Residual Behavior of S-(p-Chlorophenylthio)methyl O,O-Diethyl Phosphorodithioate (Trithion) on and in Mature Lemons and Oranges

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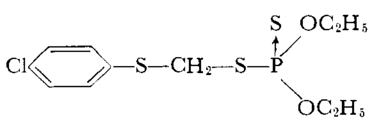
Residues of the insecticide, S-(p-chlorophenylthio) methyl O,O-diethyl phosphorodithioate, Trithion, on and in lemons and oranges, were determined by two analytical procedures. The apparent magnitudes and the residual behavior of these residues as determined by a nonspecific total-chloride method differed from those determined by the more specific colorimetric procedure. However, the magnitudes and persistence of Trithion residues determined by both methods are in general agreement with those of most other insecticides and acaricides on citrus fruits.

THE COMPOUND S-(p-chlorophenylthio)methyl O,O-diethyl phosphorodithioate, Trithion, also known as Stauffer R-1303, is a general insecticide and acaricide. Its structural formula is:



M.W. 342.86

Trithion has shown promise for the control of the citrus red mite, *Metatetranychus citri* (McG.), and other Tetranychid mites injurious to citrus (*4*), and to the California red scale, *Aonidiella aurantii* (Mask.) (*1*). This paper is concerned with magnitudes and physical fates of residues of Trithion on and in mature lemons and navel oranges treated in the field in a conventional manner with commercial-type formulations.

Two analytical procedures were used for this study: the combustion total-chloride procedure described by Gunther and Blinn (*2*) and the colorimetric procedure described by Patchett (*5*). The nonchromatographic total-chloride procedure is nonspecific and will respond to the chlorophenyl moiety, regardless of any alteration to the other portion of the molecule. The colorimetric procedure is more specific in that it is based upon hydrolysis of the chromatographically isolated parent material to p-chlorothiophenol, which reacts with 2,6-dibromo-N-chloro-p-quinoneimine at pH 6.6 to form an orange color (λ_{max} 480 mμ) (*5*). Any differences in apparent residual behavior, as determined by these two methods, may be caused by any of the many accessory ingredients in the formulation and/or by a chemical alteration of the parent compound. Data from this study indicate that residual behavior determined by the total-chloride procedure are more persistent than those determined by the colorimetric procedure. The magnitudes of residues and their half-life values by both methods are in the range of those previously established (*2*, *3*) for other pesticides on and in citrus fruits.

Materials and Methods

Mature navel orange trees were sprayed February 21, 1956, with 1, 3, and 6 pounds of a 25% wettable-powder formulation of Trithion per 100 gallons of water, or with 24 fluid ounces of an emulsifiable concentrate formulation of Trithion (4 pounds of Trithion per gallon of formulation) per 100 gallons of water. Mature Eureka lemon trees were sprayed March 6, 1956, with the dosages listed for navel oranges. Applications were made as conventional sprays, using a high-pressure reciprocating pump and manually operated spray guns. Sprays were applied at the rate of approximately 1500 gallons per acre to the lemon trees and 2500 gallons to the orange trees.

Mature lemon fruit samples for assay of residues were collected 1, 6, 9, 15, 23, 29, 43, and 58 days after treatment. Mature orange fruit samples for assay of residues were collected 1, 3, 7, 14, 21, 35, 42, 56, and 70 days after treatment. Four fruits (one from each quadrant) were picked from each of eight trees in each plot, and the resulting 32 fruits were processed as a unit sample. The two replicates for each treatment were processed separately.

The unwashed fruit was peeled and processed with petroleum ether, in the manner and with the equipment previously described (*2*), to afford final stripping solutions. Aliquots of the stripping solutions were analyzed for Trithion by colorimetry (*5*), and for organic chloride by combustion (*2*).

Results

Navel Oranges. Residue values for Trithion on and in navel orange peel, determined by both the colorimetric and the total-chloride procedures are collated in Table I.

