Multiresidue Analysis of 48 Pesticides in Agricultural Products by Capillary Gas Chromatography

Yumiko Nakamura,*,† Yasuhide Tonogai,† Yukihiro Sekiguchi,† Yukari Tsumura,† Nobuyuki Nishida,‡ Kazunori Takakura,§ Mamoru Isechi,|| Kazuo Yuasa,|| Munetomo Nakamura,⊥ Nobuyuki Kifune,⊥ Kohei Yamamoto,# Shinji Terasawa,# Tatsuyuki Oshima,# Masahiro Miyata,○ Kazumasa Kamakura,○ and Yoshio Ito△

Division of Food Chemistry, National Institute of Health Sciences, Osaka Branch, 1-1-43 Hoenzaka, Chuo-ku, Osaka 540, Japan, Food Safety Division, Kobe Center for Quality Control and Consumer Service, 1-4 Onohama-cho, Chuo-ku, Kobe 651, Japan, Frozen Food Inspection Association, 1-chome, Koyo-cho Nishi, Higashinada-ku, Kobe 658, Japan, The Japan Canned Food Inspection Association, Kobe Office, 3-2-1 Minatojima, Chuo-ku, Kobe 650, Japan, Japan Food Research Laboratories, 3-1 Toyotsu-cho, Suita 564, Japan, Japan Oilstuff Inspectors' Corporation, 1-10-4 Tsukamachi, Mikage, Higashinada-ku, Kobe 658, Japan, Kobe Quarantine Station, Center for Inspection of Imported Foods and Infectious Diseases, 1-1 Toyahama-cho, Hyogo-ku, Kobe 652, Japan, and Faculty of Pharmaceutical Sciences, Mukogawa Women's University, 11-68 Koshien, Kyuban-cho, Nishinomiya 663, Japan

A method for multiresidue analysis of 48 pesticides (20 organophosphorus pesticides, 7 organochlorine pesticides, 14 organonitrogen pesticides, and 7 pyrethroid pesticides) permitted in Japan was systematically developed on the basis of capillary GC. Pesticides were simultaneously extracted with acetone from vegetable and fruit samples or with acetonitrile from lipid-containing crops and then re-extracted into ethyl acetate (test solution). Pesticides in the test solution were determined by capillary GC: Organophosphorus pesticides were directly determined by FPD-GC. Organonitrogen pesticides were determined by FTD-GC (NPD-GC) following cleanup by silica gel chromatography. Organochlorine and pyrethroid pesticides were measured by ECD-GC after cleanup by Florisil column chromatography. Recoveries for 10 crops at fortification levels of 0.05–0.25 ppm were 42.5–128.5%. No pesticides tested here were detected except for banana, in which bitertanol was detected at 0.31 ppm.

Keywords: *Multiresidue analysis; organophosphorus pesticides; organochlorine pesticides; organonitrogen pesticides; pyrethroid pesticides; capillary GC*

INTRODUCTION

Much attention has been directed to the pesticide residues in foods in Japan, especially postharvest-applied pesticides, because of the increase in the import of foods. The Ministry of Health and Welfare in Japan has specified pesticide residue limits: 90 pesticide residues have been legislated by the Law of Food Sanitation on December 1, 1993 (Japanese Food and Hygienic Society, 1993; Ministry of Health and Welfare of Japan, 1993a,b).

In Japan, there is a separate method for each pesticide for analysis of pesticide residues in foods (Ministry of Health and Welfare of Japan, 1992, 1993a,b; Countermeasure Society for Environmental Preservation of Pesticides, 1990), which does not provide data on many different pesticide residues. Thus, a method for multiresidue analysis of pesticides, especially those permitted in Japan, is desirable.

Several researchers have investigated the methods for multiresidue analysis of pesticides in foods by GLC (Hsu et al., 1991; Garcia et al., 1991; Lee and Wylie, 1991; Leoni et al., 1992), HPLC (Miles et al., 1990; Hernandez-Hernandez et al., 1991), GC/MS (Liao et al., 1991), and LC/MS (Liu et al., 1991). Florisil column chromatography (Kadenczki et al., 1992) and gel permeation chromatography in conjunction with silica gel column chromatography (Holstege et al., 1991) have been proposed for cleanup in multiresidue analysis. These methods, however, are attended by limitations.

We have established a method for multiresidue analysis of pesticides in agricultural products permitted in this country.

MATERIALS AND METHODS

Materials. *(1) Pesticide Standards.* All pesticide standard reference materials were purchased from Hayashi Pure Chemical Industries, Ltd. (Osaka, Japan) or Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The purity of these pesticides was more than 95% by GLC or HPLC.

The following pesticides were tested.

(a) Organophosphorus Pesticides (23): dichlorvos, diazinon, acephate, fenthion, quinalphos, parathion-methyl, fenitrothion, parathion, fensulfothion, EPN, phosalone, malathion, methamidophos, ethoprophos, terbufos, etrimfos, chlorpyrifos, dimethoate, prothiofos, edifenphos (EDDP), α-CVP (chlorfenvinphos *E*-isomer), β-CVP (chlorfenvinphos *Z*-isomer), and phenthoate.

(b) Organochlorine Pesticides (15): α-BHC, β-BHC, γ-BHC, δ-BHC, *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, dicofol, and chlorobenzilate.

† National Institute of Health Sciences.
‡ Kobe Center for Quality Control and Consumer Service.
§ Frozen Food Inspection Association.
|| The Japan Canned Food Inspection Association.
⊥ Japan Food Research Laboratories.
Japan Oilstuff Inspectors' Corp.
○ Kobe Quarantine Station.
△ Mukogawa Women's University.

0021-8561/94/1442-2508$04.50/0

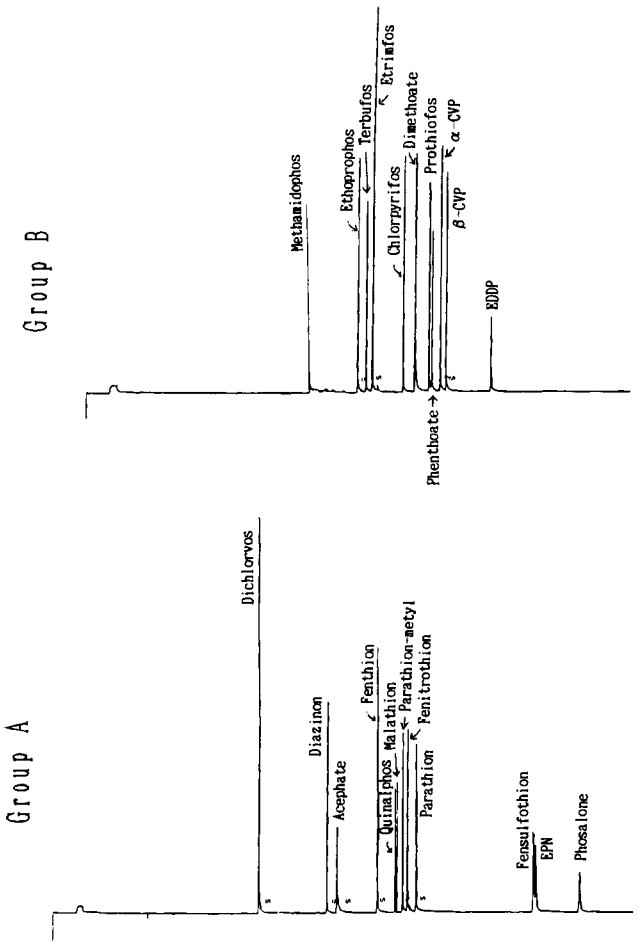


Figure 1. Gas chromatogram of the standard solution of organophosphorus pesticides (FPD-GC). Group A: DDVP, diazinon, acephate, fenthion, quinalphos, malathion, parathion-metyl, fenitrothion, parathion, fensulfothion, EPN, phosalone, 1 μg/mL each. Group B: methamidophos, ethoprophos, terbufos, etrimfos, chlorpyrifos, dimethoate, prothiofos, phenthoate, α-CVP, β-CVP, EDDP, 1 μg/mL each.

(c) Organonitrogen Containing Carbamate Pesticides (16): chlorpropham, esprocarb, diethofencarb, pendimethalin, pretilachlor, flutoluanil, mepronil, bitertanol, aldicarb, bendiocarb, pirimicarb, ethiofencarb, chinomethionat, triadimenol, propiconazole, and mefenacet.

(d) Pyrethroid Pesticides (7): pyrethrins, permethrin, flucythrinate, deltamethrin, cyhalothrin, cypermethrin, and fluvalinate.

(2) Pesticide Working Solutions. Pesticide standard solutions (1000 μg/mL) were prepared by dissolving the pesticide standards in ethyl acetate (organophosphorus and organonitrogen pesticides) or *n*-hexane (organochlorine and pyrethroid pesticides).

The following pesticide solutions were prepared by diluting pesticide standard solutions with acetone for recovery tests.

(a) Organophosphorus Pesticides. Group A: mixtures of DDVP, diazinon, acephate, fenthion, quinalphos, parathion-methyl, fenitothion, parathion, fensulfothion, EPN, phosalone, and malathion, 1 μg/mL each. *Group B*: mixtures of methamidophos, ethoprophos, terbufos, etrimfos, chlorpyrifos, dimethoate, prothiofos, α-CVP, β-CVP, and phenthoate, 1 μg/mL each.

(b) Organochlorine Pesticides. Group A: mixtures of α-BHC, γ-BHC, heptachlor, heptachlor epoxide, *p,p'*-DDE, and *p,p'*-DDD, 2 μg/mL each; dicofol and chlorobenzilate, 5 μg/mL each. *Group B*: mixtures of β-BHC, δ-BHC, aldrin, dieldrin, endrin, *o,p'*-DDT, and *p,p'*-DDT, 2 μg/mL each.

(c) Organonitrogen Pesticides (Containing Carbamate Pesticides). Group A: mixtures of chloropropham, esprocarb, diethofencarb, pendimethalin, pretilachlor, flutoluanil, mepronil, and bitertanol, 5 μg/mL each. *Group B*: mixtures of aldicarb, bendiocarb, pirimicarb, ethiofencarb, chinomethionat, triadimenol, propiconazole, and mefenacet, 5 μg/mL each.

(d) Pyrethroid Pesticides. Group A: mixtures of pyrethrins, permethrin, flucythrinate, deltamethrin, 5 μg/mL each. *Group B*: mixtures of cyhalothrin, cypermethrin, and fluvalinate, 5 μg/mL each.

(3) Organic Solvents and Reagents. Acetone, acetonitrile, ethyl acetate, dichloromethane, and *n*-hexane were of special grade for pesticide residue analysis.

Celite 545 (Johns-Manville Sales Corp.) and Florisil PR (60-100 mesh, Floridin Co.) were obtained from Wako Pure Chemical Industries, Ltd. Kieselgel 60 (70-230 mesh) was obtained from Merck & Co., Inc. (Darmstadt, Germany). Anhydrous sodium sulfate (Na_2SO_4) and sodium chloride (NaCl) were of analytical grade. These reagents were used without prewashing. Florisil PR and anhyrdous Na_2SO_4 were heated overnight at 130 °C and desiccated before use. Kieselgel 60 was used without any treatment.

