

Gas Chromatography of Pesticides

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Gas chromatography is a promising technique for rapid pesticide analysis. Aldrin, dieldrin, *p,p'*-DDT, lindane, parathion, malathion, and Systox show suitable gas chromatographic behavior between 220° to 280° C. for separation of mixtures. This technique should be very useful as a rapid method of cleanup and separation of pesticides from vegetable extracts.

RESIDUES OF CHEMICALS used to control insects on plants used as food during the growing period become more difficult to analyze because of the many new chemicals being used as pesticides. This problem is particularly difficult in the case of perishable leafy vegetables because of the limited time available for analysis. In addition, without a systematic approach to the problem of residue analysis it is virtually impossible to determine if a dangerous amount of an unknown chemical is present.

In the present work, a gas chromatographic method of separating, identifying, and measuring pesticide residues was undertaken. This should be considered as a preliminary report, however, its broad applicability should make it helpful to others engaged in residue research. Although residue analysis involves several important steps—sampling, extraction, cleanup, separation, and measurement—the present report involves only the cleanup, separation, and measurement steps.

Gunther and Blinn (4) have discussed sampling, pointing out the importance of such factors as sample size and replication of sample, and methods of extraction suitable for use with various residue methods. A polar solvent that is miscible with water, such as isopropyl alcohol or tetrahydrofuran, for the extraction of leafy vegetables, permits a single extraction to deal with a large number of pesticides of the chlorinated hydrocarbon and phosphate types. Phase separation can then be accomplished by the addition of a non-polar solvent such as hexane. Gunther (3) stresses the need for an equilibration period after the mincing and extraction operations.

Experimental and Discussion

The gas chromatograph used in these studies was similar to that described by Felton (1, 2) and was specially constructed for the current work. The column consisted of 1/4-inch outside diameter aluminum tubing, 6 feet in length, packed with 30/60 mesh Johns-Manville Chromosorb coated with 25% by weight of Dow-Corning high-vacuum silicone grease. The introduction block was also made of aluminum. Helium was used as the carrier gas. Glow plugs with plat-

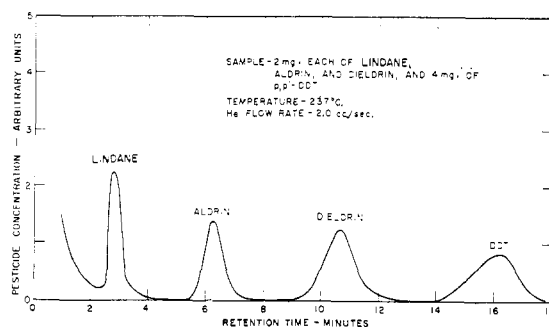


Figure 1. Gas chromatogram on a mixture of chlorinated hydrocarbons

Table I. Gas Chromatographic Results for Several Pesticides at 240° C.

Pesticide	Retention Vol., Cc. of He ^a
Systox	560
Lindane	650
Malathion	1030
Parathion	1150
Aldrin	1270
Dieldrin	2150
<i>p,p'</i> -DDT	2800
Chlordan	610, 1050, 1230, 1800, 2700
Toxaphene	Continuum, 500 to 3000

^a Measured at room temperature and atmospheric pressure.

inum filaments, of the type used in model airplanes, were used as detectors in a Wheatstone bridge circuit.

Retention volumes representing the amount of helium required to elute various pesticides from the gas chromatographic column at 240° C. are given in Table I. These data and the typical gas chromatogram (Figure 1) show that gas chromatography is potentially a very powerful tool for the separation of pesticides from one another and from other materials extracted from food products. Of the compounds listed in Table I, lindane, parathion, aldrin, and DDT have been passed through the gas chromatograph, quantitatively collected in carbon disulfide, and subjected to infrared analysis. In each case, quantitative recovery of the parent compound was obtained with no evidence of decomposition. Similar studies on the other compounds have not yet been undertaken. However, it is probable that these compounds may also be successfully gas-chromatographed.

With the exception of Systox (tempera-

Table II. Constants^a for Calculation of Retention Volumes for the Equation

Pesticide	a	b
Lindane	-3.12	3040
Aldrin	-4.49	3900
Dieldrin	-4.50	4020
<i>p,p'</i> -DDT	-4.55	4100
Parathion	-3.96	3600
Malathion	-2.26	2700
Systox	-3.48	2700

^a For a 6-foot × 1/4-inch column at temperatures between 220° and 280° C.

ture range, 220° to 250° C.), all of the compounds listed in Table I have been studied by gas chromatography in the temperature range from 220° to 280° C. In each case, the retention volume decreased as the temperature increased. This temperature effect can be expressed adequately by the empirical equation:

$$\log \left[\text{retention volume} \right] = a + \frac{b}{T}$$

where the retention volume is expressed in milliliters of carrier gas and T is the absolute temperature, °K. Values of a and b for several pesticides are given in Table II.

Figure 2 shows gas chromatograms for a mixture of lindane, parathion, and dieldrin; a mixture of Systox and malathion; chlordan; and toxaphene. In all cases, the solvent peak which represents the major component of each solution was completed in less than 1 minute and is not shown. Xylene was a satisfactory solvent for the preparation of 10% solutions of most of the pesticides studied.

