

Isolation of TDE from Cigarette Smoke

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The utilization of TDE, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)-ethane, as an insecticide for the control of the tobacco hornworm makes it of some interest to determine whether residues of this material on the tobacco find their way into the main stream of cigarette smoke. Quantitative studies of the amounts of this material on tobacco and in smoke have been recently reported by Bowery and Guthrie (1957). These workers have utilized the colorimetric procedure described by Schechter and Haller (1945), to determine quantities of TDE and its combustion products in tobacco and smoke after preliminary fractionations to remove interfering materials.

In the course of studies in this laboratory to determine the constitu-

ents of cigarette smoke TDE has been isolated in purified crystalline form and its identity established by comparison of its ultraviolet and infrared spectra (figures 1 and 2) and melting point with these data for an authentic sample of TDE. An estimation of the total amount of TDE present in the smoke of cigarettes of a cased commercial blend of tobaccos based on the ultraviolet absorption at 269 $m\mu$ is 1.6 mg per 1000 cigarettes or 0.007 per cent of the total non-volatile solids in the main stream smoke. This is of the same order of magnitude as the amounts reported by Bowery and Guthrie (1957) for the main stream smoke of cigarettes.

Infrared absorption spectra gave some evidence for dehydrochlorinated TDE in fractions where this com-

pound would be expected (figure 3). We did not isolate this material, but judge it to be present in lesser amount than TDE.

Experimental

Thirty-four thousand regular length (70 mm) cigarettes of a cased commercial blend of tobaccos were smoked mechanically on a constant volume type cigarette smoking machine (Liggett and Myers Tobacco Co.) Thirty-five milliliter puffs, each of two seconds duration, were taken at one minute intervals from each cigarette. Eight puffs were taken on each cigarette. The smoke was condensed in a series of all-glass traps cooled in liquid air. The condensate was rinsed out of the traps with ethyl ether. Two hundred milliliters each of water and hexane were added, and the ether removed *in vacuo*. The smoke condensate, containing 780 grams of non-volatile materials, was then washed in a counter-current fashion with three additional 50 ml portions of hexane and water. The filtered hexane layers were combined, and the solution evaporated *in vacuo* at less than 50°C to a concentration of 200 mg per ml. This solution, containing 280 grams of non-volatile materials, was extracted ten times with volumes of 84 per cent (W/W) methanol in water equal to the volume of hexane solution. The aqueous methanol was equilibrated with hexane prior to its use.

The combined aqueous methanol extracts, containing 115 grams of non-volatile materials, were concentrated *in vacuo* at 50°C to remove the methanol, and the aqueous suspension remaining was then extracted with ether until the final ether extract was nearly colorless. The ether extracts were evaporated to dryness, the residue redissolved in 170 ml of acetone, and the solution mixed with 920 grams of alumina (100-200 mesh, Merck acid-washed, activated at 110°C for 16

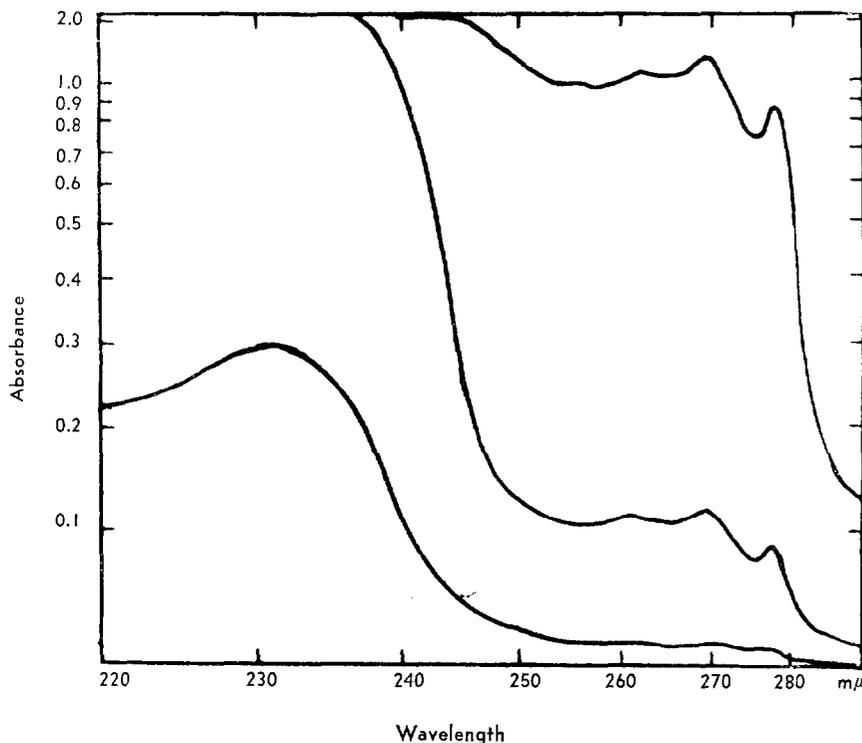


Figure 1. Ultraviolet absorption spectrum of TDE isolated from cigarette smoke, at several concentrations in cyclohexane ($E_{269} = 720 \pm 15$). The spectrum for authentic TDE was identical, with $E_{269} = 733 \pm 5$.