Ashless filter papers No. 5A and 5C were obtained from Advantec Toyo (Tokyo, Japan).

(4) Samples. Brown rice, potato, cabbage, lettuce, carrot, cucumber, shiitake (mushroom), apple, strawberry, and banana were obtained from retail sources.

Apparatus. *(1) Homogenizer.* An Excel DX-3 Autohomogenizer (Nihon Seiki Kaisha Ltd., Japan) was used for sample preparation.

(2) Rotary Evaporator. Rotavapor RE 111 (Büchi, Shibata Kagaku Kikai Kogyo, Japan) equipped with a Büchi 461 water bath and vacuum pump JS-75A (Advantec) were used to concentrate the organic solvents. A water bath was set at 35–40 °C.

(3) Chromatographic Tube for Column Chromatography. A glass column of 30 cm × 15 mm i.d. was used in silica gel or Florisil column chromatography for purification of sample solutions.

(4) Gas Chromatograph. A Yanaco Model G-6800 (Kyoto, Japan) or Hewlett-Packard Model HP 5890II (Palo Alto, CA)

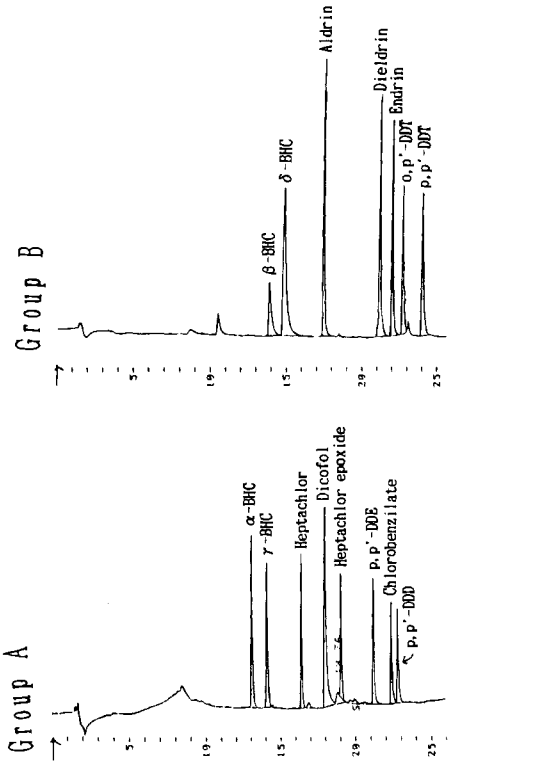


Figure 2. Gas chromatogram of the standard solution of organochlorine pesticides (ECD-GC). Group A: α-BHC, γ-BHC, heptachlor, heptachlor epoxide, *p,p'*-DDE, *p,p'*-DDD, 0.1 μg/mL each; dicofol, chlorobenzilate, 1 μg/mL each. Group B: β-BHC, δ-BHC, aldrin, dieldrin, endrin, *o,p'*-DDT, *p,p'*-DDT, 0.1 μg/mL each. Conditions for ECD-GC are described in the text.

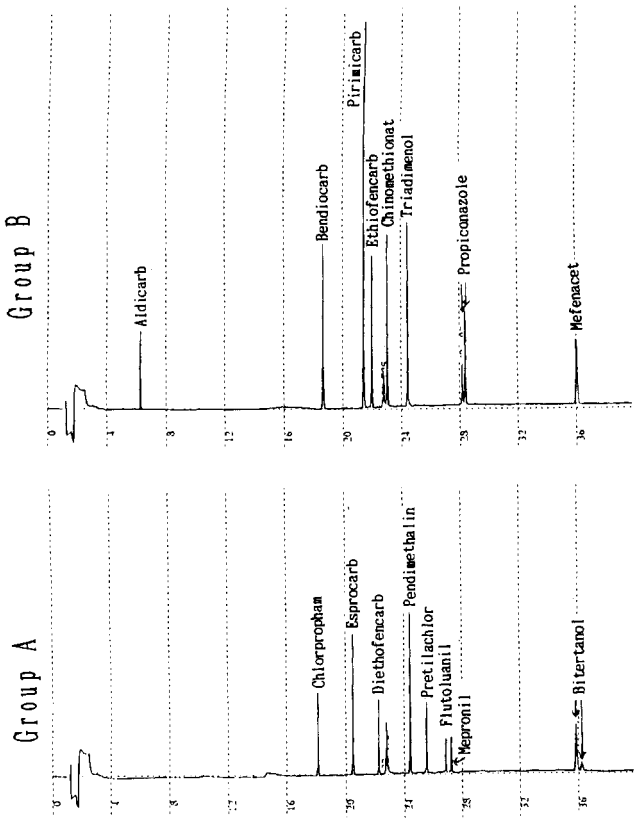


Figure 3. Gas chromatogram of the standard solution of organonitrogen pesticides (FTD-GC). Group A: chlorpropham, esprocarb, diethofencarb, pendimethalin, pretilachlor, flutoluanil, mepronil, bitertanol, 2 μg/mL each. Group B: aldicarb, bendiocarb, pirimicarb, ethiofencarb, chinomethionat, triadimenol, propiconazole, mefenacet, 2 μg/mL each. Conditions for FTD-GC (NPD-GC) are described in the text.

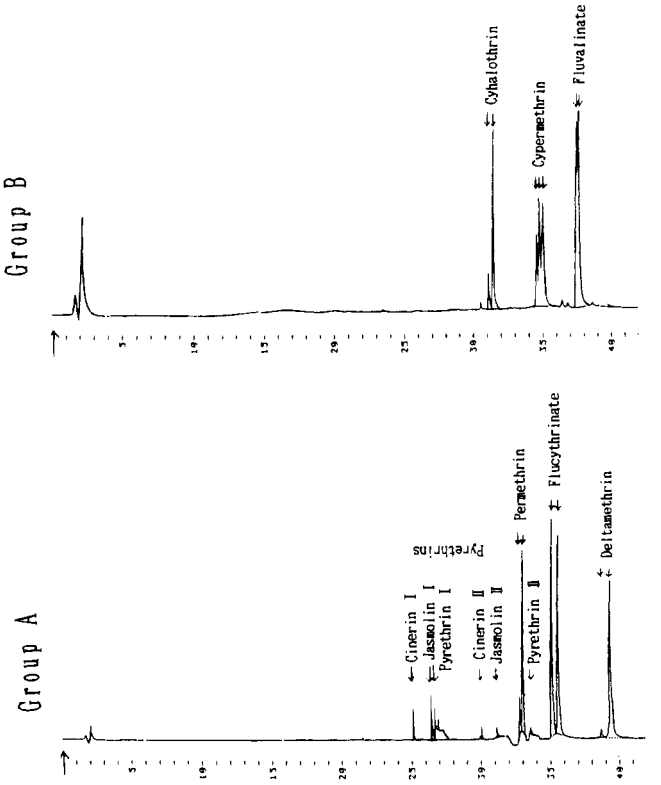


Figure 4. Gas chromatogram of the standard solution of pyrethroid pesticides (ECD-GC). Group A: pyrethrins, permethrin, flucythrinate, deltamethrin, 1 μg/mL each. Group B: cyhalothrin, cypermethrin, fluvalinate, 1 μg/mL each. Conditions for ECD-GC are described in the text.

equipped with an electron capture detector (ECD, ^{63}Ni) was used for determination of organochlorine and pyrethroid pesticides.

With a Hewlett-Packard Model HP 5890II equipped with a flame photometric detector (FPD) operated in the phosphorus mode (P-mode), determination was made of organophosphorus pesticide contents.

By a Shimadzu Model GC-14A (Kyoto, Japan) equipped with a flame thermionic detector (FTD), organonitrogen pesticide content was determined.

(5) GLC Column. Fused-silica caillary columns DB-5 and DB-210 (30 m × 0.25 mm i.d., film thickness 0.25 μm, J&W Scientific, Folsom, CA) were used for pesticide content determination.

Methods. *(1) Extraction. (a) Vegetables and Fruits.* Twenty grams of the minced vegetables or fruits was placed in a blender cup. One hundred milliliters of acetone was added and homogenized at 10^4 rpm for 3 min. The homogenate was filtered through No. 5A filter paper, and the residue was rehomogenized with 100 mL of acetone and then filtered again. The filtrate was combined and concentrated to 50 mL using a rotary evaporator. The concentrate was filtered under vacuum after the addition of 5 g of Celite 545. The filter cake was washed with 50 mL of an acetone/water mixture (1:1 v/v), and the filtrates were combined.

(b) Brown Rice. Twenty grams of the ground brown rice was placed in a blender cup. One hundred milliliters of acetonitrile was added and homogenized at 10^4 rpm for 3 min. The homogenate was filtered through No. 5A filter paper, and the residue was rehomogenized with 100 mL of acetonitrile and then filtered again. The filtrates were combined, and then 50 mL of *n*-hexane saturated with acetonitrile was added to the filtrate and shaken for 5 min. The acetonitrile layer (lower layer) was collected and concentrated to ca. 30 mL using a rotary evaporator.

(2) Liquid–Liquid Partition. One hundred milliliters of 10% NaCl solution and 100 mL of ethyl acetate were added to the extracts prepared in (a) and (b) and shaken vigorously for 5 min. The organic layer was collected. Another 100 mL of ethyl acetate was added to the aqueous layer (lower layer) and shaken again. The pesticides were partitioned in ethyl acetate. The organic layers were collected, dehydrated with ca. 20 g of anhydrous Na_2SO_4, and concentrated to 5 mL using the rotary evaporator (the sample solution).

(3) Column Chromatography. (a) Florisil Column Chromatography. Ten grams of Florisil PR suspended in adequate amounts of *n*-hexane was placed in a chromatographic tube plugged with cotton wool, and then 10 g of anhydrous Na_2SO_4 was added continuously and *n*-hexane drained.

Two milliliters of the sample solution prepared in (2) was evaporated to almost dryness and transferred completely to a Florisil column along with 5 mL of the ethyl acetate/*n*-hexane mixture (3:7 v/v). Organochlorine and pyrethroid pesticides were eluted with 100 mL of this mixture. The eluate was concentrated using a rotary evaporator, and the volume was adjusted to 1 mL with the ethyl acetate/*n*-hexane mixture (3:7 v/v) (the test solution).

(b) Silica Gel Column Chromatography. Ten grams of Kieselgel 60 suspended in adequate amounts of *n*-hexane was placed in a chromatographic tube plugged with cotton wool, and then 10 g of anhydrous Na_2SO_4 was added continuously and *n*-hexane drained.

Two milliliters of the sample solution prepared in (2) was evaporated to almost dryness and transferred completely to a silica gel column along with 5 mL of the acetone/*n*-hexane mixture (3:7 v/v). Organonitrogen pesticides were eluted with 100 mL of this mixture. The eluate was concentrated using a rotary evaporator, and the volume was adjusted to 1 mL with the acetone/*n*-hexane mixture (3:7 v/v) (the test solution).

