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GAS CHROMATOGRAPHIC CHARACTERISTICS OF CHLORDANE

II. OBSERVED COMPOSITIONAL CHANGES OF THE PESTICIDE IN AQUEOUS AND NON-AQUEOUS ENVIRONMENTS*

ARTHUR BEVENUE

Department of Agricultural Biochemistry, University of Hawaii, Honolulu, Hawaii (U.S.A.)

AND

CHEE YEE YEO

Department of Food Science and Technology, University of Hawaii, Honolulu, Hawaii (U.S.A.)

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SUMMARY

Studies were made on the vaporization and adsorptive properties of chlordane when the pesticide was exposed to water and organic solvent environments. Within thirty days of exposure to water, the heptachlor component of chlordane was completely changed to 1-hydroxy-chlordane. Over a period of sixty days, water adsorbed increasing amounts of vaporized chlordane; the α -chlordane, γ -chlordane and nonachlor components of the pesticide were markedly stable. No apparent chemical changes in the pesticide were observed when it was exposed to an isooctane environment for an equivalent period of time; the more volatile components of chlordane were adsorbed to a greater degree in the organic solvent.

Hexachlorocyclopentadiene, a component of chlordane, dissipated or degraded, with time, in water solution. However, in an organic solvent environment, this chemical displayed multi-component characteristics.

Gas chromatography was used to observe the changes in the characteristics of the pesticide, with time, in aqueous and non-aqueous media.

INTRODUCTION

Data were acquired by gas chromatography on some of the apparent chemical changes and vaporization and adsorption properties of the pesticide chlordane (a mixture of octachloro-4,7-methanotetrahydroindane and related compounds including hexachlorocyclopentadiene) in organic solvent and aqueous media, which were considered necessary prerequisites to a study of the adsorptive effects of this chemical on stored foodstuffs. Comparable data were also acquired on hexachlorocyclopentadiene which may exist in an amount as large as 1% in commercially available chlordane.

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MATERIALS AND METHODS

Gas chromatograph

F & M Model 810, electron capture detector; column $\frac{1}{4}$ in. \times 4 ft. borosilicate glass containing 3% SE-30 silicone on Chromosorb W, 80-100 mesh, acid-washed and treated with dimethyldichlorosilane; column temperature 190°, injection temperature 200°, detector temperature 200°; argon-methane (90-10) carrier gas, flow rate 75 ml/min; Leeds and Northrup Speedomax H recorder, 1 mV full scale, chart speed $\frac{1}{2}$ in. per min.

Reagents

Hexane and isooctane, Mallinckrodt Nanograde.

Pesticide chemicals

Chlordane, technical grade; α -chlordane, γ -chlordane, heptachlor, heptachlor epoxide (the foregoing chemicals supplied through the courtesy of the Velsicol Corp., Chicago, Ill.), chlordene and nonachlor. 1-Hydroxychlordene was supplied through the courtesy of Dr. M. C. BOWMAN, USDA, ARS, Tifton, Ga

Hexachlorocyclopentadiene (Aldrich Chemical Co., Milwaukee, Wisc.). All of the pesticide chemicals were 99.4 to 99.8% purity with the exceptions of technical grade chlordane and hexachlorocyclopentadiene.

Experimental

(a) A glass vial containing 50 mg technical grade chlordane was placed in each of 15 8-oz. glass jars (60 mm diameter) which contained 20 ml isooctane; the vial extended above the solvent surface to permit only the vaporized components of the chlordane to contact the solvent. The jars were sealed with aluminum foil including a bleed hole to allow equilibration with the atmosphere. The jars were selected at 2-day intervals over a period of 30 days for analysis of the isooctane contents to determine the characteristics of the gas chromatographic curve of the vaporized chlordane components adsorbed by the solvent. Another set of jars was prepared, replacing the isooctane with 20 ml distilled water, for similar analysis of the water for adsorbed chlordane vapors.

(b) Two series of jars were prepared (one of isooctane and one of distilled water, 20 ml of each solvent) as described in (a), but 0.5 mg hexachlorocyclopentadiene (Hex) was substituted for the chlordane component. The amount of Hex selected was considered to be relative to the maximum amount that was present in the technical chlordane¹ used in (a).

(c) Twenty milliliters of distilled water containing 1 p.p.m. (20 μ g) technical grade chlordane was added to each of twelve 50-ml glass-stoppered erlenmeyer flasks and stored. Flasks were selected at 2-day intervals over a period of 30 days for chlordane analysis. The contents of the twelfth flask were analyzed after 60 days of storage.

