

- Lichtenstein, E. P., Fuhremann, T. W., Scopes, N. E. A., Skrenty, R. F., *J. AGR. FOOD CHEM.* **15**, 864 (1967).
- Lukaszczuk, A., Ciba-Geigy Ltd., Basle, Agrochemicals Division, internal report, May 1971.
- Malone, C. R., Winnett, A. G., Helrich, K., *Bull. Environ. Contam. Toxicol.* **2**, 83 (1967).
- Margot, A., Gysin, H., *Helv. Chim. Acta* **40**, 1562 (1957).
- Matsumura, F., Boush, M. G., *J. Econ. Entomol.* **61**, 610 (1968).
- Miles, J. R. W., Manson, G. F., Sans, W. W., Niemczyk, H. D., *Pest. Progr.* **2**, 153 (1964).
- Miyazaki, H., Tojinbara, J., Watanabe, Y., Osaka, T., Okui, S., *Proc. Symp. Drug Metab. Action*, 135 (1969).
- Mortland, M. M., Raman, K. V., *J. AGR. FOOD CHEM.* **15**, 163 (1967).
- Mücke, W., Alt, K. O., Esser, H. O., *J. AGR. FOOD CHEM.* **18**, 208 (1970).
- Nelson, L. L., Hamilton, E. W., *J. Econ. Entomol.* **63**, 874 (1970).
- Onsager, J. A., Rusk, H. W., *J. Econ. Entomol.* **60**, 586 (1967).
- Pardue, J. R., paper presented at 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sep 1968.
- Pardue, J. R., Hansen, E. A., Barron, R. P., Chen, J.-Y. T., *J. AGR. FOOD CHEM.* **18**, 405 (1970).
- Ralls, J. W., Gilmore, D. R., Cortes, A., *J. AGR. FOOD CHEM.* **14**, 387 (1966).
- Ralls, J. W., Gilmore, D. R., Cortes, A., Schutt, S. M., Mercer, W. A., *Food Technol.* **21**, 1030 (1967).
- Randolph, N. M., Dorough, H. W., Teetes, G. L., *J. Econ. Entomol.* **62**, 462 (1969).
- Sethunathan, N., paper presented at First Annual Convention of the Pest Control Council of the Philippines, Iloilo City, May 5-8, 1970.
- Sethunathan, N., MacRae, I. C., *J. AGR. FOOD CHEM.* **17**, 221 (1969).
- Sethunathan, N., Yoshida, T., *J. AGR. FOOD CHEM.* **17**, 1192 (1969).
- Trela, J. M., Ralston, W. J., Gunner, H. B., *Bacteriol. Proc.* **6** (1968).
- Voss, G., *Automat. Analysis, Technicon Intern. Congr.* **2**, 11 (1969).

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Determination of Residues of Fensulfothion and its Sulfone in Muck Soil

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A method is described for determining fensulfothion {*O,O*-diethyl *O*-[*p*-(methylsulfinyl)phenyl] phosphorothioate} and its sulfone in muck soils, using Soxhlet extraction with a 9:1 chloroform-ethanol mixture. Cleanup and fractionation was on an alumina-silica gel column and determination was by gas chromatography with flame-photometric detection. Optimum recoveries were obtained when

the moisture content of the soil was between 20 and 60%. Recoveries from soils fortified at 0.1, 1.0, and 10.0 ppm were 80% or greater. Residues in soils field-treated with fensulfothion for protection against carrot rust fly ranged from 19.9 to 90.5 ppm for the parent compound and from 5.9 to 21.8 ppm for its sulfone.

Fensulfothion {*O,O*-diethyl *O*-[*p*-(methylsulfinyl)phenyl] phosphorothioate} is an insecticide showing considerable promise for the control of carrot rust fly, *Psila rosae* (F.) (Finlayson *et al.*, 1964, 1966). Residues of this insecticide in carrots treated at various rates have been determined (Finlayson *et al.*, 1970) and it was desirable to relate these results to residues of fensulfothion in the muck soil in which the carrots were grown.

Pesticide residues in soils high in organic matter are not easily extracted because of the strong adsorptive properties of such soils. Fensulfothion and its sulfone, being relatively polar compounds, are particularly difficult to extract. Cleanup of the extract for gas chromatographic (gc) analysis also presents a problem because high concentrations of extraneous matter are coextracted and these, if not removed, would quickly foul the gc column.

