Microdetermination of Phosphine by Gas–Liquid Chromatography with Microcoulometric, Thermionic, and Flame Photometric Detection

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Microcoulometric, thermionic, and flame photometric (phosphorus mode) detectors used with GLC were compared for minimum detectability, accuracy, reproducibility, and rapidity for the measurement of ppb and ppt levels of phosphine, PH_3, in foodstuffs, air, and water. Based on a response at 10% of recorder scale with a reproducibility to within ±10%, the lower limits of detectability were: microcoulometric (peak area), 5 nanograms; thermionic (peak height), 20 picograms; flame photometric (peak height), 5 picograms. With a 10-g. sample of foodstuff or water, these amounts correspond to a relative minimum detectability of 500, 2, and 0.5 ppt for the microcoulometric, thermionic and flame photometric detection methods, respectively. By appropriate choice of operational parameters, PH_3 can be determined within 30 seconds by these supersensitive methods. Examples are given of application of the flame photometric method to determine sorption of PH_3 by foodstuffs and insects, and the solubility of PH_3 in various solvents. Relatively large concentrations of SO_2, H_2S, CH_3SH, and other S gases or vapors can interfere; counteractive measures are discussed.

The purpose of this report is to call attention to various alternative techniques for rapid microdetermination of phosphine, PH_3, and to indicate several applications to PH_3 research.

PH_3 is a reactive and highly toxic gas that yields numerous chemical derivatives. It is also an effective fumigant against insects that infest cereal grains, tobacco, spices, cocoa, and other stored products (Dieterich *et al.*, 1967). Relatively small amounts of PH_3 are lethal to insects (Lindgren and Vincent, 1966; Berck, 1969b). PH_3 has a high fugacity that is reflected in its relatively low b.p. of −88°C. (*cf.* +4°C. for methyl bromide). Thus, the amount of free or physically bound PH_3 remaining in cereals and many other products after fumigation and aeration is insignificant, generally of the order of 10 ppb or less (Bruce *et al.*, 1962; Dieterich *et al.*, 1967).

By exposing test materials in closed systems for periods up to 7 days and then aerating with N_2 at 180 cc./min. for 30 minutes, Berck (1968b) obtained presumptive evidence of chemisorption based on irreversible uptake of PH_3 when cereal products were treated with relatively small dosages of PH_3. As the adequacy of this aeration period has been questioned (Rauscher and Mayr, 1968), further sorption studies were conducted (Berck and Gunther, 1970), in which PH_3 was applied directly to cereal substrates packed in a GC column, and N_2 under continuous flow was used as the carrier gas. The direct on-column application of PH_3 permitted rapid microfumigation under dynamic conditions, with a minimum of residence or contact time between PH_3 and the cereal substrate, and continuous aeration with N_2 as a sweep gas. Depending on the column parameters, the total exposure or contact time was only 0.5 to 6 seconds.

The combination of short exposure periods and continuous aeration with N_2 required lower limits of detection of PH_3 than had been used heretofore (Berck, 1965; Berck, 1968a; Bruce *et al.*, 1962; Dumas, 1964). Rapid, reproducible, and sensitive methods of detection that could be used with GLC were therefore sought. Gas chromatographic methods that employed thermal conductivity (Berck, 1965), or electron capture, or hydrogen flame detection (Berck, 1966) were not suitable for current experimental requirements.

This report deals with the usefulness of three alternative detection methods—namely, microcoulometric detection (MCD), thermionic detection (TD), and flame photometric detection (FPD) in the phosphorus mode. Of these, the FPD had the best combination of rapid response, reproducibility, sensitivity, and linearity of response. The FPD method was accordingly used in a reinvestigation of possible chemisorption affinities of cereal products toward PH_3 under dynamic conditions (Berck and Gunther, 1970). It was also applied to measure the uptake of PH_3 by two species of insects (Berck, 1970b), and the solubility of PH_3 in 25 solvents (Berck, 1970a).

EXPERIMENTAL

Apparatus and Auxiliary Equipment. A Coulson T 300 titration cell and a C-200 coulometer (Dohrmann Instruments Co., 1062 Linda Vista Ave., Mountain View, Calif. 94040) were used in the MCD method. The recorder was equipped with a Disc area integrator, Model 201-5B. Since PH_3 could be measured directly in the titration cell, use of GLC and auxiliary GC apparatus were omitted in the MCD method.