(4) Determination of Pesticides. Test solutions prepared in (2) and (3) were subjected to GLC for pesticide content determination under the following conditions.

(a) Organophosphorus Pesticides. Conditions: apparatus, HP 5890II; column, DB-210; column temperature, 60 °C (2

Table 1. Retention Times of Pesticides Investigated

organophosphorus pesticides[a]		organochlorine pesticides[b]		organonitrogen pesticides[c]		pyrethroid pesticides[d]		
group	retention time (min)	group	retention time (min)	group	retention time (min)	group	retention time (min)	
A		A		A		A		
dichlorvos	13.97	α-BHC	13.02	chlorpropham	18.15	pyrethrins	25.19	(cinerin I)
diazinon	18.62	γ-BHC	14.03	esprocarb	20.51		26.53	(jasmolin I)
acephate	19.30	heptachlor	17.05	diethofencarb	22.27		26.82	(pyrethrin I)
fenthion	22.11	dicofol	17.92	pendimethalin	24.43		30.08	(cinerin II)
quinalphos	23.32	heptachlor epoxide	19.00	pretilachlor	25.56		31.05	(jasmolin II)
malathion	23.47	*p,p'*-DDE	21.14	flutoluanil	26.90		33.81	(pyrethrin II)
parathion-methyl	23.84	chlorobenzilate	22.33	mepronil	27.27	permethrin	32.74	
fenitrothion	24.17	*p,p'*-DDD	22.76	bitertanol	35.85		32.97	
parathion	24.77	B			36.23	flucythrinate	35.06	
fensulfothion	32.82	β-BHC	13.89	B			35.51	
EPN	32.90	δ-BHC	14.82	aldicarb	6.26	deltamethrin	38.63	
phosalone	36.04	aldrin	17.44	bendiocarb	18.70		39.32	
B		dieldrin	21.18	pirimicarb	21.44	B		
methamidophos	15.11	endrin	22.01	ethiofencarb	22.00	cyhalothrin	31.07	
ethoprophos	18.37	*o,p'*-DDT	22.73	chinomethionat	23.06		31.09	
terbufos	18.96	*p,p'*-DDT	24.04	triadimenol	24.47	cypermethrin	34.57	
etrimfos	19.38			propiconazole	28.20		34.77	
chlorpyrifos	21.47				28.42		35.03	
dimethoate	22.26			mefenacet	36.08	fluvalinate	37.45	
prothiofos	23.21						37.59	
phenthoate	23.50							
α-CVP	23.96							
β-CVP	24.37							
EDDP	27.49							

[a] Conditions for GC are as follows. apparatus, HP 5890 II; column, DB-210; column temperature, 60 °C (2 min) → 8 °C/min → 235 °C; inlet and detector temperature, 240 °C; carrier gas, He; flow rate, 2 mL/min; detector, FPD (P mode); injection method, splitless; injection volume, 2 μL. [b] Conditions for GC are as follows: apparatus, Yanaco G-6800 or HP 5890 II; column, DB-5; column temperature, 60 °C (2 min) → 30 °C/min → 160 °C → 5 °C/min → 280 °C; inlet temperature, 220 °C; detector temperature, 260 °C; carrier gas, He; flow rate, 2 mL/min; detector, ECD; injection method, splitless; injection volume, 2 μL. [c] Conditions for GC are as follows: apparatus, Shimadzu GC-14A; column, DB-210; column temperature, 60 °C (2 min) → 8 °C/min → 235 °C; inlet and detector temperature, 240 °C; carrier gas, He; flow rate, 2 mL/min; detector, FTD (NPD); injection method, splitless; injection volume, 2 μL. [d] Conditions for GC are as follows: apparatus, Yanaco G-6800 or HP 5890 II; column, DB-210; column temperature, 60 °C (2 min) → 8 °C → 280 °C; inlet temperature, 240 °C; detector temperature, 280 °C; carrier gas, He; flow rate, 2 mL/min; detector, ECD; injection method, splitless; injection volume, 2 μL.

min) → 8 °C/min → 235 °C; inlet and detector temperature, 240 °C; carrier gas, He; flow rate, 2 mL/min; detector, FPD (P-mode); injection method, splitless; injection volume, 2 μL.

(b) Organochlorine Pesticides. Conditions: apparatus, Yanaco G-6800 or HP 5890II; column, DB-5; column temperature, 60 °C (2 min) → 30 °C/min → 160 °C → 5 °C/min → 280 °C; inlet temperature, 220 °C; detector temperature, 260 °C; carrier gas, He; flow rate, 2 mL/min; detector, ECD; injection method, splitless; injection volume, 2 μL.

(c) Organonitrogen Pesticides. Conditions: apparatus, Shimadzu GC-14A; column, DB-210; column temperature, 60 °C (2 min) → 8 °C/min → 235 °C; inlet and detector temperature, 240 °C; carrier gas, He; flow rate, 2 mL/min; detector, FTD; injection method, splitless; injection volume, 2 μL.

(d) Pyrethroid Pesticides. Conditions: apparatus, Yanaco G-6800 or HP 5890II; column, DB-5; column temperature, 60 °C (2 min) → 8 °C/min → 280 °C; inlet temperature, 240 °C; detector temperature, 280 °C; carrier gas, He; flow rate, 2 mL/min; detector, ECD; injection method, splitless; injection volume, 2 μL.

(5) Recovery Test. Recovery of 52 pesticides in brown rice, potato, cabbage, lettuce, carrot, cucumber, shiitake, apple, strawberry, and banana was assessd in three separate tests by the fortification of each pesticide working solution to each sample.

The values for this parameter were compared for ethyl acetate and dichloromethane at the liquid–liquid partition step.

Fortification levels were settled according to the sensitivity of each pesticide and the degree of the interferences. Fortification levels were as follows: 0.05 ppm for organophosphorus pesticides; 0.1 ppm for BHC, DDT, endrin, dieldrin, aldrin, heptachlor, and heptachlor epoxide (1 ppm for carrot and shiitake); 0.25 ppm for dicofol and chlorobenzilate (2.5 ppm for carrot and shiitake); 0.25 ppm for organonitrogen pesticides; and 0.25 ppm for pyrethroid pesticides.

The sum of the peak areas of all components or isomers of some organonitrogen and pyrethroid pesticides (bitertanol, propiconazole, pyrethrin, permethrin, flucythrinate, deltamethrin, cyhalothrin, cypermethrin, fluvalinate) was applied for the calculation of the recovery.

RESULTS AND DISCUSSION

GC Conditions for Pesticide Determinations. Optimal conditions for the determinations of organophosphorus, organochlorine, organonitrogen, and pyrethroid pesticides were investigated.

Gas chromatograms of these pesticide standards are shown in Figures 1–4. Retention times of pesticides investigated here (mean of three trials) are indicated in Table 1.

Organophosphorus pesticides, organochlorine and pyrethroid pesticides, and organonitrogen pesticides were determined by FPD-GC, ECD-GC, and FTD-GC (NPD-GC), respectively. NPD-GC could also be used to determine organonitrogen pesticides and N-containing pyrethroid pesticides such as flucythrinate, deltamethrin, cyhalothrin, cypermethrin, and fluvalinate.

Pesticides were divided into two groups and added as fortified samples for the complete separation of pesticides in the recovery tests.

GC/MS is recommended for the precise determination of pesticides in the test solution, particularly for those for which the retention times are very similar.

Preparation of Test Solutions for Sample Analysis. Pesticides in vegetables and fruits were extracted with acetone, and those in crops and other lipid-containing materials, with acetonitrile. Soaking of grains with water was omitted to prevent bumping.

Table 2. Recoveries of Organophosphorus Pesticides[a]

