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LC-MS/MS와 GC-MS/MS를 이용한 사과와 쌀 시료에서 320종 농약의 다성분 분석

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Development of Multi-residue Analysis of 320 Pesticides in Apple and Rice Using LC-MS/MS and GC-MS/MS

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Abstract A new analytical method has been developed to determine 320 pesticides in apple and rice. The extraction of pesticides was carried out based on QuEChERS sample extraction, and determination was performed using LC-MS/MS and GC-MS/MS. 320 pesticides were selected for experiments. 251 and 110 pesticides among them were analysed by LC-MS/MS and GC-MS/MS, respectively. 41 pesticides of them were analyzed by both GC-MS/MS and LC-MS/MS. Among pesticides analysed by LC, 242 pesticides (96% of total number) in apple and 237 pesticides (94% of total number) in rice showed recoveries in the range of 70~120% with RSD ≤20%. In case of pesticides analyzed by GC-MS/MS, 103 pesticides (94% of total number) in apple and 83 pesticides (76% of total number) in rice were successfully validated. These results indicated that LC-MS/MS and GC-MS/MS analysis with the QuEChERS sample preparation can be partly applied to multi-residue pesticides in agricultural products.

Key words GC-MS/MS, LC-MS/MS, Multiresidue analysis, Pesticide, QuEChERS

서 론

농약은 현대 농업에 있어 작부체계 및 재배방법 개선, 품질과 저장성의 향상 및 노동력 절감, 생산량 증대 등을 위한 중요하고도 필수적인 농업자재이다(Fenik 등, 2011; Lee 등, 2013). 그러나 농작물에 살포된 농약은 사용목적을 달성한 후 환경에서 분해되어 잔류하지 않는 것이 가장 이상적이지만 농약은 대부분 유기합성물질로서 자체의 물리화학적 특성에 따라 농작물 및 토양 등 재배환경 중에 잔류하게 된다(Do 등, 2010; Lee 등, 2008). 잔류농약은 농산물을 섭취하는 단계에서 인체에 흡수, 축적되어 안전성 문제를 발생시킬 가능성이 있으므로 효율적인 농산물 안전관리를 위해서는 잔류농약에 대한 지속적인 연구와 모니터링이 필요하다.

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현재 세계 각국에서는 농산물 안전성 확보를 위하여 자국에서 생산된 농산물 뿐만 아니라 수입산 농산물에 대해서도 유해물질 규제와 검역기준을 대폭 강화하고 있으며, 농산물을 통해 섭취될 수 있는 잔류농약에 대한 안전성을 확보하기 위하여 국가마다 농산물에 대한 농약안전사용기준과 농약의 최대잔류허용기준(Maximum Residue Limits, MRLs)을 설정하여 관리하고 있다(Bhanti 등, 2007). 또한, 농식품의 안전성에 대한 소비자의 높은 관심에 따라 농식품 내의 유해물질을 신속 정확하게 분석하는 기술이 중요시 되고 있다. 그 중에서도 대표적인 유해 물질인 잔류농약 분석은 다양한 매트릭스 내에 존재하는 극미량의 성분을 분석하기 위해 농약 이외의 복잡한 불순물을 선택적으로 제거해야하는 정제방법이 복잡할 뿐만 아니라 분석결과의 공적, 법적 사용을 위하여 높은 신뢰성이 요구되기 때문에 많은 시간과 비용, 분석자의 숙련된 기술이 요구된다(Lee 등, 2012).

최근 농식품 중의 잔류농약 분석을 위해 전처리방법을 간

소화 시키면서 고감도 질량분석기를 이용하여 신속하게 분석하는 방법이 필수적이기에 대부분 다종다성분 분석법이 적용되고 있다(Guana 등, 2010; Ju 등, 2011; Kwon 등, 2011; Zhang 등; 2011). QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) 전처리법은 미농무성 농업연구소(Agricultural Research Service)에서 개발되어 AOAC 및 European Committee에서 농약다성분 분석법으로 인정받았으며(Anastassiades 등, 2003; Lehotay 등, 2010), 기존 농약 잔류분석법과 달리 분석방법이 간단하고 개발이 쉬운 장점을 가지고 있어 다양한 시료를 대상으로 농약의 다성분분석 뿐만 아니라 농약의 대사물질을 동시 분석하는데도 적용이 가능하다(Cajka 등, 2008; Ju 등, 2011; Koesukwiwat 등, 2010; Seo 등, 2013). 또한, 최근 국외 잔류 농약 분석에 관한 연구는 GC/MS/MS와 LC/MS/MS를 동시에 적용한 농약 다성분 분석연구가 수행되어지고 있다(Chamkasem 등, 2013; Lehotay 등, 2005; Pang 등, 2006).

따라서 본 연구에서는 최근 사용 빈도가 높은 국내 등록 농약에 대한 잔류분석법을 확립하기 위하여 LC-MS/MS와 GC-MS/MS를 이용하여 다종농약 다성분 동시분석법 적용 시험을 수행하였다.

재료 및 방법

농약표준용액 및 시약

분석에 사용한 표준품은 HPC Standards GmbH (Cunnersdorf, Germany), AccuStandard (New Haven, CT, USA), LGC Standard (Teddington Middlesex, UK), Wako Pure Chemical (Osaka, Japan)로부터 구입하였으며 각각의 농약 표준품은 acetone, acetonitrile으로 1,000 mg/L의 용액을 LC-MS/MS 및 GC-MS/MS 분석용 혼합표준용액(5 mg/L) 조제하여 4℃ 냉장보관 하여 사용하였다.

분석에 사용된 용매인 formic acid (98%)는 Junsei Chemical (Tokyo, Japan), ammonium formate (99.995%)는 Sigma-Aldrich (Steinheim, Germany) 제품을 구입 하였다. 시료 추출 및 정제를 위해 사용한 acetonitrile, acetone, methanol은 Burdick&Jackson (Muskegon, MI, USA)로부터 구입하여 사용하였고, QuEChERS법 추출을 위해 QuEChERS Extract Kit (magnesium sulfate; 98.5~101.5%, sodium chloride; ≥99.5%, sodium citrate; 99.9%, disodium citrate sesquihydrate; 99%)와 정제를 위해 사용된 QuEChERS dispersive SPE 2 mL (primary secondary amine (PSA), octadecysilane end-capped, magnesium sulfate; 98.5~101.5%)은 Agilent (Boblingen, Germany)로부터 구입하여 사용하였다.

전처리방법

시험에 사용된 사과와 쌀은 친환경인증을 받은 무농약 시료로 분쇄기를 이용하여 균질화한 후 회수율 시험 및 blank 시료로 사용하였고 쌀시료의 경우 분쇄한 시료 5 g을 칭량하여 증류수 10 mL 넣고 1시간 습윤화 시켜 분석시료로 사용하였으며, 칭량된 각 시료에 acetonitrile 10 mL을 넣고 1분간 진탕하였다. 사과와 쌀 추출액에 4 g의 anhydrous magnesium sulfate, 1 g의 sodium chloride, 1 g의 sodium citrate, 0.5 g의 disodium citrate sesquihydrate 를 첨가 후 ceramic homogenizers를 이용하여 1분간 강하게 진탕 하였으며, 진탕한 시료는 원심분리기를 이용하여 4,500 rpm에서 5분간 원심분리를 하였다. Acetonitrile층과 water층을 분리 후, GC-MS/MS 분석을 위해서는 시료의 상징액 1 mL을 25 mg PSA, 150 mg magnesium sulfate ($MgSO_4$), 25 mg C18EC (octadecysilane, end-capped)가 충진되어 있는 dispersive SPE tube에 넣고 1분간 진탕 후 12,000 rpm으로 2분간 원심분리하여 시액으로 사용하였고, LC-MS/MS 분석을 위해서는 상징액을 0.2 μm syringe filter (Whatman, PTFE)로 여과하여 시액으로 사용하였다(Fig. 1).

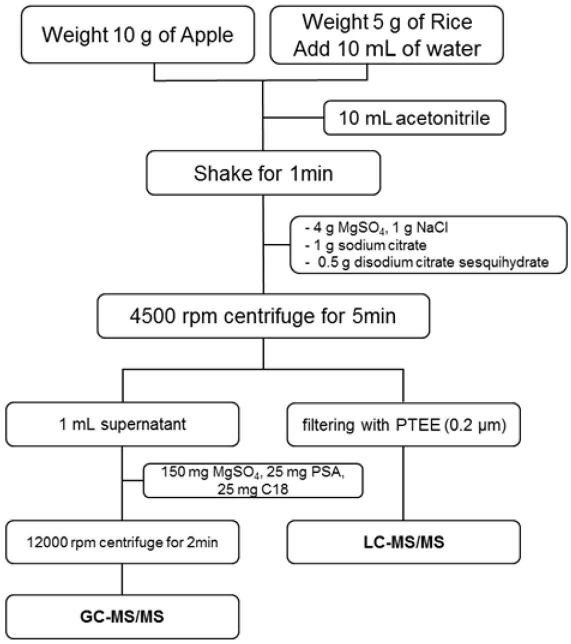

Fig. 1. Flow chart diagram of QuEChERS preparation for pesticides analysis.

농약성분의 정량분석을 위한 검량선은 각각의 표준품을 acetonitrile에 녹여 1,000 mg/L의 stock solution을 조제한 후 무처리 시료 추출액과 혼합하여 10, 25, 100, 150, 200 및 250 μg/L 농도로 matrix matched calibration을 작성하였다. 각 농약성분에 대한 회수율 시험은 50 및 200 μg/kg 수준에서 결과를 확인하였다.

기기분석 조건

LC-MS/MS는 Agilent Technologies사의 6460 Triple Quad

Table 1. Analytical conditions of LC-MS/MS

Instrument	: Agilent 6460 Triple Quad LC/MS with Agilent 1260 series HPLC			
Column	: Agilent Poroshell 120 EC-C18, 2.1 × 100 mm, I.d., 2.7 μm			
Mobile phase A	: 5 mM ammonium formate & 0.1% formic acid in water			
Mobile phase B	: 5 mM ammonium formate & 0.1% formic acid in methanol			
Gradient program	Time (min)	A (%)	B (%)	Flow (mL/min)
	Initial	85	15	0.3
	1	85	15	0.3
	1.5	40	60	0.3
	10	10	90	0.3
	15	10	90	0.3
	20	2	98	0.3
	20.1	85	15	0.3
	25	85	15	0.3
Injection volume	: 1 μL			
Column temperature	: 40°C			
Sample Tray Temp.	: 10°C			
Ionization mode	: ESI positive			
Gas temperature	: 325°C			
Gas Flow	: 6 mL/min			
Nebulizer gas pressure	: 35 psi			
Ionspray voltage	: +4000 V			
Scan type	: Dynamic MRM mode			

Table 2. Analytical conditions of GC-MS/MS

Instrument	: Bruker SCION TQ			
Column	: BR-5ms, 30 m × 0.25 mm i.d., 0.25 μm			
Flow rate	: Helium (99.999%) at 1.5 mL/min			
Injection vol., mode	: 1 μL, split ratio 50:1, 260°C			
Column oven	Temperature (°C)	Rate (°C/min)	Hold (min)	Total (min)
	90		3	3
	120	20	0	4.5
	300	8	3	30
Source temperature	: 200°C			
Transfer line	: 280°C			
Manifold	: 40°C			
Ionization	: Electron ionization (EI), 70 eV			
Scan mode	: MRM (Multiple Reaction Monitoring) mode			

LC/MS 기기를 사용하였고, 데이터 처리는 MassHunter Quantitative Analysis 소프트웨어를 사용하였다. GC-MS/MS는 Bruker사의 SCION TQ 기기를 사용하였고, 데이터 처리는 MS Work Station 8을 사용하였다. 분석 조건은 Table 1과 2에 나타내었다. LC-MS/MS 분석대상 농약 251종과 GC-MS/MS 분석대상 농약 110종에 대한 MRM 조건은 각각 Table 3과 4에 나타내었다.

