Colorimetric Microdetermination of the Acaricide 2,4,5,4′-Tetrachlorodiphenyl Sulfone

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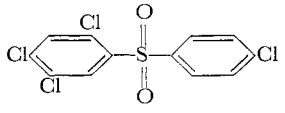
A microanalytical method for the determination of the new acaricide 2,4,5,4′-tetrachlorodiphenyl sulfone, Tedion, is presented. Nitrated Tedion produces a red color with an absorption maximum at 520 mμ when treated with alkali in the presence of pyridine. The method responds in the range of 5 to 50 γ of Tedion.

THE COMPOUND 2,4,5,4′-TETRACHLORODIPHENYL SULFONE, also known as Tedion, has high acaricidal activity against several species of plant feeding mites. The pure material is a white crystalline compound having a molecular weight of 356.06, a melting point of 148–9° C., and the following structural formula:



The magnitudes of Tedion residues existing on and in treated edible products are important and necessary for the establishment of tolerances so that the compound may be registered for use as a pesticide. The colorimetric method herein presented is well suited for the determination of such residues. It is based on the measurement of a red color which is produced when nitrated Tedion is treated with alkali in the presence of pyridine. This color has a maximum absorption value at 520 mμ (Figure 1).

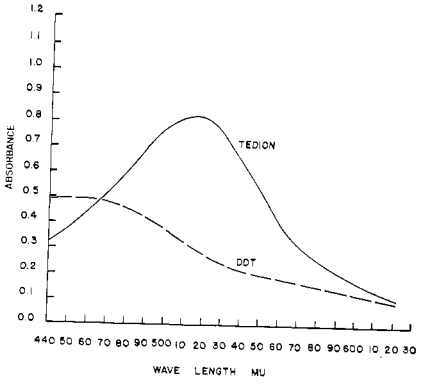


Figure 1. Absorption curves for Tedion and DDT

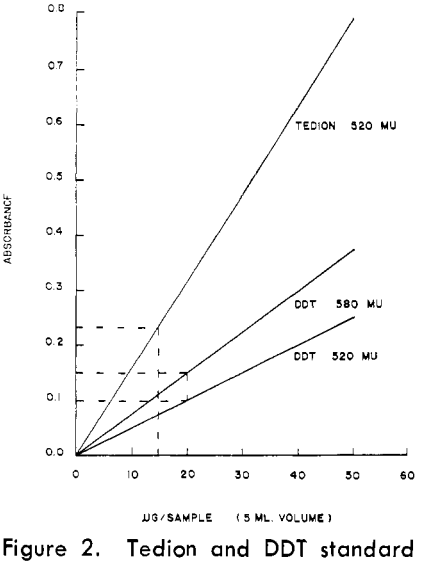


Figure 2. Tedion and DDT standard curves

Procedure

Reagents. Chloroform, U.S.P. grade.

Nitrating acid. A 2 to 1 mixture of fuming nitric acid (specific gravity 1.50) and concentrated sulfuric acid (specific gravity 1.84 ACS grade). Mix just before use.

Pyridine. ACS grade (must be checked before use. See Discussion). Add 4 ml. of water to 96 ml. of pyridine.

Potassium hydroxide solution, 33%, 33 grams of potassium hydroxide in 67 ml. distilled water.

Lanolin reagent. U.S.P. anhydrous and odorless grade (1 gram per 100 ml. of chloroform).

Special Apparatus. Spectrophotometer or colorimeter. Any type that responds satisfactorily at 520 mμ.

Preparation of a Standard Extinction Curve. Weigh accurately 20 mg. of Tedion, transfer to a 200-ml. volumetric flask, dissolve in chloroform, and make up to volume. Transfer a 5-ml. aliquot (500 γ of Tedion) to a 100-ml. volumetric flask and make up to volume with chloroform (1 ml. = 5 γ of Tedion). Add 0, 2, 5, and 10 ml. (0, 10, 25, and 50 γ) to 50-ml. Erlenmeyer flasks and duplicates if desired.

