A Method for the Determination of 1,3-Dichloropropene, 1,2-Dibromoethane, and 1,2-Dibromo-3-chloropropane in Food Crops

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1,3-Dichloropropene (DCP), 1,2-dibromoethane (EDB), and 1,2-dibromo-3-chloropropane (DBCP) were determined concurrently in foods by extraction with acetonitrile, partitioning into hexane, column chromatography on Florisil, and gas–liquid chromatography with electron-capture detection. Overall mean recoveries (% ± standard deviation) were 89.6 ± 7.7 for *trans*-DCP from 0.05 to 5.1 ppm, 93.0 ± 7.3 for *cis*-DCP from 0.05 to 5.0 ppm, 92.3 ± 7.6 for EDB from 0.025 to 2.5 ppm, and 97.5 ± 5.4 for DBCP from 0.008 to 0.81 ppm. Minimum detectable limits were estimated to be 3 ppb for DCP, 14 ppb for EDB, and 0.3 ppb for DBCP.

1,3-Dichloropropene (DCP), 1,2-dibromoethane (EBD), and 1,2-dibromo-3-chloropropane (DBCP) are registered for use as fumigants for soils in which a variety of fruit and vegetables may be grown. Although several methods for the analysis of these compounds in dried materials such as grain and grain products have been described (e.g., Berck, 1974; Heuser and Scudamore, 1969; Malone, 1970), relatively few are available for residues in fresh commodities. Gas–liquid chromatographic procedures have been presented for DBCP in brussels sprouts (Beckman and Bevenue, 1963) and for DCP in potatoes (Karasz and Gantenbein, 1970) but for our purposes, neither was found applicable to a wide range of commodities with sufficient sensitivity. The present method was developed to permit the simultaneous determination of three commonly employed soil fumigants in a variety of foods.

EXPERIMENTAL SECTION

Materials. *cis*- and *trans*-1,3-dichloropropene were purchased from Chemicals Procurement Laboratories Inc., College Point, N.Y. Each contained a significant proportion of the other isomer in addition to other impurities and was redistilled before use. The distillate was collected manually in ten fractions. Fractions containing only *cis*- and *trans*-DCP were combined and the ratio of cis to trans determined by 60-MHz NMR. Since this ratio agreed with that determined by gas–liquid chromatography with electron-capture detection, it was assumed that the detector responded equally to each compound on a weight basis.

1,2-Dibromoethane was supplied by Aldrich Chemical Co., Milwaukee, Wis., and was labeled as being 99% pure.

1,2-Dibromo-3-chloropropane was purchased from Fairfield Chemical Co., Blythewood, S.C., and was found to be 97.5% pure by gas–liquid chromatography against a standard labeled as assaying 100%.

Florisil used for column chromatography was washed with chloroform, dried at 90 °C, and activated by heating at 300 °C for 20 h.

Samples of crop (5 g) were fortified by adding 0.50 mL or less of an acetonitrile solution of the fumigants to the samples immediately before the initial extraction.

Analytical Procedure. The sample (5.0 g) was homogenized with acetonitrile (25 mL) by blending at high speed for 30 s in a Sorvall Omni-Mixer. The homogenate was filtered by gravity flow through Whatman No. 1 paper and an aliquot (15 mL) of the filtrate added to 5 M NaCl (80 mL) in a 125-mL separatory funnel. The aqueous phase was shaken with hexane (5.0 mL) and the extract dried over anhydrous sodium sulfate. An aliquot (4.0 mL) of the dry hexane extract was passed through a column

