Potentiometric Determination of Phosphine

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The White and Bushey method was modified to permit measurement of phosphine, PH_3, in amounts as small as 10 μg. The PH_3 is removed from a closed system by exhaustive flushing with dry N_2 and is trapped in chilled ethanolic mercuric chloride solution ($PH_3 + 3HgCl_2 \rightarrow P(HgCl)_3 + 3HCl$). The HCl released is determined by potentiometric titration with NaOH solution. No interference was observed when AsH_3, SO_2, HCN, or H_2S was present at concentrations one seventh that of PH_3. Extra HCl was released, apparently by hydrolysis of the $P(HgCl)_3$ complex, after 6 hours' storage at room temperature. This subsequent release of HCl was inhibited for at least 3 days and 3 weeks by storage at 4° and −14° C., respectively.

Phosphine, PH_3 (also known as hydrogen phosphide, H_3P), is a reactive and highly toxic gas from which numerous organic and inorganic compounds are derived. It may be an industrial hazard in various industries where phosphorus compounds are used (Jacobs, 1949). It is produced by hydrolysis of metal phosphides. Hence, it may appear in toxic levels in impure acetylene (Jacobs, 1949), in ferrosilicon stockpiles (Ziemer, 1963), and in cement (Phillips, 1954). The minimum warning concentration is 2 to 4 μg. per liter (Jacobs, 1949) and the maximum allowable concentration during an 8-hour exposure is 0.4 μg. per liter, equivalent to 0.3 p.p.m. (Threshold Limit Values, 1965).

Phosphine is an effective fumigant gas against insects that infest wheat, barley, rice, tobacco, and other stored products (Dieterich *et al.*, 1967). Phostoxin (manufactured by Degesch Co., Ltd., Frankfurt, West Germany, and available as 3-gram tablets and 0.6-gram coated pellets from Phostoxin Sales, Ltd., Montreal, Canada, and Hollywood Termite Control Co., Alhambra, Calif.) is a convenient source of phosphine for fumigation of grain in bulk storages, boxcars, and bags. Each 3-gram tablet or 0.6-gram pellet contains enough aluminum phosphide, which slowly hydrolyzes upon contact with moist air, to release 1 gram or 0.2 gram of phosphine, respectively. Ammonium carbamate, which yields CO_2 upon hydrolysis, is included in the Phostoxin formulation as a combustion inhibitor.

EXPERIMENTAL

Analytical Methods. A semimicro potentiometric method for PH_3 determination was developed to expedite an investigation of sorption of PH_3 by cereal products (Berck, 1968). The method is a modification of those of White and Bushey (1944) and Wilmet (1927). Free and physically sorbed PH_3 is removed from the cereal substrate by exhaustive flushing with dry N_2 and is trapped in chilled ethanolic $HgCl_2$ solution. Phosphine complexes with $HgCl_2$ [$PH_3 + 3HgCl_2 \rightarrow P(HgCl_3) + 3HCl$], and the HCl released is determined by potentiometric titration with standard NaOH solution.

Gas chromatographic methods (Berck, 1965; Dumas, 1964) were examined and rejected because the advantage of their sensitivity (0.1 μg. of PH_3) was offset by restriction on the size of sample that could be used. Concentration of the total amount of free and physically bound PH_3 by vacuum and freeze-trapping for subsequent measurement by gas chromatography was not undertaken because manipulation of PH_3 by vacuum poses the hazard of explosion (Rauscher *et al.*, 1965). Trapping the residual PH_3 in ethanolic solution containing $HgCl_2$ as a PH_3-complexing agent, as used here, was considered to be free from explosion hazard and equally effective and more convenient than freeze-trapping.

The method of Nelson and Milum (1957), which employed tubes of silica gel impregnated with $AgNO_3$, was not sufficiently reproducible to measure PH_3 at the low concentrations used (Berck, 1968). The method of Bruce *et al.* (1962), in which PH_3 is oxidized to phosphate by aqueous bromine solution and measured colorimetrically as phosphomolybdate, is sensitive to 0.8 μg. of phosphorus (0.878 μg. of PH_3). Similarly, PH_3 may be oxidized to phosphate with acid $KMnO_4$ and measured colorimetrically as phosphomolybdate (Muller, 1943). According to Rauscher *et al.* (1965), however, such oxidation procedures are not as specific for PH_3 as the $HgCl_2$ method, and yield incorrect values when gases such as HCN, SO_2, H_2S, and NO_2 are present. Similarly, the silver diethyl dithiocarbamate colorimetric method (Vasak, 1956) gives incorrect values when HCN, SO_2, or Br_2 is present (Rauscher *et al.*, 1965). With the modified $HgCl_2$ method described here, no interference was noted when HCN, SO_2, H_2S, or AsH_3 was present as a contaminant at concentrations as high as one seventh that of the PH_3.

