RESIDUES AND TRACE ELEMENTS

Multiresidue Method for the Determination of Pesticides in Korean Domestic Crops by Gas Chromatography/Mass Selective Detection

OCK KYOUNG CHUN, HEE GON KANG, and MYUNG HEE KIM
Seoul Health and Environmental Research Institute, Garak Agricultural Products Inspection Team, Garak dong 600, Songpa Ku, Seoul 138-701, Korea

The multiresidue method used in this study allows the determination of 101 pesticides, including organophosphorus, organochlorine, and nitrogen-containing pesticides, in crops by gas chromatography with mass selective detector. Analysis was performed in the selected–ion monitoring mode, and the identities of the positive analytes were confirmed by retention time and the ratios of selected ions. The selected ion mode demonstrated an acceptable selectivity for most of the pesticides determined in 3 kinds of samples (*Chrysanthemum coronarium*; *Perilla japonica*, leaf; and *Lactuca savita*, which are very popular vegetables eaten raw in Korea), and very minor interferences were observed in the elution area of the pesticide analytes. Samples were spiked with pesticides at 0.1–1.0 mg/kg. The recoveries of 90% of the pesticides were between 70 and 110%; however, the recoveries of acephate and folpet were very poor, i.e., <50%. The limits of detection (LODs) for most pesticides were between 0.02 and 0.3 mg/kg, and the LODs for about half of the pesticeds studied were <0.05 mg/kg.

Pesticides are necessary and essential in agricultural production. However, because of their potential to affect the environment and public health, a main concern is the identification and quantification of hundreds of pesticides with widely different physicochemical properties in very different types of matrixes. Therefore, a major task of analytical technology is to provide reliable and cost-effective methods.

With the introduction in the late 1960s of gas chromatography (GC) and its remarkable application to multireside analysis on packed columns, the technique was rapidly adopted. Further important developments, such as capillary columns, which provided high separation capacity, coupled with both sensitive and selective detectors, significantly enlarged the number of pesticides that could be efficiently determined in one run. These attractive features and the favorable development of both the performance and the costs of the instruments make capillary GC the most widely applied and productive technique in pesticide residue analysis. GC has proved to be an effective and selective major analytical technique for monitoring pesticide residues in agricultural foods, because of its high separation power and the presence of GC-amenable pesticides in a wide variety of samples (1). However, GC also has limited coverage of pesticides because they require specific detectors, such as those used in electron capture, nitrogen–phosphorus, and flame photometric detection.

Many studies have reported the use of GC with mass selective detection (GC–MSD) to monitor pesticide residues in matrixes, such as fruits and vegetables, with either the full-scan or the selected-ion monitoring (SIM) mode (2–5). The ease of coupling GC columns to a mass selective detector and the large number of standardized electron-impact spectra obtained by laboratories involved in pesticide residue analysis have increased the prevalence of GC–MSD over other analytical techniques (6–11).

Multiresidue methods (MRMs) that determine pesticides in food are needed to protect the environment and evaluate food quality. To supply safe agricultural products for Seoul citizens and to promote proper pesticide application practices in cultivation areas, the Seoul Health and Environmental Research Institute (SHERI) has monitored pesticide residues in agricultural products sold in Seoul city marketplaces since 1992; the results are published annually (12). The Garak Agricultural and Fishery Inspection Office founded in February 1999 provides more rapid and accurate analysis of samples and collection of violative products before their circulation by means of a 24 h inspection system. Regulatory agencies involved in the monitoring of pesticide residues in foods require fast and efficient MRMs with a broad application of analytical technology to maximize the scope of their monitoring activities.

This paper presents a rapid and efficient MRM that uses GC–MSD to determine 101 pesticides in the 3 kinds of crops that are most widely consumed in Korea.

Received November 8, 2002. Accepted by JS January 18, 2003.
Corresponding author's present address: New York State Agricultural Experiment Station, Cornell University, Department of Food Science & Technology, Food Analysis Laboratory, Geneva, NY 14456; e-mail: oc28@cornell.edu.

Table 1. Retention times (RT), ions monitored, and abundance ratios for pesticides determined by the MRM