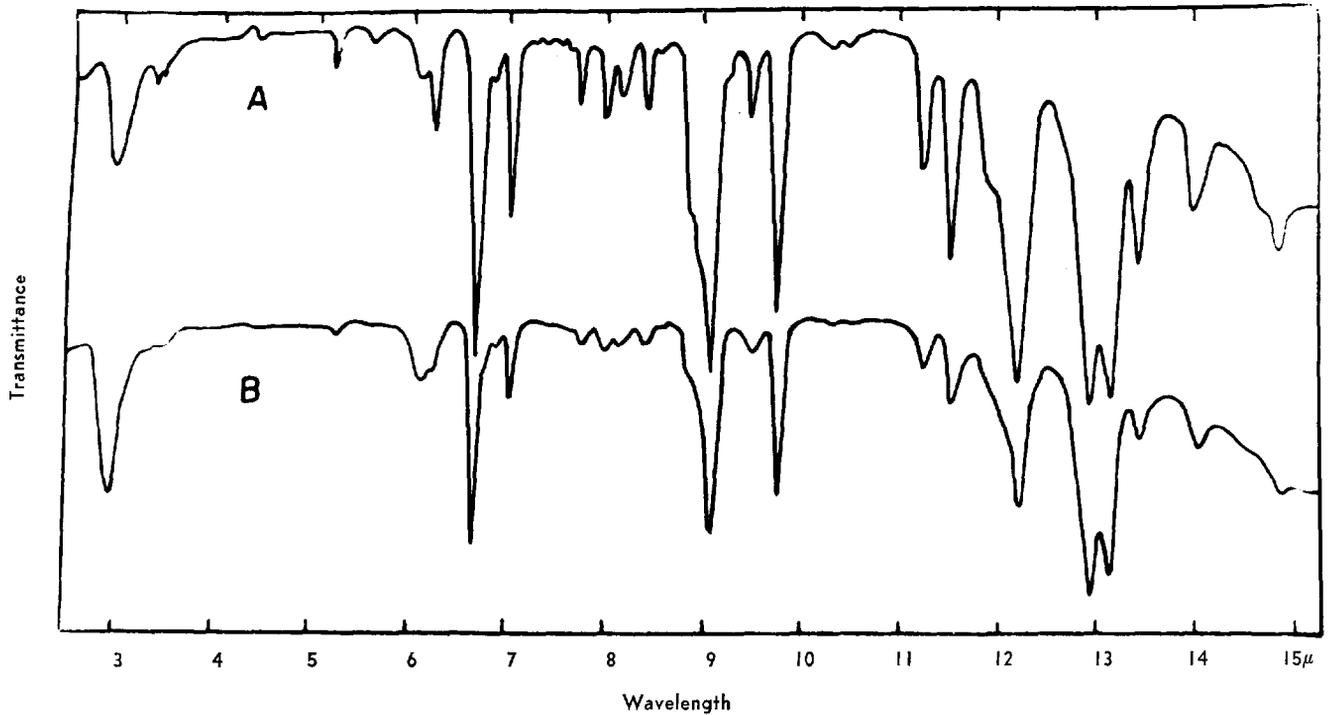


Figure 2. Infrared absorption spectra for (A) authentic TDE, and (B) TDE isolated from cigarette smoke. The spectra were determined by the KBr pellet technique.

hours). This mixture was spread in a $\frac{1}{2}$ inch layer and the acetone allowed to evaporate in air, then *in vacuo* over CaCl_2 overnight. The dried material was applied as a slurry in hexane to the top of a column prepared with 2300 grams of the alumina. Elution was carried out with 32 liters of benzene and the solvent evaporated *in vacuo* to yield 18 grams of elutable material.

This material was redissolved in

acetone and evaporated on 180 grams of alumina (100-200 mesh, Merck acid-washed, dried from methanol at 25°C). The dried material was applied to the top of a column prepared with 720 grams of the 25°C dried alumina. Elution was carried out with 2.7 liters of hexane and the solvent evaporated *in vacuo* to yield 4.2 grams of residue.

