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Original Article

A Method for Residue Analysis of Benfuracarb and Its Metabolites Carbofuran, 3-Hydroxy-carbofuran and 3-Keto-carbofuran in Crops by Gas Chromatography

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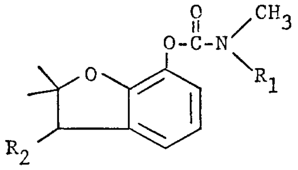
A procedure has been developed for the analysis of residues of benfuracarb and its metabolites, carbofuran, 3-hydroxy-carbofuran (3–OH–CF) and 3-keto-carbofuran (3–C=O–CF) in eleven crops. The crops were homogenized after addition of silver nitrate solution (or milled in a case of rice grain) and extracted with solvents. The extract was cleaned up by column chromatography and subjected to gas chromatography (GC). The silver nitrate solution was used to prevent the decomposition of benfuracarb by N–S bond cleavage during the homogenization and extraction. Of the four compounds benfuracarb and carbofuran were extracted with methanol from the crops. The extract was concentrated, water was added and the extract was again extracted with dichloromethane. The extraction of 3–OH–CF and 3–C=O–CF were accomplished by the aid of hydrolysis of conjugated 3–OH–CF and 3–C=O–CF by dipping the homogenate in 0.25 N hydrochloric acid and refluxing, followed by the extraction with dichloromethane. The extract containing benfuracarb and carbofuran or 3–OH–CF and 3–C=O–CF was then subjected to a cleanup procedure using silica gel and Florisil column chromatography. The concentrated eluate was analyzed by GC employing a quartz capillary column. Recoveries from fortified samples were 75–100% for benfuracarb, 73–100% for carbofuran, 76–99% for 3–OH–CF and 76–99% for 3–C=O–CF at 0.05 and 0.5 ppm levels. The overall detection limit was 0.005 ppm for all compounds.

INTRODUCTION

Benfuracarb (trade name: Oncol®, see Fig. 1 for its structure and chemical name) is a new carbamate insecticide which has been marketed by Otsuka Chemical Company. It is a new type of sulfenylated derivative of carbofuran which has outstanding insecticidal activity against a number of economically important insects.[1] The residues of the parent compound benfuracarb, and its metabolite carbofuran, 3–OH–CF and 3–C=O–CF (Fig. 1) have been reported in cottons, bush beans and corn plants[2,3] following the treatment with benfuracarb.

In the previous paper[4] we have reported the analytical procedure for the determination of benfuracarb and carbofuran in soil and water by employing high-performance liquid chromatography (HPLC). HPLC using a Zorbax ODS column was initially examined as an analytical procedure for the determination of crop residues of benfuracarb, carbofuran, and also 3–OH–CF and 3–C=O–CF. However, extensive attempts to obtain the aimed sensitivity of detection (0.005 ppm) for the four compounds were unsuccessful. There are many reports on the methods for the determination of crop residues of carbofuran, 3–OH–CF and



Where:

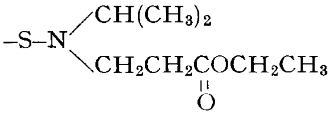
R_1	R_2	Name
 $-S-N(CH(CH_3)_2)CH_2CH_2COCH_2CH_3$	H_2	2,3-Dihydro-2,2-dimethyl-7-benzofuranyl *N*-[*N*-[2-(ethoxycarbonyl)-ethyl]-*N*-isopropylsulfenamoyl]-*N*-methylcarbamate (Benfuracarb, BC)
H	H_2	2,3-Dihydro-2,2-dimethyl-7-benzofuranyl *N*-methylcarbamate (Carbofuran, CF)
H	H,OH	2,3-Dihydro-3-hydroxy-2,2-dimethyl-7-benzofuranyl *N*-methylcarbamate (3-Hydroxy-carbofuran, 3-OH-CF)
H	O	2,3-Dihydro-2,2-dimethyl-3-oxo-7-benzofuranyl *N*-methylcarbamate (3-Keto-carbofuran, 3-C=O-CF)

Fig. 1 Structures, chemical names and abbreviations of four compounds.

