Multiresidue Procedures for the Determination of Pesticides in Food Using Capillary Gas Chromatographic, Flame Photometric, and Mass Spectrometric Techniques

Makoto Miyahara,*,† Yutaka Okada,‡ Hisashi Takeda,§ Gaku Aoki,§ Akihiko Kobayashi,|| and Yukio Saito†

Division of Foods, National Institute of Health Sciences, 1-18-1 Kamiyoga, Setagaya-ku, Tokyo 158, Japan, Food Inspection Center, Japan Medical Foods Association, 5-3-11 Maesawa, Higashikurume 203, Japan, Center for Inspection of Imported Foods and Infectious Disease, Yokohama Quarantine Office, 107-8 Nagahama, Kanazawa-ku, Yokohama 236, Japan, Narita Airport Quarantine Office, 2159 Komaino-Aza-Ten'namino, Narita 282, Japan

Organophosphorus pesticides are important for protecting many crops from insects. Multiresidue procedures for 10 organophosphorus pesticides were studied to establish analytical methods using capillary gas chromatography with flame photometric (FPD) and mass spectrometric detector (GC–MS). Quantitative gas chromatography with a FPD was examined to determine suitable chromatographic conditions for various GC columns. Gas chromatography with GC–MS was studied to choose proper fragment ions for determination and identification.

Keywords: *Multiresidue procedures; determination of organophosphorus pesticides; capillary GC; flame photometric detection; mass spectrometric detection*

INTRODUCTION

We have been studying pesticide residues in food. Nearly 45% of the food consumed in Japan is imported. This fact presents a challenging problem for pesticides residue monitoring since pesticides applied in foreign countries must be identified as well as quantified. An efficient, precise and suitable procedure is necessary for the pesticide screening. There are many procedures proposed to screen pesticides in or on food and used to conduct inspection or monitoring (FDA, 1991; OVR, 1988; DFG, 1987; FDI, 1991; Maybury, 1980; McLeod and Graham, 1986; Leoni et al., 1992). For enforcement of pesticide residue regulations, local and federal governments have developed multiresidue methods for monitoring organophosphorus pesticides in food (Lee et al.,1991; Luke and Masumoto, 1986). These methods which are simple and rapid are desired to screen a wide range pesticides; therefore, large amounts of contaminants and coextractives from the sample matrix are inevitable (Miyahara et al., 1991; FDA, 1994a). Therefore, selective detectors for gas chromatograph and capillary gas chromatography are required to avoid interferences (Miyahara et al., 1992a,b; Miyahara and Saito, 1993). With those selective detectors, it is possible to analyze tens of organophosphorus pesticides simultaneously (CDFA, 1991; EPA, 1986). However, the reliability and accuracy of these methods must be monitored carefully, because some organophosphorus pesticides are unstable at the high temperatures required for gas chromatography and readily adsorb carbonized contaminants or coextractives injected with the samples into the gas chromatograph (FDA, 1994b; Szelewski, 1989). Oily materials from coextractives will accumulate in the gas chromatograph and may change retention times of pesticides and cause ghost peaks under the temperature gradient conditions. Thus, materials that are not observable as chromatographic peaks will interfere with analysis even with element selective detector (FPD) (flame photometric detector), AED (atomic emission detector), etc.) (Miyahara et al., 1992a). There is always doubt about how long a gas chromatograph will work properly under these operating conditions.

Gas chromatography with mass spectrometric detection has been utilized for environmental samples for

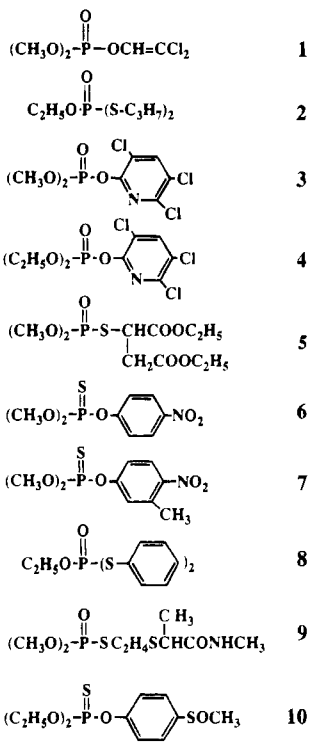

Figure 1. Structures of pesticides: **1**, dichlorvos; **2**, etoprofos; **3**, chlorpyrifos-methyl; **4**, chlorpyrifos; **5**, malathion; **6**, parathion-methyl; **7**, fenitrothion; **8**, edifenfos; **9**, vamidothion; **10**, fensulfothion.

† National Institute of Health Sciences.
‡ Japan Medical Food Association.
§ Yokohama Quarantine Office.
|| Narita Airport Quarantine Office.

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Table 1. Gas Chromatographic Conditions for Calibration Curves

	column				
	DB-1	DB-5	DB-17	DB-210	DB-1
diameter (mm)	0.25	0.25	0.55	0.25	0.55
length (m)	30	30	15	30	10
film thickness (μm)	1	1	1	0.25	0.55
carrier gas: He (mL/min)	6	6	15	3	10
makeup gas: N_2 (mL/min)	50	50	20	50	–
injector temperature (°C)	235	235	235	235	220
detector temperature (°C)	235	235	235	235	250
injection volume (μL)	1	1	2	1	3
detector	FPD	FPD	FPD	FPD	MSD
initial oven temperature (°C)	80	80	140	90	90
hold time (min)	1	1	1	1	1
rate (°C/min)	10	8	3	10	8
final oven temperature (°C)	250	250	210	235	250
hold time (min)	20	10	20	25	20

many years and is a promising technique for residue analysis of food (Ruso and Draper, 1986; Hites and Budde, 1991). This detection procedure has been utilized for the simultaneous detection of organophosphorus pesticides in food. The preconcentration factor of environmental analysis is usually ca. 1000 times (EPA, 1986). Enrichment of the pesticides in the injection solutions make it possible to achieve to lower detection limits for pesticides in samples. This is relatively easy with analytes in environmental samples because air, water, and soil which are generally readily separated from the analytes. This makes it possible to analyze environmental samples using a GC–MS. Several trials have been proposed to apply this technique to food samples (Lee et al., 1991; Boer et al., 1992), but none of them are employed in official multiresidue quantitative methods (FDA, 1994c). Applicability of the technique to the food samples are not clear (Boer et al., 1992; Voogt et al., 1994).