pesticide	brown rice	potato	cabbage	lettuce	carrot	cucumber	shiitake	apple	strawberry	banana
					Extracted with Ethyl Acetate					
dichlorvos	81.6 ± 2.5	83.6 ± 4.5	75.8 ± 0.8	113.0 ± 9.9	77.6 ± 7.0	83.9 ± 6.5	85.0 ± 8.5	88.1 ± 8.3	93.7 ± 8.0	77.7 ± 7.7
diazinon	83.4 ± 8.3	86.9 ± 5.9	79.8 ± 6.9	87.8 ± 5.8	79.4 ± 8.0	85.0 ± 5.0	79.5 ± 7.9	86.7 ± 8.9	83.4 ± 7.9	80.4 ± 5.9
acephate	21.1 ± 5.0	17.8 ± 3.0	14.1 ± 2.3	17.5 ± 4.2	10.7 ± 2.5	13.7 ± 3.4	–[b]	17.7 ± 5.0	10.2 ± 0.5	16.1 ± 4.5
fenthion	83.1 ± 7.5	83.7 ± 6.6	77.5 ± 5.0	76.5 ± 5.6	74.6 ± 1.5	91.5 ± 6.5	69.2 ± 7.1	82.5 ± 7.1	93.2 ± 7.3	101.0 ± 2.5
quinalphos	83.1 ± 8.0	82.2 ± 7.0	74.9 ± 5.0	87.5 ± 7.0	70.8 ± 7.1	80.2 ± 5.9	68.7 ± 6.3	80.8 ± 8.3	77.8 ± 8.0	99.8 ± 5.9
malathion	79.9 ± 3.5	81.9 ± 7.4	78.7 ± 3.3	88.4 ± 6.5	79.5 ± 6.8	84.2 ± 5.5	79.6 ± 8.0	78.7 ± 5.9	85.0 ± 7.3	87.1 ± 7.5
parathion-methyl	84.7 ± 5.0	81.2 ± 7.5	81.5 ± 0.4	93.0 ± 5.5	73.3 ± 5.9	89.4 ± 4.5	91.2 ± 9.2	94.4 ± 9.1	88.8 ± 5.6	99.3 ± 9.9
fenithrothion	86.4 ± 4.5	84.6 ± 6.6	70.9 ± 6.4	90.8 ± 3.5	72.9 ± 6.0	85.2 ± 7.0	79.1 ± 6.5	78.7 ± 6.5	79.5 ± 7.9	103.0 ± 9.8
parathion	85.0 ± 6.1	83.9 ± 5.9	80.9 ± 1.3	81.3 ± 7.6	75.6 ± 5.5	82.2 ± 7.9	72.5 ± 6.5	82.2 ± 6.5	85.4 ± 5.0	74.8 ± 4.6
fensulfothion	73.5 ± 5.9	87.5 ± 5.8	91.4 ± 3.8	98.5 ± 7.9	69.0 ± 7.0	86.0 ± 6.5	74.3 ± 8.0	98.6 ± 9.9	50.0 ± 4.7	85.0 ± 15.0
EPN	86.0 ± 8.9	90.3 ± 6.5	66.7 ± 7.3	77.7 ± 5.5	61.8 ± 5.5	71.6 ± 2.3	51.8 ± 6.8	77.1 ± 6.6	68.3 ± 5.1	93.9 ± 2.5
phosalone	71.6 ± 5.0	93.8 ± 8.3	61.5 ± 5.9	83.1 ± 4.6	59.2 ± 4.0	109.0 ± 6.5	71.4 ± 6.3	78.0 ± 7.9	67.4 ± 3.6	100.0 ± 6.6
methamidophos	26.6 ± 2.5	19.8 ± 2.5	3.4 ± 2.4	18.5 ± 3.1	13.9 ± 1.2	13.5 ± 2.0	–[b]	21.2 ± 1.2	–[b]	19.2 ± 3.5
ethoprophos	83.0 ± 7.7	92.8 ± 6.0	93.7 ± 7.6	92.6 ± 6.0	87.3 ± 2.3	88.3 ± 6.8	–[b]	100.0 ± 9.0	77.8 ± 4.3	86.8 ± 7.2
terbufos	83.7 ± 7.3	92.3 ± 6.0	88.5 ± 8.3	68.1 ± 4.5	79.1 ± 4.5	76.7 ± 5.7	77.1 ± 5.0	85.6 ± 2.0	79.0 ± 8.0	77.8 ± 8.0
etrimfos	83.9 ± 7.9	93.7 ± 7.3	96.3 ± 9.3	96.7 ± 5.0	83.8 ± 6.0	85.9 ± 5.3	80.3 ± 6.9	96.0 ± 4.5	73.4 ± 5.9	89.8 ± 4.5
chlorpyrifos	78.9 ± 6.1	90.8 ± 5.5	89.9 ± 6.5	87.5 ± 4.6	79.5 ± 7.0	87.0 ± 7.9	75.2 ± 6.5	100.0 ± 6.6	75.1 ± 7.0	66.5 ± 6.9
dimethoate	95.0 ± 6.9	87.2 ± 4.6	93.3 ± 8.5	103.0 ± 2.5	86.2 ± 6.8	88.3 ± 8.0	79.3 ± 6.3	104.0 ± 7.3	81.2 ± 4.5	96.1 ± 2.5
prothiofos	71.7 ± 5.9	88.6 ± 6.5	82.9 ± 3.0	82.6 ± 4.5	80.2 ± 7.5	78.0 ± 4.5	92.4 ± 5.7	86.2 ± 5.7	78.3 ± 1.9	66.6 ± 5.4
phenthoate	78.1 ± 7.5	88.3 ± 9.0	97.1 ± 6.5	84.1 ± 5.3	82.2 ± 6.0	83.3 ± 8.0	88.2 ± 6.5	102.0 ± 2.5	76.8 ± 3.9	64.6 ± 4.2
α-CVP	80.0 ± 4.5	88.1 ± 7.5	99.7 ± 6.9	99.1 ± 6.0	85.9 ± 7.2	79.3 ± 3.7	95.8 ± 6.8	91.7 ± 8.7	83.2 ± 5.0	64.6 ± 7.0
β-CVP	93.9 ± 5.0	90.1 ± 4.7	94.2 ± 2.3	100.0 ± 5.2	87.1 ± 6.9	84.0 ± 6.5	90.1 ± 9.7	84.9 ± 6.7	81.9 ± 4.5	73.0 ± 5.5
EDDP	58.5 ± 3.7	93.8 ± 6.0	93.7 ± 1.5	111.0 ± 7.8	87.5 ± 5.5	94.6 ± 5.9	82.6 ± 7.6	88.7 ± 1.6	84.6 ± 6.0	55.0 ± 6.5
					Extracted with Dichloromethane					
dichlorvos	76.5 ± 5.5	84.9 ± 5.0	80.7 ± 4.1	76.2 ± 7.2	77.5 ± 6.5	78.8 ± 3.6	86.2 ± 8.2	84.9 ± 8.3	82.5 ± 7.4	85.4 ± 6.4
diazinon	77.6 ± 6.8	81.5 ± 7.5	79.2 ± 7.0	73.0 ± 6.5	76.1 ± 5.9	79.7 ± 4.2	88.8 ± 8.0	83.7 ± 8.9	75.5 ± 6.5	86.5 ± 6.2
acephate	23.0 ± 6.5	10.0 ± 2.8	17.7 ± 2.5	18.9 ± 4.1	14.5 ± 3.1	18.9 ± 3.5	–[b]	27.0 ± 5.0	13.5 ± 2.7	16.6 ± 5.1
fenthion	79.9 ± 4.5	76.3 ± 5.8	82.1 ± 4.1	80.7 ± 7.2	75.5 ± 2.5	78.0 ± 6.0	90.0 ± 7.4	87.9 ± 7.1	87.9 ± 6.4	90.7 ± 3.7
quinalphos	69.1 ± 5.7	78.3 ± 8.1	76.0 ± 6.5	82.1 ± 5.8	77.4 ± 7.0	75.3 ± 7.2	90.1 ± 2.8	87.9 ± 8.3	81.7 ± 5.0	89.8 ± 6.2
malathion	77.0 ± 5.8	80.7 ± 5.9	78.7 ± 4.5	85.2 ± 5.8	83.1 ± 7.0	81.4 ± 6.2	96.6 ± 8.2	103.0 ± 5.9	86.2 ± 7.2	93.0 ± 6.8
parathion-methyl	79.2 ± 6.2	81.1 ± 7.0	78.3 ± 2.5	84.3 ± 6.0	78.9 ± 6.9	80.8 ± 5.8	86.0 ± 7.8	102.0 ± 9.1	84.1 ± 6.5	88.3 ± 4.5
fenitrothion	79.8 ± 4.3	82.8 ± 7.0	79.3 ± 5.9	82.9 ± 4.0	79.7 ± 7.0	76.8 ± 6.1	89.7 ± 9.4	92.0 ± 6.5	80.8 ± 4.9	88.2 ± 7.2
parathion	81.2 ± 3.6	80.0 ± 6.0	77.4 ± 4.5	80.5 ± 5.8	77.1 ± 6.4	77.7 ± 4.7	85.6 ± 8.8	99.1 ± 6.5	83.7 ± 6.4	85.2 ± 6.4
fensulfothion	61.2 ± 5.7	87.8 ± 6.5	61.4 ± 5.0	92.1 ± 8.2	94.9 ± 7.3	66.5 ± 6.2	77.0 ± 7.4	105.0 ± 9.9	91.7 ± 7.2	73.4 ± 8.9
EPN	81.6 ± 6.6	80.4 ± 3.6	61.9 ± 4.6	92.4 ± 6.1	86.6 ± 6.2	67.9 ± 3.8	66.8 ± 7.3	86.7 ± 6.6	78.1 ± 5.8	87.2 ± 5.1
phosalone	86.7 ± 7.6	88.3 ± 7.6	54.6 ± 5.5	90.6 ± 5.5	95.1 ± 5.8	68.8 ± 5.4	71.8 ± 4.7	85.2 ± 7.9	79.8 ± 4.5	90.9 ± 7.2
methamidophos	13.0 ± 3.1	9.2 ± 3.1	14.3 ± 3.0	10.2 ± 4.0	8.8 ± 3.2	10.7 ± 2.1	–[b]	17.2 ± 1.2	15.1 ± 3.7	11.5 ± 2.5
ethoprophos	78.7 ± 5.9	91.2 ± 7.4	90.2 ± 6.8	84.9 ± 7.2	82.5 ± 5.1	79.4 ± 5.8	–[b]	90.2 ± 9.0	93.8 ± 5.5	86.6 ± 7.0
terbufos	80.0 ± 6.6	88.4 ± 7.0	78.4 ± 7.9	67.9 ± 5.0	79.2 ± 6.1	78.1 ± 6.4	90.8 ± 9.1	83.8 ± 2.0	86.1 ± 7.2	87.4 ± 5.8
etrimfos	80.0 ± 5.8	87.8 ± 6.9	85.1 ± 8.0	78.5 ± 4.9	78.3 ± 4.9	79.1 ± 7.0	87.8 ± 6.6	88.5 ± 4.5	93.8 ± 6.3	82.6 ± 3.7
chlorpyrifos	78.5 ± 6.5	89.3 ± 4.6	82.8 ± 7.1	80.2 ± 5.2	77.8 ± 6.5	76.6 ± 5.9	85.2 ± 6.5	93.4 ± 6.6	91.1 ± 8.2	72.6 ± 4.2
dimethoate	83.0 ± 5.8	86.5 ± 5.4	96.3 ± 8.0	84.2 ± 5.3	82.1 ± 7.0	85.1 ± 7.9	77.5 ± 8.5	102.0 ± 7.3	101.0 ± 6.2	89.8 ± 6.1
prothiofos	68.9 ± 7.1	91.0 ± 7.1	81.6 ± 4.5	84.6 ± 6.0	74.9 ± 5.8	82.7 ± 5.2	81.8 ± 7.4	87.4 ± 1.8	85.7 ± 3.5	78.2 ± 7.0
phenthoate	74.0 ± 6.8	93.0 ± 8.5	94.0 ± 7.0	79.1 ± 5.9	72.7 ± 6.5	80.6 ± 7.2	84.4 ± 5.4	87.9 ± 4.0	96.3 ± 4.9	75.1 ± 3.7
α-CVP	79.7 ± 6.9	94.6 ± 6.9	81.7 ± 7.1	73.7 ± 6.0	76.4 ± 7.0	79.0 ± 4.0	86.0 ± 3.6	87.5 ± 0.7	94.8 ± 5.2	75.7 ± 6.8
β-CVP	79.2 ± 5.8	94.7 ± 5.2	88.9 ± 5.5	73.3 ± 7.2	78.2 ± 7.0	83.8 ± 6.2	87.5 ± 4.5	86.1 ± 1.8	95.7 ± 4.3	85.2 ± 7.0
EDDP	62.7 ± 4.2	99.8 ± 7.0	73.6 ± 4.7	83.7 ± 7.8	73.4 ± 4.0	85.9 ± 4.8	69.1 ± 4.6	99.4 ± 3.0	87.8 ± 7.2	58.2 ± 5.2

[a] Data are means ± SD for three experiments. Fortified level is 0.05 ppm for each pesticide. Conditions for GC are as follows: apparatus, HP 5890 II; column, DB-210; column temperature, 60 °C (2 min) → 8 °C/min → 235 °C; inlet and detector temperature, 240 °C; carrier gas, He; flow rate, 2 mL/min; detector, FPD (P mode); injection method, splitless; injection volume, 2 μL. [b] –, measurement is impossible. There is an interfering peak.

