

COMMUNICATIONS

Identification of the Gas Chromatographic Dieldrin and Endrin Peaks by Chemical Conversion

A simple and rapid method is described for the simultaneous confirmation of dieldrin and endrin residues in soil, sediment, water, corn grain, corn stalks, and soybeans. This technique employs a one-step sample treatment with 10% boron trichloride in 2-chloroethanol for the conversion of dieldrin and endrin into their corresponding derivatives.

The dieldrin and endrin conversions require 2 hr and 10 min reaction times, respectively, and parent residues can be confirmed at the 0.01-ppm level. This method has been employed in the Pesticides Monitoring Program on various types of samples and has been very helpful in identifying these pesticides when suspected.

In the Pesticides Monitoring Program, initiated by the Plant Protection Division of the United States Department of Agriculture in 1964, analyses are performed on numerous soil, water, sediment, and crop samples for a wide variety of pesticides. Two of the more common pesticides for which analyses are made are dieldrin (1,2,3,4,10,10-hexachloro-*exo*-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo*-, *exo*-5,8-dimethanonaphthalene) and endrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo*-, *endo*-5,8-dimethanonaphthalene). Although there is no evidence of buildup of these two pesticides, such widespread use and because of their persistence in soil and the rapid conversion of aldrin to dieldrin requires that a simple, reliable identification method be available to confirm any suspected dieldrin or endrin gc peak.

Identification methods for these and other pesticides have become of increasing importance with the finding of polychlorinated biphenyls in environmental samples (Jensen and Widmark, 1967). Frazier *et al.* (1970) also reported on "apparent" organochlorine insecticide content of soil samples with the conclusion that additional procedures are needed for identifying gc peaks in environmental samples.

Various identification methods have been employed in this laboratory. These methods include: partitioning coefficients (*p*-values), developed by Bowman and Beroza (1965); thin-layer chromatography (tlc), as described by Schutzmann *et al.* (1966); colorimetric methods published by Fahey and Schechter (1961); and multiple gc column methods, as described by Bann *et al.* (1958).

A chemical conversion method used for the identification of endrin has been reported by Woodham (1967). The derivatization of dieldrin and endrin with zinc chloride-hydrochloric acid reagent has been described by Wiencke and Burke (1969). Chau and Cochrane (1969) have reported a conversion method for the identification of various pesticides, using several reagents.

Certain disadvantages in all of the above methods became apparent when they were applied to field samples. These disadvantages included lack of sensitivity to residual pesticides, interference from other pesticides or other compounds present in sample, difficulty in obtaining the desired conversion product, the necessity of using elaborate reagents or equipment, and a lack of consistency of formation of conversion products.

It was found, however, that dieldrin and endrin would form derivatives when reacted with a 10% BCl_3 :2-chloroethanol solution. These derivatives produce characteristic gc peaks

with longer retention times. The reaction times required for these conversions are relatively short (2 hr for dieldrin and 10 min for endrin).

MATERIALS AND METHODS

(a) Conversion reagent—10% boron trichloride (Matheson Co., Inc.) in 2-chloroethanol (Distillation Products ACS grade). The reagent is prepared as follows. Freshly distilled 2-chloroethanol (900 g) is weighed into a 2-l. Erlenmeyer flask and cooled in an ice water bath. BCl_3 (100 g) is bubbled into the cooled 2-chloroethanol with stirring. (Caution: A trap is placed in the gas line to prevent liquid from being drawn back into the gas cylinder valve. The preparation of this reagent should be carried out in a good fume hood and the BCl_3 gas flow should be slow enough to prevent the emergence of white fumes from the reaction flask.) Since BCl_3 is toxic and also corrosive, small quantities of the reagent should be prepared.

