oligophagous ones, depend on a few distinct chemical cues for host-plant selection (Thorsteinson, 1960).

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Gas–Liquid Chromatographic Methods for the Determination of Disulfoton, Phorate, Oxydemeton-methyl, and Their Toxic Metabolites in Asparagus Tissue and Soil

Sunny Y. Szeto* and Marilyn J. Brown

GLC methods were developed for the determination of individual insecticide residues in asparagus tissue and soil for three groups of compounds: (I) disulfoton and (II) phorate and their sulfoxides, sulfones, oxons, oxon sulfoxides, and oxon sulfones and (III) oxydemeton-methyl and its sulfone. Residues were extracted by blending with ethyl acetate, except soil samples fortified with III, which were extracted with a mixture of 20% methanol in ethyl acetate. Cleanup and separation of individual compounds within each group were achieved by column chromatography using a 2:5 (w/w) mixture of Nuchar C charcoal and Whatman CF-11 cellulose. After separation, disulfoton sulfoxide, disulfoton oxon sulfoxide, and oxydemeton-methyl were oxidized with aqueous $KMnO_4$ to their corresponding sulfones. Gas chromatographic detection was accomplished by using an alkali flame ionization detector and a GLC column (75 cm × 2 mm i.d.) packed with 2% OV-101 on 80–100-mesh Ultra-Bond 20M. Recoveries of the individual compounds ranged from 83.7 to 110%.

Disulfoton [*O,O*-diethyl *S*-[2-(ethylthio)ethyl] phosphorodithioate] is a systemic insecticide and acaricide marketed in North America by the Mobay Chemical Corp. under the trade name Di-Syston. It is used mainly as emulsifiable concentrates for foliage treatment and as granules for soil application to protect plants from insect attack. Currently disulfoton and two other structurally related systematic insecticides, phorate [*O,O*-diethyl *S*-(ethylthio)methyl phosphorodithioate, Thimet] and oxydemeton-methyl [*S*-[2-(ethylsulfinyl)ethyl] *O,O*-dimethyl phosphorothioate, Metasystox-R], are under evaluation as control agents against the asparagus aphid, *Brachycolus asparagi*, in British Columbia.

In order to investigate the degradation, metabolism, and persistence of the three pesticides following their applications for the control of asparagus aphid, sensitive analytical methods for these chemicals and their toxic metabolites were essential. Using gas–liquid chromatography (GLC) and flame photometry, Bowman et al. (1969a) individually determined disulfoton and oxydemeton-methyl with their toxic metabolites, after these had been separated by liquid chromatography on silica gel. The same methods with minor modifications were successfully applied in the determination of phorate and five of its metabolites in corn (Bowman et al., 1969b). The major disadvantage of these methods was the poor chromatographic response of the metabolites, especially of the two sulfoxides. Reproducible response was difficult to obtain even after conditioning of the GLC column by injecting successively several plant extracts. So that this disadvantage could be overcome, residues of these compounds were all oxidized to the more stable oxygen analogue sulfone with *m*-chloroperbenzoic acid (Bowman and Beroza, 1969) or to their corresponding sulfones with aqueous $KMnO_4$ (Thornton and Anderson,

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Chart I

	solvent	compound eluted
	(I) Disulfoton and Its Metabolites	
fraction 1	20 mL of 40% ethyl acetate in hexane	disulfoton, disulfoton oxon, disulfoton sulfone, and disulfoton oxon sulfone
fraction 2	30 mL of 20% methanol in ethyl acetate	disulfoton sulfoxide and disulfoton oxon sulfoxide
	(II) Phorate and Its Metabolites	
fraction 1	30 mL of 20% methanol in ethyl acetate	phorate, phorate oxon, phorate sulfone, phorate oxon sulfone, phorate sulfoxide, and phorate oxon sulfoxide
	(III) Oxydemeton-methyl and Its Sulfone	
fraction 1	20 mL of 60% ethyl acetate in hexane	oxydemeton-methyl sulfone
fraction 2	30 mL of 40% methanol in ethyl acetate	oxydemeton-methyl

1968; Thornton et al., 1977) and then analyzed by GLC as the total residue. However, this approach could not determine and quantify the parent compound and its metabolites individually. Recently, many compounds that are susceptible to on-column decomposition, such as carbamate insecticides, have been successfully chromatographed intact on Chromosorb W support, surface-modified with Carbowax 20M (Aue et al., 1973; Lorah and Hemphill, 1974).