Table 3. Recoveries of Organochlorine Pesticides (Purified with Florisil Column)[a]

pesticide	brown rice	potato	cabbage	lettuce	carrot	cucumber	shiitake	apple	strawberry	banana
					Extracted with Ethyl Acetate					
α-BHC	97.8 ± 4.3	86.5 ± 7.2	96.7 ± 7.4	91.7 ± 4.8	91.8 ± 8.2	90.2 ± 5.8	86.1 ± 6.7	81.2 ± 5.6	93.5 ± 7.5	91.0 ± 9.1
γ-BHC	101.0 ± 7.2	100.0 ± 5.8	103.0 ± 6.0	94.5 ± 7.5	90.5 ± 4.6	94.9 ± 7.6	83.0 ± 7.5	86.5 ± 6.9	95.0 ± 6.8	92.8 ± 8.9
heptachlor	68.7 ± 5.8	30.4 ± 4.3	20.5 ± 4.3	33.3 ± 4.3	33.2 ± 5.4	18.6 ± 2.7	43.0 ± 3.1	52.3 ± 2.4	93.1 ± 8.2	37.2 ± 4.7
dicofol	83.6 ± 7.2	97.8 ± 5.6	91.6 ± 7.2	94.5 ± 6.8	94.9 ± 5.8	76.8 ± 6.2	79.9 ± 4.9	98.4 ± 9.6	101.0 ± 8.5	94.7 ± 9.3
heptachlor epoxide	97.1 ± 8.0	101.0 ± 6.0	97.0 ± 2.5	91.8 ± 9.2	90.2 ± 6.2	96.5 ± 8.9	86.6 ± 3.7	88.7 ± 9.5	95.0 ± 8.5	87.2 ± 8.1
p,p'-DDE	73.5 ± 4.5	43.6 ± 3.8	22.5 ± 3.7	43.4 ± 3.8	78.4 ± 7.5	26.1 ± 1.6	66.5 ± 5.3	53.9 ± 1.4	94.0 ± 3.6	55.6 ± 4.8
chlorobenzilate	99.3 ± 7.5	103.0 ± 8.5	101.0 ± 8.2	101.0 ± 9.3	100.0 ± 4.8	95.8 ± 4.3	89.4 ± 8.2	91.4 ± 9.1	95.8 ± 4.8	89.3 ± 7.3
p,p'-DDD	89.7 ± 5.6	96.0 ± 4.4	101.0 ± 7.5	93.7 ± 8.9	93.4 ± 7.3	81.6 ± 7.0	89.1 ± 7.8	76.8 ± 8.2	103.0 ± 5.1	89.3 ± 8.3
β-BHC	101.0 ± 7.8	102.0 ± 8.8	103.0 ± 8.2	103.0 ± 3.9	94.6 ± 8.9	91.1 ± 8.9	86.2 ± 6.5	96.0 ± 9.3	96.3 ± 6.8	93.9 ± 8.9
δ-BHC	103.0 ± 9.7	98.6 ± 8.2	97.5 ± 7.5	94.2 ± 4.9	92.6 ± 9.3	91.4 ± 7.2	92.4 ± 9.0	99.2 ± 5.6	98.0 ± 8.0	94.8 ± 9.5
aldrin	32.3 ± 4.8	11.9 ± 2.5	4.0 ± 2.7	8.6 ± 2.3	33.9 ± 3.0	7.8 ± 1.5	19.1 ± 2.7	13.9 ± 3.5	99.1 ± 9.0	12.6 ± 3.5
dieldrin	99.8 ± 7.2	103.0 ± 6.5	99.3 ± 5.2	95.5 ± 7.5	90.2 ± 8.0	86.8 ± 7.5	81.2 ± 8.0	91.1 ± 9.4	95.8 ± 4.9	89.3 ± 9.1
endrin	98.9 ± 5.6	100.0 ± 5.8	101.0 ± 6.7	101.0 ± 8.7	90.9 ± 6.9	98.7 ± 8.9	81.8 ± 7.9	96.7 ± 6.1	102.0 ± 3.8	99.1 ± 9.0
o,p'-DDT	93.5 ± 8.2	99.8 ± 7.2	91.2 ± 7.5	82.7 ± 8.5	83.0 ± 5.8	81.3 ± 7.3	84.0 ± 4.8	89.5 ± 6.3	97.2 ± 8.2	94.7 ± 8.3
p,p'-DDT	97.8 ± 7.2	94.9 ± 5.5	98.5 ± 7.8	91.8 ± 9.0	80.9 ± 7.2	90.0 ± 6.5	84.8 ± 5.1	92.3 ± 2.8	106.0 ± 6.5	99.0 ± 6.5
					Extracted with Dichloromethane					
α-BHC	100.0 ± 5.4	95.6 ± 5.8	93.2 ± 6.8	96.0 ± 8.2	94.3 ± 6.3	97.2 ± 6.5	91.7 ± 8.0	83.2 ± 6.8	99.6 ± 8.2	98.3 ± 7.8
γ-BHC	99.9 ± 5.7	101.0 ± 7.5	96.7 ± 7.5	87.9 ± 6.9	97.5 ± 5.8	100.0 ± 8.2	88.9 ± 5.9	87.9 ± 1.2	98.0 ± 5.3	98.6 ± 9.2
heptachlor	69.3 ± 6.2	16.8 ± 3.6	34.7 ± 3.4	23.5 ± 2.7	24.3 ± 2.7	21.4 ± 3.5	58.1 ± 6.0	40.1 ± 8.2	89.7 ± 6.9	48.7 ± 5.3
dicofol	87.6 ± 6.5	94.2 ± 4.7	95.1 ± 8.1	87.6 ± 5.4	95.5 ± 6.5	86.2 ± 8.2	84.5 ± 5.3	100.0 ± 7.4	98.7 ± 7.0	102.0 ± 9.9
heptachlor epoxide	96.0 ± 7.5	101.0 ± 6.5	94.9 ± 7.2	100.0 ± 8.9	96.2 ± 4.1	101.0 ± 9.1	94.7 ± 1.8	88.7 ± 5.5	94.2 ± 4.9	94.8 ± 6.8
p,p'-DDE	73.7 ± 5.0	27.7 ± 2.0	41.9 ± 4.3	29.1 ± 3.5	71.4 ± 5.5	32.5 ± 3.6	75.0 ± 2.7	38.3 ± 5.3	100.0 ± 5.3	62.9 ± 7.2
chlorobenzilate	94.8 ± 7.2	103.0 ± 7.2	98.7 ± 5.8	96.6 ± 8.2	102.0 ± 9.2	97.8 ± 5.4	95.8 ± 7.6	95.3 ± 2.5	84.4 ± 5.8	98.3 ± 6.5
p,p'-DDD	92.7 ± 6.1	96.9 ± 6.0	94.8 ± 8.5	87.2 ± 7.3	99.0 ± 5.9	93.4 ± 4.7	95.6 ± 8.9	82.9 ± 1.7	88.9 ± 6.2	99.5 ± 9.3
β-BHC	102.0 ± 8.2	102.0 ± 7.8	102.0 ± 9.2	103.0 ± 6.1	96.6 ± 7.6	97.2 ± 6.5	91.6 ± 7.5	98.1 ± 9.1	96.2 ± 3.9	101.0 ± 6.7
δ-BHC	100.0 ± 8.5	104.0 ± 9.2	96.7 ± 6.8	88.5 ± 8.2	95.6 ± 8.9	97.4 ± 6.8	85.9 ± 8.1	96.0 ± 9.4	98.0 ± 7.9	103.0 ± 8.5
aldrin	30.0 ± 4.5	4.1 ± 1.5	8.5 ± 3.1	5.0 ± 2.1	24.7 ± 4.2	10.2 ± 2.7	30.5 ± 3.5	11.5 ± 3.4	98.6 ± 8.0	23.1 ± 2.0
dieldrin	97.6 ± 8.1	103.0 ± 7.2	97.7 ± 6.8	103.0 ± 4.8	92.3 ± 6.5	94.1 ± 8.5	85.8 ± 7.4	94.8 ± 7.4	90.4 ± 5.3	98.1 ± 8.3
endrin	101.0 ± 5.2	102.0 ± 7.5	98.4 ± 7.3	95.2 ± 6.7	91.8 ± 8.0	104.0 ± 7.7	88.0 ± 8.2	99.3 ± 2.0	94.2 ± 4.9	103.0 ± 8.9
o,p'-DDT	90.2 ± 8.0	104.0 ± 5.3	102.0 ± 8.2	85.1 ± 7.5	86.1 ± 7.5	92.1 ± 6.3	89.4 ± 5.3	96.1 ± 5.6	89.8 ± 7.3	101.0 ± 7.8
p,p'-DDT	98.4 ± 4.9	99.1 ± 6.2	97.1 ± 8.5	84.1 ± 4.9	84.5 ± 8.0	101.0 ± 4.8	90.1 ± 4.8	102.0 ± 9.5	92.0 ± 8.5	102.0 ± 8.5

[a] Data are means ± SD for three experiments. Fortified levels are 0.1 ppm for BHC, DDT, endrin, dieldrin, aldrin, heptachlor, and heptachlor-epoxide (1 ppm in the case of carrot and shiitake) and 0.25 ppm for dicofol and chlorobenzilate (2.5 ppm in the case of carrot and shiitake). Conditions for GC are as follows: apparatus, Yanaco G-6800 or HP 5890 II; column, DB-5; column temperature, 60 °C (2 min) → 30 °C/min → 160 °C → 5 °C/min → 280 °C; inlet temperature, 220 °C; detector temperature, 260 °C; carrier gas, He; flow rate, 2 mL/min; detector, ECD; injection method, splitless; injection volume, 2 μL.

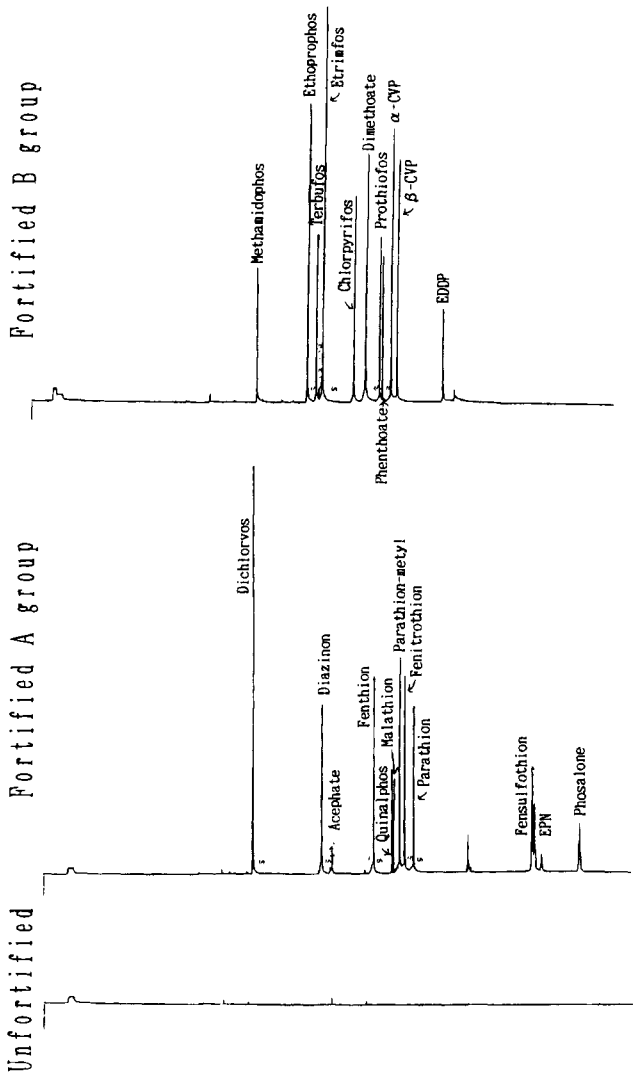


Figure 5. Gas chromatograms of the sample solutions of unfortified and fortified apple. Sample solutions were prepared as described in the text. Pesticides were extracted with ethyl acetate and determined by FPD-GC. See the text for details.