(b) Gas-liquid chromatograph—MT-220 (Tracor, Inc.), equipped with electron capture detector (tritium source) and a 6 ft \times 4 mm i.d. glass column packed with mixture of an 11% OV-17:QF-1 on 80-100 mesh Gas Chrom Q (Applied Science Cat. No. 12970) operated under the following conditions: 90 ml/min N_2 carrier gas flow, column, detector, and injector temperatures of 225° C, 210° C, and 250° C, respectively, and sufficient detector sensitivity to give half-full scale recorder response with 0.5 ng of aldrin.

Conversion of Dieldrin and Endrin. Aliquots of sample extract containing dieldrin and/or endrin were transferred to 15-ml graduated centrifuge tubes. Soil, sediment, and water samples did not normally require prior cleanup. Oily crop samples were first subjected to a CH_3CN :hexane partitioning procedure, as modified from the Mills procedure (1961). The partitioned samples were then eluted through a chromatographic column containing *ca.* 2 g of anhydrous Na_2SO_4 and 18 g of PR grade activated Florisil. This was also a modification of the Mills procedure (1961). Non-oily samples (less than 2% fat or oil) required only the Florisil column cleanup. One milliliter of a 0.01% solution of mineral oil in hexane was added to the extracts which were then evaporated just to dryness in a 60° C water bath, using a gentle air stream to facilitate evaporation.

One milliliter of the BCl_3 :2-chloroethanol reagent was added to each of the sample tubes, which were then placed, unstoppered, in a 90° C water bath for the conversion. Samples containing dieldrin or endrin were left in the water

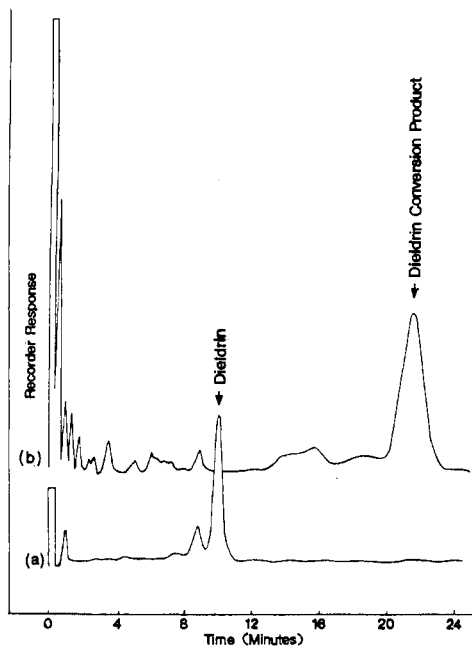


Figure 1. Chromatographic tracing of a soil sample fortified with 0.10 ppm (0.33 μg) of dieldrin (a) before and (b) after conversion. Column used was an 11% OV-17:QF-1 mixture on 100-120 mesh Gas Chrom Q

bath for 2 hr or for 10 min, respectively, while samples suspected of containing both pesticides were allowed to react for 2 hr. The sample tubes were cooled after the reaction period and exactly 5 ml of Nanograde hexane and 10 ml of a 7% aqueous Na_2SO_4 solution were added to each sample. The samples were then mixed thoroughly and allowed to settle until the hexane and aqueous layers completely separated. Appropriate injections (usually 5-10 μl) were made from the upper hexane layer into the gas chromatograph.

Sample weights used in the derivation procedure varied with the sample type. Aliquots representing 5 g were used for crops and 6.67 g were used for soil samples. Experimental work indicated that a minimum sample weight of 1.0 g and a maximum of 10 g would be possible.

The lower limit of sensitivity using this procedure is *ca.* 0.01 ppm for both soil and crop samples.