A number of methods of extracting organophosphate residues from organic soils have been reported. Beynon *et al.* (1966) used a 20% acetone-hexane mixture to extract Birlane from a peat soil, and obtained maximum recovery after 2 hr of tumbling. However, the mixture was fortified by adding Birlane to the solvent just prior to extraction so that adsorption was minimal. Suett (1971) used a 9:1 chloroform-methanol mixture with 2 hr of tumbling to extract phorate from a peaty loam. Fortification was by the addition of an acetone solution of the pesticide to the soil 1 hr before extraction. Recovery at the 0.1-ppm level averaged

85%. Getzin and Rosefield (1966) extracted C₁₄-labeled diazinon and Zinophos from an organic soil by shaking it for 15-min periods with three 50-ml portions of a 1:1 mixture of 0.05 N calcium chloride and acetone. A recovery of 98% was obtained from soil freshly fortified with Zinophos, but after 2 weeks 12% was nonextractable. Similar results were obtained for diazinon.

In this laboratory a number of extraction procedures were tested. These included Soxhlet extraction with a 1:1 hexane-acetone mixture, dichloromethane, and a 9:1 chloroform-methanol mixture. Extraction by prolonged shaking with dichloromethane was also tried. The final method of choice was Soxhlet extraction with chloroform-methanol.

EXPERIMENTAL SECTION

Materials. Two field-treated muck soils designated S and K and their corresponding untreated checks were used. The chemical and physical analyses of these soils are shown in Table I.

The silica gel and eluting solutions A and B used in the cleanup and fractionation step have been previously described (Williams *et al.*, 1971).

Alumina, Woelm, Grade W200 acid (Waters Associates, Framingham, Mass.), deactivated to activity II by the addition of 4% water, was also used in the cleanup step.

Solvents were redistilled from reagent grade material.

Apparatus. A 50-mm i.d. Soxhlet extractor with a 300-ml receiving flask was used. A pad of glass wool at the base of the extraction tube took the place of the normal filter thimble.

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Table I. Chemical and Physical Analysis of the Soils Used in the Experiments

Soil	pH	% organic matter	% nitrogen (total)	Cation exchange capacity, mequiv/100 g	% base saturation
		% sand ^a	% silt ^b	% clay ^c	% fine clay ^d
S	4.5	82.2	2.2	130.2	57.4
K	4.0	44.3	1.8	84.5	37.7
S		24.2	47.2	19.5	9.1
K		14.6	62.3	19.2	3.9

^a 2.00–0.05 mm. ^b 0.05–0.002 mm. ^c <0.002 mm. ^d <0.2 μ.

Table II. Recovery of Fensulfothion (F) and its Sulfone (FS) from Fortified Muck Soil^a

Fortification level, ppm		Recovery, ppm	
F	FS	F	FS
0.10	0.10	0.11	0.08
0.10	0.10	0.12	0.10
1.0	1.0	0.89	0.86
1.0	1.0	0.81	0.84
10.0	10.0	9.30	10.95
10.0	10.0	8.55	9.60

^a 8 hr chloroform–methanol Soxhlet extraction.

The gas chromatograph, flame photometric detector, gc column, and operating conditions used in analyzing the soil extracts have been previously described (Williams *et al.*, 1971).

Soil Fortification. To test extraction and cleanup procedures, untreated samples of soils S and K were air-dried, screened through a 20-mesh sieve, and fortified as follows. From a 200-g sample of soil a 20-g subsample was removed and slurried with acetone containing known amounts of fensulfothion and its sulfone. The solvent was evaporated, the fortified soil was added to the remainder of the sample, and the whole thing was thoroughly mixed by rolling. Samples thus fortified were held in sealed glass jars at 10° for at least 2 weeks before being used.

Analytical Procedure. SOXHLET EXTRACTION. Weigh 25 g of undried soil into a 250-ml beaker, add sufficient water to adjust the moisture content to between 20 and 60%, and then add 10 g of anhydrous sodium sulfate and 5 g of Hyflo Super Cel. Thoroughly mix and transfer to the Soxhlet apparatus. Extract with 250 ml of a 9:1 chloroform–methanol mixture for 8 hr at a rate of approximately 4 cycles per hr. Remove the heat source while most of the solvent is in the extraction tube. Transfer the contents of the receiver to a beaker and evaporate almost to dryness over a water bath at 40° in a gentle current of air. Add 5 ml of ethyl acetate to the residue, stir well to dissolve as much as possible of the residue, and then add sufficient Celite 545 to absorb the liquid and form a dry homogeneous powder. The sample is now ready for cleanup and fractionation.

