

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).

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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.

**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**

Fruit	Dosage, Lb./100 Gal. Water <sup>a</sup>	Degradation Half-Life		Persisting Half-Life	
		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

<sup>a</sup> 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.

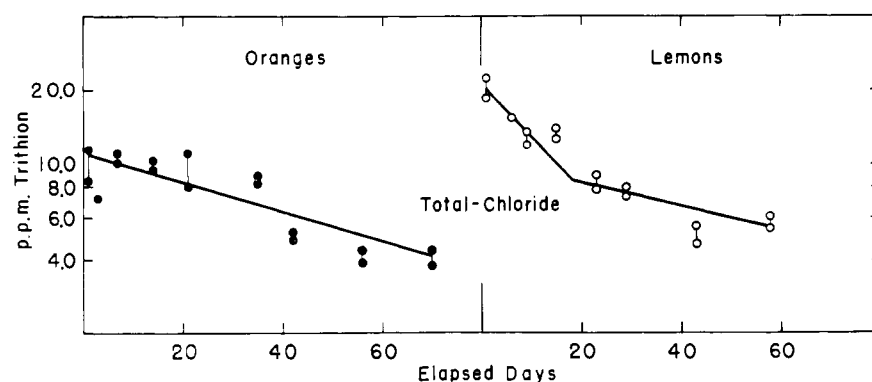


Figure 4. Residual behavior of Trithion on and in peel of citrus fruit

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

## 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

Vacuum pump, Sargent, S-71270  
Chromatographic column, 50-ml. Mohr buret

Spectrophotometer, Beckman DU (Beckman Instruments, Co., Fullerton, Calif.), fitted with a special microcell carriage (Pyrocell Manufacturing Co., New York 28, N. Y.)

Microcuvettes, quartz microcells, 1.5 × 10 × 25 mm., 0.375 ml. (Pyrocell Manufacturing Co.)

Hot water bath, thermostated at 50° C., with provision to support 250-ml. Erlenmeyer flasks immersed to a depth of 2 cm.

Hot water bath, 40° C., with provision for supporting micro reaction tubes

Reaction bath, oil bath thermostatically controlled at 100° C., with provision for support of micro reaction tubes

Micro reaction tubes, Figure 2, A (Walter Podbielniak, Inc., Chicago, Ill.)

Micro transfer filter pipet, Figure 2, B

### Procedure

**Sample Collection.** To each of the two traps are added 30 ml. of *n*-butyl alcohol and then the apparatus is assembled as shown in Figure 3. The vacuum pump is started and the flow rate of the air drawn through the traps is set by adjusting the bleeder valve, at 5 liters per minute. The air is drawn through the solvent traps until 1000 liters of air have been sampled (200 minutes). The vacuum pump is stopped and the butyl alcohol from the two traps is combined in a tightly stoppered glass bottle.

**Pentane Extraction.** The combined solvent from the traps is poured into a 500-ml. separatory funnel. *n*-Pentane (100 ml.) is added to the funnel and the contents are swirled to effect solution. The pentane solution of the alcohol is washed with seven to eight 200-ml. portions of distilled water to remove the butyl alcohol. Gentle swirling of the water with the pentane is sufficient to effect an extraction and will prevent emulsification. When all the alcohol has been removed from the pentane, the pentane is transferred to a 250-ml. Erlenmeyer flask and dried by the addition of 5 to 10 grams of anhydrous sodium sulfate. The pentane is filtered or decanted from the sodium sulfate and concentrated to 10 ml. on the 50° C. water bath.

**Chromatography.** To the chromatographic column are added 10 grams of Florisil. The column is tamped gently with a wooden dowel as the Florisil is poured in. The adsorbant is wet down with pentane, allowing 25 to 50 ml. of the pentane to pass through the column. When the head of pentane just passes into the top of the column, the concentrated pentane solution of the sample is added to the top of the column. When the sample just sinks into the top of the adsorbant the sides of the column are washed down with 5 ml. of pentane. The column is then eluted with 200 ml. of pentane. The entire elutriate is collected in a 250-ml. flask and concen-