For the thermionic detection method, an Aerograph Model 1520B Gas Chromatograph (Varian Aerograph Division, Varian Associates, Walnut Creek, Calif.) was used. The instrument was equipped with a pelleted cesium bromide thermionic detector attachment (Hartmann, 1966) obtained from Varian Associates, and a 5-ft. × 1/8-inch i.d. stainless steel column packed with 4.5% QF-1 on Chromosorb G, 70–80 mesh. The column, detector, and injection port temperatures were 65°, 205°, and 190°C., respectively. With a carrier gas (N_2) flow rate of 30 cc./min., the retention time of the PH_3 peak was 16.2 seconds.

For the FPD method, an Aerograph Model 1520B Gas Chromatograph equipped with a MicroTek FPD assembly (MicroTek Instruments, Inc., Baton Rouge, La.), and an 18-inch × 1/4-inch o.d. stainless steel column packed with 3% Carbowax 20 M on Gas-Chrom Q, 60–80 mesh, was used. Flow rates for H_2, O_2, and N_2 were 158, 25, and 100 cc./minute, respectively, and temperatures were 65°, 190°, and 220° C. for the column, injection port, and detector, respectively.

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Under these conditions, the retention time of the PH_3 peak was 6.0 seconds.

Materials. PHOSPHINE SOURCES. Two sources were used: (a) Phostoxin tablets, 3-gram, stored in a closed glass tube in a freezer. Phostoxin is manufactured by the Degesch Co., Frankfurt, W. Germany, and is distributed by the Hollywood Termite Control Co., 2221 Poplar Blvd., Alhambra, Calif. 91802. Each 3-gram Phostoxin tablet contains enough aluminum phosphide, which hydrolyzes upon contact with water or moist air, to release 1 gram of phosphine [$AlP + 3H_2O \rightarrow Al(OH)_3 + PH_3$]. (b) Phosphine, 99.5% pure, from a cylinder of the compressed gas (Matheson Co., Inc., Cucamonga, Calif. 91730). (*Caution.* Near-pure PH_3 is inflammable when in contact with air. Copper tubing and brass fittings apparently catalyze such conflagrations. No difficulties were experienced with nitrogen-diluted PH_3.)

GAS CONCENTRATE FLASKS. These consisted of volume-calibrated 6.3-liter flat bottom boiling flasks with ⅁ 24/40 necks (Cat. No. JF-2050, Scientific Glass Apparatus (S.G.A.) Co., Fullerton, Calif. 92632) that were fitted with JA-7970 gas inlet vacuum connection adapters (S.G.A.) to enable thorough flushing with dry, purified N_2 either before making required PH_3 atmospheres or to discharge them in due course into the fume hood for flask-cleaning purposes. A few grams of quartz glass chips, 20–30 mesh, were put into each flask beforehand which, upon vigorous swirling of the flask immediately before sampling, ensured a homogeneous gas mixture. After flushing of the flask with N_2, the JA-7970 adapter was replaced with a JA-3150 angle adapter (S.G.A.) fitted with a 2-way stopcock and a rubber septum at the hose connection end. PH_3 was generated by addition of 0.5 ml. of water to 0.4 gram of powdered Phostoxin in a 100-cc. syringe (Berck, 1965). The gas thus generated was transferred with a separate syringe into a 6.3-l. flask from which an equivalent amount of N_2 had first been withdrawn through the rubber septum. The syringe was pumped manually for about 30 seconds to assist uniform dispersal. Phosphine from the cylinder was transferred similarly. For higher concentrations, weighed amounts of Phostoxin tablets were placed directly into the 6.3-l. flask. The flask was swept with N_2, the N_2 atmospheric pressure was reduced to a desired manometric level, and water was added for slow generation of PH_3. The PH_3 content of the gas concentrate flasks was determined potentiometrically (Berck, 1968a).

SYRINGES. Four types were used: Hamilton Microliter syringes (Hamilton Co., Whittier, Calif.) in 10-, 50-, and 100-μl. sizes; Hamilton Gas-Tight (G-T) syringes in 2.5-, 5-, and 10-cc. sizes, all-glass B-D (Becton-Dickinson) syringes in 20-, 30-, 50-, and 100-cc. sizes; 100-cc. all-glass B-D syringes fitted with a rubber septum and used for the generation of PH_3 (Berck, 1965). All syringes were tested for gastightness and were calibrated with water. The dead volume of the microliter syringes was allowed for in taking gas samples (Dal Nogare and Juvet, 1962).