		Ions monitored, *m/z*				Abundance ratio of qualifier ion/target ion		
Compound	RT, min	Target	Q1	Q2	Q3	Q1/tgt[a]	Q2/tgt	Q3/tgt
Propamocarb	9.75	58.10	188.10	129.10	—	13.60	12.96	—
Mevinphos	10.77	127.00	192.00	109.00	164.00	41.08	26.60	11.45
Nitrapyrin	11.14	193.90	195.90	197.90	132.90	96.96	28.76	9.40
Acephate	11.26	136.00	94.00	79.00	—	44.54	9.02	—
Omethoate	15.54	156.00	110.00	79.00	126.00	75.74	17.60	11.51
Tecnazene	15.70	202.90	214.80	260.80	177.90	82.85	80.05	39.27
Ethoprophos	16.67	157.90	96.90	125.80	139.10	79.85	52.63	50.58
Ethalfluralin	17.85	276.00	316.10	55.10	292.00	89.63	84.76	49.18
Diphenylamine	18.22	169.10	—	—	—	—	—	—
Trifluralin	18.56	306.00	264.00	290.00	248.00	73.00	12.22	10.44
Phorate	18.80	75.00	121.00	97.00	260.00	43.76	25.53	23.84
Monocrotophos	19.20	127.00	192.00	67.00	97.00	16.62	16.44	13.86
Dicloran	20.12	206.00	124.00	176.00	160.00	69.74	68.89	43.29
Dimethoate	20.38	87.00	125.00	143.00	229.00	57.09	12.64	9.83
Dimethipin	21.31	54.10	118.00	76.00	210.00	36.12	23.07	8.19
Terbufos	22.05	231.00	57.10	153.00	103.10	58.62	23.50	22.32
Chlorothalonil	23.19	265.90	109.10	229.00	193.90	7.40	7.36	6.59
Disulfoton	23.36	88.00	142.00	61.00	152.90	22.20	21.66	20.52
Diazinon	23.47	179.10	137.00	152.10	304.10	89.95	62.84	61.43
Tri-allate	24.03	86.10	268.00	128.10	142.90	67.74	25.11	21.54
Etrimfos	24.58	291.90	181.00	153.00	277.00	79.90	65.56	46.35
Iprobenfos	24.74	91.00	204.00	123.00	246.00	90.60	19.87	16.20
Phosphamidon	26.49	127.00	264.10	77.10	109.00	62.36	27.88	19.01
Propanil	26.81	161.00	217.00	57.10	—	21.58	21.28	—
Heptachlor	26.82	271.80	100.00	236.80	336.80	69.59	33.05	24.79
Vinclozolin	27.11	212.00	198.00	186.90	285.00	84.63	75.07	70.93
Alachlor	27.53	160.10	188.10	146.00	237.10	95.53	27.69	27.47
Metalaxyl	28.18	206.00	249.10	146.10	192.20	58.41	54.61	52.50
Prometryn	28.29	241.10	184.00	226.10	105.50	67.29	53.26	25.78
Metribuzin	29.19	198.00	57.00	—	—	19.71	—	—
Terbutryn	29.20	226.10	185.10	241.10	170.00	70.11	62.70	51.89
Fenitrothion	29.42	277.00	125.00	109.00	260.00	76.25	61.85	55.41
Aldrin	29.53	262.80	66.10	91.00	292.90	69.82	—	—
Dichlofluanid	29.66	123.00	167.00	223.90	92.00	49.14	46.51	20.09
Metolachlor	30.44	162.10	238.10	146.10	211.10	65.69	12.08	9.61
Fenthion	30.90	278.00	125.00	108.90	92.90	34.12	24.41	23.09
Chlorpyrifos	31.03	196.90	313.90	97.00	257.80	74.75	61.41	46.80
Parathion	31.16	291.00	109.00	96.90	139.00	69.50	56.86	54.96
Triadimefon	31.60	57.10	208.00	85.10	128.00	76.55	28.61	25.46
Diphenamid	32.62	167.10	72.00	239.10	152.00	92.42	26.19	16.62
Cyprodinil	33.23	224.10	210.10	77.10	—	11.03	6.58	—
Pirimiphos-ethyl	33.43	318.10	333.10	304.10	168.00	99.79	69.77	46.79
Pendimethalin	33.78	252.10	162.10	—	—	12.28	—	—
Penconazole	34.03	248.00	158.90	213.00	—	79.38	13.22	—

Table 1. (*continued*)