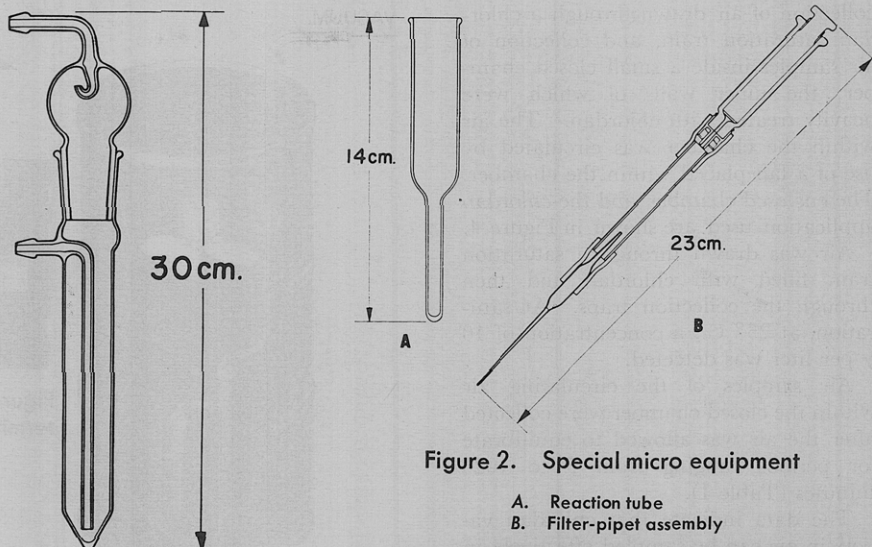


Figure 1. Air sampling trap

trated to 5 ml. on the 50° C. water bath.

**Colorimetric Determination.** The concentrated elutriate is transferred to a micro reaction tube, evaporated to dryness on the 40° C. hot water bath, and assayed by the method of Davidow (7), as modified in this laboratory (6). The modified Davidow reagent (0.2 ml.) is added to the reaction tube, and the tube is placed in an 100° C. oil bath for 15 minutes, and then cooled by placing in a beaker of cold water. The reaction product is diluted to 0.5 ml. with 90% methanol, filtered, and transferred to a microcuvette by use of the transfer pipet assembly, and its absorption at 550 m $\mu$  is measured. The absorption is converted to micrograms of chlordan from a standard curve prepared from reference grade chlordan as described.

### Discussion of Method

**Solvent Traps.** The solvent, *n*-butyl alcohol, was chosen for use as the trapping solvent after consideration of several factors. It was desired that the sampling apparatus be completely portable, so that an analyst could easily carry it to the site of testing. No refrigerant was desired. Thus the solvent must have a vapor pressure low enough so that bubbling 1000 liters of air through it would not vaporize excessive quantities of the solvent. At 20° C., 22 ml. of butyl alcohol will vaporize when 1000 liters of air are bubbled through it. This fact can be used in lieu of a flowmeter. A second demand of the solvent is that the trace quantities of chlordan be easily separated from it. Butyl alcohol can be quantitatively removed by water washing. In addition, the solvent must be readily available in a pure form. The trap is of such design as to give a maximum of contact time with a minimum of splashing. The bulbs prevent carry over of the liquid. Two traps are con-

Figure 2. Special micro equipment

- A. Reaction tube
- B. Filter-pipet assembly

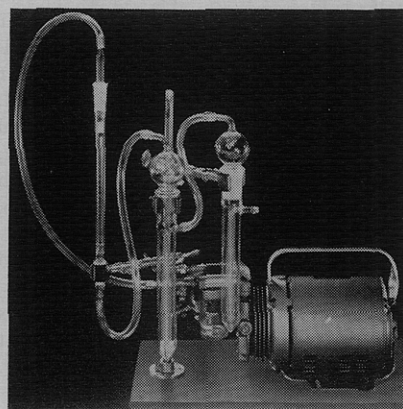


Figure 3. Sampling apparatus

nected in series to ensure complete trapping of the vapors.

**Pentane Extraction.** The chlordan must be separated from the alcohol in which it is trapped. Concentration by merely evaporating the solvent is not acceptable, because losses of chlordan will occur due to codistillation. The use of only low boiling solvents is permissible. A pentane extraction followed by evaporation of pentane on a 50° C. water bath results in little or no losses of chlordan. The last traces of alcohol must be removed, as well as small traces of water in the pentane layer, or subsequent chromatographic separation may be affected.