This paper describes a simple cleanup procedure used in conjunction with a capillary gas chromatography and a flame photometric and/or mass spectrometric detector for the simultaneous determination of organophosphorus pesticides (Figure 1) in fruits, vegetables, and grains. Also the results of studies of utilization of mass spectrometric determination of pesticides in food will be described.

EXPERIMENTAL PROCEDURES

Apparatus. *(a) A Shimadzu Model GC14A gas chromatograph with flame photometric detector* (FPD) and with splitter was used. A DB-210 capillary column (30 m × 0.32 mm i.d.) with a film thickness of 0.25 μm was used with helium carrier gas at 3 mL/min and a helium septum purge at 3 mL/min. A split ratio of 20 was used. Injector and detector temperatures, and the column oven temperature programs are listed in Table 1. A 1 μL injection in the splitless mode followed by waiting time of 1 min was utilized. Makeup gas consisted of nitrogen at 50 mL/min.

Table 2. Calibration Curves for Several GC Columns

column	pesticide	rel[a] retention time R/R	slope (a)	intercept (b)	correl coeff (r)	range (ng)	LOQ (ng)
DB-1	dichlorvos	0.42					
	etoprofos	0.74	8761	−168	0.999	0.0625–1	0.03
	chlorpyrifos-methyl	0.93	8775	−121	0.999	0.0625–1	0.03
	chlorpyrifos	1	8551	−4	0.999	0.0625–1	0.03
	malathion	0.98	7152	−36	0.999	0.0625–1	0.03
	parathion methyl	0.92	8775	−121	0.999	0.0625–1	0.03
	fenitrothion	0.96	8791	−59	0.999	0.0625–1	0.03
	edifenfos	1.21	1703	−98	0.999	0.0625–1	0.03
	vamidothion	1.07				0.5–1	0.25
	fensulfothion	1.15				0.5–1	0.25
DB-5	dichlorvos	0.31	3167	−79	0.988	0.25–1	0.125
	etoprofos	0.73	5895	0.5	0.994	0.25–1	0.125
	chlorpyrifos-methyl	0.93					
	chlorpyrifos	1	5423	303	0.990	0.25–1	0.125
	malathion	0.98	5120	125	0.993	0.25–1	0.125
	parathion methyl	0.93					
	fenitrothion	0.97	6473	185	0.993	0.25–1	0.125
	edifenfos	1.29	1353	10	0.998	0.25–1	0.125
	vamidothion	1.20	1001	−104	0.999	0.25–1	0.25
	fensulfothion						
DB-17	dichlorvos	0.09	5896	−109	0.999	0.0625–2	0.03
	etoprofos	0.41	2991	7	0.999	0.0625–2	0.03
	chlorpyrifos-methyl	0.85	2557	12	0.998	0.0625–2	0.03
	chlorpyrifos	1	2058	10	0.998	0.0625–2	0.03
	malathion	1.05	1768	−18	0.999	0.0625–2	0.03
	parathion-methyl	0.91	2604	−11	0.997	0.0625–2	0.03
	fenitrothion	1.02	2503	−18	0.998	0.0625–2	0.03
	edifenfos	1.95	446	−10	0.993	0.0625–2	0.03
	vamidothion	1.71	392	−47	0.986	0.0625–2	0.03
	fensulfothion	1.51	138	−30	0.997	0.25–2	0.125
DB-210	dichlorvos	0.26	10485	−416	0.999	0.0625–2	0.014
	etoprofos	0.83	2618	74	0.999	0.0625–2	0.028
	chlorpyrifos-methyl	0.96	6783	−61	0.999	0.0625–2	0.012
	chlorpyrifos	1	5606	2	0.999	0.0625–2	0.013
	malathion	1.11	2559	−22	0.999	0.0625–2	0.037
	parathion-methyl	1.14	5718	−21	0.999	0.0625–2	0.016
	fenitrothion	1.16	5654	−11	0.999	0.0625–2	0.017
	edifenfos	1.43	442	59	0.993	0.5–20	0.225
	vamidothion	1.59	880	−2680	0.998	4–30	1
	fensulfothion	1.86	6.01	−24	0.998	0.5–20	0.281

[a] The absolute retention times for DB-1, DB-5, DB-17, and DB-210 were 15.57, 19.28, 16.22, and 15.01 min, respectively.

