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A Multiresidue Method for Determining 136 Pesticides and Metabolites in Fruits and Vegetables: Application of Macroporous Diatomaceous Earth Column

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ABSTRACT

A fast and easy multiresidue method using the macroporous diatomaceous earth (MDE) column for determining 136 pesticide and metabolite residues in fruits and vegetables was developed. The MDE column was used instead of the separation funnel for liquid/liquid partition in sample preparation. Through MDE columns, the preparation of test solution became easier and faster than traditional funnel liquid/liquid partition. The emulsion problem can also be avoided. Fifty one pesticides including acephate were determined by gas chromatography (GC) with a pulsed flame photometric detector (GC/PFPD) and 63 pesticides including aldrin were detected by GC with electron capture detection (GC/ECD). Twenty carbamate peticides and metabolites including aldicarb were determined by high performance liquid chromatography with a post-column derivaization system and a fluorescence detector (HPLC/FLD) and two benzimidazole pesticides including carbendazim and thiabendazole were detected by HPLC with an ultraviolet detector (HPLC/UV). Recovery studies were performed by spiking pesticides (0.05~2.0 ppm) in fruit and vegetable samples, and the triplicate results showed satisfactory recoveries and repeatability. The detection limits ranged from 0.003 to 0.2 ppm. The developed multireside method can be employed to other pesticides or matrices with an easier and less solvent consumption way to prepare sample solution. It is an environment-friendly and useful method for routine pesticide analysis.

Key words: vegetable, fruit, pesticide, macroporous diatomaceous earth column, multiresidue analysis

INTRODUCTION

The most convenient and economical way to increase production and reduce cost for farmers is applying pesticides on crops. However, because of the potential hazard effect on public health, Department of Health (DOH) in Taiwan set up the "Tolerances for the Residues of Pesticides in Crops" in 1976, which is validated and revised every year to ensure the food safety and protect consumers' health. Currently, MRLs (maximum residue levels) of more than 300 pesticides in various crops have been established by DOH and must be enforced[(1)]. Monitoring programs for pesticide residues in fruits and vegetables have been the routine work of food safety related authorities. For this type of target analysis, multiresidue analytical methods are preferred to reduce workload and costs[(2)]. DOH official multiresidue methods for monitoring pesticides in fruits and vegetables[(3,4)], modified from Luke method[(5)], have been used for many years in Taiwan. However, there are some drawbacks in these official methods, such as different procedures for fruits and vegetables, and large volume of organic solvents including dichloromethane, a carcinogenic solvent, used. A multiresidue method with time economical, environment-friendly, high recovery, satisfactory reproducibility, and high sensitivity in detection limit needs to be developed.

Liquid-liquid extraction by separation funnel is traditionally used as the pretreatment for the detection of pesticide residues in agricultural products. This liquid/liquid partition method, however, is time and solvent consuming. Macroporous diatomaceous earth column (MDE column), a commercial liquid/liquid extraction cartridge, was used to replace the separation funnel for liquid-liquid extraction to analyze the pesticide residues in agricultural products[(2,6,7)]. The advantages of using MDE column include simple device, simultaneous processing multiple samples, avoiding emulsion, and no anhydrous sodium sulfate being needed during the dehydration of the eluant[(7)]. In this study, MDE column was used for liquid/liquid extraction, and solvents of lower toxicity were chosen through the analytical procedures. One hundred and thirty-six pesticides and metabolites including organochlorine, organophosphate, carbamate and synthetic pyrethroid pesticides were detected by gas chromatography (GC) or liquid chromatography (LC) and tested for recovery, repeatability and sensitivity in the developed method.

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MATERIALS AND METHODS

I. *Materials*

Chinese Cabbage, tomato, grape, starfruit and orange samples were purchased from supermarkets or traditional markets. MDE column (Chem Elut, 20 mL) was made by Varian (USA) and florisil SPE cartridge (1000 mg, 6 mL) was purchased from J&W Scientific (CA, USA). Membrane filter (Nylon, 13 mm, 0.22 μm) was purchased from Amchro (Hattersheim, Germany).

II. *Reagents*

Acetone used in this study were of residual grade. Methanol, *n*-hexane, ethyl acetate, and acetonitrile were of LC grade. Acetic acid, *o*-phthaldehyde (OPA), sodium borate and 2-mercaptoethanol were of reagent grade. Pesticide standards were purchased from Dr. Ehrenstorfer, ChemService, AccuStandard or Riedel-de Haen AG (Germany). The purities of pesticide standards were higher than 94% except for formothion (74%).

III. *Instruments and Analytical Conditions*

(I) *GC*

A Varian 3600 GC equipped with both pulsed flame photometric detector (PFPD) and electron capture detector (ECD) (Varian Technologies, CA, USA) was used. The analytes were separated on a DB-608 megabore capillary column, 30 m by 0.53 mm, with a 0.83 μm film thickness (J&W Scientific, CA). Injections were made by using a CombiPAL autosampler (CTC Analytics, Zwingen, Switzerland). Data processing was conducted by using a Chromatography Data Station Software (Scientific Information Service Corp., Taipei, Taiwan).

The chromatographic conditions for GC/PFPD were as follows: carrier gas, N_2 (10 mL/min); flow rate of air 1, air 2, and H_2, 21, 10, and 16 mL/min, respectively; temperature of injection port, 250°C; temperature of detector, 280°C; sample injection volume, 2 μL; injection mode, splitless. The oven temperature was programmed as follows: 150°C for 2 min, raised to 280°C at 4°C/min, held for 15 min.

The chromatographic conditions for GC/ECD were as follows: carrier gas, N_2 (10 mL/min); temperature of injection port, 250°C; temperature of detector, 300°C; sample injection volume, 1 μL; injection mode, splitless. The oven temperature was programmed as follows: 150°C for 2 min, raised to 230°C at 4°C/min, held for 10 min, raised to 250°C at 10°C/min, and then held for 18 min.

(II) *HPLC*

Hitachi HPLC system equipped with a Hitachi L-6200 pump, a Luna C_{18} analytical column (25 cm × 4.6 mm i.d., 5 μm, Hypersil, Runcon, UK), a Hitachi L-4250 UV detector, and a Shimadzu C-R4A integrator was used. The UV detector was set at 280 nm. The mobile phase system was 5% acetic acid/methanol (95/5, v/v) pumped at 1.0 mL/min. The injection volume was 20 μL.