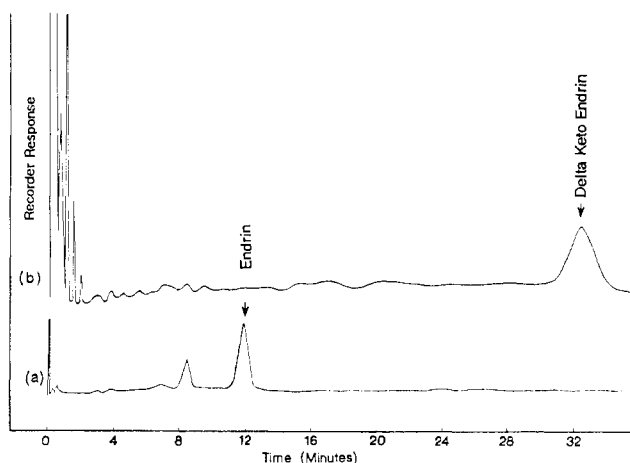


Figure 3. Chromatographic tracing of a soil sample fortified with 0.10 ppm (0.33 μg) of endrin (a) before and (b) after conversion. Column used was an 11% OV-17:QF-1 mixture on 100-120 mesh Gas Chrom Q

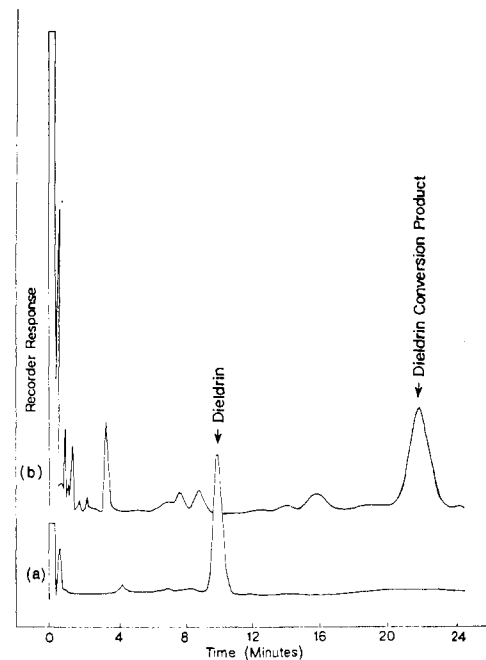


Figure 2. Chromatographic tracing of a corn grain sample fortified with 0.10 ppm (0.40 μg) of dieldrin (a) before and (b) after conversion. Column used was an 11% OV-17:QF-1 mixture on 100-120 mesh Gas Chrom Q

Identical results were also obtained when this procedure was applied to sediment, water, and other crop samples.

This identification method has been employed by our laboratory on a large number of samples with reproducible results.

RESULTS AND DISCUSSION

In experimental work, sample extracts of soil and field corn (grain) were fortified separately with 0.1 ppm of dieldrin and endrin and were carried through the conversion procedure. These extracts were analyzed on the gc before and after conversion, the results are shown in Figures 1 through 4. Figure 1 shows chromatograms of a soil sample fortified with 0.10 ppm of dieldrin, while Figure 2 is chromatograms of a corn grain sample fortified with 0.10 ppm of dieldrin, both before and after conversion.

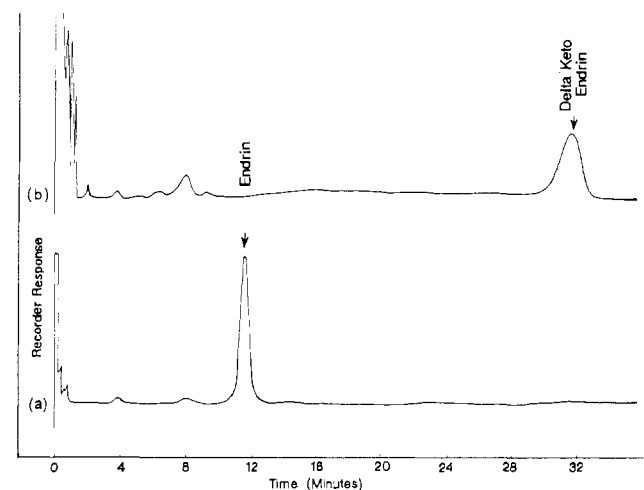


Figure 4. Chromatographic tracing of a corn grain sample fortified with 0.10 ppm (0.40 μg) of endrin (a) before and (b) after conversion. Column used was an 11% OV-17:QF-1 mixture on 100-120 mesh Gas Chrom Q