Toxaphene and chlordan gave complex gas chromatograms indicating the presence of several components in each

case. Systox which is a mixture of two isomers, was a crude product and contained a large portion of relatively volatile components that were eluted with the solvent peak. The other compounds were 95% pure or better. There was some evidence that the column required conditioning with a given pesticide before good recoveries could be obtained. This was especially true for parathion, *p,p'*-DDT, and lindane.

Because of this problem, recoveries may be poorer at the microgram level available in actual residue samples than at the milligram level used in the present study. On the other hand, the conditions for elution and elution times can probably be accurately predicted at the microgram level from data taken for milligram quantities. Work is going forward, to be reported later, on the development of sensitive and specific detectors necessary for the detection of microgram quantities of the various pesticides. The present thermal conductivity detectors have a sensitivity limit of approximately 200 γ .

Studies on the improvement of gas chromatographic columns and other conditions are being continued. As soon as sufficient background information on the gas chromatography and measurement of microquantities of pesticides is developed, the practical application of this method as a systematic approach to residue analysis in foods will be undertaken.

Projected Applications

Using the thermal conductivity type of detector, which is relatively insensitive, direct analysis of pesticide preparations and formulations may be made. With residues of known pesticides gas chromatography will undoubtedly find wide usage as a combined cleanup and separation method, to be followed by conventional measurement techniques. Its major ad-

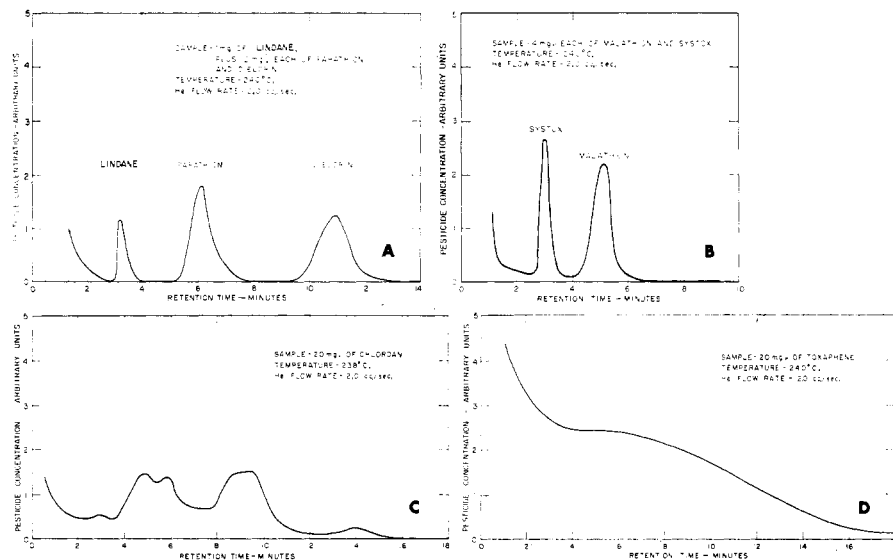


Figure 2. Gas chromatograms on mixed and unmixed pesticides

A. Mixture of lindane, parathion, and dieldrin. B. Mixture of malathion and Systox. C. Chlor-dan. D. Toxaphene

vantage for this purpose is its speed. In many cases, such a procedure could be completed within minutes. Finally, as suitably sensitive, specific direct detection methods are developed, complete residue analyses may be performed by gas chromatography. Where spray histories of the food are known, only those components known to be present need be looked for. Materials with unknown spray histories, but with the possibility of only certain residues being present, such as those included in this study, can be identified by the gas chromatographic elution time, and the amount present by the magnitude of the detector signal.

Acknowledgment

This work was carried out on a grant from the John A. Hartford Foundation

and the present paper is based, in part, on the work reported in Technical Report No. I, "Pesticide Residues on Fresh Vegetables," May 1, 1958, prepared on that research project.

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Received for review January 6, 1959. Accepted February 24, 1959.

ORGANOPHOSPHORUS INSECTICIDES

Some New Organophosphorus Compounds with Insecticidal Properties

SINCE THE DISCOVERY of bis-*N*-dimethyl phosphorodiamidic fluoride and octamethylpyrophosphoramidate by Schrader, numerous compounds have been prepared and tested as systemic insecticides. The majority of systemic phosphorus compounds are not inherently powerful anticholinesterases, but are metabolized to active com-

pounds either in the plant or after ingestion by the insect. Some general insecticides also act through a labile metabolite, but many of them are active inhibitors *per se*. In the case of octamethylpyrophosphoramidate (schradan), which has been extensively investigated by numerous workers, the insecticide can be metabolized in vivo

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or in vitro by liver preparations of certain mammals or converted by chemical oxidation with potassium permanganate to an extremely active anticholinesterase (4, 9, 13, 24). This metabolite was regarded as being either an amine oxide or an *N*-methylol compound, both of which would be very labile and readily decomposed (4, 19, 24). Spencer *et al.* (21, 23) have recently demonstrated that it is not the *N*-oxide and have advanced fresh evidence for the

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