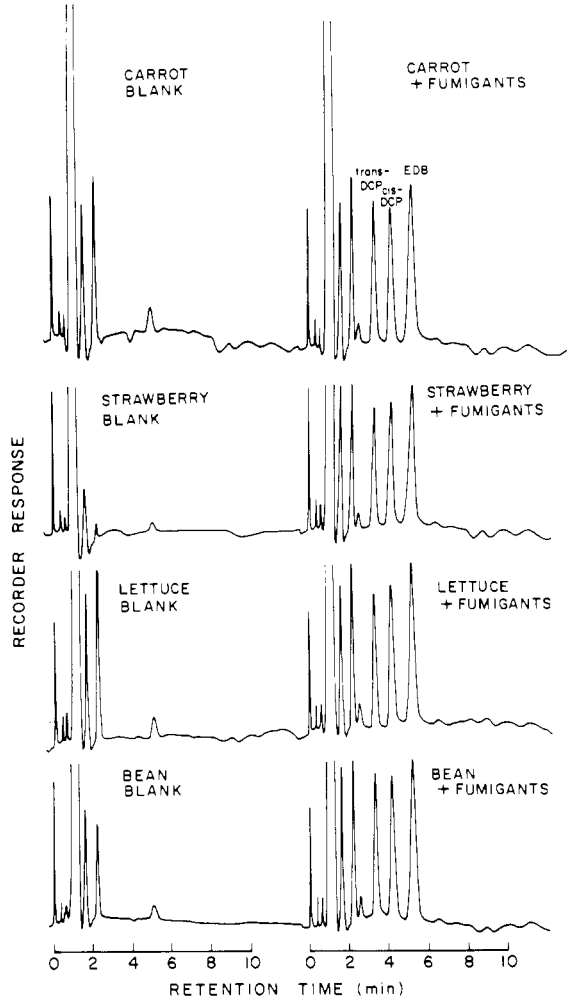

Figure 1. Gas–liquid chromatograms of processed extracts of various commodities with and without the addition of 0.051 ppm of *trans*-1,3-dichloropropene (*trans*-DCP), 0.050 ppm of *cis*-1,3-dichloropropene (*cis*-DCP), 0.025 ppm of 1,2-dibromoethane (EDB), and 0.008 ppm of 1,2-dibromo-3-chloropropane (DBCP). Column temperature was 60 °C. The peak for DBCP does not appear because of its long retention time. Each injection (7 μL) represents the equivalent of 2.8 mg of tissue.

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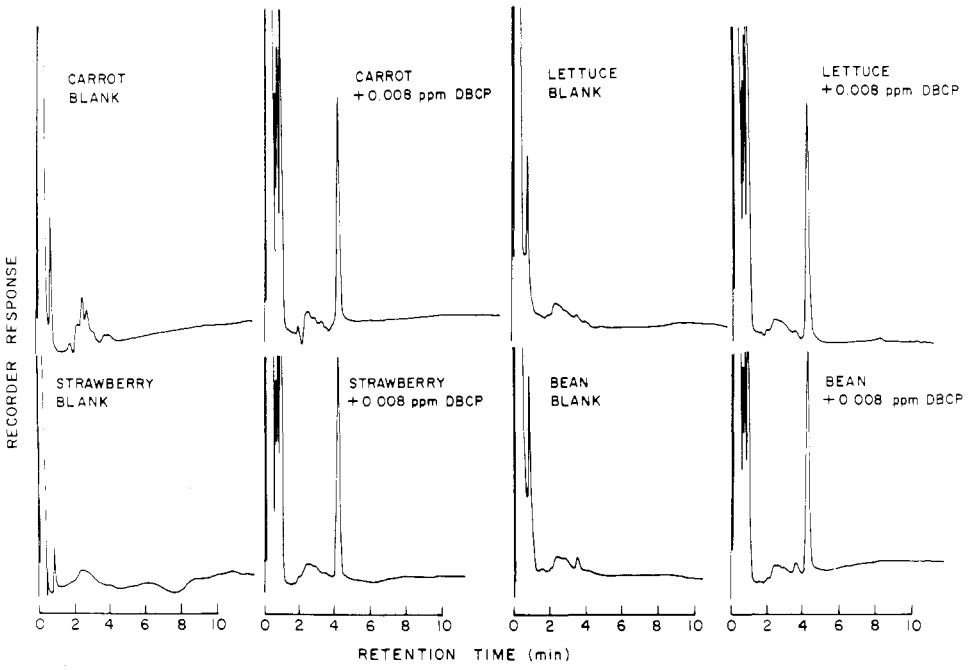

Figure 2. Gas–liquid chromatograms of processed extracts of various commodities with and without the addition of *trans*-1,3-dichloropropene (*trans*-DCP), *cis*-1,3-dichloropropene (*cis*-DCP), 1,2-dibromoethane (EDB), and 1,2-dibromo-3-chloropropane (DBCP). Column temperature was 130 °C. Each injection (5 μL) represents the equivalent of 2.0 mg of tissue. *trans*-DCP, *cis*-DCP, and EDB emerge near the solvent peak.

