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An Improved Method for Multiresidue Analysis of Pesticides in Lettuce, Chinese Cabbage and Green Pepper by Gas Chromatography

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ABSTRACT : For the improvement of gas chromatographic analysis of multiple pesticide residues in green pepper, lettuce and Chinese cabbage, multiresidue test mixtures (MRTMs) of 10 groups (ECD 5 groups and NPD 5 groups) and a recovery test mixture (RTM) of 18 compounds (11 compounds for ECD and 7 compounds for NPD) were established based on retention time and response to relevant detectors. A new extraction solvent (acetone : acetonitrile=1 : 9) and a clean up eluent (hexane : dichloromethane : acetonitile = 50 : 48.5 : 1.5) for solid-phase extraction (SPE) cartridge were selected to test two types of multiresidue methods (MRM I and MRM II). MRM II provided high recovery better than MRM I when RTM was tested. Recovery experiment with MRTMs which was conducted using MRM II resulted in that more than seventy percents of compounds were recovered in the range of 50~140%, while 9% of compounds were over 140% of recovery and only 7~8 compounds failed to detect. MRM II, an improved method, could be employed for screening residues of 190 pesticides in those vegetables.

Key words: pesticide, residue, analysis, green pepper, lettuce, Chinese cabbage.

INTRODUCTION

Pesticides are necessary and essential to maintain steady agricultural production. With their use, however, the risk of residues remaining on the consumed food has been suspected. For this reason, a number of methods have been developed and applied routinely for management of the pesticide residue in food[1,2].

Multiresidue method (MRM) development is difficult in the aspect that diverse compounds of different polarities, solubilities, volatilities and pK_a values have to be simultaneously extracted and analyzed. Several MRMs for determination of organophosphorus, organochlorine and organonitrogen pesticides in crops using gas-liquid chromatography (GLC) for separation of individual compounds followed by detection with selective and sensitive detectors (ECD, NPD, FPD, or MSD) have been proposed[1] .

A GLC method that employed of combination of different column and different detectors for testing residues of over 150 pesticides was proposed by Sicbaldi *et al.*[3], and the determination of 251 pesticides in fruits and vegetables using GLC-MSD, and HPLC with fluorescence detection was reported[4]. MRMs are commonly used by governmental organizations to surveil and monitor what kinds of pesticides are detected and how much residues are present. Subsidiary laboratories of U.S. Food and Drug Administration (FDA), the California Department of Food and Agriculture (CDFA), and the Florida Department of Agriculture and Consumer Services have routinely employed multiresidue methods utilizing either GC, HPLC or GC/MS in the determinative step[5]. In Korea, Korea Food and Drug Administration (KFDA), National Institute of Health & Environment (NIHE) and National Agricultural Products Quality

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Management Service (NAQS), have been carried out multiresidue analysis of pesticides in raw agriculture commodities (RACs).

KFDA employs a MRM for 162 pesticides by GLC while 119 pesticides are analyzed by NAQS. KFDA mainly adopted CDFA method, and NAQS method is based on PAM 302 method with some modification[6].

The purpose of the present work is to develop an improved multiresidue GLC method suitable for screening the greater number of pesticides than those investigated so far in Korea because the numbers of pesticides and RACs have been increased since those methods were established. Through the study, a new set of recovery test mixture (RTM) and 10 groups of multiresidue test mixtures (MRTMs) were established with 199 pesticides. For practical application recoveries of those pesticides in three kinds of vegetables (green pepper, lettuce, Chinese cabbage) were investigated.

MATERIALS AND METHODS

Reagents and crop samples

Total of 199 pesticide standards were purchased from commercial companies (Wako Pure Chemical and Merck), or kindly provided from institutes having stocks of certified grade.

Acetone, acetonitrile, n-hexane and dichloromethane were HPLC grade and purchased from Duksan chemical (Korea). Sodium chloride and sodium sulfate were purchased from Junsei Chemical (Japan). SPE cartridge (Florisil, 1.0 g) was from Supelco (USA). Filter papers (No. 41) were from Whatman International (UK). Green pepper, Chinese cabbage and lettuce which were certified as "residue-free" (*i.e.* no pesticide applied or the residue is present below the detection) were purchased from a local market.

Each pure standard was dissolved in acetone to prepare a concentrated stock solution of 1000 mg/L before diluting to 10 mg/L with acetone.

GLC analysis

The GC system was Agilent model 6890 (USA) equipped with a dual detector [ECD (electron-capture detector) and NPD (nitrogen-phosphorus detectors)]. GLC was set up with a fused silica capillary column (DB-5, 0.25 mm ID × 30 mm, 0.25 μm, J&W Scientific). Injector and detector temperature were 260℃ and 280℃ respectively, and carrier gas (N_2) flow rate was 1.0 mL/min. Inlet mode was splitless (purge time 1.0 min) for NPD and split (50 : 1) for ECD. The column temperature was programmed as follows; at 80℃ for 2 min, increased to 280℃ by 10℃/min, and held for 10 min.

Preparation of recovery test mixture (RTM) and multiresidue test mixtures (MRTMs)

Pesticides were divided into 10 groups (ECD 5 groups and NPD 5 groups) for MRTMs based on retention time and response to detector (Fig. 1). RTM (50 ppm) of 18 compounds (11 compounds for ECD and 7 compounds for NPD) was prepared based on the chemical class, Log P, and responding detector (Table 1)[7].

Table 1. Recovery test mixture of pesticides

Compound	Group	Detector	Log P
Esfenvalerate	Pyrethroid	ECD	6.22
Benfluralin	2,6-dinitroaniline	ECD	5.29
beta-Endosulfan	cyclodiene organochlorine	ECD	4.79
Chlorpyrifos	Organophosphate	ECD	4.7
Bitertanol	Azole	NPD	4.1, 4.4 (Isomer)
Oxyfluorfen	diphenyl ether	ECD	4.47
Pretilachlor	Chloroacetanilide	ECD	4.08
Tolylfluanid	Sulfamide	ECD	3.9
Fenitrothion	Organophosphate	ECD	3.5
Napropamide	Alkanamide	NPD	3.3
Fenothiocarb	Carbamate	NPD	3.28
Terbuthylazine	1,3,5-triazine	NPD	3.21
Nuarimol	pyrimidinyl carbinol	ECD	3.18
Vinclozolin	Dicarboximide	ECD	3.0
Molinate	Thiocarbamate	NPD	2.88
Metobromuron	Urea	ECD	2.41
Metalaxyl	Phenylamide	NPD	1.75
Acephate	Organophosphate	NPD	-0.89

