104.0(3.7)	89.0(4.9)
175	Oxamyl	4.5	173.3(6.7)	180.7(7.1)	146.0(5.5)	227.5(8.9)	154.0(5.7)	194.0(1.7)
176	Oxaziclomefon	4	108.3(9.6)	91.0(7.0)	111.7(3.7)	140.0(1.7)	96.0(8.3)	115.7(7.4)
177	p,p'-DDD	4	96.0(2.4)	80.1(3.7)	80.4(2.4)	102.0(4.7)	99.0(2.5)	93.0(3.1)
178	p,p'-DDE	4	90.1(2.2)	82.2(3.1)	83.7(3.8)	109.0(4.8)	100.0(2.3)	88.0(4.2)
179	p,p'-DDT	8	87.2(4.7)	81.1(4.0)	82.3(9.6)	77.0(6.2)	96.0(3.9)	94.0(5.1)
180	Paclobutrazol	9	82.7(3.2)	94.7(4.1)	91.8(4.3)	108.0(4.4)	99.0(2.3)	89.0(3.1)
181	Parathion-ethyl	6	116.0(1.1)	79.7(3.7)	74.1(4.1)	87.9(4.6)	83.0(2.0)	80.9(3.8)
182	Parathion-methyl	5	80.4(1.8)	96.2(4.8)	84.0(2.4)	95.0(4.8)	94.0(3.3)	98.0(3.4)
183	PCTA	4.5	79.5(2.8)	78.4(4.2)	80.2(3.7)	102.0(4.0)	96.0(1.3)	90.0(4.3)
184	Penconazole	4.5	78.3(1.5)	96.0(6.1)	110.7(7.6)	87.5(4.5)	98.7(6.1)	88.3(4.8)
185	Pencycuron	9	91.7(4.7)	97.0(1.2)	96.0(7.8)	91.7(8.2)	108.7(3.0)	119.0(1.2)
186	Pendimethalin	8	119.2(8.3)	104.0(1.6)	111.8(6.7)	72.5(2.3)	106.7(1.9)	93.3(2.2)
187	Pentachloroaniline	4	86.3(2.8)	82.8(4.4)	83.9(5.0)	107.0(3.3)	93.0(2.4)	89.0(2.5)
188	Pentoxazone	4	78.7(1.8)	78.2(5.5)	81.4(4.6)	107.0(3.7)	100.0(1.7)	89.0(3.6)
189	Permethrin	8	98.4(1.0)	85.0(4.0)	85.4(4.8)	45.2(4.2)	60.4(4.6)	99.2(7.3)
190	Phenthoate:PAP	9	108.1(2.7)	86.5(2.2)	85.1(3.1)	100.0(4.4)	95.0(2.0)	82.0(3.5)
191	Phorate	9	64.8(6.8)	66.3(6.4)	68.8(6.0)	47.4(6.0)	59.8(6.4)	76.3(2.0)
192	Phosalone	4	101.7(6.9)	113.0(6.4)	95.0(1.7)	117.5(4.1)	102.7(1.9)	114.3(3.3)
193	Phosphamidone	4	106.9(5.3)	90.2(6.2)	88.4(3.2)	108.9(1.3)	88.1(1.3)	116.2(7.3)
194	Phoxim	4.5	200.0(1.5)	154.0(1.0)	101.0(8.7)	180.0(1.8)	109.0(5.8)	128.7(1.5)
195	Piperophos	4.5	116.7(9.9)	100.0(4.1)	113.3(6.1)	115.0(1.7)	113.3(3.4)	107.3(7.5)
196	Pirimicarb	7	111.7(2.4)	118.7(1.5)	110.3(3.0)	101.7(5.0)	117.3(4.6)	102.7(1.6)
197	Pirimiphos-ethyl	4.5	93.1(3.0)	81.9(4.8)	81.8(3.9)	107.0(5.1)	99.0(3.5)	86.0(3.3)
198	Pirimiphos-methyl	4.5	83.3(2.0)	83.0(5.9)	85.3(7.4)	85.0(3.6)	84.7(3.1)	89.2(2.2)
199	Pretilachlor	4	151.7(6.9)	115.3(9.1)	111.3(5.6)	113.3(1.5)	106.7(1.5)	107.7(1.2)
200	Probenazole	4.5	82.2(5.2)	85.2(2.3)	82.5(2.2)	82.2(6.5)	85.2(10.5)	89.2(1.2)
201	Prochloraz	4	113.3(6.7)	118.0(4.4)	101.3(1.1)	80.0(6.3)	99.3(8.1)	101.3(1.9)
202	Procymidone	9	75.0(6.2)	79.9(3.9)	84.7(4.3)	113.0(3.5)	101.0(1.4)	89.0(0.8)
203	Profenofos	4.5	111.7(5.0)	106.0(8.3)	93.0(6.3)	104.5(1.7)	98.0(10.0)	97.3(5.3)
204	Propamocarb	6	115.0(7.4)	111.0(8.9)	79.0(10.2)	103.5(4.0)	113.3(1.8)	83.0(1.7)
205	Propanil	4	89.1(1.7)	85.6(2.5)	88.2(3.3)	166.8(1.1)	145.8(6.4)	207.7(6.4)
206	Propoxur	4	79.5(2.5)	77.8(4.5)	78.8(3.7)	88.6(8.9)	105.5(6.1)	116.6(4.0)
207	Prothiofos	4.5	90.6(2.6)	86.0(4.4)	87.3(3.3)	110.0(4.1)	103.0(0.9)	91.0(3.1)
208	Pyraclofos	4.5	105.0(3.8)	92.0(3.4)	118.5(1.3)	75.2(10.2)	77.5(5.2)	77.5(10.5)
209	Pyraclostrobin	4	98.0(7.4)	111.0(1.1)	113.0(1.5)	113.3(2.5)	107.3(5.1)	115.3(5.3)
210	Pyrazophos	4.5	78.8(3.5)	77.5(3.4)	80.5(4.9)	106.1(4.3)	98.0(2.6)	88.0(4.0)
211	Pyributicarb	4.5	85.0(3.7)	80.0(4.4)	83.0(5.7)	86.7(9.8)	88.0(6.7)	83.7(4.6)
212	Pyridaben	4.5	85.0(3.7)	91.0(3.8)	93.3(6.5)	86.7(1.1)	80.0(11.2)	80.7(6.2)
213	Pyridaphenthion	4.5	105.0(5.1)	116.7(8.0)	119.7(5.9)	88.3(9.0)	86.0(1.9)	76.0(1.9)
214	Pyriftalid	4.5	181.7(5.7)	137.0(5.2)	126.7(7.0)	127.5(4.6)	106.7(1.7)	168.5(2.1)
215	Pyrimethanil	4	140.0(3.6)	142.0(5.9)	137.0(1.5)	138.3(7.5)	156.7(2.9)	153.7(5.3)
216	Pyrimidifen	4	84.8(2.6)	89.9(3.8)	82.9(3.7)	90.5(1.6)	95.2(6.2)	82.4(6.4)
217	Pyriminobac-methyl	4	88.2(0.9)	79.4(4.2)	80.6(3.2)	109.0(3.9)	101.0(2.3)	91.0(3.6)
218	Pyriproxyfen	9	94.4(1.7)	86.0(4.3)	86.0(4.0)	114.0(2.5)	102.0(2.8)	88.0(5.0)
219	Pyroquilon	10	98.1(5.5)	87.6(4.6)	83.8(6.3)	106.0(6.7)	92.0(2.0)	88.0(1.2)

