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Gas Chromatographic Quantitative Analysis and Persistence of Dimethoate and Dimethoxon Residues on and in Wheat Plants

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Wheat plants fortified with dimethoate and dimethoxon were blended and extracted with chloroform. The concentrated extract was passed through a silica gel column, evaporated, and injected into a gas chromatograph equipped with a flame photometric detector and a column containing 12% OV-101 and 1.2% Carbowax 20M on Chromosorb W. Recoveries of dimethoate and dimethoxon were about 92% and 89%, respectively, in the range of 0.03–10 ppm. Dimethoate was applied to wheat plants seeded on three dates. Samples were collected 0–17 days after application. The dimethoate residues were 63.2, 41.5, and 17.4 ppm immediately after application and were 0.02, 0.36, and 0.62 ppm by 17 days after application. Dimethoate concentration decreased more rapidly on the younger wheat plants. Dimethoxon concentrations increased and then decreased more rapidly on the younger wheat plants.

Dimethoate, *O,O*-dimethyl *S*-(*N*-methylcarbamoylmethyl)phosphorodithioate, is an organophosphorous insecticide that is registered in Canada for insect control in cereal, oilseeds, commercial and home gardens, forage crops, trees, shelterbelts and shrubs (Agriculture Canada, 1979). In the province of Saskatchewan one of the main uses of dimethoate is for grasshopper control in wheat.

A number of analytical methods for dimethoate and its oxygen analogue, dimethoxon [*O,O*-dimethyl *S*-(*N*-methylcarbamoylmethyl)phosphorothioate] residues have appeared in the literature based on gas chromatography. Storherr and Watts (1969) described a method for the gas chromatographic (GC) analysis of dimethoate and dimethoxon in field-sprayed kale using a 2% diethylene glycol succinate column, and Woodham et al. (1974a,b) determined dimethoate and dimethoxon residues in citrus crops by using a DC-200 column. Steller and Pasarela (1972) used a column based on a light loading Versamid 900 and a heavier loading of DC-200. Also small quantities of poly(ethylene glycol) needed to be added to every injection to maintain satisfactory performance. MacNeil (1975) described the use of OV-17 for determing dimethoate and dimethoxon residues on cherries.

The following method was developed to determine dimethoate and dimethoxon on and in wheat plants by using a column of OV-101 and Carbowax 20M double coating, and this method was used for the determination of the rate of disappearance of dimethoate and dimethoxon residues on and in field-sprayed wheat plants.

EXPERIMENTAL SECTION

Apparatus. A Beckman GC-5 gas chromatograph fitted with a Melpar flame photometric detector and phosphorous filter (526 nm) was used. The chromatographic column was a 1.8-m glass column, 4-mm inside diameter. The column packing was prepared by first coating Chromosorb W (100–200 mesh; acid wash; dimethylchlorosilane treated) with 1.2% Carbowax 20M and then applying a second coating of 12% OV-101.

The operating conditions were column, injector, and detector temperatures of 180, 210, and 160 °C, respectively. The flow rate of carrier gas, helium, was 100 mL/min, whereas those of hydrogen, air, and oxygen were 190, 90, and 30 mL/min, respectively.

Reagents. All solvents were glass-distilled residue-free grade. Analytical standards of dimethoate (99.8% purity), dimethoxon (analytical standard), and malathion (99.1% purity) were obtained from American Cyanamid Co., and stock solutions were prepared in ethyl acetate. Malathion was used as the internal standard. Hyflo Super-Cel (Fischer Scientific Co.) and silica gel, Davison grade 12 (Fischer Scientific Co.), were used as received.

Wheat Treatments. Field experiments were carried out at Saskatoon, Saskatchewan, Canada, where wheat was seeded on May 1, May 15, and June 1. The experimental plots were 20 × 20 m, and there were four plots for each seeding date. On June 28, the date of application of dimethoate, the wheat was in three stages of development: the "boot" stage, second node visible, and tillering for the May 1, May 15, and June 1 plots, respectively. Dimethoate was applied by a self-propelled boom sprayer at the recommended rate of 420 g of active ingredient/ha (6 oz/acre). The first samples were taken ~2 h after aplication, with further samples being taken at several intervals over the next 3 weeks. Samples of wheat foliage were cut off at ground level, transferred to plastic bags, sealed, and frozen at −20 °C until analyzed.