A Shimadzu HPLC equipped with a solvent delivery system (Model L6200 pump) which delivers mobile phase, sodium hydroxide solution, and OPA solution was used. A post-column reactor including a thermal static device kept at 90°C, a sodium hydroxide solution reaction loop (2 m × 0.5 mm i.d., stainless steel), and a OPA solution reaction loop (2 m × 0.5 mm i.d., stainless steel) was used. RT-551 Spectrofluorometric detector was used and set at Ex 340 nm and Em 455 nm. The analytical column was Lichrospher 60 RP-Select B (5 μm, 250 × 4.0 mm i.d., Merck). Mobile phase of acetonitrile/water (40/60, v/v) was pumped at flow rate of 1.0 mL/min. Both sodium hydroxide and the OPA solution were pumped at 0.5 mL/min. Sample injection volume was 20 μL.

IV. *Methods*

(I) *Preparation of Standard Solutions*

Pesticides were divided into four main groups according the measuring instruments including GC/PFPD, GC/ECD, HPLC/FLD, and HPLC/UV. The stock solutions for GC/PFPD, GC/ECD and HPLC determination were prepared by acetone, *n*-hexane, and methanol, respectively. Each pesticide standard (10 mg) was accurately weighed into a 100-mL volumetric flask and solvent was then added up to the volume to make the stock solution (ca. 100 μg/mL) individually. Mix standard solutions were divided into 12 groups which were prepared by mixing and diluting the stock solution with acetone, *n*-hexane, methanol or 5% acetic acid/acetonitrile (9/1, v/v) as listed in Table 1. The grouping was determined using the chromatograms of the pesticides by GC and HPLC.

(II) *Preparation of Sample Solutions*

1. *Extraction*

The fruit and vegetable samples were homogenized and 20 g of which was then sampled and extracted with 70 mL of acetone for 3 min. The extraction solution was then filtered under suction. The residues and container were then washed with another 30 mL of acetone, which was then filtered. The filtrates were combined into an evaporation bottle and evaporated at 35°C under vacuum. The concentrate (ca. 18 mL) was applied onto a MDE column and kept standing for 10 min allowing the concentrates evenly dispersed in MDE column. The concentrate in MDE column was eluted with 80 mL of ethyl acetate, evaporated to dryness, and then dissolved in 5 mL of acetone [test solution (I)] for

Table 1. The targeted 136 pesticides/metabolites in this study and their grouping for multiresidue determination

Analytical instrument		Pesticide or metabolite
GC/PFPD (51)		
	Group 1	bromophos-methyl, EPN, ethoprophos, fenamiphos, fensulfothion, iprobenfos, isoxathion, mephosfolan, mevinphos, monocrotophos, omethoate, parathion-ethyl, phosphamidon, pirimiphos-methyl, pyrazophos, quinalphos, trichlorfon
	Group 2	acephate, chlorpyrifos, chlorpyrifos-methyl, cyanofenphos, demeton-s-methyl, dichlorvos, dimethoate, ethion, fenthion, fonofos, malathion, methacrifos, methidathion, phosalone, prothiofos, pyrazophos, salithion, terbufos
	Group 3 (in acetone)	azinphos-methyl, bromophos-ethyl, carbophenothion, diazinon, disulfoton, ditalimfos, fenitrothion, formothion, methamidophos, parathion-methyl, phenthoate, phorate, phosmet, pirimiphos-ethyl, triazophos, vamidothion
GC/ECD (63)		
	Group 4	bifenox, bifenthrin, chinomethionat, chlorfenapyr, chlorfluazuron, chlozolinate, cyhalothrin, cypermethrin, esfenvalerate, iprodione, permethrin, procymidone, triadimefon
	Group 5	alphacypermethrin, bromopropylate, chlorothalonil, cyfluthrin, dichlofluanid, fenvalerate, isoprothiolane, myclobutanil, profenofos, pyrifenox, tetradifon, trifluralin
	Group 6	bupirimate, captan, dicloran, deltamethrin, dicofol, endosulfan, flucythrinate, hexaconazole, propiconazole, pyridaben, pyridaphenthion, vinclozolin
	Group 7	benfluralin, butralin, captafol, chloropropylate,difenoconazole, diniconazole, dinitramine, fenarimol, fenpropathrin, fluvalinate, penconazole, pretilachlor, prochloraz
	Group 8 (in *n*-hexane)	α-BHC, β-BHC, β-chlordane, α-chlordane, aldrin, dieldrin, endrin, heptachlor epoxide, heptachlor, lindane, mirex, pp'-DDE, pp'-DDT
HPLC/FLD (20)		
	Group 9	3-OH carbofuran, aldicarb sulfoxide, butocarboxim, XMC , promecarb, propoxur
	Group 10	1-naphthol, 3-keto carbofuran, aldicarb sulfone, bendiocarb, fenobucarb, metolcarb
	Group 11 (in methanol)	aldicarb, carbaryl, carbofuran, isoprocarb, methiocarb, methomyl, oxamyl, thiodicarb
HPLC/UV (2)	Group 12 (in 5% HOAc:CH_3CN =9:1, v/v)	carbendazim, thiabendazole

GC/PFPD determination. One milliliter of test solution (I) was evaporated and reconstituted with 1 mL of methanol and filter through a Nylon membrane filter [test solution (II)] for HPLC/FLD determination or 1 mL of 5% acetic acid/acetonitrile (9/1, v/v) filter through a Nylon membrane filter [test solution (III)] for HPLC/UV determination. One milliliter of test solution (I) was evaporated and reconstituted with 1 mL of *n*-hexane for florisil cleanup.

2. *Solid Phase Extraction for Sample Cleanup*

The above concentrate (1 mL) for cleanup was loaded into a florisil cartridge, which was rinsed with *n*-hexane prior to applying samples. The concentrate in cartridge was then eluted with 20 mL of 30% acetone in n-hexane. The eluant was evaporated to dryness and resuspended with 1 mL of *n*-hexane for GC/ECD determination. A flow diagram for the whole analytical procedures in this study is shown in Figure 1.

(III) *Recovery Test*

Mix pesticide standards were spiked into homogenized Pai-Tsai, tomato, grape, starfruit, and orange samples separately. The spiked samples were then kept in a hood for 30 min to evaporate the solvent residues. The test samples containing 0.05~2.0 ppm pesticides were thus prepared. Each spiked sample was prepared in triplicate. A blank sample without standards was also prepared. The preparation of sample solution was as described. Recoveries for pesticides were calculated after GC or HPLC analysis.

