Sorption of Phosphine by Cereal Products

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Phosphine gas (PH_3) was applied at concentrations of 0.15 to 0.60 mg. per liter to wheat, oats, barley, flax, and milled grain products in closed containers. No free PH_3 remained in any of the substrates after accelerated aeration with nitrogen. Irreversible sorption, considered chemisorption by the author, was reproducibly obtained under the experimental conditions employed. The amount of PH_3 chemisorbed was mainly affected by the type, moisture content, and physical form of the substrate, as well as by temperature and contact time. With milled wheat products, the uptake of PH_3 by wheat gluten powder, middlings, bran, and shorts was greater than that by wheat starch, flour, and wheat germ. For four different concentrations used, the absolute amounts of PH_3 sorbed were directly proportional to the amounts applied, as for first-order reactions. Presumptive evidence that PH_3 binds with proteins and complexes with mineral components of the substrates is discussed.

Phosphine, PH_3 (also known as hydrogen phosphide, H_3P), is a highly toxic gas that may be obtained by hydrolysis of metal phosphides by water or moist air. Phostoxin, a commercial product manufactured by Degesch Co., Ltd., Frankfurt, West Germany, is formulated as tablets and pellets that contain aluminum phosphide, and is a convenient source of PH_3 to combat insect infestations of grain, flour, and other stored products. The effectiveness of small amounts of PH_3 for insect control is well established (Dieterich et al., 1967). For example, Lindgren and Vincent (1966) showed that 99% of adult confused flour beetles, Tribolium confusum Duv., were killed when exposed to concentrations of PH_3 as small as 0.02 mg. per liter of air for 24 hours at 80° F.

In an earlier study (Sinha et al., 1967), the effectiveness of PH_3 against mites, insects, and microorganisms in stored wheat was investigated. The PH_3 concentration in the interstitial air of the treated grain was smaller than expected, and it was felt that sorption by the grain was responsible, at least in part, for the low levels of free PH_3 gas. Sorption of other fumigants is reviewed by Lindgren and Vincent (1962) and by Berck (1964) and is known to be affected by the nature, particle size, and moisture content of the substrate, as well as fumigant dosage, temperature, and contact time. The present report deals with the effect of the foregoing factors on sorption of phosphine by wheat, oats, barley, flax, and a variety of milled cereal products in closed systems.

This paper deals with nonrecoverable or irreversible sorption of PH_3 by cereal substrates, and which is designated chemisorption, as distinct from physisorption (amount recovered after prolonged aeration). The differentiation of chemisorption (also called chemical sorption) from physisorption (physical sorption, which includes both adsorption and absorption) is treated in texts by Garner (1957), Gregg and Sing (1967), Hayward and Trapnell (1964), and Young and Crowell (1962), among others.

To test the hypothesis that PH_3 is nonreactive with foodstuffs, permitting 100% recovery of applied PH_3, 750 determinations of recovery were made. Gaseous PH_3 was applied in sealed glass bottles at four concentrations

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to wheat, oats, barley, and flax under different conditions of moisture, temperature, particle size, and period of exposure to PH_3. After exposure, free and physically sorbed PH_3 were removed from the system by flushing exhaustively with purified N_2. The PH_3 in the effluent was trapped in ethanolic $HgCl_2$, and was determined potentiometrically (Berck, 1968). The conditions used permitted 100% recovery of PH_3 when PH_3 was added to the empty test chambers and was stored for the duration of each experiment. The difference between the amount of PH_3 applied and the amount recovered was thus an index of sorptive capacity of the substrate under test. The uptake of PH_3 by flour, wheat germ, bran, shorts, middlings, powdered gluten, wheat starch, groats, and rolled oats was also measured. Dosages applied were based on field results obtained previously (Sinha et al., 1967), and also on the comparatively low levels of PH_3 required for insect control (Lindgren and Vincent, 1966).