회수율, 검출한계 및 정량한계의 측정

본 연구에서 잔류농약 분석법의 효율과 신뢰성을 검정하기 위하여 회수율 시험을 진행하였다. 회수율 시험은 무처리 사과와 쌀 시료에 첨가농도가 50 μg/kg, 200 μg/kg이 되도록 표준용액을 첨가한 다음 상기 전처리방법에 따라 회수율 시험을 3반복 수행하였다. 검출한계(limits of detection, LOD)와 정량한계(limits of quantification, LOQ)는 각 농도별 표준용액을 시료에 spiking하여 분석

Table 3. Parameters for 251 pesticide residue analysis by LC-MS/MS

No.	Pesticides	Retention time (min)	Parent ion	Quantitative ion (m/z)	Collision energy (V)	Qualitative ion (m/z)	Collision energy (V)	Fragmentor Voltage (V)
1	Abamectin B1	12.3	890.5	145.0	30	113.2	50	140
2	Acephate	1.0	184.0	143.0	5	95.0	20	90
3	Acetamiprid	4.1	223.1	126.0	20	56.2	20	100
4	Acibenzolar-S-methyl	6.2	211.0	136.1	28	91.2	16	120
5	Alachlor	7.2	270.1	238.1	10	162.1	15	80
6	Aldicarb	4.5	116.1	89.0	5	70.1	5	80
7	Ametoctradin	8.7	276.1	176.1	30	149.0	30	170
8	Amisulbrom	9.2	466.0	227.0	18	107.8	18	100
9	Amitraz	11.2	294.0	163.0	9	121.9	30	90
10	Azimsulfuron	5.4	424.9	181.9	10	155.9	34	110
11	Azinphos-methyl	5.8	318.0	132.1	8	77.0	40	80
12	Azoxystrobon	6.0	404.2	372.2	11	344.2	20	100
13	Bendiocarb	4.8	224.1	167.1	5	109.0	10	80
14	Benfuracarb	9.42	411.0	251.9	8	194.9	20	100
15	Benfuresat	14.9	391.2	149.1	16	65.2	84	104
16	Bensulfuron-methyl	5.8	410.9	148.9	15	181.9	20	120
17	Benthiavalicarb-Isopropyl	6.6	382.2	180.1	29	116.1	20	120
18	Benzobicyclon	6.5	446.9	256.9	24	228.9	40	160
19	Benzoximate	8.4	364.1	199.0	10	105.1	31	100
20	Bifenazate	6.8	301.2	198.0	4	170.0	16	75
21	Bitertanol	8.4	338.2	70.1	10	99.1	10	100
22	Boscalid	6.3	343.1	307.1	20	140.0	20	100
23	Bromacil	4.8	261.0	204.9	4	131.9	44	80
24	Buprofezin	9.7	306.2	116.1	14	201.1	14	100
25	Cadusafos	8.7	271.1	159.0	10	97.0	49	90
26	Cafenstrol	6.7	351.2	100.1	3	72.1	28	50
27	Carbarl (NAC)	5.0	202.1	145.0	4	127.0	20	60
28	Carbendazim	3.7	192.1	160.1	20	132.1	30	110
29	Carbofuran	4.8	222.2	165.0	14	123.0	16	100
30	Carboxin	5.0	236.1	142.9	8	87.0	20	85
31	Carfentrazone-ethyl	7.7	412.1	345.9	20	365.9	12	150
32	Carpropamid	7.9	334.1	139.0	20	103.0	40	100
33	Chlorantraniliprole	5.8	484.0	285.9	13	452.8	15	100
34	Chlorfluazron	11.3	540.0	382.9	20	347.0	50	120
35	Chlorpyrifos	10.2	350.0	97.1	25	197.9	25	60
36	Chlorsulfuron	4.9	358.0	141.0	16	167.0	12	105
37	Chromafenozide	6.9	395.2	175.1	20	147.0	55	100
38	Clethodim	6.6	360.1	164.1	16	136.1	24	97
39	Clofentezine	8.3	303.0	138.0	20	102.0	55	100
40	Clomazone	5.9	240.1	124.9	16	89.0	52	105
41	Clothianidin	3.9	250.0	132.0	20	169.0	20	100
42	Cyazofamid	7.2	325.1	108.0	11	261.2	11	100
43	Cyclosulfamuron	6.8	422.1	260.9	12	217.9	24	110
44	Cyflufenamid	8.4	413.2	203.1	38	241.2	13	120
45	Cyhalofop-butyl	9.0	358.2	256.0	28	120.0	8	90

Table 3. Continued

No.	Pesticides	Retention time (min)	Parent ion	Quantitative ion (m/z)	Collision energy (V)	Qualitative ion (m/z)	Collision energy (V)	Fragmentor Voltage (V)
46	Cymoxanil	4.2	199.1	128.0	4	111.0	12	61
47	Cyproconazole	6.6	292.1	70.1	16	125.0	30	100
48	Cyprodinil	7.4	226.2	77.1	50	93.1	50	120
49	Cyromazine	0.9	167.1	85.0	16	125.1	16	100
50	DDVP (Dichlovos)	4.8	221.0	109.0	19	126.9	19	120
51	Dinotefuran	2.3	203.1	129.2	4	114.2	8	81
52	Diafenthiuron	11.0	385.2	329.1	16	278.1	32	140
53	Diazinon	8.0	305.1	169.1	20	153.1	20	160
54	Dichlofluanid	6.8	350.0	224.1	10	123.1	35	100
55	Diethofencarb	6.1	268.2	180.1	13	226.1	13	80
56	Difenoconazole	8.8	406.1	251.0	20	337.1	19	100
57	Diflubenzuron	7.4	311.1	158.2	8	141.1	36	90
58	Dimepiperate	8.9	264.1	119.0	10	146.0	5	100
59	Dimethametryn	7.2	256.0	186.0	18	91.0	26	130
60	Dimethenamid	6.3	276.1	244.1	16	168.2	16	80
61	Dimethoate	4.1	230.0	199.0	5	171.0	10	80
62	Dimethomorph (1)	6.2	388.2	301.1	20	165.0	25	120
	Dimethomorph (2)	6.5	388.2	301.1	20	165.0	25	120
63	Dimethylvinphos	6.8	331.0	127.0	15	170.1	47	90
64	Demeton-S-methyl	4.9	231.1	89.1	2	61.1	30	50
65	Diniconazole	8.6	326.1	70.1	25	159.0	30	120
66	Diphenamid	5.7	240.2	134.1	20	167.0	20	100
67	Dithiopyr	9.1	402.1	271.9	30	353.9	24	135
68	Diuron	5.6	233.1	72.1	25	160.0	25	100
69	Dymron	6.6.	269.0	151.0	16	119.0	25	90
70	Edifenphos	7.8	311.1	109.0	35	111.0	25	80
71	EPN	8.8	324.1	157.1	20	295.9	12	50
72	Esprocarb	9.7	266.2	91.1	20	65.1	79	110
73	Ethaboxam	5.2	321.1	183.1	35	200.1	35	160
74	Ethiofencarb	5.2	226.1	107.1	15	164.2	7	50
75	Ethofenprox	12.7	394.3	177.2	21	135.1	33	100
76	Ethoprophos	7.1	243.1	97.0	30	131.0	20	100
77	Ethoxyquin	6.0	218.0	159.9	32	173.9	18	130
78	Ethoxysulfuron	6.6	398.9	260.9	10	217.8	22	120
79	Etoxazole	10.7	360.2	141.0	35	63.1	129	150
80	Etrimfos	7.8	293.1	125.0	24	265.1	25	120
81	Famoxadone	8.1	397.1	353.0	8	261.2	8	120
82	Fenamidone	6.2	312.2	92.1	25	65.1	40	100
83	Fenamiphos	7.4	304.2	217.0	20	202.0	40	110
84	Fenarimol	7.0	331.1	268.0	25	81.0	30	120
85	Fenazaquin	11.4	307.2	161.2	25	147.1	25	100
86	Fenbuconazole	7.3	337.1	70.0	20	125.0	20	120
87	Fenhexamid	7.1	302.1	97.2	20	55.2	40	134
88	Fenobucarb (BPMC)	6.1	208.1	95.1	15	152.1	9	40
89	Fenothiocarb	7.5	254.2	72.1	14	160.1	12	100

Table 3. Continued

No.	Pesticides	Retention time (min)	Parent ion	Quantitative ion (m/z)	Collision energy (V)	Qualitative ion (m/z)	Collision energy (V)	Fragmentor Voltage (V)
90	Fenoxanil (1)	7.4	329.1	302.1	4	86.3	20	80
	Fenoxanil (2)	7.5	329.1	302.1	4	86.3	20	80
91	Fenoxaprop-ethyl	9.4	362.1	288.1	12	121.1	28	138
92	Fenoxycarb	7.5	302.0	116.0	7	256.0	7	90
93	Fenpyroximate	11.0	422.2	366.2	24	135.0	35	100
94	Fenthion (MPP)	7.8	279.0	169.1	12	247.0	8	115
95	Fentrazamide	7.9	350.0	83.0	20	154.0	8	80
96	Ferimzone	5.9	255.2	124.1	30	132.1	30	120
97	Flomicamid	3.6	230.0	203.0	14	148.0	30	100
98	luaxrypyrim	8.8	427.2	145.1	25	205.1	5	100
99	Flubendiamide	7.7	408.0	273.8	17	255.8	22	100
100	Flucetosulfuron	6.0	488.1	156.0	16	273.0	24	125
101	Fludioxonil	6.3	266.2	229.1	10	158.1	47	100
102	Flufenacet	7.1	364.1	152.0	16	194.0	4	85
103	Flufenoxuron	10.8	489.1	158.1	17	141.2	35	150
104	Flumioxazin	5.8	355.1	299.1	32	327.0	32	135
105	Fluopiolide	6.5	383.0	172.9	25	108.9	91	100
106	Fluopyram	6.9	397.1	173.0	20	207.9	32	125
107	Fluquinconazole	6.9	376.0	307.0	30	108.1	69	100
108	Flusilazole	7.4	316.1	247.1	15	165.0	20	120
109	Flutolanil	6.5	324.2	262.1	15	242.1	25	120
110	Forchlorfenuron	5.6	248.1	129.1	18	155.1	19	100
111	Fosthiazate	5.2	284.1	104.0	20	228.0	9	70
112	Furathiocarb	9.6	383.2	195.1	10	252.0	10	100
113	Gibberrellic acid	4.1	364.2	239.3	14	221.2	20	90
114	Halosulfuron-methyl	6.8	434.9	182.1	10	139.1	50	120
115	Haloxyfop	7.7	362.0	316.1	12	91.2	36	120
116	Hexaconazole	8.2	314.1	70.1	20	159.1	20	120
117	Hexaflumuron	9.1	461.0	158.0	20	141.0	48	134
118	Hexazinone	4.9	253.2	171.0	12	71.1	36	100
119	Hexythiazox	10.3	353.2	168.0	22	228.2	15	100
120	Imazalil	5.3	297.1	159.0	30	69.1	30	100
121	Imazosulfuron	6.3	413.1	152.9	8	156.0	16	110
122	Imibenconazole	10.0	411.0	124.9	27	170.8	25	100
123	Imicyafos	4.6	305.1	201.0	16	235.0	14	120
124	Imidacloprid	3.9	256.1	175.1	20	209.1	20	100
125	Inabenfide	6.2	339.1	321.0	12	80.0	32	125
126	Iprobenfos	7.6	289.2	91.1	17	205.1	6	50
127	Iprovalicarb	6.8	321.3	119.1	20	203.1	5	80
128	Isoprocarb (MIPC)	5.4	194.2	95.1	10	137.1	10	70
129	Isoprothiolane	6.5	291.1	189.0	15	231.1	12	70
130	Isopyrazam	8.8	360.2	244.0	20	320.1	16	130
131	Kresoxim-methyl	7.7	314.0	222.0	10	267.0	5	80
132	Linuron	6.1	249.0	159.9	16	182.0	8	100
133	Lufenuron	10.2	511.0	157.8	10	140.9	30	100

Table 3. Continued

No.	Pesticides	Retention time (min)	Parent ion	Quantitative ion (m/z)	Collision energy (V)	Qualitative ion (m/z)	Collision energy (V)	Fragmentor Voltage (V)
134	Malathion	6.5	331.0	127.0	5	99.0	10	80
135	Mandipripamid	6.4	412.2	328.2	12	125.0	40	100
136	Mefenacet	6.7	299.1	148.1	15	120.2	25	100
137	Mepanipyrim	6.9	224.2	77.1	45	106.1	40	100
138	Mepronil	6.6	270.2	119.0	20	91.0	45	100
139	Metalaxyl	5.5	280.2	160.1	22	220.2	14	100
140	Metamifop	9.5	441.1	288.0	22	180.1	22	150
141	Metazosulfuron	6.1	476.1	182.1	20	295.1	10	110
142	Metconazole	8.3	320.2	70.1	25	125.1	50	100
143	Methabenzthiazuron	5.4	222.1	165.1	17	150.1	35	100
144	Methidathion	5.7	303.0	85.0	15	145.0	10	70
145	Methiocarb	6.2	226.1	169.1	5	121.1	10	80
146	Methomyl	3.6	163.1	88.1	5	106.1	5	50
147	Methoxyfenozide	6.5	369.2	149.1	13	133.1	15	100
148	Metobromuron	5.4	259.0	170.0	18	148.2	18	100
149	Metolachlor	7.3	284.2	252.2	15	176.1	25	100
150	Metolcarb	4.6	166.1	109.1	10	94.1	25	50
151	Metrafenone	8.5	40.91	209.0	8	226.9	16	105
152	Metribuzin	4.9	215.1	187.2	28	60.0	53	100
153	Mevinphos-1	4.1	225.1	127.1	10	193.1	0	50
	Mevinphos-2	4.3	225.1	127.1	10	193.1	0	50
154	Milbemectin A3	12.0	511.3	95.0	30	105.0	60	100
	Milbemectin A4	12.6	525.4	55.2	80	91.0	114	120
155	Molinate	6.7	188.1	55.1	25	126.1	10	120
156	Monocrotophos	3.7	224.1	127.0	10	193.0	0	100
157	Myclobutanil	6.7	289.2	70.1	27	125.0	27	100
158	Napropamide	7.1	272.2	171.1	18	129.1	18	100
159	Nicosulfuron	4.7	411.1	182.0	16	106.0	36	120
160	Novaluron	9.3	493.0	158.2	16	141.2	52	90
161	Nuarimol	6.1	315.1	81.0	30	251.9	25	120
162	Ofurace	4.8	282.1	160.2	18	254.2	13	100
163	Omethoate	2.0	214.0	125.0	20	183.0	5	80
164	Oxadiazon	9.9	345.1	220.0	18	177.0	19	135
165	Oxadixyl	4.5	279.1	219.0	32	177.0	4	75
166	Oxamyl	3.2	237.1	72.1	10	90.1	10	80
167	Oxaziclomefon	9.4	376.1	190.1	11	133	27	100
168	Paclobutrazole	6.5	294.1	70.1	20	125.0	48	100
169	Penconazole	7.8	284.1	70.1	20	159.0	39	80
170	Pencycuron	8.6	329.0	125.0	24	89.0	60	100
171	Pendimethalin	10.3	282.1	212.1	13	194.1	17	70
172	Penoxsulam	5.0	484.1	195.0	28	164.0	36	160
173	Penthiopyrad	7.8	360.1	275.9	8	177.0	36	110
174	Pentoxazone	9.5	354.2	286.0	15	186.0	15	135
175	Phenthoate	7.6	321.1	79.0	55	135.0	20	100
176	Phorate	8.3	261.0	75.0	4	199.1	0	60