(b) A JEOL Model MS-DC06 gas chromatograph with mass spectrometer (GC–MS) and splitter was used. A DB-1 capillary column (15 m × 0.53 mm id.) with a film thickness of 1 μm was used with helium carrier gas at 20 mL/min. Injector temperature, detector temperature and the column oven temperature program are listed in Table 1. A 5 μL injection in the splitless mode followed by a waiting time of 2 min was utilized. EI (Electron impact ionization) was utilized at 70 eV. A JEOL GC–MS data processor was used. The five fragment ions for each pesticide were selected for identification. The ions for dichlorvos are *m/z* 109 (100), 79 (33), 185 (18), 220 (4), 187 (4); for etoprofos, *m/z* 97 (100), 158 (76), 131 (45), 200 (28), 242 (26); for chlorpyrifos-methyl, *m/z* 286 (100), 125 (92), 288 (69), 270 (18), 323 (10); for chlorpyrifos, *m/z* 97 (100), 197 (62), 199 (60), 314 (38), 316 (26); for malathion, 93 (100), 125 (88), 173 (84), 127 (72), 331 (3); for parathion-methyl, *m/z* 109 (100), 125 (74), 263 (29), 93 (29), 200 (5); for fenitrothion, *m/z* 109 (100), 93 (61), 277 (28), 260 (20), 93 (24); for edifenfos, *m/z* 109 (100), 173 (49), 310 (28), 201 (22), 218 (9); for vamidothion, *m/z* 145 (100), 109 (69), 142 (55), 169 (26), 287 (14); for fensulfothion, *m/z* 293 (100), 73 (95), 308 (93), 125 (83), 141 (89). The number in parentheses after *m/z* is relative intensity to the base peak of the pesticide in each mass spectrum.

(c) VG Zab Model Data process equipment was used for analysis of the mass spectra.

Reagents. *(a) Pesticide standards* were all 95–100% pure and included dichlorvos, *O,O*-dimethyl *O*-(2,2-dichlorovinyl) phosphate; trichlorfon, dimethyl 2,2,2-trichloro-1-hydroxylphosphate; ethoprophos, *O*-ethyl *S,S*-dipropyl phosphorodithioate; chlorpyrifos-methyl, *O*-3,5,6-trichloro-2-pyridyl *O,O*-dimethyl phosphorothioate; chlorpyrifos, *O*-3,5,6-trichloro-2-pyridyl *O,O*-diethylphosphorothioate; malathion, *S*-(1,2-dicarboxyethyl) *O,O*-dimethyl dithiophosphate; parathion-methyl, *O,O*-dimethyl *O*-4-nitrophenyl phosphorothioate; fenitrothion, *O,O*-dimethyl *O*-4-nitro-3-methylphenyl phosphorothioate; edifenphos, *O*-ethyl *S,S*-diphenyl phosphorodithioate; vamidothion, *O,O*-dimethyl *S*-2-(1-methylcarbamoylethylthio)ethyl phosphorothioate; fensulfothion, *O,O*-diethyl *O*-4-methylsulfinylphenyl phosphorothioate. These standards were purchased from Wako Pure Chemicals Co, Osaka, Japan, or Riedel-de Haen Co., Hannover, Germany.

(b) All organic solvents for analysis were of pesticide residue grade.

Samples. Samples were obtained from Yokohama Quarantine Office, Narita Airport Quarantine Office, and retail stores in Tokyo. Those included lettuce (U.S.A.), celery (U.S.A.), five broccoli samples (U.S.A.), three garlic samples (China), two batches of carrots (U.S.A.), cauliflower (U.S.A.), lemon (U.S.A.), bananas (Ecuador), and soybeans (Australia).

Analytical Procedure for Vegetable and Fruits. Sample (20 g) was ground with sodium sulfate (30 g) in a Waring blender for 10 min. Pesticides were extracted from the sample with ethyl acetate (50 mL). After filtration, sodium sulfate was added to the solution. After 30 min, the mixture was filtered and the solvent was evaporated under reduced pressure. The residue was dissolved in 5 mL of acetone.

Analytical Procedure for Soybeans and Wheat. Pesticides were extracted from the ground sample (20 g) with acetonitrile (100 mL). After filtration, solvent was evaporated under reduced pressure. The residue was dissolved in 15 mL of hexane and pesticides were removed by extraction with three 30-mL portions of acetonitrile. The combined acetonitrile extracts were evaporated under reduced pressure, and the residue was dissolved in 5 mL of acetone.

RESULTS AND DISCUSSION

Gas Chromatographic Conditions for Flame Photometric Detection. Several capillary columns for determination of organophosphorus pesticides were examined. Column conditions are important for organophosphorus pesticide analysis. Some pesticides decompose easily in high temperature and adsorb on the wall of gas chromatographic column (Miyahara et al., 1992b). Therefore, separation as well as sensitivity depend upon the column used. Parameters of merit for the columns are the slope of calibration curve, LOQ (limit of quantitation) (defined as a response 10 times the average height of the base line noise) (ACS, 1980), and the relative retention times. Separations between peaks varied as the oven temperature program is changed. In Table 2, the best separation results of the conditions listed in Table 1 are shown. Thus, column which is bonded with a nonpolar liquid phase such as DB-1, is not suitable for the analysis using FPD because pesticides with the necessary elements have very short retention times (dichlorvos and trichlorfon) or very long retention times (edifenfos, vamidothion, and fensulfothion). However, pesticides with mid-range retention times give good responses and potentially can be detected at low levels with less polar column. Indeed, the LOQ of 0.03 ng for these pesticides was the lowest for all of the columns we examined.

All 10 pesticides are not separated by DB-5; however, this column is quite suitable for pesticides with long retention times. It yielded relatively good responses compared to the other columns studied.

DB-210 was inadequate for our purposes. A chromatogram of the standards is shown in Figure 2. Although good separations were achieved, the responses for the pesticides were not optimum exhibited considerable pesticide-to-pesticide variation.