This paper describes simplified and sensitive methods for the extraction and individual determination of disulfoton, phorate, oxydemeton-methyl, and their toxic metabolites in asparagus and soil.

EXPERIMENTAL SECTION

Apparatus. A Sorvall Omni-Mixer was used for the extraction of asparagus and soil. The GLC analysis was performed on a Tracor MT 222 gas chromatograph equipped with a Tracor 702-NP alkali flame ionization detector and a Hewlett-Packard Model 3385A reporting computing integrator.

Reagents. Activated charcoal (Nuchar C, Fisher Scientific) was acid-washed prior to use (Brown, 1975) and a 2:5 (w/w) mixture of charcoal–Whatman CF-11 cellulose powder was prepared. All solvents were distilled in glass. Anhydrous Na_2SO_4 was heated at 260 °C overnight prior to use. GLC column packings were 2% OV-101, 1% OV-225, 1% OV-101 plus 2% OV-210, or 1% OV-17 plus 1% OV-210, all on 80–100-mesh Ultra-Bond 20M and 100–120-mesh Ultra-Bond II (Ultra Scientific). Analytical grades of disulfoton (98.6%), disulfoton oxon (96.4%), their corresponding sulfoxides and sulfones (all >90%), oxydemeton-methyl (97.4%), and oxydemeton-methyl sulfone were obtained from the Mobay Chemical Corp., Kansas City, MO. Phorate, phorate oxon, and their corresponding sulfoxides and sulfones were supplied by the American Cyanamid Co., Princeton, NJ.

Sample Preparation and Fortification. Stock solutions (100 μg/mL) for sample fortification were prepared with ethyl acetate for disulfoton, phorate, and their metabolites or with acetone for oxydemeton-methyl and its sulfone. They were appropriately diluted with ethyl acetate as the reference standards for GLC analysis.

Untreated sandy loam soil (pH 6.8, organic content 1.2%, sand 68.3%, silt 25.2%, and clay 5.3%) from the Research Station, Agriculture Canada at Summerland, British Columbia, was sieved to pass a 10-mesh screen. Aliquots of 20 g of moist soil (moisutre content 8.9%) were weighed into 250-mL beakers. They were fortified separately with appropriate volumes of the 100 μg/mL stock solutions of three groups of compounds: (I) disulfoton and its sulfoxide, sulfone, oxon, oxon sulfoxide, and oxon sulfone; (II) phorate and its sulfoxide, sulfone, oxon, oxon sulfoxide, and oxon sulfone; (III) oxydemeton-methyl and its sulfone. The solvents were evaporated at room temperature in a fume hood and the soil samples were mixed frequently during drying. When no trace of the solvent remained, they were stored at 4 °C for 12 h before extraction.

Asparagus ferns or spears collected from the Research Station, Agriculture Canada at Summerland, British Columbia, were cut up with shears or in a Braun vegetable shredder and then thoroughly mixed in a plastic bag. Aliquots of asparagus tissues equivalent to 10 g of fern or 25 g of spear were fortified in 400-mL Sorvall Omni-Mixer containers by adding appropriate volumes of the 100 μg/mL stock solutions directly onto the tissues as described for soil. They were allowed to stand at room temperature in a fume hood for about 1 h before extraction.

Sample Extraction. Fortified asparagus tissue and soil samples were extracted by blending with 100 mL of ethyl acetate for 5 min, except soil samples fortified with oxydemeton-methyl and its sulfone, which were extracted with 100 mL of 20% methanol in ethyl acetate. Prior to being blended, tissue samples were mixed with anhydrous Na_2SO_4, 20 g for the fern and 50 g for the spear. The Sorvall Omni-Mixer container was immersed in an ice water bath while blending. The extracts were filtered through a Büchner funnel lined with glass fiber filter paper into 500-mL round-bottom flasks. The filter cakes were extracted twice more with 50 mL of extracting solvent, and all extracts were combined. The combined extracts were concentrated to 10 mL under nitrogen in a flash evaporator at 35 °C, except the soil extracts containing oxydemeton-methyl and its sulfone, which were concentrated just to dryness under nitrogen in a flash evaporator, and the residues were dissolved in 10 mL of ethyl acetate for cleanup.