No free PH_3 remained in any of the cereal substrates in the closed systems after accelerated aeration with N_2, but recovery was incomplete (less than 100% of the applied PH_3) in many instances. Recoveries of the PH_3 applied varied from 100 to 0% (Figure 1) and were reproducible for given conditions. After aeration, no additional PH_3 was recovered in freeze-traps after prolonged vacuum treatment at 1 to 2 mm. of Hg. The amount of PH_3 sorbed was mainly affected by the type of substrate, temperature, moisture content, and exposure of reactive surfaces by coarse grinding of the cereal seeds.

EXPERIMENTAL

Materials and Apparatus. POTENTIOMETRIC TITRATION. The pH meter, magnetic stirrer assembly, microburet, standard NaOH and HCl solutions, nitrogen, and beakers, have been described (Berck, 1968).

PHOSPHINE SOURCES. Two sources were used: Phostoxin tablets, 3-gram, 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 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, trap bottles, and fittings have been described (Berck, 1968).
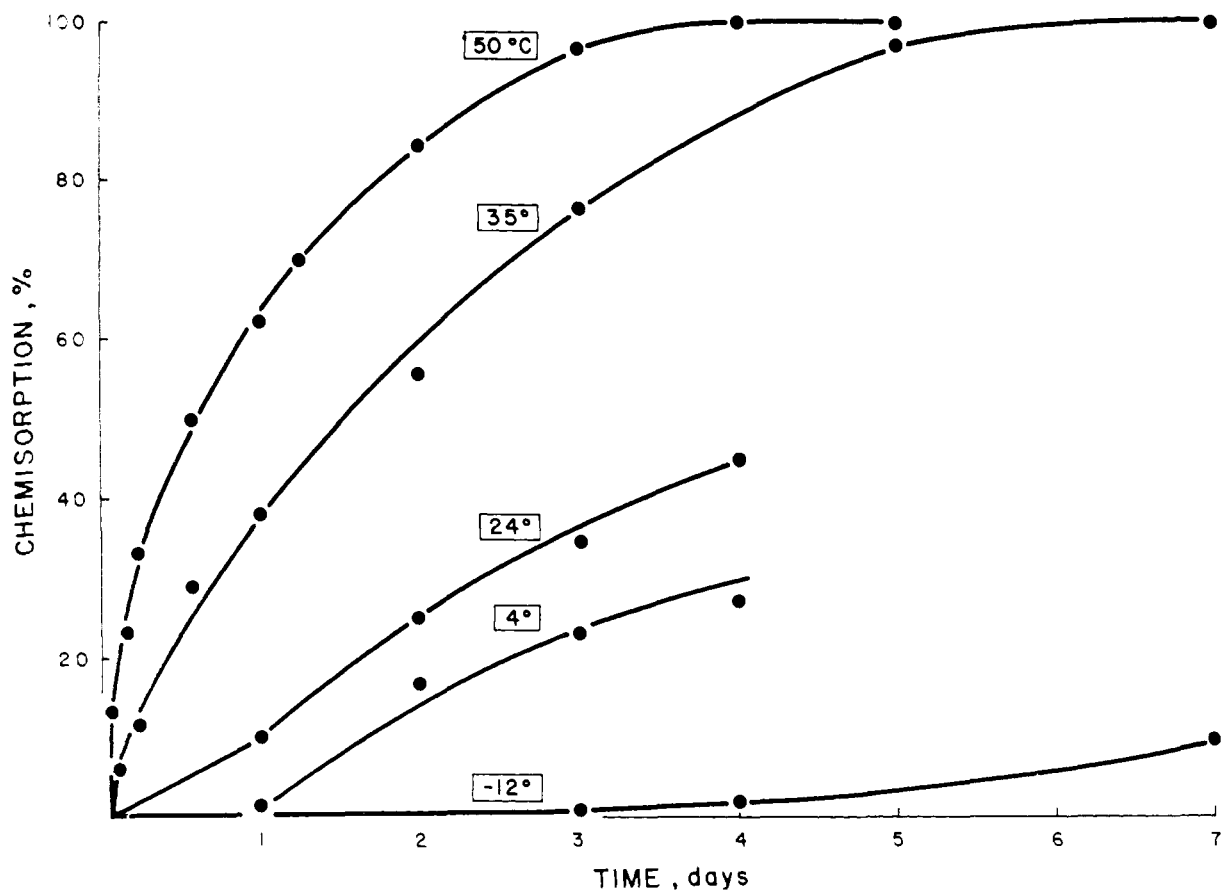
Figure 1. Effects of temperature of fumigation and contact time on per cent chemisorption of PH_3 by wheat (coarse ground, 15.0% moisture content)

