

ACARICIDE RESIDUES

Infrared Procedure for Quantitative Determination of Residues of 2,4,4',5-Tetrachlorodiphenyl Sulfone (Tedion) on and in Citrus Fruit Peel

F. A. GUNTHER, R. C. BLINN, and
J. H. BARKLEY

University of California Citrus
Experiment Station, Riverside, Calif.

The acaricide 2,4,4',5-tetrachlorodiphenyl sulfone, Tedion, is stable in the presence of chromic anhydride in glacial acetic acid. Use of this oxidizing mixture minimizes interference from the natural products extracted from citrus peel. Measurement of the strong sulfone absorption peak at 1160 cm.^{-1} permits the determination of as little as $20\ \gamma$ of Tedion in the presence of 100 grams of citrus peel.

THERE HAVE BEEN few published reports of the utilization of infrared techniques for the determination of micro quantities of an insecticide or acaricide found as field residues on and in treated crops (3, 4, 6, 8, 9). Only the procedure for *p*-chlorobenzyl *p*-chlorophenyl sulfide and its sulfone on field-treated pears (6) presented actual residue values.

The use of infrared absorption for residue studies has been limited by poor access to instrumentation and the requirement of almost complete isolation of the pesticide from the complex mixture of coextracted normal plant constituents. The recent availability of more economically priced instruments should stimulate the compilation of procedures adequate for the require-

ments of infrared techniques. Identification of an intact pesticide or its metabolic products by the use of infrared absorption in the "fingerprint" region, wherever the necessary degree of isolation can be realized, gives a highly desirable degree of specificity which is not possible with the more conventional microanalytical methods.

For an infrared spectrophotometer to respond to a pesticide in the 10- to 100- γ range, a cell of long light path (1 to 3 mm.) and small capacity (0.2 to 0.5 ml.) is required. Any extraneous material is thus a potential interference either by its absorbance at the wave length of interest or by volume dilution of the final solution. Carefully evaluated isolation procedures are therefore essential for the successful utilization of

infrared techniques for pesticide residues. Procedures described for this type of infrared analysis with particular substrates included steam distillation to remove the pesticide from its substrate (8), spontaneous evaporation to remove volatile oils (8), saponification to break down fats and esters and render them water soluble (8), and partition distribution (6) and chromatography to separate the pesticide selectively from many plant constituents (6, 8). These and other isolative procedures may be required in combination.

The acaricide 2,4,4',5-tetrachlorodiphenyl sulfone, or Tedion, is promising for the control of tetranychid mites on citrus. Its effectiveness in the field is long lived (7). Any of the several existing total-chloride methods (4) will es-

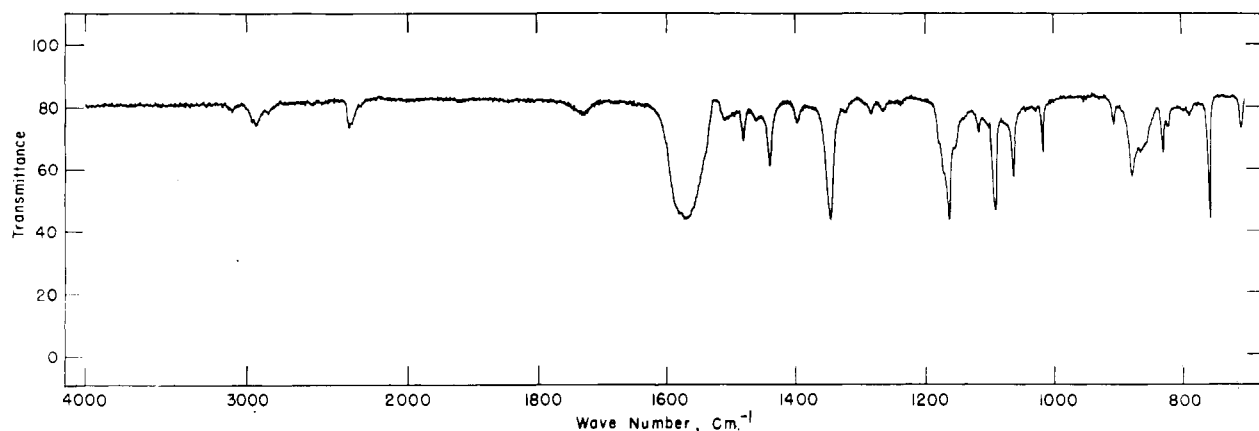
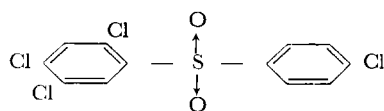


Figure 1. Infrared characteristics of 2,4,4',5-tetrachlorodiphenyl sulfone in carbon disulfide

tablish the maximum amount of parent Tedium that could exist as a residue on and in treated fruit, regardless of alterations from metabolism or degradation. A semispecific colorimetric procedure for Tedium has also been described (2), based upon the color produced by the alkaline solution of nitrated Tedium. The more specific infrared analytical procedure was investigated so that the possible residual degradation behavior would be elucidated.

