Determination of DDT in the Presence of Toxaphene Residues[1]

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With the declaration in January 1969 of a one-year moratorium on the agricultural use of DDT in Arizona, our laboratory was asked to monitor the primary irrigated areas for changes in residues of DDT and its related degradation products (DDTR). The purposes of such monitoring would be to determine whether use violations were occurring and to measure the decline of environmental DDTR residues following 20 years of continuous agricultural use. Because of our previous monitoring experience (1) we elected to sample growing alfalfa and the upper 10" of soil in these alfalfa fields on a quarterly basis.

These determinations proceeded smoothly through January and May. However, during the September sampling we encountered substantial residues of toxaphene in practically every alfalfa specimen resulting from its use on cotton alone or in combination with organophosphate insecticides.

The DDTR normally measured in our laboratory by ECGC are p,p'- and o,p'-DDT, and their respective DDE. DDD is not a metabolite commonly found in plant tissues or soil in Arizona. Toxaphene, both in laboratory standards and field-aged residues, contains numerous components whose peaks interfere with all of the above and make quantitation difficult if not impossible. Consequently it became necessary to devise a technique which would permit the measurement of very small residues of DDTR in the presence of high toxaphene residues.

After numerous failures to separate these components by combinations of column and gas chromatography, dehydrochlorination of DDT to DDE was decided upon as the most efficacious.

The following steps evolved in the search and are presented in outline form:

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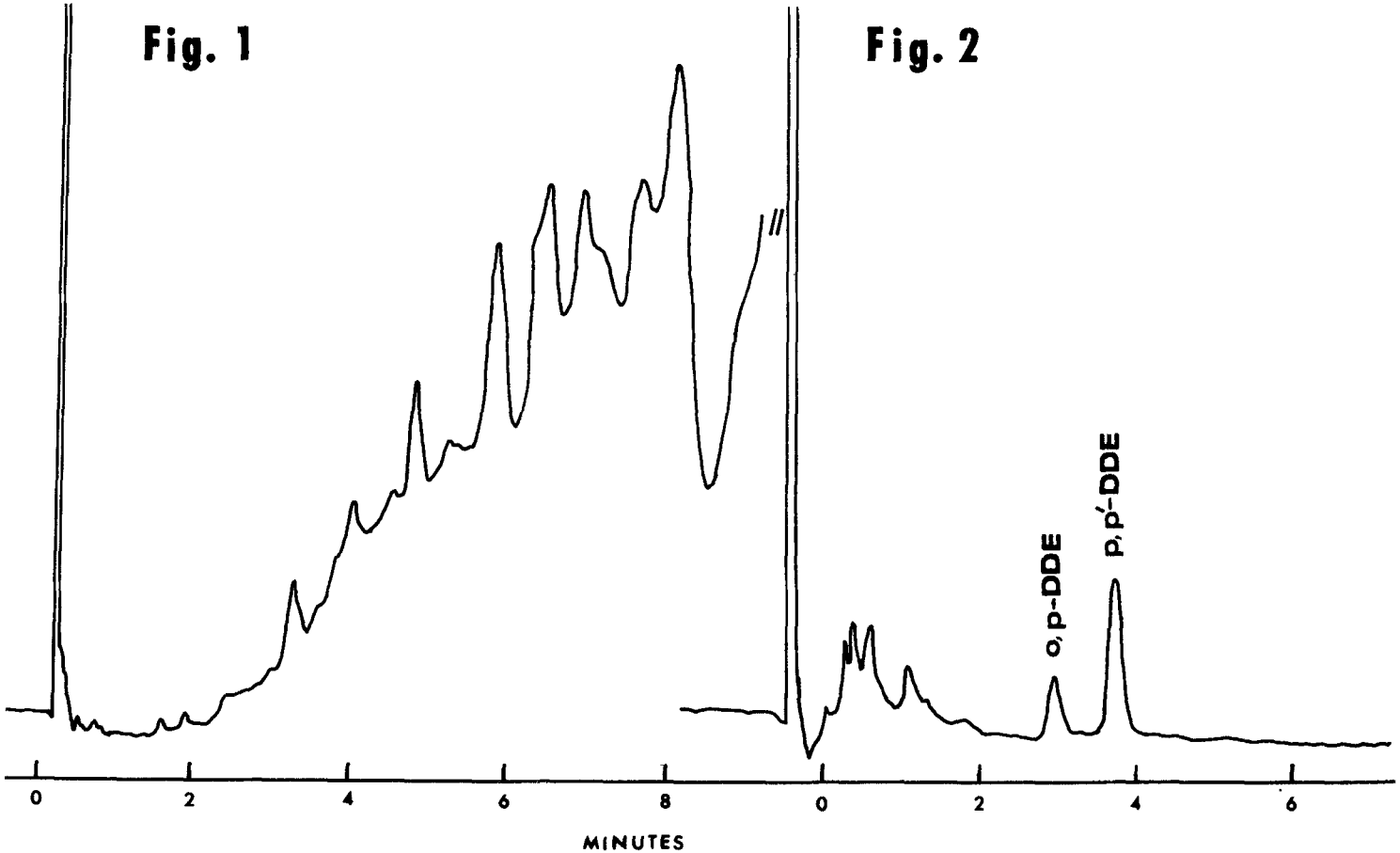

Figure 1. Toxaphene (21 ng) on standard ECGC column of Chromosorb-W + SE-30 and QF-1, as described.

Figure 2. Toxaphene (21 ng), o,p-DDE (0.03 ng), and p,p'-DDE (0.06 ng) on same column + $CdCl_2$ and Na_2CO_3 after alcoholic-NaOH dehydrochlorination.

1. The hexane-diethyl ether eluate from a standard Florisil column cleanup containing the mixture of DDTR and toxaphene residues is reduced to approximately 5 ml by evaporation.

2. The concentrated eluate is transferred with three hexane rinses totaling no more than 30 ml, to a 250 ml separatory funnel containing 30 ml of a saturated solution of ethanolic sodium hydroxide. The combination is mixed thoroughly and allowed to stand at room temperature for 1 hour.

3. An additional 30 ml of hexane is added and mixed thoroughly. The separatory is then filled with distilled water, shaken until the hexane layer clears, and allowed to stand for 10 minutes.

4. The aqueous layer is discarded followed by two additional water rinses, allowing 5 minutes for layering.

5. The hexane is passed through an anhydrous Na_2SO_4 plug directly into an appropriate volumetric flask, followed by rinsing the separatory and plug with hexane.

6. The sample is then injected onto an appropriate gas chromatographic column heated to 230°, packed with a 1" plug of anhydrous cadmium chloride followed by a 1" plug of sodium carbonate at the injection end (2).

It was found that neither the wet nor the gas column dehydrochlorination alone gave the desirable isolation, and that an occasional interfering peak was encountered. For our analyses an 8', 1/4" O.D. Pyrex glass column, containing 60-80 mesh acid-washed Chromosorb-W treated with 4% SE-30 and 6% QF-1 was operated at 225°, 230° and 210°C for the injection port, column, and detector respectively.

Analytical recovery from this dual dehydrochlorination was 94% for o,p'-DDE and 100% for p,p'-DDE, while conversion of o,p'- and p,p'-DDT to their respective DDE was essentially 100%. Conversion of DDD to DDMU and its analytical recovery were 100%.

Typical "before and after" chromatograms are illustrated, indicating ideal separation of the surviving toxaphene components and the p,p'- and o,p'-DDE and DDMU.

REFERENCES

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2. J. P. Minyard and E. R. Jackson, J. Agr. Food Chem. 13, 51 (1965).