PHOSPHINE STANDARDS. Standards in the range 2 ng. to 10 μg. PH_3/cc. N_2 were made by serial dilution of the gas concentrate flasks. Precalibrated boiling flasks (Cat. No. JF-2050, S.G.A. Co.) with ⅁24/40 necks in 125-, 250-, 500-, and 1000-cc. sizes were used to contain the standards. Each flask was fitted with Cat. No. JA-3150 adapters (S.G.A. Co.), septums, and quartz chips for gas-mixing, and contained an atmosphere of dry N_2. Predetermined aliquots were taken from the gas concentrate flasks by syringe, and were transferred with pumping to the smaller flasks from which similar volumes had been removed previously. Each gas standard flask was pumped manually with a 50-cc. syringe just before use.

NITROGEN. Compressed nitrogen, high purity, dry, 99.99% pure (Linde Company, Division of Union Carbide Corp., Los Angeles, Calif. 90058) was used.

SULFUR COMPOUNDS. To check specificity of the FPD method, standards were made of the following compressed gases (Matheson Co., Cucamonga, Calif.): SO_2 (99.98% purity), H_2S (99.6%), methyl mercaptan (99.5%), and carbonyl sulfide (97.5%). Standards were also prepared of CS_2 (spectrochemical grade, Mallinckrodt).

PROCEDURE

For calibration trials by the MCD method, PH_3-N_2 mixtures were introduced in triplicate directly into the MCD cell with N_2 as carrier gas at a flow rate of approx. 75 cc./min. Standard volumes of PH_3 in the range 2 ng. to 50 μg. PH_3/cc. N_2 were injected into a septum-capped glass T-tube fitted at the cell-connecting end with a 12/5 semi-ball glass joint. Alternatively, for the range 5–100 ng., the PH_3 was injected via a glass protective sheath directly into the cell with a 10-μl. syringe fitted with a 6-inch needle. A Coulson microcoulometer titration cell, Model T-100 and a Model C-100 microcoulometer were used initially. Improved determination, particularly for the range 5–100 ng. PH_3, was obtained with a Model T-300-S titration cell using 70% acetic acid and a Model C-200 microcoulometer. The speed of the magnetic stirrer was varied to obtain symmetrical peak profiles with a minimum of tailing or overshoot. The Disc integrator enabled reading of peak areas as 0.1 square inch per stroke of integrator pen. The C-200 microcoulometer was used in the C-100 mode, with the generator gain adjusted to 80 at a microcoulometer setting of 20 A. The position of the sensor electrode was approximately 30° in relation to the capillary inlet.

For calibration tests by the TD and FPD methods, PH_3-N_2 mixtures in the range 1–500 ng. PH_3/cc. N_2 were injected directly into the GLC columns. Response was measured as peak height. Retention time comprised the time span in seconds from the point of injection to the appearance of the peak maximum.

In the use of a 10-μl. syringe for gas sampling, the syringe needle was introduced about $^3/_4$ inch past the septum of the flask containing a well-mixed gas atmosphere, and the syringe piston was pumped 10 times before an aliquot was taken. One microliter more than the volume desired was thus withdrawn from the flask, and this excess was then discharged immediately before the adjusted sample was injected into the column. Results over the working range of a standard curve were highly reproducible when a clean 10-μl. syringe was used and corrections for the dead volume of the syringe were applied. Sudden or gradual lowering of the response for a given amount of standard by either the TD or FPD method was generally due to development of contamination on the internal walls of the syringe cylinder, evidently as a cumulative effect of hundreds of samplings and injections through silicone rubber septums. If the lowered response persisted after a septum was renewed, the syringe piston was removed, and a suction line was applied to the cylinder to pull through in succession warm ethanol–water solution (1:9, 65° C. approx.), acetone, and clean air as a vacuum-assisted cleaning. As an additional check for accuracy, the responses of the 10-μl. syringes after injection of 20, 50, and 100 pg. PH_3 standards were regularly compared with those of a precalibrated 10-μl. syringe used solely as a reference standard.