On the basis of the results with the above, a DB-17 wide bore column offered considerable promise. All retention times were are less than 15 min. To improve the separation capability of the column, a thick film was chosen. And the injection volume was increased to 2 μL to maintain the LOQ. As the result separation and sensitivity comparable to longer and narrower columns was realized. Thus, column selection in capillary gas chromatography era is still as important as it was in packed column age. Absorption and decomposition of analytes in chromatographic column must be given careful consideration with capillary columns.

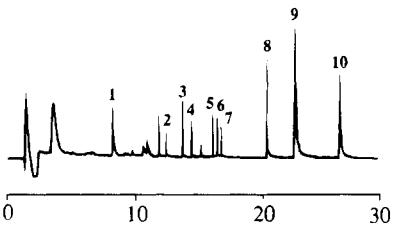


Figure 2. Chromatogram for standard solution: **1**, dichlorvos (2 ng); **2**, etoprofos (2 ng); **3**, chlorpyrifos-methyl (2 ng); **4**, chlorpyrifos (2 ng); **5**, malathion (2 ng); **6**, parathion-methyl (2 ng); **7**, fenitrothion (2 ng); **8**, edifenfos (10 ng); **9**, vamidothion (15 ng); **10**, fensulfothion (10 ng).

Table 3. Unvolatile Materials[a] from Coextractives in Sample Solution

	material weight (mg)		
crop	procedure	procedure + H-A partitioning	method 2[b]
soybean	1568	42	798
wheat	784	76	172
grapefruit	26		30
red salad	21		25
cucumber	18		15
banana	23		

[a] The unvolatile material was determined gravimetrically after evaporation of sample solution. The solution was obtained via the process presented in the text. [b] The values were obtained by the Luke (1986) procedure.

Table 4. Recovery of 10 Pesticides from 9 Crop Samples

pesticide	spiking level (ppm)	recovery (%) (CV%, $n = 3$) grapefruit	lemon	cucumber	red salad	mushroom	cherry	asparagus	wheat	soybean
dichlorvos	0.5	61 (16)	93 (3.2)	87 (4)	86 (6.0)	94 (2.9)	85 (2.3)	76 (7.0)	73 (5.0)	111 (18.0)
	1	97 (0.1)	94 (3.4)	63 (11.3)	66 (2.4)	71 (3.1)	74 (2.3)	90 (5.1)	87 (8.1)	89 (17.5)
etoprofos	0.5	79 (12.5)	93 (5.1)	84 (2.7)	78 (6.7)	95 (5.5)	101 (5.1)	80 (6.0)	92 (1.6)	83 (11)
	1	96 (0.5)	101 (2.3)	83 (7.8)	68 (2.5)	75 (5.4)	90 (5.1)	88 (7.5)	81 (7.1)	82 (3.6)
chlorpyrifos-methyl	0.5	62 (16.0)	80 (6.5)	68 (3.8)	61 (4.5)	78 (4.5)	83 (4.9)	64 (5.8)	129 (31.3)	58 (8.1)
	1	81 (5.1)	90 (2.3)	70 (8.2)	68 (3.2)	63 (1.6)	79 (3.5)	75 (5.9)	131 (12.3)	71 (2.3)
chlorpyrifos	0.5	68 (15.1)	138 (11.7)	75 (2.4)	65 (5.0)	79 (3.6)	82 (2.4)	72 (5.8)	85 (3.0)	63 (13.5)
	1	89 (4.5)	99 (2.5)	75 (6.9)	77 (2.0)	67 (3.5)	100 (4.9)	79 (7.0)	92 (3.8)	73 (4.4)
malathion	1	64 (18)	81 (5.1)	74 (5.1)	75 (6.8)	97 (4.6)	97 (6.7)	85 (6.3)	120 (16.9)	52 (8.0)
	2	85 (2.3)	98 (2.2)	70 (4.5)	70 (2.2)	66 (2.3)	82 (3.8)	83 (7.3)	70 (9.0)	88 (4.2)
parathion-methyl	0.5	69 (13.6)	76 (4.6)	72 (1.7)	70 (3.9)	88 (5.2)	92 (5.1)	77 (5.5)	51 (9.8)	47 (35.2)
	1	80 (3.5)	95 (5.2)	72 (5.0)	72 (0.7)	67 (1.4)	65 (4.2)	81 (2.0)	85 (1.9)	74 (4.6)
fenitrothion	0.5	66 (16.1)	93 (5.7)	81 (1.8)	67 (4.6)	85 (4.2)	94 (4.1)	86 (12.4)	58 (7.7)	42 (27.8)
	1	79 (8.0)	102 (2.5)	77 (5.8)	67 (1.8)	65 (2.0)	81 (5.4)	78 (7.9)	90 (1.7)	82 (5.6)
edifenfos	10	56 (20.5)	69 (8.2)	71 (6.7)	77 (8.2)	111 (9.6)	111 (11.8)	102 (10.1)	46 (20.8)	51 (24.2)
	20	79 (12.0)	67 (7.4)	68 (3.3)	67 (2.6)	77 (2.6)	50 (10.3)	97 (3.5)	66 (6.0)	78 (3.4)
vamidothion	15	44 (15.3)	10 (0.9)	88 (9.5)	96 (10.0)	114 (10.0)	100 (12.2)	93 (10.0)		
	30	44 (14.5)	11 (5.1)	80 (5.4)	70 (2.6)	76 (0.7)	92 (4.7)	81 (9.1)	37 (13)	44 (15.2)
fensulfothion	10	51 (12.3)	43 (8.4)	80 (9.8)	115 (13.6)	125 (9.4)	82 (9.6)	101 (9.5)	69 (6.1)	69 (12.1)
	20	61 (11.0)	49 (10.9)	70 (9.2)	57 (3.0)	84 (2.0)	76 (2.3)	80 (9.0)	81 (4.0)	88 (7.2)