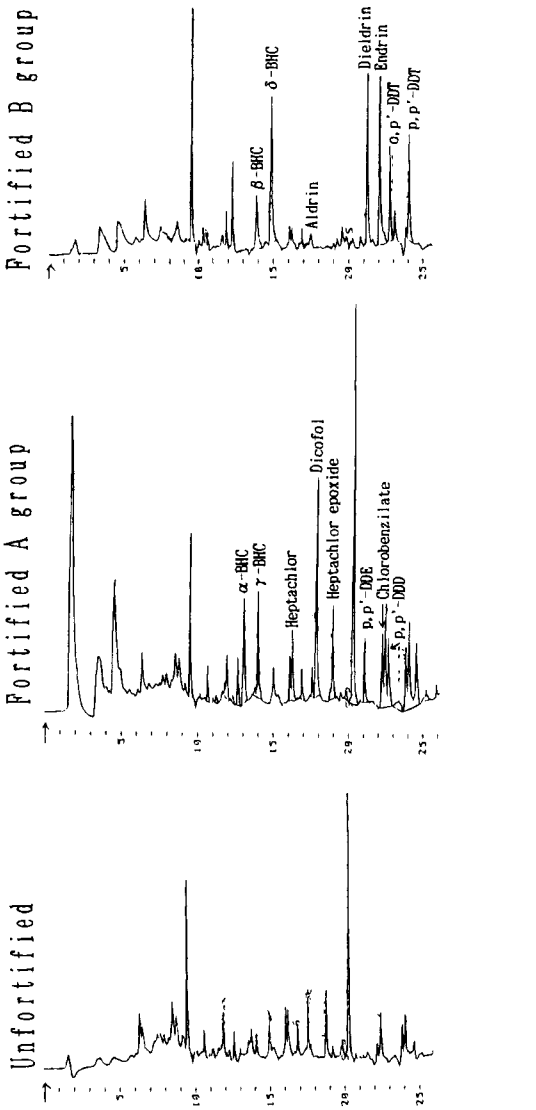


Figure 6. Gas chromatograms of the test solutions of unfortified and fortified apple. Sample solutions were prepared as described in the text. Pesticides were extracted with ethyl acetate, cleaned up by Florisil column chromatography, and determined by ECD-GC. See the text for details.

Lipids were removed from the acetonitrile extracts by the acetonitrile/*n*-hexane partition.

The volume of acetone after concentration in the extraction step had to be adjusted to 50 mL to obtain good recovery reproducibility, particularly in the case of organochlorine and pyrethroid pesticides. The concentrate was filtered under vacuum following the addition of 5 g of Celite 545. The addition of Celite 545 could be omitted in most case of fruits and vegetables.

Column chromatography was not necessary for the quantitation of organophosphorus pesticides. The quantitation of organochlorine and pyrethroid pesticides could not be conducted without cleanup, and thus Florisil column chromatography was performed. Cleanup by silica gel column chromatography was necessary in the quantitation of organonitrogen pesticides.

Determination of organonitrogen pesticides and certain pyrethroid pesticides was possible by NPD-GC (FTD-GC). A decrease in the number of interfering peaks in the NPD-GC gas chromatograms was observed in the case of pyrethroid pesticides.

Recovery Test. *(1) Organophosphorus Pesticides.* Figure 5 shows the gas chromatograms of the unfortified and fortified apple sample solutions (extracted with ethyl acetate). No interfering peaks were observed in any sample solutions except for shiitake.

Recovery data are indicated in Table 2. Recoveries of organophosphorus pesticides, except for acephate and methamidophos, were 50.0–113.0% (with ethyl acetate) and 54.6–105.0% (with dichloromethane). The recoveries of acephate (10.0–27.0%) and methamidophos (3.4–26.6%) was lower than those of other pesticides.

No significant difference in the recovery of organophosphorus pesticides could be detected regardless of the organic solvents used at the liquid–liquid partition step.

(2) Organochlorine Pesticides. Figure 6 shows the gas chromatograms of the unfortified and fortified apple test solutions (extracted with ethyl acetate). No interfering peak was observed in the sample solution except for shiitake (near BHC) and carrot (near DDT). The fortification levels were higher for shiitake and carrot than for other samples.

Recovery data are indicated in Table 3. Recoveries of organochlorine pesticides except for heptachlor, *p,p'*-DDE, and aldrin were 76.8–106.0% (with ethyl acetate) and 82.9–104.0% (with dichloromethane). The recoveries of heptachlor (16.8–69.3%), *p,p'*-DDE (22.5–78.4%), and aldrin (4.0–33.9%) in all samples except strawberry were relatively less than for other pesticides.

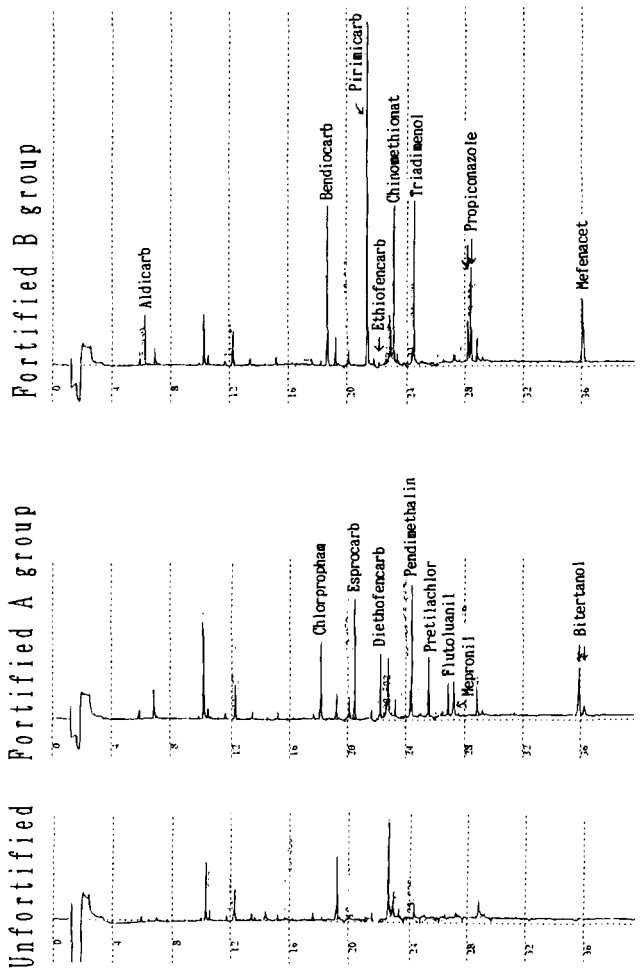


Figure 7. Gas chromatograms of the test solutions of unfortified and fortified apple. Sample solution was prepared as described in the text. Pesticides were extracted with ethyl acetate, cleaned up by silica gel column chromatography, and determined by FTD-GC (NPD-GC). See the text for details.

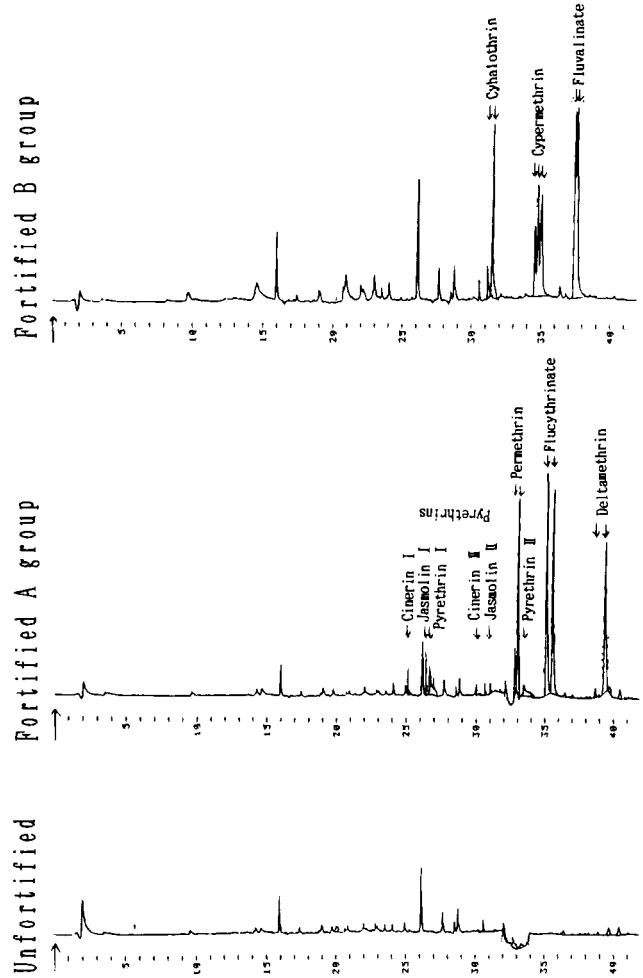


Figure 8. Gas chromatograms of the test solutions of unfortified apple. Sample solutions were prepared as described in the text. Pesticides were extracted with ethyl acetate, cleaned up by Florisil column chromatography, and determined by ECD-GC. See the text for details.

No significant difference in the recovery of organochlorine pesticides was seen regardless of the organic solvent used at the liquid–liquid partition step.

(3) Organonitrogen Pesticides. Figure 7 shows the gas chromatograms of the unfortified and fortified apple test solutions (extracted with ethyl acetate). No interfering peak was detected for the sample solution except cabbage.

Recovery data are indicated in Table 4. Recoveries of organonitrogen pesticides except for aldicarb and ethiofencarb were 50.6–119.0% (with ethyl acetate) and 51.1–118.0% (with dichloromethane). Those of aldicarb and ethiofencarb extracted with ethyl acetate were 17.9–91.9% and 0–46.0%, and with dichloromethane, 75.8–97.7% and 15.2–64.7%, respectively.

No significant difference in the recovery of organonitrogen pesticides except for aldicarb and ethiofencarb was evident regardless of organic solvent used at the liquid–liquid partition step. Recovery of aldicarb and ethiofencarb was somewhat better when extracted with dichloromethane than with ethyl acetate. Recovery of certain organonitrogen pesticides was less in shiitake, particularly when extracted with dichloromethane, compared to other samples.

(4) Pyrethroid Pesticides. Figure 8 shows the gas chromatograms of the unfortified and fortified apple test solutions (extracted with ethyl acetate). No interfering peaks were observed in any sample solutions except for carrot and apple, but several interfering peaks were observed near pyrethrins in sample solutions of carrot and apple.

Recovery data are indicated in Table 5. Recoveries of pyrethroid pesticides were 63.1–107.5% (with ethyl acetate) and 60.0–112.4% (with dichloromethane).

