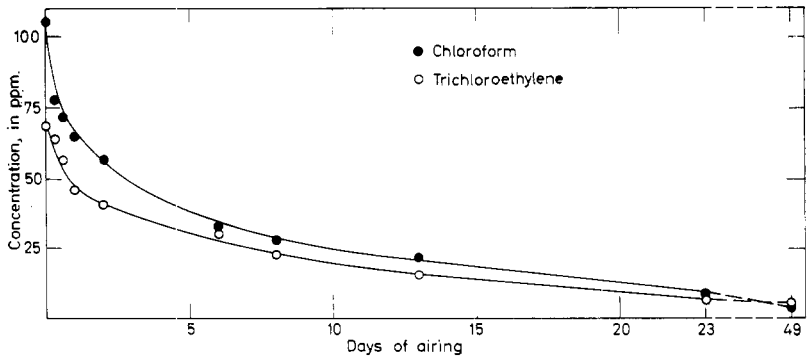


Figure 5. Residues of fumigants during airing of corn

**Table II. Residues of Fumigants in Wheat and Barley Treated with Fumigant Mixture (40 Grams per Cu. Meter) for 72 Hours**

| Days of Airing | Quantities, P.P.M. | | | | | |
|---|---|---|---|---|---|---|
| | Chloroform | | Carbon Tetrachloride | | Trichloroethylene | |
| | Wheat | Barley | Wheat | Barley | Wheat | Barley |
| 0 | 21.0 | 27.9 | 1.53 | 2.2 | 12.7 | 21.9 |
| 1 | 17.6 | | 1.47 | | 12.0 | |
| 2 | 16.8 | 11.1 | 1.4 | 1.2 | 11.2 | 9.4 |
| 5 | 8.9 | | 1.38 | | 7.7 | |
| 7 | 8.1 | 7.8 | 1.3 | 0.8 | 7.3 | 4.9 |
| 17 | 4.6 | 5.3 | 0.7 | 0.6 | 3.7 | 2.3 |

form and carbon tetrachloride, a 6-foot stainless steel column, 1/4-inch o.d., packed with 10% w./w. SE 30 silicone gum rubber on 60 to 80 Chromosorb W HMDS was used. The separation of the components on this column is illustrated in Figure 4, which shows that the column gave an improved separation of the mixture components. A glass or steel column could be used interchangeably.

The results obtained with corn, fumigated with 240 grams per cu. meter of the mixture for 72 hours, are illustrated in Figure 5. The fumigation was performed in two containers and duplicate analyses were made from each container separately. The results were very close, the maximum difference being ±5% from the average.

Airing curves for only trichloroethylene and chloroform are given in Figure 5, since carbon tetrachloride was present in very small amounts, from 7 p.p.m. at the beginning to 1 p.p.m. at the end of the airing period.

After 45 days of airing, the corn still contained about 4 p.p.m. of chloroform and 5 p.p.m. of trichloroethylene.

Results of determination of the fumigant residues in wheat and barley are given in Table II. The fumigation was carried out with 40 grams per cu. meter for 72 hours.

The quantities of residual fumigants present in grain fumigated with small amounts of the mixture are negligible after 2 days of airing (Table II).

The sensitivity of the gas chromatographic method described is in the nanogram range; this corresponds to parts per million concentrations of residual fumigants in the grain. However, the full sensitivity of the detector was not utilized, and much smaller quantities can be detected.

The method presented is more sensitive than the known chemical methods, especially for mixtures of halogenated hydrocarbons, where chemical determination of constituents is difficult and time-consuming.


### Acknowledgment

The authors thank P. Budowski and M. Katz for their valuable advice. The technical assistance of Chava Genige and Pia Holstein is gratefully acknowledged.


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**ANALYTICAL METHOD**

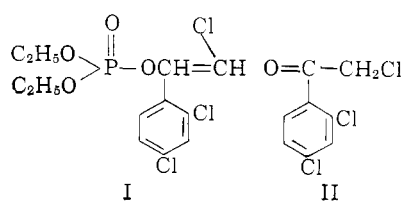
# Gas Chromatographic Determination of Compound 4072 and Shell SD-8447 by Electron-Capture and Flame-Photometric Detection


**MORTON BEROZA and M. C. BOWMAN**

**Entomology Research Division, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Md., and Tifton, Ga.**


A gas chromatographic method has been developed for Compound 4072 [2-chloro-1-(2,4-dichlorophenyl)-vinyl diethyl phosphate], an insecticide as effective as DDT against insects that attack corn (*8*). Data are also presented on the hydrolysis product of the insecticide Shell Compound SD-8447 [2 - chloro - 1 - (2,4,5 - trichlorophenyl)-vinyl diethyl phosphate].