RESULTS AND DISCUSSION

Microcoulometric Detector Method. The MCD method, utilizing GLC for resolution of mixtures of pesticides, drugs, natural products, etc. and a pyrolysis furnace operated in either an oxidation or reduction mode, enables measurement of halogenated compounds as halides (except fluoride), sulfur compounds including mercaptans, as H_2S or SO_2, (Coulson and Cavanagh, 1960; Coulson *et al.*, 1960), and P as PH_3 when the reduction mode is used (Burchfield *et al.*, 1965; Burchfield and Wheeler, 1966). Martin (1966) and Cassil *et al.* (1969) have extended the MCD method to determination of as little as 1 ng. of organically bound N as NH_3 by reductive combustion with H_2 in the presence of a Ni-MgO (Martin) or Ni-BaO (Cassil) catalyst.

Additional aspects of the MCD, TD, FPD, and other detectors used with GLC to determine pesticide residues are discussed in a critical review by Westlake and Gunther (1967).

Burchfield *et al.* (1965) applied MCD to measure the PH_3, H_2S and HCl evolved from pesticide residues containing P, S, and Cl. A Fisher micro combustion pyrolysis furnace at 950° C. was used under reductive conditions with H_2. PH_3 was quantitatively separated from H_2S and HCl by an Al_2O_3 subtraction tube, and was measured in a T-300-S coulometric titration cell.

Combustion or reduction was obviously unnecessary for measurement of PH_3 as such, hence PH_3-N_2 mixtures were applied directly to the titration cell, as was indicated above.

A linear relationship between peak area and nanograms of PH_3 was obtained in the range 5–500 ng. based on the mean of the areas recorded for the response obtained from PH_3 standards injected in triplicate directly into the titration cell. The lower limit of absolute detectability, based on a reproducibility to within $\pm 10\%$, is 5 ng. when the sensitive T-300 cell and C-200 coulometer were used.

When the T-100S titration cell and C-100 coulometer were used, resistance applied to the electrodes in the titration cell varied from 64 Λ to 256 Λ (4 × more sensitive than 64 Λ). Attempts to increase sensitivity by 8 × (512 Λ) produced excessive noise and erratic base lines.

Difficulty was generally encountered in attempts to obtain a stable base line in the 5–40 ng. range. Stirring rate and amplifier gain were adjusted to minimize tailing or excessive overshoot of the descending side of a given peak. Symmetrical peak contours were obtained at the higher concentrations (40 ng. and above), with a reproducibility between triplicate injections of ± 2 to 5%.

It was concluded that amounts of PH_3 in excess of 5 ng. could be measured satisfactorily by the MCD method.

Thermionic Detector Method. The thermionic detector (TD), introduced by Karmen (1964), Giuffrida (1964), and Karmen and Giuffrida (1964), permits measurement of P in organophosphorus pesticide residues with high specificity and lower limits of detectability, either in the presence or absence of S or halogens in the organophosphorus molecule. The TD is used as an extension of the HF detector, and may be regarded as a modification of it. The response of the TD is greatly influenced by the H_2 flow rate (Beckman and Gauer, 1966; Karmen, 1964; Giuffrida, 1964). The latter can be varied so that the TD is tuned to respond preferentially to P-containing, halogen-containing, or normal (unsubstituted) hydrocarbons analogous to the HF detector (Karmen, 1964). Various modifications of the original TD design were developed by Abel *et al.*, (1966), Coahran (1966), Giuffrida *et al.*, (1966), and Hartmann (1966). The overall lower limit of detectability of the TD for P compounds was enhanced at least 8 × by replacing N_2 as carrier gas with helium (Ford and Beroza, 1967).