3-C=O-CF using HPLC[5-7] or GC,[8-11] which also indicate that the sensitivity of detection is relatively poor, being 0.02-0.5 ppm by HPLC and 0.01-0.03 ppm by GC. In order to obtain better separation and higher sensitivity of detection, an alternative analytical procedure was designed to use GC employing a quartz capillary column equipped with a flame thermionic detector.

This report is on a gas chromatographic analysis procedure developed for the determination of residues of benfuracarb, carbofuran, 3-OH-CF and 3-C=O-CF with a detection limit of 0.005 ppm in eleven crops, *i.e.*, the rice, cucumber, green pepper, water melon, melon, eggplant, Japanese radish (root, leaf), corn, cabbage, spinach and orange.

MATERIALS AND METHODS

1. *Reagent*

All organic solvents and inorganic chemicals were guaranteed reagent purchased from Wako Pure Chemical Industries, Ltd. Florisil (100-200 mesh) and silica gel (Wako gel C-200) were also purchased from Wako Pure Chemical Industries, Ltd., and aluminum oxide (Neutral W200 for column chromatography) from ICN Pharmaceutical GmbH Co. Analytical grade benfuracarb, carbofuran, 3-OH-CF and 3-C=O-CF were available from previous studies.[2-4] Stock standard solutions of benfuracarb, carbofuran, 3-OH-CF and 3-C=O-CF were prepared in benzene at necessary concentrations. Phosphate buffer (pH 8.0) was prepared by mixing 5.3 ml of 0.2 M sodium phosphate monobasic and 94.7 ml of 0.2 M sodium phosphate dibasic to bring the final volume of 200 ml with distilled water.

2. *Apparatus*

A gas chromatograph (Model 7-AG, Shimadzu) equipped with a solventless sample injector and a flame thermionic detector (FTD-8) was used for quantitation. A 25-m flexible quartz capillary column (0.2 mm inner diameter) coated with OV-101 was used for the separation. The inlet and detector temperatures were both 300°C. The operating temperatures of a column oven were 265°C for benfuracarb, 180°C for carbofuran, 195°C for 3-OH-CF and 3-C=O-CF. Helium was used as carrier and makeup gases with a flow rate of 1.5 and 40 ml/min, respectively. The detector gases were air with a 150 ml/min flow rate and hydrogen with a flow rate of 4 ml/min. The injection sample size was 8 μl.

Other apparatuses were a rotary evaporator (Model N-1, Tokyo Rika Kikai), a shaker (Model SR-2, Taiyo Kagaku), a speed cutter (Model MK-101, Matsushita Electric) and a coffee mill (Model LHF/7, Shibata Scientific Technology).

3. *Crop Samples and Fortification*

Twelve different crop samples (11 crops) each from two different locations in Japan (Table 3) were used for the recovery study. In a case of the Japanese radish, two portions *i.e.*, the root and leaf, were used separately. To fortify each crop, except for the rice grain, at different concentrations, 0.5 ml acetonitrile solution containing different amounts of benfuracarb, carbofuran, 3-OH-CF or 3-C=O-CF were poured into the sliced crops in a speed cutter and the crop was subjected to homogenization and extraction. In a case of the rice grain, 0.5 ml of acetonitrile solution containing different amounts of each compound was added to the milled grain sample.

4. *Extraction and Cleanup Procedure of Benfuracarb and Carbofuran*

4.1 Extraction

Each crop sample, except for the rice grain (50 g in fresh weight), 2 ml of 0.1 N silver nitrate ($AgNO_3$) solution and 25 ml of phosphate buffer solution (pH 8.0) were taken into a speed cutter and homogenized. The rice grain (50 g) was milled with a coffee mill and sieved through a 42 mesh screen. Each homogenized or milled sample was placed in a 300-ml Erlenmeyer flask, and 150 ml of methanol (or acetonitrile in a case of the rice grain) was added. The flask was stoppered and shaken for 10 min using a shaker. The $AgNO_3$ solution was used to prevent the cleavage of the N-S bond in benfuracarb during the homogenization and extraction. The mixture was filtered by suction through a 25G-4 glass filter. The residue was washed with an additional 50 ml of methanol (or acetonitrile). The extract and washing were combined and an additional 2 ml of $AgNO_3$ solution was added to the mixture. The mixture was then concentrated to about 10–20 ml on a vacuum rotary evaporator at a water-bath temperature below 35°C. All concentrations were carried out in the same manner.