Liquid Column Chromatography for Cleanup and Fractionation. Glasss columns (30 cm × 1.1 cm i.d.) with Teflon stopcocks were packed from the bottom with a glass wool plug, 1.5 cm of Na_2SO_4, 4 cm of a 2:5 (w/w) mixture of Nuchar C–Whatman CF-11 cellulose, 1.5 cm of Na_2SO_4, and a glass wool plug. The packed columns were prewashed with 10 mL of ethyl acetate followed by 10 mL of hexane. Two-milliliter aliquots of crude extracts equivalent to 2 g of asparagus fern, 5 g of asparagus spear, or 4 g of soil were mixed with 3 mL of hexane and then transferred quantitatively to the cleanup columns. The resulting eluates were collected. The fractionation of the constituents present in the crude extracts was accomplished by eluting the columns with various solvent mixtures according to Chart I. All fraction 1's containing the parent compounds and the oxons were concentrated under nitrogen in a flash evaporator at 35 °C for GLC analysis.

Oxidation Procedure. The fraction 2's containing the two sulfoxides of disulfoton or oxydemeton-methyl were evporated just to dryness in a flash evaporator at 35 °C and the residues were dissolved in 2 mL of acetone. The

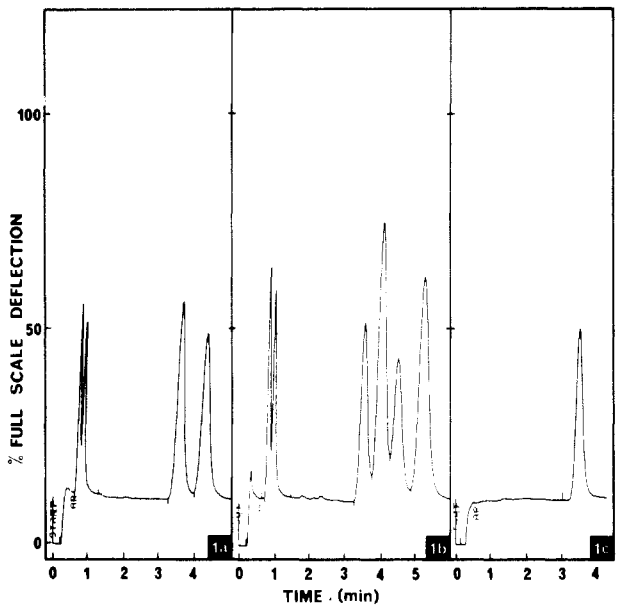

Figure 1. Gas chromatograms of (a) 0.1 ng each of disulfoton oxon and disulfoton and 0.4 ng each of disulfoton oxon sulfone and disulfoton sulfone, (b) 0.1 ng each of phorate oxon and phorate and 0.5 ng each of phorate oxon sulfoxide, phorate sulfoxide, phorate oxon sulfone, and phorate sulfone, and (c) 0.6 ng of oxydemeton-methyl sulfone; all are on column 1.

oxidation was carried out for 30 min by adding 5 mL of 20% (w/v) aqueous $MgSO_4$ and 20 mL of freshly prepared 0.5 N aqueous $KMnO_4$ with frequent swirling (Thornton and Anderson, 1968; Thornton et al., 1977). At the completion of oxidation the mixtures were extracted 3 times with 20 mL of chloroform in 250-mL separatory funnels. The combined extracts were filtered through anhydrous Na_2SO_4 and concentrated just to dryness in a flash evaporator at 35 °C. The residues were dissolved in ethyl acetate and analyzed by GLC as the sulfones.

Gas Chromatographic Analysis. Five Pyrex glass columns were used: (1) 75 cm × 2 mm i.d., 2% OV-101 on 80–100-mesh Ultra-Bond 20M at 185 °C; (2) 75 cm × 2 mm i.d., 1% OV-225 on 80–100-mesh Ultra-Bond 20M at 205 °C; (3) 60 cm × 2 mm i.d., 1% OV-101 plus 2% OV-210 on 80–100-mesh Ultra-Bond 20M at 185 °C; (4) 75 cm × 2 mm i.d., 1% OV-17 plus 1% OV-210 on 80–100-mesh Ultra-Bond 20M at 190 °C; (5) 36 cm × 4 mm i.d., 100–120-mesh Ultra-Bond II at 170 °C. Helium was the carrier gas at 60 mL/min. The operating parameters were as follows: detector temperature 240 °C, inlet and outlet temperatures 210 °C, and plasma gas flow rate 3.5 mL/min for hydrogen and 120 mL/min for air.