		Ions monitored, *m/z*				Abundance ratio of qualifier ion/target ion		
Compound	RT, min	Target	Q1	Q2	Q3	Q1/tgt[a]	Q2/tgt	Q3/tgt
Captan	34.13	79.10	149.00	116.90	263.90	36.22	22.14	14.73
Tolyfluanid	34.22	137.00	237.90	181.10	—	51.90	29.60	—
Folpet	34.68	259.90	104.00	130.00	76.10	61.05	47.60	39.34
Chlorfenvinphos	34.79	266.90	323.00	295.00	81.00	66.56	21.67	19.41
Phenthoate	34.94	274.00	125.00	93.00	246.00	38.07	28.53	22.91
Procymidone	35.36	96.00	283.00	67.10	53.10	85.13	36.22	14.04
Methidathion	35.88	145.00	85.10	125.00	—	54.91	14.78	—
α-Endosulfan	36.06	240.90	194.90	276.80	338.80	94.06	73.80	58.36
Triflumizole	36.07	278.00	73.10	206.00	179.00	94.03	68.12	39.11
Mepanipyrim	37.36	222.10	77.10	207.10	—	5.10	4.89	—
Napropamide	37.76	72.10	128.10	271.10	100.10	61.08	47.01	38.18
Dieldrin	38.17	79.10	262.80	276.90	108.00	42.24	35.62	18.67
Fenamiphos	38.56	303.10	154.00	288.10	217.00	44.11	29.50	27.15
Profenofos	38.80	207.90	338.90	139.00	97.00	90.48	89.30	67.56
Isoprothiolane	38.92	161.90	117.90	188.90	230.90	99.44	85.79	57.49
Imazalil	39.07	215.00	172.90	159.00	81.00	68.72	20.41	19.85
Carboxin	39.65	143.00	235.00	87.00	—	54.91	33.22	—
Oxadiazon	39.92	174.90	258.00	302.00	344.10	58.50	45.33	28.46
Flusilazole	40.26	233.00	206.00	315.00	219.90	34.79	12.18	9.01
Oxyfluorfen	40.68	252.00	361.00	300.00	280.00	37.73	31.36	15.51
Cyproconazole	40.79	222.00	139.00	125.00	83.10	44.22	19.97	16.52
β-Endosulfan	41.05	194.90	236.80	158.90	266.90	87.34	58.89	54.24
Chlorfenapyr	41.73	59.10	247.00	—	—	8.69	—	—
Chlorobenzilate	41.81	251.00	139.00	111.00	—	61.52	23.56	—
Fensulfothion	42.39	293.00	308.00	141.00	97.00	36.40	30.33	25.48
Ethion	43.26	230.90	97.00	153.00	121.10	51.17	49.02	33.17
Oxadixyl	43.38	163.10	105.00	132.10	119.90	96.21	86.44	63.41
Carbophenothion	44.83	157.00	341.90	121.00	97.00	46.39	43.49	38.65
Endosulfan sulfate	44.85	271.80	386.80	228.90	169.90	56.02	46.82	17.63
Edifenphos	44.91	109.00	173.00	310.00	201.00	94.32	75.48	33.19
Propiconazole	46.07	259.00	172.90	69.10	190.90	98.01	70.93	30.41
Norflurazon	46.28	303.00	145.00	102.00	173.00	88.24	39.34	19.70
Tebuconazole	46.90	250.10	125.00	70.10	163.00	82.70	40.10	14.10
Diclofop-methyl	47.58	253.00	340.00	281.00	120.10	99.29	47.23	21.27
Phosmet	49.75	160.00	77.10	317.00	—	5.54	5.01	—
Bromopropylate	50.09	340.90	184.90	155.00	207.00	47.24	18.75	6.90
EPN	50.14	157.00	185.00	141.00	323.00	32.26	28.86	14.40
Methoxychlor	50.77	227.10	113.50	195.00	152.10	5.03	3.45	3.28
Bifenthrin	50.95	181.10	166.10	—	—	35.69	—	—
Fenazaquin	51.21	145.10	160.10	117.10	—	51.30	13.70	—
Fenpropathrin	51.34	97.10	181.00	265.00	125.10	86.46	46.01	43.09
Tebufenpyrad	51.43	318.10	171.00	276.10	145.00	77.14	40.65	24.17
Tetradifon	51.76	159.00	355.90	228.90	111.00	72.87	69.07	64.62
Phosalone	52.37	182.00	121.00	367.00	154.00	36.23	31.17	19.08
Fenarimol	53.47	139.00	219.00	107.00	251.00	73.60	65.48	64.23

Table 1. (*continued*)

Compound	RT, min	Ions monitored, *m/z*				Abundance ratio of qualifier ion/target ion		
		Target	Q1	Q2	Q3	Q1/tgt[a]	Q2/tgt	Q3/tgt
Cyhalothrin	53.71	181.00	197.00	208.00	141.00	80.32	55.73	19.18
Pyrazophos	54.06	221.10	373.10	265.10	193.00	27.16	11.55	9.76
Pyraclofos	54.29	360.00	194.00	139.00	97.00	56.11	40.90	26.20
Bitertanol	54.76	170.10	112.10	141.10	—	15.23	10.44	—
Pyridaben	55.02	147.20	117.10	309.00	364.10	17.83	14.83	13.94
Permethrin	55.14	183.10	163.00	91.10	127.00	32.22	8.46	7.97
Prochloraz	55.40	180.10	308.00	70.00	265.90	59.97	48.58	18.18
Cyfluthrin	56.09	163.00	206.00	226.00	91.10	71.54	63.51	23.23
Cypermethrin	56.56	163.00	181.10	209.10	91.10	87.85	29.26	23.67
Fenvalerate	57.92	167.10	125.00	225.10	419.10	94.29	59.11	45.68
Fluvalinate	58.33	250.10	181.10	208.00	—	17.18	8.17	—
Deltamethrin	59.47	252.90	181.00	209.10	77.10	92.50	26.94	22.59

[a] Q = Qualifier ion; tgt = target ion.