**Chromatography.** Chromatography of the pentane extract was necessary, because traces of contaminants present in the air (such as paint solvents in freshly decorated homesites) interfered with the colorimetric procedure. Certain contaminants form yellow colors with the reagent and others prevent color formation.

**Colorimetric Determination.** The modified Davidow reagent is extremely sensitive and will form a pink-reaction product with as little as 5  $\gamma$  of chlordan. No material normally found in the air will react in this manner.

**Sampling Efficiency.** The efficiency of the air-sampling technique was studied by the use of two techniques:

collection of air drawn through a chlordan saturation train, and collection of air samples inside a small closed chamber, the inner walls of which were heavily treated with chlordan. The air within the chamber was circulated by use of a fan placed within the chamber. The enclosed chamber and the chlordan application used are shown in Figure 4.

Air was drawn through a saturation train filled with chlordan and then through the collection traps. At saturation, at 25° C., a concentration of 10  $\gamma$  per liter was detected.

Air samples of the circulating air within the closed chamber were collected after the air was allowed to equilibrate for periods ranging from 5 to 1020 minutes (Table I).

The data indicate that chlordan vapors in air can be sampled effectively in this manner, and that when the air within the chamber is allowed to equilibrate for longer periods of time, higher concentrations of chlordan are found. The fact that chlordan vaporizes at an extremely slow rate is evident when, after 17 hours in a closed chamber, which has a high surface area-volume ratio, saturation has not been attained.

Recovery of the trapped chlordan through the extraction, chromatographic, and pentane concentration steps was investigated and found to be about 80%. This agrees with earlier work (6).

#### Application of Chlordan to Termite Control

Five homes commercially treated with chlordan for residual termite control were studied. These homes were located in Georgia, South Carolina, and Arkansas. Applications were made during various seasons of the year.

The homes were of two basic types of construction: (1) built directly on top of a concrete slab, and (2) built on foundation and piers with a crawl space between the ground and the flooring. These are the most common types of construction used in the areas studied.

Chlordan was applied by commercial pest control operators and followed the methods suggested by the U. S. Department of Agriculture Forest Service (8). Water emulsions at a concentration of 1% chlordan were used (Figure 5).

1. Slab-on-Ground Type of Construction. Apply 1 gallon for each 10 square feet of soil surface as an over-all treatment prior to pouring the slab which may serve as a floor, attached porch, terrace, or entrance platform. In critical areas, where termites are frequently found entering floors, such as at expansion joints and utility entrances in the slab, apply emulsion at the rate of 2 gallons per 5 lineal feet. Treat the exterior of the foundation wall at the same rate.

2. Crawl-Space Homes (or crawl space portion of homes). Apply 2 gallons of the emulsion per 5 lineal feet of foundation wall to the critical areas

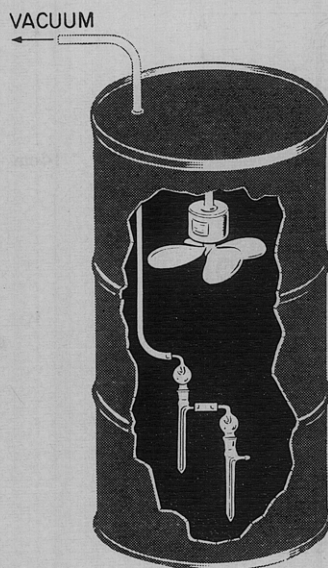


Figure 4. Enclosed chamber

Size.	30-gal. drum, 18-inch diameter, 28 inches high
Volume.	4 cu. ft.
Surface area.	15 sq. ft.
Fan.	2040 r.p.m., 8-inch blade
Chlordan application.	200 mg. per sq. ft., 150 grams 2% in oil