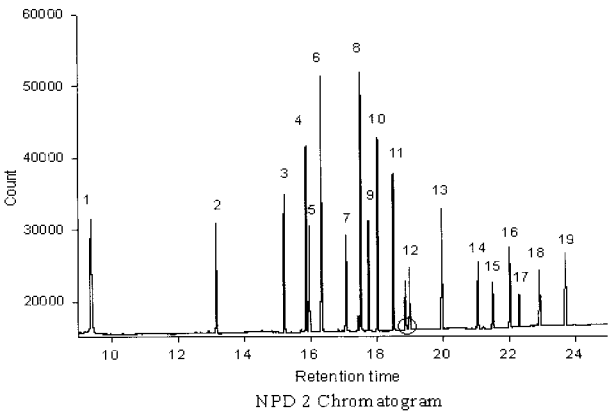

Fig. 1. Gas chromatogram of NPD group 2.
1, Trichlorfon; 2, Isoprocarb; 3, Thiomefon; 4, Terbufos; 5, Pyroquilon; 6, Isazofos; 7, Chlorpyrifos-methyl; 8, Terbutryn; 9, Malathion; 10, Parathion; 11, Cyprodinil; 12, Triadimenol; 13, Buprofezin; 14, Carbophenothion; 15, Terbuconazole; 16, Pyridaphenthion; 17, Etoxazole; 18, Azinphos-Methyl; 19, Pyraclofos.

Selection of extraction solvent

RTM (1 mL, 50 ppm) was added to water (50 mL) and extracted with various extraction solvents (Table 2) and filtered. Sodium chloride (10 g) was added to filtrates and allowed to stand for 1 hr. The upper phase (20 mL) was concentrated by rotary evaporator at 40℃ to dryness. Then the residue was dissolved in 20% acetone/hexane (2 mL), before an aliquot (1 μL) was analyzed with GC-ECD or NPD.

Modification of SPE clean up method

SPE cartridge containing Florisil (1.0 g) was pre-washed with hexane (5 mL) and washed with 20% acetone in hexane (5 mL). Then RTM (100 μL) was loaded and eluted with CLE-1 (20% acetone in hexane, 5 mL) or CLE-2 (hexane : dichloromethane : acetonitrile = 50 : 48.5 : 1.5, 5 mL) or CLE-3 (hexane : dichloromethane : acetonitrile = 50 : 45 : 5, 5 mL). Each eluent was collected and evaporated with gentle stream of N_2. The residue was dissolved in hexane (2 mL) before GLC-ECD or GLC/NPD analysis.

Evaluation of MRM I and MRM II with vegetables using RTM

MRM I ; RTM (1 mL, 50 ppm) was added to vegetables (50 g), blended with extraction solvent B (acetone : acetonitrile = 1 : 9) and extraction was followed as described above to obtain residue solution (2 mL) in 20% acetone/hexane. SPE cartridge clean up with CLE-1 and analysis with GLC-ECD or GLC/NPD were followed after loading of residue solution.

MRM II ; RTM (500 μL, 50 ppm) was added to vegetables (25 g) and the extraction was followed as described above except the 10 mL of upper phase of filtrate and CLE-2 (5 mL) were used as elution solvent.

Recovery test with MRTMs in vegetables using MRM II

MRTMs (500 μL, 50 ppm) were spiked on vegetable samples (25 g), and then each sample was extracted and analyzed using MRM II.

Table 2. Solvent mixtures for extraction efficiency tests of pesticides from agricultural products

Solvent System	Extraction solvent ratio	
	Acetone	Acetonitrile
A	0	100
B	10	90
C	30	70
D	50	50
E	70	30
F	90	10
G	100	0

RESULTS AND DISCUSSION

Establishment of standard analytical condition

GC analytical conditions of Food Code (2002)[8] and other methods were tried and GC condition of Food Code (2002) was chosen as a standard GC condition because it has shorter analysis time than the other methods.

Selection of backbone MRM

MRMs of KFDA and NAQS have their characteristics in sample preparation and clean up procedure (Fig. 2). MRM of NAQS uses less amount of sample, partitioning and glass column clean up procedures to give a chromatogram of less impurity peaks. MRM of KFDA also has few advantages such as shorter sample preparation and clean up time by using salting out procedure and SPE cartridge. In this study, MRM of KFDA was chosen as a backbone procedure because of shorter analytical time, which is one of important factors for a screening purpose.

Preparation of RTM

Compound classifications based on chemical structure, Log P, molecular weight, detector and solubility have been useful in defining analytical strategies[7,9]. Among them, Log P plays an important role in classifying of compounds depending on polarity and solubility and it is a useful distribution constant in pesticide chemistry, underlying calculations of bioconcentrations, structure-activity relationships, and the choice of solvent condition for extraction. Partition

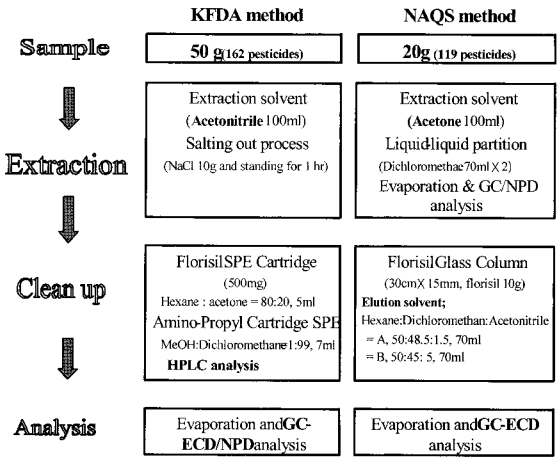

Fig. 2. Comparison of MRMs adopted by KFDA and NAQS.

coefficient compilations for a variety of organic compounds are available in the literature[10].

To select RTM, Log P of the subject pesticides was divided into three levels; log P >3, 1~3, and <1. Number of compounds of log P >3 was 124, those of log P 1~3 was 32, and 9 compounds have log P <1. Considering of the number of compound in three different Log P levels, 16 compounds were selected from various chemical classes. Two organophosphorus compounds (OPs) were added in the list because they belong to the biggest chemical class. As a result, RTM of total 18 compounds (11 compounds for ECD and 7 compounds for NPD) was established (Table 1).

Establishment of sample preparation method using RTM

Selection of extraction solvent

In the preparation of a sample for analysis, it is common practice to first extract the analyte away from the bulk of the matrix material and then to remove potentially interfering coextractives that will inevitably be present in the extract, by one or more clean up steps. The strategy in choosing the proper extraction, clean up condition, and methods for separate determination involved taking advantage of unique physical and chemical properties of the analyte that will allow it to stand out from the bulk of substances that occur in the matrix that could interfere in the determination step by responding to the detection system employed[10].

For the initial multiresidue analysis, acetonitrile was used as the extraction solvent. Use of acetonitrile as an extracting solvent was extended to cover organochlorine as well as organophosphorus residue for a number of high moisture-low fat products. The resulting multiresidue procedure eliminated the need for multiple extractions to completely extract the residues by including a recovery factor based on the volume of acetonitrile used in the extraction plus the moisture content of the product[11].