The concentrated solution was then transferred to a 300-ml separatory funnel with the aid of 150 ml of distilled water, and then 20 g of potassium chloride and 50 ml of dichloromethane were added to the funnel. The funnel was shaken for 5 min and allowed to stand for 5 min in order to separate the mixture into two phases. The lower phase (dichloromethane) was separated and the residual aqueous phase was extracted again with 50 ml of dichloromethane. The dichloromethane extracts were combined, concentrated by rotary evaporator to dryness, and the residue was dissolved in 20 ml of carbon tetrachloride.

4.2 First column cleanup

Five grams of Florisil was transferred to a 15×300 mm chromatographic column fitted with a sintered glass disc and containing 15 ml of carbon tetrachloride. The column was gently shaken until the Florisil settled and all air bubbles were dispelled. The inner wall of the column was rinsed with 2–3 ml of carbon tetrachloride and the solvent was drained from the column until the solvent surface reached the top of the Florisil bed.

The crop extract (carbon tetrachloride solution) was added and rinsed with 2 ml of carbon tetrachloride and 35 ml of *n*-hexane–ethyl acetate (9: 1, v/v). Benfuracarb was eluted with 45 ml of *n*-hexane–ethyl acetate (9: 1) at a flow rate of 1.5 ml/min. The same flow rate was kept through all cleanup processes after the elution of the column by the solvent. The column was then rinsed with 10 ml of *n*-hexane–ethyl acetate (4: 1) and carbofuran was eluted with 30 ml of *n*-hexane–ethyl acetate (4: 1). Both eluates were combined and concentrated to dryness, and the residue was dissolved in 10 ml of carbon tetrachloride.

4.3 Second column cleanup

A silica gel column was prepared using a 15×300 mm chromatographic column and 7 g of silica gel by the same method as the Florisil column. The eluate from the Florisil column (carbon tetrachloride solution) was added and rinsed with 2 ml of carbon tetrachloride and 30 ml of *n*-hexane–ethyl acetate (17: 3). Benfuracarb was eluted with 30 ml of *n*-hexane–ethyl acetate (17: 3). The column was then rinsed with 10 ml of *n*-hexane–ethyl acetate (7: 3) and carbofuran was eluted with 25 ml of *n*-hexane–ethyl acetate (7: 3). Both eluates were concentrated and the residues were dissolved in 2.5 ml of benzene for GC-analysis.

5. *Extraction and Cleanup Procedure of 3-OH-CF and 3-C=O-CF*

5.1 Extraction

The homogenized or milled samples (50 g each) of each crop prepared as described in Section *4.1* was taken into a 1-*l* round bottom flask, and 400 ml of 0.25 N hydrochloric acid was added. The mixture was refluxed for 2 hr on a mantle heater with stirring and filtered through glass wool into a 1-*l* Buchner flask. The residue was washed with an additional 100 ml of hot 0.25 N hydrochloric acid. The extracts and washings were combined and cooled in an ice bath. The cooled extract was transferred to a 1-*l* separatory funnel, and 5 ml of 4% sodium dodecylsulfate solution and 200 ml of dichloromethane were added. The mixture was shaken for 15 min and allowed to stand for 10 min in order to separate the mixture into two phases. The lower phase (dichloromethane) was separated and the residual aqueous phase was extracted twice with another 200 ml each of dichloromethane by following the same procedure. The dichloromethane extracts were combined and dried over 30 g of anhydrous sodium sulfate and filtered through a 25G-4 glass filter into a 1-*l* round bottom flask. The filtrate was evaporated to dryness at 35°C and the residue was dissolved in 20 ml of dichloromethane–carbon tetrachloride (1 : 1).