Detector response was calibrated daily with authentic analytical standards. Quantification was based on average peak heights of these external standards, injected before and after the sample.

RESULTS AND DISCUSSION

Performance of the GLC Columns. The parent compound, the oxon and the two sulfones of disulfoton, phorate and its metabolites, and oxydemeton-methyl sulfone were chromatographed successfully on all five columns tested. Oxydemeton-methyl and the two sulfoxides of disulfoton were chromatographed successfully on column 5 (Ultra-Bond II) only but without separation. The isolation of these three sulfoxides from other compounds within the same group was achieved by liquid column chromatography with a 2:5 (w/w) mixture of Nuchar C–CF-11 cellulose. Column 1 (2% OV-101 on Ultra-Bond 20M) proved to be the best overall because it

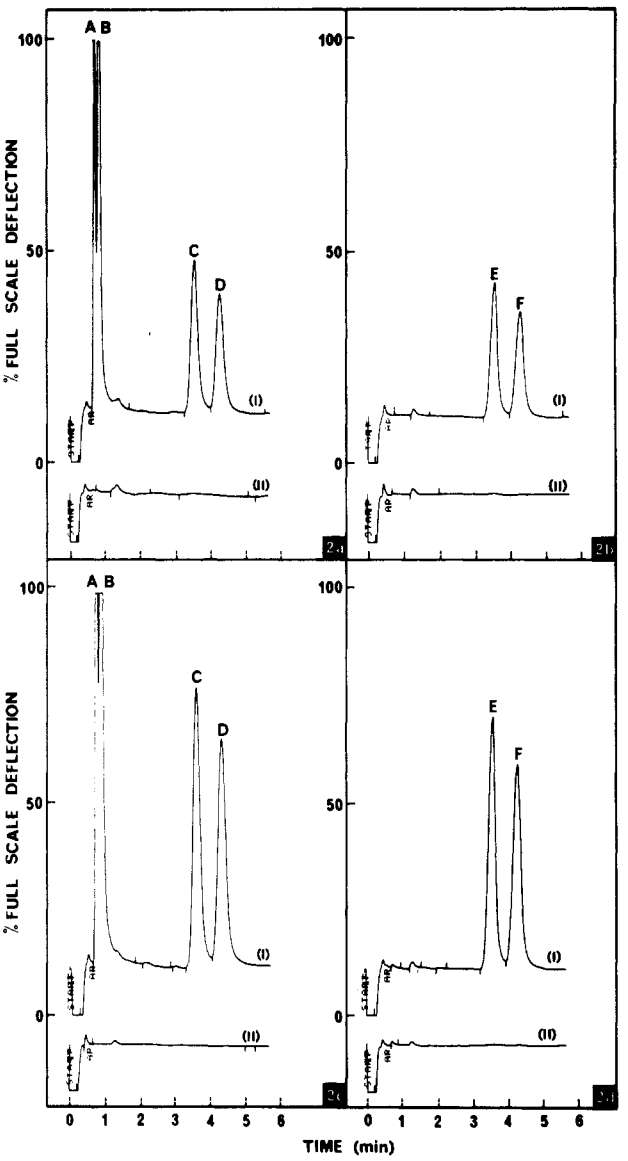

Figure 2. Gas chromatograms of fraction 1 [(a) I] and 2 [(b) I] of 2 g of asparagus tissue fortified with 0.1 ppm of disulfoton oxon (A), disulfoton (B), disulfoton oxon sulfone (C), disulfoton sulfone (D), disulfoton oxon sulfoxide (E), and disulfoton sulfoxide (F) and the corresponding unfortified asparagus blanks [(a) II and (b) II]; fraction 1 [(c) I] and 2 [(d) I] of 4 g of soil fortified with 0.1 ppm of A–F and the corresponding unfortified soil blanks [(c) II and (d) II]. Fraction 2 contained the sulfoxides (E, F), which are analyzed as the sulfones.

provided good sensitivity and separation of disulfoton and its oxon and sulfones, phorate and its oxon, sulfoxides, and sulfones, and oxydemeton-methyl sulfone (Table I; Figure 1). Because the sulfoxides chromatographed poorly on this column, they were first isolated from other compounds, oxidized with aqueous $KMnO_4$, and then analyzed as their corresponding sulfones. Other column packings, Gas-Chrom Q or Chromosorb W "HP", coated with various liquid phases, were also evaluated. It was apparent that the chromatographic response of the sulfoxides and sulfones on these columns was about 1–10% of that on column 1 depending on the extent of on-column decomposition. The superior performance of column 1 was probably due to the inertness of the Cabowax 20M bonded solid support (Aue et al., 1973).

