primarily mercury vapor, and EMA pots, which gave both mercury and EMA vapors, the MMD and MMC pots gave primarily the methylmercury vapor. The minute amount of mercury vapor detected indicated that methylmercury compounds are quite stable to degradation in soil over a 35-day period. After the aeration period, 86 to 94% of the original mercury remained. All of the loss was recovered as the methylmercury compound captured in the carbonate absorbers. Comparison of the total mercury column with the extractable mercury column again suggested an absorption of the organomercury by the soil, especially when the insignificant amount of metallic mercury obtained during this period is considered.

The cumulative vapor (Figure 3) for methylmercury compounds appeared abnormally low. This was due to compacting of the soil surface by periodic watering to bring the pots to their original weights and also to impervious glass pots used. The compacted surface then acted as a vapor barrier. The ratio of the volatility of MMD to MMC was apparently about one to two.

The data, thus far, indicate gross differences in the tendencies of the three organomercurials toward degradation in soil and their mode of loss from soil. The nonvolatile PMA was degraded to mercury and was lost as mercury vapor. The volatile EMA was also degraded in soil to mercury, but its loss from soil occurred both as mercury vapor and the organomercury vapor. MMD and MMC gave no significant metallic mercury vapor and their loss from soil was due entirely to the volatility of the organomercury compound. If biological inactivation and mercury evolution are assumed to be intimately related, this would be inconsistent with the results of Spanis *et al.* (*8*), who found that Panodrench 4, a commercial preparation containing 0.6% MMD, was inactivated by soil microorganisms. Thus, one must assume that biological inactivation and mercury evolution do not necessarily occur together. Most of the mercurial remaining in soil could be extracted undegraded by using mild reagents, indicating that the mercurial fungicide, whether biologically active or inactive, persists in soil for a considerable time.

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FUMIGANT MEASUREMENT

Determination of Phosphine in Air by Gas Chromatography

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Phosphine was determined in air by gas chromatography of sample sizes of 0.05 to 1 ml. for concentrations of 10 mg. of PH_3 to less than 0.5 mg. of PH_3 per liter. Analysis took less than 4 minutes.

HYDROGEN phosphide (PH_3), also known as phosphine, is highly toxic to insects infesting grain (*2*) and, by modern methods of application, may be safely used for control in such material. Several methods for phosphine analysis have been published: the method of White and Bushey (*5*) is not accurate with small samples at low concentrations; the colorimetric phosphorus determination by King (*3*) is more accurate but it is complicated and time consuming; the technique of Nelson and Milum (*4*) requires a sample of several liters. A rapid and simple method using small samples was required in view of the shortcomings of the above methods; therefore, gas chromatography was investigated.

Experimental

Apparatus. The Perkin-Elmer 154-D gas chromatograph with thermistor cell was used. The column was of stainless steel, 160 inches long and $^1/_4$ inch diameter, and filled with firebrick 40-60 mesh as the solid phase and Apiezon L 30% as the liquid phase. Column temperature was 35° C., and the flow rate of helium carrier gas was 25 cc. per minute. A 1-mv. recorder was used with pen speed of 1 second for full 10-inch scale.

Reagents. For the generation of phosphine, Phostoxin tablets produced by Degesch Co., Frankfurt Am-Main, W. Germany, were used. Each tablet weighs about 3 grams and generates 1 gram of phosphine. The tablet composition was 70% aluminum phosphide, 26% ammonium carbamate, and 4% solid paraffin. To avoid ignition, phosphine is generated from a tablet of the above composition by reaction with water, which produces, in addition, ammonia and carbon dioxide.

The solid support packing in the column with Apiezon L was obtained from Wilkins Instruments and Research, Calif.

Procedure. Phosphine was generated in a 525-liter fumigation chamber by introducing Phostoxin tablets in a beaker and adding sufficient water to cover them. Subsequent to the generation of the phosphine gas, samples of the phosphine-air mixture were drawn from the fumigation chamber at various intervals of time by a gas syringe and