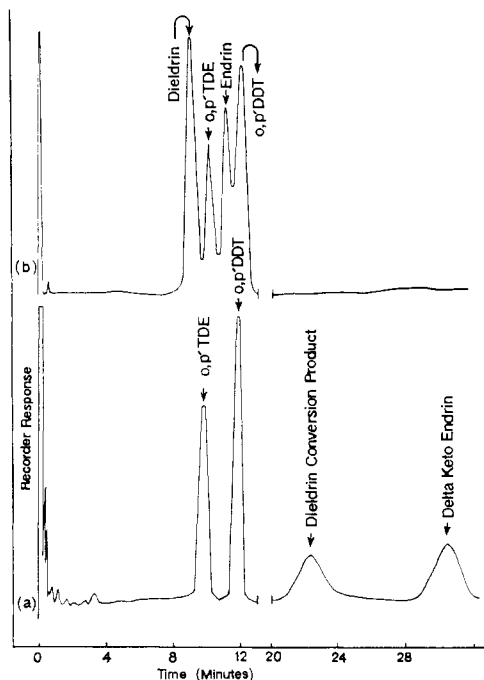


Figure 5. Chromatographic tracing of a pesticide standard containing dieldrin, *o,p'*-TDE, endrin, and *o,p'*-DDT (a) before and (b) after conversion. Column used was an 11% OV-17:QF-1 mixture on 100–200 mesh Gas Chrom Q

Figure 3 depicts chromatographic tracings of a soil sample fortified with 0.10 ppm of endrin. Figure 4 shows tracings of a corn grain sample fortified with 0.10 ppm of endrin, again, both before and after conversion.

Figure 5 shows chromatograms of a mixture of dieldrin (1.0 ng), endrin, *o,p'*-DDT and *o,p'*-TDE (5.0 ng of each) before and after conversion.

Note that dieldrin and endrin are distinguished from pesticides having nearly the same glc retention times by virtue of their derivatives; the other two pesticides are virtually unchanged after the reaction. This standard contains a combination of pesticides frequently encountered in environmental monitoring, and the conversion procedure has proven useful in the analysis of such combinations. In addition to the pesticides listed, *p,p'*-DDE, Endosulfan II and Captan also exhibit similar or identical retention times on this column and also the DC-200 column.

Confirmation analyses using thin-layer chromatography, partitioning coefficients, dual-column glc, and other methods have shown that the conversion product of endrin is Δ -keto

endrin. This fact is substantiated in some of the above-mentioned publications. The dieldrin conversion product has not been identified by our laboratory. The product may be the dieldrin "ketone" previously reported by Chau and Cochrane (1969). A standard was not available at the time to confirm this theory.

The conversion procedure provides a rapid and reliable method for the confirmation of dieldrin and endrin residues in a wide variety of samples. The dieldrin and endrin conversion products have retention times beyond most of the common organochlorine pesticides and sample interferences. Because of this longer retention time and lack of interference from other compounds, this procedure has become a most useful tool in our laboratory. Dieldrin and endrin may easily be detected at the 0.05 ppm (0.05 ppb in water) level, and by concentration of the sample, a lower level of 0.01 (0.01 ppb in water) ppm can be reached. Other organochlorine pesticides tested are not destroyed in the reaction nor do they result in interferences with the conversion products.

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Received for review February 1, 1971. Accepted August 2, 1971. Trade names are used in this publication solely to provide specific information. Mention of a trade name does not constitute a guarantee or warranty by the U. S. Department of Agriculture and does not signify that the product is approved to the exclusion of other comparable products. ¹ Pesticides Regulation Division, Environmental Protection Agency, Washington, D.C. 20250. ² Pesticide Residue Laboratory, Agricultural Research Service, Brownsville, Texas 78520.