No.	Compound	LOQ (ug/kg)	Recovery,% (RSD,%)			Recovery,% (RSD,%)		
			<i>Zizyphi Fructus</i>			<i>Cnidii Rhizoma</i>		
			20 ug/kg	50 ug/kg	100 ug/kg	20 ug/kg	50 ug/kg	100 ug/kg
220	Quinoclamine	4	165.9(6.1)	129.0(4.1)	124.4(4.7)	21.7(9.2)	35.2(6.2)	45.2(1.5)
221	Quintozene	4.5	84.5(3.1)	72.5(4.6)	70.9(4.7)	97.0(3.7)	84.0(9.4)	93.0(5.2)
222	Quinzalofop-ethyl	9	111.7(7.1)	113.0(1.3)	96.0(3.6)	97.5(10.9)	114.7(8.8)	103.2(2.9)
223	Sethoxydim	10	107.5(4.1)	115.0(2.4)	113.3(1.4)	119.2(1.8)	76.0(1.6)	85.0(3.3)
224	Silafluofen	4	85.2(10.2)	89.6(2.4)	108.0(5.3)	107.5(5.4)	116.7(4.4)	115.3(3.4)
225	Simazine	4	84.1(2.6)	82.8(2.7)	85.2(4.8)	165.4(6.2)	155.1(1.1)	166.1(8.6)
226	Simeconazole	5	75.8(3.6)	80.5(7.0)	86.3(5.3)	135.2(4.3)	192.6(3.4)	168.1(3.7)
227	Simetryn	6	143.3(6.5)	133.3(3.5)	112.7(1.0)	185.0(2.7)	165.3(3.0)	149.0(3.5)
228	Spirodiclofen	4.5	116.7(9.3)	107.0(6.7)	91.3(4.1)	85.0(6.9)	106.7(6.1)	93.3(4.7)
229	Spiromesifen	9	97.5(3.4)	107.0(3.8)	98.5(2.2)	110.0(7.7)	94.0(4.2)	78.0(10.8)
230	Tebuconazole	4.5	110.0(8.0)	106.0(3.5)	81.5(7.8)	70.0(4.7)	74.0(9.8)	71.3(1.9)
231	Tebufenozide	4.5	72.5(2.5)	79.0(1.1)	77.5(2.4)	72.5(2.7)	74.7(5.4)	76.5(3.9)
232	Tebufenpyrad	4.5	130.0(8.5)	115.0(5.7)	104.0(7.4)	277.5(1.1)	149.2(6.7)	128.3(9.0)
233	Tebupirimfos	4.5	115.0(1.5)	119.0(9.9)	109.0(6.2)	115.0(6.9)	118.0(1.4)	102.0(1.4)
234	Teflubenzuron	10	43.2(3.6)	116.0(4.9)	107.3(8.4)	52.5(5.1)	183.0(1.2)	103.7(9.3)
235	Tefluthrin	9	85.4(2.1)	82.0(3.9)	82.5(4.1)	81.8(1.8)	102.3(3.0)	107.7(3.5)
236	Terbufos	9	102.5(8.6)	93.3(8.7)	83.0(8.4)	107.5(2.3)	97.0(1.5)	84.0(1.8)
237	Terbuthylazine	4.5	88.7(3.3)	84.4(4.3)	86.0(4.7)	152.1(8.8)	165.2(9.2)	163.2(7.3)
238	Tetraconazole	7	95.0(3.1)	109.0(6.3)	118.3(8.0)	105.0(1.2)	98.7(7.0)	105.7(4.3)
239	Tetradifon	4.5	79.3(6.1)	79.7(5.8)	79.5(2.4)	84.5(6.0)	84.0(7.1)	85.2(8.3)
240	Thiabendazole	4.5	100.0(8.7)	102.0(1.1)	103.7(5.3)	119.2(7.2)	115.3(4.0)	105.0(5.0)
241	Thiacloprid	4.5	118.3(9.1)	102.0(1.7)	110.7(9.7)	151.7(6.9)	97.3(5.5)	131.3(4.2)
242	Thiamethoxam	10	143.3(5.3)	103.3(1.5)	99.7(8.5)	97.5(1.4)	112.7(1.9)	106.7(9.4)
243	Thiazopyr	9	93.7(3.8)	83.7(3.7)	81.6(2.8)	106.0(5.0)	101.0(3.5)	97.0(9.2)
244	Thifluzamide	10	163.6(1.6)	111.3(3.2)	118.2(3.5)	56.2(1.2)	59.0(1.2)	51.0(4.1)
245	Thiobencarb	4.5	68.0(4.8)	75.8(6.8)	78.9(3.9)	107.0(4.1)	98.0(2.6)	91.0(4.0)
246	Thiodicarb	4.5	101.7(1.2)	117.0(1.2)	103.3(1.6)	175.2(5.2)	170.3(3.9)	190.2(9.4)
247	Tiadinil	7	49.2(5.2)	176.0(3.0)	108.0(1.6)	157.5(3.7)	63.0(3.7)	144.5(6.2)
248	Tolclofos-methyl	7	76.8(2.4)	79.5(5.1)	81.5(4.2)	102.0(4.1)	95.0(3.2)	83.0(4.0)
249	Tolyfluanid	4	90.7(3.8)	81.5(6.9)	80.6(8.4)	73.0(3.3)	93.0(3.7)	86.0(3.1)
250	Tralomethrin	4.5	137.9(1.8)	90.2(1.9)	85.1(0.4)	86.0(4.3)	102.0(3.5)	100.0(2.6)
251	Triadimefon	4.5	107.5(1.2)	119.0(3.6)	109.0(4.3)	133.3(1.8)	197.3(1.5)	172.7(1.9)
252	Triadimenol	4.5	98.3(1.9)	84.7(1.8)	95.7(10.5)	85.0(1.2)	88.0(1.7)	75.7(8.0)
253	Triazophos	9	82.5(4.3)	105.0(1.2)	115.3(8.0)	105.0(9.5)	86.7(3.2)	98.7(2.2)
254	Trichlorfon	4.5	88.3(3.7)	86.0(6.5)	114.3(5.5)	90.0(8.8)	116.7(3.3)	101.3(1.2)
255	Tricyclazole	4.5	91.7(1.8)	117.3(1.8)	110.7(1.6)	86.7(8.6)	89.3(4.3)	82.3(5.0)
256	Trifloxystrobin	4.5	115.0(5.7)	114.0(1.8)	125.7(4.8)	102.5(4.4)	148.7(5.4)	112.0(5.8)
257	Triflumizole	4.5	103.3(9.1)	95.0(10.4)	116.0(3.4)	117.8(4.0)	94.0(1.5)	114.3(3.7)
258	Triflumuron	9	136.7(1.5)	115.3(8.4)	124.0(0.8)	115.0(1.6)	112.7(7.4)	149.0(6.4)
259	Trifluralin	4.5	102.7(1.5)	74.5(4.8)	69.3(3.1)	89.0(4.9)	85.0(2.2)	95.0(1.9)
260	Vamidotion	4	118.3(1.6)	83.0(8.7)	83.7(9.2)	111.7(1.6)	118.0(4.7)	103.7(5.8)
261	Vinclozolin	4	85.0(4.8)	81.1(4.6)	84.7(4.1)	106.0(3.7)	82.0(5.2)	83.0(2.1)