5.2 *First column cleanup*

A Florisil column was prepared using a 15 × 300 mm chromatographic column and 10 g of Florisil in the same manner as described. The crop extract was added and rinsed with 40 ml of *n*-hexane–ethyl acetate (7 : 3). 3–C=O–CF was eluted with 50 ml of *n*-hexane–ethyl acetate (7 : 3). The column was then rinsed with 10 ml of *n*-hexane–ethyl acetate (6 : 4) and 3–OH–CF was eluted with 70 ml of *n*-hexane–ethyl acetate (6 : 4). Both eluates were combined and concentrated to dryness, and the residue was dissolved in 10 ml of dichloromethane–carbon tetrachloride (1 : 1).

5.3 *Second column cleanup*

A silica gel column was prepared using a 15 × 300 mm chromatographic column and 10 g of silica gel in the same manner as described. The eluate from a Florisil column (dichloromethane-carbon tetrachloride solution) was added and rinsed with 30 ml of *n*-hexane–ethyl acetate (7 : 3). 3–C=O–CF was eluted with 60 ml of *n*-hexane–ethyl acetate (7 : 3). The column was then rinsed with 30 ml of *n*-hexane–ethyl acetate (6 : 4) and 3–OH–CF was eluted with 60 ml of *n*-hexane–ethyl acetate (6 : 4). Both eluates were concentrated and the residues were dissolved in 2.5 ml of benzene to be subjected to GC analysis.

6. *Gas Chromatographic Analysis*

Residues were quantitated with gas chromatography equipped with an FTD detector by comparing the peak height of response in a sample to the peak height of response in an external standard of benfuracarb, carbofuran, 3–OH–CF or 3–C=O–CF. Detector linearity was checked daily for each compound.

7. *Calibration and Calculation*

Before an unknown sample was analyzed, the linearity of the detection system was established for the amount of benfuracarb, carbofuran, 3–OH–CF or 3–C=O–CF ranging from 1.6 to 8 ng. The amount of each compound was obtained from each calibration curve.

The amount of each compound in different crop samples was calculated from the following formula:

$$\text{Compound (ppm)} = C \times V/G$$

where C = concentration (μg/ml) of benfuracarb, carbofuran, 3–OH–CF or 3–C=O–CF obtained from the calibration curve, V = final sample volume (ml) and G = sample weight (g) of the crop.

RESULTS AND DISCUSSION

1. *Extraction and Cleanup Procedure*

1.1 *Addition of silver nitrate solution*

Our previous studies on soil residue analysis[4] indicated that the N–S bond in benfuracarb was susceptible to thiolytic cleavage when the sulfur atom was attacked by sulfhydryl-containing agents, and that the addition of silver nitrate ($AgNO_3$) solution was necessary to prevent the cleavage of the N–S bond during the extraction procedure of soil samples. The current studies also indicated that without the addition of sulfhydryl inhibitor the recovery of benfuracarb fortified at a level of 0.05 ppm was only 18% (Japanese radish), 6% (orange) and 33% (cabbage).

Therefore, the $AgNO_3$ solution was used to prevent the decomposition of benfuracarb during the homogenization and concentration. Table 1 summarizes the data on the effect of different amount of 0.1 N $AgNO_3$ solution on the recovery of benfuracarb from six repre-

Table 1 Effects of different volume of 0.1 N silver nitrate ($AgNO_3$) solution on the recovery of benfuracarb from the Japanese radish, green pepper, orange, cabbage, corn and rice grain.[a]

Crop	Volume (ml) of $AgNO_3$ solution added		% recovery
	At homogenization	At concentration	
Cabbage	0	0	44, 23
	2	2	88, 92
Japanese radish	0	0	26, 9
	2	2	18, 32
	0	5	20, 26
	5	0	54, 61
	5	5	84, 81
Green pepper	0	0	63, 58
	2	2	92, 88
Orange	0	0	3, 8
	2	2	13, 1
	5	5	5, 10
Corn	0	0	88, 94
Rice grain	0	0	90, 88

[a] Fortified level: 0.05 ppm.