Table 3. Continued

No.	Pesticides	Retention time (min)	Parent ion	Quantitative ion (m/z)	Collision energy (V)	Qualitative ion (m/z)	Collision energy (V)	Fragmentor Voltage (V)
177	Phosalone	8.4	368.1	181.9	10	75.1	100	100
178	Phosphamidone	4.5	300.1	127.0	20	174.1	17	120
179	Phoxim	8.2	299.1	77.0	36	129.0	4	70
180	Picoxystrobin	7.5	368.1	145.0	16	205.1	4	75
181	Piperophos	8.8	354.1	171.0	20	255.1	12	90
182	Pirimicarb	4.8	239.2	72.1	20	182.2	18	100
183	Pirimiphos-methyl	8.3	306.2	108.1	22	164.1	32	100
184	Probenazole	6.9	224.0	77.3	88	51.2	40	62
185	Prochloraz	8.2	376.1	308.0	13	70.0	22	50
186	Profenofos	9.4	373.0	302.9	15	127.9	50	90
187	Prometryn	6.5	242.2	158.1	27	200.1	27	100
188	Propamocarb	2.2	189.2	102.1	15	73.9	20	100
189	Propanil	6.2	218.0	162.0	15	127.0	20	120
190	Propaquizafop	9.8	444.1	100.0	12	56.1	36	115
191	Propiconazole	8.0	342.1	159.0	20	69.0	20	120
192	Propoxur	4.8	210.2	111.1	10	93.1	25	50
193	Pymetrozine	1.9	218.1	105.2	20	79.0	30	110
194	Pyraclofos	8.3	361.1	138.1	40	111.0	50	100
195	Pyraclostrobin	8.2	388.1	194.1	10	163.1	20	120
196	Pyrazolate	8.5	439.0	91.2	36	173.1	16	118
197	Pyrazophos	8.4	374.1	222.1	20	194.1	30	120
198	Pyribenzoxim	9.8	413.2	119.0	35	289.1	30	100
199	Pyributicarb	10.1	331.2	108.0	30	181.1	19	70
200	Pyridaben	11.6	365.2	147.1	18	309.2	13	100
201	Pyridaphenthion	6.7	341.1	189.1	24	205.1	24	100
202	Pyrifluquinazon	6.7	465.1	423.0	20	107.0	32	145
203	Pyriftalid	5.9	319.1	139.0	28	179.0	32	155
204	Pyrimethanil	6.0	200.1	77.1	50	181.1	43	100
205	Pyrimidifen	9.6	378.1	184.1	27	150.0	45	150
206	Pyriminobac-methyl (*E*)	6.4	362.2	330.2	10	284.1	30	100
	Pyriminobac-methyl (*Z*)	5.9	362.2	330.2	15	75	110	100
207	Pyrimisulfan	5.6	420.1	369.9	16	254.8	24	100
208	Pyriproxyfen	10.1	322.1	96.0	16	185.0	16	100
209	Pyroquilon	4.7	174.1	117.0	41	130.0	41	100
210	Quinalphos	7.6	299.1	96.9	32	163.0	24	110
211	Quinmerac	4.1	222.0	203.9	8	141.0	36	95
212	Quinoclamine	4.7	208.1	77.0	37	105.0	35	100
213	Quizalofop-ethyl	9.4	373.1	298.9	16	162.9	36	145
214	Saflufenacil	5.9	501.1	348.9	24	197.9	48	140
215	Sethoxydim	9.7	328.2	282.2	4	178.1	16	116
216	Silafluofen	14.8	426.1	287.2	0	168.1	34	90
217	Simeconazole	7.1	294.1	73.0	25	134.9	25	100
218	Simetryn	5.1	214.1	68.1	35	124.0	29	100
219	Spinetoram (j)	9.2	748.5	142.0	28	98.0	60	180
	Spinetoram (L)	9.9	760.5	142.0	28	98.0	60	180

Table 3. Continued

No.	Pesticides	Retention time (min)	Parent ion	Quantitative ion (m/z)	Collision energy (V)	Qualitative ion (m/z)	Collision energy (V)	Fragmentor Voltage (V)
220	Spirodiclofen	11.1	411.2	71.0	10	313.1	10	120
221	Spiromesifen	10.6	371.1	273.1	15	255.0	19	40
222	Sulfoxaflor	4.2	278.1	174.2	4	154.2	28	50
223	Tebuconazole	7.9	308.2	70.0	20	125.0	30	120
224	Tebufenozide	7.5	297.0	133.0	10	104.9	18	100
225	Tebufenpyrad	9.7	334.1	117.0	37	145.0	37	150
226	Tebupirimfos	9.8	319.0	153.1	30	277.0	18	100
227	Teflubenzuron	9.9	381.2	141.1	30	158.0	12	100
228	Terbuthylazine	6.3	230.1	174.1	15	104.0	35	120
229	Terbutryn	6.6	242.1	186.1	15	71.0	20	120
230	Tetraconazole	7.1	371.9	159.0	28	70.0	28	120
231	Thenylchlor	7.0	324.1	127.0	4	97.0	48	70
232	Thiabendazole	3.9	202.0	131.1	40	175.0	30	120
233	Thiacloprid	4.2	253.0	126.0	20	186.0	10	90
234	Thiamethoxam	3.7	292.0	211.0	10	181.1	20	80
235	Thiazopyr	7.8	397.2	377.1	20	355.1	28	170
236	Thidiazuron	4.8	221.0	102.0	12	127.8	12	107
237	Thifensulfuron-methyl	4.6	388.0	167.0	10	204.9	25	110
238	Thiobencarb	8.5	258.1	125.0	13	89.1	67	50
239	Thiodicarb	5.0	355.1	88.0	15	108.0	10	80
240	Thiophanate-methyl	4.7	343.1	151.0	16	93.1	50	96
241	Triadinil	6.8	268.0	100.7	20	101.2	20	50
242	Toclofos-methyl	8.3	301.0	125.0	15	175.0	24	110
243	Tolylfluanid	9.8	371.1	73.1	20	355	12	120
244	Triadimefon	6.6	294.1	69.0	15	197.0	20	120
245	Triazophos	6.8	314.1	162.1	17	119.0	35	100
246	Tricyclazole	4.4	190.1	136.0	42	163.1	42	120
247	Trifloxystrobin	9.0	409.2	186.1	14	206.1	14	100
248	Triflumizole	9.0	346.1	73.1	11	278.1	11	100
249	Triflumuron	8.3	359.1	155.9	16	138.9	40	90
250	Uniconazole	7.3	292.2	70.1	22	125.0	30	110
251	Vamidothion	4.0	288.1	146.0	4	118.0	20	85

Table 4. Parameters for 110 pesticide residue analysis by GC-MS/MS

No.	Pesticides	Retention time (min)	Parent ion	Quantitative ion (m/z)	Collision energy (V)	Qualitative ion (m/z)	Collision energy (V)
1	Acrinathrin-1	24.862	290	93	20	95	20
	Acrinathrin-2	25.060	290	93	20	95	20
2	Alachlor	17.976	188	160	15	131	15
3	Aldrin	19.005	263	193	30	228	30
4	Anilofos	24.726	226	157	10	184	10
5	BHC (alpha)	15.254	181	145	25	109	25
	BHC (beta)	15.983	181	145	25	109	25
	BHC (delta)	16.960	181	145	25	109	25
	BHC (gamma)	16.188	181	145	25	109	25

Table 4. Continued

No.	Pesticides	Retention time (min)	Parent ion	Quantitative ion (m/z)	Collision energy (V)	Qualitative ion (m/z)	Collision energy (V)
6	Bifenox	24.759	341	189	15	281	15
7	Bifenthrin	24.380	181	166	15	167	15
8	Bromobutide	17.749	119	91	30	65	15
9	Bromoproylate	24.411	341	185	10	183	10
10	Butachlor	20.770	176	147	15	134	15
11	Captan	20.189	149	105	10	79	10
12	Cabofuran	6.586	164	149	10	103	25
13	Carbophenothion	22.974	342	157	10	296	5
14	Chinomethionat	20.566	234	206	15	148	10
15	Chlordane (*cis*)	20.864	375	266	15	301	15
	Chlordane (*trans*)	20.547	375	266	15	301	15
16	Chlorfenapyr	21.806	247	227	30	200	30
17	Chlorfenvinphos (*cis*)	20.044	267	159	15	203	15
	Chlorfenvinphos (*trans*)	19.795	267	159	15	203	15
18	Chlorfluazuron	17.553	321	304	20	286	15
19	Chlorobenzilate	22.184	251	111	30	139	30
20	Chlorothalonil	16.639	266	231	15	133	35
21	Chlorpropham	14.682	213	127	10	171	10
22	Chlorpyrifos-methyl	17.764	286	93	20	271	10
23	Cyflufenamid	18.389	412	223	15	294	10
24	Cyfluthrin-1	27.220	206	151	25	177	25
	Cyfluthrin-2	27.350	206	151	25	177	25
	Cyfluthrin-3	27.420	206	151	25	177	25
	Cyfluthrin-4	27.480	206	151	25	177	25
25	Cyhalothrin-1	25.370	197	141	5	161	5
	Cyhalothrin-2	25.590	197	141	5	161	5
26	Cypermethrin-1	27.620	181	127	30	152	25
	Cypermethrin-2	27.750	181	127	30	152	25
	Cypermethrin-3	27.820	181	127	30	152	25
	Cypermethrin-4	27.870	181	127	30	152	25
27	Cyprodinil	19.806	224	208	25	224	10
28	o,p-DDT	22.390	235	165	15	199	15
	p,p-DDD	22.389	235	165	15	199	15
	p,p-DDE	22.184	246	176	20	211	20
	p,p-DDT	23.262	235	165	15	200	10
29	Deltamethrin	26.128	253	93	20	172	10
30	Dichlofluanid	15.352	224	77	15	123	10
31	Diclofop-methyl	23.605	253	162	15	190	15
32	Dicloran	15.628	206	148	20	176	20
33	Dicofol	19.327	139	75	25	111	25
34	Dieldrin	21.506	263	193	30	228	20
35	Dimethoate	15.639	125	79	20	93	20
36	Dimethylvinphos	19.021	295	109	15	295	15
37	Diphenylamine	14.162	169	115	40	139	40
38	Disulfoton	16.814	142	81	15	109	10

