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Sorption and Recovery of Phosphine

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Minute quantities of phosphine were added to several cereal products and inert materials to investigate if temperature, duration of contact, and various aeration conditions would alter recovery. Previous experiments had shown that phosphine could diffuse through porous materials quite readily, so diffusion studies were also conducted at room temperature and elevated temperature conditions. Loss of added phosphine and poor recovery were shown to occur at elevated temperatures from systems containing cereal products or inert materials when proper precautions were not taken to insure an airtight system. Loss of phosphine was prevented and recovery greatly improved when an airtight system was used in the experiment.

Phosphine has gained a continuously rising importance as a fumigant for the last few years, initially being used as a grain fumigant and later as a fumigant for a vast number of human food products, animal feeds, and tobacco.

The development of Phostoxin tablets and pellets has provided a safe means of fumigating with phosphine, and registration of this product was previously based on the assumption that following adequate aeration no residual phosphine would be found in the final manufactured commodity.

Various experiments reported by Dieterich *et al.* (1967) have demonstrated that a residue can exist if adequate aeration has not been employed. This paper also reported the analysis of a large number of commodities which showed that, following proper aeration, no residue can be detected. Sullivan *et al.* (1969a,b) conducted additional studies on tobacco and a series of whole in-shell nuts and nut meats which showed that, immediately following fumigation, a residue can be detected but falls off rapidly following proper aeration. Robinson and Bond (1970) used radioactive phosphine ($^{32}PH_3$) in studying recovery of the applied fumigant from wheat. They found that small residues would exist and showed that the residue consisted of oxyacids of phosphorus and that oxygen was necessary for this reaction. Bond (1971) reported similar results, and again oxygen was necessary for the formation of the oxyacids of phosphorus. The formation of these acids is greatly decreased in a nitrogen atmosphere. Hilton (1971) also confirmed the results reported by Robinson and Bond (1970).

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Additional studies are being conducted at the present time to determine if the reaction rate of radioactive phosphine ($^{32}PH_3$) to oxyacids of phosphorus is faster than nonradioactive phosphine, and if exchange is possible in both insect systems and various commodities. These studies will be reported at a later date.

Two papers were published by Berck (1968a,b) describing recovery experiments following fumigation of raw and processed commodities, which reported a different result than those found by Dieterich *et al.* (1967), but which also stated that no organoleptic change between treated and untreated commodities could be detected and no evidence of residues could be found in the products.

The analytical procedure used by Berck (1968a) was perfectly acceptable and has also been reported by White and Bushey (1944). The authors of these papers found similar results as far as recovery from an empty vessel was concerned, and also reported similar solubility of phosphine in water.

As a result of the differences reported by Berck (1968a) and Dieterich *et al.* (1967), a study was conducted to establish if different methods were necessary to show that added phosphine could be recovered. The major differences that existed between the two series of studies reported were the volume of the vessels employed for fumigation, the method of aeration, and the dosage rates. Dieterich *et al.* (1967) used either an 8- or an 11-l. desiccator with a tight-fitting seal as a fumigation vessel and an accelerated aeration with warm nitrogen and mechanical stirring of the commodity, and a dosage rate of 1.5 to 5.7 mg/l. Berck (1968a) used a flask with a volume of 1.13 l., a dosage rate of 0.1 to 0.6 mg/l., and aerated with nitrogen with occasional shaking.

Since Robinson and Bond (1970) had reported that residues of oxyacids of phosphorus increased as the concentration of

Table I. Recovery of PH_3 after Fumigation of Wheat Flour

Flask no.	Dosage PH_3, mg	Recovered from space, mg	Recovered from flour, mg	Total recovery, mg	Percent of dosage
1	3.40	3.30	0.06	3.36	98.82
2	3.40	3.27	0.08	3.35	98.53
3	3.60	3.50	0.08	3.58	99.44
4	3.60	3.52	0.05	3.57	99.17
5	3.63	3.54	0.05	3.59	98.89
6	3.63	3.52	0.08	3.60	99.17
7	3.92	3.77	0.10	3.87	98.72
8	3.92	3.81	0.06	3.87	98.72
9	4.00	3.91	0.06	3.97	99.25
10	4.00	3.92	0.07	3.99	99.75
11	4.10	4.00	0.07	4.07	99.26
12	4.10	4.02	0.06	4.08	99.51
13	8.65	8.51	0.09	8.60	99.42
14	8.65	8.48	0.09	8.57	99.07
15	8.74	8.60	0.06	8.66	99.08
16	8.74	8.50	0.08	8.58	98.16
17	8.74	8.58	0.09	8.67	99.19