Acetonitrile has two significant advantages over other solvents in trace pesticide residue analysis. One advantage is that acetonitrile exhibits a very strong dissolving ability and is readily miscible with water. The other advantage of acetonitrile solution can be separated from water by a simple salting out procedure. A two phase azeotrope of acetonitrile and hexane can easily be concentrated and has a boiling point of 52℃. Thus the sample concentration is relatively simpler in this case than with an aqueous alcohol or aqueous acetone solution[12]. However, the disadvantages of acetonitrile were its high price and toxicology.

Luke *et al.*[12] used acetone instead of acetonitrile as extraction solvent in multiresidual method and it has bec- ome a major extraction solvent. Acetone is more volatile than acetonitrile and easier to concentrate and remove than acetonitrile. Acetone has been used in a Swedish study monitoring pesticide residues since 1981.

Therefore, acetonitrile was selected as primary extraction solvent based on the advantages of acetonitrile described above. And then acetonotrile was modified with acetone by various proportion to find out better extraction solvent system for recovery of RTM (Table 2).

From RTM, acephate and bitertanol were not recovered by any solvent system. Recoveries of chlorpyrifos, matalaxyl, benfluralin, terbutylazine, vinclozolin, fenitrothion, tolyfluanid and beta-endosulfan decreased with the increase of acetone when it was above 10%. Molinate was recovered only by solvent system B. From the overall results (Fig. 3), solvent system B (acetone : acetonitrile = 1 : 9) was selected as extraction solvent in this study because about 80% of recovery was obtained for most of the compounds.

Modification of SPE clean up method

Whichever technique is used for extraction, various components with a high molecular size such as lipids, pigments and resins are always present and need to be eliminated to permit a more definitive identification of lower limit residues and to minimize adverse on the detection instruments. Although some MRMs (multiresidue methods) eliminate the clean up step, most do not. Many clean up procedures employ fractionation of extracts based on polarity, as in liquid-liquid partitioning (LLP), column chromatography (CC),

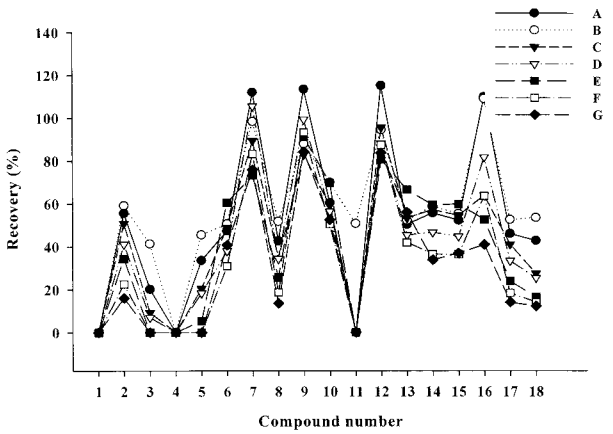

Fig. 3. Extraction efficiency of a various solvent systems (A~G).
1, Acephate; 2, β-Endosulfan; 3, Benfluralin; 4, Bitertanol; 5, Chlorpyrifos; 6, Esfenvalerate; 7, Fenithiocarb; 8, Fenitrothion; 9, Metalaxyl; 10, Metobromuron; 11, Molinate; 12, Napropamid; 13, Nuarimol; 14, Oxyfluofen; 15, Pretilachlor; 16, Terbutylazine; 17, Tolyfluanid; 18, Vinclozolin.

or adsorption chromatography using either florisil, neutral alumina or silica gel column, gel permeation chromatography (GPC), steam distillation, or low temperature precipitation. LLP is a very commonly used method, and hydrophobic analyte is extracted into a non polar solvent. However, the major drawbacks of LLP were: it is sub-optimal for oily crops, which require additional sample clean up; the low sample throughput due to manual concentration steps; and the large amounts of organic solvents used; resulting in a large volume waste[13]. This method is laborious, time-consuming, evaporation of large solvent volumes, and the disposal of toxic solvents. Recent regulations pertaining to the use of organic solvents have made LLP techniques unacceptable[14]. And, at present, the use of dichloromethane is being avoided because the solvent is known to be carcinogenic[12]. The column chromatography is less environment-friendly and efficient work than SPE cartridges because the clean up method uses to large solvent, time and labor[5].

The use of adsorption chromatography for clean up of samples using alumina, silica gel and Florisil in different mesh size, levels of activity and column sizes, either separately or in a combination, to reduce sample handling and analysis time is well established. Florisil is most popular sorbent employed today, and is particularly suited for fatty foods. Florisil SPE cartridges had been used to clean up OCP residues in fat, environmental samples, and agricultural crops[14].

For very polar residues, non-specific hydrophobic sorbents such as charcoal or graphitized carbon black (GCB) are used[13].

The ideal sample preparation methodology is fast, accurate, precise, and consumes little solvent[15]. Furthermore, it is easily adapted for field work, and requires less costly materials. Therefore, LLP and column clean up procedure was discarded in this study to save time and solvent and SPE (florisil) was adapted because the SPE method may be the isolation technique that is capable of meeting all these expectations[14].

However, two clean up eluents (CLE-2 and CLE-3) of glass column method[16] were used in addition to CLE-1[8] to evaluate better elution solvent for SPE cartridge. In SPE clean up procedure, three compounds (acephate, metalaxyl and bitertanol) were not eluted by all eluents while recoveries of 15 compounds were > 80% with CLE-1 and CLE-2 (Fig. 4). After careful comparison of their results, CLE-2 selected as elution solvent for SPE because it gave better recovery than the others.

Evaluation of MRM I and MRM II with vegetables using RTM

MRM I is mainly based on KFDA method except a new extraction solvent system B, SPE cartridge (1.0 g) clean up procedure was carried out with CLE-1 eluent, keeping the amount of sample by 50 g. However, MRM II used a half of the sample amount of MRM I, and volume of acetonitrile

Table 3. Number of RTM pesticides recovered by MRM I or MRM II

Recovery rate	Green pepper		Lettuce		Chinese cabbage	
	MRM I	MRM II	MRM I	MRM II	MRM I	MRM II
ND[a]	1	1	3	2	2	3
< 50%	1	4	2	3	1	3
50~140%	11	12	6	12	9	9
> 140%	5	1	7	1	6	3

[a] Not detected

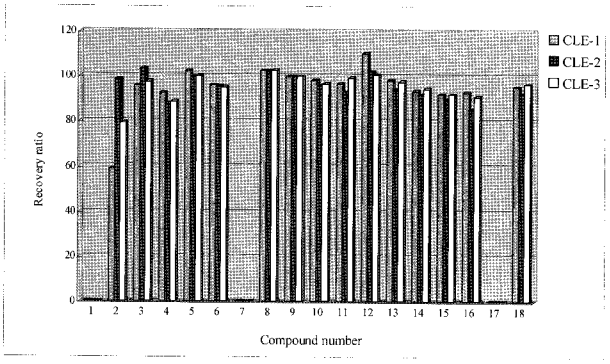

Fig. 4. Recovery of RTM from SPE clean up with CLE-1,-2 and -3. 1, Acephate; 2, Molinate; 3, Benfluralin; 4, Terbutylazine; 5, Metobromuron; 6, Vinclozolin; 7 , Metalaxyl; 8, Fenitrothion; 9, Chlorpyrifos; 10, Tolyfluanid; 11, Fenithiocarb; 12, Napropamid; 13, Pretilachlor; 14, Oxyfluofen; 15, beta-Endosulfan; 16, Nuarimol; 17, Bitertanol; 18, Esfenvalerate.