METHOD

To analyze large numbers of samples with a pesticide treatment history that is usually unknown, we use analytical methods that can simultaneously determine numerous pesticide residues. We developed MRMs that can determine ca 101 pesticides by GC–MSD. Table 1 lists the 101 pesticides determined by this MRM.

Reagents

(**a**) *Solvents*.—Acetonitrile, acetone, toluene; Riedel-de Haën Co. (Pardubice, Germany) and Wako Co. (Osaka, Japan); pesticide residue analysis grade (guaranteed purity by GC with electron capture detection after 300-fold concentration).

(**b**) *Purified water*.—Barnstead (Dubuque, IA).

(**c**) *Sodium chloride*.—Wako Co.

(**d**) *Sodium sulfate anhydrous*.—ACS grade Wako Pure Chemicals (Osaka, Japan).

(**e**) *Octadecyl (C_{18}) solid-phase extraction (SPE) cartridge*.—Sep Pak C_{18}, 6 mL (Waters Corp., Milford, MA).

(**f**) *Carbon SPE cartridge*.—Envi-Carb 6 mL, 500 mg (Supelco, Inc., Bellefonte, PA).

(**g**) *Filter*.—Disposable membrane disk; 0.25 μm, 25 mm, nylon Acrodisc (Gelman Sciences Inc., Ann Arbor, MI).

(**h**) *Helium*.—Ultrapure grade (Dongil Co., Seoul, Korea).

(**i**) *Analytical standards*.—Riedel-de Haën Co. and Wako Co. Individual stock standard solutions were prepared at concentrations of 20 000 ng/μL in acetone.

(**j**) *Spiking solutions*.—Mixed-compound solutions were freshly prepared daily from stock solutions at concentrations ranging from 40 to 80 ng/μL, according to their respective sensitivities.

Apparatus

(**a**) *Food chopper*.—Robot Coupe Blixer 5 (Robot Coupe USA Inc., Jackson, MS).

(**b**) *Homogenizer*.—Omni Macro Homogenizer Model 17505 (Omni International, Inc., Warrenton, VA).

(**c**) *Filter paper*.—Shark skin, 15 cm id (Schleicher & Schuell Inc., Keene, NH).

(**d**) *Jar*.—Glass, 1 pint (Mason).

(**e**) *Bottle*.—4 oz, glass, Corning No. 1367 (Corning, Inc., Corning, NY).

(**f**) *Graduated centrifuge tube*.—Glass, 15 mL.

(**g**) *Graduated cylinder*.—50 mL.

(**h**) *Autopipet*.—Eppendorf (Madison, WI).

(**i**) *Finntip*.—10 mL (Labsystems, Vantaa, Finland).

(**j**) *Rotary evaporator*.—With water bath set at 40°C in a well-ventilated hood.

Instrumentation

To confirm the identity of each pesticide residue, we used a Hewlett-Packard gas chromatograph HP 5973 MSD (equipped with HP6890 autosampler) system under the following conditions: splitless injection mode; injection volume, 2 μL; injector temperature, 250°C; carrier gas, helium. The flow was 0.9 mL/mm and controlled by constant flow mode. The oven temperature was programmed as follows: hold 2 min at 70°C; 70 to 130°C at 20°C/min; 130 to 220°C at 2°C/min; 220 to 280°C at 10°C/min; hold 8 min at 280°C. The analytical column was an HP-5 (5% phenyl methyl siloxane, 30 m × 250 μm × 0.25 μm). The workstation software was HP Chemstation (Rev. B.02.05).

The ion groups in each injection are listed in Table 2 along with their start and dwell times. Compounds were identified according to their retention times and ion ratios. Table 1 lists the compounds, their retention times, the target and qualifier