There was no significant difference in the recovery of pyrethroid pesticides regardless of the organic solvents at the liquid–liquid partition step. The recovery of pyrethroid pesticides was less for carrot and banana.

Pesticide Residue Monitoring Studies. The 48 kinds of pesticide residues examined in this study were monitored by the proposed method of multiresidue analysis for 10 kinds of agricultural products:, brown rice, potato, cabbage, lettuce, carrot, cucumber, shiitake (Japanese mushroom), apple, strawberry, and banana.

The detection limits (ppm or μg/g for each sample) were 0.001 ppm for organophosphorus and organochlorine pesticides and 0.01 ppm for organonitrogen and pyrethroid pesticides by the proposed method.

No pesticide was detected from any unfortified sample except bitertanol in banana, from which bitertanol was detected at the level of 0.31 ppm.

Application of the Proposed Multiresidue Method. Chart 1 provides a summary of the proposed method for multiresidue analysis.

This method was found to be effective for all 48 pesticides: 20 organophosphorus pesticides, 7 organo-

Table 4. Recoveries of Organonitrogen Pesticides (Purified with Silica Gel Column)[a]

pesticide	brown rice	potato	cabbage	lettuce	carrot	cucumber	shiitake	apple	strawberry	banana
					Extracted with Ethyl Acetate					
chlorpropham	70.1 ± 6.3	93.3 ± 7.4	78.8 ± 8.0	74.3 ± 6.3	81.8 ± 8.3	89.0 ± 5.6	88.1 ± 4.7	84.2 ± 9.8	93.5 ± 8.3	94.9 ± 9.3
esprocarb	86.6 ± 4.8	92.9 ± 4.1	85.9 ± 7.9	87.3 ± 8.3	82.1 ± 3.9	82.1 ± 9.3	79.2 ± 2.1	89.9 ± 3.0	91.8 ± 3.6	82.2 ± 8.0
diethofencarb	42.5 ± 5.3	97.7 ± 1.2	119.0 ± 13.0[b]	91.3 ± 9.1	87.4 ± 7.5	84.9 ± 9.4	83.1 ± 8.7	94.0 ± 2.4	96.1 ± 7.3	50.6 ± 6.0
pendimethalin	69.7 ± 3.9	79.3 ± 8.6	79.9 ± 9.5[b]	88.7 ± 8.9	83.7 ± 8.5	63.7 ± 7.2	73.8 ± 1.3	76.3 ± 7.4	98.7 ± 4.9	79.1 ± 7.8
pretilachlor	67.0 ± 5.5	90.9 ± 2.4	87.9 ± 7.3	92.2 ± 1.3	82.2 ± 3.9	88.5 ± 8.7	73.9 ± 9.3	90.7 ± 4.5	99.5 ± 6.5	82.7 ± 6.3
flutoluanil	65.9 ± 6.4	90.8 ± 5.9	85.2 ± 5.9	92.8 ± 7.3	84.2 ± 7.3	98.8 ± 1.0	72.1 ± 6.6	92.2 ± 9.2	101.1 ± 8.3	87.9 ± 8.3
mepronil	73.1 ± 7.3	83.9 ± 9.1	109.0 ± 12.9[b]	97.9 ± 9.6	111.0 ± 11.5[b]	88.6 ± 9.4[b]	90.0 ± 3.7	97.0 ± 5.9[b]	113.0 ± 8.6[b]	103.0 ± 5.8
bitertanol	103.0 ± 8.3	93.2 ± 8.9	96.9 ± 10.5[b]	85.7 ± 8.7[b]	83.4 ± 8.3	119.0 ± 13.4[b]	92.1 ± 10.3	102.5 ± 3.4[b]	100.0 ± 9.9[b]	109.2 ± 8.9[c]
aldicarb	56.2 ± 4.9	68.9 ± 7.3	60.9 ± 6.3	59.7 ± 6.3	22.1 ± 3.5	17.9 ± 3.5	64.2 ± 9.6	43.3 ± 7.2	70.4 ± 7.3	91.9 ± 9.3
bendiocarb	101.0 ± 8.9	74.7 ± 8.7	83.1 ± 8.3	83.5 ± 8.2	83.6 ± 5.3	89.4 ± 2.8	67.2 ± 8.0	89.9 ± 7.3	77.9 ± 8.3	88.5 ± 7.3
pirimicarb	80.0 ± 7.3	69.4 ± 8.0	79.5 ± 7.0	81.4 ± 7.8	85.8 ± 8.5	90.9 ± 1.8	63.7 ± 9.0	80.1 ± 9.9	55.3 ± 4.9	98.4 ± 8.3
ethiofencarb	6.7 ± 2.5	17.1 ± 7.3	29.5 ± 5.9	17.0 ± 3.5	1.5 ± 1.5[b]	0.0 ± 0.0	29.7 ± 5.3	0.9 ± 0.9	40.3 ± 6.3	46.0 ± 4.7
chinomethionat	81.1 ± 6.3	72.5 ± 7.7	65.7 ± 6.3	83.8 ± 8.3	82.8 ± 8.3	85.6 ± 9.9	54.6 ± 9.9	78.3 ± 9.7	71.1 ± 7.3	95.8 ± 9.3
triadimenol	99.1 ± 5.9	67.9 ± 7.2	39.8 ± 6.0	92.7 ± 3.9	74.6 ± 5.3	96.9 ± 9.8	70.0 ± 6.9	84.6 ± 3.7	71.5 ± 6.9	112.0 ± 10.5
propiconazole	78.5 ± 5.0	77.2 ± 7.3	80.1 ± 7.9	91.7 ± 2.6	88.2 ± 5.3	98.4 ± 9.2	69.5 ± 8.6	87.6 ± 9.6	79.5 ± 5.3	109.0 ± 9.3
mefenacet	82.6 ± 7.3	79.4 ± 8.2	83.0 ± 8.9	96.2 ± 8.6	80.1 ± 3.9	93.3 ± 4.7	70.5 ± 8.0	90.3 ± 9.3	78.9 ± 5.3	67.5 ± 7.3
					Extracted with Dichloromethane					
chlorpropham	107.0 ± 5.5	84.7 ± 3.9	96.3 ± 9.9	64.1 ± 7.3[b]	79.9 ± 8.0	91.4 ± 3.5	62.1 ± 1.8	90.8 ± 10.4	94.9 ± 9.3	99.3 ± 10.5
esprocarb	60.2 ± 5.3	103.0 ± 10.0	98.5 ± 7.9[b]	62.9 ± 8.3	80.0 ± 5.1	90.0 ± 9.1	54.0 ± 2.9	89.5 ± 5.1	90.4 ± 6.6	89.4 ± 9.3
diethofencarb	55.4 ± 2.7	104.0 ± 7.5	115.0 ± 12.6	72.3 ± 1.6	85.2 ± 4.9	93.2 ± 9.0	53.7 ± 8.3	92.6 ± 10.3	89.1 ± 8.3	58.7 ± 5.8
pendimethalin	96.8 ± 4.3	95.3 ± 5.7	103.3 ± 9.9[b]	61.7 ± 7.5	82.3 ± 7.5	89.8 ± 9.9	62.4 ± 9.6	78.8 ± 8.6	93.1 ± 5.5	86.7 ± 8.3
pretilachlor	78.6 ± 6.5	95.7 ± 3.4	101.3 ± 7.6	65.1 ± 6.8	80.9 ± 3.1	95.5 ± 10.1	41.1 ± 8.9	79.6 ± 9.2	92.3 ± 7.3	90.8 ± 7.3
flutoluanil	95.6 ± 8.1	93.6 ± 6.8	91.4 ± 4.8	69.0 ± 7.1	94.5 ± 6.9	91.7 ± 7.6	37.6 ± 8.9	94.1 ± 10.8	105.1 ± 9.3	98.4 ± 7.9
mepronil	92.2 ± 6.9	99.0 ± 9.3	115.0 ± 16.9[b]	94.1 ± 9.7	112.0 ± 13.1[b]	100.0 ± 14.5[b]	54.1 ± 7.1[b]	96.5 ± 11.7[b]	105.0 ± 9.9[b]	105.4 ± 8.3
bitertanol	118.0 ± 9.9	99.5 ± 7.7	92.4 ± 10.6[b]	87.0 ± 7.5	91.8 ± 8.3	88.7 ± 10.1[b]	37.2 ± 6.3	102.2 ± 8.7	92.3 ± 9.9[b]	108.5 ± 9.1[c]
aldicarb	92.5 ± 5.3	85.9 ± 8.5	88.1 ± 8.8	83.9 ± 9.1	83.5 ± 4.9	93.5 ± 6.6	75.8 ± 9.3	84.2 ± 9.0	86.3 ± 6.6	97.7 ± 8.9
bendiocarb	82.1 ± 7.0	78.9 ± 4.7	104.2 ± 10.2	86.0 ± 8.3	91.7 ± 6.5	94.9 ± 1.1	66.2 ± 5.4	88.6 ± 6.7	81.3 ± 5.7	87.7 ± 8.4
pirimicarb	86.9 ± 5.9	74.5 ± 7.2	96.6 ± 9.7	81.1 ± 8.9	97.8 ± 4.7	97.7 ± 1.1	64.8 ± 1.1	84.1 ± 9.1	73.9 ± 8.3	92.5 ± 5.9
ethiofencarb	44.2 ± 4.3	36.0 ± 7.0	47.1 ± 6.2[b]	64.7 ± 6.9	43.8 ± 5.3[b]	15.2 ± 2.3	32.7 ± 6.9	57.0 ± 7.7	47.5 ± 4.7	43.6 ± 5.3
chinomethionat	76.9 ± 5.9	85.0 ± 6.9	91.3 ± 9.2	79.4 ± 8.3	90.7 ± 7.9	91.6 ± 8.1	66.0 ± 1.4	80.7 ± 9.5	80.1 ± 8.5	81.9 ± 4.6
triadimenol	101.0 ± 8.3	72.5 ± 8.0	85.4 ± 10.7[b]	88.6 ± 7.1	81.9 ± 6.3	105.8 ± 10.2	67.1 ± 4.2	79.9 ± 9.6	81.5 ± 4.1	104.0 ± 10.0
propiconazole	75.0 ± 4.2	83.5 ± 9.7	96.2 ± 6.8	85.0 ± 5.3	82.6 ± 4.7	104.1 ± 10.0	68.7 ± 4.5	87.8 ± 7.6	90.2 ± 3.9	92.4 ± 9.0
mefenacet	82.6 ± 3.9	78.4 ± 2.5	93.3 ± 9.1	84.4 ± 3.6	85.0 ± 6.3	101.8 ± 3.2	73.6 ± 9.7	91.0 ± 8.9	90.4 ± 7.3	51.1 ± 6.5