Table 4. Continued

No.	Pesticides	Retention time (min)	Parent ion	Quantitative ion (m/z)	Collision energy (V)	Qualitative ion (m/z)	Collision energy (V)
39	Endosulfan (alpha)	20.862	241	206	15	170	25
	Endosulfan (beta)	22.243	241	206	15	170	25
	Endosulfan-sulfate	22.394	272	237	15	143	25
40	Endrin	21.981	263	193	30	228	15
41	EPN	24.373	157	77	20	110	15
42	Ethalfuralin	14.579	276	202	10	248	5
43	Ethion	23.141	272	237	20	119	25
44	Etridiazole	8.690	211	183	10	140	20
45	Fenamidone	24.611	238	103	30	238	30
46	Fenamiphos	21.042	303	154	25	288	10
47	Fenitrothion	18.561	277	109	20	260	10
48	Fenothiocarb	20.777	160	72	15	160	5
49	Fenpropathrin	24.591	265	181	20	210	10
50	Fenvalerate-1	28.700	225	119	15	147	15
	Fenvalerate-2	28.950	225	119	15	147	15
51	Ferimzone (*E*,*Z*)	20.431	239	107	10	82	10
52	Fipronil	19.924	367	213	30	255	20
53	Flucyrhrinate-1	27.819	199	157	15	107	15
	Flucyrhrinate-2	28.070	199	157	15	107	15
54	Fludioxonil	21.204	248	154	10	182	10
55	Fluopyram	16.681	396	223	10	173	10
56	Folpet	20.332	260	130	10	232	10
57	Fthalide	19.362	272	215	25	243	25
58	Halfenprox	27.688	263	235	15	115	20
59	Heptachlor	18.106	272	235	15	237	15
	Heptachlor-epoxide	19.970	353	263	15	282	15
60	Imazalil	21.195	215	145	25	173	25
61	Indanofan	24.704	174	131	20	159	20
62	Indoxacarb	29.425	218	134	20	203	20
63	Iprodione	24.171	314	245	15	271	10
64	Isofenphos	20.005	213	121	15	185	10
65	Lufenuron	10.586	353	203	5	174	25
66	Mecarbam	20.105	131	86	15	74	15
67	Methidation	20.499	145	85	5	58	15
68	Methoxychlor 1	20.115	227	169	25	212	15
	Methoxychlor 2	21.076	227	169	25	212	15
	Methoxychlor	24.534	227	169	25	212	15
69	Metobromuron	17.404	170	143	25	91	50
70	Metolachlor	18.920	162	134	10	133	10
71	Metribuzin	17.767	198	82	15	110	10
72	Mevinphos	10.723	192	127	10	164	10
73	Novaluron	7.367	168	140	15	112	20
74	Oxyfluorfen	21.572	361	252	20	300	20
75	Parathion	19.161	291	109	15	137	10
76	Parathion-methyl	17.917	263	109	10	246	5

Table 4. Continued

No.	Pesticides	Retention time (min)	Parent ion	Quantitative ion (m/z)	Collision energy (V)	Qualitative ion (m/z)	Collision energy (V)
77	Pendimethalin	19.784	252	162	10	191	10
78	Penthiopyrad	18.889	302	152	5	302	5
79	Permethrin-1	26.560	183	153	10	168	10
	Permethrin-2	26.715	183	153	10	168	10
80	Phorate	15.177	260	75	5	231	5
81	Picoxystrobin	17.510	335	173	10	303	10
82	Pirimiphos-ethyl	19.538	333	163	10	180	10
83	Probenazole-1	12.961	130	77	20	103	20
	Probenazole-2	15.530	130	77	20	103	20
84	Procymidone	20.263	283	96	10	67	25
85	Prometryn	18.256	241	184	10	226	10
86	Propiconazole-1	23.090	259	69	10	191	10
	Propiconazole-2	23.240	259	69	10	191	10
87	Prothiofos	21.204	267	221	20	239	20
88	Pyridalyl	28.055	204	148	20	176	20
89	Pyridaphenthion	24.137	340	199	10	109	20
90	Quinoclamine	18.794	207	172	10	144	20
91	Quintozene	16.053	237	143	20	117	20
	Methyl Pentachlorophenyl sulfide	18.638	296	263	20	246	20
	Pentachloroanilline	17.362	265	193	20	229	10
92	Silafluofen	28.178	179	151	10	286	20
93	Simazine	15.889	201	173	5	186	5
94	Simeconazole	17.962	211	121	10	195	10
95	Simetryn	18.067	213	170	10	185	10
96	Spiromesifen	23.980	272	209	15	254	10
97	Tebupirimfos	17.205	261	137	15	153	15
98	Tefluthrin	17.010	177	127	10	157	10
99	Terbufos	16.362	231	175	15	157	20
100	Terbutryn	18.549	185	170	10	111	20
101	Tetradifon	24.999	159	131	10	111	25
102	Thiazopyr	18.882	327	263	30	277	30
103	Thifluzamide	21.466	194	125	25	166	15
104	Tolclofos-methyl	17.943	265	250	15	93	20
105	Tolyfluanid	19.994	238	137	15	110	25
106	Tralomethrin	29.595	253	172	10	199	25
107	Triadimenol	20.270	168	70	10	112	10
108	Trifluralin	14.854	306	264	10	160	25
109	Vinclozolin	17.873	212	145	20	172	20
110	Zoxamide	23.912	187	159	20	123	20

하여 얻은 크로마토그램을 기초로 하여 LOD는 S/N ratio가 3 이상, LOQ는 S/N ratio 10 이상을 기준으로 측정하였다.

결과 및 고찰

검출한계 및 정량한계

분석을 위한 검출한계(limit of detection, LOD) 및 정량

Table 5. Average recovery and RSD of 251 pesticides spiked in apple and rice at two different concentrations with LC-MS/MS (n=3)

No.	Compound	LOD (μg/kg)	LOQ (μg/kg)	Recovery, % (RSD, %) Apple		Recovery, % (RSD, %) Rice	
				50 μg/kg	200 μg/kg	50 μg/kg	200 μg/kg
1	Abamectin B1	3	5	91.3(5.9)	101.3(2.8)	59.7(9.7)	92.1(5.4)
2	Acephate	0.1	0.5	93.1(5.6)	93.4(0.8)	84.3(2.3)	94.5(1.2)
3	Acetamiprid	0.01	0.05	114.9(2.7)	99.3(1.1)	78.0(3.7)	108.0(0.5)
4	Acibenzolar-S-methyl	3	5	101.7(13.4)	94.7(5.4)	81.2(6.8)	111.5(5.6)
5	Alachlor*	5	10	110.4(1.7)	92.3(0.7)	83.3(13.8)	100.2(8.3)
6	Aldicarb	0.01	0.05	105.8(1.2)	99.3(0.9)	94.0(5.9)	105.1(3.6)
7	Ametoctrdin	0.03	0.05	100.1(1.1)	98.5(0.9)	89.2(6.1)	101.7(3.2)
8	Amisulbrom	1	2	87.2(9.9)	99.6(0.4)	92.4(4.8)	99.9(2.9)
9	Amitraz	0.03	0.05	2.56(11.8)	1.36(8.9)	72.3(2.4)	64.5(10.0)
10	Azimsulfuron	0.03	0.05	109.6(4.8)	102.3(3.3)	89.5(9.1)	93.4(9.4)
11	Azinphos-methyl	0.1	0.5	104.1(3.1)	95.7(3.0)	93.0(3.5)	100.6(2.6)
12	Azoxystrobin	0.05	0.1	101.6(2.9)	97.8(0.8)	83.3(1.4)	101.7(1.1)
13	Bendiocarb	0.05	0.5	112.6(3.7)	99.6(1.8)	83.7(3.6.)	110.2(0.8)
14	Benfuracarb	0.03	0.05	-	-	-	1.7(58.5)
15	Benfuresate	0.005	0.01	115.7(1.7)	94.1(4.3)	442.8(39.0)	165.4(18.5)
16	Bensulfuron-methyl	0.01	0.05	109.3(2.8)	107.5(0.4)	83.9(2.5)	94.7(9.4)
17	Benthiavalicarb-Isopropyl	0.05	0.1	105.6(3.3)	95.6(1.4)	86.4(5.1)	104.7(2.5)
18	Benzobicyclon	0.03	0.05	96.0(8.7)	85.5(2.1)	82.3(3.2)	92.8(8.7)
19	Benzoximate	0.05	0.1	102.7(0.8)	101.8(1.1)	91.3(1.9)	104.2(0.3)
20	Bifenazate	0.005	0.01	35.0(2.7)	33.6(1.8)	69.8(3.0)	80.1(2.5)
21	Bitertanol	0.5	1	97.5(3.1)	95.4(1.0)	104.5(4.9)	96.1(2.9)
22	Boscalid	0.1	0.5	106.1(6.0)	102.0(0.2)	84.9(8.9)	108.9(1.6)
23	Bromacil	0.005	0.01	103.3(3.9)	106.4(1.0)	86.6(2.0)	118.1(1.8)
24	Buprofezin	0.01	0.05	100.8(5.6)	96.8(2.6)	83.8(2.0)	101.2(1.5)
25	Cadusafos	0.05	0.1	102.3(2.8)	92.7(1.8)	92.6(1.7)	101.3(1.9)
26	Cafenstrole	0.03	0.05	110.2(5.1)	100.1(2.4)	81.1(4.1)	110.5(2.0)
27	Carbaryl(NAC)	0.05	0.1	105.6(3.2)	97.9(1.6)	86.9(2.5)	113.3(1.7)
28	Carbendazim	0.01	0.05	93.8(2.2)	90.6(0.4)	77.0(0.4)	92.3(0.3)
29	Carbofuran*	0.05	0.1	104.0(5.7)	93.9(0.8)	83.7(1.8)	97.0(0.9)
30	Carboxin	0.03	0.05	91.0(1.7)	90.2(0.8)	86.4(1.8)	110.7(1.0)
31	Carfentrazone-ethyl	0.008	0.01	160.3(3.2)	102.6(1.0)	91.5(3.4)	104.1(1.0)
32	Carpropamide	0.01	0.05	103.6(2.0)	100.7(1.2)	77.4(6.4)	107.8(0.9)
33	Chlorantraniliprole	0.5	1	99.1(5.2)	98.0(1.5)	91.7(5.2)	100.4(1.2)
34	Chlorfluazuron*	0.05	0.5	78.8(2.2)	76.0(1.4)	73.7(2.8)	81.2(6.6)
35	Chlorpyrifos	1	2	93.4(1.1)	92.1(4.6)	91.3(1.8)	98.6(1.2)
36	Chlorsulfuron	0.1	0.5	107.6(3.7)	117.4(1.9)	89.1(1.6)	91.1(1.4)
37	Chromafenozide	0.05	0.1	105.9(3.1)	100.7(0.9)	92.1(3.3)	106.4(1.2)
38	Clethodim	0.05	0.5	101.5(0.9)	102.8(1.3)	79.6(2.5)	85.3(4.1)
39	Clofentezine	0.5	1	105.1(5.1)	107.3(1.2)	97.2(6.2)	115.1(2.1)
40	Clomazone	0.03	0.05	100.7(4.2)	94.9(0.6)	85.0(3.3)	105.8(1.0)
41	Clothianidin	0.1	1	80.7(4.0)	85.6(3.1)	86.4(3.8)	100.8(3.8)
42	Cyazofamid	0.05	0.1	113.5(0.4)	109.9(0.9)	100.1(1.8)	117.0(0.5)
43	Cyclosulfamuron	0.01	0.05	98.3(4.8)	88.8(1.9)	87.0(0.6)	95.3(4.5)
44	Cyflufenamid*	0.1	0.5	104.6(1.7)	99.9(0.1)	76.1(10.0)	108.9(0.9)