Oxidation of Sulfoxides. Disulfoton sulfoxide, disulfoton oxon sulfoxide, and oxydemeton-methyl were oxidized with aqueous $KMnO_4$ to their corresponding

Table I. Absolute Retention Times of Disulfoton, Phorate, Their Metabolites, and Oxydemeton-methyl Sulfone on GLC Column 1[a]

compound	column temp, °C	absolute retention time, min
I		
disulfoton	185	0.84
disulfoton oxon		0.71
disulfoton sulfone		4.12
disulfoton oxon sulfone (II)		3.43
phorate	165	0.97
phorate oxon		0.83
phorate sulfoxide		3.85
phorate oxon sulfoxide		3.39
phorate sulfone		5.00
phorate oxon sulfone (III)		4.30
oxydemeton-methyl sulfone	185	3.25

[a] 75 cm × 2 mm i.d., 2% OV-101 on 80–100-mesh Ultra-Bond 20M.

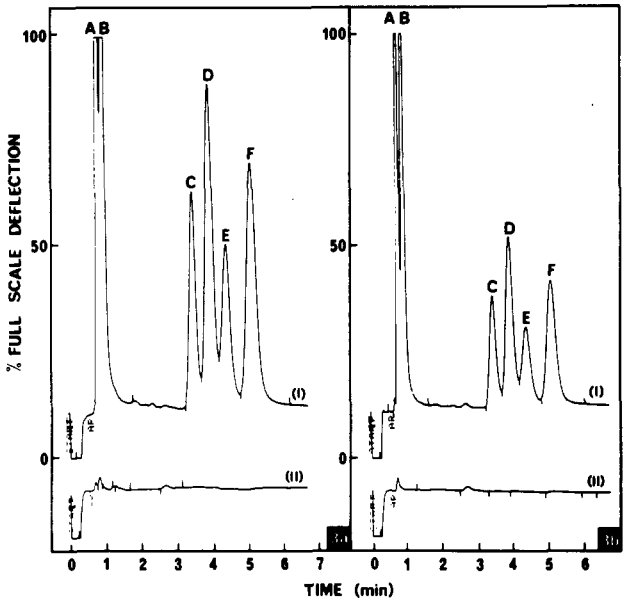

Figure 3. Gas chromatograms of 4 g of soil [(a) I] and 2 g of asparagus tissue [(b) I] fortified with 0.1 ppm each of phorate oxon (A), phorate (B), phorate oxon sulfoxide (C), phorate sulfoxide (D), phorate oxon sulfone (E), and phorate sulfone (F) and the corresponding soil [(a) II] and asparagus [(b) II] blanks.

