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*Received for review November 8, 1957. Accepted May 7, 1958. Approved for publication by the director of Wisconsin Agricultural Experiment Station. This study was supported in part by a research grant from AEC.*

**FUNGICIDE RESIDUES**

# Determination of Phygon Residues on Food Crops

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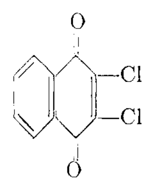
**A colorimetric method of analysis for microgram quantities of residual Phygon on food crops is based upon the reaction of Phygon with dimethylamine to produce an intense orange color. The method is sensitive to 1 γ per ml. and detectable to 0.5 γ per ml., and it has been applied to five food crops. Eighteen untreated samples charged at 0.4 to 1.0 p.p.m. have given recoveries of 85 to 101% averaging 91% recovery. Interference values obtained from untreated samples, in terms of parts per million of Phygon, have averaged 0.02 p.p.m. with a high of 0.12 and a low of —0.02 p.p.m. The color reaction is specific for Phygon.**

The fungicidal properties of Phygon were discovered by the United States Rubber Co.'s General Laboratories, Passaic, N. J., in 1940 (*7*, *8*).



Considered one of the most potent organic fungicides (*5*), Phygon gives outstanding control of apple scab, brown rot of stone fruits (*4*), botrytis, late blight of tomatoes (*2*), celery blight, potato seed piece rot, and many other plant diseases caused by fungi (*3*, *9*). It has been granted a residue tolerance of 3 p.p.m. under the Miller Amendment for use on apples, celery, peaches, and tomatoes (*6*).

The reaction between Phygon and dimethylamine to produce an orange color is taken from a colorimetric method, described by Burchfield and McNew (*1*), wherein analysis is made for fractions of a per cent of Phygon on seed. In order to adapt the above color reaction from fractions of a per cent of Phygon on seed to fractions of a part per million of Phygon on food crops, several modifications were made.

The aqueous acetone medium for color development used by Burchfield and McNew was replaced with an anhydrous benzene medium because acetone readily extracts colored plant matter from most crops, thereby presenting considerable background interference, whereas benzene extracts almost none. Also, the sensitivity of the method was increased by use of a considerably larger sample and by employment of 10-cm. cells in place of 1-cm. cells for spectrophotometric measurements.

The reaction between Phygon and anhydrous dimethylamine in a benzene medium to produce an orange color takes place almost instantly and is stable for 20 to 30 minutes (Figure 1). The orange color, with an absorption maximum at 495 mμ (Figure 2), is specific to Phygon. Standard curves of the orange color follow Beer's law. Natural plant components dissolved from the crop by the solvent form very weak yellow or green interference coloration with dimethylamine. Interferences obtained from untreated samples, in terms of parts per million of Phygon, have averaged 0.02 p.p.m., with a high of 0.12 and a low of −0.02 p.p.m. Typical recovery data of the crops analyzed are given in Table I.

## Experimental

**Processing of Sample.** Place a 500- to 1000-gram sample of the crop and a volume of benzene in milliliters equal to 1/2 the sample weight in a suitable glass jar, protecting the contents from the lid by a piece of cellophane or polyethylene sheet. Roll the jar on an automatic rolling device for 15 minutes to dissolve the Phygon from the surfaces of the sample. Decant the benzene and dry over anhydrous sodium sulfate for 10 minutes. Filter the benzene through a fast filter paper and retain a pint for analysis. Analysis should be carried out the same day the samples are processed, as Phygon tends to decompose slowly in crop washes when stored.

**Special Reagent.** Phygon, purified. Filter a saturated benzene solution of technical Phygon through an alumina chromatographic column; concentrate benzene filtrate to 1/4 its volume, chill, collect crystalline precipitate of Phygon on a sintered glass funnel, and air dry.