A recent article (*6*) indicated that Compound 4072 (I) could not be determined by gas chromatography (GLC) directly; it was therefore hydrolyzed with dilute sulfuric acid to give 2,2′,4′-trichloroacetophenone (II), which was determined gas chromatographically.

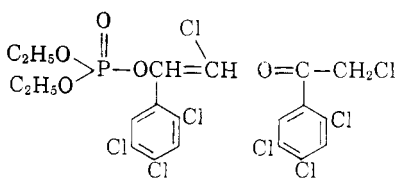



I II

Since the authors had already used GLC to determine directly the closely

The insecticidal compounds designated Compound 4072 [2-chloro-1-(2,4-dichlorophenyl)-vinyl diethyl phosphate] and Shell SD-8447 [2-chloro-1-(2,4,5-trichlorophenyl) vinyl diethyl phosphate] may be determined by gas chromatography without breakdown on a 90-cm. × 4-mm. i.d. stainless steel column containing 5% w./w. purified silicone grease on acid-washed Chromosorb W at 190° C. Residues of Compound 4072 and Shell SD-8447 in corn extracts could be estimated to 0.02 p.p.m. by electron-capture and to 0.002 p.p.m. by flame-photometric detection. Flame photometry was superior in detector life, freedom from background interference, cleanup required, range of linearity, stability, and ease of operation. The identity of the product formed by acid hydrolytic cleavage of Compound 4072 was confirmed as 2,2′,4′-trichloroacetophenone, and that from SD-8447 as 2,2′,4′,5′-tetrachloroacetophenone.

related Shell Compound SD-8447 (III) (*9*), similar conditions were applied to the determination of Compound 4072 and found to be suitable.



III IV

Inasmuch as the two compounds contain both chlorine and phosphorus, they offered the opportunity to compare analytical data by electron-capture (sensitive to chlorine) and flame-photometric (sensitive to phosphorus) detection (*5*) on identical extracts of the same compounds.

Spiked and unspiked samples were analyzed as follows: Fifty grams of fresh, chopped, whole sweet corn, 50 grams of sodium sulfate, and 150 ml. of distilled benzene were mixed for 5 minutes in a Waring Blendor. The slurry was filtered through Whatman No. 1 paper and stored over anhydrous sodium sulfate prior to analyses (3 ml. equivalent to 1 gram of corn). The filtrate (called the raw extract because it had no further cleanup) was subjected directly, concentrated (with a jet of dry air at room temperature) or diluted, to electron-capture and flame-photometric GLC analysis on a 90-cm. × 4-mm. i.d. (1/4-inch o.d.) stainless steel column containing 5% w./w. purified silicone grease on 80- to 100-mesh acid-washed Chromosorb W at 190° C. The column was conditioned by injecting extract and insecticide until the latter gave a constant response; standards were run frequently. A Jarrell-Ash gas chromatograph was used for the electron-capture analyses and an F & M Scientific Corp. Model 700 gas chromatograph equipped with the Melpar flame-photometric detector (526-mμ interference filter) described by Brody and Chaney (*5*) was employed for the phosphorus analysis.

In the electron-capture analyses the nitrogen flow rate was 200 ml. per minute and the injection port and detector temperature was 210° C. Retention time, $R_t$, of Compound 4072 was 3.80 minutes. Minor peaks appeared at $R_t$ 0.55 and 0.80 minutes and are believed to be due to impurities, because their areas were directly proportional to the main peak in the chromatography of differing amounts of Compound 4072. Response was linear to at least 3 ng., and analyses were based on peak height. Under these conditions the $R_t$ of Shell SD-8447 was 4.35 minutes, and the $R_t$ of the impurity in it (*9*) was 0.90 minute.