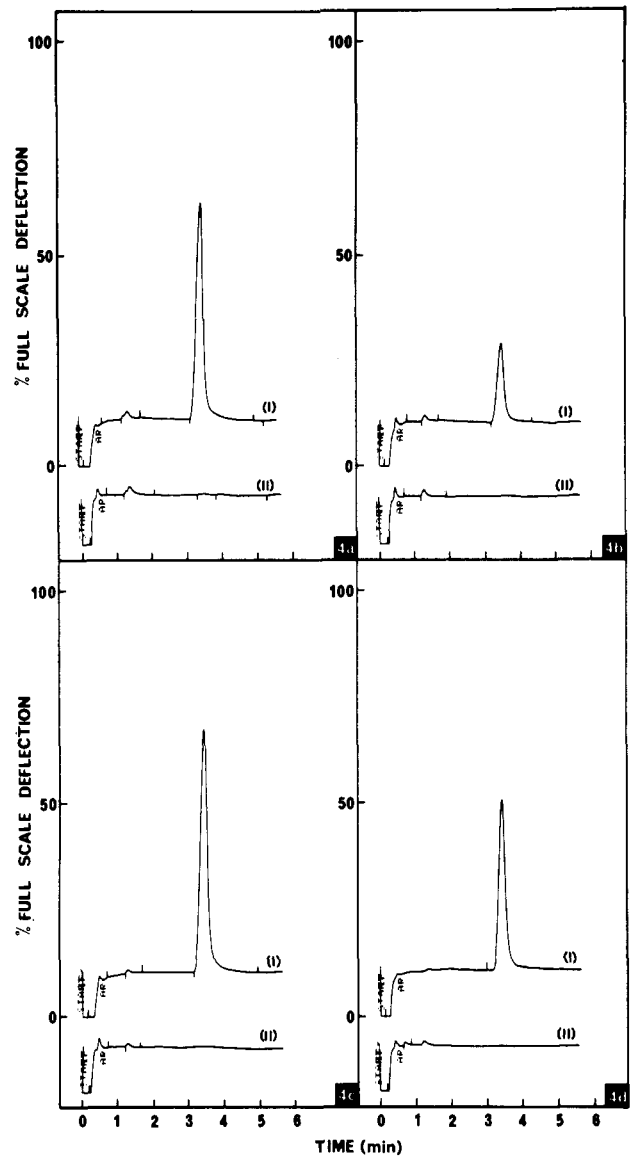

Figure 4. Gas chromatograms of fractions 1 [(a) I] and 2 [(b) I] of 3 g of asparagus tissue fortified with 0.1 ppm each of oxydemeton-methyl and oxydemeton-methyl sulfone and the corresponding unfortified asparagus blanks [(a) II, and (b) II] and fractions 1 [(c) I] and 2 [(d) I] of 6 g of soil fortified with 0.1 ppm each of oxydemeton-methyl and oxydemeton-methyl sulfone and the corresponding unfortified soil blanks [(c) II and (d) II]. Fraction 2 contained oxydemeton-methyl, which is analyzed as the sulfone.

sulfones. The conversion was quantitative in 0.5 h for the two sulfoxides of disulfoton and for oxydemeton-methyl. Therefore, the quantification of the two sulfoxides of disulfoton and oxydemeton-methyl can be achieved by comparison of the sulfone produced by oxidation against an appropriate dilution of the authentic sulfone standard or against the sulfone standard prepared from 5 μg of the sulfoxide started at the oxidation step along with the unknowns as recommended by Thorton et al. (1977).

Recoveries of Residues from Asparagus and Soil. The cleanup accomplished by the Nuchar C–Whatman CF-11 cellulose column was excellent. Both fraction 1 and fraction 2 obtained from extracts equivalent to 5 g of asparagus spear, 2 g of asparagus fern, or 4 g of soil were pigment free and contained no extraneous substances that interfered with subsequent GLC analyses of disulfoton, phorate, oxydemeton-methyl, and their metabolites (Figures 2–4). However, it is extremely important to calibrate the capacity of the cleanup column for each substrate. We found that some of the disulfoton sulfoxide was eluted in fraction 1 when crude extracts equivalent to 2 g of late-season asparagus fern were cleaned up on the columns. These crude extracts contained a significant amount of waxy substances that exceeded column capacity and altered the elution pattern. Satisfactory fractionation was obtained when crude extracts equivalent to only 1 g of late-season fern were cleaned up on these columns. So that the capacity of the cleanup column can be increased, a larger quantity of the 2:5 (w/w) Nuchar C–Whatman CF-11 cellulose will be required. The cleanup efficiency and fractionation on silica as described by Bowman et al. (1969a) were compared. The fraction collected from the elution with 20% acetone in benzene contained a significant amount of pigment. Furthermore, the oxon, the sulfoxide, and the oxon sulfone of disulfoton were all eluted in this fraction so that subsequent determination of individual compounds following oxidation was impossible.