Table 5. Continued

No.	Compound	LOD (μg/kg)	LOQ (μg/kg)	Recovery, % (RSD, %) Apple		Recovery, % (RSD, %) Rice	
				50 μg/kg	200 μg/kg	50 μg/kg	200 μg/kg
45	Cyhalofop-butyl	5	25	91.7(7.9)	91.2(10.2)	90.4(2.8)	98.3(2.3)
46	Cymoxanil*	0.05	0.1	101.5(3.0)	96.2(1.7)	82.6(3.0)	106.2(1.2)
47	Cyproconazole	0.5	1	99.3(1.3)	94.1(1.8)	90.1(0.1)	107.9(2.7)
48	Cyprodinil	5	7	93.9(0.7)	94.7(2.2)	83.3(3.3)	100.8(0.6)
49	Cyromazine	0.01	0.05	40.3(5.2)	44.3(1.7)	39.3(7.0)	39.3(5.9)
50	DDVP (Dichlovos)	1	5	98.2(1.0)	92.6(4.4	108.7(12.8)	112.0(5.2)
51	Dinotefuran	0.1	0.5	106.7(4.2)	99.6(1.9)	84.5(1.8)	97.1(1.0)
52	Diafenthiuron	0.01	0.05	-	5.87	14.0(20.6)	37.1(5.4)
53	Diazinon	0.05	0.1	101.2(2.4)	96.4(1.1)	98.9(3.7)	102.9(2.0)
54	Dichlofluanid*	0.1	0.5	108.6(2.1)	115.6(2.3)	-	-
55	Diethofencarb	0.2	0.5	89.5(13.2)	92.0(8.5)	77.9(1.1)	93.2(2.4)
56	Difenoconazole	0.5	1	103.7(1.7)	100.8(1.7)	87.2(6.1)	106.7(1.6)
57	Diflubenzuron	0.5	1	102.9(2.5)	98.2(0.9)	93.2(0.6)	97.6(1.8)
58	Dimepiperate	1	5	99.7(1.2)	96.5(1.1)	86.8(2.9)	102.9(1.9)
59	Dimethametryn	0.01	0.05	99.7(2.0)	97.3(1.0)	94.1(4.2)	102.1(3.8)
60	Dimethenamid	0.05	0.5	100.6(4.1)	96.4(0.3)	90.2(3.0)	108.0(2.1)
61	Dimethoate*	0.01	0.05	104.8(1.8)	102.5(0.7)	84.6(1.1)	106.6(0.8)
62	Dimethomorph	0.5	1	91.4(4.2)	94.6(1.4)	96.1(2.8)	101.5(1.3)
63	Dimethylvinphos*	0.5	1	78.2(6.7)	93.3(0.2)	103.6(6.6)	114.2(3.9)
64	Demeton-S-Methyl	0.01	0.05	101.1(5.1)	93.4(2.0)	90.1(3.8)	103.7(1.4)
65	Diniconazole	0.5	1	100.2(2.6)	97.5(3.4)	97.5(1.2)	103.3(2.9)
66	Diphenamid	0.05	0.1	100.1(4.2)	95.6(1.6)	86.1(3.2)	102.3(2.2)
67	Dithiopyr	1	2	94.1(4.0)	98.1(2.3)	81.0(15.0)	98.4(2.2)
68	Diuron	0.05	0.5	102.3(2.8)	96.6(1.3)	83.3(2.5)	104.1(1.3)
69	Dymron	0.01	0.05	107.3(2.6)	98.3(2.0)	89.5(5.9)	110.2(2.9)
70	Edifenphos	0.1	0.5	105.7(2.8)	100.8(0.8)	90.2(4.1)	112.5(1.2)
71	EPN*	0.7	1	95.9(14.9)	99.4(7.1)	75.2(3.5)	103.9(7.6)
72	Esprocarb	0.05	0.1	97.3(1.9)	92.3(0.4)	84.7(3.0)	102.8(1.1)
73	Ethaboxam	0.5	1	104.1(1.0)	96.9(1.0)	86.9(9.7)	99.9(1.2)
74	Ethiofencarb	0.05	0.3	95.8(3.2)	92.6(1.7)	87.2(1.2)	104.2(2.1)
75	Ethofenprox	0.1	0.5	96.7(0.7)	97.9(7.5)	81.6(1.0)	101.1(0.4)
76	Ethoprophos	0.1	0.5	100.6(4.2)	92.6(1.6)	87.0(0.6)	99.9(1.8)
77	Ethoxyquin	0.3	0.5	33.4(3.2)	34.3(2.1)	65.9(2.2)	86.4(4.0)
78	Ethoxysulfuron	0.005	0.01	101.1(7.8)	86.1(1.5)	82.8(2.8)	93.5(9.7)
79	Etoxazole	0.01	0.05	110.0(10.2)	102.6(4.3)	85.6(1.1)	95.5(2.7)
80	Etrimfos	0.1	0.5	99.1(1.6)	95.9(1.4)	99.4(3.6)	104.2(2.8)
81	Famoxadone	0.3	0.5	96.3(1.7)	95.8(3.5)	102.3(9.7)	101.7(1.9)
82	Fenamidone*	0.05	0.2	100.0(4.3)	97.3(1.3)	86.4(6.3)	98.0(3.4)
83	Fenamiphos*	0.05	0.1	102.5(3.6)	96.4(1.0)	81.0(2.8)	106.8(1.0)
84	Fenarimol	4	5	103.6(8.4)	95.6(3.6)	86.5(9.3)	101.7(4.9)
85	Fenazaquin	0.1	0.5	95.7(18.7)	96.7(4.4)	85.6(2.2)	95.5(1.5)
86	Fenbuconazole	0.5	1	103.5(1.4)	94.3(3.0)	93.4(2.9)	101.4(1.1)
87	Fenhexamid	0.1	0.3	-	-	82.9(9.6)	103.5(4.6)
88	Fenobucarb (BPMC)	0.1	1	88.7(8.0)	87.8(6.3)	78.5(5.4)	91.4(4.0)

Table 5. Continued

No.	Compound	LOD (μg/kg)	LOQ (μg/kg)	Recovery, % (RSD, %) Apple		Recovery, % (RSD, %) Rice	
				50 μg/kg	200 μg/kg	50 μg/kg	200 μg/kg
89	Fenothiocarb*	0.01	0.05	105.3(0.3)	96.1(2.1)	79.1(0.8)	106.6(2.6)
90	Fenoxanil	1	5	108.4(2.9)	95.7(0.6)	83.1(3.3)	102.5(3.0)
91	Fenoxaprop-Ethyl	0.03	0.05	103.7(4.5)	96.8(2.0)	83.7(2.4)	105.4(1.6)
92	Fenoxycarb	0.03	0.05	103.8(3.1)	97.5(0.7)	88.0(5.2)	105.4(1.1)
93	Fenpyroximate	0.7	1	97.5(2.7)	91.6(4.4)	91.6(2.1)	99.6(1.4)
94	Fenthion(MPP)	0.1	0.5	97.6(3.5)	91.4(2.0)	86.3(8.7)	103.1(4.6)
95	Fentrazamide	0.03	0.05	99.0(4.2)	96.4(2.4)	103.3(2.6)	105.4(3.8)
96	Ferimzone*	0.05	0.1	93.1(3.7)	89.4(3.2)	75.3(0.3)	87.2(1.3)
97	Flonicamid	0.1	0.5	103.2(3.7)	93.5(0.5)	93.8(3.5)	100.7(1.3)
98	Fluacrypyrim	0.05	0.1	101.9(0.3)	96.0(1.5)	84.2(3.9)	101.3(0.8)
99	Flubendiamide	0.5	1	104.9(2.9)	95.6(0.3)	94.3(3.9)	100.5(1.3)
100	Flucetosulfuron	0.04	0.05	107.3(2.4)	100.8(2.4)	102.3(5.6)	117.6(2.2)
101	Fludioxonil*	0.5	1	104.9(7.9)	96.4(0.9)	106.4(1.5)	110.5(1.2)
102	Flufenacet	0.1	0.5	103.8(3.7)	95.8(1.4)	86.9(4.0)	107.8(1.7)
103	Flufenoxuron	0.05	0.1	96.8(0.5)	89.8(10.6)	87.1(2.5)	97.6(0.1)
104	Flumioxazin	4	5	98.5(8.4)	95.7(6.6)	76.7(7.3)	105.5(3.4)
105	Fluopicolide	0.05	0.1	108.9(3.2)	94.1(1.4)	84.7(8.0)	111.8(1.9)
106	Fluopyram*	0.01	0.05	112.8(1.0)	96.6(0.9)	82.3(6.7)	110.0(2.1)
107	Fluquinconazole	0.05	0.1	99.3(5.8)	94.5(2.9)	86.2(7.4)	107.1(3.5)
108	Flusilazole	0.5	1	107.7(0.9)	95.1(1.5)	82.8(0.3)	109.7(3.5)
109	Flutolanil	0.01	0.05	102.5(4.8)	94.3(4.1)	79.7(0.4)	108.9(3.7)
110	Forchlorfenuron	0.1	0.5	98.6(2.4)	92.6(1.1)	84.2(2.4)	97.5(2.4)
111	Fosthiazate	0.01	0.05	104.6(1.7)	95.7(1.0)	90.1(1.9)	102.7(1.6)
112	Furathiocarb	0.05	0.1	101.7(1.4)	95.6(0.2)	84.7(3.7)	100.4(0.7)
113	Gibberellic acid	10	15	110.6(10.5)	100.9(6.6)	81.1(7.0)	88.4(3.9)
114	Halosulfuron-methyl	0.05	0.1	99.9(5.4)	89.2(1.9)	86.9(1.6)	93.9(8.0)
115	Haloxyfop	0.3	0.5	105.6(1.1)	91.6(1.0)	84.5(12.7)	96.6(2.8)
116	Hexaconazole	0.1	0.5	100.6(1.8)	92.5(0.8)	88.4(5.6)	100.0(0.7)
117	Hexaflumuron	5	10	89.0(14.7)	93.7(4.0)	100.1(11.6)	96.2(1.6)
118	Hexazinone	0.005	0.01	105.0(1.8)	96.0(1.0)	86.2(4.3)	103.0(2.6)
119	Hexythiazox	0.05	0.1	100.3(1.6)	92.6(3.3)	86.6(1.7)	96.5(1.6)
120	Imazalil*	0.05	0.1	99.9(0.8)	94.2(1.1)	88.1(1.5)	100.1(3.1)
121	Imazosulfuron	0.08	0.1	107.2(3.1)	101.1(3.0)	97.4(9.5)	114.9(1.1)
122	Imibenconazole	0.7	1	98.1(11.4)	102.1(6.1)	110.3(5.0)	109.9(0.5)
123	Imicyafos	0.008	0.01	110.9(3.2)	101.6(0.8)	90.4(3.3)	103.0(2.1)
124	Imidacloprid	0.5	1	77.5(5.4)	81.8(1.6)	91.2(1.7)	100.9(0.7)
125	Inabenfide	0.8	1	96.8(2.2)	92.4(2.9)	103.6(2.2)	97.7(5.3)
126	Iprobenfos	0.01	0.05	100.4(1.2)	93.8(0.8)	88.6(1.2)	100.3(0.9)
127	Iprovalicarb	0.05	0.1	95.5(3.3)	93.9(1.0)	91.4(4.4)	101.5(1.4)
128	Isoprocarb (MIPC)	0.1	1	100.6(1.0)	91.8(0.9)	87.0(4.0)	100.9(2.7)
129	Isoprothiolane	0.05	0.1	103.4(0.9)	94.9(1.6)	77.0(2.8)	105.5(3.2)
130	Isopyrazam	0.03	0.05	105.8(1.1)	96.6(0.7)	83.1(6.6)	106.1(1.6)
131	Kresoxim-methyl	0.5	1	101.8(3.9)	96.0(1.8)	99.3(5.5)	105.1(1.4)
132	Linuron	0.01	0.05	82.9(14.3)	87.6(12.2)	76.5(2.4)	91.7(6.5)

Table 5. Continued

No.	Compound	LOD (μg/kg)	LOQ (μg/kg)	Recovery, % (RSD, %) Apple		Recovery, % (RSD, %) Rice	
				50 μg/kg	200 μg/kg	50 μg/kg	200 μg/kg
133	Lufenuron*	0.1	0.5	93.7(16.8)	91.7(9.9)	84.8(10.5)	95.7(1.9)
134	Malathion	0.5	1	106.3(3.1)	94.5(2.3)	80.3(6.5)	110.0(0.8)
135	Mandipropamid	0.05	0.1	100.9(0.4)	94.0(1.5)	73.0(0.9)	100.3(1.1)
136	Mefenacet	0.05	0.1	102.5(1.6)	95.3(1.3)	87.9(2.9)	102.0(1.7)
137	Mepanipyrim	1	2	101.2(2.3)	94.2(1.2)	80.3(9.7)	101.8(3.0)
138	Mepronil	0.05	0.08	108.8(1.8)	92.5(1.3)	78.5(6.4)	111.2(2.9)
139	Metalaxyl	0.05	0.1	104.0(2.0)	94.7(0.9)	88.4(1.1)	101.5(0.8)
140	Metamifop	0.05	0.1	102.3(4.4)	98.6(2.3)	88.3(2.6)	106.2(0.1)
141	Metazosulfuron	0.08	0.1	109.4(8.1)	113.8(2.2)	92.5(1.2)	89.1(4.5)
142	Metconazole	0.1	0.5	103.8(1.0)	94.4(0.6)	88.8(4.1)	101.4(2.4)
143	Methabenzthiazuron	0.05	0.1	98.9(2.2)	92.4(0.2)	83.5(5.6)	99.5(1.6)
144	Methidathion*	0.1	0.5	103.5(1.2)	95.4(2.2)	83.6(2.4)	102.9(1.5)
145	Methiocarb	0.1	0.5	99.3(2.4)	92.2(0.7)	87.9(1.5)	104.7(1.8)
146	Methomyl	0.05	0.1	100.6(2.0)	91.9(0.2)	106.6(3.7)	114.7(0.6)
147	Methoxyfenozide	0.1	0.5	109.9(1.6)	95.0(0.1)	86.6(1.9)	112.9(0.9)
148	Metobromuron*	0.1	0.5	98.5(3.2)	93.5(0.9)	90.3(5.5)	98.7(1.6)
149	Metolachlor*	1	2	100.5(2.1)	92.0(0.7)	86.9(1.2)	100.4(2.4)
150	Metolcarb	0.1	1	104.1(1.2)	94.9(1.2)	88.4(2.5)	101.2(5.1)
151	Metrafenone	0.03	0.05	100.6(0.9)	97.7(0.5)	90.9(2.0)	100.2(0.6)
152	Metribuzin*	1	5	110.9(0.8)	97.1(2.9)	76.0(3.7)	115.2(3.4)
153	Mevinphos (*E*,*Z*)*	0.1	0.5	106.7(1.5)	95.4(0.5)	84.8(2.8)	97.9(1.1)
154	Milbemectin A3	0.3	0.5	95.4(3.2)	93.4(4.3)	86.4(5.9)	98.0(3.3)
	Milbemectin A4	0.5	1	92.2(4.0)	96.2(2.0)	79.3(3.6)	95.7(2.2)
155	Molinate	5	10	101.7(0.5)	95.9(8.9)	85.4(5.1)	95.0(6.4)
156	Monocrotophos	0.1	0.5	103.6(1.6)	97.4(0.4)	85.8(1.3)	101.1(1.9)
157	Myclobutanil	1	2	103.7(1.8)	93.2(0.9)	89.2(6.8)	109.2(1.8)
158	Napropamide	0.05	0.1	103.0(1.0)	95.0(1.4)	90.1(4.9)	103.3(1.8)
159	Nicosulfuron	0.005	0.01	84.4(1.7)	82.4(1.6)	83.7(2.4)	91.5(2.8)
160	Novaluron*	0.5	1	84.7(13.1)	91.4(4.8)	92.9(5.6)	98.4(2.9)
161	Nuarimol	2	5	325.3(0.4)	159.8(1.0)	502.4(4.2)	183.0(3.6)
162	Ofurace	0.05	0.5	108.5(3.1)	93.8(1.7)	83.4(5.4)	107.6(1.9)
163	Omethoate	0.1	0.5	91.1(2.8)	90.8(1.6)	87.8(1.4)	95.9(1.2)
164	Oxadiazon	0.1	0.5	95.8(3.9)	92.1(2.9)	92.0(2.0)	93.8(1.1)
165	Oxadixyl	0.008	0.01	109.3(2.6)	99.8(0.2)	81.0(3.9)	104.3(2.6)
166	Oxamyl	0.01	0.05	102.3(1.5)	94.1(0.3)	92.7(1.1)	100.3(1.1)
167	Oxaziclomefon	0.05	0.1	99.3(7.6)	95.7(1.6)	88.5(3.1)	101.6(0.6)
168	Paclobutrazol	0.5	1	101.3(5.1)	93.7(0.5)	95.9(7.3)	110.0(2.7)
169	Penconazole	0.1	0.5	100.2(0.7)	93.9(1.1)	88.1(3.6)	103.2(2.7)
170	Pencycuron	0.05	0.1	96.8(3.3)	94.5(1.8)	106.7(3.8)	109.2(2.6)
171	Pendimethalin*	1	2	89.3(3.8)	89.9(4.8)	100.7(7.0)	96.0(2.9)
172	Penoxsulam	0.03	0.05	101.2(3.3)	93.4(1.7)	100.7(5.2)	102.3(2.7)
173	Penthiopyrad*	0.008	0.01	104.5(2.0)	94.7(0.8)	85.8(2.6)	110.1(0.8)
174	Pentoxazone	1	5	102.6(6.6)	99.6(5.1)	98.8(12.5)	109.8(6.3)
175	Phenthoate	0.1	0.5	95.8(2.1)	93.9(1.8)	89.2(3.3)	100.4(3.4)