RESULTS AND DISCUSSION

I. *Method Development*

Due to the low detection levels required by regulatory bodies and the complex nature of the matrices in

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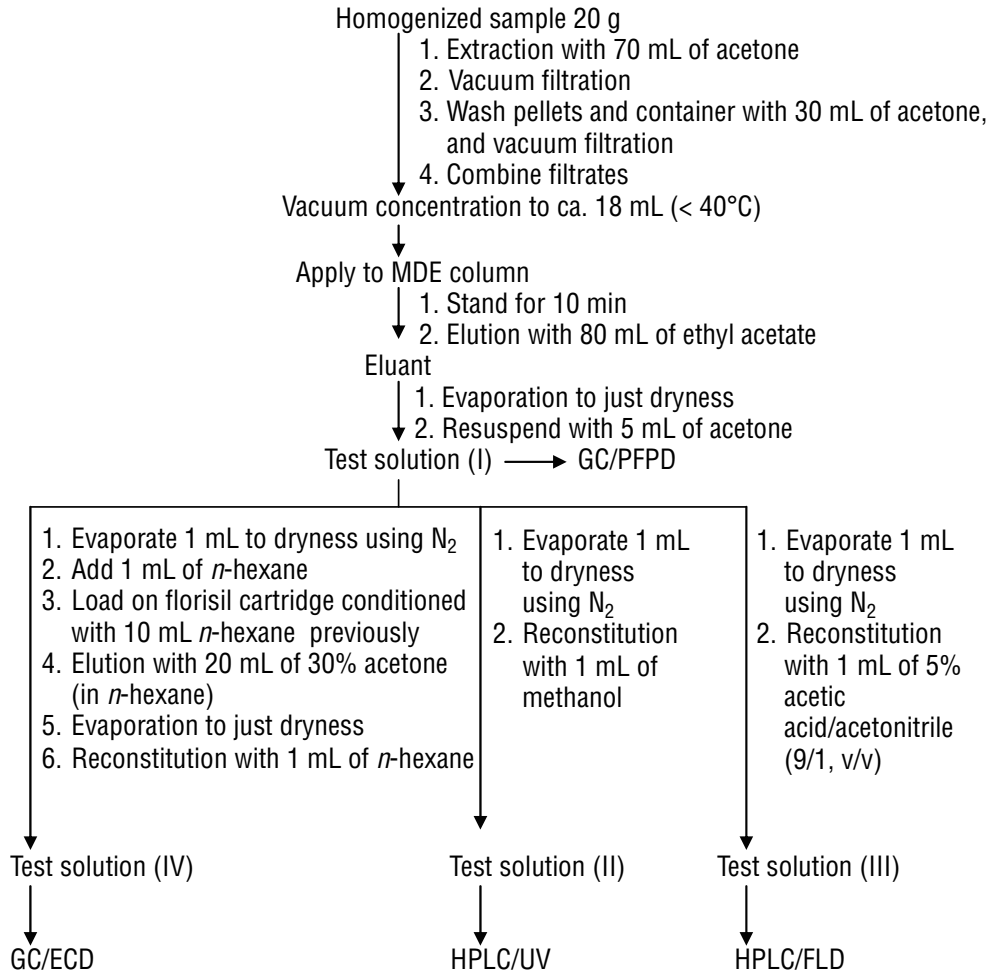

Figure 1. Analytical procedures for determining 136 pesticide and metabolite residues in fruits and vegetables.

which the target compounds are present, efficient sample preparation and trace-level detection and identification are important aspects in an analytical method[8]. In this study, according to the physico-chemical properties of pesticides, sensitive and selective detectors were used. A GC/PFPD was used for detecting organophosphate pesticides. A GC/ECD was used for detecting halogenated pesticides, synthetic pyrethroids pesticides, and other pesticides. An LC with a post-column derivatization system and a fluorescence detector was used for detecting carbamate pesticides. An LC/UV was used for detecting benzimidazole pesticides, such as thiobendazole and carbendazim. A total of 136 pesticides/metabolites was divided into four main groups and 12 subgroups based on the analytical equipments and retention times, respectively (Table 1). Fifty one pesticides were detected by GC/ECD, 63 pesticides were detected by GC/ECD, 20 pesticides were detected by LC/FLD, and 2 pesticides were detected by LC/UV. HPLC chromatograms of pesticides detected by LC/FLD with a post-column derivatization system are shown in Figure 2.

A number of solvents have been used for multiresidue extractions and the most commonly used include acetone, ethyl acetate, acetonitrile[8], and dichloromethane. The MDE column is a polypropylene (PP) cartridge packed with highly pure and inert macroporous diatomaceous earth. High surface area makes highly efficient in interaction between sample and extraction solvent without emulsion. The extraction process can be done without any suction but gravity. The column is packed with a phase-separation filtering material to protect the organic eluants from being contaminated with aqueous matrices. According to literatures[6,7, 9-11], *n*-hexane, ethyl acetate and dichloromethane were used as eluting solvents for diatomaceous earth application. The extract solvents of DOH official multiresidue methods for determining pesticides in fruits and vegetables modified from Luke method were acetone/water, followed by partition with petroleum ether and dichloromethane[3,4]. In this study, the samples containing water were extracted by acetone, followed by MDE liquid/liquid extraction and the eluting solvent was ethyl acetate. In the previous study conducted by Ficbaldi *et al.*[10], the homogenized sample was mixed with diatomaceous earth to obtain