Values for the colorimetric procedure are presented graphically in Figures

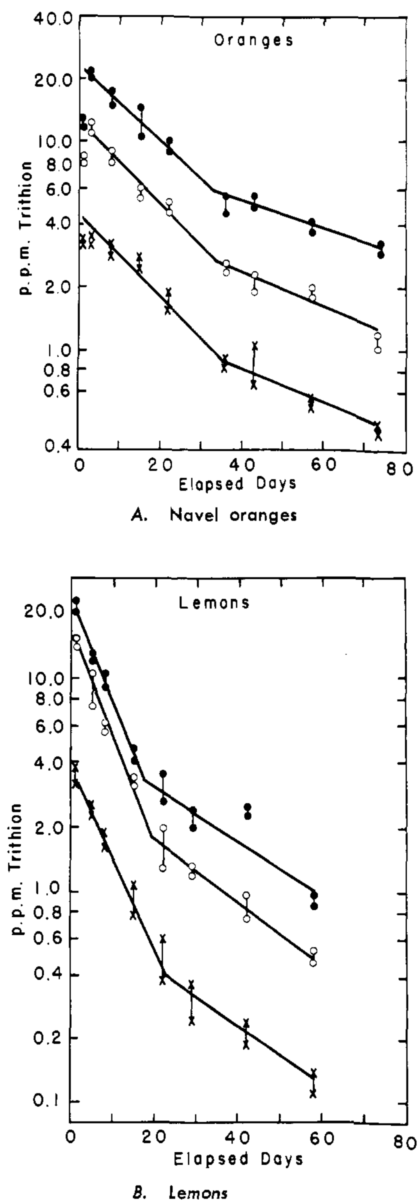


Figure 1. Residual behavior of Trithion on and in peel of citrus fruits

Determined by colorimetric method.
Lb. 25% W. P./100 Gal. Water
● 6 ○ 3 × 1

Table I. Residue Values (P.P.M.) for Trithion on and in the Peel of Field-Sprayed Citrus Fruits[a]

Days after Treatment	Dosage,[b] 1 Lb. 25% W.P./100 Gal.		Dosage,[b] 3 Lb. 25% W.P./100 Gal.		Dosage,[b] 6 Lb. 25% W.P./100 Gal.		Dosage,[b] 24 Ounces E.C./100 Gal.	
	Colorimetric	Total chloride	Colorimetric	Total chloride	Colorimetric	Total chloride	Colorimetric	Total chloride
				Navel Oranges				
1	3.2, 3.3	3.9, 6.3	8.2, 8.0	12.6, 10.7	13.0, 13.4	17.8, 17.8	7.3, 5.5	8.5, 11.4
3	3.4, 3.3	5.7, 7.0	10.6, 10.6	14.8, 12.4	20.8, 21.2	25.9, 31.4	5.3, 7.8	7.2,
7	2.8, 3.3	2.1, 1.8	8.7, 8.3	10.8, 10.3	17.6, 14.8	23.7, 24.2	7.1, 7.4	10.1, 11.1
14	2.8, 2.4	5.7, 5.3	5.8, 5.9	9.9, 11.1	12.3, 10.2	20.5, 19.7	5.7, 5.1	10.2, 9.4
21	1.9, 1.6	4.9, 4.9	5.1, 4.7	10.6, 12.4	9.2, 9.6	18.8, 18.6	4.5, 5.1	8.0, 11.1
35	0.9, 0.8	3.7, 3.5	2.4, 2.6	7.9, 8.5	5.5, 4.6	13.4, 15.6	2.4, 1.9	8.6, 8.5
42	0.7, 1.0	3.0, 3.0	1.9, 2.4	7.5, 7.5	5.0, 5.5	13.9, 14.0	2.4 2.6	5.0, 5.0
56	0.6, 0.6	2.2, 1.1	2.0, 1.9	5.3, 5.9	3.8, 3.8	9.1, 9.7	2.0, 2.1	3.9, 4.4
70	0.4, 0.4	1.9, 1.8	1.2, 1.0	5.0, 4.6	3.0, 3.1	10.1, 10.2	1.7, 1.4	4.4, 3.8
				Lemons				
1	3.8, 3.2	3.5, 5.2	14.7, 15.4	17.1, 21.0	21.3, 22.9	38.1, 39.6	14.4, 15.4	22.6, 22.3
6	2.3, 2.6	6.0, 5.1	7.5, 10.6	16.9, 17.3	12.8, 12.5	30.4, 12.1	8.9, 10.6	15.4
9	1.8, 1.9	0.9, 5.6	6.3, 6.1	12.5, 12.4	9.4, 10.4	22.1, 24.1	8.8, 7.5	13.5, 11.9
15	0.8, 1.1	3.2, 1.7	3.3, 3.4	11.9, 12.6	4.7, 4.2	17.3, 17.8	5.0, 5.5	12.6, 13.8
23	0.6, 0.4	2.4, 2.8	1.3, 2.1	5.5, 7.6	3.6, 2.6	12.3, 11.6	4.2, 4.4	7.8, 8.9
29	0.3, 0.4	1.3, 0.7	1.4, 1.3	3.2, 5.1	2.0, 2.4	10.8, 11.4	2.9, 2.7	7.8, 7.5
43	0.2, 0.2	0.9, 0.1	0.8, 1.0	4.1, 3.7	2.4, 2.4	7.4, 5.6	2.9, 2.7	4.7, 5.5
58	0.1, 0.1	0.7	0.5, 0.5	0.3	0.9, 1.0	2.7, 3.5	1.2, 1.1	5.4, 6.1