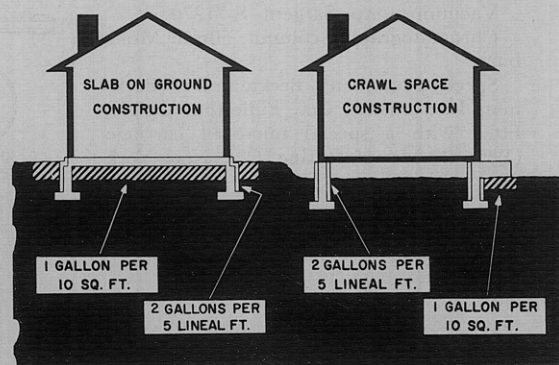


Figure 5. Typical chlordan application for termite control

Table I. Analysis of Air from Enclosed Chamber for Chlordan Content

Time Chamber Closed Prior to Sampling, Minutes	Air Sampled, Liters	Chlordan Found	
		$\gamma$	$\gamma$ /liter
5	144	250	1.74
10	288	620	2.15
60	216	580	2.69
1020	162	680	4.18

Table II. Air from Homes Treated with Chlordan for Termite Control

Type Home	Location	Date Chlordan Applied	Time of Sampling, Days after Applications	Chlordan Assay, $\gamma$ /Liter
Slab	Savannah, Ga.	9-22-55	106	0.000
Slab	Aiken, S. C.	5-24-56	12	0.000
			47	0.000
			83	0.000
			131	0.000
Crawl space	Savannah, Ga.	9-15-55	112	0.000
Crawl space	Aiken, S. C.	4-19-56	48	0.006
			82	0.000
			117	0.000
			166	0.000
Crawl space	Hot Springs, Ark.	12-1-55	126	0.000
			126	0.040

under the house, such as along the inside of the foundation walls, and around piers and utility entrances.

Apply 2 gallons per 5 lineal feet to the exterior of the foundation walls, including the part opposite entrance platforms, porches, etc., where the footing is shallow, and 4 gallons per 5 lineal feet where the footing is deep. Apply 1 gallon per 10 square feet of ground surface as an over-all treatment, only where attached porches, entrance platforms, etc., have concrete on the ground or fill.

**Results.** Samples of air were collected in the treated homes from 2 weeks to 6 months subsequent to application of chlordan. All samples were collected and analyzed in duplicate (Table II).

#### Discussion of Results.

A great deal of work has been published on studies of the toxicity of chlordan vapors to man (1, 3, 7) and other warm-blooded animals (2, 4, 5). These works indicate that concentrations of 1 to 2  $\gamma$  per liter in air show no toxic effects.

The air in homes treated with chlordan for termite control, reported in this study, contained no detectable quantities of chlordan, even though the sensitivity of this method is one hundredth of the concentrations reported to be safe. It must be concluded, therefore, that no danger is involved in the use of chlordan in this manner.

#### Acknowledgment

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## HERBICIDAL ACTIVITY AND STRUCTURE

# Preliminary Evaluation of Some Quaternary Ammonium Salts as Phytotoxic Agents

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Some 60 quaternary ammonium salts  $RR_1R_2R_3N-X$  were prepared by standard chemical methods. Many of these quaternary salts exhibit considerable phytotoxicity in seed germination tests. In a series of 1-substituted pyridinium bromides, maximum phytotoxicity was noticed when R was  $C_{12}$  to  $C_{14}$ . Other active types of similar compounds are also mentioned. Lack of selectivity towards mono- or dicotyledenous species is evident from these examples.

QUATERNARY ammonium salts in general exhibit considerable activity in many biological applications. The bactericidal-germicidal applications are very numerous and are well known. Attempts to correlate the mode of activity of various quaternary ammonium salts as bacteriostatic agents with their colloidal and detergency activity have been presented (3, 6, 7).

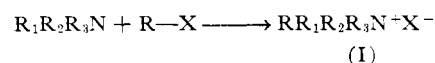
However, prior to the disclosure of the potentialities of a few certain select quaternary salts as herbicides (5), little has been reported concerning this phase of their biological activity.

The laurylpyridinium salts of 2,4-D and 2,4,5-T are phytotoxic, but this type of salt combines a quaternary compound with known herbicides (7).

Decyldimethyl-2-methoxyethylammonium chloride is strongly "phytohormonal" (2).