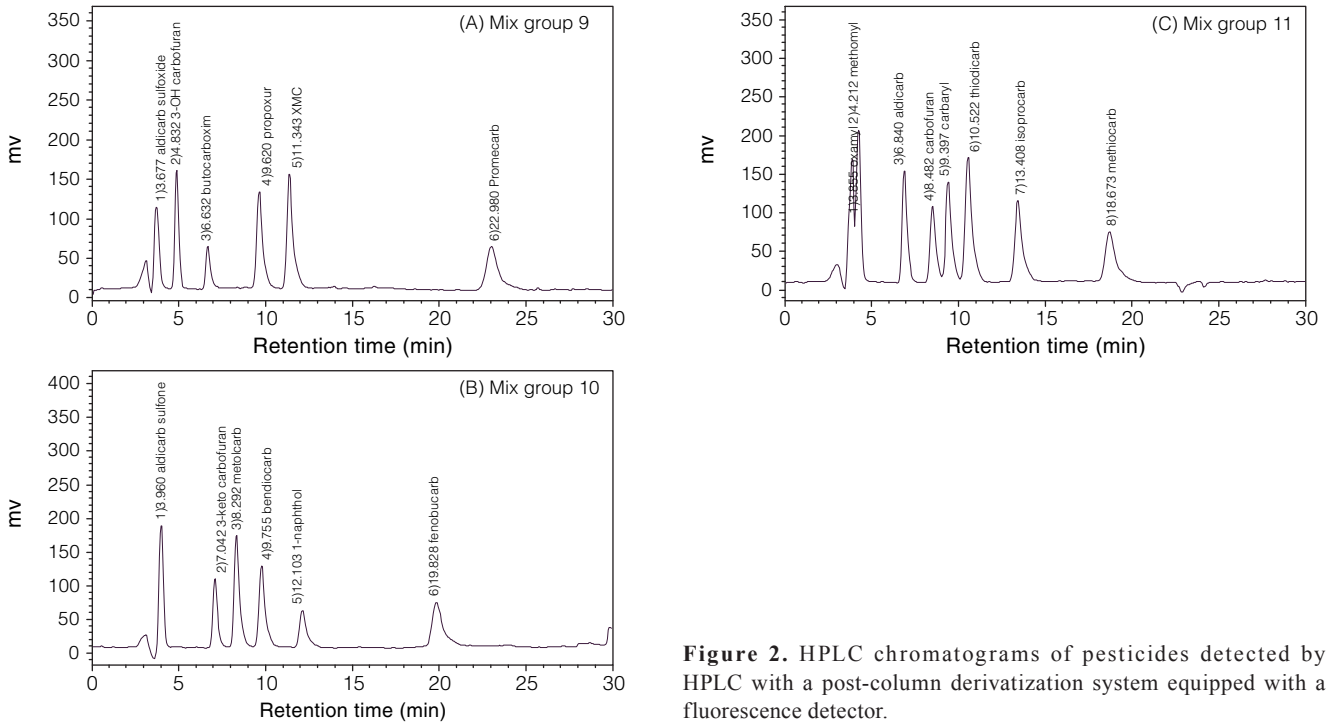

Figure 2. HPLC chromatograms of pesticides detected by HPLC with a post-column derivatization system equipped with a fluorescence detector.

a free-flowing powder, which was extracted with ethyl acetate. Compared with this previous study[10], the MDE column is more stable and easier to use. The eluant from the MDE column is clearer than the extraction solution processed by the separation funnel. To bring the liquid/liquid extraction efficiency into full play, the sample was loaded into an MDE column and kept standing for 10 min allowing the sample solution to evenly disperse in the column. A stopcock was installed upon the column to control the elution speed at 3~5 mL/min after applying the extraction solution. This could improve the recovery and reproducibility.

A cleanup process was necessary before GC/ECD determination to eliminate matrix interferences. The optimal organic eluant for the cleanup process was assessed by using mix standard solution (in *n*-hexane), which was loaded on a florisil SPE cartridge, conditioned with *n*-hexane, followed by eluants with increasing polarities. Various combinations of *n*-hexane (H) and acetone (A) were prepared to study the eluting conditions. Initially, the cartridge was eluted stepwise with 10 mL each of *n*-hexane, 15% A/H, 30% A/H and 45% A/H. It is showed that 30% A/H could completely elute out all pesticides. Further elution with more polar solvents (such as 45% A/H), did not improve the recovery. Thirty percent A/H was thus chosen as the eluting solvent and the elution scheme was tested for pesticides in fruit and vegetable samples and showed satisfactory cleanup effect (data not shown).

The solvents, acetone, *n*-hexane, and ethyl acetate, used in this study are all low in toxicity and capable of replacing chloroform and dichloromethane, the carcinogenic and highly polluting agents, for routine pesticide analysis.

II. *Method Validation*

The performance of this developed method was evaluated by recovery, repeatability, matrix interference, and detection limit. The recoveries of 136 pesticides and metabolites from fruits and vegetables spiked at 0.05~2.0 ppm standards are listed in Table 2 and shown in Figure 3. The recoveries of pesticides detected by GC/PFPD, LC/FLD and LC/UV mainly ranged 80~120%. The recoveries of pesticides detected by GC/ECD were mainly distributed across 60 to 100%, lower than other chromatographic methods due to chemical character and loss during MDE partition and florisil clean-up procedures. Recoveries of most pesticides from MDE column were satisfactory except for a few unstable compounds or high polar compounds. Recoveries of aldicarb sulfoxide were 35.2~69.9% due to loss in the MDE liquid-liquid partitioning because of the polarity of this compound. The coefficients of variation for recoveries of pesticides were mostly below 10%, and not higher than 30% (Table 2). The above data indicated that both satisfactory recovery and reproducibility were achieved for a multiresidue method.

The limit of detection (LOD) of the developed method was defined as the amount of each analyte in sample that would produce a signal/noise ratio of at least 3:1 ($S/N \geq 3$) in the chromatogram. The LODs of 136 pesticides/metabolites ranged from 0.003 to 0.2 ppm (Table 2). Further confirmation by GC/MS or LC/MS is needed in this screen method.

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Table 2. Recoveries of pesticides spiked in fruits and vegetables and limits of detection