CLEANUP AND FRACTIONATION. To a 300 × 20 mm i.d. chromatographic column add, in order from the bottom, 1 cm of anhydrous sodium sulfate, 10 g of silica gel, 0.5 cm of anhydrous sodium sulfate, 10 g of alumina, 1 cm of anhydrous sodium sulfate, and a small plug of glass wool. Prewash the column with 25 ml of ethyl acetate and then transfer the sample to it. Wash out the beaker with several 1-ml portions of ethyl acetate and add these to the column. Elute the first fraction containing the fensulfothion with 75 ml of eluting solution A (20:80 v/v ethyl acetate–benzene). Change the

receiver and elute the second fraction containing the sulfone with 100 ml of eluting solution B (40:60 v/v acetone–benzene). Evaporate both fractions almost to dryness over a water bath at 40° in a gentle stream of air. Take up with ethyl acetate and dilute to an appropriate volume (10 to 50 ml, depending on the residue level) for gc analysis as previously described (Williams *et al.*, 1971).

ADDITIONAL CLEANUP. Some coextractants in soils exceptionally high in organic matter may elute in the first fraction and eventually foul the gc column. In such cases, indicated by the yellow color of the eluate, carry out the following additional cleanup. Evaporate the eluate almost to dryness as described above, add 25 ml of acetonitrile, and transfer the solution to a 125-ml separatory funnel. Extract the acetonitrile with 25 ml of hexane, return it to the original beaker, and discard the hexane layer. Evaporate almost to dryness, add 1–2 ml of ethyl acetate, and again evaporate almost to dryness. Take up with ethyl acetate and dilute to an appropriate volume for gc analysis.

Effect of Soil Moisture on Soxhlet Extraction. Four samples of untreated air-dried muck soil were fortified with 2 ppm of fensulfothion and its sulfone. One sample was extracted by the procedure described but without the addition of water. Moisture levels of the other three samples were adjusted to 10, 25, and 50%, respectively, before extraction. After gc analysis of all four samples, recoveries were compared.

Comparison of Extraction Efficiencies. DICHLOROMETHANE vs. CHLOROFORM–METHANOL. Duplicate samples of soil K, known to contain 39% moisture and high residues of fensulfothion and its sulfone, were Soxhlet-extracted with dichloromethane for 8 hr. The extracts were removed and analyzed. The extracted soils, still in the Soxhlet tubes, were allowed to remain covered by solvent overnight. Sufficient fresh solvent was added to make up the original volume and the soils were reextracted for 4 hr. Again the extracts were removed and analyzed. This procedure was repeated at intervals until recoveries of 1% or less of the total pesticides were obtained.

The experiment was repeated in duplicate with a 9:1 chloroform–methanol mixture as the extractant. In this instance, extraction for 8 hr was so effective that a 4-hr extraction, after 40 hr of standing with solvent, recovered less than 0.1% of the total pesticides found. No further extractions were made.

HEXANE–ACETONE. An 8-hr Soxhlet extraction with a 1:1 hexane–acetone mixture was carried out on the same field-treated soil as that used in the previous experiment. Attempts to remove the acetone by the addition of water, as normally used in this method of extraction, produced such a persistent emulsion due to the organic nature of the soil that further study of this solvent was abandoned.

EXTRACTION BY SHAKING. Duplicate 25-g samples of the soil used in the previous extraction experiments were transferred to 500-ml flasks and 250 ml of dichloromethane was added. The flasks were stoppered and shaken for 48 hr on an oscillating table. The extracts were then analyzed by the procedure described.

RESULTS AND DISCUSSION

Recoveries of fensulfothion and its sulfone from a muck soil fortified at three levels are shown in Table II. While this is not a true indication of extraction efficiency as applied to weathered soil, it does show that little loss is experienced during cleanup.