Table II. Recovery of PH_3 after Fumigation of Wheat Flour at Room Temperature and at 50°C

Flask no.	Dosage PH_3, mg	Exposure time, hr	Recovered, mg	Percent of recovery
Wheat flour at room temperature				
1–5	0.376	20	0.380	101.06
6–10	0.376	48	0.376	100.00
11–15	0.204	72	0.205	100.49
16–20	0.254	7 days	0.254	100.00
Wheat flour at 50°C				
1–5	0.425	24	0.346	81.41
6–8	0.452	24	0.215	47.56
9–14	0.425	72	0.241	56.70
15–17	0.452	72	0.188	41.59

Table III. Recovery of PH_3 from Inert Material at 50°C

Flask no.	Material	Dosage PH_3, mg	Recovered, mg	Percent of recovery
1–2	Silicone dioxide	0.463	0.221	47.73
3–4	Glass rings	0.496	0.243	48.99

radioactive phosphine ($^{32}PH_3$) was increased, and the recoveries reported by Berck (1968a) and Dieterich *et al.* (1967) differed, a series of experiments was carried out to further investigate the problem.

EXPERIMENTAL

Two methods of phosphine generation were employed. In the first method, Phostoxin tablets were placed in an airtight, 2000-l. tank. Air samples were taken from the tank by means of a syringe; the first two syringefuls were rejected, the third was used for control analysis, and the fourth was used for injection into the fumigation bottle. In the second method employed, phosphine was generated in a container and a calculated amount transferred, following the same procedure described in the first method.

The possibility of recovering small quantities of phosphine from commodities at higher temperatures (approximately 50°C), using the equipment described in the report by Dieterich *et al.* (1967), was studied. Eleven-liter fumigation vessels containing 250 g of wheat flour with a 15% moisture content were used for this experiment. The administered dose, analyzed prior to injection, was introduced by means of a syringe. The vessels were exposed by varying amounts of phosphine (3.4 to 8.74 mg) for 72 hr at a temperature of 50°C. The flasks were then aerated for 2 hr with nitrogen at a rate of 18 l. per hour with strirring. The results are shown in Table I. Recovery approximated 100%.

Table IV. Recovery of PH_3 from Wheat Bran, Oat Flakes, and Wheat Flour at 50°C with Paraffin-Coated Stoppers

Commodity	Flask no.	Dosage PH_3, mg	Recovered, mg	Percent of recovery
Wheat bran	1	0.136	0.136	100.00
	2	0.496	0.486	97.98
	3	0.496	0.475	95.76
Oat flakes	4	0.068	0.068	100.00
	5	0.486	0.486	100.00
	6	0.486	0.475	97.73
Wheat flour	7	0.147	0.136	92.51
	8	0.147	0.147	100.00
	9	0.520	0.509	97.88

The recovery of phosphine from fumigated commodities at 24 and 50°C, using equipment equivalent to that described in the reports published by Berck, was studied, but a sufficient nitrogen flow and aeration time which, from previous studies were known to be necessary, were used.

Flasks having a 1.13-l. capacity were then employed, with each containing 250 g of wheat flour having a 10% moisture content. The neoprene-stoppered flasks were exposed to small amounts (0.204 to 0.376 mg) of phosphine, introduced by syringe, for time periods ranging from 20 hr to 7 days. The administered phosphine was recovered by aerating for 1 hr with 18 l. of nitrogen with continuous shaking. The mean doses administered and the mean recoveries are presented in Table II. This experiment demonstrated that the length of exposure time would not cause any change in recovery.

An identical experiment was performed with the exception that the temperature of the flasks was maintained at 50°C rather than room temperature. In this experiment, phosphine (0.425 to 0.452 mg) was injected into the neoprene-stoppered flasks and the exposure time was either 24 or 72 hr. The recoveries were accomplished by aerating for 1 hr with 18 l. of nitrogen and continuous shaking. The mean recoveries, which are also presented in Table II, show the remarkable lowering of the recovery values due to diffusion of the phosphine through the neoprene stopper at this elevated temperature. In order to demonstrate that diffusion, rather than sorption, had occurred, the experiment was repeated with the exception that either 500 g of silicon dioxide or 250 g of glass rings were placed in the fumigation vessel instead of wheat flour containing 15% moisture. Recovery values, which did not improve, are shown in Table III.