FUMIGATION CHAMBERS. Quart-size square-type glass milk bottles (1.13 ± 0.003 liter capacity) containing gastight neoprene rubber stoppers, 2-hole, No. 9, and fitted as described (Berck, 1968).

CEREAL PRODUCTS. The cereal seeds and milled cereal products used in this investigation are listed in Table I. The wheat used was Average 2 Northern Grade, cleaned to a dockage level of approximately 0.3%, and obtained from the Fort William terminal elevators by the Inspection Branch of the Board of Grain Commissioners for Canada. Cleaned barley, oats, and flax (Conquest, Garry, and Raja varieties, respectively) were obtained from the Cereal Breeding Section of this research station. The two moisture levels of each of the four types of cereal seed were chosen to represent straight or acceptable as against tough or undesirable grades suitable for storage. In this regard, the upper limits of moisture content allowed under the Canada Grain Act for the grades designated as straight and tough, respectively, are: wheat, 14.5, 17.0%; barley, 14.8, 17.0%; oats, 14.0, 17.0%; flax, 10.5, 13.5%. The upper levels of moisture shown in Table I were obtained by calculated tempering (moistening) of the wheat, barley, oats, and flax. Moisture equilibrium was reached within 2 days, after which the seeds were treated with PH_3 in closed systems.

The wheat and barley were coarsely cracked in a mechanical hammer mill, omitting use of a sieve. The flax was coarsely ground in a Waring Blendor. The whole oats were squeeze-rolled through a crimping machine used in processing oats for animal feeds. The aim was to expose the surfaces of coarsely ground seed endosperm to PH_3 with a minimum of grinding that would produce small particles.

The flour, bran, shorts, middlings, and wheat germ were conventional run-of-the-mill grades, as were the wheat starch, wheat gluten, groats, and rolled oats. The wheat starch powder was of a fine particle size (<200-mesh). The wheat gluten, known as vital gluten powder, was considerably coarser. Groats are green oats (raw, or as received) that have been kilned and dehulled for manufacture into rolled oats. The main difference between the slow-cooking or old-fashioned rolled oats and the rapid-cooking or quick rolled oats is that the latter are milled at a slightly thinner setting of the rolls.

General Procedure. Glass bottles (1.13 ± 0.003 liter capacity) that served as fumigation chambers were loaded with 250 grams of cereal or cereal product, sealed, treated with PH_3, stored at 4°, 24°, and 35° C. for variable periods, degassed with N_2, and analyzed for total PH_3 recovered in the effluent, as described. For each condition of time, temperature, cereal product, particle size, and moisture content, four different concentrations in the range 0.15 to 0.60 mg. of PH_3 per liter of air were applied to determine the effect of gas concentration on sorption. Except for the groats and rolled oats, the milled cereal products were

stored at 24° and 35° C. only. Cereals of greater economic importance, such as wheat and barley, were investigated more extensively than the other cereal products listed in Table I.

Supplementary Tests. The following auxiliary tests were made for additional information about PH_3 behavior:

To supplement findings on the role of temperature and time on sorption of PH_3 by wheat, a series of determinations was made at 50° and −12° C. with coarse ground wheat of 15% moisture content (Figure 1).

To supplement data on the role of gas concentration in which the dosage applied to a fixed weight (250 grams) of substrate was progressively increased from 1 to 4 times in the range 0.15 to 0.60 mg. of PH_3 per liter of air (Table I), a limited number of tests were made in which the amount of substrate was doubled (500 grams) and the PH_3 applied was 0.44 to 0.48 and 0.66 to 0.72 mg. per liter (Table II).