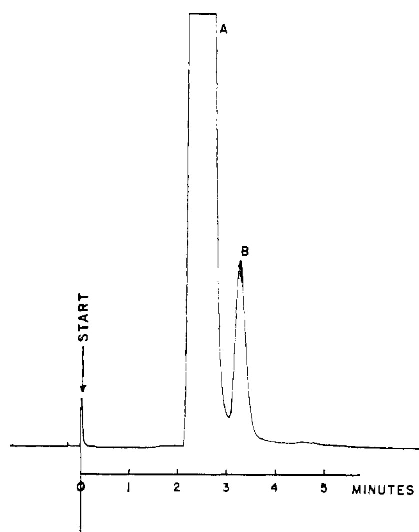

Figure 1. Chromatogram of phosphine, 1.5 mg. per liter in air, using thermistor detector at 1-mv. sensitivity

Sample size: 0.25 ml.; peaks: A, air and carbon dioxide; B, phosphine

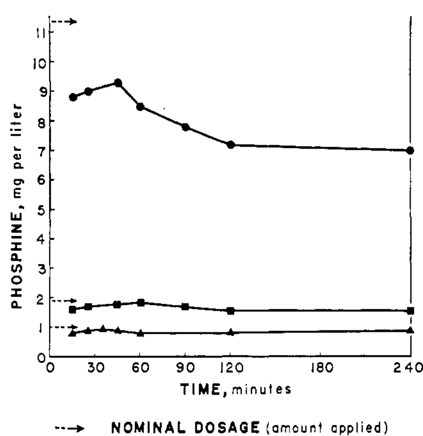

Figure 2. Phosphine concentration during fumigation

injected into the instrument. The sample size was 0.05 ml. for about 10 mg. of PH_3 per liter of air, 0.25 ml. for about 2 mg. per liter of air, and 1 ml. for below 0.5 mg. per liter of air.

The amount of phosphine represented by the area under the curve obtained by gas chromatography was determined as follows. Gas samples were drawn into special evacuated flasks (*1*) of 230 ml. volume. The flasks were then connected to the fumigation chamber through two gas-washing bottles, one filled with 20% H_2SO_4 solution and the other with 20% NaOH solution. In this way, the ammonia and carbon dioxide produced with phosphine from Phostoxin tablets was eliminated. Each flask had an outlet with a rubber septum so that a small gas sample could be withdrawn for the analysis by gas chromatography. The remaining gas in the flask was analyzed by the White and Bushey method (*5*), which was considered satisfactory as a standard for comparative purposes at the concentration of 10 mg. of PH_3 per liter of air. In this method, phosphine was reacted with mercuric chloride, and the resulting HCl was titrated by standard NaOH solution.

Results and Discussion

When the sample was introduced into the gas chromatograph, the retention time for phosphine was 3 minutes and 21 seconds, for carbon dioxide 2 minutes and 42 seconds, and for air 2 minutes and 28 seconds. For very low concentrations of phosphine in air, the carbon dioxide peak does not separate from the air peak. Figure 1 shows a gas chromatogram of a 0.25-ml. gas sample of 1.5 mg. of PH_3 per liter of air. In this experiment, the standard deviation for seven consecutive determinations was 0.05. This shows that this method is very accurate even at low concentrations of fumigant.

The concentrations of phosphine determined during a 2-hour fumigation experiment at nominal dosage (initial amount applied) of 11.4, 1.9, and 1 mg. of PH_3 per liter of air, assuming 1 gram phosphine per tablet of Phostoxin, are shown in Figure 2.

These results indicate that analysis of phosphine by gas chromatography gives good separation of this compound from air in the presence of other contaminants such as ammonia and carbon dioxide, which might be encountered in fumigation practice.

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INSECT ATTRACTANTS

tert-Butyl and *tert*-Pentyl Esters of 6-Methyl-3-cyclohexene-1-carboxylic Acid as Attractants for the Mediterranean Fruit Fly

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Gertler *et al.* (*3*) reported on the synthesis of 31 esters of 6-methyl-3-cyclohexene-1-carboxylic acid that were tested as attractants for the Mediterranean fruit fly [*Ceratitis capitata* (Weidemann)]. The *sec*-butyl ester, known as siglure, played an important role in the eradication of an infestation of the insect from the state of Florida in 1957.

Table I. Physical and Chemical Data for the *tert*-Butyl and *tert*-Pentyl Esters of 6-Methyl-3-cyclohexene-1-carboxylic Acid

Ester	Boiling Point, ° C./mm. Hg	n_D^{25}	Carbon		Hydrogen		Yield, %
			Calcd.	Found	Calcd.	Found	
tert-Butyl	99/14	1.4445	73.43	73.58	10.27	10.38	65
tert-Pentyl	114–115/12	1.4503	74.24	74.17	10.54	10.38	79