Add 5 ml. of lanolin reagent to each flask and evaporate to dryness with a gentle air current. Chill in ice, add 3 ml. of chilled acid mix, and rotate the flasks to make sure that the acid comes in contact with all the Tedion. After 5 minutes in an ice bath, remove the flasks and allow them to stand for 0.5 hour to reach room temperature. Place the flasks in a cold water bath (20° to 25° C.) and increase the temperature gradually to 90° C. during a half-hour period. Continue to nitrate at approximately 90° C. on a steam bath for an additional 45 minutes. Cool the samples in an ice bath, and transfer the contents of each flask to separate 200-ml. separatory funnels with chilled distilled water (5° to 10° C.) to give a final volume of 50 to 60 ml. in the separatory funnel.

Add 18 ml. of 33% potassium hydroxide and mix. Within 2 minutes after addition of the alkali, add exactly 25 ml. of chloroform to the nitrating flask, swirl briefly, and transfer to the separatory funnel. Shake cautiously but vigorously for 1 minute, releasing the pressure as necessary. Let stand and allow the layers to separate. Drain as much of the clear chloroform layer as possible through a small fluted filter paper into a 50-ml. flask, taking care not to drain any of the emulsion at the water-chloroform interface on the filter paper. (Trials have shown that 23 ml. of the chloroform can consistently be recovered from the initial 25 ml.)

Transfer exactly 20 ml. of this filtered chloroform extract to a clean 125-ml. flask. Evaporate to dryness on a steam bath and aspirate to remove the last traces of chloroform completely. (Complete removal is essential.) Cool to room temperature.

To develop color, add exactly 5 ml. of pyridine to each flask, and cap each one with aluminum foil to prevent possible condensation of the chloroform vapor from the room or the hood into the flasks. Heat each flask on the steam bath for 0.5 hour at 80° C. Swirl the pyridine in the flasks intermittently during the heating period to make sure that all the nitrated Tedion is dissolved in the pyridine. Cool the flasks to room temperature, add 1 ml. of 33% potassium hydroxide and swirl occasionally during a 2- to 5-minute period.

Transfer the supernatant clear pyridine to measuring cells of a suitable size and read the extinctions in a photoelectric colorimeter at 520 mμ, using a blank prepared from the same reagents. The red color is stable for at least 30 minutes. Make a standard curve (Figure 2) from the data thus obtained by plotting the extinction coefficient or transmittance value *vs.* the corresponding quantity of Tedion.

Residue Determinations. In making actual residue determinations, place a volume of chloroform fruit extract containing 10 to 50 γ of Tedion plus 5 ml. of lanolin reagent in a 50-ml. Erlenmeyer flask, take to dryness, chill, nitrate, extract, and develop the color as indicated under preparation of a standard extinction curve.

Table I. Recovery of Tedion from 5-Ml. Aliquots of Fruit Extract

Tedion Added, γ	Tedion Recovered, γ				Av. Recovery, %
	Apples	Peaches	Pears	Plums	
10	11.0	10.0	10.0	11.0	106.3
		10.0	10.0	11.5	
	10.5	10.0	11.0	11.0	
		9.0	11.5	12.0	
20	19.0	19.5	20.0	19.5	97.0
	18.0	19.0	20.0	19.5	
	..	19.5	..	..	
	..	20.0	..	..	
30	30.0	30.0	32.0	28.0	99.7
	28.5	30.0	32.0	28.0	
	30.0	30.0	30.0	30.0	
		30.0	32.0	28.0	
40	34.0	38.0	42.0	42.0	96.4
	36.0	38.0	44.0	40.0	
	34.0	32.0	40.0	46.0	
		38.0	42.0	40.0	
				Av.	99.8

Average blank on 5-ml. aliquots of fruit extract approximates 2.2 γ Tedion

Table II. Recovery of Tedion from 10-Ml. Aliquots of Orange Juice Extract

Tedion Added, γ	Recovered	
	γ	%
3	4.0	133
5	5.5	110
	4.5	90
10	8.9	89
	9.0	90
	10.0	100
	Av.	102

No correction for the 20/25 aliquot is necessary when reading the unknown from the standard extinction curve, because the same aliquot is used when preparing the standard curve.

Sample Preparation for Surface Residues. Surface residues on fruits such as apples, pears, peaches, plums, and citrus may be suitably extracted with U.S.P. chloroform in a tumble- or roll-type extraction apparatus. A convenient procedure is to extract 2 kg. of fruit with 500 ml. of chloroform for 5 minutes in a tumble-type extractor. The chloroform extract is then filtered through a fast fluted filter paper to remove the insoluble solids.