One-kilogram samples of wheat that had been fumigated in boxcars with Phostoxin tablets at a commercially recommended dosage were analyzed after a 2-week aeration period for residual PH_3 by the method described (Berck, 1968).

To determine whether treatment of cereal products with PH_3 would leave residues that might kill insects or affect insect development, tests were conducted with adults and 1-day-old larvae of the confused flour beetle, *Tribolium confusum* Duv. Flour, bran, shorts, middlings, wheat germ, groats, rolled oats, wheat gluten powder, and wheat starch, all of which had been treated at a dosage of 0.60 mg. of PH_3 per liter for 3 days at 4°, 24°, and 35° C., respectively, and then aerated with N_2, were used as substrates. The insects were exposed on the products for 28 days.

Organoleptic tests were conducted by a five-man panel on PH_3-treated cereal products that had been aerated in the glass fumigation chambers with N_2 at 180 cc. per minute for 30 minutes. The object was to determine whether trace amounts of PH_3 that might be present in the products due to incomplete aeration could be detected by smell. A comparison bottle containing PH_3 diluted to a concentration of 0.002 mg. per liter of air was used for cross-reference in these tests.

To determine the solubility of PH_3 in water, 10 mg. of PH_3 in nitrogen were bubbled slowly through 250 ml. of ice-cooled distilled water in an Erlenmeyer flask for 5 minutes. The residual PH_3 in the flask space above the water was removed with N_2 and discarded. The water was then degassed with nitrogen for 45 minutes, and the recovery of dissolved PH_3 was determined.

RESULTS AND DISCUSSION

Table I shows the per cent of nonrecoverable PH_3—i.e., the relative amount of PH_3 applied that was not recovered after accelerated aeration of the cereal substrates with N_2— as a function of the substrate, particle size, moisture content, temperature of fumigation, and duration of exposure or contact time.

The nonrecoverable PH_3 is considered to be irreversibly adsorbed (Young and Crowell, 1962), which is synonymous with chemisorption, as described by Hayward and Trap-

nell (1964) and Gregg and Sing (1967). Each value in Table I is the mean of the chemisorptions obtained at four different dosages in the range 0.15 to 0.60 mg. of PH_3 per liter. The deviations shown in Table I indicate a combined effect of the error of the method (Berck, 1968) and the variability of uptake with the four dosages applied to replicates of test substrates under stated conditions of time and temperature. The latter may be regarded as time points on a reaction rate curve (Figure 1). Checks with wheat made 7 to 10 days after a given series was processed showed that the nonrecoverable PH_3 of whole kernel wheat and of coarsely ground wheat of 15.0% moisture content exposed for 3 days at 35° C. was within ±2.8 and ±6.3%, respectively, of the initial value. Variation between repeated determinations was greatest with coarsely ground cereals at the high moisture levels, and was possibly due in part to variation in particle size.

Table I shows a relative constancy of PH_3 uptake at any given time point, where $\dfrac{PH_3 \text{ sorbed}}{PH_3 \text{ applied}} = k$. This indicates that the absolute amounts of PH_3 sorbed increase in direct proportion to the amounts applied, as for first-order chemical reactions. A somewhat similar finding was obtained in previous research with ethylene dibromide, ethylene dichloride, and carbon tetrachloride applied singly and in admixture to wheat in closed systems (Berck, 1965), although in the latter instance the substrates were not aerated.

Table I and Figure 1 show that sorption of PH_3 by cereal products rises when the temperature is increased. This is characteristic of chemisorption, while the reverse effect occurs with physical sorption. A lag or induction period is indicated (Figure 1) at −12° and 4° C., respectively; this disappears when the temperature is raised. The influence of temperature on chemisorption was also manifested when recoveries of free and physically bound PH_3 by flushing PH_3-treated wheat with N_2 were greater and more consistent at room temperature than at higher temperatures obtained by use of a steam bath or modified pressure cooker.