분석법의 농약의 회수율

품목별 261성분에 대한 회수율 시험결과는 Tables 3과 4에 나타내었다. 구기자에서 70~120% 이내이고 표준편차가 20% 이내인 농약은 20 ug/kg에서 228종, 50 ug/kg에서 234종, 100 ug/kg에서 244종이었다. 당귀에서 70~120% 이

내이고 표준편차가 20% 이내인 농약은 20 ug/kg에서 185종, 50 ug/kg에서 204종, 100 ug/kg에서 224종이었으며, 대추에서 70~120% 이내이고 표준편차가 20% 이내인 농약은 20 ug/kg에서 219종, 50 ug/kg에서 228종, 100 ug/kg에서 231종이었다. 천궁에서 70~120% 이내이고 표준편차가

20% 이내인 농약은 20 ug/kg에서 198종, 50 ug/kg에서 205종, 100 ug/kg에서 214종이었다. 각국 및 국제기구 등에서 연구수행에 활용된 분석방법에 대한 적합성은 회수율과 상대표준편차 등의 범위를 이용하여 판단하고 있으며, 국내는 회수율 70~120% 및 상대표준편차 20% 이하(Rural Development Administration, 2009), 유럽연합에서 제시한 회수율은 70~120%와 상대표준편차 20% 이하 (Document N SANCO/12495, 2011)로 규정하고 있다. 본 연구결과에서 생약재 중 구기자, 당귀, 대추, 천궁 품목에 대하여 GC-MS/MS와 LC-MS/MS를 이용한 다중농약다성분 분석법의 회수율은 국내 및 국제적 기준에 충족하였다. 하지만 일부 불량한 회수율의 결과를 가진 농약성분(Table 5)의 경우 생약재 시료에 존재하는 matrix의 영향에 의해 suppression과 enhancement의 결과로 정확한 정량은 어렵지만 10 ug/kg 이하까지 정량 한계를 낮춤으로써 충분히 검출 가능하기에 screening 용도로 활용 가능하다고 판단되었다. LC-MS/MS 분석 대상 농약 중 chlorfluzuron, etofenprox 등의 분석불가 성분으로 분류하였으나[11], Hernando 등[12]의 연구결과 macrocyclic lactone 화합물은 LC-MS/MS의 desolvation 온도에 따라 감도의 변화가 있다고 보고하였다. 이들의 연구결과를 바탕으로 desolvation 온도를 600°C에서 400°C로 설정하여 회수율을 시험하였을 경우 chlorfluzuron의 회수율은 70.2-118.0%, etofenprox의 회수율은 70.5-109.6%의 회수율을 보임으로써 회수율 기준인 70-120% 이내를 만족하는 결과를 나타내었다. 또한 식품의약품안전처(2010)의 보고에 의하면 QuEChERS 분석법을 이용할 경우 carbendazim, tricyclazole 및 sulfonyleurea 계통의 농약은 다중농약다성분 분석이 불가능한 농약들로 분류하

였으나, 본 실험에서는 회수율이 각각 70.0-117.3% 및 상대 표준편차 1.0-10.2%로 기준을 만족하는 결과를 나타내었다. 따라서, 본 연구에서 검토된 생약재 중 GC-MS/MS와 LC-MS/MS를 이용한 농약의 다성분 동시분석법은 앞으로 생약재의 농약잔류 모니터링 연구에 적용될 수 있을 것으로 판단 되었다.