Table I

Compound analyzed	DCP, EDB	DBCP
Column temp	60 °C	130 °C
Carrier gas	Argon–methane (95:5)	Nitrogen
Carrier flow rate	33 mL min^{-1}	26 mL min^{-1}
Injector temp	150 °C	170 °C
Detector temp	300 °C	180 °C

(1.5 cm diameter) of activated Florisil (2.0 g) in hexane. The column was washed with hexane (2.0 mL) and the washings discarded. The fumigants were then eluted with a further portion of hexane (6.0 mL) and an aliquot of the eluent analyzed by GLC.

Gas–Liquid Chromatography. Two instruments were used, one operating at 60 °C for the analysis of DCP and EDB and the other at 130 °C for the analysis of DBCP. In the former case a Hewlett Packard 5700 A equipped with a ^{63}Ni electron-capture detector was employed while DBCP was determined on a Varian Aerograph 1400 fitted with a ^{3}H electron-capture detector. Both instruments contained 6 ft × 4 mm i.d. glass columns packed with 6% QF-1 and 4% SE-30 on 80–100 mesh Supelcoport. The columns were heated at 50 °C above the operating temperature for 24 h before use. The operating parameters were as shown in Table I. Under these conditions and with routine working attenuation, approximately 50% full-scale deflection was given by 0.14 ng of *cis*- or *trans*-DCP, 0.07 ng of EDB, and 0.015 ng of DBCP. Compounds were quantitated by comparison of the peak height to that of a standard of similar concentration.

GLC–Mass Spectrometry. Samples were analyzed on a Varian MAT 311A double-focusing spectrometer coupled to a Varian 1440 GLC. The GLC contained a 6 ft × 4 mm i.d. glass column packed with 6% OV-210 and 4% SE-30 on 80–100 mesh Gas-Chrom Q. The column temperature was 70 °C for the analysis of DCP or EDB and 130 °C for DBCP. The mass spectrometer was operated with the interface at 220 °C, the source at 200 °C, and an ionizing voltage of 66 eV. For DCP, the $C_3H_4{}^{35}Cl$ fragment ion at m/e 75 was monitored with a resolution of 5000. The $C_2H_4{}^{79}Br$ ion at m/e 107 and $C_3H_5{}^{35}Cl{}^{79}Br$ ion at m/e 155 were monitored with a resolution of 5000 in the cases of EDB and DBCP, respectively.

Table II. Recoveries of Fumigants Added to Various Commodities[a]

Amount added, ppm	Recovery, %			
	Carrot	Lettuce	Strawberry	Bean
		trans-DCP		
0.051	91.2	88.8	76.5	95.9
0.103	80.4	80.0	81.4	90.1
0.513	84.5	90.6	100	79.2
1.03	92.8	86.4	98.8	97.8
5.13	84.6	94.7	103	94.8
		Overall mean ± SD		89.6 ± 7.7
		cis-DCP		
0.050	97.8	86.0	87.8	107
0.100	82.2	85.7	87.8	91.4
0.501	88.5	91.4	103	82.8
1.00	95.4	92.0	101	102
5.01	88.0	94.3	103	93.2
		Overall mean ± SD		93.0 ± 7.3
		EDB		
0.025	100	97.1	79.6	100
0.051	78.8	88.1	83.2	94.9
0.254	84.1	95.3	99.7	86.2
0.508	95.3	94.8	94.7	101
2.54	81.4	94.3	102	93.1
		Overall mean ± SD		92.3 ± 7.6
		DBCP		
0.008	103	105	101	100
0.016	91.5	95.3	89.5	94.2
0.081	95.9	100	104	88.4
0.162	104	103	94.4	102
0.810	93.3	99.1	97.7	88.7
		Overall mean ± SD		97.5 ± 5.4

[a] Values are the means of duplicate determinations.