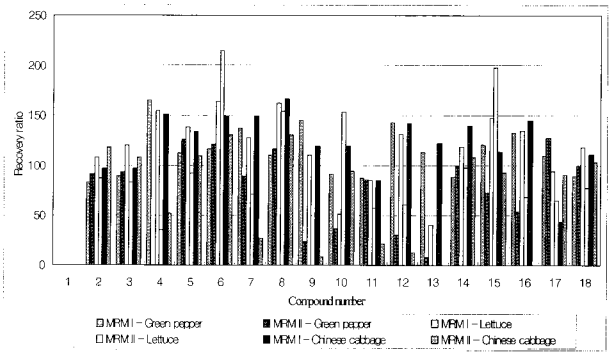

Fig. 5. Recovery of RTM in vegetables samples by MRM I and II. 1, Acephate; 2, β-Endosulfan ;3, Benfluralin; 4, Bitertanol; 5, Chlorpyrifos; 6, Esfenvalerate; 7, Fenitrocarb; 8, Fenitrothion; 9, Matalaxyl; 10, Metobromuron; 11, Molinate; 12, Napropamid; 13, Nuarimol; 14, Oxyflufen; 15, Pretilachlor; 16, Terbuthylazine; 17, Tolyfluanid; 18, Vinclozolin.

extract for evaporation was also reduced to a half of that of MRM I for reducing of analytical time, and CLE-2 for clean up. By the MRM II, 9~12 compounds (benfluralin, vinclozolin, napropamid etc) were recovered by 50~140% while 6~11 compounds were recovered by MRM I (Table 3 and Fig. 5). Small number of compounds (1~3) were not detected by both of the methods. Acephate was not detected in all vegetables, and bitertanol was detected only in green pepper. MRM I gave less number (1~2) of low recovery (< 50%) than MRM II (3~4), however, much higher number (5~7) of excess recovery (>140%) was observed by MRM I than MRM II (1~3). In overall considering, MRM II gave better results than MRM I. Therefore, recovery test with MRTMs was conducted using MRM II.

Comparing with the conventional methods, MRM II was improved in various aspects. For example, sample amount (50 g) was reduced to 25 g and acetone was added in extraction solvent (acetonitrile) for better recovery. Analytical time was reduced by evaporation of 10 mL of extract and SPE elution solvent was improved by combination of hexane, acetonitrile and dichloromethane.

Recovery test of MRTMs in vegetables using MRM II (Table 4 and Fig. 6)

Imibenconazole in ECD group 5 was removed from analysis because it had relatively longer retention time, and

Table 4. MRL, recovery, LOD and RT of pesticides from vegetable samples

Compound	Green pepper		Lettuce		Chinese cabbage		LOD[c]	RT[d]	Detector & group
	MRL[a]	Recovery[b]	MRL[a]	Recovery[b]	MRL[a]	Recovery[b]			
alpha-BHC		101.2±10.9		109.2±1.9	0.20	64.4±4.0	0.10	16.4	ECD 3
Acephate	4.00	ND[e]	5.00	ND	5.00	ND		10.5	RE-NPD
Acetochlor		112.2±2.96		161.8±4.4		101.9±1.8	0.10	18.4	ECD 3
Acrinathrin		114.0±7.6		160.9±5.2		131.6±9.2	0.04	24.6	ECD 4
alpha-Endorsulfan	1.00	114.2±2.8	1.00	117.0±6.1	2.00	119.8±9.0	0.10	21.3	ECD 2
Alachlor	0.20	98.4±5.4		98.8±5.2		96.6±3.8	0.10	18.7	ECD 1
Aldrin	0.01	83.9±3.8	0.01	91.7±3.1	0.01	76.1±0.7	0.10	19.6	ECD 3
Alpha-cypermathrin		236.0±15.1		147.2±22.7		194.1±10.9	0.05	27.6	ECD 3
Amitraz		13.7±13.2		13.3±3.1		2.85±4.6	0.10	22.9	NPD 3
Anilazine		79.3±16.73		58.7±6.5		82.4±8.0	0.10	20.5	ECD 2
Anilofos		74.7±1.2		152.3±7.9		104.4±1.24	0.10	25.1	ECD 2
Azinophos-methyl	0.30	72.1±3.6		95.2±0.9	0.20	94.5±5.9	0.10	22.7	NPD 2
beta-BHC	0.20	71.2±3.4	0.20	82.0±5.1	0.20	53.9±7.1	0.10	17.0	ECD 3
beta-endosulfan	1.00	82.8±8.5	1.00	108.5±11.3	2.00	97.2±2.2	0.10	22.5	RE-ECD
Benfluralin		89.6±13.9		119.8±21.4		97.2±5.5	0.10	15.9	RE-ECD
Benfuracarb	0.20	ND		92.1±8.9		96.9±2.2	0.50	23.4	NPD 1
beta-cyfluthrin		116.4±3.7		110.3±9.6		109.9±9.9	0.04	29.1	ECD 4
Bifenox		177.5±2.3		287±0.0		185.7±0.7	0.10	25.0	ECD 5
Bifenthrin	0.50	100.1±2.9		104.4±13.3	0.50	98.9±2.8	0.10	24.4	ECD 5
Bitertanol	0.70	164.5±5.6		154.5±6.0		150.0±9.0	0.10	23.9	RE-NPD
Bromacil		77.6±1.9		74.5±11.2		85.1±5.3	0.10	19.1	ECD 3
Bromopropylate	1.00	125.6±4.5	1.00	133.4±0.7	1.00	122.2±2.3	0.10	24.0	ECD 3
Buprofezin	1.00	83.5±1.5		88.0±1.1	1.00	83.1±2.44	0.10	19.8	NPD 2
Butachlor		90.0±11.2		101.1±4.7		125.9±2.9	0.10	21.1	ECD 1
Captafol	1.00	106.0±3.8		82.1±2.0		102.2±1.4	0.50	23.6	ECD 2
Captan	5.00	85.9±1.7	5.00	83.8±1.5	2.00	95.0±2.2	0.10	20.7	ECD 4
Carbophenothion	0.80	88.7±1.6		91.4±2.2		87.1±2.6	0.10	20.8	NPD 2
Carbosulfan		14.9±3.2		22.1±2.1		7.6±7.1	0.10	21.8	NPD 3
Chinomethionat	0.50	95.2±4.9	0.50	117.7±3.7	0.50	102.4±1.9	0.10	20.9	ECD 3
Chlomethoxyfen		152.1±1.9		195.2±14.4		143.0±11.2	0.10	24.2	ECD 5
Chlorfenapyr	0.70	125.7±1.0		159.9±15.0	0.50	120.2±1.8	0.10	22.0	ECD 5
Chlorfenvinphos		3.4±7.5		4.3±10.3		11.5±14.2	0.10	18.5	NPD 4
Chlornitrofen		114.6±2.4		136.2±21.6		109.9±2.4	0.10	23.0	ECD 5
Chlorobenzilate		78.2±3.6		81.2±1.4		87.4±5.4	0.10	22.2	ECD 1
Chlorothalonil	1.00	52.7±2.2	5.00	34.1±86.6	5.00	54.7±0.6	0.10	17.8	ECD 1
Chlorpropham	0.05	81.2±9.1	0.05	90.3±1.6	0.05	84.3±5.4	0.10	14.2	NPD 1