The stability of the $P(HgCl)_3$ complex was examined because the acidity produced in the complexing reaction increased with time. The rate of increase at 23° C. in titration value after a standard amount of PH_3 had been introduced is shown in Table I. Test samples stored at 23° C. in the light and dark, respectively, showed identical rates of increase. The increase in acidity, presumably from hydrolysis of the complex, was prevented by storing samples at −14° C.; no increase above the expected titration value was shown after a three-week storage period. Storage at 4° C. delayed detectable changes for three days. Thus, in either field or laboratory investigations where test samples cannot be titrated within 6 hours, storage at 4° C. or lower is recommended.

The modified $HgCl_2$ method was used to determine the amount of PH_3 that was recovered from closed systems after cereal substrates were fumigated (Berck, 1968). Methods of removing and trapping PH_3 were accordingly explored. With dry, purified nitrogen as a sweep gas,

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Table I. Increase in Apparent PH_3 Due to Hydrolysis of $P(HgCl)_3$ Precipitate Stored in Trapping Solution at 23° C.

Storage Period, Days	PH Applied, μg.	PH_3 Recovered, μg.	Gain in Storage, μg.	Increase, %
0	240	240	0	0
1/12	240	240	0	0
1/6	240	238	0	0
1/4	240	240	0	0
1/3	240	250	10	4.2
1	240	274	34	14.2
2	240	302	62	25.8
3	240	337	97	40.4
5	240	380	140	58.4
8	240	440	200	83.5
12	240	460	220	91.8

recoveries from fumigated cereals were consistently higher and more reproducible at room temperature than at steam bath temperature. A drastic reduction in recovery was obtained when a modified pressure cooker was used experimentally in an attempt to drive out residual PH_3 that presumably was strongly bound physically by high moisture wheat. The low recoveries of PH_3 obtained at higher temperatures were subsequently attributed to chemical bonding (chemisorption) between PH_3 and cereal components (Berck, 1968). Consequently, PH_3 is routinely swept from the fumigation chambers with nitrogen at room temperature.

Purified nitrogen was passed through each 1.13-liter fumigation chamber at a constant flow rate of 180 cc. per minute. The effluent was bubbled into the $HgCl_2$ solution through a 6-mm. O.D. glass tube bent at 90° and drawn to about 0.75-mm. bore at the discharge end. The simple discharge tube did not impede gas flow, and was preferred to commercially available sintered or fritted glass tips, because even the extra-coarse porosity type clogged quickly with $P(HgCl)_3$ precipitate. Stainless steel tubes with bubble-fractionating tips (Berck, 1962) were unsatisfactory as they were corroded by the $HgCl_2$ solution. Small-bore Teflon tubing was satisfactory for the discharge outlet.

After known amounts of PH_3 were injected into empty fumigation chambers, they were held at 4°, 24°, or 35° C. for four to seven days. Regardless of temperature and time, 100% of the PH_3 was recovered in a single trap bottle after 30 minutes of flushing with N_2. With chambers that contained cereal substrates, recoveries after 1/2, 1, 2, or 3 hours' flushing were almost identical. Prolonged flushing, up to 6 hours, did not lower the titration value of the trapping solution due to possible volatilization of the HCl. This was confirmed with HCl standards added directly to the trapping solution.

No alkaline volatiles were trapped when 100-cc. aliquots of PH_3–air mixture from a 6.3-liter gas concentrate flask were injected directly into receiving flasks containing 0.035*N* H_2SO_4. Alkaline vapors were similarly absent in the cereal substrates that were tested (Berck, 1968). However, since NH_3 or other alkaline vapor in the effluent of the fumigation chambers would reduce the titration value, a fore-trap that contained 8 ml. of 6*N* H_2SO_4 was interposed between the fumigation chamber and the trap bottle as a precautionary measure.

Materials and Apparatus. Potentiometric Titration Assembly. pH meter, sensitive to 0.001 pH; microburet, Koch, 5-ml. capacity, 0.01-ml. divisions, with offset tip; magnetic stirrer assembly, with Teflon-coated stirring bars.

Phosphine Sources. Two sources were used: Phostoxin tablets, 3 gram, uncoated, stored in a closed jar in a freezer; and phosphine, 99.5% pure, in a No. 5 cylinder of the compressed gas (Matheson Co. of Canada, Ltd., Whitby, Ont.). (*Caution.* Near-pure PH_3 is flammable when in contact with air. Copper tubing and brass fittings apparently catalyze this effect. No difficulties were experienced with PH_3 diluted with nitrogen.)