Table 2 Effects of pH of homogenate on the recovery of benfuracarb from the orange.[a]

Reagent for pH adjustment	pH of homogenate	Volume (ml) of $AgNO_3$ solution added		% recovery
		At homogenization	At concentration	
None	3.7	0	0	3, 8
None	3.7	2	2	13, 1
10% NaOH	8.5	0	0	27, 29
10% NaOH	8.5	2	2	51, 53
10% NaOH	6.8	2	2	76, 86
Buffer (pH 8.0)	—	2	2	92, 99

[a] Fortified level: 0.05 ppm.

sentative crops. The recovery of benfuracarb was satisfactory in the green pepper and cabbage when 2 ml of 0.1 N $AgNO_3$ solution was added before homogenization and concentration, while in a case of the corn and rice grain, the recovery was good without the addition of $AgNO_3$ solution. In general, 2 ml each of $AgNO_3$ solution was added before homogenization and concentration to all crops except for the Japanese radish, which required of 5 ml each of $AgNO_3$ solution. In a case of the orange, the recovery was very poor even 5 ml of $AgNO_3$ solution was added.

1.2 Addition of pH 8.0 buffer

The recovery of benfuracarb from the orange fortified at a level of 0.05 ppm was still very poor (less than 13%) even after addition of the $AgNO_3$ solution. Such poor recovery was presumed to be caused by the lower pH in the orange homogenate. Therefore, 10% sodium hydroxide solution or phosphate buffer (pH 8.0) was added when the orange was homogenized. As expected, the recovery significantly increased, as seen in Table 2. The recovery was most stable and satisfactory when 25 ml of phosphate buffer (pH 8.0) along with 2 ml each of $AgNO_3$ solution was added during the homogenization and concentration. Therefore, for the residue analysis of the orange 25 ml of phosphate buffer (pH 8.0) is necessary in addition to the general extraction procedure described in "Materials and Methods," Section *4.1.*

1.3 Cleanup

Combination of the Florisil and the silica gel column chromatography was necessary to remove coextractives which showed large peaks on the gas chromatograms and prevented quantitation of benfuracarb and carbofuran or 3-OH-CF and 3-C=O-CF. The concentrated crop extracts to be subjected to the Florisil column chromatography were dissolved in carbon tetrachloride (for the analysis of benfuracarb and carbofuran) or in a dichlorometane-carbon tetrachloride (1 : 1) mixture (for the analysis of 3-OH-CF and 3-C=O-CF), because of good solubility of these compounds in the solvent or the solvent mixture.

The quantitation of benfuracarb in the eggplant, spinach, Japanese radish and rice grain among the eleven crops tested required an additional or alternative cleanup procedure. In a case of the Florisil column chromatography of the extract from the eggplant, 10 g of Florisil, instead of 5 g, was needed to separate benfuracarb from interferences, as confirmed by comparative gas chromatograms shown in Fig. 2-a. For the silica gel column chromatography of the extracts from the spinach and Japanese radish, 2 g of aluminum oxide containing 0.5% of $AgNO_3$ on top of the silica gel (7 g) layer was useful in separating benfuracarb from interferences. Comparative chromatograms of the spinach were shown in Fig. 2-b. In a case of the rice grain, coextractives in the