Therefore, it became of interest to prepare a broad series of quaternary ammonium salts and attempt to correlate structure with phytotoxic activity, if any was present.

The quaternary ammonium salts were obtained by the standard reaction of the appropriate amine and organic halide in an anhydrous solvent, usually in ethyl alcohol.



The salts (I) were examined for phytotoxicity by a slight modification of the method of Thompson, Swanson, and Norman (9). Cucumber and wheat seeds (representing di- and monocotyledenous species) were germinated in Petri dishes in the presence of aqueous solutions of the test chemical. The results (Table I) are expressed as per-

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Table I. Phytotoxicity of Quaternary Ammonium Salts to Germinating Cucumber and Wheat Seeds

	Percentage Root Growth			
	100 p.p.m. Cucumber	10 p.p.m.	100 p.p.m. Wheat	10 p.p.m.
Pyridinium Bromide				
1-Methyl <sup>a</sup>	40	81		
1-Methyl <sup>b</sup>	10	86		
1-Ethyl	65	94		
1-Propyl	64	93		
1-( <i>iso</i> -butyl)	74	86		
1-( <i>n</i> -Hexyl)	34	72		
1-( <i>n</i> -Heptyl)	10	63		
1-(2-Ethylhexyl)	20	72		
1-( <i>n</i> -Octyl)	5	37	13	65
1-(3,5,5-Trimethylhexyl)	14	42		
1-( <i>n</i> -Decyl)	2	23		
1-( <i>n</i> -Dodecyl)	2	25		
1-( <i>n</i> -Tetradecyl)	4	43		
1-Propargyl	48	99		
1-Cyanomethyl <sup>c</sup>	73	97		
1-(2-Chloroethyl)	68	92		
1-( $\beta$ -Ethoxyethyl)	83	101		
1-( $\beta$ -Butoxyethyl)	68	93		
1-( $\beta$ -Butoxyethoxy)ethyl	74	99		
1-( $\beta$ -Phenylethyl)	67	102		
1-Benzyl <sup>c</sup>	36	59		
1-(2,4-Dichlorobenzyl) <sup>c</sup>	26	69		
1-( $\gamma$ -Phenylpropyl)	50	98		
1-Phenacyl	82	89		
1-(6-Cyanoethyl)	54	80		
1-Carbobutoxymethyl <sup>c</sup>	90	99		
1-Methoxymethyl <sup>c</sup>	61	89		
1-( <i>m</i> -Xylol)	32	52	22	84
1-( <i>p</i> -Ethylbenzyl) <sup>c</sup>	23	65	16	58
1-(2,4-Diethylbenzyl) <sup>c</sup>	5	53	4	38
1-( <i>p</i> -Isopropylbenzyl) <sup>c</sup>	7	48	9	70
1-(2,4-Diisopropylbenzyl) <sup>c</sup>	3	26	5	30
1-( <i>p</i> - <i>sec</i> -Amylbenzyl) <sup>c</sup>	4	25	3	22
1-(2-Cyclohexylethyl)	32	66	34	78
1-(1-Naphthylmethyl) <sup>c</sup>	13	57		
1-(2-Hydroxyethyl) <sup>c</sup>	60	82		
1-(2,4-Dinitrophenyl) <sup>c</sup>	44	86		
1-(3,5,5-Trimethylhexyl)-4-methyl	14	37	8	46
1-(3,5,5-Trimethylhexyl)-2-methyl-5-ethyl	92	97	94	105
1-(3,5,5-Trimethylhexyl)-2-chloro	41	81	64	98
1-( <i>p</i> - <i>sec</i> -Amylbenzyl)-2-methyl-5-ethyl <sup>c</sup>	4	27	7	36
Ammonium Bromide				
Triethyl-(3,5,5-trimethylhexyl)	15	52	23	81
Tri-( <i>n</i> -butyl)-3,5,5-trimethylhexyl	4	30	10	61
Tri-( <i>n</i> -Amyl)-3,5,5-trimethylhexyl	2	22	4	47
Trimethyl- <i>p</i> - <i>sec</i> -butylbenzyl <sup>c</sup>	36	84	34	103
3,5,5-Trimethylhexyldimethylphenyl	10	46	15	63

(continued on page 34)