Table 4. Continued.

Compound	Green pepper		Lettuce		Chinese cabbage		LOD[c]	RT[d]	Detector & group
	MRL[a]	Recovery[b]	MRL[a]	Recovery[b]	MRL[a]	Recovery[b]			
Chlorpyrifos	0.50	112.4±17.2	0.10	138.0±9.1	1.00	133.7±5.0	0.10	19.6	RE-ECD
Chlorpyrifos-methyl	0.10	94.6±0.9		105.8±1.7		96.3±2.3	0.10	16.9	NPD 2
Cyfluthrin	2.00	110.0±21.1	2.00	129.4±0.4	2.00	132.2±4.5	0.10	28.9	ECD 1
Cyhalothrin		135.1±5.3	2.00	167.1±2.3	1.00	126.2±3.6	0.10	26.0	ECD 5
Cypermethrin	0.50	103.2±12.0	2.00	95.2±4.3	5.00	118.2±8.0	0.01	30.0	ECD 1
Cyproconazole		3.4±7.5		ND		6.9±4.5	0.10	20.1	NPD 1
Cyprodinil		79.7±3.1		83.8±1.1		80.5±3.5	0.10	18.3	NPD 2
delta-BHC	0.20	120.8±3.0	0.20	125.4±3.5	0.20	104.0±0.9	0.10	17.6	ECD 3
Deltamethrin	0.20	108.2±1.2	0.50	135.0±18.7	0.50	98.3±5.9	0.50	35.0	ECD 2
Demeton-s-methyl		2.5±2.0		2.8±11.5		10.3±2.3	0.10	14.0	NPD 1
Diafenthiuron		34.9±5.0		8.6±14.9		83.0±4.3	0.10	20.7	NPD 3
Diazinon	0.50	86.9±4.5	0.10	95.8±9.8	0.10	90.2±1.3	0.10	14.2	NPD 5
Dichlobenil		26.2±124.8		13.5±50.8		ND	0.10	11.5	ECD 2
Dichlofluanid	2.00	87.0±0.7	10.0	116.8±2.3	15.0	95.4±2.5	0.10	19.3	ECD 1
Dichlorvos	0.30	5.2±8.3	0.30	7.4±9.1	0.30	31.5±4.4	0.10	9.2	NPD 1
Diclfop-methyl		43.7±6.6		48.1±3.3		56.7±2.9	0.10	23.2	ECD 3
Diclomezine		102.2±12.5		113.2±5.4		113.2±1.5	0.50	23.2	ECD 4
Dicloran		101.8±11.9		104.0±0.9		78.3±1.9	0.10	16.6	ECD 3
Dicofol	1.00	108.5±3.1	1.00	110.0±1.3	1.00	103.7±1.1	0.10	19.7	ECD 4
Dieldrin	0.01	118.9±2.9	0.01	117.4±1.5	0.01	119.7±1.1	0.10	21.8	ECD 1
Diethofencarb	1.00	70.9±7.1	5.00	89.7±0.8		94.6±3.9	0.10	17.6	NPD 1
Difenconazole	0.30	ND		ND		ND	0.04	34.5	ECD 4
Dimepiperate		82.9±3.1		97.6±1.5		99.7±1.7	0.10	18.7	NPD 4
Dimethametryn		69.2±5.7		49.9±9.8		68.6±4.6	0.10	18.4	NPD 3
Dimethenamid		86.8±2.0		59.6±44.6		93.6±0.7	0.10	18.4	ECD 4
Dimethoate	1.00	6.6±2.9	2.00	4.6±1.5	2.00	3.4±1.7	0.10	13.6	NPD 5
Dimethylvinphos		16.7±9.4		29.9±3.5	0.05	72.5±3.5	0.10	16.1	NPD 5
Dinocap		1453.1±1.1		1596.6±1.8		1691.9±9.8	0.06	24.0	ECD 1
Diphenamid	0.10	20.6±5.4		3.6±4.4		48.9±5.0	0.10	18.2	NPD 3
Diphenylamine		52.3±0.9		58.5±4.2		75.2±6.7	0.10	14.0	NPD 4
Disulfoton	0.50	93.3±44.6	0.50	81.9±21.3	0.50	95.4±21.8	0.10	17.5	ECD 2
Dithiopyr		117.6±4.4		114.7±3.9		109.2±3.1	0.10	18.9	ECD 4
Edifenphos		74.6±9.2		74.3±17.1		108.7±3.8	0.10	21.0	NPD 3
Endorsulfan-sulfate	1.00	90.1±11.9		118.8±3.7		121.9±4.2	0.10	23.4	ECD 1
Endrin	0.01	90.8±1.6	0.01	109.5±8.1	0.01	98.3±3.0	0.10	22.3	ECD 3
EPN	0.10	95.1±0.4	0.10	110.4±4.3	0.20	103.1±3.0	0.10	22.0	NPD 1
Esfenvalerate		116.3±13.1		163.7±5.6		149.5±19.2	0.10	30.2	RE-ECD
Esprocarb		84.7±4.6		96.7±2.4		92.0±1.4	0.10	15.8	NPD 5
Ethalfluralin	0.05	128.1±3.3		133.0±6.0		78.5±13.4	0.10	15.6	ECD 2
Ethion	1.00	81.8±3.4		96.7±6.5		83.3±5.9	0.10	20.4	NPD 1
Ethoprophos	0.02	7.8±67.5	0.02	31.3±7.6		68.0±1.6	0.10	12.4	NPD 5
Etoxazole		76.9±1.7		87.9±1.2		80.3±2.9	0.10	22.1	NPD 2
Etridiazole		658.3±6.2		624.8±12.0		731.7±10.3	0.10	13.4	ECD 4
Etrimos		90.4±3.5		98.3±7.2	0.10	96.8±1.7	0.10	14.5	NPD 5
Fenamphos		ND		ND	0.05	ND	0.10	19.3	NPD 1
Fenarimol	1.00	ND		23.4±52.3		ND	0.10	26.6	ECD 1

Table 4. Continued.

