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Phosphine Sorption and Desorption by Stored Wheat and Corn

Theodore Dumas

The sorption and desorption of PH_3 from wheat treated with concentrations of 0.5–5 mg/kg of wheat was determined at 25, 45, and 85 °C. The desorbed PH_3 was extracted from the air by passing through a cold trap; here sufficient quantities of the gas could be accumulated for accurate analysis by GLC. Most of the PH_3 was desorbed in the first 2–3 days but small amounts continued to desorb for many weeks following treatment. After 220 days of aeration, PH_3 was still present in the grain and desorbing at the rate of ppt (10^{-12} g). For a wide range of concentrations, about 10% of the PH_3 applied was found to be adsorbed. The amount of physically sorbed PH_3 increased with the fumigant concentration applied and with the length of exposure. Because of reduced reactivity even when the temperature was increased to 85 °C for several days, unreacted PH_3 still desorbed slowly from wheat. Corn aerated 26 days desorbed 0.004 ng/g in 2 days.

Hydrogen phosphide (PH_3), also known as phosphine, is toxic at very low concentrations and it is used in fumigation of grains and other stored products. Because of its wide use as a fumigant it was necessary to investigate the behavior of PH_3 insofar as sorption and desorption could occur during and after fumigation. In previous publications Berck (1968) and Berck and Gunther (1970) attributed to chemisorption the PH_3 portion which could not be recovered after fumigation. On the other hand, Rauscher and Mayr (1968) found complete recovery when they fumigated wheat with PH_3 for short periods of time. Robinson and Bond (1970) after fumigation with radioactive $^{32}PH_3$ showed that small amounts of residual radioactive ^{32}P remained for days following the treatment. To investigate this apparent difference in results, low levels of PH_3 desorbing from treated materials were determined using an extremely sensitive method that could measure amounts down to ppt (10^{-12} g).

MATERIALS AND METHODS

Soft winter wheat of 13.1% and field corn of 8.8% moisture content were fumigated with 0.5 and 5 mg of PH_3/kg of commodity at 25 °C. The fumigation of wheat was made in 240-mL gas-adsorbing bottles by injecting with a syringe 1–100 μg of PH_3 gas. The PH_3 gas was generated from Phostoxin tablets by the method described by Kashi and Bond (1975). Because very small quantities of fumigant were involved in these experiments and because the concentration in air was always well below the lower explosive limit of 1.79% by volume in air, no hazards were created by handling this fumigant. After treatment the materials were left to aerate with laboratory environment for a period of several weeks, and the rate of desorption was determined at selected time intervals. This was done by placing wheat or corn samples in a glass desorption chamber consisting of a 240-mL gas adsorption bottle fitted with stopcocks. The desorbed PH_3 was collected in a cold trap (Dumas, 1978) and analyzed by gas chromatography. A sample size of 1–100 g of fumigated commodity was used depending on the level of PH_3 absorbed. The rate of desorption for a range of concentrations and exposure times was determined mainly at 25 °C, but it was also investigated at 45 and 85 °C to determine if desorption or reaction could be accelerated at higher temperatures. The sorption on the empty desorption chambers was determined and found to be less than 3% in 24 h for 50 μg of PH_3 applied.

Phosphine retention in wheat was determined by treating wheat with a dosage of 5 mg/kg of PH_3 using Phostoxin pellets which were placed at the bottom center of a 25-L container containing 13.7 kg of wheat and

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Table I. Residual Phosphine Desorbed from Wheat Fumigated with PH_3 (5 mg/kg) for 19 Days

aeration, days	desorption, days	top, ng/g	bottom, ng/g
4	4 h	0.2	
4	1	2	
6	1	0.02	0.01
6	3	0.1	0.2
15	1	0.005	0.05
15	4	0.06	0.1
35	1	0.004	
35	4	0.02	0.01
42	2	0.006	
42	7	0.02	0.01
71	4	0.02	0.01
130	6	0.002	0.008
220	3	0.0002	0.004

Table II. Residual Phosphine Desorbed from Corn Fumigated with PH_3 (0.5 mg/kg) for 4 Days

aeration, days	desorption, days	PH_3 desorbed, ng/g
1	1	0.08
2	1	0.03
3	3	0.02
26	2	0.004

phosphine was slowly released to fumigate the wheat. Phostoxin is an aluminum phosphide product of Degesch Frankfurt on Main, West Germany. After 19 days of exposure, the lid was removed and the wheat was allowed to aerate. Wheat samples were taken at various intervals of time after the treatment and analyzed to determine the quantity of fumigant desorbing from the wheat per unit of time. Samples of wheat were taken from two points: the top 2-cm layer and from an opening on the side of the container 2 cm from the bottom. For the analysis of the phosphine desorbed, 10 g of fumigated wheat was taken from the top after 4 days of aeration. The sample was placed in the desorption chamber for a selected length of time, then the space was analyzed by the method previously described (Dumas, 1978).