In the flame-photometric analysis gas flow rates were 160 ml. per minute for the nitrogen carrier gas, 40 ml. per minute for oxygen, and 200 ml. per minute for hydrogen; the injection port and detector temperatures were 210° and 200° C., respectively. $R_t$ of Compound 4072 was 4.50 minutes, and the $R_t$ of Shell SD-8447 was 5.10 minutes. The response of both pesticides was linear over at least three decades of concentration and linear to at least 250 ng.

Results of analyses are given in Table I. Individual results of duplicate analyses are listed to give an idea of reproducibility. Typical chromatograms of the two insecticides alone and in the presence of raw corn extracts are shown in Figure 1 for the electron-capture runs. Figure 2 presents similar chromatograms obtained with flame-photometric detection. Residues in the extract could be estimated to about 0.02 p.p.m. by electron-capture and to at least 0.002 p.p.m. by flame-photometric analysis. The sensitivity of the latter

**Table I. Gas Chromatographic Determination of Compound 4072 and Shell SD-8447 in Raw Benzene Extracts of Whole Sweet Corn Plants by Electron-Capture and Flame-Photometric Detection**

| Pesticide | Added P.p.m. | Added μg.[a] | Mg. Equivalent of Corn/Analysis | Recovered μg.[a] | Recovered % |
|---|---|---|---|---|---|
| | | ELECTRON-CAPTURE | | | |
| Compound 4072 | 0.0 | 0.0 | 1.67 | <1.0 | ... |
| | | | | <1.0 | ... |
| | 0.50 | 25.0 | 1.67 | 24.4 | 98 |
| | | | | 24.1 | 96 |
| | 5.00 | 250.0 | 0.56 | 255.0 | 102 |
| | | | | 253.0 | 101 |
| Shell SD-8447 | 0.0 | 0.0 | 1.67 | <1.0 | ... |
| | | | | <1.0 | ... |
| | 0.50 | 25.0 | 1.67 | 23.5 | 95 |
| | | | | 24.2 | 97 |
| | 5.00 | 250.0 | 0.56 | 251.0 | 100 |
| | | | | 247.0 | 99 |
| | | FLAME-PHOTOMETRIC | | | |
| Compound 4072 | 0.0 | 0.0 | 16.7 | <0.1 | ... |
| | | | | <0.1 | ... |
| | 0.05 | 2.50 | 16.7 | 2.35 | 94 |
| | | | | 2.40 | 96 |
| | 0.50 | 25.0 | 16.7 | 24.8 | 99 |
| | | | | 24.2 | 97 |
| | 5.00 | 250.0 | 1.67 | 250.0 | 100 |
| | | | | 253.0 | 101 |
| Shell SD-8447 | 0.0 | 0.0 | 16.7 | <0.1 | ... |
| | | | | <0.1 | ... |
| | 0.05 | 2.50 | 16.7 | 2.37 | 95 |
| | | | | 2.35 | 94 |
| | 0.50 | 25.0 | 16.7 | 24.5 | 98 |
| | | | | 24.0 | 96 |
| | 5.00 | 250.0 | 1.67 | 249.0 | 100 |
| | | | | 246.0 | 98 |

[a] Per 50 grams of plant material.

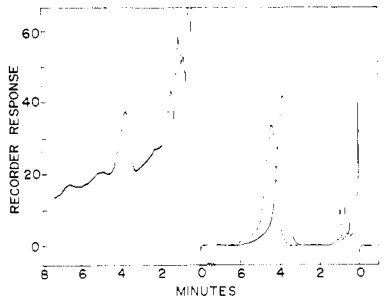



Figure 1. Chromatograms with electron-capture detection

— Compound 4072
- - - - Shell SD-8447
*Right.* 2-ng. amounts of pesticides injected in 5 μl. of benzene
*Left.* Raw benzene extract of corn (1.67 mg. equiv.) containing 0.833 ng. of Compound 4072 (0.50 p.p.m.).
Range setting $10^{-9}$ ampere, attenuation 3X with 10-mv. recorder

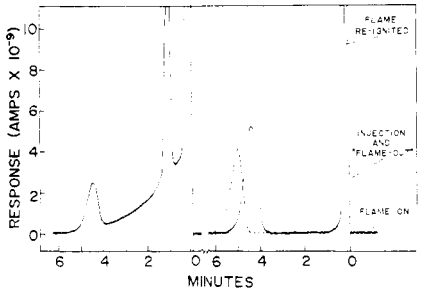


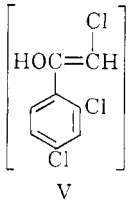

Figure 2. Chromatograms with flame-photometric detection

—— Compound 4072
- - - - Shell SD-8447
*Right.* 2-ng. amounts of pesticides injected in 5 μl. of benzene.
*Left.* Raw benzene extract of corn (16.67 mg. equiv.) containing 0.833 ng. of Compound 4072 (0.05 p.p.m.)

analysis could be further increased by injecting volumes larger than the 5 μl. used in this study and raising the column temperature to increase peak height.