All of the samples were stored at room temperature (22-25°) and a relative humidity of 60-80%. No direct sunlight contacted the samples, and fluorescent light was the primary light source in the laboratory in which these experiments were conducted.

Preparatory to gas chromatographic analysis, the chlordane-isooctane solutions

were transferred to 50-ml volumetric flasks and made to volume with isooctane. The Hex-*isooctane* solutions were made to 100-ml volumes. The water solutions were extracted three times with hexane, the combined hexane extracts were filtered through a plug of anhydrous sodium sulfate directly into 50-ml volumetric flasks and made to volume with hexane. Suitable aliquots were applied to the gas chromatograph and the recorded data were compared to data obtained from the technical chlordane and related chemical standards.

RESULTS AND DISCUSSION

Technical grade chlordane, described by the manufacturer to be composed of a mixture of octachloro-4,7-methanotetrahydroindane and related compounds with a maximum of 1% hexachlorocyclopentadiene¹, contains at least ten components² including heptachlor and γ - and α -chlordane (see Fig. 1, curve 1). Although chlordane is a complex mixture of chlorinated hydrocarbons, the product is surprisingly uniform in composition as determined by acceptable methods of quality control³.

Gas chromatograph curves of chlordane have appeared only recently in the literature^{2,4-7}, which is not surprising considering the complex pattern of the chromatographed material. KAWAHARA *et al.*⁸ presented a study of gas chromatograph retention times of some chlordane components but they did not include any illustrative curves. The number of characteristic gas chromatograph peaks of chlordane obtained by different workers have varied from seven⁶ to fourteen²; such differences were due, no doubt, to variable gas chromatograph techniques and not to any characteristic differences in the chlordane material used by each worker. In all instances, including the data reported herein, the predominant peak areas (Fig. 1, curve 1) were heptachlor (E), the peak preceding heptachlor (D), and γ -chlordane and α -chlordane (J, K).

Fig. 1 illustrates the adsorption pattern of vaporized technical chlordane exposed to isooctane for time periods of 2 to 30 days. The greater volatility of the heptachlor component (peak E) of chlordane and the fractions that emerged from the gas chromatograph column prior to heptachlor are readily apparent. The gas chromatograph curve pattern of technical chlordane in isooctane solution was unchanged over a period of 30 days stored at room temperature (20-25°) with exposure to artificial light, except that the more volatile components of the pesticide became magnified by continued adsorption of these components by isooctane. This stability characteristic is in agreement with BURKE AND HOOVER⁹ who noted that other chlorinated pesticides, including heptachlor and heptachlor epoxide, exhibited no characteristic changes in composition over a period of 8 months when isooctane solutions of the pesticides were stored under similar room conditions.

The data obtained from isooctane solutions of the adsorbed vapors from Hex showed an unexpected gas chromatograph pattern. After 24 h of exposure to isooctane, the chromatographic characteristics of Hex were similar to the standard material obtained directly from the reagent bottle (Fig. 2, curves 2 and 3). However, the curves 4, 5, and 6 (Fig. 2) for the solutions exposed 7 through 21 days showed a multiple-peak phenomena up to and including the D-peak area of technical chlordane; this latter peak area (D) has been described as the Diels-Alder adduct of pentachlorocyclopentadiene and cyclopentadiene². The degree of purity of hexachlorocyclopentadiene was not determined; however, the source of this reagent (Aldrich Chemical Co.)