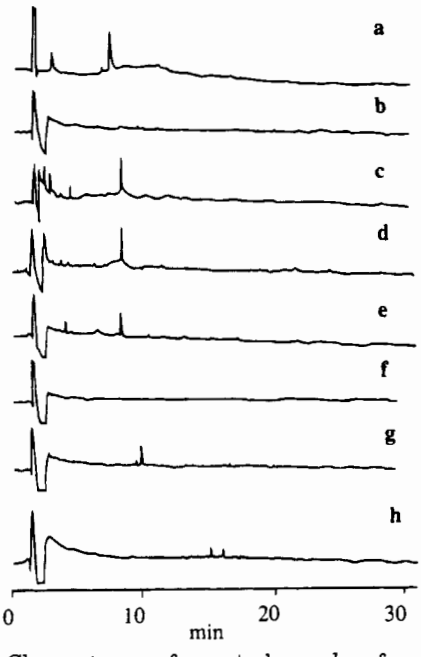


Figure 3. Chromatogram for control samples of vegetable and fruits: a, red salad; b, orange; c, asparagus; d, cherry; e, mushroom; f, cucumber; g, grapefruit; h, lemon.

Extraction and Cleanup Procedure. Minimum cleanup procedures were employed. Samples were classified according to fat content. Samples with less than 2% fat were treated as nonfatty; Fatty sample contain more than 5% fat. Nonfatty samples were homogenized with sodium sulfate and ethyl acetate in a Waring blender. After filtration, the solution was dried and evaporated. The residue was dissolved in acetone. This simple extraction is adequate for a screening procedure with nonfatty samples and 18–76 mg unvolatile materials from 20 g samples remained after extraction (see Table 3). Fatty samples were required for the cleanup the after extraction. This cleanup procedure is also simple and consists of partitioning the residue between hexane and acetonitrile (AOAC, 1990). The efficiency of this procedure is comparable with other methods (Miyahara et al., 1991; Luke and Masumoto, 1986) and the results are also shown in Table 3. Thus, the performance of this commonly employed procedure is adequate for an organophosphorus pesticide screening procedure.

Recovery Test by FPD. The recoveries of the pesticides are shown in Table 4. The chromatograms for the controls and the recovery tests are shown in Figures 3–5. Thus, no interferences were observed in the chromatogram. The chromatograms for soybeans and wheat revealed several residual peaks. Recoveries of vamidothion from citrus fruits such as grapefruit and lemon are low, but the recovery from vegetables was quantitative. This suggests that the pesticide is not extracted quantitatively under the acidic conditions due to protonation of nitrogen. Further study of the recovery of the analytes as a function of pH will be necessary to optimize the recoveries. The recoveries from wheat and soybeans were fair at 15 ppm but were much poorer at 1 ppm (the data at this level are not shown). This may be due to adsorption and/or decomposition of the analyte in the chromatographic column as a result of accumulated oily material. The decreased recoveries of several pesticides from soybeans were observed. The recovery tests were conducted after the gas chromatograph had been extensively used for other recovery tests without any cleaning. The relative adequacy of the recovery results suggests that the capillary gas chromatographic system is rugged enough for a minimum cleanup for a screening of organophosphorus pesticides in food. However, a more efficient cleanup is desired to reduce gas chromatograph maintenance and improve the accuracy (Szelewski, 1989).

Mass Spectrometric Detection. Gas chromatographic conditions for mass spectrometric detection must necessarily differ from those for flame photometric detection. The GC–MS is less sensitive than the FPD because column eluent must be cleaner and the GC–MS is limited to molecular ion and its fragments. Decomposition of analytes into fragment ions in the ionization cavity reduces the intensity of each ion. Mass scanning procedures also reduces the intensity of each ions. These instrumental limitations can be overcome with various techniques. Short column with a thin film was used with a steep temperature gradient for the oven. Those conditions minimize decomposition of the analyte in the gas chromatograph, however, at the expense of reduced separation. To compensate for low sensitivity, large amounts of analytes should be injected into the gas chromatograph by adjusting the sample volumes. With these considerations and experimented results of our studies the optimum gas chromatographic