Table I shows that reduction of particle size through cracking favors increased sorption. This effect is further enhanced by an increase in moisture content and exposure period (contact time). Nevertheless, the increase in gas uptake is not entirely due to multiplication of surface area by a decrease in particle size. Thus, even a minor decrease in particle size may yield a significant increase in sorption, as seen by comparing whole kernel oats with groats, or with coarse ground oats, which in this investigation were merely crimped and squeeze-rolled mechanically, with no appreciable change in particle size.

The role of chemical forces, as related to the chemical nature of the substrate and to the exposure of reactive sites within cereal seeds through grinding, is more readily discerned with other substrates listed in Table I. Thus, flour and wheat starch consist of finely divided particles (<200-mesh), but their uptake of PH_3 is only modest compared to that of wheat gluten powder, which is both coarser and of lower moisture content. Similarly, bran, shorts, and middlings sorbed substantially more PH_3 than raw wheat germ, flour, and starch. Similar differences were shown in the sorption profiles of these and other substrates

Table I. Chemisorption of Phosphine (Nonrecoverable PH₃) as a Function of the Nature of the Cerea

Cereal Substrate	Moisture Content, %	Temp., ° C.	% Chemisorption,[a] Days			
			1	2	3	4
Wheat, whole kernel	12.5	4	0.0 ± 0.0	1.1 ± 0.6	4.8 ± 1.7	
		24	2.2 ± 0.7	6.1 ± 1.8	18.6 ± 3.5	
		35	4.8 ± 2.3	22.5 ± 2.0	33.2 ± 1.6	
Wheat, coarse ground	12.5	4	0.0 ± 0.0		5.5 ± 2.4	
		24	5.4 ± 2.5		20.4 ± 1.5	37.2 ± 3.8
		35	18.2 ± 1.2		57.2 ± 2.7	
Wheat, whole kernel	15.0	4	0.0 ± 0.0	12.2 ± 2.8	20.8 ± 3.9	29.5 ± 1.3
		24	12.6 ± 0.7	26.8 ± 2.1	34.8 ± 1.3	47.7 ± 1.2
		35	29.4 ± 2.0	53.5 ± 2.3	69.7 ± 2.3	81.7 ± 1.7
Wheat, coarse ground	15.0	4	5.8 ± 0.3	18.5 ± 1.3	28.0 ± 2.2	35.2 ± 4.2
		24	22.8 ± 2.4	37.6 ± 2.1	43.8 ± 1.9	58.0 ± 1.4
		35	40.5 ± 1.2	54.7 ± 3.4	71.2 ± 2.5	86.7 ± 3.4
Barley, whole kernel	10.0	4	0.0 ± 0.0		5.5 ± 1.7	
		24	0.0 ± 0.0	2.0 ± 1.4		16.9 ± 0.8
		35	8.2 ± 2.5		29.0 ± 2.9	38.8 ± 2.4
Barley, coarse ground	10.0	4	0.3 ± 0.2		14.3 ± 1.1	
		24	2.4 ± 0.6		18.5 ± 0.2	
		35	10.0 ± 3.0		33.1 ± 1.8	
Barley, whole kernel	15.0	4	0.3 ± 0.3		2.9 ± 0.8	
		24	2.0 ± 1.0		15.3 ± 1.4	
		35	13.6 ± 0.6		37.3 ± 1.3	
Barley, coarse ground	15.0	4	0.9 ± 0.4		35.8 ± 0.6	
		24	29.9 ± 2.2		74.7 ± 0.4	
		35	55.5 ± 2.0		91.2 ± 1.6	
Oats, whole kernel	10.2	4	0.0 ± 0.0		6.8 ± 2.2	
		24	3.4 ± 1.3		24.2 ± 2.1	
		35	14.0 ± 2.4		37.6 ± 1.0	
Oats, coarse ground	10.2	4	0.2 ± 0.1			
		24	6.5 ± 2.1			
		35	19.0 ± 1.0			
Oats, whole kernel	15.5	4	0.7 ± 0.1			
		24	10.9 ± 0.9			
		35	23.9 ± 1.3			
Oats, coarse ground	15.5	4	0.2 ± 0.2			
		24	22.4 ± 2.6			
		35	34.9 ± 2.0			