Known amounts of Tedion have been recovered from such extracts (Table I) using the procedure outlined above. Using such surface extracts, it is feasible to run aliquots up to 20 ml. per sample (2- to 5-ml. aliquots are generally in the right range) without undue interference from fruit waxes. Because a 20-ml. aliquot represents 80 grams of sample and the method as described is sensitive to at least 5 γ of Tedion, residues as low as 0.06 p.p.m. with a precision of approximately ±15% can be determined.

Residues from orange juice (Table II) have been successfully recovered using benzene as a solvent. Weigh 200 grams of orange juice (filtered through a sieve to remove large particles of pulp and any seeds present) into a 500-ml. glass-stoppered flask. Add 100 grams of anhydrous sodium sulfate. Then add 100 ml. of benzene (ACS grade) and tumble the flask in a laboratory shaker for 1 hour. Centrifuge the sample. Decant and save the benzene extract for analysis.

Determination of Tedion in Presence of DDT. When DDT is carried through the Tedion method, it interferes by producing a yellow color which absorbs at 520 mμ (Figure 1). A correction for DDT must therefore be made. Because the yellow color is proportional to the amount of DDT present, this correction is readily made. Extinction curves for DDT carried through the Tedion procedure and measured at 520 mμ as well as for DDT carried through a modified Schechter-Haller method and measured at 580 mμ are given in Figure 2.

A typical example for the determination of Tedion in the presence of DDT is given under Figure 2.

In determining DDT in fruit extracts containing Tedion, it is convenient to modify the Schechter-Haller procedure (*5*) by carrying out the extraction of the nitrated DDT under alkaline conditions using chloroform as the solvent. This procedure is identical with the one described above under the Tedion procedure, up to the color development step. Instead of using pyridine and potassium hydroxide as the final color development reagents, a mixture of benzene and sodium methylate (as called for in the Schechter-Haller procedure) is used. When the extraction is carried out with chloroform under strongly basic conditions, it is possible to determine DDT accurately using up to 20 ml. of peach, apple, pear, plum, or citrus extract without interference from fruit waxes. These waxes interfere in the standard Schechter-Haller procedure, where the extraction of the nitrated DDT is carried out under acid conditions using diethyl ether. Tedion does not interfere with the determination of DDT by the Schechter-Haller method.

DDT and Tedion can be determined on a single aliquot taken from the fruit extract by this method.

Typical recoveries of Tedion and DDT from pear extract are given in Table III.

Discussion

Nitration. The uniform nitration of small amounts of Tedion (below 100 γ) is not possible without the addition of a "keeper." This problem has also been encountered with DDT. Gunther and Blinn (*3*) recommend the use of stearic acid as a keeper, when nitrating small amounts of DDT. Oleic acid is also suggested for this use (*1*). Neither material is suitable for use with Tedion, because both form soaps under the alkaline conditions necessary for the extraction of nitrated Tedion. These soaps interfere with the extraction by forming emulsions which are not readily broken up.

A number of materials were evaluated as keepers for the nitration step. Lanolin was found to be effective and is used. Chloroform surface extracts of most fruits—i.e., apple, pear, peach, lemon, and orange—are effective. Lanolin is used in all samples and standards to maintain a constant reagent blank. Recoveries of Tedion with and without lanolin are presented in Table IV.

Extraction. Under the conditions described, the extraction of nitrated Tedion with chloroform is complete. As shown in Table V, it is necessary to carry out the extraction shortly after the addition of the potassium hydroxide, or low values result. These low values are probably caused by the hydrolysis of the nitrated Tedion in the basic medium.

Table III. Tedion and DDT Recoveries from 5-Ml. Aliquots of Surface Pear Extract

Tedion Added, γ	DDT Added, γ	DDT Recovered		Tedion Recovered	
		γ	%	γ	%
10	10	12.0	120	8.5	85
		13.0	130	8.5	85
20	20	20.5	102	20.0	100
		18.5	92	21.5	107
40	40	41.0	102	41.0	102
		41.0	102	43.0	107
			Av. 108		98