Pesticide	Recovery[a] (%)						MDL (ppm)	Detector[c]
	Spike level (ppm)	Pai-Tsai	Tomato	Grape	Starfruit	Orange		
Acephate	0.5	81.1(16.9)[b]	66.8 (8.6)	82.4 (0.9)	79.5 (15.9)	82.1 (5.3)	0.1	PFPD
Azinphos-methyl	0.5	114.0 (4.3)	119.3 (3.4)	102.0 (2.0)	103.0 (3.0)	83.1 (4.5)	0.1	PFPD
Bromophos-ethyl	0.5	91.4 (1.8)	82.2 (2.7)	77.7 (4.2)	76.5 (7.3)	94.8 (3.6)	0.03	PFPD
Bromophos-methyl	0.75	104.4 (2.3)	61.7 (16.4)	84.5 (0.4)	61.5 (11.6)	99.7 (1.3)	0.03	PFPD
Carbophenothion	0.5	114.4 (6.8)	58.7 (15.7)	110.3(10.1)	71.0 (2.7)	108.2 (9.3)	0.02	PFPD
Chlorpyrifos	0.5	106.8 (4.3)	78.5 (9.9)	91.1 (6.1)	76.7 (11.2)	115.5 (0.3)	0.05	PFPD
Chlorpyrifos-methyl	0.5	83.8 (4.5)	90.5 (1.5)	80.7 (1.0)	78.3 (3.5)	85.1 (3.6)	0.03	PFPD
Cyanofenphos	1.5	122.1 (6.5)	74.7 (7.8)	87.8 (4.1)	66.7 (7.9)	109.8 (1.4)	0.02	PFPD
Demeton-s-methyl	0.5	30.3 (8.2)	101.7 (3.2)	100.7 (23.2)	121.8 (2.1)	111.5 (18.0)	0.03	PFPD
Diazinon	0.5	105.6 (6.7)	90.4 (8.2)	106.5 (1.5)	97.4 (3.0)	119.1 (4.8)	0.02	PFPD
Dichlorvos	0.5	80.7 (4.5)	91.6 (5.4)	81.6 (15.8)	94.8 (6.9)	79.4 (4.7)	0.01	PFPD
Dimethoate	1.0	113.5 (5.2)	126.3 (0.5)	113.1 (10.1)	107.7 (14.7)	116.2 (4.7)	0.02	PFPD
Disulfoton	0.5	75.5 (6.1)	59.4 (15.0)	79.5 (5.1)	59.5 (13.4)	85.5 (18.6)	0.01	PFPD
Ditalimfos	0.5	99.1 (6.2)	111.7 (3.7)	102.8 (7.6)	106.5 (10.3)	100.8 (6.2)	0.025	PFPD
EPN	1.25	111.6 (2.8)	125.7 (1.6)	94.0 (5.6)	72.3 (4.4)	106.3 (5.5)	0.01	PFPD
Ethion	0.5	113.2 (6.5)	60.4 (15.5)	109.0 (11.9)	67.3 (3.4)	132.9 (2.82)	0.01	PFPD
Ethoprophos	0.5	100.3 (5.1)	112.1 (1.2)	99.2 (14.4)	116.1 (4.5)	112.6 (5.6)	0.01	PFPD
Fenamiphos	0.5	97.0 (6.1)	117.3 (3.4)	116.8 (5.4)	95.1 (6.7)	109.5 (3.4)	0.05	PFPD
Fenitrothion	1.0	107.1 (3.8)	99.0 (9.4)	118.0 (1.4)	103.1 (3.1)	106.4 (1.3)	0.01	PFPD
Fensulfothion	0.5	115.4 (6.0)	117.5 (3.3)	122.9 (2.5)	118.2 (2.2)	103.5 (3.8)	0.05	PFPD
Fenthion	0.5	106.1 (6.4)	79.5 (14.7)	103.9(15.3)	81.3 (1.9)	101.6 (17.5)	0.02	PFPD
Fonofos	0.5	83.3 (3.8)	75.1 (6.6)	91.3 (15.5)	118.93 (7.9)	100.9(25.7)	0.02	PFPD
Formothion	0.5	91.5 (3.2)	118.6 (4.8)	98.4 (4.2)	85.1 (3.8)	81.0 (1.0)	0.03	PFPD
Iprobenfos	0.5	112.3 (7.7)	114.0 (5.5)	109.1 (8.2)	109.8 (7.1)	110.7 (8.1)	0.03	PFPD
Isoxathion	0.75	120.2(10.7)	115.1 (4.3)	22.3 (6.7)	24.7 (25.8)	68.0 (7.0)	0.02	PFPD
Malathion	1.0	116.5 (4.5)	73.3 (9.0)	116.8 (7.7)	92.3 (2.6)	89.4 (9.4)	0.01	PFPD
Mephosfolan	0.75	127.2 (0.9)	124.3 (3.5)	114.9 (12.3)	106.9 (6.0)	98.8 (13.6)	0.02	PFPD
Methacrifos	0.5	89.9 (2.4)	101.0 (3.4)	88.4 (4.2)	90.5 (3.1)	92.9 (3.8)	0.02	PFPD
Methamidophos	0.5	67.8 (5.5)	82.0 (6.7)	106.3 (16.3)	86.13 (6.4)	83.6 (11.2)	0.02	PFPD
Methidathion	1.0	117.1 (5.8)	126.4 (1.2)	120.4 (0.8)	109.5 (1.0)	108.1 (3.5)	0.02	PFPD
Mevinphos	0.75	86.7 (6.0)	113.6 (1.7)	112.1 (8.4)	109.0 (10.5)	95.2 (4.8)	0.02	PFPD
Monocrotophos	0.5	127.1 (2.3)	105.6 (8.5)	145.1 (2.9)	135.6 (3.2)	151.3 (3.7)	0.05	PFPD
Omethoate	0.5	85.9 (5.9)	89.3 (14.8)	123.5 (2.4)	124.1 (1.3)	114.0 (3.3)	0.05	PFPD
Parathion-ethyl	0.5	105.1 (9.2)	69.4 (4.5)	86.3 (15.7)	66.2 (9.8)	111.5 (11.6)	0.01	PFPD
Parathion-methyl	0.75	121.6 (2.3)	97.2 (3.2)	115.3 (4.8)	103.3(12.2)	101.7 (14.8)	0.01	PFPD
Phenthoate	0.5	122.5 (1.0)	102.5 (12.4)	116.3 (2.0)	88.0 (3.8)	113.7 (2.8)	0.02	PFPD
Phorate	1.0	81.3 (5.8)	73.2 (1.5)	85.7 (0.6)	66.5 (0.4)	98.2 (11.4)	0.01	PFPD
Phosalone	1.0	121.0 (1.2)	84.4 (9.2)	99.1 (9.0)	70.7 (14.2)	115.7 (4.5)	0.03	PFPD
Phosmet	1.0	127.4 (1.6)	128.3 (1.7)	125.0 (1.5)	108.5(10.7)	118.7 (1.9)	0.02	PFPD
Phosphamidon	0.5	88.0 (4.1)	101.1 (5.2)	111.4 (8.6)	115.9 (5.2)	98.0 (5.0)	0.05	PFPD
Pirimiphos-ethyl	0.5	96.5 (5.4)	69.9 (5.6)	80.1 (0.7)	57.2 (8.6)	101.5 (0.6)	0.01	PFPD
Pirimiphos-methyl	0.5	122.6 (2.2)	105.0 (0.4)	109.4 (2.5)	106.8 (13.7)	106.3 (8.6)	0.01	PFPD
Prothiofos	0.5	98.1 (8.9)	41.6 (15.0)	92.6 (7.5)	43.2 (4.4)	89.2 (1.1)	0.01	PFPD
Pyrachlofos	1.0	123.8 (2.8)	99.8 (12.8)	108.9 (18.8)	99.3 (14.5)	120.3 (1.4)	0.03	PFPD
Pyrazophos	0.5	112.3 (7.5)	110.5 (3.9)	91.6 (3.1)	98.0 (4.9)	105.4 (1.4)	0.1	PFPD

Table 2. (continued)