[a] Per cent chemisorption, as used here, is the relative amount of PH₃ applied that was not recovered after prolonged aeration of the cereal substrate with nitrogen. Each value is the average ± absolute deviation from the mean of the per cent of irreversible sorption obtained from 4 different concentrations applied in the range 0.15 to 0.60 mg. PH₃ per liter of air.

Table II. Effect of Doubling the Weight of Substrate on Recovery and Per Cent Uptake of PH₃

Substrate	Conditions	Wt. of Substrate, G.	PH₃ Dosage, Mg./1.13 Liters	PH₃ Recovered, μg.	PH₃ Sorbed, %	Free PH₃, %
Wheat, whole kernel, 15.0% moisture content	Exposed 3 days, 35° C.	250	0.44	160	63.6	36.4
		250	0.66	240	63.6	36.4
		500	0.44	80	81.9	18.1
		500	0.66	120	81.9	18.1
Wheat, coarse ground, 15.0% moisture content	Exposed 2 days, 35° C.	250	0.48	180	62.6	37.4
		250	0.72	272	62.3	37.7
		500	0.48	86	82.0	18.0
		500	0.72	133	81.5	18.5

Substrate, Particle Size, Moisture Content, Temperature of Fumigation, and Duration of Exposure

Cereal Substrate	Moisture Content, %	Temp., ° C.	% Chemisorption,[a] Days			
			1	2	3	4
Flax, whole kernel	6.2	4	3.0 ± 3.0			
		24	16.4 ± 1.9			
		35	41.6 ± 1.6			
Flax, coarse ground	6.2	4	34.0 ± 1.3			
		24	42.5 ± 0.4			
		35	60.1 ± 0.8			
Flax, whole kernel	11.5	4	14.6 ± 1.5			
		24	33.3 ± 0.2			
		35	52.2 ± 1.1			
Flax, coarse ground	11.5	4	47.6 ± 2.4			
		24	62.0 ± 2.0			
		35	75.3 ± 0.4			
Flour, 1st patent	14.1	24	2.8 ± 0.8		4.9 ± 1.0	
		35	7.1 ± 2.1		11.1 ± 0.5	
Flour, 2nd patent	14.0	24	2.3 ± 2.3		8.2 ± 0.5	
		35	13.7 ± 3.4		20.1 ± 1.2	
Wheat starch, commercial	9.3	24	8.0 ± 0.6		12.1 ± 0.8	
		35	12.3 ± 1.2		16.8 ± 0.5	
Wheat gluten powder, commercial	5.5	24	35.0 ± 0.8		51.2 ± 0.5	
		35	48.9 ± 0.7		77.8 ± 0.2	
Wheat germ, raw	13.0	24	1.3 ± 1.3		18.3 ± 2.3	
		35	12.1 ± 0.6		37.3 ± 1.3	
Wheat bran, commercial	14.0	24	24.4 ± 1.2		58.3 ± 0.7	
		35	46.2 ± 0.3		77.0 ± 0.2	
Wheat shorts, commercial	14.0	24	37.2 ± 0.7		56.1 ± 0.5	
		35	56.6 ± 3.0		79.5 ± 1.9	
Wheat middlings, commercial	13.5	24	25.2 ± 1.1		33.3 ± 0.3	
		35	37.9 ± 0.2		60.4 ± 1.2	
Groats, commercial	8.0	4	13.3 ± 2.5		20.0 ± 1.6	
		24	19.3 ± 3.9		23.3 ± 1.6	
		35	25.8 ± 2.6		30.0 ± 1.7	
Rolled oats, slow-cooking	8.5	4	5.5 ± 0.3		17.4 ± 1.2	
		24	6.9 ± 0.4		22.9 ± 3.2	
		35	16.7 ± 1.2		34.8 ± 1.5	
Rolled oats, rapid-cooking	8.7	4	5.6 ± 1.2		17.7 ± 2.5	
		24	9.5 ± 1.5		23.2 ± 1.5	
		35	16.4 ± 0.4		36.3 ± 1.4	