In general, the flame-photometric detector was vastly superior to the electron-capture detector in terms of detector life, freedom from background interference, cleanup required, range of linearity, stability, and ease of operation. It would appear then that the flame-photometric detector is to be preferred if the application of either detector is possible and no specific interferences occur. One other advantage of the flame-photometric detector, which should prove of interest in the analysis of biological materials, is its insensitivity to water. The presence of water affects the electron-capture detector adversely.

The peak at 0.55 minute in the electron-capture runs of I appears to be the acid hydrolysis product (II) by its retention time and its $p$-value (*2,4*) in the hexane–acetonitrile system. The peak does not contain phosphorus or it would have appeared in the flame-photometric analysis. Since the structure of the hydrolysis product was not established, we prepared it by acid hydrolysis of I and found its melting point to be 54.5–55° C., which agreed with its reported value of 57° (*7*). The NMR spectrum, also in agreement with the structure of II, showed a singlet at $\delta$4.70 (two methylene protons) and a complex multiplet at ca. $\delta$7.50 (three aromatic protons). Its infrared spectrum showed a carbonyl absorption at 1706 $cm^{-1}$. [Subsequently, H. V. Claborn of this division informed us that he had identified II by comparing its infrared spectrum and $R_f$ by his procedure (*6*) with the spectrum and $R_f$ of a sample of II supplied by the General Chemical Co. His method of analysis of Compound 4072 cannot be used with the phosphorus detector.] The formation of II appears to take place by hydrolytic cleavage of I to give V, the enol form of II, which rearranges to give II.




V

In a similar manner Shell SD-8447 was hydrolyzed to give a compound melting at 64–65° C. Its NMR spectrum, in agreement with structure IV, showed a singlet at $\delta$4.66 (two methylene protons) and two singlets at $\delta$7.59 and 7.69 (one aromatic proton each; para protons do not couple). Its infrared spectrum showed carbonyl absorption at 1717 $cm^{-1}$. Since the compound could not be found in the literature, elemental analyses were run and found in agreement with IV:

ANALYSIS. Calculated for $C_8H_4OCl_4$: C, 37.2; H, 1.56; Cl, 54.9. Found: C, 37.19; H, 1.58; Cl, 53.78.

The carbon skeleton of IV was verified by carbon-skeleton chromatography (*1, 3*), a technique known to strip off chlorine and oxygen atoms; the expected product, ethylbenzene, was obtained. Compound IV and the impurity of Shell SD-8447 have the same retention time and the same $p$-value in the hexane–acetonitrile system (0.18) and therefore appear to be the same compound.

The extraction $p$-values (*4*) of Compound 4072 in the hexane–acetonitrile and hexane–dimethyl formamide systems are 0.058 and 0.026, and those of its hydrolysis product (IV) are 0.12 and 0.057, respectively. Extraction $p$-values of Shell SD-8447 and its hydrolysis product have been published (*4*).

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**RESIDUE DETERMINATION**

# Residue Analysis of 4-Chlorophenoxyacetic Acid in Tomato Fruit

**CRAIG M. ASMUNDSON, JAMES M. LYONS, and FRANK H. TAKATORI**

**Department of Vegetable Crops, University of California, Riverside, Calif.**

THE ADVANTAGEOUS USE of 4-chlorophenoxyacetic acid (4-CPA) as a chemical to induce fruit set in tomatoes (*3*) has prompted the development of a sensitive analytical method for residue determinations of this plant growth hormone. Attempts to adapt the methods of Marquardt and Luce (*4, 5*) for determination of 2,4-dichlorophenoxyacetic acid (2,4-D) residues in grain and in sugar cane juice, and that of Erickson and Hield (*7*) for 2,4-D in citrus fruit proved unsatisfactory. A technique was developed whereby the 4-CPA is cleaved by pyridine hydrochloride to give 4-