Table III shows the effect of moisture on recovery. It

Table III. Effect of Moisture on the Recovery of Fensulfothion and its Sulfone from Fortified Soil

Moisture, %	Recovery, %	
	On air-dried basis	On oven-dried basis
0	71	92
10	91	100
25	90	100
50	89	100

Table IV. Efficiencies of Two Solvent Systems for Soxhlet Extracting Fensulfothion and its Sulfone from Field-Treated Muck Soil

	F		Recovery ^b FS		F + FS, ppm
	ppm	%	ppm	%	
Extraction with CH ₂ Cl ₂ ^a					
8-hr extraction	18.3	64.3	8.3	62.8	26.6
4-hr extraction after 16 hr of standing	7.6	26.8	3.9	29.7	11.5
4-hr extraction following previous extraction	1.1	3.9	0.4	3.0	1.5
4-hr extraction after 80 hr of standing	1.2	4.0	0.5	3.7	1.7
4-hr extraction following previous extraction	0.3	1.0	0.1	0.8	0.4
Total recovery	28.5		13.2		41.7
Extraction with 9:1 CHCl ₃ /CH ₃ OH ^a					
8-hr extraction	29.1	99.7	12.7	100	41.8
4-hr extraction after 16 hr of standing	0.08	0.3	0.02		0.1
Total recovery	29.2		12.7		41.9

^a Successive extractions of the same sample. ^b Average of duplicate samples.

would appear that a certain amount of moisture does facilitate extraction. Similar results were observed in extracting organochlorine pesticides from soil (Williams, 1968). The residual soil moisture in this particular air-dried soil, as found by oven drying at 105°, was 12.6%. Thus, a total moisture content of between 20 and 60% would appear satisfactory for good extraction.

The relative efficiency of the dichloromethane and chloroform-methanol solvent systems is compared in Table IV, where extraction recoveries after various time intervals are shown. A comparison of the total amounts of fensulfothion and its sulfone extracted by either method shows them to be almost identical. However, the time required for complete extraction by chloroform-methanol is so much less than

Table V. Fensulfothion and its Sulfone Found in Field-Treated Muck Soils in Which Carrots Were Grown

Treatment, ^a days after seeding	Recovery, ppm ^b			
	Soil S		Soil K	
	F	FS	F	FS
40-70	19.9	5.9	48.5	21.2
40-70-100	52.5	15.2	39.4	13.0
30-50-70	90.5	21.5	39.7	16.5
30-50-70-90	78.0	21.8	52.9	18.4

^a In furrow application at 1 oz active/1000 row ft (approx 2 lb/acre), plus sprays at the days after seeding indicated, at 1 lb active/acre. Soil samples taken 150 days after seeding. ^b On oven-dried basis.

that required by dichloromethane that it is obviously the more suitable solvent. The one advantage in using dichloromethane is that a much cleaner extract is produced.

Extraction by shaking with dichloromethane for 48 hr was extremely inefficient, with little more than 50% of either compound being recovered. No further experiments with shaking were carried out.

The addition of anhydrous sodium sulfate to the soil had no significant effect on the extraction efficiency of either solvent system, though it did render the soil more friable and is therefore recommended.

Recoveries from a number of samples of field-treated soils which were used for the carrot experiments are given in Table V. No attempt was made to recover fensulfothion oxygen analog or its sulfone, since neither of these compounds was found in other than trace amounts in the carrots.

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LITERATURE CITED

- Beynon, K. I., Davies, L., Elgar, K., Stoydin, G., *J. Sci. Food Agr.* **17**, 162 (1966).
 Finlayson, D. G., Fulton, H. G., Noble, M. D., *Proc. Entomol. Soc. Brit. Columbia* **61**, 13 (1964).
 Finlayson, D. G., Fulton, H. G., Noble, M. D., *J. Econ. Entomol.* **59**, 1082 (1966).
 Finlayson, D. G., Fulton, H. G., Kore, R., Williams, I. H., *J. Econ. Entomol.* **63**, 1304 (1970).
 Getzin, L. W., Rosefield, I., *J. Econ. Entomol.* **59**, 512 (1966).
 Suett, D. L., *Pestic. Sci.* **2**, 105 (1971).
 Williams, I. H., *J. Ass. Offic. Anal. Chem.* **51**, 715 (1968).
 Williams, I. H., Kore, R., Finlayson, D. G., *J. AGR. FOOD CHEM.* **19**, 456 (1971).

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