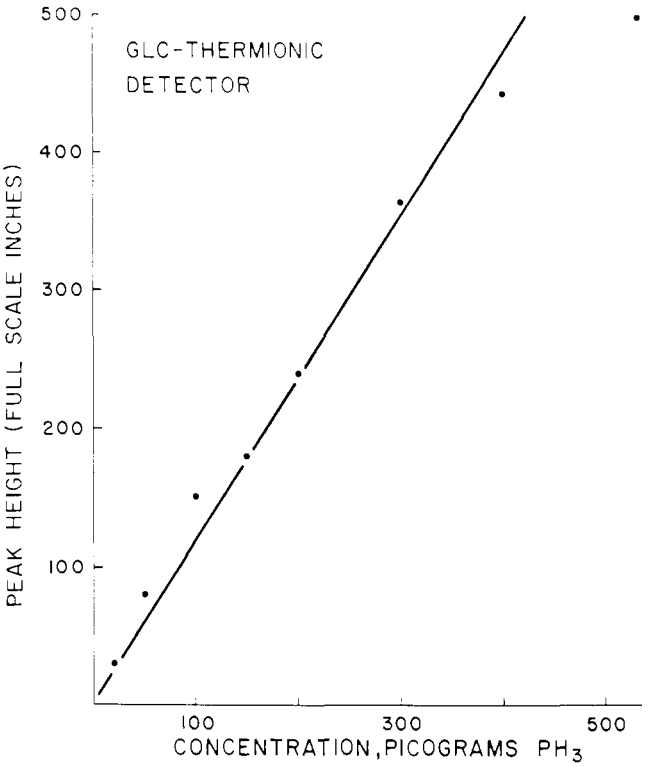

Figure 1. Standard curve, 20–400 picograms of PH_3 by TD

Figure 1 shows the relationship between peak height and picograms of PH_3 in the range 20–400 pg. based on the mean of the peak heights recorded for the response obtained from PH_3-N_2 standards injected in triplicate directly into the column. The lower limit of detectability based on reproducibility within $\pm 7.8\%$, is 20 pg. Although the response of the TD is at least 250 × more sensitive than that obtained by the MCD, it is nonlinear above 400 pg. and the deviation from linearity between points in the 20–400 pg. range is greater than with the MCD. The base line noise level of the TD was excessive at attenuations below 16×. Because of concurrent use of the TD for P-containing compounds other than PH_3, adjustments in flow rate and temperature settings to achieve maximum reproducibility and lower limits of detectability of response of PH_3 with least fluctuation in base line were not made.

It was concluded that PH_3 in amounts from 20 pg. upward can be measured satisfactorily by the TD method, and that more work should be done to improve reproducibility and sensitivity of response at levels below 20 pg.

Flame Photometric Detector Method. The FPD (also known as the flame-emission detector) is operated at hydrogen flame temperatures higher than for the TD, and enables specific detection of P, S, and other elements by photometric measurement at their characteristic emission lines. For the latter purpose, specific spectral bands in the hydrogen-rich flame can be selected with a monochromator (Juvet and Durbin, 1966; Zado and Juvet, 1966) or with interference filters. The FPD method of Brody and Chaney (1966) employs a Melpar, Inc. (Falls Church, Va.), narrow-band 526-mμ optical interference filter that specifically isolates the band for P emission and a 394-mμ narrow-band filter that selectively permits passage of emissions confined to the S

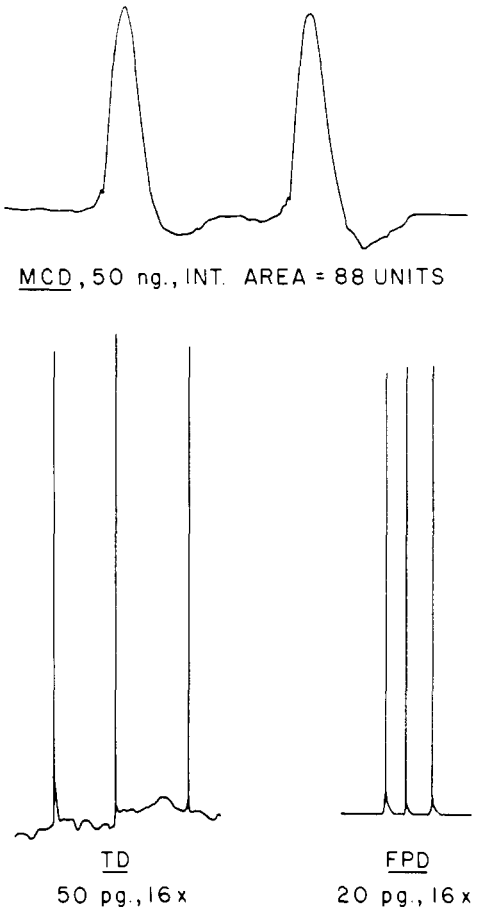

Figure 2. Comparative peak areas in duplicate for 50 nanograms of PH_3 by MCD *vs.* peak heights in triplicate for 50 picograms by TD and 20 picograms by FPD

spectral band. Bowman and Beroza (1968) combined two such Melpar interference filters as a single unit in their dual FPD for simultaneous sensing of P- and S-containing compounds.