Table IV. Effectiveness of Lanolin as a Keeper during Tedion Nitration

	Tedion Added, γ							Tedion Added, γ					
	10	20	30	50	100[a]	200[a]	400[a]	5	10	20	20[b]	30	40
	No Lanolin							Lanolin, 75 Mg.					
Tedion recovered, γ	5.2	3.5	8.5	40.0	82.0	186	392	4.4	10.0	18.8	18.0	28.5	45.6
	5.3	7.0	10.8	39.6	82.0	188	403	5.0	10.6	16.9	20.0	30.0	44.0
	4.0	8.0	16.1	40.5	90.0	178	400		9.5	18.0	19.5		41.2
	5.0	4.0	11.6	41.6					10.5	17.0	18.0		39.6
	3.0	16.6	22.3	43.5					8.5	22.0	19.5		42.0
									9.6	19.8	20.0		41.2
									11.0	20.0	18.0		
									11.5	22.6	16.0		
										22.0	23.0		
										20.4	19.5		
Recovery, %	45	39	46	82	85	92	99	94	102	99	98	98	105

[a] 1/10 aliquots taken after extraction from alkali solution.
[b] 50 mg. of lanolin used.

Table V. Recovery as Function of Time Lapse between Addition of Potassium Hydroxide to Nitrated Tedion and Extraction with Chloroform

Added, γ	Time Lapse, Minutes	Recovery γ	Recovery %
20	0	19.7	
		20.5	100.5
20	5	19.7	
		19.7	98.5
20	15	12.5	
		15.0	67.5

Color Development. In preparation for the color development step, it is extremely important to eliminate chloroform from the sample prior to the addition of pyridine. Chloroform and pyridine react to give a red color very similar to the Tedion color according to the Fujiwara reaction (*2*). This reaction has recently been made the basis of an analytical method for the determination of Kelthane (*4*).

It is necessary to check each bottle of pyridine prior to use. Some samples will develop a red color in the presence of potassium hydroxide and should not be used.

Anhydrous pyridine will not develop a satisfactory color with nitrated Tedion; therefore water must be added to the pyridine. A maximum color per microgram of Tedion is obtained when the water content of the pyridine is approximately 4%.

The Tedion color reaches a maximum intensity about 2 minutes after the potassium hydroxide is added and remains stable for at least 30 minutes.

Interfering Pesticides. DDT interferes with the method and a correction must be made. TDE (DDD) also interferes, but not to the same extent. The miticide, 4-chlorodiphenyl sulfone (Sulfenone), reacts quantitatively by this method. Methoxychlor, ovex, Perthane, parathion, malathion, ziram, ethion, Thiodan, and Captan do not interfere.

Acknowledgment

The authors are indebted to K. H. Hanewaldt of the Analytical Department, N. V. Philips-Roxane Pharmaceutisch Industrie, Amsterdam, Holland, for basic information on the development of this procedure.

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Received for review March 27, 1958. Accepted August 11, 1958. Division of Agricultural and Food Chemistry, 133rd Meeting, ACS, San Francisco, Calif., April 1958.

ACARICIDE RESIDUES

Persistence of Tedion Residues on Fruits

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TEDION WAS DISCOVERED in the laboratories of N. V. Philips-Roxane of the Netherlands. Tedion is very effective in the control of several species of mites, which include the citrus red mite, *Metatetranychus citri* (Mc G.), the European red mite, *Metatetranychus ulmi* (Koch), the Willamette mite, *Eotetranychus willamettei* (Mc G.), the Pacific mite, *Tetranychus pacificus* (Mc G.), the two-spotted mite, *Tetranychus telarius* (Linn), and the Atlantic mite, *Tetranychus atlanticus* (Mc G). In addition, Tedion shows promise for the control of clover mite, *Bryobia praetiosa* (Koch), and of the peach silver mite, *Vasates cornutus* (Banks).

A colorimetric microanalytical method is available for the determination of Tedion. This method is suitable for residue determinations and was used exclusively in obtaining the data given here. Data illustrating recoveries from four different fruit extracts by this method of analysis are to be published in another paper (*2*).

Materials and Methods

Apple, pear, peach, lemon, and orange trees bearing fruit were sprayed with either 1.0 or 3.0 pounds of 25% Tedion wettable powder per 100 gallons of water. The sprays were applied to the pears and peaches with air carrier-type orchard equipment using approximately 500 gallons of spray per acre. The oranges and lemons were sprayed with conventional high pressure spray machines using approximately 1000 gallons per acre. The apples were