Another experiment was conducted to demonstrate that diffusion could be prevented at an elevated temperature. In this experiment, three different commodities were fumigated for 24 hr with varying amounts of phosphine (0.068 to 0.520 mg). The commodities used for this experiment were wheat bran (11.4% moisture), oat flakes (11.4% moisture), and wheat flour (8.8% moisture). In addition, melted paraffin was poured over the neoprene stopper and outlet tube prior to heating to 50°C. Previous experiments had demonstrated that phosphine gas would not diffuse through paraffin. The

Table V. Recovery of PH_3 after Fumigation of Wheat Flour in Partially Evacuated Vessels

Flask no.	Nitrogen, °C	Dosage PH_3, mg	Recovered, mg	Percent of recovery
1	20	0.339	0.305	89.97
2	20	0.339	0.316	93.21
3	20	0.339	0.328	96.75
4	40	0.339	0.336	99.11
5	40	0.339	0.332	97.93
6	40	0.339	0.321	94.69

fumigation vessels were maintained at 50°C for 24 hr and then were aerated for 1 hr with 18 l. of nitrogen with continuous shaking. These results are presented in Table IV and clearly demonstrate that diffusion did not occur and the administered amount of phosphine could be recovered.

Diffusion had been shown to occur in the previous experiments due to elevated temperatures and shown not to occur at room temperature. The authors then performed an experiment where the flasks were partially evacuated prior to heating to allow for the expansion of the gases, including the injected phosphine which was present in the fumigation vessels. The exposure period for 250-g samples of wheat flour was 72 hr with similar amounts of phosphine (0.305 to 0.366 mg) administered immediately after the flasks were evacuated. Aeration with nitrogen at a rate of 18 l. per hour for 3 hr at 16-hr intervals was carried out with the nitrogen at 20°C for half the samples and at 40°C for the remaining samples. The recoveries obtained are presented in Table V and indicate that diffusion did not occur due to expansion of the gases in the partially evacuated vessels.

Berck stated that recoveries were poor at room temperature due to chemisorption and that heating did not increase the recoveries; therefore the phosphine could not be physisorbed. The authors of this paper realized that the insufficient aeration of 180 cm^3 for 30 min and only surface rinsing resulted in the low recoveries reported by Berck. In order to prove this, fumigation vessels containing 250 g of wheat flour were treated with varying amounts of phosphine (0.362 to 1.017 mg) and the neoprene stoppers coated with melted paraffin. The vessels were then heated at 50°C for a 24-hr period. Aeration was carried out by using 18 l. of nitrogen per hour for 1, 3, and 6 hr without stirring. The cumulative recoveries are presented in Table VI. This experiment demonstrated that recoveries are poor after 1 hr, even with an aeration rate of 18 l. per hour, but that longer aeration times can increase the recoveries significantly. This experiment also showed that stirring the fumigated product is an absolute necessity when shorter aeration periods are employed.

Table VI. Cumulative Recovery of PH_3 after Fumigation of Wheat Flour at 50°C

Flask no.	Dosage PH_3, mg	Recovered after 1 hr, mg	Recovered after 3 hr, mg	Recovered after 6 hr, mg	Percent recovery
1	0.441	0.158	0.328	0.396	89.79
2	0.418	0.146	0.336	0.415	99.28
3	0.407	0.181	0.294	0.362	88.94
4	0.486	0.192	0.384	0.476	97.94
5	0.452	0.169	0.372	0.395	87.38
6	0.396	0.136	0.271	0.384	96.96
7	0.384	0.146	0.259	0.327	85.15
8	0.362	0.136	0.317	0.353	97.51
9	1.017	0.893	1.006	1.006	98.91
4	0.938	0.813	0.937	0.937	99.89
11	0.859	0.723	0.859	0.859	100.00
12	0.441	0.158	0.328	0.396	89.79
13	0.418	0.146	0.336	0.415	99.28
14	0.407	0.181	0.294	0.362	88.94
15	0.486	0.192	0.384	0.476	97.94
16	0.452	0.169	0.372	0.395	87.38
17	0.396	0.136	0.271	0.384	96.96
18	0.384	0.146	0.259	0.327	85.15
19	0.362	0.136	0.317	0.353	97.51

CONCLUSIONS

The results of this investigation have clearly demonstrated that minute quantities of phosphine can be recovered if proper aeration rates, accompanied by stirring, are applied. These data have also demonstrated that elevated temperatures can result in loss by diffusion of the phosphine through a porous stopper. This can be prevented by using an airtight system for fumigation. The simple coating of a porous stopper with melted paraffin can insure airtightness and prevent loss by diffusion. These data have also shown that phosphine gas is not chemisorbed to the fumigated products and the applied amounts can be recovered when sufficient precautions are used during the experiment.

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