We used the Brody-Chaney method to measure picogram amounts of PH_3 and 0.15–300 ng. amounts of SO_2, H_2S, CH_3SH, COS, and CS_2. Results with PH_3 were more reproducible, with a longer linear range, with a short GLC column (18 inches × 1/4-inch o.d. stainless steel, packed with 3% Carbowax 20M on Gas-Chrom Q, 60–80 mesh) than with an equivalent 8-ft. column.

A linear relationship between peak height and picograms of PH_3 was obtained in the range 2–600 pg. based on the means of the height response obtained from PH_3-N_2 standards injected in triplicate directly into the column. Reproducibility was excellent, with deviations ranging from ±0.0 to ±6.0%, and an average response of 3.8 F.S. (full scale) inches/picogram. As is shown in Figure 2, the PH_3 signal is both fast and sharp, with a very narrow base line. While 2 pg. of PH_3 can readily be detected, use of an attenuation of 4× for that purpose significantly decreased the signal-to-noise ratio. Compared to the TD, the FPD chromatograms of PH_3 had a more stable base line, and at an attenuation of 8×, the sensitivity of response was at least fourfold higher. However, as was previously stated, the TD was not adjusted for maximum response. While the insensitivity to air and water vapor was complete and equal for both detectors, the range of linearity of the FPD was greater, with no significant deviation between points.

The responses to the S gases with the 394-mμ filter were nonlinear, except in narrow segments of the 150–600 pg. range, and was only about 3 to 5% of the sensitivity shown for PH_3 measurement. Linearity can be achieved by plotting the relationship of S-gas concentration *vs.* response on a log-log scale.

We found that S gases, if present in high enough amounts, yield a response in the P mode and, conversely, PH_3 can respond in the S mode, if enough PH_3 is injected. This posed the question of the specificity that was claimed for the FPD method. In any event, we attempted comparative tests in measuring 10 pg. of PH_3 in the presence of 500 and 1000 pg. amounts of H_2S, SO_2, and CH_3SH, with and without a short trapping or subtraction column positioned immediately in front of the analytical column. Al_2O_3 (Merck, chromatographic grade) was the most suitable of the trapping materials tested for the S gases, but approximately 25% of the 10 pg. of PH_3 was also retained. Without a trap, the S gases gave a false response for PH_3 with the P filter. Some separation of S gases from PH_3 can be obtained by using longer columns. The percentage of PH_3 retained by the trap decreased as the amount of PH_3 injected increased. Interference in the P channel was not detectable when less than 150 pg. of S gases were present.

Figure 2 shows the comparative profiles of peaks obtained from triplicate injections of 50 nanograms, 50 picograms, and 20 picograms of PH_3 by the MCD, TD, and FPD methods, respectively. The FPD method was the most suitable for our purpose because of its greater sensitivity, freedom from background interference and consequent steady base line, and the rapid, highly reproducible elution of PH_3 when applied to a short column. The greater range of linearity and the exact proportionality of attenuation settings enabled picogram amounts of PH_3 to be measured with accuracy. We were thus able to miniaturize our fumigation experiments.

The high response-concentration ratio of the FPD method for quantitative measurement of PH_3 in amounts as low as 5 picograms, with 2 picograms as the lowest practical limit of detectability, is the most sensitive yet reported for any P compound. The sensitivity of response may be partly due to properties of the PH_3 molecule itself, such as its low molecular weight, which in turn is reflected in short retention time and unusually sharp peaks of narrow base. The short retention time of 6.0 seconds obtained under the conditions described above appeared to enhance the remarkable replicability obtainable with multiple injections by microliter syringe of samples containing 5–600 pg. of PH_3.

The FPD method described here was applied in 3 ways: A rapid method of measuring sorption affinity of PH_3 was developed (Berck and Gunther, 1970). Appropriate amounts of flour, ground cereal, or other powdered or granular substrate were vibration-packed into short GC columns. After a brief conditioning period, 500 pg. of PH_3 were injected into the N_2 stream flowing through the column. The comparative response on packed *vs.* unpacked columns was correlated with the sorption affinity of the substrate for PH_3. Although 500 pg. is a relatively small amount, it is nevertheless ample for this method, since differences in uptake down to 5 pg. (a 1% level in this instance), can be accurately and reproducibly measured. Detection of 5 picograms in 1 gram of cereal product would correspond to 5 ppt. Second, a new and simple micro method was developed (Berck, 1970a) whereby known amounts of PH_3 were dispensed into fixed volumes of different solvents placed beforehand into septum-capped tubes. The PH_3 remaining in the headspace of the tubes

was measured by the FPD method described. Third, insects were exposed to PH_3 in the range 4 to 160 μg./l. air at 4 temperatures in micro-fumigation cells fitted with silicone rubber septums (Berck, 1970b). The LC_{50}, LT_{50}, and rate of uptake were determined simultaneously.