Pesticide	Recovery[a] (%)						MDL (ppm)	Detector[c]
	Spike level (ppm)	Pai-Tsai	Tomato	Grape	Starfruit	Orange		
Quinalphos	0.5	118.5 (6.7)[b]	98.1 (8.7)	110.4 (10.5)	89.8 (10.4)	106.8 (0.5)	0.02	PFPD
Salithion	0.5	95.3 (4.3)	100.0 (10.6)	94.3 (6.1)	92.3 (2.80	87.4 (3.2)	0.02	PFPD
Terbufos	0.5	79.8 (15.9)	120.4 (7.8)	139.1 (1.0)	126.6 (2.8)	127.7 (5.5)	0.01	PFPD
Triazophos	0.75	121.0 (6.1)	121.3 (7.4)	105.4(13.8)	99.5 (8.0)	119.9 (0.5)	0.02	PFPD
Trichlorfon	1.5	86.5 (7.0)	59.1 (13.6)	94.1 (4.3)	61.3 (3.8)	106.5 (8.2)	0.05	PFPD
Vamidothion	0.5	121.8 (2.6)	113.5 (6.1)	118.9 (4.9)	81.5 (1.3)	73.0 (4.8)	0.1	PFPD
α-BHC	0.05	66.2 (2.0)	79.4 (1.4)	83.8 (6.1)	72.9 (4.3)	47.3 (9.4)	0.003	ECD
β-BHC	0.05	72.0 (3.0)	83.0 (2.6)	91.6 (9.2)	107.8 (5.8)	51.2 (3.7)	0.01	ECD
α-chlordane	0.05	85.6 (3.4)	59.6 (2.0)	86.5 (6.4)	64.4 (7.5)	50.0 (3.5)	0.005	ECD
β-chlordane	0.05	83.6 (3.6)	67.7 (5.7)	116.8 (5.3)	67.9 (4.6)	61.4 (2.3)	0.003	ECD
Aldrin	0.05	76.8 (2.7)	47.0 (5.0)	86.4 (2.1)	47.6 (15.0)	45.1 (7.4)	0.005	ECD
Alphacypermethrin	0.25	103.8 (7.9)	68.5 (13.4)	75.8 (11.0)	64.0 (6.1)	66.7 (2.4)	0.05	ECD
Benfluralin	0.05	67.9 (18.9)	86.4 (24.7)	73.7 (8.9)	69.9 (39.9)	38.8 (22.4)	0.01	ECD
Bifenox	0.10	90.6 (12.8)	97.1 (23.4)	78.8 (10.1)	68.9 (17.1)	46.5 (9.5)	0.01	ECD
Bifenthrin	0.25	97.5 (6.5)	59.0 (16.7)	83.0 (17.4)	71.7 (9.4)	47.5 (9.4)	0.03	ECD
Bromopropylate	0.25	105.0 (14.9)	89.0 (12.6)	97.7 (14.1)	64.5 (14.8)	79.4 (3.0)	0.02	ECD
Bupirimate	0.25	92.4 (16.8)	86.8 (9.0)	77.6 (12.2)	90.7 (22.9)	12.9 (14.3)	0.03	ECD
Butralin	0.50	73.3 (15.9)	65.6 (10.6)	83.3 (20.0)	56.0 (6.3)	43.2 (13.8)	0.05	ECD
Captafol	0.10	105.8 (14.3)	84.4 (5.1)	112.0 (14.5)	83.6 (7.0)	56.0 (10.1)	0.05	ECD
Captan	0.05	82.7 (16.8)	51.6 (11.1)	79.3 (23.9)	46.4 (2.9)	54.6 (7.3)	0.005	ECD
Chinomethionat	0.05	30.8 (25.9)	80.7 (7.6)	29.3 (21.6)	31.4 (13.7)	78.7 (4.9)	0.005	ECD
Chlorfenapyr	0.5	109.5 (4.2)	70.1 (6.7)	99.7 (1.7)	69.7 (10.4)	63.0 (10.5)	0.01	ECD
Chlorfluzuron	0.05	92.0 (1.0)	85.9 (5.0)	102.6 (2.5)	81.9 (11.4)	73.4 (5.6)	0.03	ECD
Chloropropylate	1.0	81.8 (19.4)	87.7 (23.2)	102.0 (10.6)	55.4 (18.2)	66.0 (14.1)	0.1	ECD
Chlorothalonil	0.05	109.7 (20.1)	80.1 (10.5)	100.5 (18.2)	74.4 (16.3)	33.1 (18.1)	0.005	ECD
Chlozolinate	0.10	102.5 (14.9)	78.4 (10.5)	67.4 (12.1)	79.6 (27.7)	49.9 (32.5)	0.01	ECD
Cyfluthrin	0.25	25.5 (20.1)	54.8 (14.3)	36.3 (33.5)	56.0 (14.9)	48.3 (11.3)	0.05	ECD
Cyhalothrin	0.10	47.8 (35.0)	85.8 (4.1)	78.3 (20.2)	68.7 (17.7)	73.0 (15.3)	0.01	ECD
Cypermethrin	0.25	44.7 (32.0)	76.0 (15.9)	99.3 (11.0)	65.7 (16.7)	86.7 (6.4)	0.05	ECD
Deltamethrin	0.20	51.8 (19.0)	55.8 (20.9)	86.2 (13.0)	89.9 (7.9)	79.8 (26.5)	0.02	ECD
Dichlofluanid	0.05	54.4 (27.6)	72.6 (1.1)	70.9 (7.1)	71.8 (3.2)	47.9 (37.1)	0.01	ECD
Dicloran	0.125	112.1 (12.3)	96.5 (16.2)	87.4 (8.9)	73.9 (14.4)	49.0 (20.7)	0.01	ECD
Dicofol	0.15	71.6 (9.1)	66.0 (26.3)	60.9 (15.3)	66.8 (28.1)	81.8 (15.3)	0.02	ECD
Dieldrin	0.05	69.6 (2.4)	75.0 (20.0)	111.5 (17.5)	114.8 (28.8)	41.5 (2.9)	0.005	ECD
Difenoconazole	0.5	76.6 (3.5)	91.4 (9.1)	78.1 (23.3)	72.8 (7.7)	27.1 (8.4)	0.1	ECD
Diniconazole	0.125	99.1 (12.5)	98.0 (21.7)	87.7 (15.1)	84.1 (10.1)	50.6 (30.7)	0.025	ECD
Dinitramine	0.05	92.0 (20.8)	92.7 (25.6)	83.5 (3.1)	63.8 (8.0)	46.0 (9.4)	0.005	ECD
Endosulfan	0.10	60.8 (9.2)	79.2 (9.1)	82.8 (14.9)	47.1 (28.9)	49.5 (10.5)	0.01	ECD
Endrin	0.05	87.0 (7.5)	71.6 (1.9)	94.5 (7.0)	77.1 (7.1)	44.2 (8.5)	0.005	ECD
Esfenvalerate	0.25	101.6 (26.1)	71.4 (16.1)	78.0 (17.6)	72.4 (12.5)	66.7 (9.8)	0.02	ECD
Fenarimol	0.125	88.4 (10.6)	84.8 (12.7)	89.7 (17.8)	79.8 (13.2)	32.8 (12.6)	0.02	ECD
Fenpropathrin	0.15	72.4 (21.2)	83.0 (13.4)	91.9 (14.5)	91.2 (15.9)	89.1 (20.2)	0.08	ECD
Fenvalerate	0.25	84.9 (17.8)	63.0 (16.8)	99.9 (2.0)	81.5 (9.2)	92.8 (13.7)	0.03	ECD
Fucythrinate	0.25	55.7 (20.4)	100.7 (10.2)	90.2 (6.9)	82.6 (9.4)	80.4 (14.2)	0.1	ECD
Fluvalinate	0.10	57.3 (14.2)	66.7 (8.9)	71.7 (2.1)	94.3 (11.9)	72.4 (1.0)	0.1	ECD
Heptachlor	0.05	79.8 (1.7)	61.5 (2.9)	110.1 (11.5)	63.7 (6.2)	69.6 (7.8)	0.003	ECD
Heptachlor epoxide	0.05	94.9 (7.9)	63.3 (3.0)	90.5 (9.3)	58.5 (4.9)	64.2 (5.8)	0.005	ECD