Table 5. Continued

No.	Compound	LOD (μg/kg)	LOQ (μg/kg)	Recovery, % (RSD, %) Apple		Recovery, % (RSD, %) Rice	
				50 μg/kg	200 μg/kg	50 μg/kg	200 μg/kg
176	Phorate	0.05	1	96.6(5.9)	91.8(4.0)	95.1(6.3)	108.2(4.6)
177	Phosalone	0.1	0.5	99.3(1.1)	95.7(0.7)	81.2(2.4)	106.7(0.1)
178	Phosphamidone	0.05	0.1	105.2(1.4)	97.0(0.7)	94.4(1.7)	100.8(2.3)
179	Phoxim	0.03	0.05	95.2(1.6)	93.7(1.4)	91.7(1.8)	102.1(0.9)
180	Picoxystrobin*	0.01	0.05	100.7(1.8)	94.9(1.3)	94.8(2.2)	89.6(0.9)
181	Piperophos	0.05	0.1	99.8(0.2)	92.2(1.0)	85.6(1.7)	99.8(1.7)
182	Pirimicarb	0.01	0.05	100.2(1.4)	93.4(0.5)	90.6(1.9)	102.4(2.7)
183	Pirimiphos-methyl	0.1	0.5	99.3(1.9)	94.2(1.4)	92.8(3.1)	102.2(1.4)
184	Probenazole*	5	15	100.6(2.5)	94.2(1.1)	81.0(6.7)	100.9(3.1)
185	Prochloraz	0.5	1	95.8(0.3)	92.8(0.7)	93.6(5.2)	99.6(1.9)
186	Profenofos	0.1	0.5	101.1(1.5)	95.1(0.8)	86.3(1.5)	101.6(1.8)
187	Prometryn*	0.1	0.5	97.1(1.8)	90.7(0.6)	89.2(2.6)	102.2(0.9)
188	Propamocarb	0.005	0.01	86.1(6.4)	85.6(1.5)	82.2(2.5)	92.2(1.1)
189	Propanil	1	5	94.5(3.4)	91.8(1.4)	89.3(4.0)	104.8(2.5)
190	Propaquizafop	0.03	0.05	99.2(2.2)	97.6(1.2)	87.6(2.9)	81.5(1.4)
191	Propiconazole*	0.7	1	97.1(0.4)	91.8(1.0)	93.9(1.4)	106.4(1.1)
192	Propoxur	0.05	0.1	105.3(2.5)	92.6(1.3)	87.5(3.1)	104.9(1.4)
193	Pymetrozine	0.03	0.05	53.0(0.6)	52.8(1.1)	62.8(0.7)	73.5(3.0)
194	Pyraclofos	0.5	1	96.2(2.2)	91.8(0.5)	94.6(0.9)	97.6(2.5)
195	Pyraclostrobin	0.05	0.2	97.7(1.5)	95.0(0.8)	93.8(1.9)	102.7(1.9)
196	Pyrazolate	0.05	0.1	101.6(1.1)	97.3(0.2)	81.4(3.7)	105.2(0.4)
197	Pyrazophos	0.1	0.5	96.3(1.9)	94.1(0.3)	99.8(3.2)	98.2(0.8)
198	Pyribenzoxim	1	2	98.0(2.3)	94.7(2.0)	86.1(4.7)	104.0(1.8)
199	Pyributicarb	0.05	0.1	93.7(12.1)	94.5(1.9)	88.9(0.8)	101.8(0.1)
200	Pyridaben	0.05	0.1	97.9(3.0)	92.5(9.3)	57.4(1.2)	72.2(2.1)
201	Pyridaphenthion*	0.1	0.5	102.4(1.1)	95.1(1.3)	90.0(4.6)	103.5(2.1)
202	Pyrifluquinazon	0.005	0.01	95.6(2.4)	97.6(1.4)	87.0(1.1)	107.1(4.2)
203	Pyriftalid	0.5	1	103.2(4.2)	96.4(0.9)	88.4(3.3)	105.4(2.7)
204	Pyrimethanil	1	5	97.6(5.6)	97.1(1.4)	109.7(9.3)	95.9(4.8)
205	Pyrimidifen	0.05	0.1	100.3(1.4)	96.9(0.2)	98.6(4.9)	104.7(0.9)
206	Pyriminobac-methyl (*Z*)	0.1	0.5	100.3(2.5)	93.2(0.7)	87.9(1.7)	101.9(1.2)
	Pyriminobac-methyl (*E*)	0.1	0.5	99.9(2.3)	92.7(0.6)	90.9(4.1)	102.0(2.8)
207	Pyrimisulfan	0.008	0.01	99.5(1.7)	93.5(1.0)	96.9(1.7)	100.6(1.5)
208	Pyriproxyfen	0.05	0.1	92.3(15.1)	94.4(3.5)	93.7(2.3)	102.9(0.7)
209	Pyroquilon	0.05	0.1	97.6(1.2)	92.0(0.4)	81.3(3.4)	103.9(2.6)
210	Quinalphos	0.03	0.05	100.5(0.3)	94.4(0.5)	92.5(4.2)	103.9(0.4)
211	Quinmerac	0.005	0.01	105.6(7.6)	94.7(0.8)	71.5(0.5)	88.7(2.2)
212	Quinoclamine*	1	5	95.0(6.1)	94.9(2.4)	88.2(7.4)	103.4(5.0)
213	Quizalofop-ethyl	0.01	0.05	100.4(2.8)	95.2(1.5)	88.8(2.5)	106.9(1.6)
214	Saflufenacil	0.03	0.05	99.7(6.6)	94.4(3.1)	99.7(6.6)	100.2(5.6)
215	Sethoxydim	0.03	0.05	91.4(1.1)	93.4(0.5)	95.6(2.9)	95.3(1.3)
216	Silafluofen*	0.03	0.05	91.6(1.3)	97.9(0.3)	99.4(0.6)	101.3(0.6)
217	Simeconazole*	1	3	98.5(6.4)	93.1(1.3)	86.6(7.2)	107.6(4.9)
218	Simetryn*	0.05	0.1	98.1(1.7)	91.0(0.2)	90.8(3.0)	101.3(1.0)

Table 5. Continued

No.	Compound	LOD (μg/kg)	LOQ (μg/kg)	Recovery, % (RSD, %) Apple		Recovery, % (RSD, %) Rice	
				50 μg/kg	200 μg/kg	50 μg/kg	200 μg/kg
219	Spinetoram (j)	0.03	0.05	91.6(2.5)	90.3(0.8)	100.3(0.3)	101.1(3.1)
	Spinetoram (L)	0.03	0.05	91.0(1.0)	91.6(2.3)	101.1(1.2)	98.4(4.9)
220	Spirodiclofen	0.05	0.1	94.9(9.3)	93.1(6.9)	83.3(2.8)	100.6(1.9)
221	Spiromesifen*	0.7	1	97.8(14.1)	91.0(6.2)	92.3(4.2)	98.4(0.5)
222	Sulfoxaflor	0.005	0.01	81.3(0.7)	88.6(1.8)	81.0(3.6)	90.3(1.6)
223	Tebuconazole	0.1	0.5	101.3(2.2)	94.4(1.0)	92.6(3.6)	101.2(1.7)
224	Tebufenozide	0.1	0.5	101.5(2.5)	95.6(2.2)	92.9(6.4)	108.7(1.7)
225	Tebufenpyrad	0.1	0.5	97.0(12.4)	101.8(5.4)	90.1(3.1)	86.3(1.9)
226	Tebupirimfos*	0.05	0.1	93.2(3.9)	92.5(0.7)	104.7(2.5)	102.4(0.9)
227	Teflubenzuron	4	5	91.7(6.6)	99.5(2.9)	86.7(6.8)	98.3(2.2)
228	Terbuthylazine	0.5	1	105.4(0.7)	94.4(1.1)	89.2(2.5)	112.4(2.4)
229	Terbutryn*	0.05	0.1	97.7(0.5)	92.6(0.3)	89.6(2.9)	101.7(2.5)
230	Tetraconazole	0.1	1	97.8(5.1)	93.9(1.7)	113.0(4.1)	112.3(2.3)
231	Thenylchlor	0.03	0.05	104.5(2.8)	94.5(1.3)	90.9(1.4)	103.8(1.9)
232	Thiabendazole	0.5	1	95.3(1.8)	92.9(1.2)	86.1(3.3)	93.3(0.9)
233	Thiacloprid	0.03	0.05	100.6(3.4)	94.9(0.4)	89.2(2.5)	100.7(2.0)
234	Thiamethoxam	0.1	0.5	99.8(1.8)	92.4(1.1)	83.2(1.2)	107.3(1.3)
235	Thiazopyr*	0.5	1	100.4(3.2)	93.4(1.8)	88.4(2.6)	105.9(0.8)
236	Thidiazuron	0.1	0.5	111.0(2.6)	96.8(1.2)	81.6(8.8)	107.0(2.8)
237	Thifensulfuron-methyl	0.01	0.05	106.2(4.2)	99.4(1.8)	113.4(4.0)	113.8(2.3)
238	Thiobencarb	0.1	0.5	97.9(1.5)	90.9(1.4)	93.3(5.2)	102.9(1.0)
239	Thiodicarb	0.05	0.2	105.5(2.8)	97.5(1.2)	45.2(2.9)	79.6(0.9)
240	Thiophanate-methyl	18	20	111.6(6.5)	106.5(0.5)	99.4(0.8)	116.5(0.5)
241	Triadinil	3	5	98.4(15.0)	93.3(7.6)	105.6(10.4)	115.7(1.6)
242	Tolclofos-methyl*	5	10	88.2(6.6)	90.4(4.8)	97.0(15.1)	101.6(2.4)
243	Tolylfluanid*	4	5	259.6(55.8)	66.7(45.2)	314.2(10.9)	184.7(19.2)
244	Triadimefon	0.5	1	105.7(2.6)	93.3(1.4)	87.3(4.9)	108.4(2.2)
245	Triazophos	0.01	0.05	103.1(1.6)	94.5(0.4)	88.8(1.0)	104.5(1.8)
246	Tricyclazole	0.01	0.05	107.4(4.0)	100.4(0.5)	88.7(5.2)	102.4(1.5)
247	Trifloxystrobin	0.05	0.1	99.5(1.7)	93.5(1.0)	86.7(2.4)	102.0(0.8)
248	Triflumizole	0.05	0.1	112.1(3.0)	104.9(2.1)	103.5(1.9)	107.0(0.7)
249	Triflumuron	0.05	0.5	100.4(4.7)	92.9(1.3)	87.4(3.1)	107.0(0.7)
250	Uniconazole	0.8	1	97.4(1.7)	92.3(2.1)	95.3(2.3)	100.0(3.0)
251	Vamidothion	0.005	0.01	105.2(1.4)	96.2(0.7)	90.1(1.3)	101.0(1.7)

*41 pesticides were analyzed by both GC-MS/MS and LC-MS/MS.