Table 2. Groups of ions for SIM acquisition

Group	Start time, min	Ions, *m/z*	Dwell time, ms
1	4.00	109, 185, 171, 136, 188, 129	23
2	10.20	127, 192, 109, 136, 94, 79, 194, 196, 198	23
3	13.29	156, 110, 79, 203, 215, 158, 97, 126, 276, 316, 55	23
4	18.10	169, 306, 264, 290, 75, 121, 127, 192, 67	20
5	19.81	206, 124, 176, 87, 125, 143, 54, 118, 76	23
6	21.90	231, 57, 153, 266, 109, 229, 88, 142, 179, 137	20
7	23.84	86, 268, 128, 292, 181, 153, 91, 204, 123	23
8	25.76	127, 264, 161, 217, 272, 100, 212, 198, 160, 188	23
9	28.00	206, 249, 241, 184, 198, 57, 226, 185	25
10	29.45	277, 125, 263, 66, 123, 167, 162, 238, 146	20
11	30.80	278, 125, 93, 197, 314, 258, 291, 139	25
12	31.52	57, 208, 85, 167, 72, 239	25
13	33.11	224, 210, 77, 318, 333, 304	40
14	33.75	252, 162, 248, 159, 79, 149, 137, 238	20
15	34.65	260, 104, 267, 323, 274, 125, 96, 283, 67	40
16	35.80	145, 85,125, 241, 195, 277, 278, 73, 206	23
17	37.02	222, 77, 207, 72, 128, 271, 79, 263, 277	23
18	38.54	303, 154, 208, 339, 162, 118, 215, 173	40
19	39.40	143, 235, 87, 175, 258, 302, 233, 206, 315	23
20	40.65	252, 361, 300, 222, 139, 125, 195, 237, 159	23
21	41.59	59, 247, 251, 139, 111, 293, 308, 141	25
22	42.90	231, 97, 153, 163, 105, 132	40
23	44.38	157, 342, 121, 272, 387, 229, 109, 173, 310	23
24	45.40	259, 173, 303, 145, 250, 125, 253, 340	23
25	48.67	160, 77, 341, 155, 157, 141, 227, 114, 195	23
26	50.92	181, 166, 145, 160, 97, 265, 318, 171, 276	25
27	51.62	341, 310, 173, 159, 356, 229, 182, 121, 367	40
28	53.00	139, 219, 107, 181, 197, 208, 221, 373, 265	23
29	54.17	360, 194, 139, 170, 112, 141, 183, 163, 91, 147, 117, 309	20
30	55.28	180, 308, 70, 266, 163, 206, 226	40
31	56.46	163, 181, 209, 91	95
32	57.32	167, 125, 225, 250, 181, 208	40
33	58.75	253, 209, 77	95

ions, and the abundance ratio of the first qualifier ion to the target ion. Quantification was based on the target ion.

Sample Preparation

The sample preparation, sample extraction, and cleanup procedure reported by Fillion et al. (3) were adapted for use in this MRM.

Prepare representative portion of sample by using a knife, and mix thoroughly with food chopper. Place 50 g aliquot (fresh weight) into 1 pint jar. To obtain sample for recovery test at 3 levels (0.1–1.0 mg/kg), add 1.0 mL spiking solution for each pesticide to 50 g known blank, and let stand for 15 min before extraction. Add 100 mL acetonitrile, and blend with homogenizer for 5 min. Add 10 g NaCl, and homogenize for another 5 min. Precondition C_{18} SPE cartridge with acetonitrile. Further condition tube by loading ca 2 mL acetonitrile extract (top layer) into C_{18} cartridge, elute, and discard eluate. Load ca 15 mL acetonitrile layer onto C_{18} cartridge, and elute by gravity into 15 mL centrifuge tube until collection volume reaches 13 mL. Add sodium sulfate to make the volume 15 mL. Cap tube and shake tube well. Centrifuge at 3000 rpm for 5 min. Transfer 10 mL aliquot (equiva-

Table 3. Recoveries (%) and LODs for pesticides determined by the MRM

Compound	*Chrysanthemum coronarium*	*Perilla japonica*, leaf	*Lactuca savita*	Mean ± SD, %[a]	LOD, mg/kg
Propamocarb	85.81	88.92	88.50	87.4 ± 13.3	0.17
Mevinphos	88.33	90.63	88.02	88.9 ± 4.3	0.04
Nitrapyrin	58.86	62.38	60.48	60.3 ± 5.1	0.17
Acephate	42.51	39.72	41.97	41.6 ± 14.4	0.39
Omethoate	69.14	52.82	74.38	66.1 ± 20.1	0.26
Tecnazene	66.04	61.75	63.08	64.1 ± 4.4	0.23
Ethoprophos	88.93	90.74	92.45	90.4 ± 5.1	0.02
Ethalfluralin	85.55	87.90	85.77	86.2 ± 5.4	0.01
Diphenylamine	93.60	88.08	91.14	91.4 ± 26.3	0.07
Trifluralin	70.60	81.52	76.04	75.1 ± 5.7	0.13
Phorate	62.25	75.96	70.22	68.2 ± 16.2	0.25
Monocrotophos	75.83	69.36	66.35	71.5 ± 9.3	0.24
Dicloran	82.69	81.08	79.89	81.5 ± 4.5	0.12
Dimethoate	96.42	97.02	96.25	96.5 ± 6.5	0.02
Dimethipin	98.07	98.81	99.92	98.8 ± 7.0	0.03
Terbufos	67.45	60.92	70.52	66.5 ± 5.3	0.19
Chlorothalonil	72.80	75.10	71.34	73.0 ± 12.3	0.25
Disulfoton	69.47	68.79	66.74	68.5 ± 7.9	0.17
Diazinon	86.84	87.37	85.50	86.6 ± 9.2	0.15
Tri-allate	74.74	75.44	70.32	73.7 ± 5.6	0.16
Etrimfos	84.63	89.36	87.43	86.7 ± 9.3	0.04
Iprobenfos	90.02	89.85	89.11	89.7 ± 5.4	0.02
Phosphamidon	82.95	82.69	85.43	83.6 ± 11.0	0.04
Propanil	91.20	89.49	88.18	89.9 ± 9.7	0.03
Heptachlor	69.19	67.54	65.46	67.7 ± 2.9	0.18
Vinclozolin	89.62	89.29	91.60	90.1 ± 3.1	0.02
Alachlor	93.30	98.10	99.01	96.2 ± 6.9	0.02
Metalaxyl	94.34	93.93	94.26	94.2 ± 4.7	0.02
Prometryn	97.66	95.24	99.49	97.5 ± 6.7	0.02
Metribuzin	85.56	82.89	78.40	82.9 ± 11.3	0.03
Terbutryn	107.67	107.83	115.58	109.9 ± 27.9	0.07
Fenitrothion	90.40	92.75	92.49	91.6 ± 5.8	0.02
Aldrin	95.63	95.35	93.95	95.1 ± 7.3	0.01
Dichlofluanid	66.91	74.19	77.33	71.7 ± 7.9	0.25
Metolachlor	99.87	105.72	109.46	104.1 ± 14.9	0.06
Fenthion	89.28	91.38	88.98	89.8 ± 7.4	0.05
Chlorpyrifos	86.30	88.26	88.62	87.5 ± 5.6	0.03
Parathion	96.78	97.45	105.73	99.4 ± 8.3	0.02
Triadimefon	96.55	106.19	103.00	100.9 ± 9.9	0.04
Diphenamid	99.13	102.53	97.76	99.7 ± 6.2	0.03
Cyprodinil	76.38	79.24	73.61	76.4 ± 8.5	0.15
Pirimiphos-ethyl	109.25	95.88	100.12	103.1 ± 8.0	0.02
Pendimethalin	97.80	90.42	101.31	96.7 ± 12.0	0.03
Penconazole	93.92	95.14	92.26	93.8 ± 7.7	0.02
Captan	77.47	86.90	79.65	80.6 ± 14.6	0.14
Tolyfluanid	80.47	75.98	74.49	77.6 ± 7.2	0.16

