The Examination of Toxaphene by Gas Chromatography

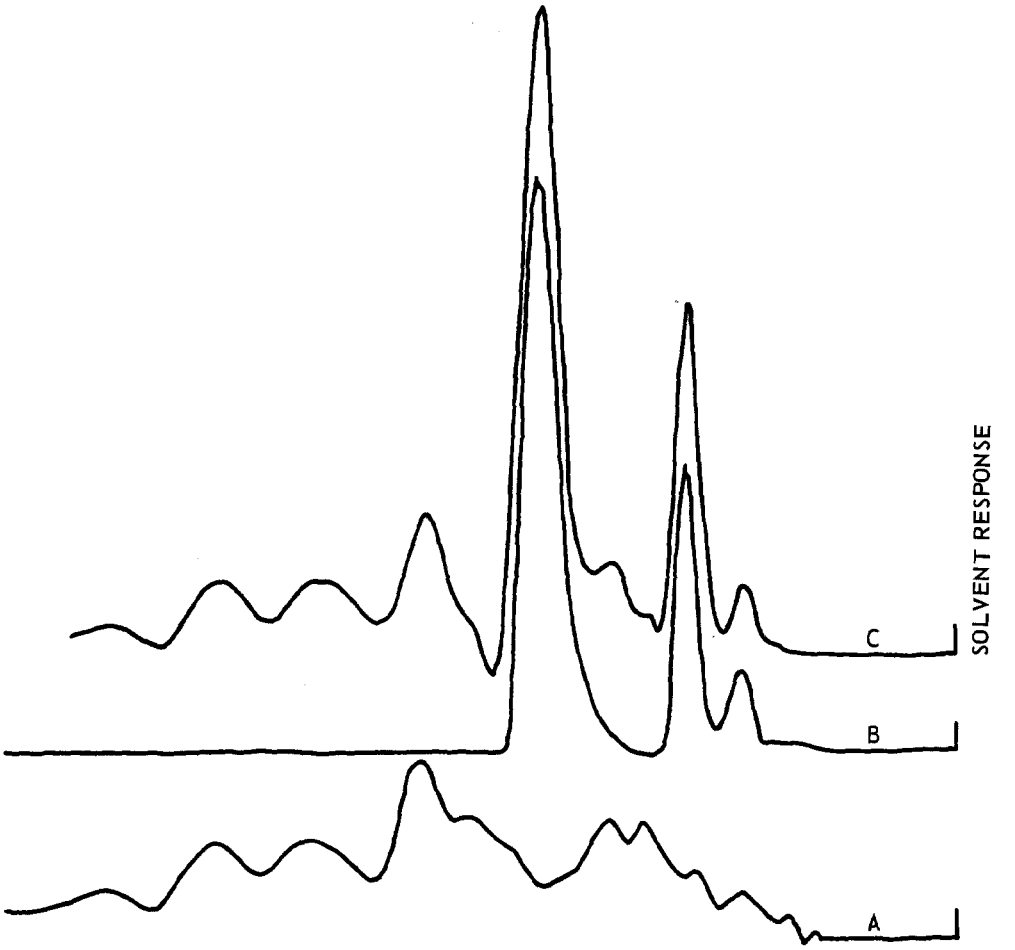
by ARTHUR BEVENUE
Pacific Biomedical Research Center
University of Hawaii, Honolulu, Hawaii

and HERMAN BECKMAN
Agricultural Toxicology and Residue Research Laboratory
University of California, Davis, California

Considerable data have been published as tables on the retention times of various pesticides obtained by gas chromatography. Such data usually includes three or more "peaks" (or retention-time values) for the insecticide toxaphene. The paucity of published gas chromatographic curves on toxaphene, alone or in combination with other pesticides, can be explained by the continuum-like curves reproduced in Figure 1. The difficulty in classifying this type of curve qualitatively and estimating the amount quantitatively is obvious.

Toxaphene is a mixture of related compounds and isomers, with a chlorine content of 67 to 69 per cent. Therefore, well-defined separations of mixtures containing toxaphene cannot be successful because it is not a discrete compound (1). However, in an effort to find some reproducible, well-defined characteristic, or fingerprint, gas chromatographic studies were made of toxaphene alone, and in combination with technical grade DDT.

Bulletin of Experimental Contamination & Toxicology,
Vol. 1, No. 1, 1966, published by Springer-Verlag New York Inc.