in a previous investigation (Berck, 1965) in which ethylene dibromide, ethylene dichloride, and carbon tetrachloride were applied in the vapor phase. The sorption profiles of the two types of rolled oats (last two items, Table I) are interesting because of their similarity. In this regard, the composition and manufacture of each type are essentially identical, except for the roll settings used.

Based on the foregoing examples from Table I, the chemical nature of the substrate is a major factor with selective properties, and may predominate over physical factors such as particle size. Within this context, it is suggested that PH_3 has a greater affinity for substances that are rich in protein and mineral components. The reactivity of PH_3 with Cu, Fe, Hg, Ca, Mg, Zn, Al, and other metals is established (Van Wazer, 1958). Bran, shorts, and middlings are relatively high in both protein and minerals (ash). The greater uptake of PH_3 by second

patent (bakers') flour as compared with first patent flour (Table I) may be a reflection of the greater ash content of the former. The protein content of gluten powder is more than six times that of flour, but differences in the protein constitution may also account for the greater chemisorption of PH_3 by gluten powder compared to that of flour or wheat germ. In this connection, chemisorption of methyl bromide has been related to –SH groups in flour protein (Lewis and Eccleston, 1946; Page and Lubatti, 1940), and to methylation of amino acids of wheat protein (Bridges, 1956; Winteringham et al., 1955). Bromide residues that resulted from fumigation with methyl bromide increased with increasing protein content of mill fractions (Gibich and Pedersen, 1963). The type of wheat was a factor in the bromide levels. Lindgren et al. (1962) found little or no loss in bromide residues of fumigated wheat after 6 hours' accelerated aeration, indi-

cating that the residues were more or less permanently fixed. Bromide residues increased with an increase in the moisture content of the wheat, fumigation temperature, and exposure period. Their data indicate that fumigation with methyl bromide at lower temperatures and high dosages may result in lower bromide residues than fumigation at higher temperatures and lower dosages. Other fumigants with demonstrated chemisorption capabilities include ethylene dibromide (Bridges, 1956; Metcalf, 1963), hydrogen cyanide (Page and Lubatti, 1940), sulfur dioxide (Burroughs and Sparks, 1964), ethylene oxide and propylene oxide (Gordon et al., 1959; Wesley et al., 1965), and trichloroethylene (McKinney et al., 1957).

In summary, irreversible uptake of PH_3 (Table I) has these chemisorption features: The rate of uptake is relatively slow, but increases when the temperature is raised. Differences in affinity for PH_3 are shown by related cereal substrates, especially by different fractions of milled cereal seeds. Compared to this aspect of chemisorption, physical sorption is nonspecific. A large increase in sorption is effected by modest reduction in particle size of substrate and is presumably due to exposure of additional and more active reaction sites. This effect is enhanced by increase in moisture content of the substrate. The absolute amounts of PH_3 chemisorbed by a substrate at a given temperature and point of time are a function of the amounts applied. After aeration, no additional PH_3 is recovered in freeze-traps after prolonged vacuum treatment. This suggests that the residues are permanently fixed. Investigations with other fumigants, cited above, indicate various common features with those shown by PH_3 in this investigation. In the latter regard, the evidence for chemisorption of PH_3 is presumptive until isolation and characterization of the reaction products can be undertaken.