한계(limit of quantitation, LOQ)를 측정하기 위해 제조한 표준품 혼합용액을 0.005~100 μg/L로 희석하여 각각 3반복으로 분석하였다. 각 농약의 LOD는 LC-MS/MS 분석에서 0.005~18 μg/kg, GC-MS/MS에서 0.08~80 μg/kg 수준이었으며, LOQ는 LC-MS/MS분석에서 0.01~20 μg/kg, GC-MS/MS의 경우 0.1~100 μg/kg 범위로 나타나 시료 중에 함유된 ppb 수준의 미량 농약성분의 검출이 가능할 것으로 판단되었다(Table 5, 6).

농약성분별 회수율

회수율 실험은 친환경인증을 받은 사과와 쌀 시료에 최종 농도가 50 μg/kg, 200 μg/kg 되도록 표준품 혼합용액을 시료에 첨가하여 QuEChERS 전처리 방법으로 추출한 시험용액을 LC-MS/MS와 GC-MS/MS에 적용하여 회수율을 검증

Table 6. Average recovery and RSD of 110 pesticides spiked in apple and rice at two different concentrations with GC-MS/MS (n=3)

No.	Compound	LOD (μg/kg)	LOQ (μg/kg)	Recovery, % (RSD, %) Apple		Recovery, % (RSD, %) Rice	
				50 μg/kg	200 μg/kg	50 μg/kg	200 μg/kg
1	Acrinathrin	20	30	85.9(4.9)	90.1(5.9)	72.2(1.7)	54.5(2.8)
2	Alachlor*	1	5	79.3(7.3)	92.0(5.0)	100.3(6.0)	91.2(12.5)
3	Aldrin	3	5	77.9(5.1)	91.3(7.3)	93.8(5.0)	92.6(8.6)
4	Anilofos	1	5	83.5(4.4)	95.2(4.7)	78.9(1.6)	35.9(2.8)
5	BHC	1	5	76.9(8.3)	92.3(4.6)	94.4(8.9)	88.9(12.0)
6	Bifenox	0.08	0.1	89.4(2.1)	92.5(5.1)	91.2(1.3)	81.3(1.0)
7	Bifenthrin	1	5	95.0(5.4)	102.6(5.8)	72.2(1.5)	54.5(0.9)
8	Bromobutide	1	3	80.7(7.4)	95.6(5.8)	102.9(4.7)	94.0(11.1)
9	Bromopropylate	0.08	0.1	86.0(6.3)	97.6(5.2)	88.3(2.4)	87.2(0.9)
10	Butachlor	1	2	85.8(5.6)	99.8(5.2)	101.9(3.1)	92.3(6.7)
11	Captan	20	30	37.6(1.7)	27.0(4.8)	65.0(6.6)	37.3(14.2)
12	Carbofuran*	0.3	0.8	101.5(14.7)	105.7(6.8)	101.5(13.4)	112.9(5.2)
13	Carbophenothion	5	10	86.0(5.6)	98.4(5.6)	88.5(2.1)	79.5(0.5)
14	Chinomethionat	30	50	34.6(3.5)	22.7(5.7)	44.5(1.5)	30.1(1.5)
15	Chlordane	0.3	0.5	85.0(7.1)	93.2(5.1)	94.2(5.9)	89.8(7.4)
16	Chlorfenapyr	5	10	98.1(7.3)	101.1(6.0)	98.0(1.7)	89.2(3.8)
17	Chlorfenvinphos	1	5	79.4(7.1)	96.7(5.3)	95.7(3.8)	86.9(5.9)
18	Chlorfluazuron*	3	5	104.8(9.1)	111.1(6.4)	126.1(4.2)	130.5(9.7)
19	Chlorobenzilate	1	5	86.3(6.6)	99.9(5.2)	89.8(0.4)	83.6(2.4)
20	Chlorothalonil	5	10	80.5(2.7)	86.0(6.4)	90.7(10.2)	87.2(12.8)
21	Chlorpropham	1	5	74.0(9.6)	91.9(2.4)	96.7(10.1)	91.1(13.4)
22	Chlorpyrifos-methyl	1	5	75.7(8.6)	91.2(5.3)	96.8(6.9)	85.5(11.8)
23	Cyflufenamid*	8	10	81.3(7.8)	93.8(1.6)	62.7(1.4)	49.5(1.6)
24	Cyfluthrin	30	50	84.1(4.1)	88.3(5.6)	77.3(1.2)	64.3(2.9)
25	Cyhalothrin (lambda)	3	5	88.6(5.3)	92.3(6.5)	76.8(0.3)	68.5(1.4)
26	Cypermethrin	10	30	84.1(2.5)	88.6(6.0)	82.0(1.0)	66.2(1.8)
27	Cyprodinil	5	8	84.5(7.9)	95.9(6.7)	99.1(3.8)	93.7(9.6)
28	DDT	0.1	0.3	90.0(6.1)	98.4(5.9)	91.8(1.8)	83.7(4.0)
29	Deltamethrin	10	30	76.1(4.4)	83.0(5.1)	70.7(3.6)	44.3(8.1)
30	Dichlofluanid*	1	3	24.0(0.1)	37.2(1.0)	55.1(0.2)	19.5(5.8)
31	Diclofop-methyl	10	30	93.8(9.5)	100.1(6.2)	88.8(1.1)	87.0(0.8)
32	Dicloran	8	10	86.0(1.1)	92.2(6.1)	94.3(5.8)	86.0(13.7)
33	Dicofol	10	30	89.5(6.9)	105.2(5.4)	96.5(4.1)	92.6(10.5)
34	Dieldrin	1	3	88.6(6.1)	93.8(5.3)	90.1(6.5)	88.8(6.0)
35	Demethoate*	20	30	79.8(3.4)	94.1(5.3)	85.2(4.6)	76.8(10.6)
36	Dimethylviphos*	5	8	74.0(7.5)	91.1(3.8)	86.0(3.8)	75.7(8.5)
37	Diphenylamine	3	5	73.8(8.5)	84.9(2.5)	92.5(10)	92.2(17.9)
38	Disulfoton	0.5	0.8	75.2(6.5)	92.0(3.8)	104.5(5.7)	96.4(13.2)
	Endosulfan sulfate	25	50	84.8(7.2)	97.6(3.4)	81.3(4.4)	76.9(1.8)
39	Endosulfan-α	1	3	82.4(6.9)	94.4(6.3)	89.5(4.8)	89.0(9.8)
	Endosulfan-β	0.8	1	90.9(5.0)	97.2(6.6)	92.6(2.9)	86.1(4.4)
40	Endrin	3	5	89.0(7.7)	95.5(7.8)	92.0(4.7)	83.3(5.9)
41	EPN*	1	5	89.0(4.0)	93.7(5.3)	86.1(1.6)	76.6(1.4)
42	Ethalfluralin	1	5	95.4(7.4)	102.3(1.1)	98.1(6.6)	88.9(13.4)

Table 6. Continued

No.	Compound	LOD (μg/kg)	LOQ (μg/kg)	Recovery, % (RSD, %) Apple		Recovery, % (RSD, %) Rice	
				50 μg/kg	200 μg/kg	50 μg/kg	200 μg/kg
43	Ethion	20	30	101.1(1.7)	100.3(5.2)	90.9(1.5)	82.4(1.5)
44	Etridiazole	0.3	0.5	76.8(10.7)	96.4(4.0)	88.4(9.2)	92.2(19.6)
45	Fenamidone*	1	5	85.9(7.6)	99.2(7.1)	91.2(3.2)	84.7(2.2)
46	Fenamiphos*	5	10	82.3(5.8)	92.6(6.0)	91.3(1.7)	82.4(1.7)
47	Fenitrothion	5	10	78.6(6.8)	87.7(4.6)	96.3(7.0)	88.8(9.7)
48	Fenothiocarb*	1	5	83.6(5.7)	97.4(5.6)	101.5(4.3)	91.1(4.6)
49	Fenpropathrin	5	10	91.2(5.8)	102.7(5.0)	93.1(2.0)	80.9(1.2)
50	Fenvalerate	10	30	87.9(2.1)	92.1(5.0)	80.9(1.3)	64.2(2.5)
51	Ferimzone	80	100	97.6(2.8)	71.0(1.5)	105.1(2.7)	102.0(6.8)
52	Fipronil	1	3	93.1(6.2)	95.2(6.1)	103.5(2.3)	94.6(3.1)
53	Flucythrinate	8	10	85.0(2.2)	89.9(5.3)	80.6(1.5)	67.4(3.6)
54	Fludioxonil*	1	5	87.5(6.5)	99.5(5.7)	92.1(2.5)	85.9(1.2)
55	Fluopyram*	10	30	75.5(7.5)	90.4(0.5)	62.7(1.6)	49.0(7.3)
56	Folpet	5	10	66.8(1.5)	85.9(2.5)	72.7(7.0)	46.0(7.4)
57	Fthalide	5	10	86.2(7.1)	96.9(3.9)	97.1(3.0)	95.6(8.6)
58	Halfenprox	5	10	88.0(2.1)	93.2(5.3)	86.9(0.5)	81.3(1.5)
59	Heptachlor	1	5	73.6(7.9)	87.9(6.0)	93.4(5.9)	88.2(14.7)
	Heptachlor-epoxide	1	5	79.9(8.9)	91.9(6.9)	96.9(6.2)	91.1(12.2)
60	Imazalil*	25	50	92.7(9.0)	101.9(8.5)	91.7(6.8)	86.0(2.3)
61	Indanofan	10	25	87.9(5.1)	102.6(6.6)	84.0(1.9)	81.8(3.1)
62	Indoxacarb	10	30	74.8(3.4)	84.2(4.5)	71.2(1.6)	58.4(5.3)
63	Iprodione	10	30	82.6(5.2)	92.7(2.4)	70.0(3.7)	46.4(6.0)
64	Isofenphos	1	5	79.8(5.2)	94.0(3.9)	101.8(2.5)	93.4(5.8)
65	Lufenuron*	1	5	38.4(7.1)	26.3(1.5)	31.3(5.3)	10.7(17)
66	Mecarbam	5	10	77.2(6.9)	95.5(3.6)	96.0(3.9)	89.2(5.6)
67	Methidathion*	5	8	78.6(5.9)	96.8(4.9)	97.5(2.6)	88.0(6.3)
68	Methoxychlor	0.3	0.5	93.9(4.2)	103.1(5.0)	92.0(1.3)	86.4(0.6)
69	Metobromuron*	50	80	75.9(9.1)	85.6(5.3)	90.6(4.5)	83.2(9.1)
70	Metolachlor*	1	5	86.0(5.8)	95.7(10.4)	103.4(3.8)	93.8(7.5)
71	Metribuzin*	1	5	74.2(6.3)	88.2(3.0)	97.7(5.9)	89.9(8.9)
72	Mevinphos*	5	10	70.7(11.6)	95.3(3.8)	86.1(14.1)	75.6(9.3)
73	Novaluron*	1	5	35.6(17.3)	47.2(1.5)	33.7(7.1)	16.5(9.7)
74	Oxyfluorfen	5	10	90.6(6.6)	105.1(3.5)	96.0(1.6)	86.8(2.8)
75	Parathion	3	5	79.4(5.7)	90.9(5.3)	100.1(3.7)	95.9(8.7)
76	Parathion-methyl	5	8	75.5(6.9)	85.8(3.8)	96.1(4.4)	87.4(12.2)
77	Pendimethalin*	1	5	80.8(4.6)	91.8(5.2)	98.9(2.0)	92.8(7.4)
78	Penthiopyrad*	10	30	82.8(9.3)	94.3(1.4)	54.6(2.0)	41.3(0.6)
79	Permethrin	10	25	89.6(5.3)	96.6(6.1)	84.0(2.8)	81.8(1.3)
80	Phorate*	5	10	70.3(7.5)	95.2(6.8)	106.3(4.6)	98.8(13.4)
81	Picoxystrobin*	1	5	106.1(3.6)	102.7(4.5)	63.0(1.5)	49.1(1.5)
82	Pirimiphos-ethyl	1	5	101.2(4.0)	104.7(2.5)	-	-
83	Probenazole*	5	10	81.8(13.0)	97.3(4.5)	35.1(9.4)	31.5(8.5)
84	Procymidone	10	25	90.4(4.9)	96.1(7.0)	102.4(3.7)	93.3(8.3)
85	Prometryn*	5	10	80.1(9.3)	96.8(5.4)	98.2(5.4)	92.1(8.9)