Extraction. Whole wheat plants were chopped into pieces less than 1 cm long and mixed thoroughly. A subsample (20 g) was blended with chloroform (150 mL) for 5 min at high speed in Virtis homognizer. Hyflo Super-Cel (7 g) was added to the homogenized sample and mixed. The sample was filtered through a pad of Hyflo Super-Cel (3 g) on a filter paper on a Buchner funnel with vacuum. The filter residue was scraped back into the homogenizer

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Table I. Recovery of Dimethoate and Dimethoxon from 20 Grams of Fortified Wheat Plants

fortification, ppm		recovery ± SE, %[a]	
dimethoate	dimethoxon	dimethoate	dimethoxon
0.03	0.03	84.1 ± 3.5	77.3 ± 6.0
0.51	0.68	89.2 ± 2.9	87.2 ± 2.1
1.02	1.36	93.0 ± 1.2	88.3 ± 1.1
5.12	6.81	98.4 ± 0.8	97.9 ± 0.8
10.23	13.61	97.3 ± 0.8	96.6 ± 1.3
	av:	92.4	89.4

[a] Results are the mean percentage recovery from three replicates. SE, standard error.

cup, blended with chloroform (150 mL), and filtered. The blending and filtering were then repeated once more. The blender cup and the filter residue were washed with chloroform (2 × 20 mL). All filtrates and washings were combined prior to drying over anhydrous sodium sulfate (30 g). The dried extract was filtered through a filter paper on a Buchner funnel with vacuum. The flask, sodium sulfate, and filter paper were washed with chloroform (2 × 25 mL). The filtrates and washings were combined and concentrated to ~30 mL on a rotary evaporator at a water bath temperature lower than 35 °C. All evaporations were done in this manner.

Column Cleanup. The silica gel column cleanup procedure was modified from that reviewed by Zweig and Sherma (1972). Anhydrous sodium sulfate was added to a depth of 1 cm over a glass wool plug in a column containing acetone–hexane (1:4; 50 mL). Silica gel (15 g) was added to acetone–hexane (1:4; 30 mL), allowed to stand for ~5 min, and then stirred with a glass rod to remove the trapped air bubbles and transferred to the column. The side of the column was washed down with acetone–hexane (1:4), and a glass wool plug was placed on top of the packed silica gel. The column was drained until the level of solvent was even with the top of the silica gel. The concentrated sample was transferred to the column, and the flask and side walls of the column were rinsed with acetone–hexane (1:9; 2 × 15 mL). The column flow rate was adjusted to 4–5 mL/min and eluted until the level of the solution in the column reached the top of the silica gel. Acetone–hexane (1:4; 100 mL) was added and eluted at the same flow rate until the level of the solution was at the top of the silica gel. This elute was discarded. The receiver was changed and the column eluted with acetone (300 mL). The acetone eluant was concentrated on a vacuum rotary evaporator to ~0.5–3 mL, and an internal standard (malathion) was added prior to injection into the GC.

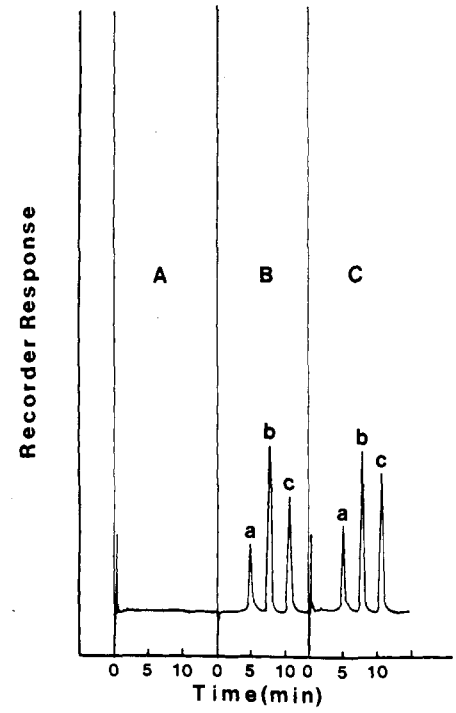

Figure 1. Chromatrogram of (a) diamethoxon, 6.81 ng, (b) dimethoate, 5.12 ng, and (c) malathion, 3.73 ng. (A) Unfortified wheat foliage (20 g); (B) standards; (C) fortified wheat foliage (20 g).