ELECTRON CAPTURE DETECTOR RESPONSES TO: A – 7 NANOGRAMS TOXAPHENE, B – 2.8 NANOGRAMS DDT, C – 7 NANOGRAMS TOXAPHENE + 3.5 NANOGRAMS DDT

COLUMN: 4 x 1/4 WITH 5% QF-1 ON CHROMASORB-W

Experimental

In an effort to find a characteristic fingerprint of toxaphene by the use of gas chromatography, the stationary liquid phase and the solid support of the gas chromatographic column were varied, both in the amount used and the type selected. The stationary phases included QF-1 (Silicone fluoro, FS 1265), Silicone Dow Corning 11, Silicone Dow Corning 200, and Silicone Gum Rubber, methyl, SE-30. In addition, columns were used containing mixtures of QF-1 and DC-200 oil in variable ratios. Column supports included Chromosorb G, Chromosorb W, and Chromosorb P, which had been variously treated with acid, hexamethyldisilazane, and/or dimethyldichlorosilane. Six different commercial types of gas chromatographs were used including the concentric and the parallel-plate type of electron capture detector (tritium radiation source), the pulse mode and the DC mode of operation, and also a coulometric type detector.

The detectable limit of toxaphene was dependent upon the newness (or cleanliness) of the detector and the efficiency of the column packing. Under ideal conditions, 2 nanograms of toxaphene could be observed with no difficulty. Using an instrument that had been exposed to considerable usage in pesticide residue analysis, the required sample size was of the order of 5 to 7 nanograms of toxaphene and 2 to 3 nanograms of DDT. Burke and Holswade (2) noted in their procedure when using a microcoulometric detector that it required about 9-fold the amount of toxaphene when compared to p, p'-DDT to attain one-half full scale recorder deflection.

Irrespective of the type of column or column packing used, no characteristic fingerprint for toxaphene could be obtained with one possible exception. One column material showed promise for a characteristic 3-peak fingerprint subsequent, timewise, to the p, p'-DDT peak. Using a 1/8" x 5' glass column of 5% QF-1 on Chromosorb W, and assigning aldrin a reference

point of 1.00, o, p'-DDT had a relative retention time of 2.7; p, p'-DDT 4.1, and toxaphene had three "peaks" at retention time of 6.0, 7.0, and 8.0. Perhaps a different stationary liquid phase might be found that would improve upon and clearly define this portion of the toxaphene continuum.

The data indicates that the use of 1/8" columns containing Dow-11 or DC 200 oil at a column temperature not greater than 190° C. gave the best resolution for the DDT components. In the pesticide mixture, DDT is clearly defined in the presence of toxaphene if toxaphene does not exceed the amount of DDT present by an approximate factor of 3. Obviously, a gas chromatographic record of toxaphene is practically meaningless unless the background of the sample under examination is known; in many instances this is highly improbable, if not impossible to obtain. If the pesticide formulation originally used was a mixture, such as toxaphene-DDT, the picture is more complex. An experienced pesticide residue analyst may be competent in interpreting the data qualitatively, but to attempt to quantify such data may be more difficult and only an approximation. Proposals have been made to estimate the amount of toxaphene residue present in a sample by the so-called characteristic three-peak fingerprint comprising the latter part of the curve. This is demonstrated in Figure 1. However, until a more precise and sharper defined picture of this area is obtained by some improved means, this technique is highly empirical and subject to a large quantitative error.

Suggestions have also been made to rearrange the structure or to partially dehalogenate toxaphene, and DDT if present, by refluxing with a basic alcoholic solution. Gas chromatographic curves obtained from such solutions are then compared with curves obtained from untreated samples. Crosby and Archer showed that this procedure is not wholly successful, especially when toxaphene and DDT are in the same mixture. The dehydrochlorinated toxaphene may show as many as 5 "peaks", by

electron capture gas chromatography, the primary peak being only about 2.0-2.5% as large as DDE, the dehydrochlorinated component of DDT (3).

In summary, the pesticide residue chemist has been placing increased reliance on gas chromatographic data for the identification of a pesticide residue. In the examination of a sample for toxaphene residue, such data is not reliable, either qualitatively or quantitatively. In particular, when State or other Regulatory agencies may wish to examine a shipment of produce suspected of excess toxaphene residue, the use of gas chromatography data alone for the basis for legal actions is an invitation for criticism and rebuttal. We believe the same thesis could be applied to the compounds chlordane and strobane. Until it can be shown by some new, and presently unknown, technique that toxaphene can be unequivocally identified, the gas chromatographic procedure for the determination of toxaphene, alone or in combination with other pesticides, is at best highly questionable. Further investigation into the "3-peak" phenomena at the latter part of the gas chromatographic curve may possibly produce a definitive fingerprint.

Acknowledgment

We acknowledge with thanks the cooperation of Mr. Fred Roth, Mr. Felix Erro, Mr. William Lewis, and Mr. R. A. Sweet, all of the California State Department of Agriculture, in supplying much of the data obtained from a variety of commercial types of gas chromatographic instrumentation.

References

1. H. F. BECKMAN and P. BERKENKOTTER, Anal. Chem. 35, 242 (1963)
2. J. BURKE and W. HOLSWADE, J. A. O. A. C. 47, 845 (1964)
3. D. G. CROSBY and T. E. ARCHER, Paper presented at the 148th National Meeting of the American Chemical Society, Chicago, September, 1964.