Gas Concentrate Flasks. Phosphine 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 generated was transferred with a separate syringe into a 6.3-liter Strand flask (Scientific Glass Apparatus Co., Bloomfield, N. J., Cat. No. JF-5230, fitted with a custom 55/50 flask head) from which an equivalent amount of air had first been withdrawn through a rubber septum fitted to one of the flask outlets. The PH_3 concentration in this stock flask was maintained in the range 15 to 20 mg. per liter by replenishment when required. Phosphine from the cylinder was transferred similarly, but a nitrogen-filled Strand flask was used.

Syringes. Three types were used: Hamilton Gas-Tight syringes (Hamilton Co., Whittier, Calif.) in 2.5-, 5-, and 10-cc. sizes; all-glass B-D (Becton-Dickinson) syringes in 20-, 30-, and 50-cc. sizes; 100-cc. all-glass B-D syringes fitted with a rubber septum and used for the generation of PH_3 from Phostoxin, as described (Berck, 1965). All syringes were tested for gastightness and were calibrated with water.

Fumigation Chambers. Quart-size square-type glass milk bottles (1.130 ± 0.003 liter capacity) containing gas-tight neoprene rubber stoppers (2-hole No. 9) and two glass tubes fitted with rubber septums were used as chambers for experimental fumigation of cereals. The inlet tube extended to 1/2 inch from the bottom of the bottle, and the outlet tube projected about 1/2 inch from the bottom of the stopper. Such bottles required less bench area, cost less, and were more convenient than all-glass assemblies that were used initially (Scientific Glass Apparatus Co., 1-liter boiling flask, Cat. No. F-4095, and a 24/40 two-outlet adapter, Cat. No. JA-6510).

Trap Bottles and Fittings. Medicine bottles (1 1/2-ounce cabinet oval style, with Bakelite screw caps), which contained 30 ml. of aqueous 1.5% $HgCl_2$–95% ethanol (2 to 1, v./v.), were used as trap bottles at ice-bath temperature. Gas dispersion tube fittings bent at 90° were made from 6-mm. glass tubing. The vertical arm was drawn at the gas discharge end to an orifice about 0.75 mm. in diameter, similar in this regard to the midget impinger used in trapping air pollutants (Jacobs, 1949). After the gas dispersion tube and trap bottle were positioned in the ice bath, the horizontal arm was connected by a butt joint to a H_2SO_4 fore-trap (Corning Glass Co., Cat. No. 91300, size 4), and the fore-trap was connected to the outlet (short tube) of the fumigation chamber, as described below.

REAGENTS. NaOH solutions, 0.01764*N* and 0.00882*N* (1 ml. = 0.2 and 0.1 mg. of PH_3, respectively), were used as titrants. HCl solutions, 0.01764*N* and 0.00882*N*, respectively, were used to standardize the NaOH solutions and to prepare phosphine equivalents (Table III).

NITROGEN. Compressed nitrogen, high purity, dry, 99.99% pure (Linde Gases Division, Union Carbide of Canada, Ltd., Toronto, Ont.) was used. The tank was fitted with a two-stage regulator and needle valve, which was connected to rubber tubing bearing a 21-gage $2^1/_2$-inch hypodermic needle at the outlet end. The nitrogen was regulated with a precision flowmeter to a constant flow of 180 cc. per minute.

PROCEDURE

Loading of Fumigation Chambers. The glass fumigation chambers contained 250 grams of cereal product and were sealed with the two-hole rubber stoppers. Empty chambers were used as controls, in which 20 cc. of PH_3 from a gas concentrate flask were injected into the chamber through the septum on the outlet tube. Residual PH_3 in the syringe was swept into the chamber with an air-wash of 20 cc. In each instance, an amount of air equivalent to the combined volume of PH_3 and air-wash introduced was first withdrawn from the chamber. For storage at temperatures above ambient, sufficient extra air was removed to allow for expansion. The loaded chambers were mixed by gentle rolling and then placed on their sides for storage at selected temperatures.

Removal of Free PH_3. With the fumigation chamber in the vertical position, 30 cc. of the gas in the chamber were drawn into a Chaney-type syringe. With the syringe locked in position, the septum of the outlet was removed and the trap inlet was coupled to the chamber outlet by a butt joint. The syringe piston was slowly depressed and was followed by a 30-cc. air wash. Nitrogen as a sweep gas at 180 cc. per minute was then injected into the inlet through a 21-gage hypodermic needle. Sweeping was continued for 30 minutes, during which the chamber was agitated three times during the first 20 minutes by sharp impacts by hand on the sides of the chamber.

