

to use a method that gives good yields of pure product with a minimum of transfers in order to avoid mechanical losses.

Nenitzescu and Scarlatesca obtained 2-ethylthioethanol by passing ethylene oxide through a packed tower containing ethyl mercaptan, and by reacting the compounds in a closed vessel with activated carbon (7). We found that both procedures gave poor yields in small scale preparations. The condensation of ethylene oxide with ethyl mercaptan was investigated further, by reacting equal molar quantities of the reagents in sealed tubes in the presence of catalytic amounts of one of the following: metallic sodium, aluminum oxide, silica, sulfuric acid, and aluminum chloride. Anhydrous aluminum chloride gave promising results, but the other catalytic materials either were not effective, or carried the condensation too far, forming highly viscous products. Condensation in the presence of aluminum chloride could be controlled, and optimum concentration, temperature, and time of reaction were determined. It was found that the reaction could be carried out in a tightly stoppered flask, thus avoiding transfer from a sealed tube.  $S^{35}$ -labeled ethyl mercaptan was used in the synthesis, but  $C^{14}$ -labeling could be effected by use of the appropriately labeled reagents.

Larger scale preparations can be made by this procedure, if a rise in

temperature during the reaction is prevented by constant stirring and cooling in a water bath.

### Experimental Procedure

One-tenth gram of anhydrous aluminum chloride was placed in a 15-ml. conical flask fitted with a 15/35 standard taper stopper that could be clamped in position. The ampoules of ethylene oxide and labeled ethyl mercaptan, two 10-ml. graduated cylinders, and the flask were chilled in a dry ice-acetone bath. After cooling, 4.0 ml. (54 mmoles) of ethyl mercaptan and 2.5 ml. (53 mmoles) of ethylene oxide were added to the flask, the contents mixed, and the stopper was clamped in place. The flask was removed from the bath and allowed to stand at room temperature (25° C.) for 24 hours. A longer period of standing produced no apparent change in yield. A small distilling head and condenser were attached to the flask and the product was distilled at 60° to 62° C. at 5 mm. of Hg pressure, yielding 4.2 grams of product (75% based on the mercaptan),  $n_D^{25}$  1.4828, and  $d_4^{25}$  1.013. The theoretical amount of bromine was absorbed when the product was titrated with standard bromate-bromide solution (5). The sample was analyzed at 120° C., by gas-liquid chromatography, on a 1/4-inch silicone column, 5 feet long with helium as carrier gas. No

impurities were observed and the retention time was the same as that of a pure, authentic sample of ethylthioethanol. Infrared absorption curves for the two samples were identical for the range 2.8 to 15  $\mu$ .

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## Chromatographic Separation of Heptachlor, Gamma Chlordan, and Heptachlor Epoxide from High-Heptachlor Residues

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ANALYTICAL methods recently developed for the determination of heptachlor and heptachlor epoxide in forage crops use chromatographic columns to separate heptachlor from its epoxide (1, 2). The column recommended is activated Florex (a specially selected form of hydrated fuller's earth) and the solvents used are pentane (colorimetric grade) for heptachlor, followed by 2% ethyl ether in pentane for heptachlor epoxide. In the application of this technique to the determination of heptachlor residues on several crops, an apparent spilling over of heptachlor into the ether-pentane fraction which contained the heptachlor epoxide was observed. With low residues the quantity of apparent heptachlor found in the epoxide residues was very small and

usually negligible. When high heptachlor residues were determined, there was an increase in the quantity of apparent heptachlor spilling over into the heptachlor epoxide fraction with resultant interference in analysis of heptachlor epoxide. Processing the residues twice on the Florex column did not decrease the contamination, indicating that it was not a simple spilling of excessive heptachlor into the epoxide.

Following a suggestion (3) that the contaminating material was gamma chlordan, a minor constituent of technical heptachlor, the authors directed their efforts toward separating gamma chlordan from heptachlor epoxide by column chromatography. Since Florisil (a synthetic magnesia-silica gel) has been observed to have a slower elution

rate than Florex, it was thought that Florisil could be used for this purpose.

### Experimental

**Procedure.** With 50-ml. Mohr burets as chromatographic tubes, columns were prepared, using 10 grams of activated Florex (washed with pentane, dried, and heated at 135° C. for 24 hours) and 15 grams of activated Florisil (washed with hexane, dried, and heated at 130° C. for 24 hours). Solutions from corn plants that contained about 300  $\mu$ g. of heptachlor, 30  $\mu$ g. of gamma chlordan (evaluated as heptachlor), and 100  $\mu$ g. of heptachlor epoxide were processed on these columns. The columns were wet with pentane and the solutions were added to the columns and eluted with

Analyses of various crops for heptachlor residues have shown a contamination of the heptachlor epoxide fraction with apparent heptachlor which interferes with the determination of heptachlor epoxide. Residues from heptachlor sprays on corn plants were placed on a Florisil column and eluted with pentane and 6% ether pentane. The pentane fraction contained all of the heptachlor. The first 45 ml. of the ether-pentane eluent contained gamma chlordan and the remaining ether-pentane eluent contained all of the heptachlor epoxide. The technique devised will eliminate interference of gamma chlordan in heptachlor epoxide determinations and will result in a more complete analysis of residues from heptachlor applications to crops.