[a] Values based on weight of peel only (mature navel oranges have 22.1 ± 7.3 weight % peel, from 567 measurements. Mature lemons have 30.0 ± 8.5 weight % peel, from 632 measurements). All values corrected for background (oranges: colorimetric method 0.4 p.p.m.; total chloride 1.5 p.p.m.; lemons: colorimetric method 0.3 p.p.m.; total chloride 1.5 p.p.m.) and recovery (oranges: colorimetric method 98%; total chloride 98%; lemons: colorimetric method 90%; total chloride 95%).

[b] W.P. Wettable powder analyzed by colorimetric procedure to be 21.7% Trithion.
E.C. Emulsifiable concentrate analyzed by colorimetric procedure to be 3.28 lb. of Trithion/gal. concentrate.

1,*A*, and 2; those for total chloride, in Figures 3,*A*, and 4. Values for the pulp (edible portion) analyses by the colorimetric procedure never exceeded an apparent 0.02 p.p.m. of Trithion throughout this study, and total chloride values never exceeded an apparent 0.5 p.p.m. of Trithion.

Lemons. Residue values for Trithion on and in lemon peel, determined by both the colorimetric and the total-chloride procedures are also collated in Table I. Values for the colorimetric procedures are presented graphically in Figures 1,*B* and 3; those for total chloride, in Figures 3,*B*, and 4. Values for the pulp (edible portion) analyses, by the colorimetric procedure, never exceeded an apparent 0.02 p.p.m. of Trithion throughout this study, and the total-chloride values never exceeded an apparent 0.5 p.p.m. of Trithion.

