Gas Chromatographic Characteristics of Chlordane

I. Effect of an Aqueous Environment on the Heptachlor Component

by ARTHUR BEVENUE
Department of Agricultural Biochemistry
University of Hawaii, Honolulu, Hawaii
and
CHEE YEE YEO
Department of Food Science and Technology
University of Hawaii, Honolulu, Hawaii

Technical grade chlordane is described by the manufacturer to be composed of a mixture of octachloro-4, 7-methanotetrahydroindane and related compounds containing a maximum of one per cent hexachlorocyclopentadiene (1). Reimschneider (2) has reported the existence of four isomers of octachloro-, two of heptachloro-, and one each of enneachloro-, and decachloro-dicyclopentadiene as well as unchanged hexachlorodicyclopentadiene in the technical material. Saha et al. (3) have separated and identified at least 10 components, including heptachlor, from a commercial chlordane dust formulation.

When chlordane vapors are exposed to water, or when chlordane is dispersed in water, changes in the chemical characteristics of the

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pesticide, with time, can be conveniently followed by gas chromatography. The changes observed in the heptachlor component of this pesticide are of special interest and is the substance of this report.

Procedure: Experiment No. 1. Twenty ml samples of distilled water containing 1 part per million (ppm) technical grade chlordane were stored in 50-ml glass-stoppered Erlenmeyer flasks.

Experiment No. 2. Glass vials containing 50 mg technical grade chlordane were placed in 8-oz. jars (60 mm diameter) containing 20 ml distilled water. The vial extended above the water surface to permit only the vaporized components of chlordane to come into contact with the water.

Experiment Nos. 3 and 4. Ten mg each of heptachlor and heptachlor epoxide (both compounds of 99+% purity) were placed in separate vials and containers of water as described in Experiment No. 2.

The jars were covered with aluminum foil including a bleed hole to allow equilibration with the atmosphere. The jars and the flasks were stored at room temperature (22-25° C). Samples of the water were taken after 24 hours, 7 days, and 14 days, and extracted three times with Nanograde hexane. The extracts were filtered through a plug of anhydrous sodium sulfate and made to suitable volumes with hexane. Aliquots of the samples were injected into the gas chromatograph, and

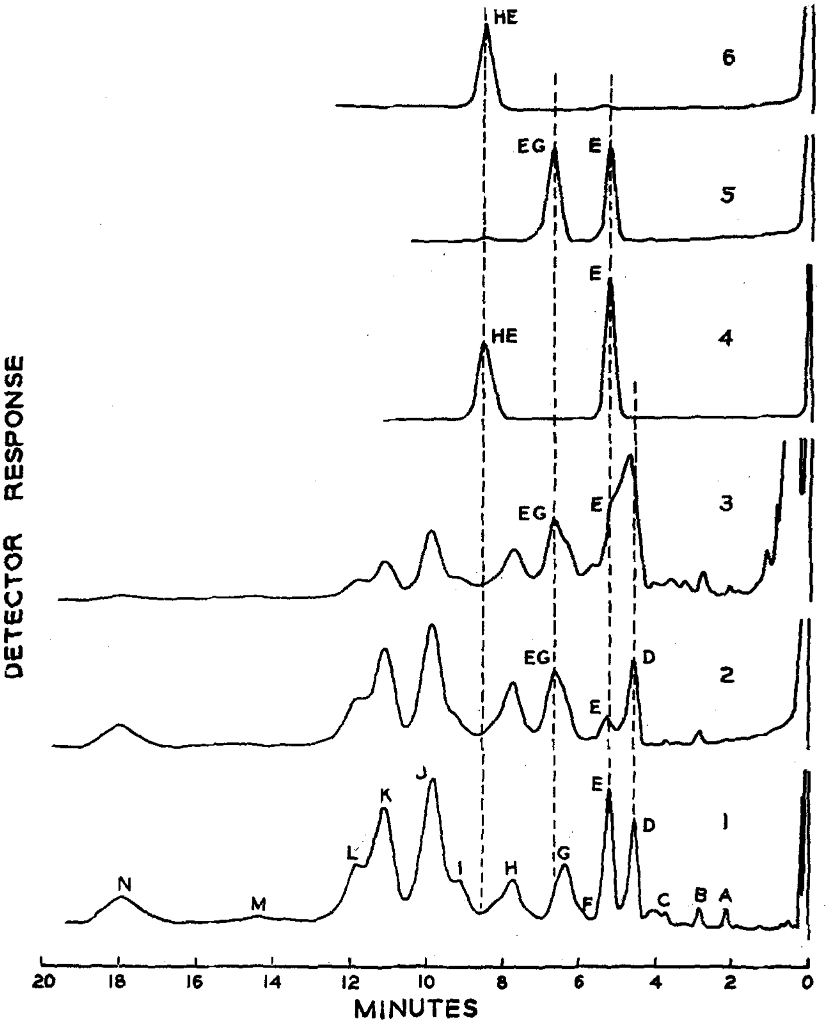

Figure 1. Curve 1, technical chlordane standard 4 ng; Curve 2, 1 ppm chlordane in water, 14-day exposure; Curve 3, chlordane vapors exposed 14 days to water; Curve 4, heptachlor (E) and heptachlor epoxide (HE) standards, each 0.2 ng; Curve 5, heptachlor vapors exposed 14 days to water; Curve 6, heptachlor epoxide vapors exposed 14 days to water.

the recorded curves were compared to the chromatographic patterns of standard samples of chlordane, heptachlor, and heptachlor epoxide.