ACKNOWLEDGMENT

The authors thank the Hollywood Termite Control Co., Alhambra, Calif., for supplying the Phostoxin tablets.

LITERATURE CITED

Abel, K., Lanneau, K., Stevens, R. K., *J. Assoc. Offic. Anal. Chem.* **49,** 1022 (1966).
Beckman, H., Gauer, W. O., *Bull. Environ. Contam. Toxicol.* **1,** 149 (1966).
Berck, B., J. AGR. FOOD CHEM. **13,** 373 (1965).
Berck, B., 49th Natl. Conf., Chemical Inst. of Canada, Anal. Chem. Div., Saskatoon, Saskatchewan, June 5–8, 1966.
Berck, B., J. AGR. FOOD CHEM. **16,** 415 (1968a).
Berck, B., J. AGR. FOOD CHEM. **16,** 419 (1968b).
Berck, B., paper in preparation (1970a).
Berck, B., paper in preparation (1970b).
Berck, B., Gunther, F. A., J. AGR. FOOD CHEM. **18,** 148 (1970).
Bowman, M. C., Beroza, M., *Anal. Chem.* **40,** 1448 (1968).
Brody, S. S., Chaney, J. E., *J. Gas Chromatog.* **4,** 42 (1966).
Bruce, R. B., Robbins, A. J., Tuft, T. O., J. AGR. FOOD CHEM. **10,** 18 (1962).
Burchfield, H. P., Rhoades, J. W., Wheeler, R. J., J. AGR. FOOD CHEM. **13,** 511 (1965).
Burchfield, H. P., Wheeler, R. J., *J. Assoc. Offic. Anal. Chem.* **49,** 651 (1966).
Cassil, C. C., Stanovick, R. P., Coon, R. F., *Residue Rev.* **26,** 63 (1969).
Coahran, D. R., *Bull. Environ. Contam. Toxicol.* **1,** 141 (1966).
Coulson, D. M., Cavanagh, L. A., *Anal. Chem.* **32,** 1245 (1960).
Coulson, D. M., DeVries, J. E., Walther, B., J. AGR. FOOD CHEM. **8,** 399 (1960).
Dal Nogare, S., Juvet, R. S., Jr., "Gas-Liquid Chromatography," Chap. IX, Interscience, New York, 1962.
Dieterich, W. H., Mayr, G., Hild, K., Sullivan, J. B., Murphy, J., *Residue Rev.* **19,** 135 (1967).
Dumas, T., J. AGR. FOOD CHEM. **12,** 257 (1964).
Ford, J. H., Beroza, M., *J. Assoc. Offic. Anal. Chem.* **50,** 601 (1967).
Giuffrida, L., *J. Assoc. Offic. Agr. Chem.* **47,** 112 (1964).
Giuffrida, L., Ives, N. F., Bostwick, D. C., *J. Assoc. Official Agr. Chem.* **44,** 8 (1966).
Hartmann, C. H., *Bull. Environ. Contam. Toxicol.* **1,** 159 (1966).
Juvet, R. S., Jr., Durbin, R. P., *Anal. Chem.* **38,** 565 (1966).
Karmen, A., *Anal. Chem.* **36,** 1416 (1964).
Karmen, A., Giuffrida, L., *Nature* **201,** 1204 (1964).
Lindgren, D. L., Vincent, L. E., *J. Stored Prod. Res.* **2,** 141 (1966).
Martin, R. L., *Anal. Chem.* **38,** 1209 (1966).
Rauscher, H., Mayr, G., Degesch Co., Frankfurt, W. Germany, unpublished report, 1968.
Westlake, W. E., Gunther, F. A., *Residue Rev.* **18,** 175 (1967).
Zado, F. M., Juvet, R. S., Jr., *Anal. Chem.* **38,** 569 (1966).

Received for review August 22, 1969. Accepted November 3, 1969. Presented in part to the Division of Agricultural and Food Chemistry, 157th Meeting, ACS, Minneapolis, Minn., April, 1969. Contribution No. 381, Canada Department of Agriculture, Research Station, Winnipeg, Manitoba, Canada.