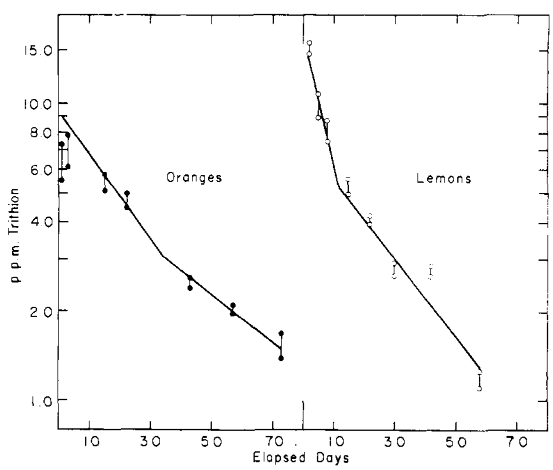
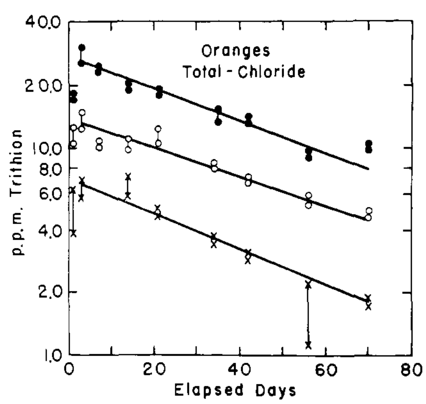


Figure 2. Residual behavior of Trithion on and in peel of citrus fruits

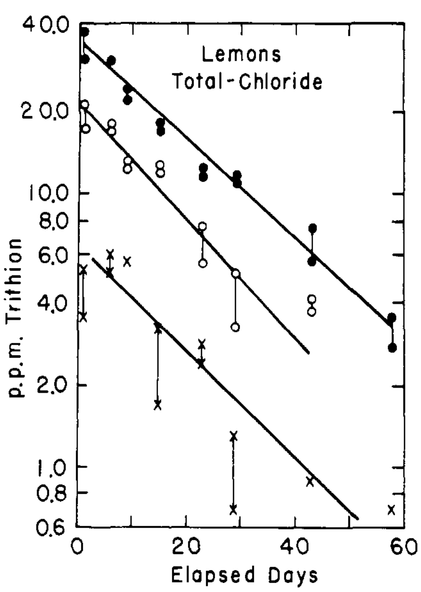
● Navel oranges
○ Lemons
Both sprayed with 24 ounces of an emulsifiable concentrate formulation of Trithion/100 gal. water, as determined by colorimetric procedure

Discussion

The degradation and persisting half-life values (*2*) for residues of Trithion on and in the peel of navel oranges and lemons, as determined by the total-chloride and colorimetric procedures, are listed in Table II. From these half-life values and from the magnitudes reported in Table I, it is evident that residue behavior determined by the nonspecific total-chloride procedure differs significantly from that determined by the specific colorimetric procedure. The consistently higher initial deposits and subsequent residue values for the total-chloride procedure indicate that some of the many accessory compounds in the formulations used for this study do respond to the total-chloride pro-



A. Navel oranges



B. Lemons

Figure 3. Residual behavior of Trithion on and in peel of citrus fruits

Determined by total chloride procedure.
Lb. 25% W. P./100 Gal. Water
● 6 ○ 3 × 1

cedure. The divergent residual behavior of Trithion on and in citrus fruits determined by the two analytical methods may be due to either the accessory materials or to the chemical alteration of Trithion. Studies of the nature of Trithion residues are indicated.

The half-life values for Trithion residues on citrus, determined by either analytical method, are of intermediate longevity in comparison with the residual behavior of many other acaricides and insecticides (*2*, *3*).

Table II. Degradation and Persisting Half-Life Values (in Days) for Residues of Trithion on and in Peel of Field-Treated Lemons and Navel Oranges

		Degradation Half-Life		Persisting Half-Life	
Fruit	Dosage, Lb./100 Gal. Water[a]	Colorimetric	Total chloride	Colorimetric	Total chloride
Lemons	1 25% W.P.	8	..	21	16
	3 25% W.P.	6	..	20	14
	6 25% W.P.	6	..	23	15
	24 ounces E.C.	9	13	21	43
Navel oranges	1 25% W.P.	16	..	41	42
	3 25% W.P.	16	..	37	45
	6 25% W.P.	16	..	38	35
	24 ounces E.C.	21	..	37	45

[a] W.P. Wettable powder analyzed by colorimetric procedure to be 21.7% Trithion. E.C. Emulsifiable concentrate analyzed by colorimetric procedure to be 3.28 lb. Trithion/gal. concentrate.