RESULTS AND DISCUSSION

The use of either acetone or absolute ethanol as an extraction solvent resulted in peaks on the GLC which

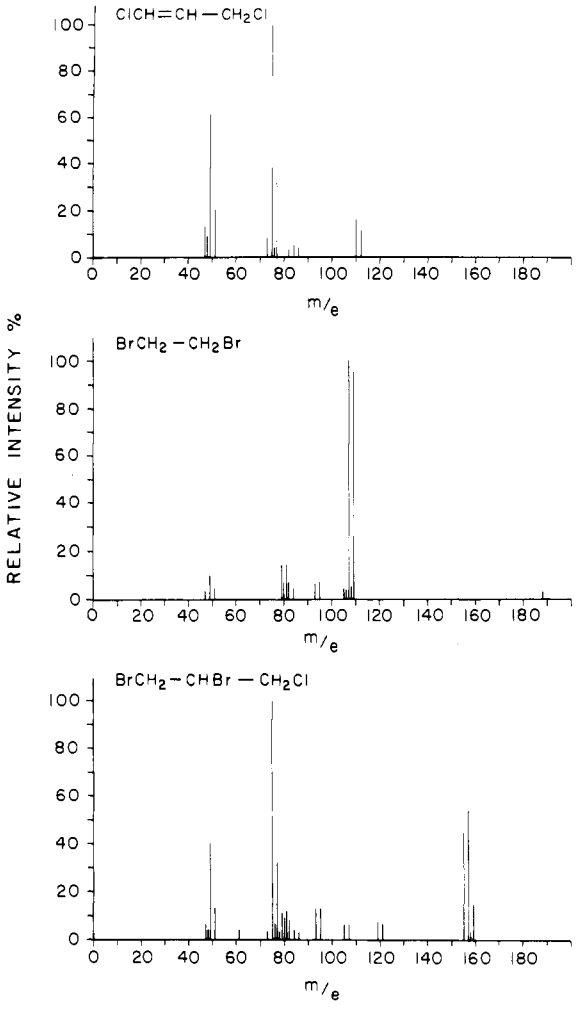

Figure 3. Mass spectra of 1,3-dichloropropene, 1,2-dibromoethane, and 1,2-dibromo-3-chloropropane. Ionization voltage was 66 eV.

interfered with the determination of DCP and EDB. Acetonitrile produced the best recoveries and the lowest background. As shown in Figure 1, a component with retention time slightly less than that of EDB occurred in extracts of all commodities at a level equivalent to approximately 7 ppb of EDB. No interfering compounds were present during the analysis of DBCP as shown in Figure 2. The minimum detectable amount of each compound was estimated to be 3 ppb for *cis*- or *trans*-DCP, 14 ppb for EDB, and 0.3 ppb for DBCP using a 2:1 signal:noise ratio.

Mean recoveries of fumigant added to various commodities were constant over a 100-fold range of concentration as indicated by the data in Table II. A salt concentration of at least 5 M was required to obtain satisfactory recoveries of DCP when partitioning into hexane. Lower concentrations did not affect the recovery of EDB or DBCP.

Confirmation of fumigant residues was carried out by GLC–mass spectrometry. As shown by the spectra in Figure 3, none of the compounds gave a molecular ion in sufficient abundance to be useful for detection by single ion monitoring. Using the stated fragment ions, and with a 2:1 signal:noise ratio, a lower limit of detection of 0.050 ppm for DCP and 0.025 ppm for EDB and DBCP was established with vegetable extracts.

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X-Ray Fluorescence Spectroscopic Determination of Br^- Residues in Crops after Soil Treatment by Methyl Bromide

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Dried samples of lettuce, pepper, and cucumber cultures, grown on soils treated with CH_3Br and on nontreated soils, have been analyzed for their Br^- content by x-ray fluorescence spectroscopy (XRFS). Variations in the Br^- concentrations in the plants have been followed during a growing period of several months. It appears that the levels for the treated soils considerably exceed at all times the maximum values admitted in most European countries and seem to be approximately inversely proportional to the total dry weight material of the crops. The x-ray fluorescent (dispersion) spectroscopic technique, used here, reveals to be perfectly adapted for analysis in this concentration range and may be used as a very rapid screening technique for the detection of bromine in crop material. In order to obtain some information about the accuracy of the technique, the results obtained by this technique have been compared with those obtained by a colorimetric method for a number of cases.

Intensive crop cultures require a careful control of the soil conditions. Futhermore, to obtain good yields in those cultures it is necessary to eliminate harmful effects of weeds and mold as much as possible. Therefore, the treatment with pesticides, fungicides, and soil disinfectants is practically unavoidable. Their use, however, gives rise to new problems, such as those related to the presence of their residues in the plant.

Among the many soil disinfectants CH_3Br takes an important place because of its efficiency against mold and weeds. After application this CH_3Br is rapidly converted to inorganic bromide in the soil and can be accumulated

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