The residue was next distilled at 50°C and 0.3 mm Hg for 15 hours

in a short-path (ca. 2 cm) distillation device. The non-distilled materials totalled 2.4 grams. A portion of this material (2.2 grams representing 31,000 cigarettes) was next distributed in an all-glass Craig countercurrent distribution apparatus through 190 transfers between hexane and 84 per cent (W/W) methanol-water. The volume of each of the upper layers was three-tenths of the volume of each lower layer. The

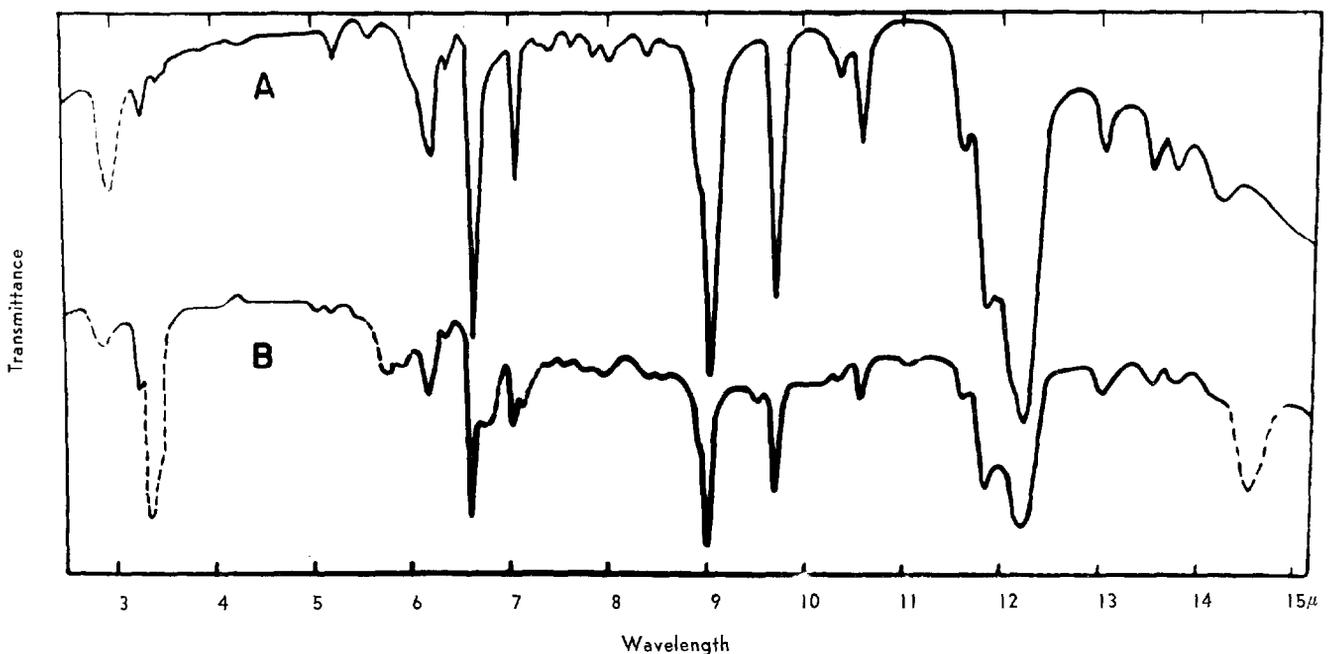


Figure 3. Infrared absorption spectra for (A) authentic dehydrochlorinated TDE, and (B) a fraction isolated from cigarette smoke. The dotted portions of the curves indicate absorption believed due to impurities present. The spectra were determined by the KBr pellet technique.

infrared spectrum for the contents of tubes 60-99 gave evidence of the maxima at 9.17 and 9.85 μ characteristic of TDE.

The contents of tubes 70-79, 27.4 mg. which appeared to contain the purest fraction of TDE, was chromatographed on a one-gram column of alumina (100-200 mesh, Merck acid-washed, activated at 110°C for 16 hours). Development and elution was accomplished with cyclohexane. The elution of TDE began after six ml of filtrate had been collected and was completed after 24 ml of filtrate had been collected. Rather good ultraviolet absorption spectra for TDE were obtained for several of these fractions. Crystallization of the TDE was accomplished from ethanol to give a product melting at 112-3° (Corr). This was identical with the melting point for an authentic sample obtained by recrystallization of the commercial product. No depression of the melting point was observed

when the isolated material was mixed with authentic TDE. Ultraviolet and infrared spectra for the TDE isolated from cigarette smoke were identical to the spectra for authentic TDE (figures 1 and 2).

The amount of TDE present in tubes 70-79 was estimated to be 13.9 mg based on the ultraviolet absorption intensity. The distribution of a substance in the Craig machine can be calculated by the binomial expansion. If one determines which tube contains the maximum concentration, it is therefore possible to calculate the total amount present in adjacent tubes. On this basis, it was estimated that 50 mg of TDE was present in all of the Craig fractions (representing the main stream smoke of 31,000 cigarettes), or 1.6 mg per 1000 cigarettes.

Acknowledgment

The smoke collection and prelimi-

nary fractionation to prepare the hexane soluble fraction was carried out under the direction of Dr. E. J. Hackney.

Infrared spectra were obtained by Mr. Ernest Sunas.

Literature Cited

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