품목별 matrix effect

품목별 261성분에 대한 matrix effect는 matrix matched standard와 solvent standard를 비교하여 산출하였다. Matrix effect 판단 시 $\pm 20\sim 50\%$ 의 수준은 약간의 영향을 받는 수준이며, 그 이상은 matrix에 강한 영향을 받는 수준으로 평가한다[13-15].

해당 기준으로 본 시험결과는 supplemental S1에 나타내었다. Matrix의 영향이 없거나 약한 영향($\pm 20\sim 50\%$)을 받는 성분들은 천궁에서는 acetamiprid 등 186종, 당귀에서는 alachlor 등 192종, 구기자에서는 aldrin 등 192종, 대추에서는 alachlor 등 211종이었다. Matrix에 의해 강한 영향을 받는 성분들은 천궁의 경우 alachlor 등 75종, 당귀의 경우 acetamiprid 등 69종, 구기자의 경우 acetamiprid 등 69종, 대추의 경우 acetamiprid 등 50종이었다. 또한, 농약의 물리화학적 특성 중 기본적인 계수인 옥탄올/물 분배계수 Kow (log P)값을 3 이하와 3이상의 두 개 그룹으로 나누어 품목별 matrix effect 영향을 알아보았다. Kow (log P)값이 3이하인 경우 구기자를 제외한 천궁, 당귀, 대추에서 suppression 되는 경향이 크다는 것을 알 수 있었으며, Kow (log P)값이 3이상에서는 구기자, 대추에 비해 천궁, 당귀가 suppression과 enhancement

Table 5. Components showing poor average recovery of 261 pesticides in herbal medicines

Herbal medicine	Compound
<i>Lycii Fructus</i>	Captan, Cyhalothrin, Deltamethrin, Dichlofluanid, Dichlorvos, Diethofencarb, Diflubenzuron, Etrimfos, Fenarimol, Myclobutanil, Napropamide, Phoxim, Pretilachlor, Tebufenpyrad, Thifluzamide
<i>Angelica gigas Nakai</i>	Acetamiprid, Alachlor, Aldicarb, Amisulbrom, Amitraz, Azoxystrobin, Bendiocarb, Bitertanol, Captan, Carbaryl, Carbofuran, Chlorantraniliprole, Cyhalofop-butyl, Cyprodinil, Dimethylvinphos, Diuron, Emamectin benzoate, Etrimfos, Fenhexamid, Fenoxycarb, Flumioxazin, Flutolanil, Isoprocarb, Metobromuron, Metolachlor, Myclobutanil, Napropamide, Pentoxazone, Propoxur, Pyrifthalid, Pyrimethanil, Quinoclamine, Simetryn, Tebufenpyrad, Teflubenzuron, Trifloxystrobin, Triflumuron
<i>Zizyphi Fructus</i>	Captan, Carbaryl, Carbosulfan, Chlorothalonil, Cypermethrin, Cyprodinil, Dichlofluanid, Dimethomorph, Ethalfluralin, Flumioxazin, Flutolanil, Imazalil, Isoprocarb, Linuron, Mefenacet, Methabenzthiazuron, Metobromuron, Metrafenone, Metribuzin, Myclobutanil, Napropamide, Novaluron, Oxamyl, Phorate, Pyrifthalid, Pyrimethanil, Quinoclamine, Trifloxystrobin, Triflumuron, Trifluralin
<i>Cnidii Rhizoma</i>	Acetamiprid, Alachlor, Amisulbrom, Amitraz, Bendiocarb, Bifenox, Bitertanol, Captan, Carbofuran, Carbosulfan, Chlorothalonil, Chlorpyrifos, Cyprodinil, Diazinon, Dichlofluanid, Dicloran, Diflubenzuron, Dimethylvinphos, Diuron, Emamectin benzoate, Etrimfos, Fenhexamid, Fenitrothion, Fenoxycarb, Flumioxazin, Imazalil, Mefenacet, Metobromuron, Metribuzin, Myclobutanil, Oxamyl, Phoxim, Propanil, Pyrifthalid, Pyrimethanil, Quinoclamine, Simazine, Simeconazole, Simetryn, Tebufenpyrad, Terbutylazine, Thiacloprid, Thifluzamide, Thiodicarb, Tiadinil, Triadimefon, Triflumuron

에 의한 matrix 영향이 다소 크다는 것을 알 수 있었다. 한편 Kow(log P)값을 기준으로 3미만인 극성 농약이 비극성농약에 비해 suppression 현상이 많이 관찰되었으며, 이와 같은 연구결과는 Helen 등[16]의 연구결과와 비슷한 경향이였다.

마지막으로, 농약성분의 화학적 성분이나 조성에 따라 품목별 matrix effect 영향을 알아보려고 261 성분을 2,6-dinitroaniline, amide, anilide, azole, organochlorine, organophosphorus, carbamate, pyrethroid, thiocarbamate 및 urea로 분류하였다. Pyrethroid계의 경우 4품목에서 모두 enhancement에 의해 잔류량이 증가된 것으로 나타났는데 이 약제들의 Kowlog P값은 4이상이었다. Carbamate계의 경우 천궁, 당귀에서 suppression에 의해 잔류량이 감소된 것으로 나타났으며, 이들 약제의 Kowlog P값이 3이하였다. Organophosphorus계의 경우 당귀에서는 suppression에 의해 잔류량이 감소된 것으로 나타났고, 대추에서는 enhancement에 의해 잔류량이 증가하는 것으로 나타났다. Organochlorine계의 경우는 대부분이 당귀에서 suppression이 일어나는 것을 확인할 수 있었지만 그 이외의 2,6-dinitroaniline, amide, anilide, azole, thiocarbamate 및 urea계 등에 속하는 농약들은 특별한 경향을 나타내지 않았다. 따라서, 생약재 중 다중농약 동시분석을 수행할 경우 질량분석기를 통한 정량분석에서는 시료 matrix의 영향을 보완하기 위하여 무처리 시료에서 동일한 전처리 과정을 통해 얻은 추출용액을 사용하여 표준물질을 만들어 정량분석 해야 하며, suppression과 enhancement에 의한 matrix 영향을 주는 요인들에 대해서는 좀 더 많은 연구가 필요하다고 본다.