**Procedure.** Transfer 38 ml. of the filtered solvent wash to a ground glass–stoppered 50-ml. mixing cylinder. Di-

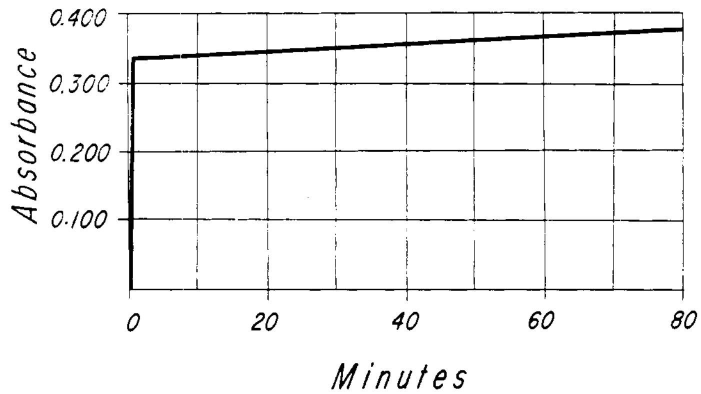



Figure 1. Rate of increase of Phygon-dimethylamine color *vs.* time

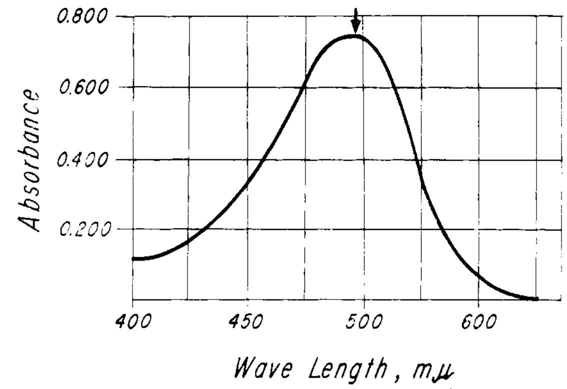



Figure 2. Absorption spectrum of orange color produced by reaction of Phygon with dimethylamine

**Table I. Recovery of Knowns**

| | P.P.M. Added | P.P.M. Recovered[a] | % Recovery |
|---|---|---|---|
| Peaches | 0.46 | 0.39 | 85 |
| | 0.46 | 0.44 | 91 |
| | 0.46 | 0.46 | 100 |
| | 0.43 | 0.41 | 94 |
| | 0.43 | 0.42 | 98 |
| | 0.43 | 0.40 | 93 |
| Apples | 0.46 | 0.47 | 101 |
| | 0.46 | 0.45 | 97 |
| | 0.46 | 0.46 | 99 |
| | 0.46 | 0.47 | 101 |
| | 0.43 | 0.41 | 95 |
| | 0.43 | 0.44 | 101 |
| Strawberries | 0.43 | 0.39 | 92 |
| String beans | 0.50 | 0.45 | 89 |
| | 1.0 | 0.88 | 88 |
| | 1.0 | 0.84 | 83 |
| Tomatoes | 0.50 | 0.48 | 97 |
| | 0.50 | 0.45 | 91 |
| | | Average | 91 |

[a] Corrected for interference due to untreated sample.

lute to 40 ml. with anhydrous dimethylamine and mix thoroughly. At the same time, dilute a second 38 ml. of the filtered solvent wash to 40 ml. with benzene (technical grade) and mix thoroughly. Against benzene as the reference, measure the absorbance of both the prepared color solutions at 495 mμ on a Beckman Model DU spectrophotometer in 10-cm. Corex cells. The color solutions should be measured 5 to 20 minutes after the addition of dimethylamine. The absorbance difference between the portion diluted with dimethylamine and the portion diluted with benzene is that at 495 mμ used in Equation 1.

**Calculations.**

P.p.m. = 2.91 × (absorbance difference at 495 mμ) (1)

P.p.m. (due to dimethylamine coloration of interferences present) = p.p.m. check (with dimethylamine) − p.p.m. check (no dimethylamine) (2)

P.p.m. treated sample (corrected)

$$= \frac{(A - B - C) \times 100}{\%\ \text{recovery of known}} \quad (3)$$

where $A$ = p.p.m. of sample treated with dimethylamine, $B$ = p.p.m. of sample treated without dimethylamine, $C$ = p.p.m. due to crop interference, from Equation 2.

Equation 1 has worked well in this laboratory, but it is advisable to run standard curves for approximately 2 weeks prior to instituting analysis. This will standardize the method to each laboratory's equipment, before formulation of an equation similar to Equation 1.

### Recovery Experiments

Two means of adding known amounts of Phygon to untreated samples were used. Initially, the untreated sample and benzene were placed in a gallon jar, the known amount of Phygon was added, and the sample was tumbled on an automatic rolling device. Later, to simplify analysis, the untreated sample was washed first with benzene alone. To an aliquot of the recovered solvent, the known amount of Phygon was added, and analysis was made. Equally good recoveries were obtained from each addition and no distinction is made in Table I.

### Acknowledgment

The author is indebted to the Agricultural Chemical Group of Naugatuck Chemical for their assistance and cooperation in making this work possible and to Dorothy R. Hill for much of the experimental data in this paper.

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*Received for review April 8, 1957. Accepted April 30, 1958. Divisions of Analytical and Agricultural and Food Chemistry, 131st Meeting, ACS, Miami, Fla., April 1957.*

**FUNGICIDE RESIDUES**

# Spectrophotometric Determination of Pentachloronitrobenzene on Food and Forage Crops

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A SPECTROPHOTOMETRIC METHOD developed to detect residues of pentachloronitrobenzene (Terraclor, Olin Mathieson Chemical Corp.) has yielded good recoveries with extracts containing 10 to 50 γ, or as little as 0.02 p.p.m. Terraclor, also field tested as PCNB and Compound 275, is an effective soil fungicide for control of many root-