Table 3. (*continued*)

Compound	*Chrysanthemum coronarium*	*Perilla japonica*, leaf	*Lactuca savita*	Mean ± SD, %[a]	LOD, mg/kg
Folpet	48.45	39.17	60.83	49.3 ± 10.0	0.39
Chlorfenvinphos	86.52	91.50	83.00	86.9 ± 16.5	0.04
Phenthoate	84.49	84.30	79.07	83.0 ± 3.7	0.05
Procymidone	92.76	93.67	92.32	92.9 ± 7.1	0.02
Methidathion	86.65	88.48	85.95	87.0 ± 9.3	0.04
α-Endosulfan	87.60	92.82	95.88	91.3 ± 5.5	0.02
Triflumizole	98.46	100.77	98.97	99.2 ± 8.4	0.02
Mepanipyrim	87.13	91.87	84.43	87.7 ± 14.1	0.14
Napropamide	91.86	89.84	87.29	90.1 ± 4.9	0.02
Dieldrin	86.02	89.81	84.28	86.6 ± 5.7	0.03
Fenamiphos	75.96	77.37	73.40	75.6 ± 9.8	0.16
Profenofos	80.72	78.21	75.57	78.6 ± 5.2	0.15
Isoprothiolane	84.97	82.50	78.91	82.6 ± 8.1	0.06
Imazalil	85.80	84.53	83.66	84.9 ± 3.3	0.03
Carboxin	77.94	80.95	76.97	78.5 ± 9.0	0.17
Oxadiazon	86.63	85.15	85.74	86.0 ± 7.7	0.09
Flusilazole	84.77	89.58	92.52	88.2 ± 7.4	0.08
Oxyfluorfen	81.75	88.47	87.64	85.2 ± 5.7	0.06
Cyproconazole	96.16	95.82	98.32	96.7 ± 4.6	0.01
β-Endosulfan	93.68	96.67	95.95	95.1 ± 7.6	0.02
Chlorfenapyr	86.86	89.80	90.60	88.7 ± 8.0	0.14
Chlorobenzilate	89.12	82.63	82.77	85.6 ± 6.7	0.14
Fensulfothion	91.83	94.88	89.43	92.0 ± 9.8	0.03
Ethion	84.39	81.37	78.37	81.9 ± 7.2	0.09
Oxadixyl	94.11	95.37	93.82	94.4 ± 4.5	0.02
Carbophenothion	69.65	69.02	82.88	73.1 ± 10.4	0.16
Endosulfan sulfate	88.30	91.03	88.83	89.2 ± 4.1	0.06
Edifenphos	91.81	88.32	90.35	90.5 ± 6.3	0.02
Propiconazole	80.49	75.36	87.05	80.9 ± 9.6	0.13
Norflurazon	88.76	88.49	86.08	88.0 ± 3.9	0.04
Tebuconazole	94.18	97.77	99.06	96.5 ± 4.6	0.02
Diclofop-methyl	96.28	97.00	98.34	97.0 ± 3.9	0.01
Phosmet	80.67	79.67	84.69	81.5 ± 5.8	0.14
Bromopropylate	73.86	67.73	62.23	69.0 ± 6.1	0.27
EPN	86.54	84.50	86.15	85.9 ± 4.5	0.15
Methoxychlor	87.81	87.53	85.67	87.1 ± 4.5	0.14
Bifenthrin	82.80	79.60	89.85	83.9 ± 11.7	0.16
Fenazaquin	70.31	75.86	72.80	72.5 ± 6.8	0.26
Fenpropathrin	80.13	76.43	77.27	78.3 ± 3.9	0.09
Tebufenpyrad	97.38	93.71	98.38	96.7 ± 4.5	0.02
Tetradifon	94.52	90.36	99.94	94.9 ± 5.8	0.02
Phosalone	92.48	100.06	99.94	96.6 ± 4.6	0.01
Fenarimol	94.50	95.25	92.17	94.1 ± 3.0	0.01
Cyhalothrin	98.08	96.81	96.56	97.3 ± 3.6	0.01
Pyrazophos	70.58	68.61	72.66	70.6 ± 15.0	0.27
Pyraclofos	86.82	89.34	82.81	86.4 ± 4.7	0.09