Table 2. (continued)

Pesticide	Recovery[a] (%)						MDL (ppm)	Detector[c]
	Spike level (ppm)	Pai-Tsai	Tomato	Grape	Starfruit	Orange		
Hexaconazole	0.25	36.2 (26.5)[b]	46.4 (7.0)	35.9 (4.2)	35.4 (19.6)	24.8 (28.8)	0.02	ECD
Iprodine	0.50	95.7 (10.5)	53.3 (24.6)	92.7 (6.7)	48.1 (17.6)	47.3 (12.7)	0.05	ECD
Isoprothiolane	0.125	86.8 (6.4)	89.7 (15.0)	76.3 (3.9)	85.0 (14.0)	125.5 (7.8)	0.02	ECD
Lindane	0.05	72.5 (4.1)	69.6 (2.4)	82.4 (3.8)	74.7 (11.8)	43.6 (3.7)	0.005	ECD
Mirex	0.05	61.6 (2.2)	78.5 (4.0)	81.1 (6.0)	71.5 (1.9)	52.0 (1.2)	0.01	ECD
Myclobutanil	0.25	100.2 (1.1)	104.1 (3.9)	120.3 (3.4)	112.0 (4.2)	35.7 (1.7)	0.05	ECD
Penconazole	0.125	97.1 (10.3)	99.9 (20.3)	91.0 (14.7)	79.1 (15.1)	36.1 (14.1)	0.02	ECD
Permethrin	0.30	47.8 (6.4)	49.8 (27.9)	92.2 (13.1)	58.5 (28.4)	43.1 (12.8)	0.2	ECD
PP'-DDE	0.05	72.6 (4.5)	77.2 (11.6)	93.6 (4.3)	108.5 (24.5)	32.1 (7.1)	0.003	ECD
PP'-DDT	0.05	88.3 (3.4)	73.5 (4.1)	103.2 (7.6)	67.8 (1.8)	48.5 (10.9)	0.01	ECD
Pretilachlor	0.25	95.7 (16.4)	92.9 (24.8)	81.3 (1.7)	49.2 (21.2)	80.1 (48.9)	0.05	ECD
Prochloraz	0.5	99.9 (2.9)	77.9 (5.5)	93.8 (0.8)	104.1 (3.8)	36.8 (13.8)	0.03	ECD
Procymidone	0.05	74.8 (17.1)	86.7 (3.8)	84.5 (5.8)	85.7 (3.7)	43.0 (6.0)	0.5	ECD
Profenofos	0.50	98.7 (3.4)	85.2 (7.8)	98.2 (7.1)	78.2 (15.2)	54.9 (6.2)	0.02	ECD
Propiconazole	0.125	67.2 (37.1)	81.8 (13.2)	78.7 (9.4)	51.7 (11.4)	14.9 (44.8)	0.03	ECD
Pyridaben	0.50	93.7 (21.2)	77.8 (12.6)	66.8 (6.2)	75.2 (7.2)	43.3 (4.6)	0.05	ECD
Pyridaphenthion	0.40	77.1 (4.8)	101.7 (8.4)	75.5 (26.6)	94.7 (19.6)	90.9 (21.4)	0.2	ECD
Pyrifenox	0.125	62.3 (12.2)	66.1 (20.0)	73.6 (6.8)	41.3 (12.2)	20.0 (23.5)	0.03	ECD
Tetradifon	0.25	94.0 (12.0)	85.2 (13.8)	70.5 (0.4)	64.2 (18.6)	42.1 (13.7)	0.02	ECD
Triadimefon	0.15	37.2 (19.1)	93.6 (8.2)	39.6 (20.1)	68.9 (10.0)	82.8 (8.8)	0.01	ECD
Trifluralin	0.5	95.8 (8.7)	86.5 (7.9)	87.0 (6.9)	86.1 (7.4)	95.6 (3.3)	0.01	ECD
Vinclozolin	0.05	103.3 (16.7)	74.6 (17.4)	92.7 (6.9)	54.3 (13.6)	41.5 (18.3)	0.005	ECD
1-naphthol	0.5	78.9 (13.9)	76.3 (4.4)	83.7 (3.9)	35.2 (3.8)	118.0 (5.5)	0.1	FLD
3-keto carbofuran	0.5	98.9 (5.7)	106.1 (2.8)	116.3 (3.8)	101.6 (0.2)	95.3 (5.8)	0.1	FLD
3-OH carbofuran	0.5	89.2 (4.6)	99.0 (2.8)	101.1 (3.3)	101.4 (2.5)	100.2 (4.7)	0.05	FLD
Aldicarb	0.5	75.6 (3.1)	117.4 (9.7)	82.2 (6.0)	89.2 (3.6)	100.7 (5.5)	0.1	FLD
Aldicarb sulfone	0.5	90.0 (3.6)	97.0 (0.2)	97.4 (3.7)	102.1 (2.8)	97.7 (7.1)	0.05	FLD
Aldicarb sulfoxide	0.5	35.2 (11.2)	69.9 (4.4)	55.9 (4.0)	40.3 (4.5)	46.2 (3.0)	0.1	FLD
Bendiocarb	0.5	91.0 (2.5)	95.4 (1.3)	97.1 (4.2)	99.8 (0.4)	87.6 (4.3)	0.03	FLD
Butocarboxim	2.0	103.8 (1.8)	85.3 (2.2)	124.5 (3.3)	93.5 (4.8)	112.0 (5.9)	0.05	FLD
Carbaryl	0.5	100.0 (5.2)	102.0 (0.4)	99.1 (3.3)	102.1 (3.5)	97.2 (3.5)	0.05	FLD
Carbofuran	0.5	98.8 (4.6)	82.8 (2.1)	96.2 (2.1)	98.8 (5.8)	79.5 (5.6)	0.05	FLD
Fenobucarb	0.5	85.5 (5.4)	93.3 (1.3)	96.5 (4.1)	94.2 (5.7)	110.2 (1.8)	0.05	FLD
Isoprocarb	0.5	87.5 (7.4)	96.8 (1.5)	97.7 (4.2)	109.1 (7.3)	98.5 (1.6)	0..05	FLD
Methiocarb	0.5	89.2 (6.6)	93.2 (3.8)	94.1 (4.0)	97.3 (0.8)	92.5 (4.3)	0.05	FLD
Methomyl	0.5	91.0 (5.3)	95.7 (0.8)	115.5 (5.3)	120.9 (16.1)	78.6 (8.8)	0.05	FLD
Metolcarb	0.5	88.7 (3.9)	100.2 (0.7)	94.7 (3.9)	95.8 (2.9)	96.6 (4.8)	0.05	FLD
Oxamyl	0.5	89.8 (3.4)	95.7 (3.7)	101.5 (3.4)	98.0 (2.6)	93.1 (4.4)	0.05	FLD
Promecarb	0.5	87.7 (5.1)	93.7 (3.1)	93.0 (4.0)	97.6 (2.4)	90.3 (4.8)	0.04	FLD
Propoxur	0.5	91.0 (2.5)	97.4 (2.2)	93.4 (4.2)	99.0 (2.2)	89.9 (4.2)	0.03	FLD
Thiodicarb	0.5	90.8 (2.6)	96.8 (3.5)	103.8 (4.8)	101.8 (5.8)	82.9 (1.9)	0.05	FLD
XMC	0.5	102.9 (1.7)	94.4 (0.8)	95.1 (4.4)	100.3 (1.3)	89.1 (3.8)	0.05	FLD
Carbendazim	1.0	85.0 (8.1)	49.8 (1.5)	89.8 (1.2)	63.4 (4.9)	30.0 (18.4)	0.05	UV
Thiabendazole	1.0	44.8 (8.1)	58.3 (0.1)	82.6 (2.0)	57.0 (0.3)	32.1 (39.3)	0.05	UV