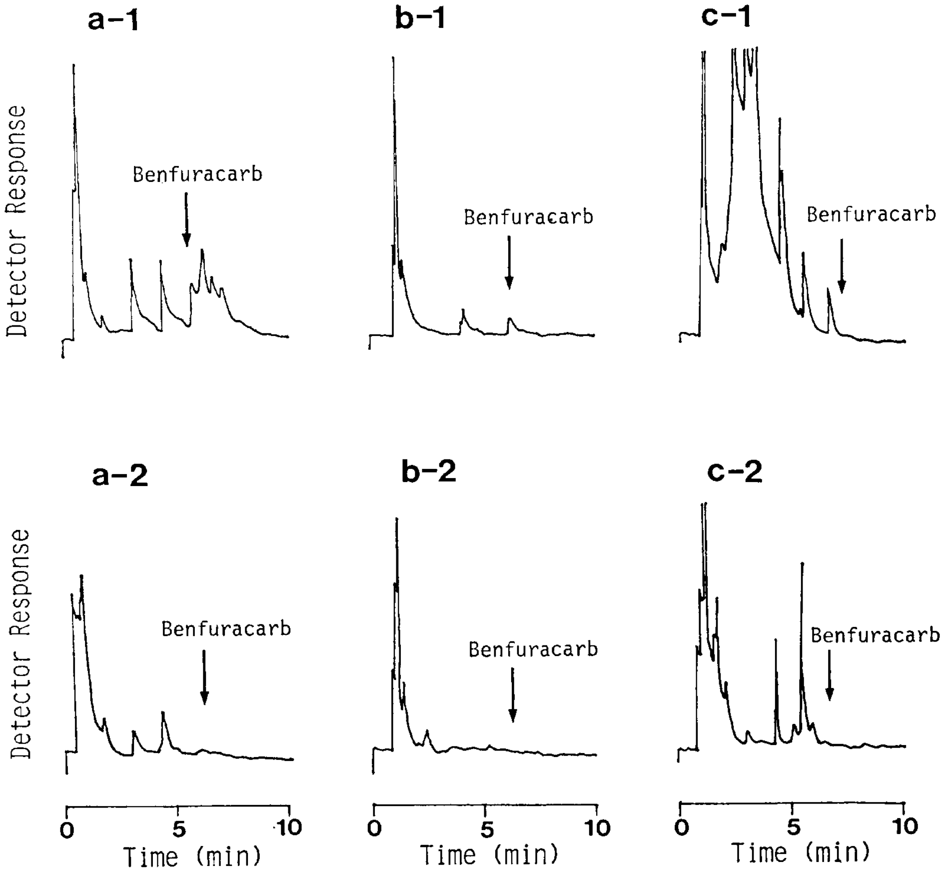


Fig. 2 Comparative gas chromatograms of the extract from unfortified samples of the eggplant (a), spinach (b) and rice grain (c) before and after alternative or additional cleanup for benfuracarb quantitation.

Arrows indicate the retention time of benfuracarb. (a-1) cleanup with 5 g of Florisil, (a-2) cleanup with 10 g of Florisil, (b-1) cleanup with silica gel only, (b-2) cleanup with silica gel and aluminum oxide containing 0.5% $AgNO_3$, (c-1) acetonitrile extraction only, (c-2) acetonitrile extraction followed by partitioning between *n*-hexane and acetonitrile.

acetonitrile extract were removed by partitioning between acetonitrile and *n*-hexane. The partitioning procedure: *n*-hexane (50 ml) was added to the combined mixture of the acetonitrile extract and washings (200 ml). The mixture was shaken for 1 min and the acetonitrile phase was taken to be subjected to the next procedure. Comparative gas chromatograms of the rice grain were shown in Fig. 2-c.

1.4 Extraction and cleanup procedure of 3–OH–CF and 3–C=O–CF

The described procedure for the extraction and cleanup of 3–OH–CF and 3–C=O–CF based on the published informations[8-11] can provide a sample pure enough to be analyzed quantitatively by GC employing a quartz capillary column.

In the extraction procedure of the refluxed sample of homogenized crops, an addition of 5 ml of 4% sodium dodecylsulfate solution into a separatory funnel with an extraction solvent (dichloromethane) was effective to separate the mixture into two phases. An addition of 20 g of potassium chloride, which was also examined, did not produce satisfactory results.

1.5 Concentration

As mentioned previously, the crop extract should be concentrated at a water-bath temperature below 35°C. The results indicated that benfuracarb significantly decomposed during the concentration procedure at a water-bath temperature of over 55°C.

2. GC Operational Conditions

For the gas chromatographic residue analysis of benfuracarb, carbofuran, 3–OH–CF and 3–

Table 3 Recovery of benfuracarb, carbofuran, 3–OH–CF and 3–C=O–CF from different crop samples.