RESULTS AND DISCUSSION

Table I shows that for a 4-h desorption time, 0.2 ng of PH_3/g was desorbed. Analysis of samples from the top and bottom showed that the amount of PH_3 desorbed from the top sample was about twice that of the bottom for the first 70 days. After that the bottom samples released up to 20 times higher amounts after 220 days aeration. The amount of PH_3 desorbed from the top decreased with time, initially fast for the first 15 days, leveling after 30 days, and still desorbing at a slow rate after 220 days of aeration. This seems to indicate that PH_3 is held in the capillaries of the wheat, delaying the desorption time. The presence of PH_3 after a long aeration time could indicate slow reactivity with the commodity fumigated and low residues from reaction products. The amounts of unreacted PH_3 found by desorption after the initial few days of aeration are below the 1-ppb (10^{-9} g) level, and this is well below the permissible residue level of 0.3 ppm (Am. Conf. of Gov. Ind. Hyg, 1964).

Table II shows the results of corn fumigation with 0.5 mg of PH_3/kg, exposed for 4 days. After aeration and analysis by desorption, corn showed a slow desorption rate similar to wheat. Although it was treated with one-tenth the amount usually used for wheat fumigation, after 26 days of aeration 0.004 ng of PH_3/g of corn was desorbed in 48 h. In this case, as in that of the wheat fumigation, we see that the desorption is slow and the PH_3 amount is not significant from the point of view of permissible residue level.

In Table III is shown the sorption of PH_3 for a range of concentrations from 1 to 100 μg/240 mL at 25 and 85 °C in an empty chamber and in one with 10 g of wheat. The sorption increase was small with the increase of temperature. At the 8-μg level sorption by wheat was similar to the empty flask, where at the 100-μg level there was 4 μg at 25 °C and 41.3 μg at 85 °C after 3 days of exposure. From these data we see also that the percent sorbed decreases with the amount applied which indicates mainly adsorption. The fact that PH_3 is mainly adsorbed and not chemisorbed or reacted is important because, with the increase of PH_3 applied, more is available for insect control for several days. This is more important because for effective insect control with PH_3 long exposure of several days is necessary at low concentrations (Monro, 1969). The amounts desorbed are low, but PH_3 is very toxic and for *S. granarius* the LD_{50} is 0.2 ppm at 504 h of exposure (Bond et al., 1977).

In Table IV is shown the desorption rate for the 1 h to 3 days of exposure of 10 g of wheat to 5.5 mg of PH_3/kg. The results show that most of the PH_3 would desorb in the first 2 h. After the initial 2 h, the wheat exposed for 1 h desorbs less than the one exposed for 3 days. This seems to indicate that for the 1 day of exposure PH_3 is adsorbed more on the surface and desorbs faster.

In Table V is shown the hourly desorption rate for 1 h and 3 days of exposure. The PH_3 desorbed at the fifth hour interval for the 1-h exposure was as low as the one at the ninth hour interval for the 3-day exposure. This indicates a deeper penetration into the capillaries of the wheat at longer exposure times.

In Table VI is shown the effect of temperature on sorption and the desorption rate. Adsorption increased with the increase in temperature to more than one-half the amount applied at 85 °C after 3 days of aeration when wheat was present. Adsorption in the empty flask was also nil. This could indicate that the loss of phosphine was due to adsorption as well as chemisorption or formation of reaction products as oxy acids of phosphorus (Robinson and Bond, 1970).