Compound	Green pepper		Lettuce		Chinese cabbage		LOD[c]	RT[d]	Detector & group
	MRL[a]	Recovery[b]	MRL[a]	Recovery[b]	MRL[a]	Recovery[b]			
Fenazaquin		43.9±2.6		62.3±4.2		84.0±3.0	0.10	22.3	NPD 4
Fenclorim		100.5±0.4		98.9±5.4		97.6±3.0	0.10	16.3	ECD 5
Fenitrocarb		137.0±1.0		128.0±8.8		149.5±11.8	0.10	19.0	RE-NPD
Fenitrothion	0.10	110.0±19.8	0.20	162.4±6.0	0.50	165.9±7.4	0.10	19.1	RE-ECD
Fenobucarb		72.1±6.1		78.5±1.7		82.9±0.5	0.10	12.2	NPD 5
Fenpropathrin	0.50	112.9±5.3		129.8±9.1		106.1±3.9	0.10	24.6	ECD 5
Fenthion		37.1±2.9	0.50	81.7±11.1	0.50	74.7±7	0.10	17.8	NPD 4
Fenvalerate	1.00	98.2±16.7	2.00	109.4±6.8	1.00	108.5±6.3	0.10	32.8	ECD 1
Fipronil		44.0±9.0		86.4±8.3		88.5±1.7	0.10	20.2	ECD 5
Fluazinam	0.30	88.2±18.9		106.8±4.9	0.05	100.4±3.0	0.10	20.3	ECD 4
Flucythrinate	0.50	120.3±2.5	2.00	105.8±49.3	0.50	115.6±4.4	0.10	30.4	ECD 2
Flufenoxuron	0.30	66.6±0.9		39.8±8.6	0.50	5299.4±9.7	0.10	16.0	NPD 3
Fluoroimide		179.4±7.7		262.4±15.8		402.5±17.5	0.50	16.7	ECD 2
Flusilazole		10.6±10.7		3.1±3.8		7.1±2.3	0.10	18.0	NPD 5
Flutolanil		71.4±1.7		90.2±7.8		98.8±3.2	0.10	19.4	NPD 4
Folpet	5.00	62.0±0.0	2.00	96.8±0.0		124.3±0.0	0.10	20.9	ECD 5
Fonofos		75.7±4.4		89.2±2.7		73.8±2.6	0.10	15.81	NPD 1
Fosthiazate		33.4±5.4		24.6±5.1		119.9±8.8	0.10	17.91	NPD 1
Fthalide		88.4±11		121.2±2.6		100.0±1.9	0.10	20.0	ECD 3
Furathiocarb		65.8±8.7		92.2±8		84.7±6	0.10	22.4	NPD 3
Halfenprox		116.2±3.1		131±0.3		132.8±2.2	0.10	30.0	ECD 4
Heptachlor	0.01	115.8±3.7	0.01	174.9±16.5	0.01	106.8±3.2	0.50	18.8	ECD 3
Heptachlor-epoxide		85.6±4.8		97.8±6.4		83.6±2.2	0.10	20.4	ECD 3
Hexaconazole		10.24±3.7		9.8±1.2		9±8	0.10	19.4	NPD 3
Hexazinone		0		0.00		2.6±6.1	0.10	21.2	NPD 1
Imazalil		112.4±7.8		0.00		0.00	0.10	21.4	ECD 2
Iprobenfos		0		24.67±6.4		55.4±1.7	0.10	16.4	NPD 1
Iprodione	5.00	116.2±16.6	10.00	119.7±12		117.3±2.4	0.10	23.6	ECD 3
Isazophos		84.4±2.1		88.6±1.5		86.7±0.7	0.10	16.2	NPD 2
Isofenphos		89.5±4.6		99.1±7	0.05	96.2±2	0.10	16.9	NPD 5
Isoprocarb		73.7±3.2		77.3±1.5		103.2±1.2	0.10	13.0	NPD 2
Isoprothiolane		112.8±3.1		171.05±8.6		89.9±3.9	0.10	21.0	ECD 5
Kresoxim-methyl	1.00	88.1±4.8		84±5.2		85.8±2.3	0.10	19.8	NPD 3
Lambda-cyhalothrin		98.6±9.0		152.7±1.2		111.6±16	0.10	24.6	ECD 3
Linuron		116.2±4.7		120.8±18.1		113.9±14	0.10	19.2	ECD 2
Malathion	0.50	89.9±1.2	2.00	98±3.5	0.50	98.9±2.3	0.10	17.6	NPD 2
Matalaxyl	1.00	145±8.8	2.00	110±3.9	0.10	119.5±17.2	0.10	17.1	RE-NPD
Mecarbam		89.3±1.2		89.3±1.9		92.8±9.2	0.10	18.6	NPD 3
Mepanipirim	0.50	81.5±4.9		93.8±5.8		87.1±3.8	0.10	17.4	NPD 5
Methidation		73.6±0.6	0.20	102.2±1.9	0.20	102.4±4	0.10	19.0	NPD 1
Methoxychlor	14.00	124.6	14.00	134.6±9.7	14.00	151.8±5.5	0.10	24.1	ECD 2
Metobromuron		91.7±22.1		51.9±0.8		119.2±6.4	0.10	18.0	RE-ECD
Metolachlor	0.50	32.87±20.2		105.2±11.8		124.7±15.8	0.10	19.5	ECD 2
Metribuzin	0.50	88.4±0.1	0.50	92.6±4.7	0.50	91.0±4.3	0.10	18.3	ECD 1

Table 4. Continued.

