

# Microdetermination of Phosphine in Air by Gas Chromatography

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A gas chromatographic method was developed for the determination of phosphine in low concentrations (0.005 to 0.5 mg. per liter) in one minute,

sampling in a range of 100  $\mu$ l. to 1  $\mu$ l. The detection limit was 0.0005 mg. per liter, for 250- $\mu$ l. sample size.

Hydrogen phosphide ( $\text{PH}_3$ ) also known as phosphine, is toxic at very low concentrations, and hence extremely sensitive methods are required for its detection and analysis. For a study of absorption and desorption of  $\text{PH}_3$ , it was necessary to analyze concentrations down to 0.005 mg. of  $\text{PH}_3$  per liter. A previous method (Dumas, 1964) gave accurate analysis in the range 0.5 to 10 mg. of  $\text{PH}_3$  per liter of air. The limiting factor was the close retention time between air and  $\text{PH}_3$ ; hence, the separation was difficult when the ratio of air to  $\text{PH}_3$  increased. For these reasons, flame ionization gas chromatography with phosphorus detector was investigated for concentrations from 0.5 down to 0.005 mg. of  $\text{PH}_3$  per liter of air.

## EXPERIMENTAL

**Apparatus.** The Aerograph 600 D was used with the flame ionization phosphorus detector. The column was of stainless steel, 96 inches long,  $\frac{1}{8}$ -inch diameter filled with Chromosorb W 30/60 mesh solid phase, and Apiezon L 30% as the liquid phase. Column temperature was 45° C., and the flow rate of nitrogen carrier gas was 10 cc. per minute. A 1-mV. recorder and the Varian Aerograph Model 475 digital integrator was used to measure the signals.

**Reagents.** Phosphine as a compressed gas was obtained from a lecture bottle cylinder (99.5% purity), or was generated from Phostoxin tablets produced by Degesch Co., Frankfurt am-Main, West Germany. The active ingredient is aluminum phosphide which generates  $\text{PH}_3$  in the presence of water.

**Procedure.** Phosphine gas from the cylinder or generated from a tablet was drawn into a gas syringe, then injected into a 250-ml. flask fitted with a silicone septum. This dilute phosphine-air mixture was used for standard curves.

For higher  $\text{PH}_3$  concentrations in the order of 0.5 mg. per liter of air, a 1- to 4- $\mu$ l. sample was taken. For these small samples, a 10- $\mu$ l. Hamilton syringe (No. 701-N), originally designed for liquids, was used in a manner which made it gas-tight. Prior to sampling the gas, distilled water was drawn into the syringe and quickly released, leaving only the needle filled with water. Following this, the sample was

drawn and injected into the chromatograph column. When used in this manner, the small water plug at the tip of the plunger provided a gas-tight seal and allowed the entire gas sample to be injected into the instrument. In sampling in the range of 0.005 mg. of  $\text{PH}_3$  per liter of air, a 100- $\mu$ l. sample was used, while in the extremely low range of 0.0005 mg. of  $\text{PH}_3$  per liter of air, a sample size of 250  $\mu$ l. was used.

The application and usefulness of the method are demonstrated by an example from an investigation on the absorption and desorption of phosphine by confused flour beetle *Tribolium confusum* Jaquelin du Val.

## RESULTS AND DISCUSSION

When the sample was introduced into the gas chromatograph, the retention time for air was 53 seconds and for  $\text{PH}_3$  63 seconds. At concentration of 0.005 mg. of  $\text{PH}_3$  per liter of air with sample size of 100  $\mu$ l. containing 0.5 ng. of  $\text{PH}_3$  the standard deviation for 10 consecutive determinations was  $\pm 0.006$  ng. Oxygen will interfere when its level exceeds 15  $\mu$ g. per sample and will give a peak 8 seconds ahead of the  $\text{PH}_3$  peak. Also, carbon dioxide above 2  $\mu$ g. per sample will