The structural formula for Tedium is:



Mol. wt. 356

The infrared characteristics of the purified compound are reproduced in Figure 1. Because diphenyl sulfones are resistant to strong oxidizing conditions, it is possible to destroy coextracted interfering natural products by oxidation with chromic anhydride in glacial acetic acid and to determine microquantities of parent Tedium by its absorption at 1160 cm^{-1} .

Special Reagent. Aluminum oxide Woelm, basic grade I.

Special Apparatus. Infrared spectrophotometer, equipped with a 3-mm. microcell with rock salt windows.

Procedure

Oxidation. Add chloroform stripping solution, obtained in the usual manner (4), to a 500-ml. Erlenmeyer flask and evaporate to dryness through a three-ball Snyder column, carefully removing the last traces of solvent with a gentle jet of air. To the cooled residue add 50 ml. of glacial acetic acid and 9 grams of chromic anhydride, and reflux vigorously for exactly 10 minutes. If the solution at this point is green, add another aliquot of chromic anhydride and reflux an additional 10 minutes, then cool for at least 5 minutes. Transfer the acetic acid solution to a 500-ml. separatory funnel, using 250 ml. of water and 150 ml. of *n*-hexane.

CAUTION. Do not use stopcock grease on the plug of the separatory funnel, as it will cause serious interference during the measuring step.

Shake the funnel vigorously for 30 seconds, then discard the aqueous layer. Wash the *n*-hexane solution successively with two 100-ml. portions of water and two 25-ml. portions of 4% sodium hydroxide solution, then pass it through 1 gram of anhydrous sodium sulfate into a Kuderna-Danish evaporative concentrator. Evaporate to dryness, removing the last traces of solvent with a gentle jet of air.

Measurement. Dissolve the residue in 0.3 ml. of spectrograde carbon disul-

Table I. Recovery of Tedium from Lemon Peel Extractives

Added		Recovered		
γ	P.p.m.	γ	P.p.m.	%
40	2.0	44	2.2	110
40	2.0	47	2.4	117
40	2.0	44	2.2	110
40	2.0	41	2.1	102
40	2.0	38	1.9	95
40	2.0	40	2.0	100

Table II. Typical Tedium Residues^a on and in Peel of Field-treated Lemons^b

Lb. 25% Wet Powder per 100 Gal. H ₂ O	P.P.M. ^c		
	Total chloride	Colorimetric	Infrared
0	0.6, 1.0	0.4, 0.4	0.6, 0.4
0.5	6.0, 7.6	1.4, 3.6	3.7, 3.7
1	5.6, 4.7	4.3, 3.4	4.9, 4.3
2	6.9, 8.7	4.2, 7.9	5.0, 6.8

^a Sampled about 1 hour after treatment.
^b Values based upon weight of peel only. (Mature lemons have 30.0 ± 8.5 weight % peel determined by 632 measurements.) Samples hand-washed in detergent solution before processing.

^c Values corrected for recovery only (total chloride 111%, colorimetric 116%, infrared 106%).

fide, transfer this solution to a 3-mm. microcell, and record the spectrum from 1200 to 1000 cm^{-1} . The absorbance of the peak at 1160 cm^{-1} is determined by the base-line techniques.

Cleanup. If the oxidation procedure requires excessive amounts of chromic anhydride for complete cleanup, a preliminary cleanup may be used to reduce the amount of extracted natural material. Concentrate the chloroform stripping solution to near dryness and dissolve in 100 ml. of *n*-hexane, then pass onto a 10×200 mm. column of aluminum oxide Woelm, basic grade I. Wash down the column with 30 ml. of *n*-hexane, then elute with 100 ml. of ethyl ether. Evaporate the ether solution to dryness, and treat exactly as described in the above procedure. (Note. Tedium is soluble in *n*-hexane to the extent of 3.3 mg. per ml. at 20° C.)

Discussion

The oxidation procedure described here is the same as previously presented (7, 5). It has proved successful on some substrates other than citrus peel. The use of grease for lubricating stopcocks, especially silicone-type greases, results in serious interferences during the optical measuring step. Teflon plugs or water-lubricated plugs are recommended for separatory funnels. The use of the alu-

minum oxide column is necessary for reducing the quantity of coextracted natural products to be oxidatively destroyed, so that the recommended amount of chromic anhydride will be sufficient.

A calibration curve for Tedium in carbon disulfide conforms to Beer's law at 1160 cm^{-1} from 10 to 400 γ of Tedium, with a slope of about 56 γ per 0.1 absorbance unit using the volume and the microcell recommended. The analytical procedure has an over-all efficiency of from 95 to 117%, based upon recovery of Tedium in the presence of citrus extractives in chloroform (see Table I).

The use of infrared techniques gives the method a high degree of specificity. Although any stable organic sulfide, sulfoxide, or sulfone would interfere with the sulfone band at 1160 cm^{-1} , the use of any of the appropriate alternate strong absorption bands (1345, 1090, 1063 cm^{-1}) would alleviate this interference.

In Table II are comparisons of some typical residues of Tedium on and in the peel of field-treated lemons as determined by the combustion-chloride (4), colorimetric (2), and infrared procedures. Background and recovery values for oranges are of the same order of magnitude as for lemons.

Acknowledgment

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