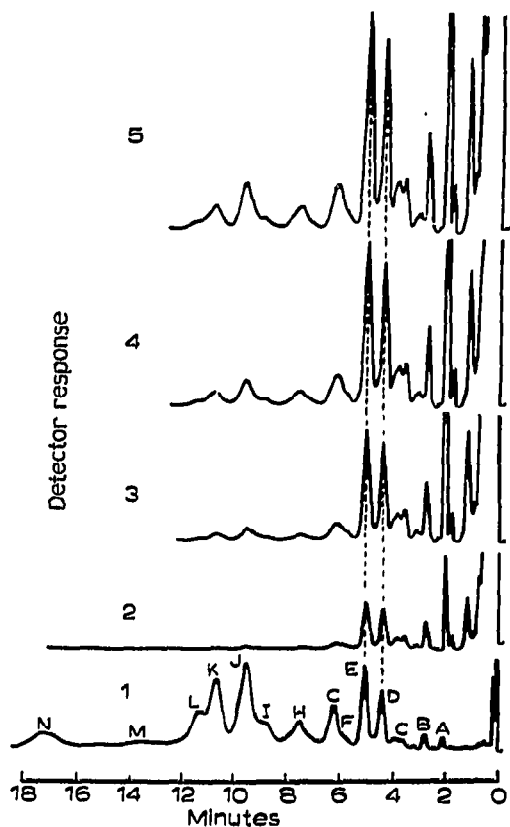


Fig. 1. Technical chlordane vapors exposed to isooctane. Curve 1, 4 ng technical grade chlordane standard; curve 2, 2 days exposure; curve 3, 10 days exposure; curve 4, 20 days exposure; curve 5, 30 days exposure.

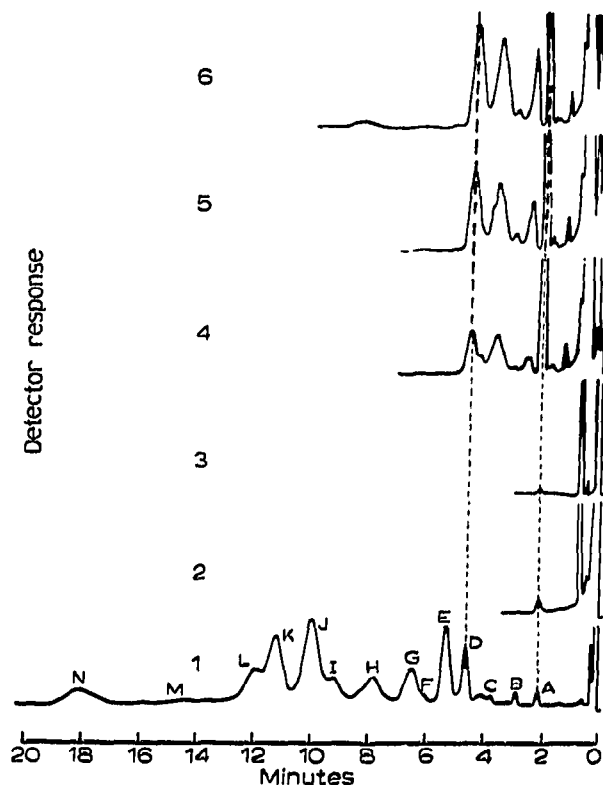


Fig. 2. Hexachlorocyclopentadiene vapors exposed to isooctane. Curve 1, 4 ng technical grade chlordane standard; curve 2, 0.1 ng hexachlorocyclopentadiene standard; curve 3, 1 day exposure; curve 4, 7 days exposure; curve 5, 14 days exposure; curve 6, 21 days exposure.

indicates a purity range of 97–100%. Also, the method of manufacture of this chemical will largely determine the number of other chlorinated hydrocarbons that may be present in the final product¹⁰. Some of the early peaks observed in isooctane solution containing adsorbed technical chlordane vapors (Fig. 1) may be attributed to the Hex fraction of the pesticide, as illustrated in Fig. 3. Fig. 4, curve 3 shows another comparison of the adsorbed Hex vapors with known standards of possible chlordane components (curve 2), and indicates that either chlordene, an intermediate product formed during the manufacture of chlordane¹¹, may be a constituent of the Hex pattern and/or the components shown in the early part of the curve may be more susceptible to atmospheric oxidation and/or light, as suggested by BROOKS AND HARRISON'S studies with chlordene¹². The data suggest that any examination of foodstuffs (especially those of low moisture content) which contain adsorbed chlordane residues would yield gas chromatograph data containing a multiple-peak picture prior to the D area similar to curves 2 and 3, Fig. 3, instead of a pattern as in curve 1, Fig. 3.

The data obtained from distilled water solutions containing adsorbed vapors of Hex was different from the comparable data for isooctane solutions. After 3 days exposure, any adsorbed Hex components had disappeared completely from the water