Recovery Studies. Aliquots of dimethaote and dimethoxon standard stock solutions were added to the chopped wheat foliage just prior to the first blending with chloroform. The remaining extraction and cleanup steps are as previously stated.

Calculations. The calculation methods are similar to those used by Lee and Westcott (1980).

RESULTS AND DISCUSSION

The 12% OV-101 and 1.2% Carbowax 20M double-coated column separated dimethoxon, dimethoate, and malathion as shown in Figure 1. Under the GC conditions the retention times of dimethoxon, dimethoate, and malathion (internal standard) were 5.2, 8.0, and 11.0 min, respectively, and the minimum detectable amounts of dimethoxon, dimethoate, and malathion were about 2.5, 0.7, and 0.7 ng, respectively. The minimum detectable concentration in a 20-g wheat sample by this method was 0.01 ppm of dimethoxon.

The recoveries of pesticides from laboratory-fortified wheat foliage samples are given in Table I. The average

Table II. Residues of Dimethoate and Dimethoxon on and in Wheat Plants following Application of Dimethoate at 420 Grams of Active Ingredient per Hectare

		residues, ppm, at seeding dates					
		May 1		May 15		June 1	
sampling date	days after spray	dimethoate	dimethoxon	dimethoate	dimethoxon	dimethoate	dimethoxon
June 28	0	17.36	ND[a]	41.50	ND	63.18	ND
29	1	7.08	T[b]	14.07	T	13.79	0.19
30	2	5.19	0.45	9.96	0.96	10.39	1.32
July 1	3	4.72	0.63	5.40	0.71	8.54	1.22
2	4	4.25	0.62	4.86	0.74	5.46	0.90
4	6	4.03	0.60	3.65	0.56	4.89	0.76
5	7	3.99	0.58	2.70	0.49	2.97	0.55
7	9	2.13	0.44	1.95	0.36	1.22	0.25
11	13	0.64	0.25	0.55	0.19	0.12	0.06
15	17	0.62	0.24	0.36	0.14	0.02	0.03

[a] ND, not detectable, less than 0.005 ppm. [b] T, trace amounts, between 0.005 and 0.009 ppm.

recoveries of dimethoate and dimethoxon added to wheat samples over the range 0.03–10.23-ppm level were 92% and 89%, respectively. Recoveries at all levels of fortification were good, and this method is suitable for the determination of dimethoate and dimethoxon residues on and in field wheat plants.

About 90% of all field wheat samples were analyzed in single and about 10% in duplicate, and average values from the four plots are reported in Table II. The results reported in Table II are not corrected for recovery. The blank foliage samples which were collected at the heading stage from both untreated field-grown and greenhouse-grown plants did not show any interfering peaks in the range of the rentention times of dimethoxon, dimethoate, or the internal standard, malathion.

Table II shows that the dimethoate concentration found in the June 1 crop, 63.18 ppm, was higher than that found on the May 15 crop, 41.50 ppm, and the May 15 crop was higher than the May 1 crop, 17.36 ppm. This is to be expected when it is realized that the mass of wheat foliage per unit area is much less for the June 1 crop than it is for the May 15 crop, and the May 15 crop is less than the May 1 crop, but yet each unit area nominally received the same quantity of dimethoate.

The rate of disappearance of dimethoate was very rapid for the first few days. About 60–80% of dimethoate was lost in the first day after application. It seems likely to propose that dimethoate is still on the surface of the foliage and the loss is mainly accounted for by evaporation. Approximately 1 week after application, the concentrations of dimethoate on May 1, May 15, and June 1 crops were nearly the same. This can be explained in part by the more rapid growth of the younger plants.

One day after dimethoate was sprayed on the wheat plants, the June 1 crop had a dimethoxon residue level of 0.19 ppm, whereas the older plants had only trace levels of dimethoxon. The more rapid rate of appearance of dimethoxon in the youngest wheat plants may be indicative of more active metabolism of dimethoate by these plants or may be a reflection that the youngest plants had the highest concentration of dimethoate immediately after spraying. It would be reasonable to propose that the plants with the highest concentration of dimethoate would also have the highest concentration of dimethoxon soon after spraying.

The rate of disappearance of dimethoxon in the youngest plants was higher than that in the older plants. This may again be a indication of more active metabolism of dimethoxon by the younger plants. However, it must be remembered that the youngest plants were growing more rapidly and that the concentration of both dimethoxon and dimethoate would be reduced because of plant growth.

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