Two different particle sizes of wheat, dosages of PH_3, and periods of exposure were used in a limited side study to estimate the influence of amount of substrate on PH_3 uptake. Table II shows that doubling the weight of the substrate reduces the amount of free or physically bound PH_3 by 50%, and increases, but does not double, the percentage of PH_3 sorbed. These tests show that the latter value will vary considerably because of the interaction of time, temperature, moisture content, and particle size. One may nevertheless infer from Table II that, at any given time point, the free or physically bound gas will be reduced by an amount more or less inversely proportional to the weight of substrate used. This is perhaps to be expected on the premise that the average total surface area of one weight increment of cereal grain is similar to that of another increment of the same weight from the same source. Although only two dosages were used in the above tests, they confirm the constant relationship between PH_3 sorbed and PH_3 applied demonstrated in Table I and previously discussed.

Samples of wheat (13.8% moisture content) that had been commercially fumigated in railway boxcars with Phostoxin tablets at a rate of six tablets per ton and aerated for two weeks were analyzed for residual PH_3 by the method described (Berck, 1968). The mean value of residual PH_3 was 0.04 p.p.m. Such traces of free PH_3 were faintly detectable by smell.

No effects on feeding behavior, egg-laying, or insect development were observed after adults and 1-day-old larvae of the confused flour beetle, T. confusum Duv., were exposed for 4 weeks to aerated cereal substrates that had been treated with PH_3 at 0.60 mg. per liter for 3 days at 4°, 25°, and 35° C. The insects survived and developed equally well on treated and untreated flour, bran, shorts, middlings, wheat germ, groats, and rolled oats. No free PH_3 remained in the substrates and the chemisorbed residues were deemed nontoxic and innocuous to this species. With wheat starch and gluten powder, however, 100% of the insects died in both the treated and control samples, since wheat starch and gluten are evidently not suitable media for this species.

The five-man panel that attempted to detect possible traces of residual PH_3 by sniff tests could find no difference in odor between untreated samples and cereal products that had been treated with PH_3 and aerated. The characteristic odor of PH_3 was readily discerned by sniffing 1 or 2 cc. of discharge from a syringe containing 0.002 mg. of PH_3 per liter.

The solubility of PH_3 in water, by the experimental method indicated in the preceding section, was 490 ± 7 μg. per 250 ml. or 0.000196% at a temperature of approximately 3° C. By use of a different experimental setup, Rauscher et al. (1965) obtained a solubility value of 0.000160 to 0.000166% at room temperature. The solubility value reported for hydrogen phosphide, H_3P, in the Handbook of Chemistry and Physics (1967) is 26 cc. per 100 ml. of H_2O at 17° C., equivalent to 37.2 mg. per 100 ml. or 0.0372%. The latter is considerably higher than the values mentioned above.

Table I indicates that the relative amounts of PH_3 irreversibly sorbed by the fumigated cereal products can be large under favorable conditions of moisture content, temperature, and time. Nevertheless, in absolute units (micrograms of PH_3 per gram of substrate), the amounts sorbed are small. Thus, with 250 grams of cereal product, a dosage of 0.6 mg. of PH_3 per liter (0.68 mg. per 1.13 liters), and an 80% uptake, the amount of PH_3 chemisorbed is equivalent to 2.16 p.p.m.

The dosages used in this investigation are well below those used in the fumigation of boxcars, grain bins, or warehouses, or where there is rapid volatilization, such as with the use of a grinder blower to treat packaged foods (Rauscher et al., 1965). Furthermore, the gastight conditions used in this laboratory investigation are normally not found in commercial fumigation. The respective concentration-time relationships in commercial fumigation and this investigation are also different. Thus, under average commercial conditions, PH_3 is generated relatively slowly from aluminum phosphide tablets, whereas in this investigation PH_3 was applied in the vapor phase for greater convenience.

Bruce et al. (1962) indicate that only insignificant amounts of free PH_3—e.g., 0.046 to 0.006 p.p.m.—may be expected in PH_3-treated grain after adequate aeration. This author's results are in agreement on this point, and with exhaustive aeration as described, no measurable PH_3 remained in the cereal substrates that were tested. Nevertheless, through the use of closed systems whereby PH_3 was confined, evidence for chemisorption of PH_3

by cereal products was obtained. This underlines the need to investigate fumigant gases for both physically bound and chemically bound residues that may result under the conditions of use.

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