To determine efficiency of recovery, PH_3 aliquots from a stock flask were injected directly into a chilled trap bottle via a septum-capped dispersion tube, followed by a 30-cc. air wash with the syringe used. Results were compared with those obtained by nitrogen-conveyed transfer of PH_3 from the fumigation chambers to the trap bottles.

Titration. The contents of the trap bottles were transferred quantitatively to 100-ml. beakers that contained Teflon-coated stirring bars and were titrated potentiometrically with magnetic stirring (Willard *et al.*, 1965). If the PH_3 content was in the 0.6- to 2.0-mg. range, 0.01764*N* NaOH was used; if the PH_3 content was lower, 0.00882*N* NaOH was used. Titration was continued to a point slightly beyond the largest increase in pH per unit volume of titrant, ΔpH per 0.05 ml. in this instance. The midpoint of the most steeply rising portion of the titration curve, determined graphically, constituted the end point which was subsequently corrected for the reagent blank.

RESULTS AND DISCUSSION

Table II shows the recoveries obtained when PH_3 from gas concentrate flasks was applied in triplicate in the range 0.210 to 1.680 mg. to empty fumigation chambers and stored for 1 hour at 24° C. prior to nitrogen-conveyed transfer to trap bottles in the manner described. The standard deviation was 0.0065 to 0.0148 mg., and the coefficient of variation was 3.1 to 0.9%, as indicated in Table II. In separate tests in which HCl standards in the range 0.20 to 1.60 mg. of PH_3 equivalents were added directly to trapping solutions and allowed to stand for one day at 4° C. prior to potentiometric measurement, the standard deviation was 0.0045 to 0.0072 mg. and the coefficient of variation was 2.25 to 0.45% (Table III). Examination of the comparative variability of Tables II and III, using the standard deviations of the recoveries around their mean values, shows that the coefficients of variation of recoveries of applications of known amounts of PH_3 (Table II) are about twice those of known increments of HCl standards applied as PH_3 equivalents (Table III). Moreover, the standard deviation of the observed values around the applied values are also higher when PH_3 gas is applied to empty fumigation chambers (Table II). This seems to indicate that operational errors were greater in the latter case.

Figure 1 shows potentiometric titration curves obtained when standards ranging from 0.1 to 0.5 mg. of PN_3 derived from gas concentrate flasks were applied directly to 30 ml. of trapping solution in an ice bath and were analyzed shortly thereafter. The role of volume of trapping solution on end-point estimation was examined. Commencing with a volume of 100 ml. (two traps used in series, each containing 50 ml. of 1.5% $HgCl_2$ aqueous

Table II. Recovery of PH_3 from Fumigation Chambers without Cereal Substrate

PH_3 Applied,[a] Mg.	PH_3 Recovered, Mg.	Std. Deviation, Mg.	Coeff. of Variation, %
0.210	0.216, 0.2055, 0.204	0.0065	3.1
0.420	0.426, 0.410, 0.412	0.0087	2.1
0.630	0.640, 0.622, 0.636	0.0095	1.5
0.840	0.826, 0.848, 0.834	0.0111	1.3
1.050	1.060, 1.054, 1.036	0.0125	1.2
1.260	1.250, 1.272, 1.268	0.0117	0.93
1.680	1.670, 1.664, 1.692	0.0148	0.88

[a] PH_3 from gas concentrate flasks applied in triplicate to empty fumigation chambers and stored at 24° C. for 1 hour.

Table III. Recovery of HCl Added as PH_3 Equivalents to Trapping Solution

PH_3 Equivalents Applied,[a] Mg.	PH_3 Equivalents Recovered, Mg.	Std. Deviation, Mg.	Coeff. of Variation, %
0.200	0.200, 0.205, 0.196	0.0045	2.25
0.400	0.395, 0.395, 0.400	0.0029	0.73
0.600	0.597, 0.605, 0.595	0.0053	0.89
0.800	0.796, 0.792, 0.805	0.0067	0.84
1.000	0.992, 1.006, 1.002	0.0072	0.72
1.200	1.206, 1.204, 1.194	0.0064	0.53
1.600	1.596, 1.592, 1.606	0.0072	0.45

[a] For the upper three applications, 2, 4, and 6 ml. of 0.00882*N* HCl (1 ml. = 0.1 mg. of PH_3) were added in triplicate to 30 ml. of trapping solution. For the lower four applications, 4, 5, 6, and 8 ml. of 0.01764*N* HCl (1 ml. = 0.2 mg. of PH_3) were added.