Table 6. Continued

No.	Compound	LOD (μg/kg)	LOQ (μg/kg)	Recovery, % (RSD, %) Apple		Recovery, % (RSD, %) Rice	
				50 μg/kg	200 μg/kg	50 μg/kg	200 μg/kg
86	Propiconazole*	5	10	89.6(8.9)	99.7(5.5)	88.8(3.8)	79.9(2.2)
87	Prothiofos	5	10	83.3(5.0)	99.4(5.3)	99.2(1.7)	92.1(4.2)
88	Pyridalyl	5	10	85.4(2.7)	92.0(5.9)	87.0(1.9)	77.2(2.1)
89	Pyridaphenthion*	5	10	85.7(4.9)	95.8(2.3)	78.4(1.8)	69.8(3.5)
90	Quinoclamine*	5	10	74.1(4.2)	83.9(4.7)	86.7(1.6)	80.2(6.6)
	Quintozene	50	80	94.5(8.4)	101.3(2.0)	91.9(6.0)	87.8(12.9)
	Propiconazole*	5	10	89.6(8.9)	99.7(5.5)	88.8(3.8)	79.9(2.2)
	Prothiofos	5	10	83.3(5.0)	99.4(5.3)	99.2(1.7)	92.1(4.2)
91	Pyridalyl	5	10	85.4(2.7)	92.0(5.9)	87.0(1.9)	77.2(2.1)
	Pyridaphenthion*	5	10	85.7(4.9)	95.8(2.3)	78.4(1.8)	69.8(3.5)
	Methyl-pentachlorophenyl sulfide	0.1	0.3	74.9(7.5)	86.7(9.1)	98.7(3.4)	83.1(12.2)
	Pentachloroaniline	1	5	74.3(7.2)	84.8(6.4)	90.9(6.5)	86.1(13.3)
92	Silafluofen*	1	5	89.3(2.9)	96.0(5.4)	87.0(0.6)	80.9(2.0)
93	Simazine	5	10	71.2(8.1)	91.3(5.6)	98.2(9.2)	90.6(14.5)
94	Simeconazole*	1	25	74.7(7.4)	91.1(3.6)	96.3(7.0)	91.2(7.9)
95	Simetryn*	5	1	82.1(7.4)	99.1(4.4)	97.8(6.4)	93.0(12.2)
96	Spiromesifen*	1	5	83.0(5.5)	97.2(3.0)	82.5(2.9)	74.6(1.3)
97	Tebupirimfos*	1	5	75.0(8.4)	91.7(5.1)	99.4(5.0)	89.7(14.4)
98	Tefluthrin	0.08	0.1	84.3(8.3)	95.5(7.4)	104.5(8.5)	94.9(15.8)
99	Terbufos	1	5	70.9(8.4)	86.6(4.2)	101.3(7.2)	94.0(15.7)
100	Terbutryn*	5	10	78.3(6.4)	94.2(5.1)	96.1(5.7)	91.4(10.4)
101	Tetradifon	1	5	97.2(1.5)	101.9(5.7)	89.5(1.1)	85.3(0.8)
102	Thiazopyr*	5	10	86.7(7.2)	99.2(5.7)	105.3(6.7)	94.9(10.5)
103	Thifluzamide	1	5	87.6(6.6)	102.6(5.6)	98.1(0.6)	89.5(2.0)
104	Tolclofos-methyl*	1	5	78.3(7.6)	92.2(5.9)	100.4(6.5)	93.2(13.1)
105	Tolylfluanid*	5	10	44.9(6.1)	52.6(5.4)	54.7(1.5)	25.6(9.1)
106	Tralomethrin	1	5	76.1(4.0)	83.4(4.9)	70.0(3.0)	44.1(8.1)
107	Triadimenol	5	10	83.8(7.3)	95.3(5.8)	99.2(2.7)	91.7(4.1)
108	Trifluralin	1	5	95.3(2.4)	101.1(1.2)	99.5(6.7)	91.9(15.8)
109	Vinclozolin	1	5	84.8(7.7)	95.7(6.0)	102.4(8.1)	95.0(12.9)
110	Zoxamide	1	5	81.0(6.4)	90.0(3.6)	69.9(3.2)	43.5(4.3)

*41 pesticides were analyzed by both GC-MS/MS and LC-MS/MS.

하였다. 분석대상 농약에 대한 분석법 확립 결과 표준곡선의 직선성은 0.05~0.2 mg/L 범위에서 $R^2 > 0.99$이었으며 회수율에 대한 결과는 Table 5과 6에 나타내었다.

LC-MS/MS분석 대상 농약성분 251성분의 회수율은 사과시료의 경우 저농도(50 μg/kg)에서는 회수율이 70~120% 이내이고 표준편차 20% 이내인 농약은 242종이었고, 정성이 가능한 성분은 248종이었으며 benfuracarb, diafenthiuron, fenhexamid 농약 성분 3종은 검출 할 수 없었다. 고농도(200 μg/kg)에서는 회수율이 70~120% 이내이고 표준편차 20% 이내인 농약은 242종이었고, 정성이 가능한 성분은 249종이었으며, benfuracarb, fenhexamid 농약 성분 2종은 검출 할 수 없었다. 쌀시료의 경우 저농도에서는 회수율이 70~120% 이내이고 표준편차 20% 이내인 농약은 238종이었고, 정성이 가능한 성분은 249종이었으며 benfuracarb, dichlofluanid 농약 성분 2종은 검출 할 수 없었다. 고농도에서는 회수율이 70~120% 이내이고 표준편차 20% 이내인 농약은 243종이었고, 정성이 가능한 성분은 250종이었으며 dichlofluanid 농약 성분 1종은 검출 할 수 없었다(Table 5).

GC-MS/MS분석 대상 농약성분 110성분의 회수율은 사과시료의 경우 회수율이 70~120% 이내이고 표준편차 20%

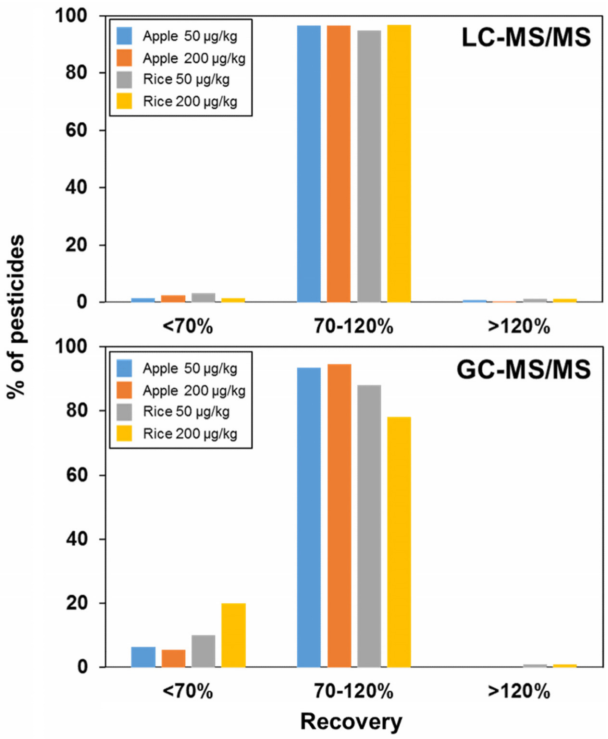

Fig. 2. Distribution of recoveries in apple and rice using two different concentrations with LC-MS/MS and GC-MS/MS.

이내인 농약은 저농도(50 μg/kg)와 고농도(200 μg/kg)에서 각각 103종과 104종이었으며, 모든 농약성분이 검출 되었다. 쌀시료의 경우 저농도와 고농도에서 회수율이 70~120% 이내이고 표준편차 20% 이내인 농약은 97종이었고, 정성이 가능한 성분은 109종이었으며 pirimiphos-ethyl 농약 성분 1종은 검출 할 수 없었다(Table 6).

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, 국제식품규격위원회는 회수율 60~120%와 상대표준편차 15~30% 이하로 규정하고 있다(Codex Alimentarius Commission, 2003). 본 연구결과에서 LC-MS/MS와 GC-MS/MS를 이용한 다종농약 다성분 분석법에서 제시한 회수율은 최소 70% 이상과 상대 표준편차 20% 이하로 나타내어 국내 및 국제적 기준을 충족하였다. 따라서 본 연구에서 적용된 분석방법은 농산물 중 잔류되는 다성분 농약을 분석하는데 적용될 수 있을 것으로 판단되었다.

LC-MS/MS 분석 대상 농약 중에서 abamectin, chlorfluazuron은 기존에 수행된 선행 연구에서 LC-MS/MS 분석조건에서 정량이 불가능한 수준의 감도를 보여 분석불가 성분으로 분류된 바 있고(Kwon 등 2001), Hernando 등(2007)은 abamectine과 같은 macrocyclic lactone 화합물은 HPLC-MS/MS의 drying gas 온도를 낮추면 감도를 높일 수 있다고 보고 하였다. Hernando 등(2007)의 연구 결과를 기기분석 조건에 반영 한 결과 사과시료에서 abamectin의 경우 90%, chlorfluazuron의 경우 75% 이상의 회수율을 보임으로써 잔류농약 다성분 분석 기준인 70~130% 이내를 만족하는 재현성이 우수한 결과를 얻을 수 있었다. 사과와 쌀시료에서 공통적으로 검출되지 않은 benfuracarb 농약은 기존의 농약잔류 연구결과에서 회수율이 잔류농약 다성분 분석 기준보다 낮은 경향을 보였다(Gwon 등, 2014; Yang 등, 2013). Benfuracarb는 중성 및 염기성 조건에서 음전하를 띄며, 음전하를 지니는 농약들은 QuEChERS 정제과정 중 PSA에 흡착되는 특성이 있어 회수율이 떨어지고 최종 시료 추출액이 pH 6이상의 조건에서는 검출이 되지 않는다는 연구 보고가 있다(Lehotay, 2003; Sannino 등, 2004). LC-MS/MS와 GC-MS/MS 분석대상 농약 dichlofluanid은 시료 추출과정 또는 시료 추출액의 pH의 증가에 의해 빠르게 분해되는 특징이 있고 질량분석기를 이용한 다성분 동시분석법에서 회수율이 낮은 성분으로 단성분 분석법으로 정량이 가능하다고 보고 된바 있다(Cho 등, 2013). 또한, GC-MS/MS 분석대상 농약인 pirimiphos-ethyl은 사과시료에서는 100% 이상의 회수율을 보였으나 쌀시료에서는 검출되지 않았다. 다른 matrix에 비해 시료 추출단계에서 쌀시료 습윤화 과정을 거치는 동안 pirimiphos-ethyl 성분이 acetonitrile 층으로 완벽하게 분리되지 않은 원인이 작용한 것으로 판단되어진다. 따라서 분석효율이 낮거나 미분석 대상 농약에 대해서는 시료 전처리법의 개선과 분석효율을 증대시키기 위한 추가적인 연구가 필요할 것으로 사료된다.

결 론

본 연구에서는 QuEChERS 시료 전처리법을 적용한 사과와 쌀 시료로부터 LC-MS/MS와 GC-MS/MS를 이용하여 잔류농약 동시다성분 분석의 가능성을 살펴보았다. LC-MS/MS 분석대상 농약성분 251종, GC-MS/MS 분석대상 농약성분 110종을 적용하여 320종 농약성분이 본 연구의 다성분 동시분석법 적용 시험을 통해 정성 및 정량이 동시에 가능함을 확인하였다. 분석대상 농약성분의 회수율은 70-120%의 적정 범위를 나타내었으나(Fig. 2), 이 범위를 벗어나는 회수율을 나타내는 성분들도 다수 존재하여 이를 개선하기 위해 분석효율이 낮은 농약성분들에 대해서는 추출방법 및 추가적인 시험법 적용과 개발이 필요하다고 판단되었으며, 본 연구에서 검토된 LC-MS/MS와 GC-MS/MS를 이용한 농약의 다성분 동시분석법은 앞으로 농산물의 농약잔류 모니터링 연구 분야에 적용될 수 있을 것으로 기대되었다.

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LC-MS/MS와 GC-MS/MS를 이용한 사과와 쌀 시료에서 320종 농약의 다성분 분석

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요 약 본 연구는 사과와 쌀에서 320성분 농약에 대한 다성분 동시분석법을 확립하고자 수행되었다. 시료의 추출은 QuEChERS법을 사용하였고, 추출 후 잔류물은 LC-MS/MS와 GC-MS/MS로 기기분석 하였다. 시험 농약은 LC-MS/MS 251성분, GC-MS/MS 110성분을 선발하였으며, 41성분은 공통적으로 적용되었다. 분석법의 정량한계는 LC-MS/MS에서 0.01~20 μg/kg, GC-MS/MS에서 0.1~100 μg/kg으로 산출되었다. 사과와 쌀에서 회수율 70~120%, 상대표준편차 20% 이내의 조건을 충족한 성분은 LC-MS/MS로 분석한 농약 중 각각 242성분(96%)과 237성분(94%)로 나타났으며, GC-MS/MS로 분석한 농약 중에는 각각 103성분(94%)과 83성분(76%)로 나타났다. 본 연구를 통해 QuEChERS 전처리와 LC-MS/MS 및 GC-MS/MS를 이용한 분석법은 농산물(사과 및 쌀) 중 잔류농약 다성분 동시분석에 효과적으로 적용될 것으로 기대된다.

색인어 농약, 다성분동시분석, QuEChERS, LC-MS/MS, GC-MS/MS