In Table VII is shown the effect of temperature on the rate of PH_3 desorption at 25, 45, and 85 °C. For the first 1-h interval the desorption rate is two times faster at 85 °C, but at the end of 14 days the total amount at 25 °C

Table III. Quantity of PH_3 (μg) after Sorption in 240-mL Flasks Function of Time and Amounts Applied at 25 and 85 °C

	recovered								
	empty flask			flask with 10 g of wheat					
	25 °C			25 °C			85 °C		
applied	1 h	24 h	72 h	1 h	24 h	72 h	1 h	24 h	72 h
1	0.73	0.66	0.63	0.75	0.78	0.8	0.88	0.68	0.5
4	3.6	3.5	3.4	3.5	3.5	3.5	3.9	3.5	2.5
8	7.1	6.7	6.1	7.1	6.7	7	7.4	5	3.2
50	41.6	39	35.9	39.3	34.5	30	44.6	25	17.3
100	89	82	79.6	82.7	78.8	74.6	65.6	44	38.3

Table IV. Phosphine Desorption from 10 g of Wheat Fumigated with 5 mg of PH_3/kg of Wheat

fumigation time	desorption time	desorbed PH_3,[a] μg
1 h	first hour	2.7
	second hour	0.24
	third hour	0.04
	first 24 hours	0.0007
1 day	first 2 hours	3
	second 2 hours	0.3
	third 2 hours	0.003
	first 24 hours	0.04
3 days	first 2 hours	3
	second 2 hours	0.9
	third 2 hours	0.04
	first 24 hours	0.07

[a] Average of eight experiments.

Table V. Desorption Rate for 10 g of Wheat Fumigated with 50 μg of PH_3 for 1 h and 3 Days

desorption time interval	desorbed PH_3 from 3 days of exposure, μg	desorbed PH_3 from 1 h of exposure, μg
first hour	3.7	2.7
second hour	0.45	0.24
third hour	0.04	0.04
fourth hour	0.04	0.004
fifth hour	0.02	0.0007
sixth hour	0.003	0.0003
seventh hour	0.003	
eighth hour	0.002	
ninth hour	0.0008	

Table VI. Sorption of PH_3 at 25, 45, and 85 °C by the Empty 240-μL Flask and 10 g of Wheat Treated with 1.36 or 54.4 μg of PH_3

temp, °C	time, h	sorption,[a] μg: flask	PH_3 applied, 1.36 μg to 10 g of wheat	flask	PH_3 applied, 54.4 μg to 10 g of wheat
25	1	0.26	0.16	13.4	13.4
25	3	0.26	0.2	12.6	14.4
45	1	0.18	0.36	7.4	9.4
45	3	0.2	0.36	5.4	12.4
85	1	0.19	0.04	13.4	16.3
85	3	0.23	0.08	14.4	17.4
85	6	0.25	0.17	16.6	20.7
85	3 days			16.6	32
85	4 days				32.5
85	5 days				36.8

[a] Sorption was determined by the decrease of PH_3 in the space during exposure.

was greater than the other temperatures. This would indicate some losses by reaction or decomposition at 45 and 85 °C. After 14 days of desorption, the total amounts of PH_3 desorbed were about the same at 45 and 85 °C and about double at 25 °C. This indicates that the desorption could be accelerated by increasing the temperature. For this reason the higher temperatures are useful for a fast test to determine if PH_3 is present and is helpful when the PH_3 amount is very low and hard to detect.

Table VII. Desorption Rate for 50 g of Wheat Fumigated with 50 μg of PH_3 for 3 Days and Aerated 3 h

desorption time interval	desorption temperature °C for 10 g of wheat: 25 °C	45 °C	85 °C
	PH_3, ng		
1 h	11	9.7	19.7
1 h	2.8	3.8	2.4
2 h	3	2.2	3.7
	25 °C	25 °C	25 °C
1 day	13	2.7	0.4
2 days	8.6	4.2	0.2
4 days	3.6	2.3	0.2
7 days	1.9	0.62	Tr[a]
14 days	2.2	1.0	Tr

[a] Trace.

Table VIII. Residual PH_3 in Wheat Fumigated in a Grain Elevator with 120 Pellets Aluminum Phosphide/1000 Bushels

aeration time, days	desorption time, days	ng/g of PH_3 desorbed: 0.3 m deep	7.5 m deep	conveyor belt
1	1	10	20	2
2	1	0.6	6	0.5
5	4	0.3	7.5	2
35	6		0.2	
44	9		0.15	
120	50		0.15	

In Table VIII is shown the PH_3 residue in the field application. Grain was treated in a grain elevator with 120 pellets of aluminum phosphide per 1000 bushels of wheat, with 14% moisture. Samples for analysis were taken from three points: 0.3 m deep, 7.5 m in the bin, and from the conveyor belt as the grain was being moved from the bin. The samples were left in the air for 1–120 days. In the 7.5-m-deep sample after 1 day of aeration 20 ng of PH_3/g of wheat desorbed in 24 h and after 120 days a small amount of PH_3 was still present, 0.15 ng of PH_3/g of wheat when kept for 50 days in the desorption chamber.

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