Table 3. (*continued*)

Compound	*Chrysanthemum coronarium*	*Perilla japonica*, leaf	*Lactuca savita*	Mean ± SD, %[a]	LOD, mg/kg
Bitertanol	93.83	95.53	96.86	95.1 ± 4.3	0.02
Pyridaben	100.20	98.43	139.40	110.4 ± 22.7	0.04
Permethrin	100.41	98.71	132.72	108.8 ± 19.2	0.03
Prochloraz	75.71	76.81	73.45	75.4 ± 6.2	0.27
Cyfluthrin	85.25	87.36	88.06	86.6 ± 4.5	0.05
Cypermethrin	83.21	88.10	83.22	84.5 ± 8.6	0.06
Fenvalerate	93.24	96.15	98.42	95.4 ± 5.1	0.02
Fluvalinate	66.69	75.06	79.67	72.5 ± 7.9	0.17
Deltamethrin	67.80	80.33	71.93	72.3 ± 9.6	0.18

[a] SD = Standard deviation; $n = 7$.

lent to 5 g sample) to second 15 mL centrifuge tube. Evaporate extract to 0.5 mL. Precondition carbon SPE cartridge with acetonitrile–toluene (3 + 1). Resuspend and transfer extract to cartridge with acetonitrile–toluene (3 + 1), and elute with 15 mL acetonitrile–toluene (3 + 1). Collect eluate in third 15 mL centrifuge tube. Evaporate elute to small volume with rotary evaporator. Add two 10 mL portions of acetone, and evaporate to <2.0 mL with gentle stream of air. Dilute the extract to 2 mL with acetone, and transfer to vial for GC–MSD analysis. The concentration of the sample represented by the extract is 2.5 g/mL.

Validation and Quantification

Calculate results in parts per million (ppm, mg/kg). The final extract used in the GC–MSD analyses represents 2.5 mg/kg of sample per 1 μL injection. All validation procedures were performed by using pesticide-free crops.

Recovery was determined for 7 replicate at 3 concentration levels (0.1, 0.5, and 1.0 mg/kg) by comparing the peak areas of analytes and corresponding standard peaks.

A least-squares linear regression line based on a minimum of 5 external standard calibration solutions was used for quantification: 0.05, 0.1, 0.5, 1.0, and 2.0 ng/μL. Quantification was based on the abundance of each ion monitored by GC–MSD. Pesticides having isomers were calculated based on major peak. Repeated injections were treated as the same sample and were averaged to generate the arithmetic average and the standard deviation.

The limit of detection (LOD) was determined as the lowest concentration giving a response of 3 times the average of the baseline noise from 3 nonfortified samples. For each analyte in each sample, the LOD was estimated as follows:

$$\mathrm{LOD} = \frac{\mathrm{CAL}_{\min} \times \upsilon}{\mathrm{W}} \times \frac{1}{\mathrm{R}}$$

where LOD is the limit of detection in mg/kg, υ is the final volume of the extract in mL, W is the sample weight in g, R is the average recovery obtained for a minimum of 3 laboratory-fortified replicates with a relative standard deviation of ≤15, and $\mathrm{Cal}_{\min}$ is the minimum standard concentration detectable by the analytical instrument as a peak. To determine $\mathrm{Cal}_{\min}$, extracts of nonfortified subsamples of each commodity (referred to as blanks in this study) were analyzed. Around each retention time of interest, signals below a certain response were considered noise, and the average noise was calculated manually. To qualify as a peak, a signal's response had to be ≥3 times the average noise.