Note

The authors declare no conflict of interest.

References

1. Choi YC, Park SK, Kim OH, Seoung HJ, Han SH, Lee YJ, Jeong HJ, Kim YH, JO HB et al. (2011) Pesticides residue monitoring of medicinal herbs in Seoul. *The Korean Journal of Pesticide Science*, 15(4), 335-349.
2. Cho JH, KIM DH, Kim HS, Oh MH, Kang IH, Shim YH, Hwang WK, Myung SW, Chio BK (2000) Monitoring research for residual pesticides as endocrine disreptors in natural medicines(I). *Korean Journal of Pharmacognosy*, 31(4), 455-458.
3. Hwang BH, Lee MR (2000) Solid-phase microextraction for organochlorine pesticide residues analysis in Chinese herbal formulations. *Journal of Chromatography A*, 898(2), 245-256.
4. Lee SH, Kim HS, Kim YM, KIM WS, Won YJ, Chae GY, Kim OH, Park HJ, Jeong SW (2006) Monitoring of pesticide residues in herbal medicines. *Journal of the Environmental Sciences*, 15(8), 811-817.
5. KIM BS, Park SG, Kim MS, Cho TH, Han CH, Jo HB, Chio BH, Kim SD (2007) A study of current status on pesticide residues in commercial dried agricultural products. *Korean Journal Food Science and Technology*, 39(2), 114-121.
6. Ock HS (2009) Developmental trend of analytical methods for pesticide residues. *The Korean Journal of Pesticide Science*, 13(4), 336-348.
7. Park JW, Kim AK, Kim JP, Lee HH, Park DW, Moon SJ, Ha DY, Seo KW (2014) Multi-residue analysis of pesticides using GC-TOF/MS, ECD, NPD with QuEChERS sample preparation. *The Korean Journal of Pesticide Science*, 18(4), 278-295.
8. Wilkowska A, Biziuk M (2011) Determination of pesticide residues in food matrices using QuEChERS methodology. *Food Chemistry*, 125(3), 803-812. <https://doi.org/10.1016/j.foodchem.2010.09.094>.
9. de Sousa Freitas S, Lancas FM (2009) Matrix effects observed during pesticides residue analysis in fruits by GC. *Journal of Separation Science*, 32(21), 3698-3705. <https://doi.org/10.1002/jssc.200900358>.
10. Hajšlová, J., Holadova, K., Kocourek, V., Poustka, J., Godula, M., Cuhra, P., & Kempný, M. (1998). Matrix-induced effects: a critical point in the gas chromatographic analysis of pesticide residues. *Journal of Chromatography A*, 800(2), 283-295.
11. Kwon HY, Kim CS, Park BJ, Jin YD, Son KA (2011) Multiresidue analysis of 240 pesticides in apple and lettuce by QuEChERS sample preparation and HPLC-MS/MS analysis. *The Korean Journal of Pesticide Science*, 15(4), 417-433.
12. Hernando MD, Suarez-Barcelona JM, Bueno MJM, Garcia-Reyes JF, Fenandez-Alba AR (2007) Fast separation liquid chromatography tandem mass spectrometry for the confirmation and quantitative analysis of avermectin residues in food. *Journal of chromatography A*, 1155(1), 62-73. <https://doi.org/10.1016/j.chroma.2007.02.120>.
13. Ferrer C, Lozano A, Agüera A, Girón AJ, Fernández-Alba AR (2011) Overcoming matrix effects using the dilution approach in multiresidue methods for fruits and vegetables. *Journal of Chromatography A*, 1218(42), 7634-7639. <https://doi.org/10.1016/j.chroma.2011.07.033>.
14. Moreno-González D, Huertas-Pérez JF, García-Campaña AM, Gámiz-Gracia L (2014) Determination of carbamates in edible vegetable oils by ultra-high performance liquid chromatography-tandem mass spectrometry using

- a new clean-up based on zirconia for QuEChERS methodology. *Talanta*, 128, 299-304.
<https://doi.org/10.1016/j.talanta.2014.04.045>.
15. Gwon JH, Kim TK, Seo EK, Hong SM, Kwon KS, Kyung HY, Kyung KS, Kim JE, Cho NJ (2014) Multiresidue analysis of 124 pesticides in soil with QuEChERS extraction and LC-MS/MS. *The Korean Journal of Pesticide Science*, 18(4), 296-313.
 16. Stahnke H, Reemtsma T, Alder L (2009) Compensation of matrix effects by postcolumn infusion of a monitor substance in multiresidue analysis with LC-MS/MS. *Analytical Chemistry*, 81(6), 2185-2192.
<https://doi.org/10.1021/ac802362s>.