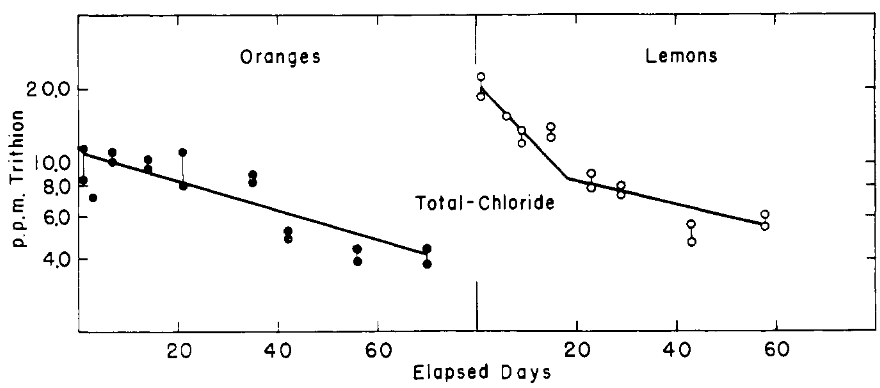


Figure 4. Residual behavior of Trithion on and in peel of citrus fruit

● Navel oranges
O Lemons

Both sprayed with 24 ounces of an emulsifiable concentrote formulation of Trithion/100 gal. water, as determined by total chloride method

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(1) Carman, G. E., unpublished data, 1956.
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(5) Patchett, G. G., "Determination of R-1303 Spray Residues in Oranges, Lemons, and Alfalfa," Stauffer Chemical Co., Richmond, Calif., Mimeo., May 16, 1956.

Received for review May 16, 1958. Accepted October 13, 1958. Paper No. 1051, University of California Citrus Experiment Station, Riverside, Calif. The pesticide chemicals discussed may not be used unless a tolerance has been established or an exemption from the requirement of a tolerance has been granted for each specific use, irrespective of the information contained in this report.

INSECTICIDE VAPORS IN AIR

Determination of Chlordan in Air of Habitations Treated for Insect Control

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A method was developed for the detection and analysis of microgram quantities of chlordan that might be present in the air of homes treated for insect control. Techniques for sampling the air and subsequent concentration and analysis are described. Concentrations lower than 0.005 p.p.m. can be measured. Assays of air samples collected in homes commercially treated for termite control are given.

When chemicals are used for the control of household pests, the question arises whether vapors of the insecticide may be present in the air of the treated home. A method for the detection and determination of micro quantities of chlordan vapor in air was developed in order to answer this question in the case of the insecticide, chlordan.

The air from five homes commercially treated for residual control of termites was analyzed. It was sampled 1 to 6 months subsequent to application.

Reagents

n-Butyl alcohol, reagent grade

n-Pentane, colorimetric grade, Philips Petroleum Co.

Methanol, 99% reagent grade

Florisil, 60/100 mesh (Floridin Co.) dried for 24 hours at 130° C.

Potassium hydroxide pellets, reagent grade

Sodium sulfate anhydrous powder, reagent grade

Chlordan, reference grade (Velsicol Chemical Corp., Chicago, Ill.

Diethanolamine (Union Carbide Chemicals Corp.) purified by distilling 1 liter at a pressure of 20 mm. of mercury. The first 100 ml. of distillate is discarded and the next 100 ml. is collected.

1.0*N* potassium hydroxide in methanol

Methanol-water solution, 90% methanol

Modified Davidow reagent, 2 parts of 1.0*N* methanolic potassium hydroxide, 1 part of diethanolamine, 9 parts of methanol by volume (*6*)

Apparatus

Air-sampling traps, as described in Figure 1

Flowmeter, Fischer Porter, No. 2-F-1/4-20-5/35