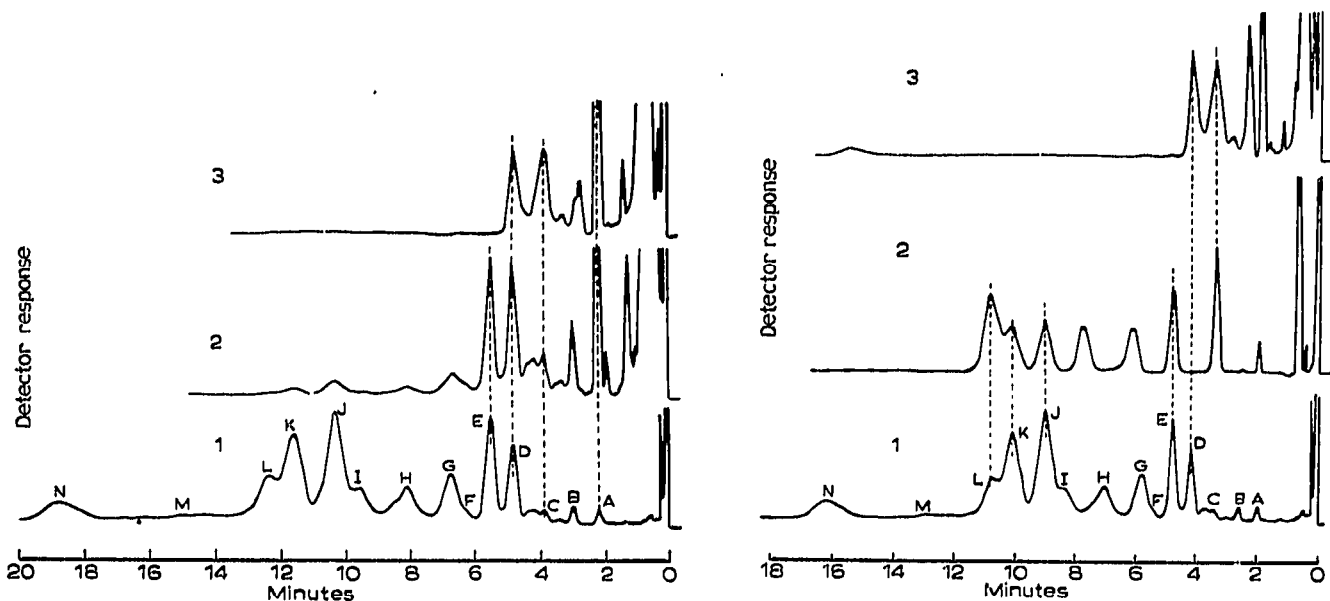


Fig. 3. Curve 1, 4 ng technical grade chlordane standard. Vapors exposed to isooctane for 14 days: curve 2, technical grade chlordane; curve 3, hexachlorocyclopentadiene.

Fig. 4. Curve 1, 4 ng technical grade chlordane standard. Curve 2, standards including possible chlordane components—the seven peaks reading from left to right on the curve, nonachlor, α -chlordane, γ -chlordane, heptachlor epoxide, γ -hydroxychlordane, heptachlor, chlordene. Curve 3, hexachlorocyclopentadiene vapors exposed to isooctane for 14 days.

(Fig. 5), suggesting dissipation or decomposition of the chemical. KAWAHARA *et al.*⁸ noted that Hex decomposed rapidly upon exposure to light or during the period of analysis of the chemical by thin layer chromatography.

Data obtained from distilled water samples which had been exposed to the vapors of technical chlordane are illustrated in Fig. 6. The noncumulative effect of the more volatile components of the pesticide is consonant with the data obtained with Hex and water. Over a period of 60 days, the water adsorbed increased amounts of the vaporized chlordane with no change in the characteristics of the gas chromatograph curves between the areas of peaks H and L, indicating a marked stability to water and light of the γ -chlordane, α -chlordane, and nonachlor components of the pesticide. A tangible difference in the gas chromatograph characteristics of the area of the curve

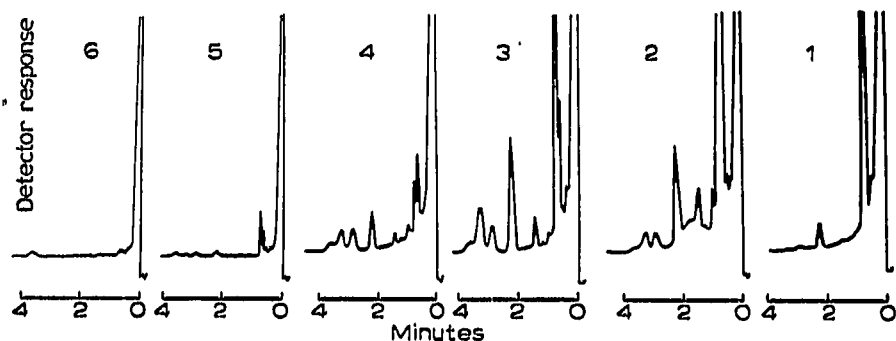


Fig. 5. Hexachlorocyclopentadiene vapors exposed to distilled water. Curve 1, 1.0 ng standard solution; curve 2, 1 day exposure; curve 3, 2 days exposure; curve 4, 3 days exposure; curve 5, 7 days exposure; curve 6, 14 days exposure.