Disulfoton, phorate, and their oxons were very unstable, and they oxidized rapidly to yield the corresponding sulfoxides. Working standards of disulfoton and disulfoton

Table II. Percent Recovery of Disulfoton, Phorate, Oxydemeton-methyl, and Their Metabolites from Soil and Asparagus Tissue

compound	% recovery ± SD (n = 4)				
	asparagus		soil		
I	5.0 ppm	0.1 ppm	5.0 ppm	0.5 ppm	0.05 ppm
disulfoton	99.5 ± 3.1	101 ± 2.7	93.8 ± 2.9	96.3 ± 5.1	100 ± 8.5
D oxon	100 ± 2.5	97.1 ± 2.8	87.9 ± 3.8	102 ± 6.1	110 ± 3.0
DSO	93.9 ± 7.5	89.4 ± 7.8	109 ± 7.3	96.2 ± 5.1	98.2 ± 0.4
D oxon SO	103 ± 12.3	99.1 ± 1.6	83.5 ± 3.5	102 ± 6.5	107 ± 11.0
DSO_2	91.4 ± 3.9	108 ± 3.0	96.5 ± 2.9	108 ± 8.8	101 ± 7.5
D oxon SO_2	97.1 ± 0.9	110 ± 3.7	83.9 ± 8.6	91.8 ± 5.7	95.3 ± 7.0
II	5.0 ppm	0.1 ppm	5.0 ppm	0.1 ppm	
phorate	83.6 ± 0.8	83.7 ± 8.0	87.2 ± 6.2	89.6 ± 5.4	
P oxon	98.9 ± 0.9	96.7 ± 1.7	89.9 ± 2.3	100 ± 10.7	
PSO	97.4 ± 2.5	94.9 ± 1.0	100 ± 4.0	94.4 ± 5.3	
P oxon SO	108 ± 5.3	95.9 ± 4.5	87.2 ± 4.7	105 ± 2.1	
PSO_2	90.2 ± 3.7	85.5 ± 1.9	99.7 ± 3.1	91.9 ± 2.2	
P oxon SO_2	99.2 ± 4.8	101 ± 4.6	99.4 ± 6.0	99.6 ± 8.6	
III	5.0 ppm	0.1 ppm	5.0 ppm	0.1 ppm	
oxydemeton-methyl	99.1 ± 5.4	97.8 ± 6.6	92.4 ± 11.3	97.4 ± 5.3	
Oxy SO_2	95.7 ± 2.5	95.7 ± 3.1	95.4 ± 0.7	92.8 ± 2.6	

oxon prepared in ethyl acetate for GC analysis showed a 20% transformation in 7 days and a 30% transformation in 18 days even though they were stored at 4 °C. All the sulfoxides were relatively stable, and they oxidzed very slowly to their corresponding sulfones, which were the most stable. Similar conversions occurred in phorate and phorate oxon standards prepared in ethyl acetate. It was also observed that 60–70% of the disulfoton, phorate, and their oxons were oxidized when the extracts were concentrated just to dryness under air in a flash evaporator. Therefore, it is critical that the crude extracts and all fractions containing disulfoton, phorate, and their oxons, collected from the Nuchar–cellulose columns, should be concentrated under nitrogen only and they should never be taken to dryness even under nitrogen.

Oxidation of disulfoton, phorate, and their oxons to the sulfoxides occurred in the fortified soil samples during storage for 12 h at 4°C for equilibration. It was therefore necessary to determine the percentage recovery of sulfoxides from soil samples fortified with these compounds alone. The percentage recovery of disulfoton, phorate, and their oxons were determined after adjusting for the in situ conversion to their corresponding sulfoxides as suggested by Brown (1981). Since the sulfones are relatively stable, no adjustment was necessary to determine their recoveries. In contrast, no significant oxidation ocurred in fortified asparagus tissue samples, probably because analyses were carried out within 1 h of fortification.

Extraction efficiency for soil was affected by soil moisture content. Recovery was poor from air-dried Summerland soil but improved significantly with the addition of up to 10% moisture. The water-holding capacity of this soil was low, and it was saturated at about 10% moisture. Therfore, all soils were adjusted to contain 10% moisture for the recovery studies.

Percentage recoveries for fortified soil and asparagus tissue are given in Table II. Each mean percentage with its standard deviation was derived from four separate analyses. The recoveries of disulfoton, phorate, oxydemeton-methyl, and their metabolites ranged from 83.7 to 110% for both soil and asparagus tissue. The extraction by blending appeared to be as efficient as Soxhlet extraction (Bowman et al., 1969a, b; Thornton and Anderson, 1968). Since 0.5 ng of the least sensitive compound, phorate oxon sulfone, gives about 40% full-scale deflection (Figure 1), the limit of detection of the described method may well be below 0.01 ppm for asparagus tissue and soil.

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