200 ml. of pentane (heptachlor fraction). The columns were then eluted with 200 ml. of 6% ethyl ether in pentane, and fractions of the eluent were collected for evaluation. To each fraction was added 0.01 ml. of Nujol (medicinal grade heavy mineral oil), in pentane, and the volume reduced to 5 ml., using 3-ball Snyder condensers. The residue was transferred to graduated centrifuge tubes and reduced to dryness in a 40° C. bath, using a gentle stream of air to assist in evaporation.

One milliliter of modified Polen-Silverman (4) reagent and a small Carborundum chip were added, and the tubes were placed in an oil bath at 100° C. for 15 minutes and then removed and cooled to room temperature. The color developed by the reaction was evaluated qualitatively.

With both adsorbents the heptachlor fraction was recovered in the pentane, but the heptachlor epoxide and gamma chlordan remained on the column. The addition of ethyl ether to the pentane removed both gamma chlordan and heptachlor epoxide from the columns. In the Florex column no heptachlor epoxide was found in the first 25 ml. of the ether-pentane eluent; the next 75 ml. of this eluent contained a mixture of heptachlor epoxide and gamma chlordan. In the Florisil column, the first 25 ml. of ether-pentane eluent was free of heptachlor epoxide or gamma chlordan. The next 20 ml.

of eluent gave a true violet color, indicating the presence of gamma chlordan and the absence of heptachlor epoxide. The remaining fractions (155 ml.) gave only the pure yellow associated with heptachlor epoxide. The Florex column did not separate gamma chlordan from heptachlor epoxide. The Florisil column released the gamma chlordan in the first 45 ml. of ether-pentane eluent, and heptachlor epoxide in the next 155 ml. of eluent.

**Calibration of Column.** For calibration of the Florisil column use an aliquot of plant extract from a sample of the untreated crop, and add 400 µg. of technical heptachlor and 30 µg. of heptachlor epoxide. Reduce the volume to 10 ml. and transfer to a 15-gram activated Florisil column previously wet with pentane. Rinse the sides of the column with about 2 ml. of pentane, and when the rinses have gone into the adsorbent, connect a reservoir containing 250 ml. of pentane and elute the column. Collect the eluent in a 500-ml. flask and reserve for heptachlor analysis. When all the pentane has reached the top of the Florisil, remove the flask and replace it with a graduated cylinder. Connect a reservoir containing 200 ml. of 6% ether-pentane to the column and continue the elution, collecting fractions to determine the rate of release and the separation of gamma chlordane and heptachlor epoxide. The ether-pentane solvent should be removed and the

column activity determined by observing the colors produced in the various fractions by the Polen-Silverman reagent.

### Results

Good column activity should produce the following results: all the heptachlor in the pentane fraction, no color in the first 25-ml. ether-pentane fraction, and violet, but no yellow, in the next two 10-ml. fractions. The last 10-ml. fraction should show only a faint violet or yellow, and the remainder of the ether-pentane eluent should contain practically all the epoxide added, when compared to a comparable quantity of epoxide run directly in a reaction tube.

With this procedure almost all the interfering gamma chlordan is recovered in the 45-ml. fraction, and a good measurement can be made of the epoxide present. Other degrees of activation or variability of the adsorbent may require different quantities of the ether-pentane eluent.

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## ACARICIDE RESIDUES

# A Modification of the Rosenthal Method for Rapid Determination of Kelthane Residues

THREE METHODS are available for the determination of residues of Kelthane [4,4'-dichloro- $\alpha$ -(trichloromethyl)benzhydrol]. Rosenthal, Frisone, and Blinn (6) and Eiduson (7) described methods in which chloroform is liberated, swept from extraneous material in a special apparatus, and

converted quantitatively to a red dye with an aqueous pyridine-alkali mixture. Gunther and Blinn (5) determined it directly by the absorption at 264 m $\mu$  or indirectly by absorption of the 2,4-dinitrophenylhydrazone in alcoholic alkali at 510 m $\mu$ . Rosenthal and co-workers established that, under mildly

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alkaline conditions, Kelthane will undergo a haloform type reaction to yield 4,4'-dichlorobenzophenone and chloroform. Griffon, Mossanen, and Legault-Demare (4) made a study of the Fujiwara (2) test for polyhalogen compounds with pyridine.

Analysis of a large number of samples