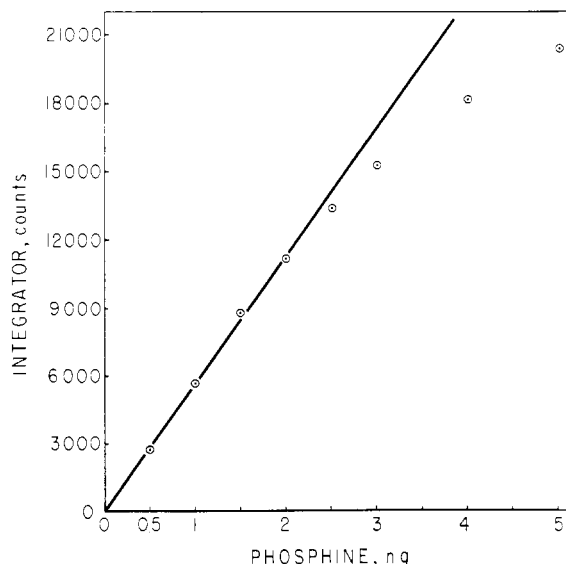


Figure 1. Detector response vs. sample weight

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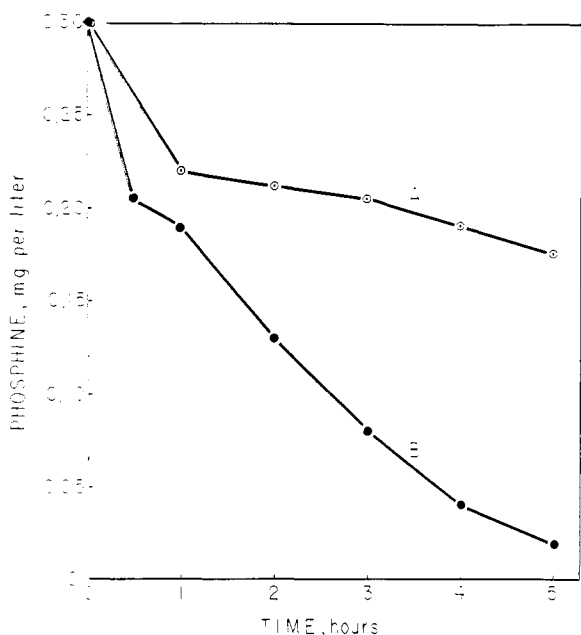


Figure 2. Phosphine uptake by insects in flasks, A. 235 ml and B. 39 ml

give a small negative peak. At a concentration of 0.5 mg. of  $\text{PH}_3$  per liter of air in a sample of 2- $\mu\text{l}$ . volume containing 1 ng. of  $\text{PH}_3$ , the standard deviation based on 10 consecutive determinations was  $\pm 0.009$  ng. The linearity at this concentration was affected above the 2-ng. sample size as is shown in Figure 1. For concentrations above 0.5 mg. per liter, the method previously published (Dumas, 1964) could be used.

The amount of  $\text{PH}_3$  absorbed by insects when exposed to the fumigant was determined by placing 1 gram of insects in each of two flasks, one 235-mg. flask and another of 39-ml. size at a concentration of 0.3 mg. per liter of air. Figure 2 shows the rate of  $\text{PH}_3$  drop during a 5-hour exposure. In the small flask the concentration of  $\text{PH}_3$  dropped to 0.02 mg. of  $\text{PH}_3$  per liter, while in the large flask it was 0.17 mg. per liter. The desorption of  $\text{PH}_3$  from insects was determined by exposing 1 gram of insects for 5 hours to 19.5 mg. of  $\text{PH}_3$  per liter in a 39-ml. flask, then transferring to another 39-ml. flask for 1 hour, where desorption took place. The concentration of  $\text{PH}_3$  in the flask was 0.0068 mg. of  $\text{PH}_3$  per liter, which represents desorption of 0.226  $\mu\text{g}$ . of  $\text{PH}_3$  per gram of insect. Bond and Dumas (1967) showed that the warning odor attributed to  $\text{PH}_3$  was really due to impurities and it could be selectively absorbed by foodstuffs leaving odorless phosphine. For this reason it is necessary to detect amounts as low as 0.3 p.p.m. which is the threshold limit for exposure of human beings.

These results demonstrate that low concentrations of phosphine can be determined accurately even with very small samples and in a short length of time.

#### ACKNOWLEDGMENT

The author thanks E. J. Bond for help in preparing the manuscript and C. T. Buckland and E. Upitis for technical assistance.

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Received for review May 9, 1969. Accepted July 25, 1969.