Gas chromatograph conditions: F&M Model 810 gas chromatograph, electron capture detector; 1/4 inch x 4 feet spiral borosilicate glass column packed with 3% SE-30 silicone on Chromosorb W, acid washed and treated with dimethyldichlorosilane, 80-100 mesh; column temperature 190° C, Injection temperature 200° C, detector temperature 200° C; argon-methane (90:10) carrier gas, flow rate 75 ml/min; 1 mV full scale recorder, chart speed 0.5 in/min.

Results and Discussion

Using in our study the same peak designations as reported by Saha et al. (3), peak D of the gas chromatograph Curve 1 of Fig. 1 is the Diels-Alder adduct of pentachlorocyclopentadiene and cyclopentadiene, peak E is heptachlor, and peak G is most probably the Diels-Alder adduct of hexachlorocyclopentadiene and cyclopentadiene. Within the first 24 hours of exposure to water, a marked decrease was noted in the heptachlor content of chlordane. After 14 days of exposure, the heptachlor component had almost disappeared from the 1 ppm solution as evident in peak E of Curve 2, Figure 1. When water was exposed to the vapors of chlordane for 14 days, the pattern of the E area (Curve 3) was dissimilar to that of the same area of the 1 ppm chlordane solution

(Curve 2); a difference due, no doubt, to the fact that heptachlor (and other components) were continuously vaporizing from the excess chlordane present in the vial. The pattern of the peak areas E and G had changed, and in both Curves 2 and 3 areas EG were quite similar but different from peak area G of the standard chlordane of Curve 1.

Curve 4 represents standard solutions of 0.2 ng each of heptachlor (peak E) and heptachlor epoxide (peak HE). Curves 5 and 6 are heptachlor (peak E) and heptachlor epoxide (peak HE), respectively, which were vaporized and adsorbed by the water over a period of 14 days. The amount of heptachlor present in the water after 14 days exposure was about 0.07 ppm (Curve 5). However, it is noted that an additional peak (EG) derived from the vaporized heptachlor, and of equal area to peak E, was present and this peak coincides with peaks EG of Curves 2 and 3 of the chlordane samples. Areas EG of Curves 2, 3, and 5 practically superimpose area G of the original chlordane pattern as shown in Curve 1. However, it is apparent that area EG and the original area G are not the same component. With increased time, no doubt peak E in Curve 5 would disappear transforming to the product EG. The vaporized heptachlor epoxide adsorbed by the water, about 0.10 ppm, remained unchanged, as evidenced in Curve 6, and was similar to the standard sample peak HE of Curve 4; this concurs with the pattern of chlordane in the same area for Curves 2 and 3, where no formation of the epoxide was indicated.

Published observations on the properties of heptachlor class the compound (4) as one of the more stable chlorinated hydrocarbons which is not affected by acid or alkaline conditions and is stable against hydrolysis. It is also one of the more volatile compounds of this group, and its loss to the air is appreciable. It has been reported (5) that heptachlor in water is very rapidly converted to heptachlor epoxide, an observation which is contrary to our findings reported herein with distilled water. If the reported observation (5) is referring to river waters or other waters containing living organisms, the epoxide may have been produced. However, Lamar et al. (6) were unable to detect either heptachlor or the epoxide conversion product thirty days after the addition of the compound to river water samples. Pionke et al. (7) noted poor recoveries of heptachlor from distilled water and lake water samples, whereas no difficulty was experienced in recovering added amounts of heptachlor epoxide. Bowman et al. (8) did not find heptachlor epoxide in heptachlor-treated soils of low organic content aged for 1, 2, 4, and 8 days at 45° C. Bowman et al. (9) were also unable to find the epoxide in an aqueous medium treated with heptachlor but they did note the formation of 1-hydroxy chlordene from heptachlor. However, they found that the presence of mosquito larvae in the aqueous medium produced the epoxide. Soloway (10) noted that epoxidation of the double bond in heptachlor cannot be effected with the usual peroxy acids, but can be transformed to heptachlor epoxide in living systems as shown by Davidow and Radomski (11) and Ely et al. (12). Park and Bruce (13), in their studies on the water solubility of pesticides, noted that solubility data on heptachlor for the first 5 days of equilibrium varied considerably for each day; data obtained by the same authors on heptachlor epoxide solubility were more consistent. With one exception (5), the data in the cited literature are consonant with our findings reported herein.

The data in Figure 1 illustrates one of the many problems encountered by the pesticide residue analyst. The effects of water or other weathering phenomena (14, 15) on the residue content of a sample may mislead the analyst's interpretation of the data, as illustrated in the areas of DE and EG of Curves 2 and 3 for chlordane, and areas E and EG of Curve 5 for heptachlor in Figure 1. Obviously, supplementary confirmatory procedures are necessary to characterize chromatographic curves of this type derived from a sample of unknown pesticide history. The gamma and alpha chlordane fractions of the pesticide (peaks J and K of Curve 1, Fig. 1) might be used to quantitate residues of chlordane obtained from crops, soil, or water if it can be shown that these two components, after exposure to "weathering" conditions, are relatively stable and related quantitatively to chlordane formulations commercially available.

There is a paucity of chlordane residue data on human or animal tissues, and such data are needed when the analyst is required to analyze blood, urine, and tissue samples of cases suspected of acute toxic symptoms derived from chlordane exposure. It can be presupposed that the gas chromatographic analytical data from such specimens would be quite different from that obtained from original commercial chlordane formulations and most probably considerably different from the observed changes in the pesticide discussed in this report.

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