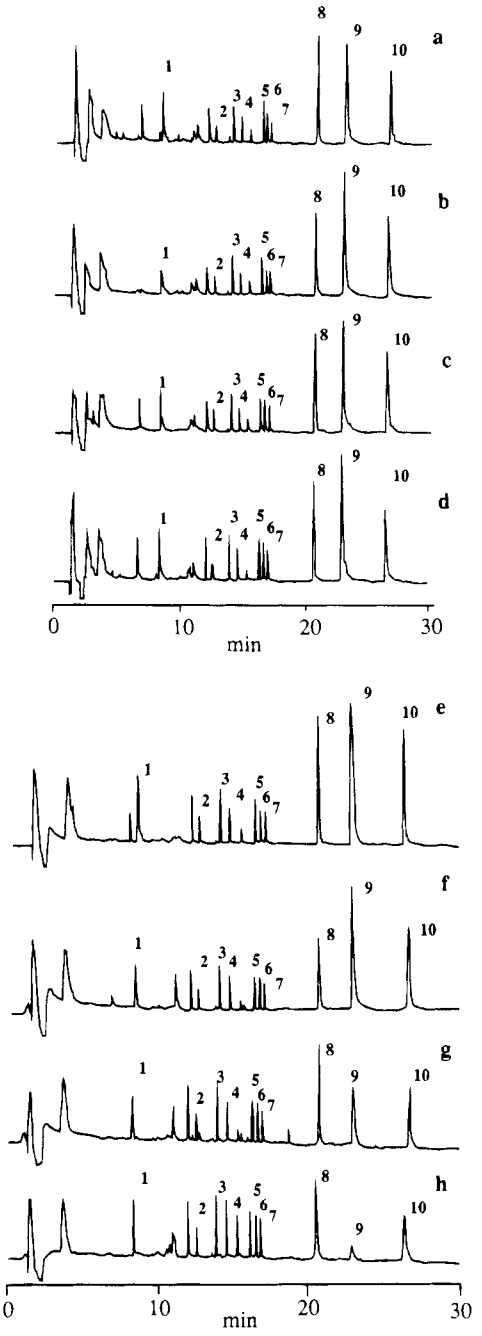


Figure 4. Chromatogram for spiked samples of vegetable and fruits: a, red salad; b, orange; c, asparagus; d, cherry; e, mushroom; f, cucumber; g, grapefruit; h, lemon.

conditions were selected. These are shown in Table 4 using the DB-1 as the liquid phase.

In order to determine what kind fragment ions can be utilized for determination of pesticides in food, the five most intense ion peaks were studied. These selected ions are shown under Experimental Procedures. These most promising candidates for ions in GC–MS detection were *m/z* 109 and 93 which are characteristic ions for organophosphorus pesticides. The fragmentation patterns were compared with reference data (Tsunoda and Kishi,1986; Skinner and Greenhalgh, 1977; Spectral Service, 1992). The principal fragment ions were the same as reported in the references. However, closer scrutiny of mass spectra reveled considerable differences. It is strongly recommended that mass patterns should be established for each instrument with pesticide standards (Eichelberger et al., 1973).

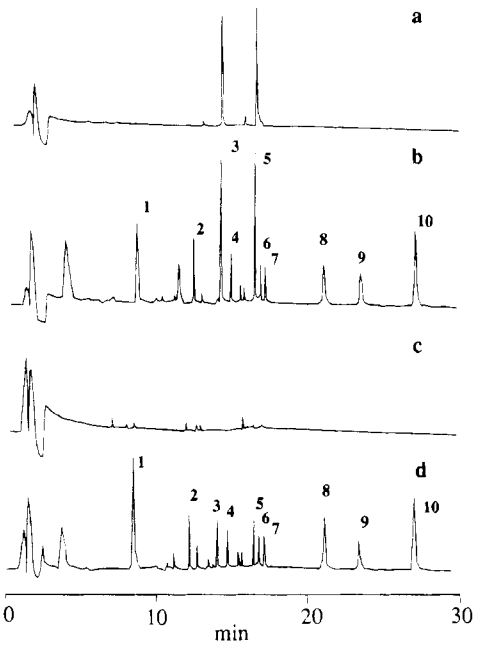


Figure 5. Chromatogram for control samples and for spiked samples of grains: a and c, control samples of wheat and soybeans, respectively; b and d, spiked samples of wheat and soybeans, respectively.

Fragment Ion Analysis. Selection of the optimum fragment ions for identification of organophosphorus pesticides required study of the structures of intense fragment ions. The results are shown in Table 5. The structures of fragment ions were postulated by well-established methods of mass spectra analysis. Ions with chlorine atoms were identified by spectrum simulation. The results are given in Table 5.

All pesticides that include of dimethyl phosphate or dimethyl thiophosphate functional group gave peaks at *m/z* 109 for dimethyl phosphate and at *m/z* 125 for dimethyl thiophosphate (EPA of Japan, 1992). These are easily detected and good markers for confirmation of organophosphorus pesticide. However, pesticides that have no such substructure give other characteristic ions.

Generally ions with double bonds give good response and constitute one major fragments. The slope of the fragment intensity versus the amount of pesticide injected provided a good parameter for comparing the analytical utility of the fragment. Sensitivities for the dimethylphosphorus ion was better than other characteristic ions. But all of the major ions are important for identification of pesticides in food. Unfortunately, vamidothion gave only the peak at *m/z* 109. In this case mass spectrometric identification can be done using a second gas chromatographic column of different polarity.

Relative Intensities of Fragment Ions. The relative intensities for the individual pesticides are given under Experimental Procedures. Three-dimensional illustrations of results for those pesticides are shown in Figure 6. The five most intense peaks [The numbers in parentheses after *m/z* are relative intensities calculated based on chloropyrifos-methyl (*m/z* 125).] in the pesticides examined are *m/z* 125 (base peak in this figure, relative intensity: 100%) for chlorpyrifos-methyl, *m/z* 109 (82%) for edifenfos, *m/z* 97 (78%) for chloripyrifos, *m/z* 109 (74%) for parathion-methyl, and *m/z* 125 (70%) for malathion. The least intense peak is *m/z* 109 (0.01%) for vamidothion. The relative intensity for the dimethyl phosphate fragment varies from pesticides to