Supplemental S1. Matrix effect results

No.	Compound	Matrix effect (%)			
		<i>Lycii Fructus</i>	<i>Angelica gigas Nakai</i>	<i>Zizyphi Fructus</i>	<i>Cnidii Rhizoma</i>
1	Acetamiprid	94.5	-50.6	-50.1	-10.2
2	Alachlor	36.3	-20.1	6.3	99.0
3	Aldicarb	54.5	31.1	25.6	50.2
4	Aldrin	-19.0	-32.1	-0.6	-2.4
5	Amisulbrom	-21.0	-29.9	-33.8	-27.1
6	Amitraz	-10.0	-14.6	-24.8	-28.7
7	Azimsulfuron	-41.0	-42.0	-34.8	-42.5
8	Azinphos-methyl	17.2	-48.1	6.5	-55.3
9	Azoxystrobin	27.1	21.1	95.8	94.3
10	Bendiocarb	5.4	-44.7	-17.4	-31.7
11	Benthiavalicarb-isopropyl	-49.5	-54.8	-31.8	-34.5
12	Benzoximate	10.2	95.8	-24.8	-26.3
13	BHC- α	88.5	-12.9	-15.5	86.7
14	BHC- β	57.0	-27.1	-9.8	59.8
15	BHC- δ	82.0	-49.0	-30.9	59.8
16	BHC- γ	131.8	-56.9	-11.5	42.7
17	Bifenox	20.5	-1.9	15.2	12.0
18	Bifenthrin	83.6	-11.9	35.0	19.6
19	Bitertanol	53.4	16.8	45.9	83.5
20	Boscalid	52.2	-26.3	59.4	47.0
21	Bromobutide	50.4	85.1	12.2	43.3
22	Bromopropylate	122.9	-41.6	89.9	22.7
23	Buprofezin	-12.2	-42.4	-21.7	5.7
24	Butachlor	61.2	-10.2	17.7	43.1
25	Cadusafos	74.5	-40.8	36.7	89.3
26	Captan	105.2	41.3	-82.9	88.4
27	Carbaryl	2.2	-64.6	-20.9	-17.1
28	Carbendazim	60.8	-56.3	48.1	-12.1
29	Carbofuran	-4.4	-61.6	-17.6	-49.4
30	Carbosulfan	-58.1	-64.3	76.3	-62.1
31	Carfentrazone-ethyl	-26.5	-63.6	-35.2	-51.0
32	Chlorantraniliprole	184.2	14.7	113.0	48.7
33	Chlorfenapyr	36.0	45.1	8.4	37.2
34	Chlorfluazuron	-43.4	-54.9	-69.4	-46.3
35	Chlorobenzilate	89.2	-29.9	57.3	20.2
36	Chlorothalonil	-54.6	-15.8	-44.3	-4.3
37	Chlorpyrifos	20.3	-47.8	-13.1	-46.6
38	Chlorpropham	22.0	-28.4	4.7	67.4
39	Chlorpyriphos-methyl	25.3	-35.1	14.5	40.9
40	Chromafenozide	2.5	-17.8	65.3	63.9
41	Clofentezine	19.5	-41.1	15.6	78.3
42	Clomazone	-11.3	-1.6	4.6	2.2
43	Clothianidin	-8.3	-53.7	-23.7	-27.4
44	Cyazofamid	-18.4	-75.1	29.1	-53.8
45	Cyclosulfamuron	-46.9	53.9	39.0	50.3
46	Cyflufenamid	-13.3	-46.8	-15.6	-20.7
47	Cyfluthrin(1)	41.5	95.4	21.5	61.4
48	Cyhalofop-butyl	3.7	-41.0	-44.8	-42.0

No.	Compound	Matrix effect (%)			
		<i>Lycii Fructus</i>	<i>Angelica gigas Nakai</i>	<i>Zizyphi Fructus</i>	<i>Cnidii Rhizoma</i>
49	Cyhalothrin(2)	58.4	57.7	59.0	41.0
50	Cymoxanil	-24.1	-65.8	49.9	-48.6
51	Cypermethrin(4)	23.8	21.2	52.1	56.5
52	Cyproconazole	-5.6	-2.6	7.4	15.0
53	Cyprodinil	9.7	-53.9	0.4	-32.6
54	Daimuron	52.7	39.2	0.6	118.9
55	Deltamethrin	76.9	-56	100	127.4
56	Diazinon	20.1	-29.5	18.2	-8.7
57	Dichlofluanid	23.4	-53.4	-30.5	55.9
58	Dichlorvos	13.5	-45.4	-28.0	-37.2
59	Diclofop-methyl	68.6	-38.2	34.4	18.3
60	Dicloran	27.9	-27.5	66.6	88.8
61	Dicofol	28.1	-20.3	10.3	3.1
62	Dieldrin	-18.2	-31.8	-2.7	46.0
63	Diethofencarb	4.0	-55.1	-26.1	-18.8
64	Difenoconazole	45.8	12.6	98.8	66.1
65	Diflubenzuron	15.5	-74.6	39.8	104.7
66	Dimepiperate	12.7	-50.4	119.1	-50
67	Dimethenamid	28.4	-28.5	20.6	11.5
68	Dimethoate	-5.5	-23.1	-52.9	-10.2
69	Dimethomorph(E,Z)	22.1	20.0	38.7	42.1
70	Dimethylvinphos	82.1	-37.1	32.9	-28.9
71	Diniconazole	-0.8	-23.0	8.7	-13.5
72	Dinotefuran	-0.7	-34.8	-16.8	27.5
73	Diphenamid	36.0	-18.2	7.7	-1.5
74	Diphenylamine	37.9	-23.5	9.0	6.8
75	Dithianon	-45.7	13.9	12.2	-45.3
76	Dithiopyr	6.4	-35.0	10.4	-17.7
77	Diuron	34.1	-6.1	11.1	29.2
78	Edifenphos	-1.8	-29.8	0.9	-26.5
79	Emamectin benzoate (B1a, B1b)	46.7	90.9	5.5	63.8
80	Endosulfan- α	-16.1	-32.0	-5.1	3.9
81	Endosulfan- β	11.6	6.8	-3.4	28.7
82	Endosulfan-sulfate	54.4	11.9	-38.3	58.5
83	Endrin	49.3	2.4	29.1	-0.2
84	EPN	67.4	-31.0	65.9	58.2
85	Esprocarb	19.9	-21.1	10.0	11.3
86	Ethaboxam	-29.8	-27.9	11.2	-43.8
87	Ethalfuralin	45.0	-58.2	73.1	7.0
88	Ethiofencarb	-5.1	-74.7	-4.3	-45.9
89	Ethoprophos	61.8	52.8	46.4	74.3
90	Etofenprox	54.5	-72.7	55.4	-15.2
91	Etoxazole	97.0	-30.8	49.8	11.1
92	Etridiazole	73.5	51.7	-24.6	116.7
93	Etrimfos	-25.6	-12.9	-22.2	-68.0
94	Fenamidone	44	-30.1	-20.5	-51.8
95	Fenamiphos	80.3	-0.6	13.5	10.0
96	Fenarimol	8.7	9.9	21.5	41.2