[a]Average of triplicate.
[b]Value in the parenthesis is coefficient of variation (CV, %).
[c]PFPD: pulsed flame photometric detector; ECD: electron capture detector; FLD: fluorescence detector; UV: ultraviolet detector.

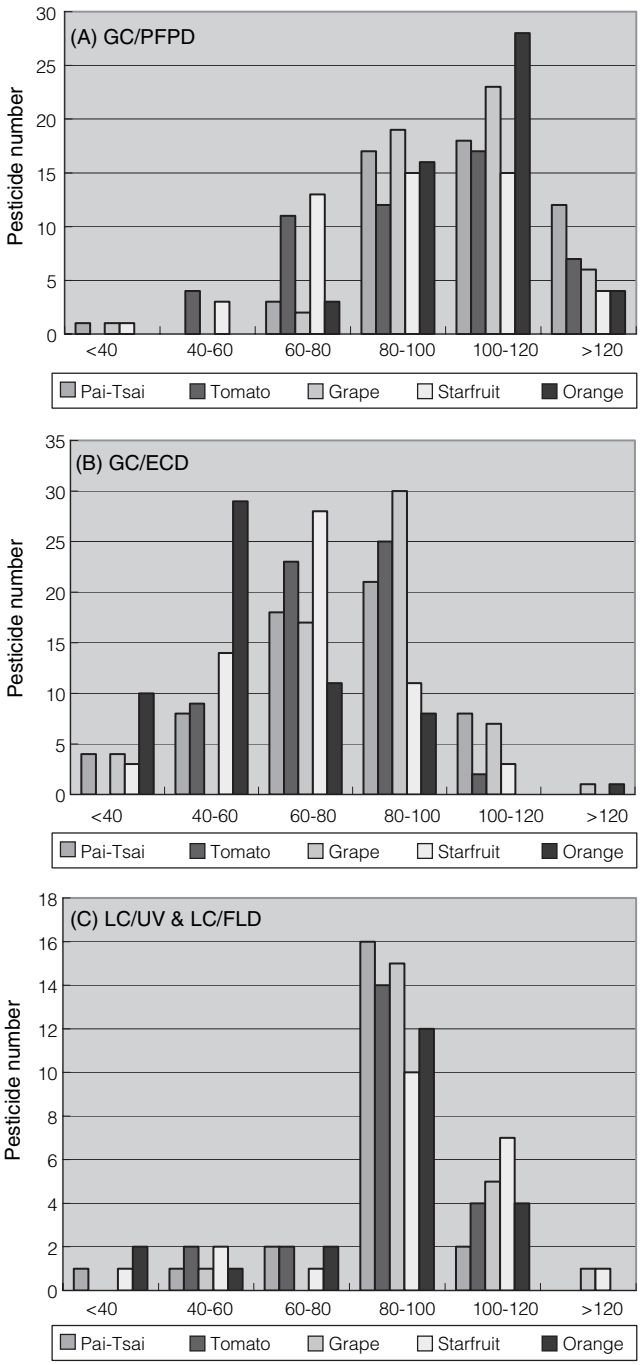

Figure 3. Recovery distribution of pesticides detected by various detectors.

CONCLUSIONS

Compared to previous DOH official methods, this new developed pesticide mutiresidue method is faster, less labor intensive and requires less solvent consumption. The proposed method in this study had been already accepted as a DOH official method in 2005[12] and used as a routine method for monitoring pesticide residues in marketed fruits and vegetables.

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