Crop sample	Location (prefecture)	Recovery (%)[a] at different fortification level (ppm)							
		Benfuracarb		Carbofuran		3–OH–CF		3–C=O–CF	
		0.05	0.5	0.05	0.5	0.05	0.5	0.05	0.5
Rice	Shizuoka	90	90	84	98	76	98		
(grain)	Yamagata	97	100	100	98	82	82		
Cucumber	Nagano	86	87	86	84	91	88		
(fruit)	Kagoshima	88	94	97	85	89	95		
Green pepper	Wakayama	88	88	96	99	98	93	87	81
(fruit)	Ibaraki	94	96	92	92	85	87	86	79
Water melon	Nagano	98	90	96	99	92	87		
(fruit)	Ibaraki	94	98	97	99	97	77		
Melon	Shizuoka	98	86	88	84	98	83		
(fruit)	Kumamoto	96	98	85	92	98	85		
Eggplant	Kochi	92	96	92	93	87	94	86	81
(fruit)	Kagoshima	93	99	98	92	96	99	93	82
Japanese radish	Nagano	93	90	91	100	86	86	85	86
(root)	Ibaraki	75	82	74	80	92	88	76	82
Japanese radish	Nagano	81	89	97	95	86	96	99	90
(leaf)	Ibaraki	81	92	95	88	86	99	95	94
Corn	Yamanashi	91	78	73	79	79	81		
(grain)	Iwate	82	80	79	77	83	90		
Cabbage	Wakayama	91	93	95	80	78	91		
(leaf)	Nara	85	96	98	97	89	86		
Orange	Wakayama	89	98	98	94	85	85		
(fruit)	Shizuoka	96	96	98	98	94	82		
Spinach	Aichi	92	80	92	82	90	92		
(leaf)	Tokushima	94	83	85	85	96	95		

[a] Means of duplicate determinations.

C=O–CF using an FTD detector, a variety of glass columns (3 m in length) packed with materials such as OV-101, OV-105 and OV-210, and a quarts capillary column (25 m) coated with OV-101 were tested. The results indicated that the best peak shape, separation and response could be achieved by using the quartz capillary column. The combination of the gas chromatograph employing the quartz capillary column and the mentioned extraction procedure could enhance the sensitivity of detection up to a 0.005 ppm level for all four compounds. Under the conditions described, the retention times of benfuracarb, carbofuran, 3–OH–CF and 3–C=O–CF were 6.0, 4.6, 5.8 and 4.8 min, respectively. Equivalent performance with other gas chromatograph units using the same column could be obtained with minor changes in the gas chromatographic conditions.

Gas chromatography using a packed glass column showed relatively broader peak shapes for all four compounds. However, the packed OV-101 column was also useful for the residue analysis of the four compounds with the same detection limit (0.005 ppm).

3. *Recovery and Detection Limit*

Recovery values of 12 different crop samples (11 crops) each collected from two different locations and fortified with benfuracarb, carbofuran, 3–OH–CF or 3–C=O–CF are presented in Table 3. Crop types, locations and spiking levels produced no significant difference in