No.	Compound	Matrix effect (%)			
		<i>Lycii Fructus</i>	<i>Angelica gigas Nakai</i>	<i>Zizyphi Fructus</i>	<i>Cnidii Rhizoma</i>
97	Fenazaquin	104.6	59.9	45.3	20.2
98	Fenbuconazole	-27	-33.2	33	-20.1
99	Fenhexamid	12.1	-49.2	14.7	-17.0
100	Fenitrothion	51.0	-18.8	56.7	72.0
101	Fenobucarb	18.3	18.2	-0.1	-34.2
102	Fenothiocarb	-33.8	-34.8	-34.0	-36.8
103	Fenoxanil	83.4	-28.0	71.3	32.4
104	Fenoxaprop-P-ethyl	-7.4	-35.4	-3.1	14.4
105	Fenoxycarb	47.6	-78.0	-9.5	26.5
106	Fenpropathrin	-35.3	-72.8	-36.9	-41.2
107	Fenpyroximat	1.8	-24.5	11.0	11.6
108	Fenthion	22.7	-25.5	8.5	12.9
109	Ferimzone	11.4	-59.5	2.9	-49.4
110	Fipronil	50.9	-27.0	14.1	50.6
111	Flonicamid	-2.4	-78.7	-23.9	-29.9
112	Fluacrypyrim	63.9	95.3	74.8	30.1
113	Fluazifop-P-butyl	-11.6	-71.4	2.9	-15.1
114	Fluazinam	-48.0	25.8	26.7	-40.0
115	Flubendiamide	63.3	22.9	79.4	-25.8
116	Fludioxonil	-10.6	64.0	52.0	57.3
117	Flufenoxuron	-45.1	9.7	7.2	-46.1
118	Flumioxazin	-5.6	-24.0	17.3	-55.9
119	Fluopicolide	14.5	40.2	11.7	45.9
120	Fluquinconazole	-17.5	-14.2	51.3	95.9
121	Flusilazole	48.1	-29.5	39.5	63.4
122	Flutolanil	31.3	-16.5	27.3	73.0
123	Forchlorfenuron	23.9	-32.9	-7.8	-23.8
124	Fosthiazate	25.4	-25.5	13.6	-13.2
125	Fthalide	25.9	-22.5	9.0	39.3
126	Furathiocarb	30.4	50.9	4.1	79.7
127	Heptachlor	8.1	-9.7	-9.0	17.5
128	Heptachlor-epoxide	-64.5	-40.7	1.5	6.7
129	Hexaconazole	86.0	-20.1	-6.0	57.6
130	Hexaflumuron	-22.3	-76.2	-9.6	-43.4
131	Hexazinone	-29.5	-72.9	-56.2	-52.1
132	Hexythiazox	-51.5	-29.0	-17.3	-35.5
133	Imazalil	-25.0	-37.3	-2.1	-24.4
134	Imazosulfuron	100.5	47.8	7.1	-26.6
135	Imibenconazole	-17.6	-41.1	19.2	18.9
136	Imidacloprid	29.8	-9.7	-23.7	92.4
137	Indanofan	-22.4	-66.3	60.2	-11.3
138	Indoxacarb	120.9	-46.2	45.8	166.3
139	Iprobenphos	27.7	-17.0	46.3	135.1
140	Iprodione	-29.3	-49.8	59.2	-26.8
141	Iprovalicarb	-7.7	33.9	-6.5	99.0
142	Isofenphos	49.8	-37.4	19.3	18.1
143	Isoprocarb	26.2	-53.3	8.0	-14.7
144	Isoprothiolane	8.5	-20.3	23.0	-55.6
145	Kresoxim-methyl	31.9	-60.2	119.8	-27.9

No.	Compound	Matrix effect (%)			
		<i>Lycii Fructus</i>	<i>Angelica gigas Nakai</i>	<i>Zizyphi Fructus</i>	<i>Cnidii Rhizoma</i>
146	Linuron	-0.3	53.3	27.5	56.8
147	Lufenuron	9.2	-29.9	4.3	66.8
148	Malathion	95.4	-30.5	42.2	66.4
149	Mandipropamid	12.6	35.9	21.2	14.1
150	Mecarbam	89.2	-5.8	41.5	24.2
151	Mefenacet	-22.7	-37.1	-9.9	14.2
152	Mepanipyrim	10.2	-25.9	11.5	-24.8
153	Mepronil	98.3	-11.1	101.9	-79.6
154	Metalaxyl	29.6	43.8	19.4	13.2
155	Metamifop	-24.4	-40.7	-6.5	-8.3
156	Metconazole	19.9	-43.9	65.4	139.3
157	Methabenzthiazuron	6.9	-27.5	-5.5	-2.0
158	Methidathion	82.3	-49.8	29.1	-26.2
159	Methiocarb	-8.1	-59.7	37.3	22.8
160	Methomyl	-41.6	-56.3	-63.2	-40.0
161	Methoxychlor	59.6	-54.7	63.8	-21.3
162	Metobromuron	42.4	-50.9	10.1	7.2
163	Metolachlor	48.3	50.6	13.9	52.5
164	Metolcarb	55.4	36.5	88.3	93.6
165	Metrafenone	-2.6	-30.7	17.4	-22.6
166	Metribuzin	-6.9	-35.8	-2.4	-35.0
167	Monocrotophos	15.3	-35.0	-1.3	4.3
168	Myclobutanil	21.2	31.2	55.2	69.0
169	Napropamide	1.3	-30.6	-3.3	19.4
170	Novaluron	-13.5	-67	9.3	-38.4
171	Nuarimol	31.9	-48.2	66.9	14.1
172	o,p'-DDT	28.2	-69	4.9	48.6
173	Ofurace	30.6	-68.6	13.7	79.8
174	Oxadiazon	22.4	-23.9	4.5	7.0
175	Oxamyl	-46.5	-47.7	-66.6	-13.5
176	Oxaziclonefon	-29.7	-54.7	-21.4	-38.4
177	p,p'-DDD	28.2	-69	4.9	48.6
178	p,p'-DDE	-6.1	6.7	-0.1	3.8
179	p,p'-DDT	59.1	-39.1	-75.3	50.8
180	Paclbutrazol	53.9	-20.0	76.5	23.0
181	Parathion-ethyl	46.6	-1.4	60.1	72.3
182	Parathion-methyl	71.6	1.9	49.1	20.6
183	PCTA	-14.9	-32.6	6.5	4.9
184	Penconazole	-36.3	-64.4	-0.4	57.1
185	Pencycuron	-21.2	-33.8	-6.7	-6.5
186	Pendimethalin	-18.2	-51.2	26.2	144.6
187	Pentachloroaniline	-8.6	-32.5	13.8	-0.4
188	Pentoxazone	83.9	-55.3	43.6	22.3
189	Permethrin	32.2	57.5	55.8	59.0
190	Phenthoate:PAP	72.7	-40.7	28.6	36.8
191	Phorate	6.1	-30.7	21.3	-2.5
192	Phosalone	-13.6	-29.0	33.3	-40.6
193	Phosphamidone(2)	85.8	77.9	82.8	36.6
194	Phoxim	-9.6	-67.1	16.6	-30.1