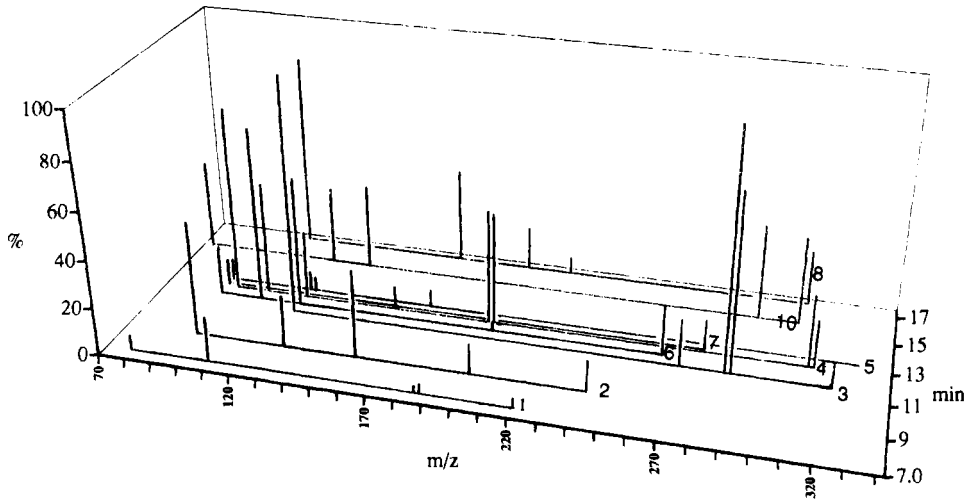
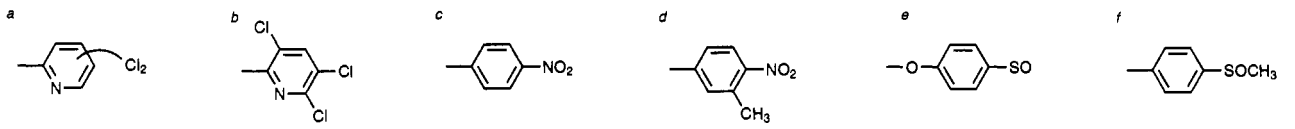


Figure 6. 3D display of GC–MS for nine organophosphorus pesticides: **1**, dichlorvos; **2**, etoprofos; **3**, chlorpyrifos-methyl; **4**, chlorpyrifos; **5**, malathion; **6**, parathion-methyl; **7**, fenitrothion; **8**, edifenfos; **10**, fensulfothion.

Table 5. Selected Ions for GC–MS Determination and Calculation Data

pesticide	*m/z*	structure	range (ng)	correl coeff (*r*)	intercept (*b*)	slope (*a*)
dichlorvos	109	$P(=O)(OCH_3)_2$	60–15	0.9965	42587.69	1559.32
	220	$Cl_2C=CHOP(=O)(OCH_3)_2$	60–15	0.9998	−6716.5	629.729
etoprofos	158	$CH_3CH_2OP(=O)(SH)_2$	60–7.5	0.9801	−6125.17	3844.02
	242	$CH_3CH_2OP(=O)(SCH_2CH_3)_2$	60–15	0.9619	−884.5	1257.39
chlorpyrifos-methyl	125	$P(=S)(OCH_3)_2$	60–7.5	0.9994	−22536.8	10565.5
	286	$(C_5HNCl_2)^aOP(=S)(OCH_3)_2$	60–7.5	0.9683	−4284.3	5294.29
	323	$(C_5HNCl_3)^bOP(=S)(OCH_3)_2$	60–15	0.9982	5431.798	343.332
parathion-methyl	93	$P(OCH_3)_2$	60–7.5	0.9998	−8610.96	6456.52
	109	$P(=O)(OCH_3)_2$	60–7.5	0.9353	−15010.7	7803.55
	125	$P(=S)(OCH_3)_2$	60–7.5	0.9945	8474.261	3285.38
	200	$(O_2NC_6H_4)^cOPOCH_3$	60–15	0.961	−1096.5	445.329
	263	$(O_2NC_6H_4)^cOP(=S)(OCH_3)_2$	60–7.5	0.9954	−28444.5	3114.35
chlorpyrifos	97	$S=P(OH)_2$	60–7.5	0.9875	−48399.2	8569.44
	197	$(Cl_3C_5HN)^bO-$	60–7.5	0.9994	−2573.91	3606.83
	314	$(Cl_2C_5HN)^aOP(=S)(OCH_2CH_3)$	60–7.5	0.9941	−944.522	1945.54
fenitrothion	93	$P(OCH_3)_2$	60–7.5	0.9989	−6268.22	1707.12
	109	$P(=O)(OCH_3)_2$	60–7.5	0.9419	−64991.5	5459.65
	125	$P(=S)(OCH_3)_2$	60–7.5	0.998	11738.87	5196.32
	260	$(O_2NC_6H_4CH_3)^dOP(=O)(OCH_3)_2$	60–7.5	0.9767	−23492.9	2367.66
	277	$(O_2NC_6H_4CH_3)^dOP(=S)(OCH_3)_2$	60–7.5	0.9863	−26338.7	3158.58
malathion	93	$P(OCH_3)_2$	60–7.5	0.9838	−499	904.952
	125	$P(=S)(OCH_3)$	60–7.5	0.9626	−88974.2	8143.64
	173	$C_2H_5OCOCH=CH_2COOC_2H_5$	60–30	0.9995	1	1
vamidothion	109	$P(=O)(OCH_3)_2$	60–30	0.9523	1	1
fensulfothion	125	C_6H_4SO	60–15	0.9867	−13244	882.476
	141	$OC_6H_4\text{-}SO^e$	60–15	0.9699	−85989	4559
	308	$CH_3SO\text{-}C_6H_4{}^fOP(=S)(OC_2H_5)_2$	60–15	0.9946	−5849.71	485.256
edifenfos	109	$P(=O)(OCH_3)$	60–7.5	0.9934	−38794.1	8868.11
	173	$C_6H_5SP(=O)OH$	60–7.5	0.9858	−33648.5	5062.94
	201	$C_6H_5SP(=O)OC_2H_5$	60–15	0.9791	−29037	2466.78
	310	$(C_6H_5S)_2P(=O)OC_2H_5$	60–7.5	0.9848	−28545.9	3069.71



pesticide. This may be influenced by the detector and column efficiency. The ratio of intensities of chlorpyrifos-methyl and vamidothion at *m/z* 109 is calculated from the data and is 10000:1. This is comparable to the practical dynamic range of the spectrometer. This means such intense peak may cause positive error when a sample containing large amount of chlorpyriphos methyl is analyzed under the conditions we used.