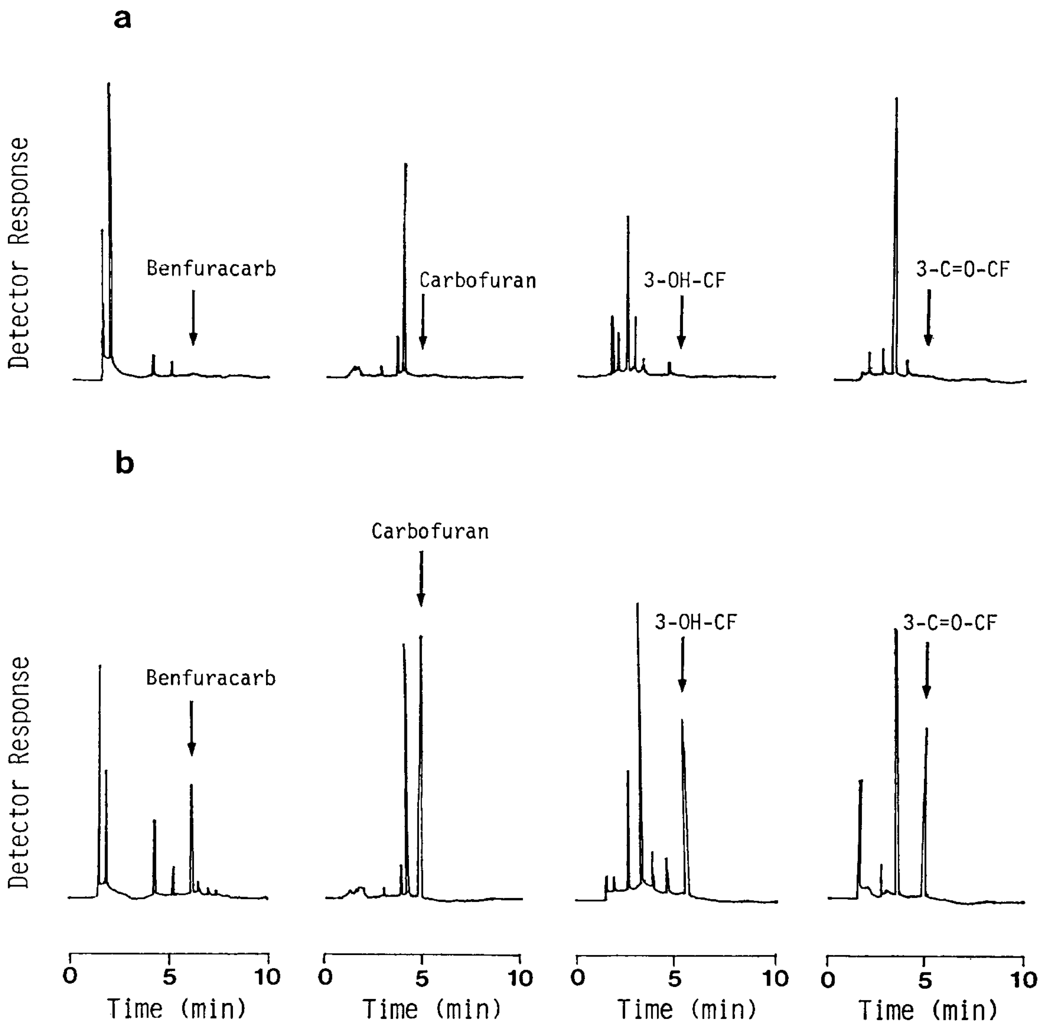


Fig. 3 Typical chromatograms for the analysis of benfuracarb, carbofuran, 3–OH–CF and 3–C=O–CF in the eggplant by GC.

(a) eggplant blank, (b) eggplant+0.05 ppm of each compound.

recovery: 75–100% with benfuracarb, 73–100% with carbofuran, 76–99% with 3–OH–CF and 76–99% with 3–C=O–CF. There were no troublesome interferences in any of the samples.

Representative chromatograms of crop extracts unfortified or fortified with benfuracarb, carbofuran, 3–OH–CF or 3–C=O–CF are shown in Fig. 3 using the eggplant as an example.

The limit of detection (quantitation of a single three times the noise level) was determined to be 0.005 ppm for all four compounds.

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要　　約

ベンフラカルブおよびその代謝物カルボフラン，3–ヒドロキシ–カルボフラン，3–ケト–カルボフランのガスクロマトグラフィーによる作物における残留分析法

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ベンフラカルブおよびその主要代謝物であるカルボフラン，3-ヒドロキシ-カルボフラン (3-OH-CF)，3-ケト-カルボフラン (3-C=O-CF) の残留分析法を11の作物について検討した．ベンフラカルブおよびカルボフランは，作物を磨砕後メタノールで抽出したが，この過程でのベンフラカルブの分解を防止するため安定剤として硝酸銀水溶液を添加した．3-OH-CF および 3-C=O-CF は抱合体を加水分解するため 0.25 N 塩酸で加熱還流して抽出した．それぞれの抽出液は，ジクロロメタンに転溶後シリカゲルおよびフロリジルカラムクロマトグラフィーにより精製し，石英キャピラリーカラムを用いる FTD-ガスクロマトグラフィーにより定量した．それぞれの化合物の回収率は，ベンフラカルブ 75～100%，カルボフラン 73～100%，3-OH-CF 76～99%，3-C=O-CF 76～99% であり，検出限界は全化合物とも 0.005 ppm であった．