No.	Compound	Matrix effect (%)			
		<i>Lycii Fructus</i>	<i>Angelica gigas Nakai</i>	<i>Zizyphi Fructus</i>	<i>Cnidii Rhizoma</i>
195	Piperophos	-12.6	-18.4	-2.8	-12.5
196	Pirimicarb	-26.5	-66.0	-30.2	-37.1
197	Pirimiphos-ethyl	28.9	-24.2	26.8	9.4
198	Pirimiphos-methyl	0.6	-39.2	3.4	-17.9
199	Pretilachlor	1.6	-13.6	-3.6	-11.6
200	Probenazole	-34.8	-23.6	-19.8	-56.1
201	Prochloraz	12.0	12.4	9.3	22.2
202	Procymidone	14.4	21.5	7.2	13.4
203	Profenofos	-12.3	-33	18.3	5.6
204	Propamocarb	-61.7	-24.6	-46.5	-28.4
205	Propanil	52.8	-25.3	35.2	4.0
206	Propoxur	52.5	-38.7	57.9	59.4
207	Prothiofos	38	-24	34.8	18.8
208	Pyraclufos	-49.8	-24.8	-23.8	-34.8
209	Pyraclostrobin	49.2	-31.9	46.7	-13.0
210	Pyrazophos	57.8	-47.9	21.3	27.1
211	Pyributicarb	-21.8	-44.4	-6.5	-14.8
212	Pyridaben	-51.3	-57.2	-9.8	-52.6
213	Pyridaphenthion	86.1	34.4	-51.1	45.9
214	Pyrifthalid	-33.9	-12.3	-6.1	59.7
215	Pyrimethanil	3.0	-56.3	0.2	-41.8
216	Pyrimidifen	14.0	27.9	48.4	37.6
217	Pyriminobac-methyl(E,Z)	58.4	-32.8	46.8	34.0
218	Pyriproxyfen	34.4	-34.5	46.9	25.4
219	Pyroquilon	46.2	-20.4	24.3	35.8
220	Quinoclamine	55.3	30.1	-50.5	19.5
221	Quintozene(PCNB)	3.4	-12.8	11.1	19.1
222	Quinzalofop-ethyl	-0.3	-48.2	-1.2	-2.1
223	Sethoxydim	-31.7	-36.6	-65.4	-64.6
224	Silafluofen	-2.8	-51.3	150.9	-73
225	Simazine	11.6	-33.6	17.5	75.9
226	Simeconazole	103	-16.1	67.9	13.0
227	Simetryn	-27	-48.8	-17.1	-66.4
228	Spirodiclofen	-59.9	-69.1	-0.3	-73.7
229	Spiromesifen	26.8	-76.7	-23.4	-69.3
230	Tebuconazole	51.8	-56.7	26.9	16.6
231	Tebufenozide	62.2	-59.7	-43.6	-25.9
232	Tebufenpyrad	52.4	-48.9	16.1	41.4
233	Tebupirimfos	-11	-54.5	0.4	-18.1
234	Teflubenzuron	-1.8	-24.8	50.5	-75
235	Tefluthrin	29.8	-27.4	2.4	9.2
236	Terbufos	-17.8	-42.6	-36.6	19.4
237	Terbuthylazine	16.8	-23.7	8.1	58.1
238	Tetraconazole	53.1	25.8	20.5	4.4
239	Tetradifon	40.1	153.1	4.6	12.8
240	Thiabendazole	-41.8	-55.4	-40.7	-40.4
241	Thiacloprid	15.0	-17.0	1.2	42.0
242	Thiamethoxam	13.7	-41.1	-42.8	-12.0
243	Thiazopyr	10.9	-23.6	12.8	7.4

No.	Compound	Matrix effect (%)			
		<i>Lycii Fructus</i>	<i>Angelica gigas Nakai</i>	<i>Zizyphi Fructus</i>	<i>Cnidii Rhizoma</i>
244	Thifluzamide	96.1	-54.1	55.9	32.8
245	Thiobencarb	-56.0	117.6	-19.4	51.2
246	Thiodicarb	44.3	47.8	9.7	93.1
247	Tiadinil	-29.5	-50.0	14.5	-34.8
248	Tolclofos-methyl	20.1	-34.5	-4.0	10.9
249	Tolyfluanid	36.0	-55.7	-25.7	60.9
250	Tralomethrin	48.3	-37.3	80.4	51.3
251	Triadimefon	62.7	-35.8	9.0	5.1
252	Triadimenol	44.1	21.5	54.0	46.1
253	Triazophos	-4.8	-12.2	15.3	37.2
254	Trichlorfon	-22.6	-44.4	-10.0	-31.4
255	Tricyclazole	33.0	-16.4	-44.1	51.9
256	Trifloxystrobin	-22.6	-30.2	-14.8	-47.3
257	Triflumizole	16.2	-43.9	14.2	18.8
258	Triflumuron	-1.4	-41.1	0.3	-51.4
259	Trifluralin	24.0	-48.7	29.1	3.9
260	Vamidothion	-24.7	-35.1	-42.9	-23.1
261	Vinclozolin	12.1	-30.9	1.2	6.4