Results and Discussion

MRMs need to cover a variety of pesticides and produce sensitive and accurate performance for effective regulation. GC has proved to be an effective and selective major analytical technique for monitoring pesticide residues in agricultural foods, because of its high separation power and the presence of GC-amenable pesticides in a wide variety of samples. The mass selective detector offers several advantages over specific detectors. GC–MSD provides universality and specificity in analysis and confirmation of the identities of positive analytes, and the number of injections required for analysis and the need for confirmation by a second injection are reduced.

The MRM in this study allows the analysis for 101 pesticides, including organophosphorus, organochlorine, and nitrogen-containing pesticides, in crops by GC–MSD. Analysis was performed in the SIM mode, which demonstrated an acceptable selectivity for most of the analyzed pesticides spiked onto *Chrysanthemum coronarium*; *Perilla japonica*, leaf; and *Lactuca savita*.

Chromatograms obtained in the SIM mode for nonfortified *C. coronarium* were compared with those obtained in the scan mode. The background obtained in the SIM mode was very low, and the extracts did not interfere with the standard fortification operation. Analysis of 3 blank samples (*C. coronarium*; *P. japonica*, leaf; and *L. savita*) revealed no trace of the pesticides studied.

Table 3 lists the recoveries of the pesticides added to *C. coronarium*; *P. japonica*, leaf; and *L. savita*, which are very popular vegetables eaten raw in Korea. The recoveries used to generate LOD of the method were obtained by spiking 3 different crops at 0.1, 0.5, and 1.0 mg/kg. There was no significant difference in the recoveries for the 3 spiking levels. Recoveries of 90% of the pesticides were between 70 and 110%, whereas acephate and folpet gave very poor recoveries of <50%. The greater water solubility of acephate in the extraction process caused its low recovery; the low recoveries of other polar compounds, such as omethoate and monocrotophos, were also due to this greater water solubility. On the other hand, enzyme degradation also certainly contributed to the lower recoveries of captan, dichlofluanid, and chlorothalonil, as well as folpet. On the other hand, some compounds showed quite different recoveries, depending on the matrix. The recoveries of omethoate, folpet, carbophenothion, pyridaben, and permethrin from *L. savita* were relatively high.

The LOD is defined as 3 times the standard deviation of a minimum 7 replicate analyses of samples fortified at 3 times the estimated LOD. The LODs for most compounds range between 0.02 and 0.3 mg/kg, and about half of the compounds studied have LODs of <0.05 mg/kg.

The present method, developed for the simultaneous determination of 101 pesticides in crops involves a rapid and nonselective extraction procedure and a specific GC–MSD determination with satisfactory recoveries and LODs. Routine use demonstrated that this method is suitable for the analysis of crops for residual amounts of pesticides.

The MRM described in this study has shown suitable sensitivity for monitoring a wide range of pesticide residues in agricultural products. This method also has demonstrated the sensitivity and accuracy needed for analysis of a large number of samples in a regulatory laboratory.

References

(1) Luke, M.A., Frodberg, J.E., Doose, G.M., & Masumoto, H.T. (1981) *J. Assoc. Off. Anal. Chem.* **64**, 1187–1195

(2) Lee, S.M., Papathakis, M.L., Feng, H.-M.C., Hunter, G.F., & Carr, J.E. (1991) *Fresenius Z. Anal. Chem.* **339**, 376–383

(3) Fillion, J., Sauve, F., & Selwyn, J. (2000) *J. AOAC Int*. **83**, 698–713

(4) Fillion, J., Hindle, R., Ladroix, M., & Selwyn, J. (1995) *J. AOAC Int*. **78**, 1252–1266

(5) Liao, W., Joe, T., & Cusick, W.G. (1991) *J. AOAC Int.* **74**, 554–565

(6) Lehotay, S.J., & Eller, K.I. (1995) *J. AOAC Int.* **78**, 821–830

(7) Kawasaki, M., Fukuhara, K., & Uchiyama, S. (1994) *J. Food Hyg. Soc. Jpn.* **35**, 479–496

(8) Colume, A., Cardenas, S., Gallego, M., & Valcarcel, M. (2001) *J. Agric. Food Chem.* **49**, 1109–1116

(9) Adou, K., Bontoyan, W.R., & Sweeney, P.J. (2001) *J. Agric. Food Chem.* **49**, 4153–4160

(10) Lacassie, E., Dreyfuss, M.F., Daguet, J.L., Vignaud, M., Marquet, P., & Lachatre, G. (1998) *J. Chromatogr. A* **805**, 319–326

(11) Cheng, C.L., Shin, S.J., Yen, G.C., Chou, S.S., & Liu, C.H. (1994) *J. Food Drug Anal.* **2**, 113–122

(12) Cho, T.H., Kang, H.G., Kim, B.S., Kim, I.Y., Shin, K.Y., Lee, J.H., Park, J.S., Hong, M.S., Kim, S.D., Hong, I.S., Chang, M.S., Jung, S.Y., Cho, S.J., Lee, E.S., Cho, S.A., Park, A.S. (2000) *Report of S.I.H.E.* **36**, 157–165