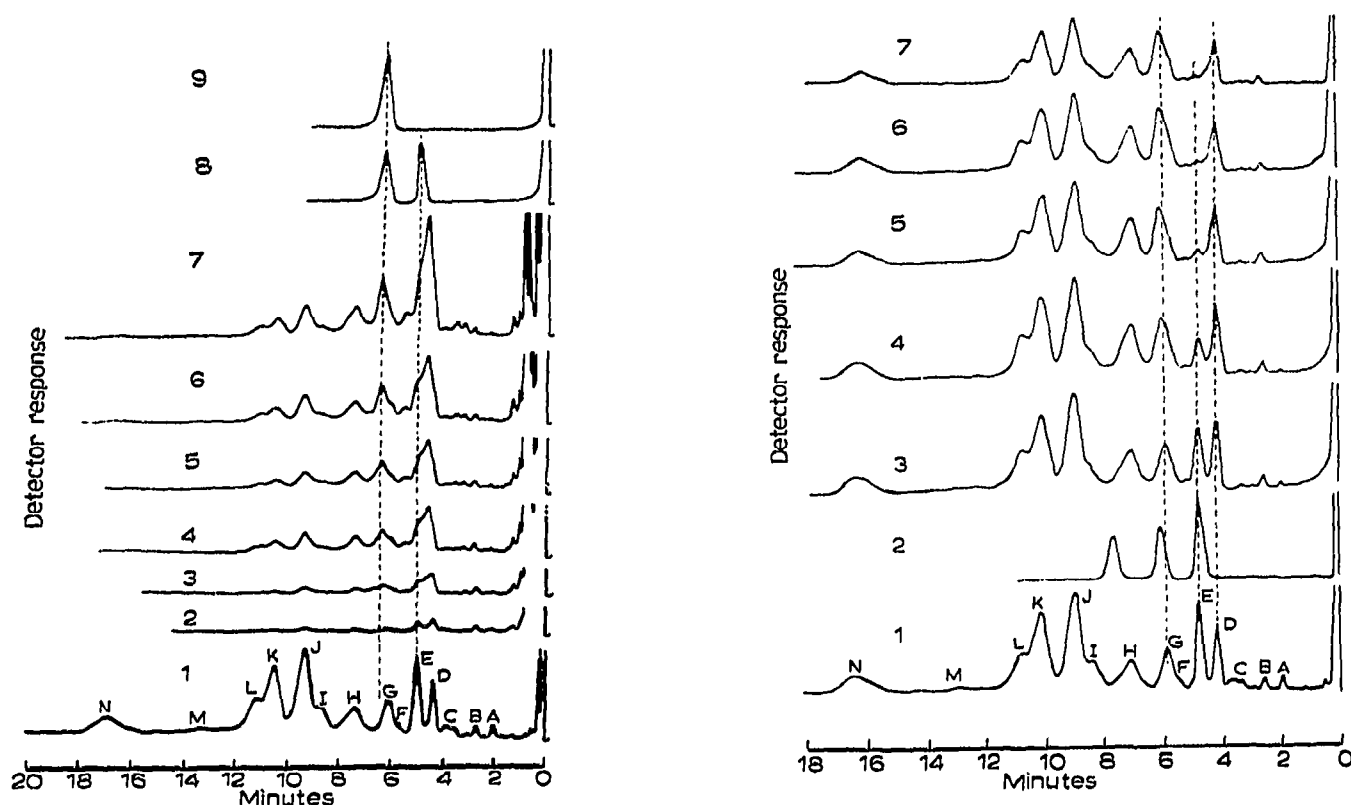


Fig. 6. Technical grade chlordane vapors exposed to distilled water. Curve 1, technical grade chlordane standard, 4 ng; curve 2, 1 day exposure; curve 3, 7 days exposure; curve 4, 14 days exposure; curve 5, 21 days exposure; curve 6, 30 days exposure; curve 7, 60 days exposure; curve 8, heptachlor vapors exposed to distilled water for 14 days; curve 9, 1-hydroxychlordene (1 p.p.m.) in water, 14 days storage.