Compound	Green pepper		Lettuce		Chinese cabbage		LOD[c]	RT[d]	Detector & group
	MRL[a]	Recovery[b]	MRL[a]	Recovery[b]	MRL[a]	Recovery[b]			
Mevinphos		3.4±1.1	0.50	0.5±21	1.00	0.00	0.10	10.1	NPD 5
Molinate		88±41.8		85.5±17.4		85.5±24	0.10	13.0	RE-NPD
Myclobutanil	1.00	119.2±1.5		101.6±3.9	1.00	102.4±4.4	0.10	21.4	ECD 5
Napropamid	0.10	143±9.9		130.5±22.2	0.10	142.0±19.9	0.10	19.4	RE-NPD
Nonachlor		101.61±3.5		114.9±3.1		96.8±1	0.10	21.4	ECD 3
Nuarimol		113.4±16.4		40±8		122.6±7.3	0.10	23.7	RE-ECD
Ofurace		15.3±7.2		89.7±2.6		41.9±3.8	0.10	20.9	NPD 1
Oryzalin		109.2±7.7		101.1±7.9		97.6±5.2	0.50	27.4	ECD 5
Oxadixyl	1.00	6.5±4.8		8.0±5.7	0.10	8±1.8		27.1	NPD 5
Oxadizon	0.10	99.8±2.6		515.7±6.7		115.2±13.1	0.10	21.5	ECD 2
Oxyflufen		88.7±13.5		118.5±15.3	y0.05	139.3±5.0	0.10	21.6	RE-ECD
p,p-DDD	0.20	121.5±6.5	0.20	142.5±7.9	0.20	110.2±1.5	0.10	22.5	ECD 3
p,p-DDE	0.20	81.3±0.9	0.20	98.0±5.3	0.20	87.2±2.2	0.10	21.6	ECD 3
Paclobutrazole		5.7±12.2		4.9±7.4		9.9±1.3	0.10	19.1	NPD 3
Parathion	0.30	93.1±1.7	0.3	97.9±2.1	0.30	97.0±0.9	0.10	17.9	NPD 2
Penconazole	0.30	7.5±3.4		17.9±108		98.7±2.6	0.10	18.6	NPD 4
Pendimethalin	0.05	88.1±2.7	0.20	98.9±0.9	0.20	89.5±0.6	0.10	18.5	NPD 1
Permethrin	1.00	520.5±19.1	3.00	700.8±7.5	5.00	640.1±0.5	0.26	25.6	ECD 3
Phenthoate		88.1±5.9		119.6±0.9		98.6±3.8	0.10	20.5	ECD 1
Phorate		54.9±2.3		78.9±0.6		72.3±3.1	0.10	14.8	NPD 1
Phosalone		83.7±9.1		117.1±1.1	2.00	118.5±0.4	0.10	22.7	NPD 4
Phosmet		99.9±12.8		108.6±3.2	2.00	111.6±2	0.10	23.5	ECD 4
Phosphamidone		80.6±1.6		84.5±6.5		0.00	1.00	16.0	NPD 4
Piperophos		1.1±15.5		0.7±8.8		0.6±13.6	0.10	20.2	NPD 5
Pirimicarb	2.00	0.8±8.1	1.00	0.4±23.3	2.00	3.8±0.5	0.10	16.4	NPD 4
Pirimiphos-ethyl	0.50	91.1±4.3	2.00	103.3±3.8	2.00	96.5±1.9	0.10	16.5	NPD 5
Pirimiphos-methyl	0.50	80.1±2.4		94.2±0.93	2.00	73.6±0.5	0.10	17.4	NPD 1
Pretilachlor		120.5±3.4		147.2±7		113.6±15.3	0.10	21.4	RE-ECD
Prochloraz	3.00	123.1±1.8		142.6±9		175.6±10	0.10	27.9	ECD 2
Procymidone	5.00	67±13	5.00	92.2±14.2		82.12±40.7	0.10	20.3	ECD 2
Prodiamine		116.6±6.1		112.4±4.2		102.9±2.7	0.10	19.0	ECD 5
Profenofos	2.00	171.9±6.8		79.5±2.3	2.00	42.4±11.2	1.00	21.5	ECD 1
Prometryn		70.6±3.2		85.1±5		85.2±2.9	0.10	15.4	NPD 5
Propamocarb-HCl	1.00	11.7±2	10.00	10.8±1	0.10	10.6±7.5	0.10	9.8	NPD 5
Propanil		31.4±17.5		88.2±7		120.8±5	0.10	18.2	ECD 2
Propiconazole		8.2±13		19.6±2.6		34.7±3.2	0.10	21.0	NPD 4
Prothiofos		111.1±4.6		138.5±9.9	0.05	134.9±2.1	0.10	21.4	ECD 4
Pyraclofos	1.00	8.7±4.9		87.6±0.8	0.10	86.9±4	0.10	23.5	NPD 2
Pyrazophos		75±10.8		155.7±3	0.10	159.4±22.5	0.10	26.5	ECD 2
Pyrazoxyfen		0.00		0.00		102.9±6.5	0.10	31.6	ECD 5
Pyributicarb		615.6±6.3		596.9±5.2		409.4±13.6	2.00	23.9	ECD 2
Pyridaben	0.70	105.4±3.8		103.3±2.1		101.6±6	0.10	26.6	ECD 4
Pyridaphenthion		10.6±4.9		20.0±2.4		18.6±1.6	0.10	21.8	NPD 2

Table 4. Continued.

Compound	Green pepper		Lettuce		Chinese cabbage		LOD[c]	RT[d]	Detector & group
	MRL[a]	Recovery[b]	MRL[a]	Recovery[b]	MRL[a]	Recovery[b]			
Pyroquilon		11±11		9.8±6.6		11.7±3.8	0.10	15.8	NPD 2
Quinalphos		90.4±3.2		98.6±7.6		95.7±2.8	0.10	16.9	NPD 5
Quintozene		124.7±5.8	3.00	129.2±6.3	0.02	96.8±11.4	0.10	17.3	ECD 1
gamma-BHC	0.20	86.5±3.0	0.20	88.1±1.3	0.20	81.9±6.1	0.10	17.1	ECD 3
Simazine		5.3±3.8		3.1±8.6		237.8±7.6	0.10	15.3	NPD 3
Simetryn		15.8±6.8		4.5±2.8		36.4±2.0	0.10	16.9	NPD 3
tau-fluvalinate		137.2±18.6		291.7±8.5		152.1±6.5	0.50	33.5	ECD 2
Tebufenpyrad	0.50	70.4±5.2		61.2±14.0		67.3±2.5	0.10	22.1	NPD 3
Tefluthrin		112.2±1.4		111.1±1.3		107.1±2.3	0.10	17.5	ECD 4
Terbuconazole	1.00	14.6±6.6		17.4±1.3		20.5±1.1	0.10	21.3	NPD 2
Terbufos	0.05	78.9±1.1		83.2±1.6	0.05	84.6±1.4	0.10	15.7	NPD 2
Terbuthylazine		132.0±1.1		134.5±10.0		145.0±13.6	0.10	15.67	RE-NPD
Terbutryn		61.1±1.0		76.7±1.1		68.4±4.0	0.10	17.35	NPD 2
Tetradifon		121.4±4.4		126.5±12.1		113.3±1.5	0.10	25.40	ECD 5
Thifluazamide		63.4±9.2		103.6±3.7		92.2±3.6	0.10	19.83	NPD 4
Thiobencarb	0.20	81.8±2.7	0.20	81.7±0.8	0.20	84.1±2.6	0.10	17.65	NPD 3
Thiomefon		47.4±2.7		69.5±1.1		52.3±2.0	0.10	15.06	NPD 2
Tolclofos-methyl		87.8±0.9		99.1±0.9		80.6±2.2	0.10	17.01	NPD 1
Tolyfluanid	2.00	109.6±10.2	1.00	94.7±6.0		43.8±17.4	0.10	20.42	RE-ECD
Tralomethrin	0.50	114.2±2.1	0.50	117.4±1.2	0.50	114.7±1.8	0.10	35.90	ECD 4
Triadimefon		79.8±3.4		64.0±8.7		81.0±0.0	0.10	19.62	ECD 1
Triadimenol		26.0±12.4		18.8±10.1		15.1±2.8	0.05	18.70	NPD 2
Triazamate		12.9±6.0		15.5±1.9		93.0±5.9	0.10	19.06	NPD 4
Triazophos		55.5±1.3		91.9±5.1	0.10	112.6±2.8	0.10	20.68	NPD 4
Trichlorfon	0.10	23.8±3.7	0.50	32.2±1.0	0.50	85.1±1.1	0.10	9.25	NPD 2
Triflumizole	1.00	2.2±10.3	1.00	2.2±12.9	1.00	16.7±4.2	0.10	18.84	NPD 4
Trifluralin	0.05	117.6±1.4	0.05	114.5±2.5	0.05	101.3±0.6	0.10	15.82	ECD 4
Vinclozolin	3.00	88.9±13.2	2.00	117.6±9.3	1.00	111.1±4.0	0.10	18.48	RE-ECD
Zeta-cypermethrin		114.5±13.4		135.4±12.6		111.9±2.9	0.06	29.79	ECD 5