Monitoring Results of FPD Quantification and of GC–MS Identification. To evaluate the performance of the procedure, a total of 18 samples (lettuce, celery, five broccoli, three garlic, two carrots, cauliflower, lemon, banana, soybeans) obtained from quarantine offices were analyzed. Low levels of organophosphorus pesticides were determined by flame photometric determination. The following pesticides were detected by flame photometric detection: fenitorothion (0.03–0.43 ppm) in broccoli, chlorpyrifos-methyl (0.028–0.038 ppm) in wheat, malathion (0.057–0.072 ppm), and chlorpyrifos (0.174 ppm) in lemon.

Several pesticides were identified as shown in Figure 7 by GC–MS during study of this method. The mass spectral patterns are similar to those of the standards. Using the intensities of the selected peaks, the pesticide levels were determined. The results are shown in Table 6. The pesticide levels which were calculated from

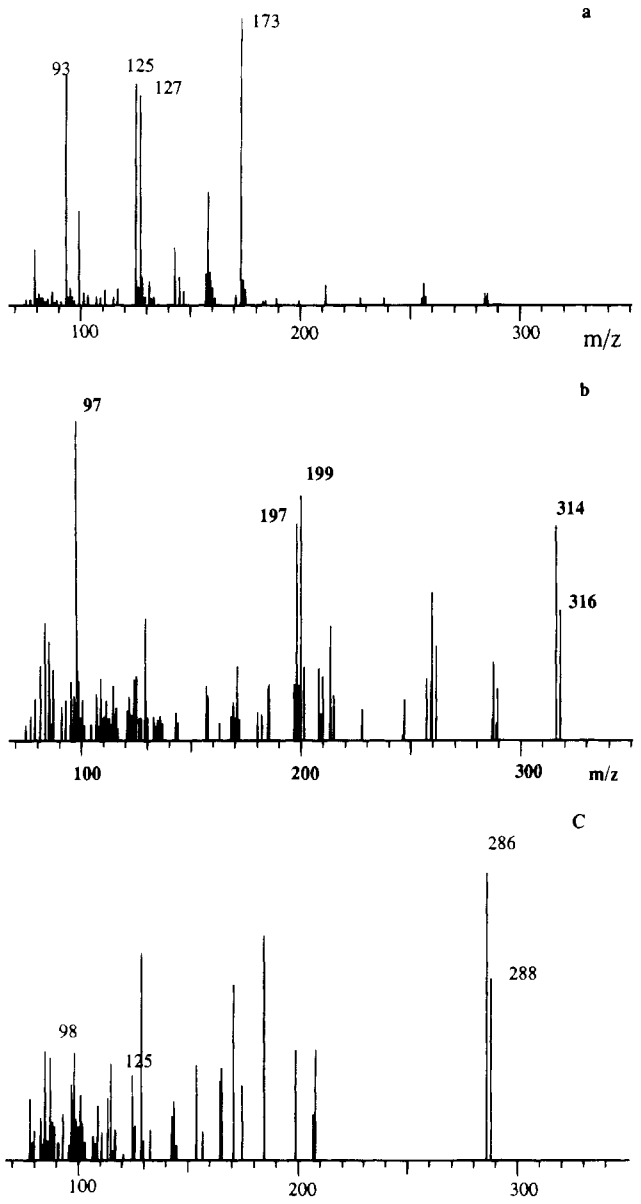


Figure 7. Mass spectra of pesticides in the samples: a, malathion in wheat; b, chlorpyrifos in lemon; c, chlorpyrifos-methyl in wheat.

Table 6. Pesticide Levels Measured by Mass Spectrometric and Flame Spectrometric Determinations

pesticide	detector		ppm
malathion	MSD	*m/z* 93	0.113
	MSD	*m/z* 125	0.987
	FPD	526 nm	0.057
chlorpyrifos	MSD	*m/z* 97	0.187
	MSD	*m/z* 197	0.050
	MSD	*m/z* 314	0.020
	FPD	526 nm	0.174
chlorpyrifos-methyl	MSD	*m/z* 286	0.028
	MSD	*m/z* 125	0.056
	FPD	526 nm	0.038

different fragment ion peaks differed considerably. This deviation increased at low levels detected by flame photometric detection. Thus, it is very difficult to determine which value is correct. Mass spectrometric determination is not adequate for quantification at the levels we examined (Lee et al., 1991; Boer et al., 1992). This conclusion is supported by other experiments of ours. Mass spectra of the pesticides extracted from sample are not free from effects of coextractive materials as shown Figure 7. Even after cleanup, the sample solution for GC analysis contains residual materials from matrix as shown in Table 3. Therefore, not only due to coextractives, but also due to bleeding of the accumulated contaminants in GC after several sample injection (FDA, 1994b), so-called similarity indexes for the mass spectra are not high at the levels we studied. Those phenomena are inevitable to multi residue procedures for food using GC–MS. However, this device can be used as a tool for identification of pesticides in food. Appropriate background subtraction may improve the similarity index and give good spectrum for identification. The traditional use of gas chromatography with mass spectrometric detection for pesticide identification will provide additional confirmation of the results in many cases. In conclusion, the mass spectrometric system is quite useful when it was used under careful control and consideration.

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