Fig. 7. Changes in characteristics of technical grade chlordane, with time, stored at a concentration of 1 p.p.m. in distilled water. Curve 1, technical grade chlordane standard, 4 ng; curve 2, heptachlor epoxide, 1-hydroxychlordene, heptachlor standards, reading from left to right, each 0.2 ng; curve 3, 4 days storage; curve 4, 12 days storage; curve 5, 20 days storage; curve 6, 30 days storage; curve 7, 60 days storage.

between peaks D and G (Fig. 6) was apparent within 7 days of exposure and the change was quite marked between the period of 21 days and 60 days of exposure. In addition to the heptachlor component of the pesticide converting to 1-hydroxychlordene, similar to an observation noted by BOWMAN *et al.*^{13,14}, the D peak area characteristic was tangibly changed. There was no evidence of the formation of heptachlor epoxide. COCHRANE AND CHAU¹⁵ recommended the conversion of 1-hydroxychlordene to its corresponding silyl ether derivative to produce a more sensitive and sharper peak on their gas chromatograph curves; this additional step was not considered necessary (see Fig. 6, curve 9), using the gas chromatograph conditions reported herein.

The storage pattern of technical chlordane in water solution (1 p.p.m.) over a period of 60 days showed somewhat different gas chromatograph characteristics (Fig. 7) than the water which was exposed to the vapors of chlordane. The gradual loss of the heptachlor component (peak E) was more apparent, and almost complete loss of this component occurred after 16 days of storage; loss was complete after 30 days of storage. Changes in the profile of peak G of the series in Fig. 7 became quite marked after 16 days of storage because of the formation of 1-hydroxychlordene which was

TABLE I

CHANGE IN CONCENTRATION OF TECHNICAL CHLORDANE IN WATER SOLUTION

Age of solution (days)	Curve areas ^a				
	Peak H	Peak I J	Peak K L	Total	Peak G-OH
2	0.20	0.64	0.65	1.49	0.20
4	0.25	0.61	0.64	1.50	0.24
6	0.26	0.70	0.69	1.65	0.30
8	0.23	0.56	0.60	1.39	0.30
10	0.25	0.70	0.70	1.65	0.30
12	0.30	0.65	0.64	1.59	0.35
14	0.27	0.60	0.60	1.47	0.30
16	0.26	0.53	0.50	1.29	0.30
18	0.27	0.58	0.58	1.43	0.30
20	0.28	0.56	0.55	1.39	0.30
30	0.27	0.53	0.53	1.33	0.30
60	0.20	0.43	0.40	1.03	0.26

^a Areas of designated peaks of curves illustrated in Fig. 7, measured by planimeter in square inches. Each curve represents an original quantity (at zero time) of 2 ng technical chlordane.

practically superimposable on the component G of the original technical chlordane. Experience has shown that some evaporation loss may occur with glass-stoppered flasks, and the data in Fig. 8 and Table I indicate some codistillation of the pesticide^{14,16}. However, in the area of peak G of the curve, this factor is not apparent, because of the increased superimposition of 1-hydroxychlordane, with time, that was formed from the degraded heptachlor component. Supplemental storage studies of 1-hydroxychlordane in water after 2, 7 and 14 days indicated no change in the gas chromatograph characteristics of the compound and there was no apparent loss of this component by codistillation. In this series, also, no heptachlor epoxide was formed during the storage period.

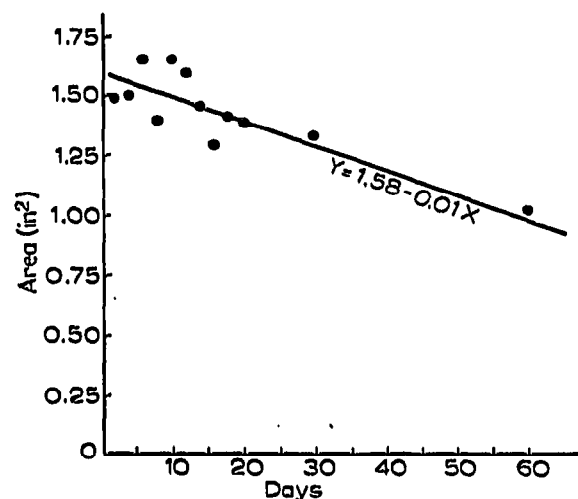


Fig. 8. Codistillation of technical grade chlordane with water (see Table I).

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