[a]Maximum residue limit, [b] % ± RSD, [c] Limit of detection, [d] Retention time, [e] not detected.

Table 5. Number of pesticides recovered by MRM II

Recovery rate	Green pepper (%)	Lettuce (%)	Chinese cabbage (%)	Average (%)
ND	8 (4)	7 (4)	7 (4)	4
< 50%	42 (21)	24 (12)	37 (18)	17
50~140 %	136 (69)	147 (74)	130 (66)	70
> 140%	12 (6)	20 (10)	24 (12)	9

therefore, total 198 pesticides tested for recovery.

Only 7~8 compounds were not detected including difenoconazole, acephate, hexazinone and fenamiphos, which were not detected in all samples (Table 5). Seventy percents of compounds was recovered by 50~140%, while 9% of compounds was over 140% of recovery.

Particularly, a few compounds (dinocap, pyributicarb, etridiazole, flufenoxuron, and permethrin) showed false recovery of more than 600%. When recovery data was analyzed according to the major chemical classes (Table 6), azole showed relatively lower recovery rate compared to other groups. The tested compounds were classified into three Log P groups (<1, 1~3 and >3). As excepted, more polar compounds of Log P <1 gave lower recovery rates than the group of higher Log P (>1).

Table 6. Distribution of recovery rates of pesticide

Chemical class	Green pepper				Lettuce				Chinese cabbage			
	ND[a]	L[b]	G[c]	H[d]	ND	L	G	H	ND	L	G	H
Azole (16)	6	57	31	6	12	57	19	12	12	57	25	12
Carbamate (9)	11	33	56	-	-	33	67	-	-	33	56	11
Dinitroaniline (6)	-	-	100	-	-	-	100	-	-	-	100	-
Diphenyl ether (4)	-	-	50	50	-	-	50	50	-	-	50	50
Oganophosphorus (50)	6	2	0	2	4	20	70	6	6	8	82	4
Oranochlorine (12)	-	-	100	-	-	8	84	8	-	-	100	-
Pyrethroid (18)	-	-	89	11	-	-	61	39	-	-	78	22
Thiocarbamate (5)	-	-	80	20	-	-	80	20	-	-	80	20
Triazine (6)	-	33	67	-	-	50	50	-	-	17	50	33
Trihalomethlthio (5)	-	-	100	-	-	-	100	-	-	20	80	-
Urea (3)	-	33	67	-	-	33	67	-	-	33	67	-

[a]not detected (%), [b]low (< 50 %), [c]good (50~140 %), [d]high (>140 %).

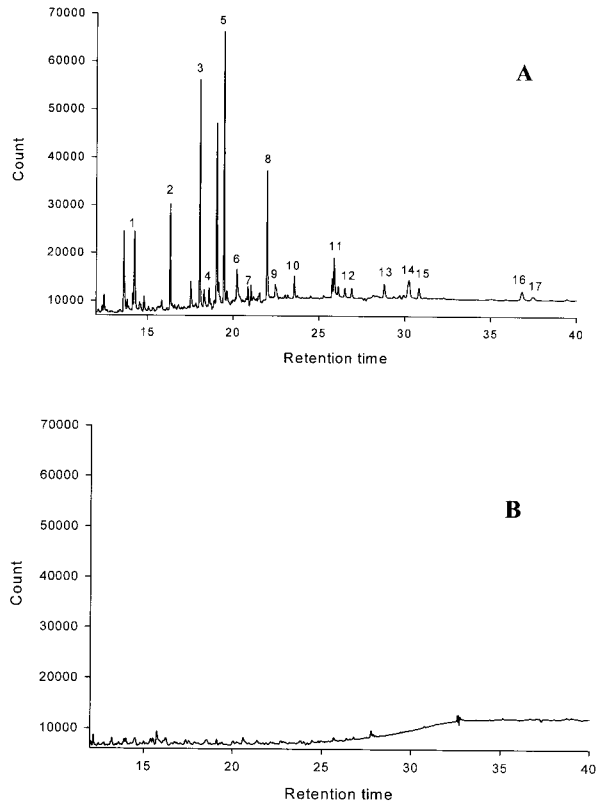

Fig. 6. Gas chromatograms of MRTMs (A, ECD group 4 from , Chinese cabbage) and control sample (B, Chinese cabbage).
1, Etridiazole; 2, Trifluralin; 3, Tefluthrin; 4, Dimethenamid; 5, Dithiopyr; 6, Dicofol; 7, Fluazinam; 8, Captan; 9, Prothofos; 10, Dichlomezine; 11, Phosmet; 12, Acrinathrin; 13, Pyridaben; 14, β-yfluthrin; 15, Halfenprox; 16, Difenconazole; 17, Tralomethr.

CONCLUSION

Multiresidue test mixtures (MTRMs) and recovery test mixture (RTM) were established to be used for developing of an improved gas chromatographic multiresidue methods for lettuce, Chinese cabbage and green pepper.

MRM II gave better recovery from vegetables than MRM I method using RTM, and therefore recovery test with MRTMs was conducted using MRM II. The results showed that seventy percents of compounds was recovered by 50~140%, while 9% of compounds were over 140% of recovery and only 7~8 compounds were not detected.

Azoles showed relatively lower recovery rate compared to other chemical groups, and more polar compounds of Log P <1 gave lower recovery rates than the group of higher Log P (>1).

Based on the improved results such as reduced sample amount and evaporation time, better extraction and elution solvents compared with conventional method, MRM II could be used for screening maximum number of 190 compounds in green pepper, lettuce and Chinese cabbage.

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