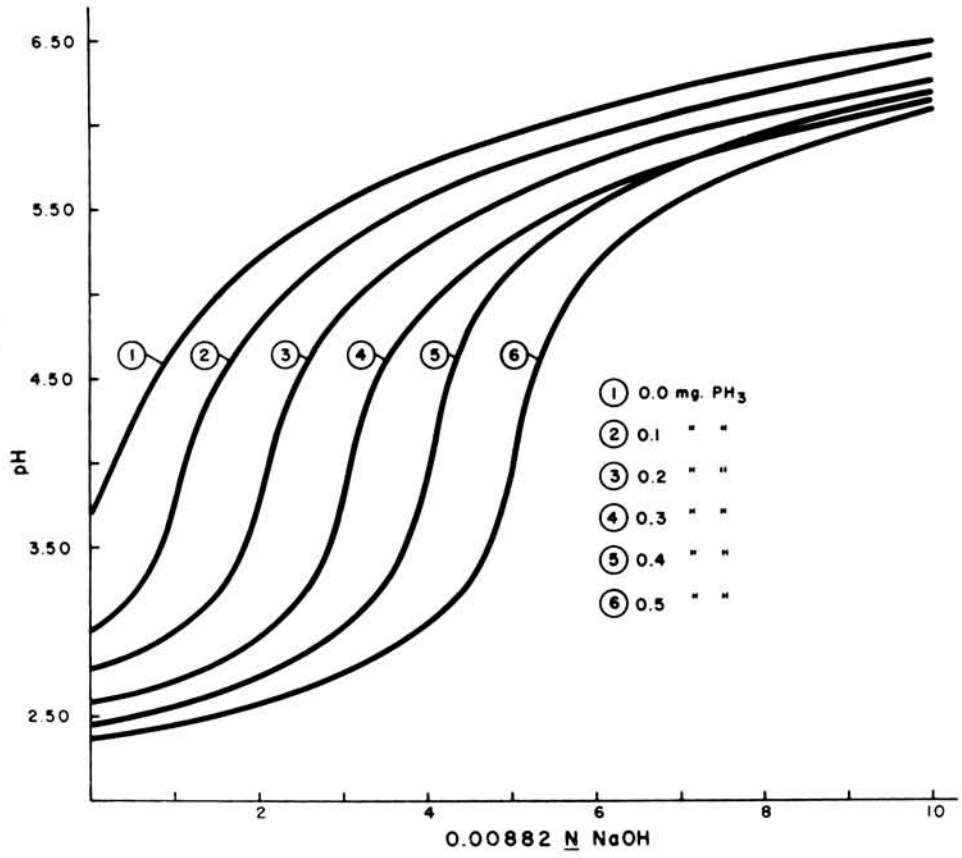

Figure 1. Potentiometric titration curves for PH_3 in the range 0.0 to 0.5 mg.

solution), progressive reduction in volume increased the magnitude of the inflection in the end-point zone. Addition of ethanol to the trapping medium further increased this effect, and a chilled mixture of 20 ml. of 1.5% $HgCl_2$ solution and 10 ml. of 95% ethanol was suitable for trapping residual PH_3 in the range 0.1 to 1.6 mg. The $HgCl_2$ content was adequate for rapid, quantitative complexing of the PH_3 conveyed in the nitrogen stream. It is not necessary to remove the $P(HgCl)_3$ precipitate by filtration before titrating the test samples. Use of an automatic titrator, such as are commercially available, was not tried, but would undoubtedly expedite the potentiometric titration procedure.

Advantages of the use of ethanol are: enhanced solubility of PH_3, thus requiring only one trap for quantitative trapping; rapid attainment of steady state during titration, permitting faster titrations, and higher and steeper titration curves in the end point zone; enhanced magnitude of the end-point break, thus increasing the sensitivity and permitting determination of PH_3 down to ± 5 μg.; improved retention of HCl generated in the complexing reaction, as shown by resistance to loss after 6 hours of continuous bubbling of N_2 gas into the ice-chilled trapping solution; stability of the $P(HgCl)_3$ complex for at least 6 hours at 24° C., 3 days at 4° C., and 3 weeks at −14° C. Thus, storage of trapped samples at sufficiently low temperatures extends the use of this method to field and laboratory investigations where analyses may not be made within 6 hours of sample injection. After the sorption investigation (Berck, 1968) was completed, additional improvement in sensitivity could be achieved by raising the 95% ethanol content of the trapping solution from 33 to 40% by volume.

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