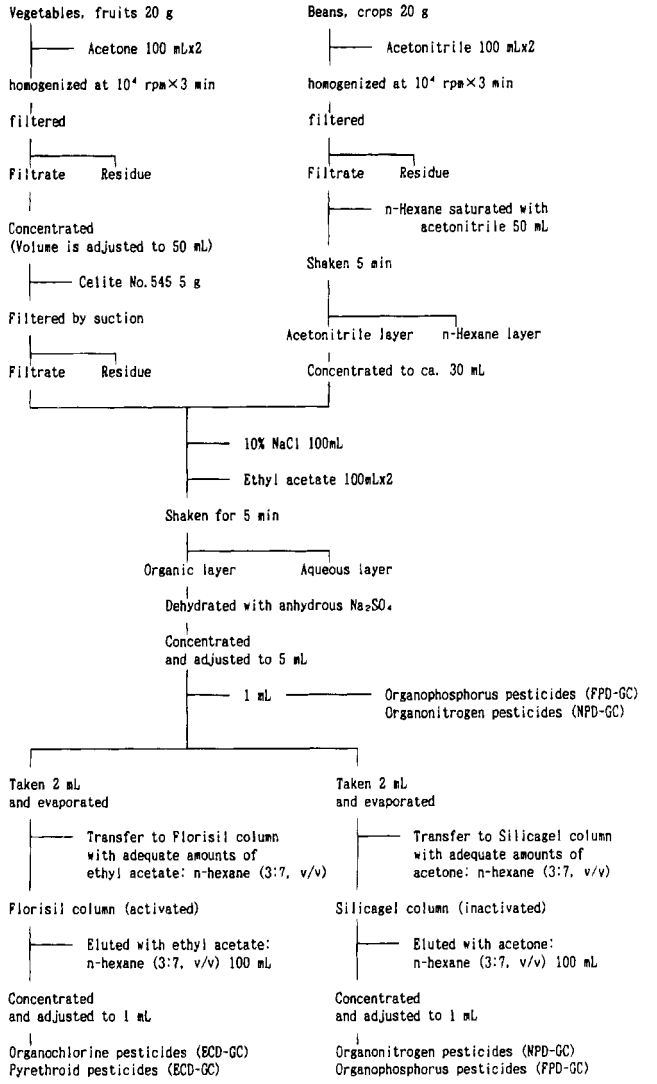
[a] Data are means ± SD for three experiments. Fortified levels are 0.25 ppm. Conditions for GC are as follows: apparatus, Shimadzu GC-14A; column, BD-210; column temperature, 60 °C (2 min) → 8 °C/min → 235 °C; inlet and detector temperature, 240 °C; carrier gas, He; flow rate, 2 mL/min; detector, FTD (NPD); injection method, splitless; injection volume, 2 μL. [b] There is an interfering peak. [c] Pesticide was detected from the unfortified sample (0.31 ppm).

Table 5. Recoveries of Pyrethroid Pesticides (Purified with Florisil Column)[a]

pesticide	brown rice	potato	cabbage	lettuce	carrot	cucumber	shiitake	apple	strawberry	banana
					Extracted with Ethyl Acetate					
pyrethrins	94.4 ± 0.8	89.0 ± 11.2	92.6 ± 9.3	98.5 ± 4.2	82.3 ± 11.6[b]	77.5 ± 4.1	63.6 ± 8.1	77.0 ± 6.7	83.6 ± 8.3	68.5 ± 9.8
permethrin	107.5 ± 2.1	89.6 ± 10.3	91.9 ± 8.9	94.3 ± 8.7	85.3 ± 7.4	83.5 ± 4.7	81.4 ± 9.2	101.0 ± 1.8	92.1 ± 9.1	63.5 ± 9.5
flucythrinate	93.5 ± 2.2	94.6 ± 9.3	87.9 ± 9.1	99.9 ± 7.8	71.2 ± 7.6	82.8 ± 6.2	65.6 ± 6.9	101.2 ± 4.6	97.7 ± 4.7	63.1 ± 10.5
deltamethrin	82.1 ± 3.5	89.1 ± 9.2	75.8 ± 9.3	93.6 ± 3.7	69.8 ± 7.0	87.9 ± 7.1	69.4 ± 7.2	89.6 ± 3.0	98.6 ± 3.4	70.7 ± 9.7
cyhalothrin	89.7 ± 5.2	91.6 ± 9.5	84.7 ± 3.5	87.5 ± 2.9	90.3 ± 11.8	88.4 ± 3.3	80.0 ± 1.1	89.8 ± 3.9	83.9 ± 0.1	68.2 ± 9.8
cypermethrin	87.3 ± 4.2	89.6 ± 9.6	87.1 ± 3.7	82.6 ± 5.8	74.5 ± 8.9	89.4 ± 2.4	75.6 ± 4.5	95.3 ± 4.7	93.5 ± 2.0	66.5 ± 8.6
fluvalinate	81.0 ± 5.9	90.7 ± 8.5	86.8 ± 3.3	89.2 ± 7.6	69.8 ± 9.3	92.7 ± 2.9	73.7 ± 5.4	95.3 ± 5.3	91.3 ± 2.1	67.6 ± 9.5
					Extracted with Dichloromethane					
pyrethrins	76.4 ± 4.7	99.5 ± 12.2	85.5 ± 2.1	80.6 ± 6.2	111.4 ± 11.3[b]	83.9 ± 3.3	71.0 ± 3.0	74.0 ± 9.9	75.6 ± 8.3	75.0 ± 9.3
permethrin	86.3 ± 0.6	83.9 ± 1.0	83.8 ± 4.6	60.8 ± 1.1	93.1 ± 8.4	91.3 ± 8.6	76.5 ± 9.0	112.4 ± 11.6	79.8 ± 8.7	61.3 ± 10.0
flucythrinate	77.9 ± 9.5	86.1 ± 1.0	88.3 ± 5.0	73.3 ± 10.9	88.5 ± 4.5	82.0 ± 8.0	60.0 ± 4.5	104.1 ± 10.4	80.7 ± 9.4	60.0 ± 9.7
deltamethrin	80.1 ± 4.8	82.3 ± 1.8	64.3 ± 3.5	64.1 ± 10.1	86.8 ± 0.2	88.5 ± 2.3	72.7 ± 6.4	84.0 ± 8.3	82.4 ± 9.7	65.3 ± 9.3
cyhalothrin	94.0 ± 1.2	91.7 ± 6.1	88.8 ± 9.3	81.3 ± 1.3	61.2 ± 10.5	77.7 ± 7.6	77.0 ± 0.8	90.5 ± 6.3	83.7 ± 10.0	64.8 ± 3.3
cypermethrin	75.7 ± 6.6	86.9 ± 8.1	89.6 ± 10.3	78.8 ± 1.1	65.3 ± 9.6	79.4 ± 8.9	73.3 ± 4.4	97.8 ± 10.6	84.7 ± 8.9	65.5 ± 7.6
fluvalinate	87.2 ± 4.2	91.8 ± 9.4	92.2 ± 9.8	91.3 ± 5.7	84.9 ± 14.0	82.1 ± 5.3	69.2 ± 4.7	93.9 ± 5.4	84.9 ± 9.7	63.1 ± 5.2

[a] Data are mean ± SD for three experiments. Fortified levels are 0.25 ppm. Conditions for GC are as follows: apparatus, Yanaco G-6800 or HP 5890 II; column, DB-210; column temperature, 60 °C (2 min) → 8 °C → 280 °C; inlet temperature, 240 °C; detector temperature, 280 °C; carrier gas, He; flow rate, 2 mL/min; detector, ECD; injection method, splitless; injection volume, 2 μL. [b] There is an interfering peak.

Chart 1. Method for Multiresidue Analysis



chlorine pesticides, 14 organonitrogen pesticides, and 7 pyrethroid pesticides.

Ethyl acetate is recommended for use at the liquid–liquid partition step because organochlorine solvents such as dichloromethane are hazardous to man, although the recovery of some pesticides such as aldicarb and ethiofencarb was better when dichloromethane was used.

The present method, however, was found not to be effective for hydrophilic or heat-unstable pesticides such as acephate, methamidophos, dimetipin, aldicarb, ethiofencarb, propamocarb, amitraz, and clofentezine. Other methods should be used for their determination.

LITERATURE CITED

Countermeasure Society for Environmental Preservation of Pesticides. *Handbook of Reservation Standards for Registered Pesticides* (in Japanese); Kagaku Kogyo Nippo-sha: Tokyo, 1990.

Garcia, A. V.; Pradas, E. G.; Vidal, J. M.; Lopez, A. A. Simple and efficient multiresidue screening method for analysis of nine halogen-containing pesticides on peppers and cucumbers by GLC-ECD. *J. Agric. Food Chem.* **1991,** *39,* 2188–2191.

Hernandez-Hernandez, J.; Sancho, J. V.; Beltran, J.; Medina, J. Study of several multiresidue methods for the determination of pesticides in citrus fruits by HPLC using diode-array detection. *Quim. Anal.* **1991,** *10,* 75–92.

Holstege, D. M.; Scharberg, D. L.; Richardson, E. R.; Moller, G. Multiresidue screen for organophosphorus insecticides using gel permiation chromatography-silica gel clean-up. *J. Assoc. Off. Anal. Chem.* **1991,** *74*, 394–399.

Hsu, J. P.; Schattenberg, H. J., III; Garza, M. Fast turnaround multiresidue screen for pesticides in produce. *J. Assoc. Off. Anal. Chem.* **1991,** *74*, 886–892.

Japanese Food and Hygienic Society. Standards of Foods and Food Additives (in Japanese). *J. Food Hyg. Soc. Jpn.* **1993,** *34* (*Suppl.*), 6–24.

Kadenczki, L.; Arpad, Z.; Gardi, I.; Ambrus, A.; Gyorfi, L.; Resse, G.; Ebing, W. Column extraction of residues of several pesticides from fruits and vegetables: A simple multiresidue analysis method. *J. AOAC Int.* **1992,** *75*, 53–61.

Lee, S. M.; Wylie, P. L. Comparison of the atomic emission detector to other element-selective detectors for the gas chromatographic analysis of pesticide residues. *J. Agric. Food Chem.* **1991,** *39*, 2192–2199.

Leoni, V.; Caricchia, A. M.; Chiavarini, S. Multiresidue method for quantitation of organophosphorus pesticides in vegetable and animal foods. *J. AOAC Int.* **1992,** *75*, 511–518.

Liao, W.; Joe, T.; Cusick, W. G. Multiresidue screening method for fresh fruits and vegetables with gas chromatographic/mass spectrometric detection. *J. Assoc. Off. Anal. Chem.* **1991,** *74*, 554–565.

Liu, C.-H.; Mattern, G. C.; Yu, X.; Rosen, R. T.; Rosen, J. D. Mulriresidue determination of nonvolatile and thermally labile pesticides. *J. Agric. Food Chem.* **1991,** *39*, 718–723.

Miles, C. J.; Zhou, M. Multiresidue pesticide determinations with a simple photoconductivity HPLC detector. *J. Agric. Food Chem.* **1990,** *38*, 986–989.

Ministry of Health and Welfare of Japan. Bulletin 239, Oct 27, 1992.

Ministry of Health and Welfare of Japan. Bulletin 68, March 4, 1993a.

Ministry of Health and Welfare of Japan. Bulletin 200, Sept 14, 1993b.

Received for review March 9, 1994. Accepted August 5, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1994.