

Figure 6. Residues of methidathion (open symbols) and its oxygen analogue (closed symbols) on Arlington fine sandy loam treated with 700 ppm methidathion under dark storage (triangles), ambient air and sunlight (squares), or 0.5 ppm ozone and sunlight (circles).

degradation and oxon production intermediate between the control samples and those exposed to 0.5 ppm ozone. On the weathered samples some of the effects were probably due to ultraviolet radiation, which has been observed by Spear (1976) to cause the thion-to-oxon conversion with parathion.

Ozone exposure experiments were conducted during March, 1977; the average maximum air temperature during this time was 66 °F (19 °C); soil sample temperatures again were considerably higher. The rate of disappearance of methidathion was greatly accelerated by 0.5 ppm ozone compared to the laboratory control samples. In general, the rate of oxon formation was increased by ozone, but this was not consistently the case, as shown by the results for the "Visalia" silt loam (Figure 1), where there is no sig-

nificant difference between the ozone exposure and normal weathering in oxon formation rates. In the cases of the Laveen loamy sand and the Arlington fine sandy loam soil, the concentration of oxon after 10 days was far greater than the concentration of parent compound.

The soil thin-layer technique is a convenient method for studying the dissipation, degradation, and alteration of pesticides on air-dry soil. Any pesticide can be incorporated into the soil and soil type and environmental variables can be altered to determine what effects are produced.

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Determination of Phosphine in Wheat by Headspace Gas-Liquid Chromatography

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A relatively fast gas chromatographic method has been developed for the determination of residual phosphine (PH₃) in wheat. The phosphine was released by grinding the grain in a gas-tight blender jar. After equilibrium had been reached, samples from the headspace gas were injected directly into the gas-liquid chromatograph and measured against standards.

Hydrogen phosphide, or phosphine, PH₃, has been used to control stored grain pests for a number of years (Dieterich et al., 1967). The gas is generated by the action of moisture on aluminum phosphide preparations.

Phostoxin, manufactured by Degesch, Frankfurt/Main, Germany, is available in tablets or pellets. A 3-g tablet or 0.6-g pellet releases 1 g or 0.2 g of phosphine, respectively.

As phosphine is toxic at low levels (LCLo: 8 ppm; Christensen and Luginbyhl, 1974), it is necessary to monitor any residual gas in the grain. This has previously been done by colorimetric (Bruce et al., 1962) or chemical

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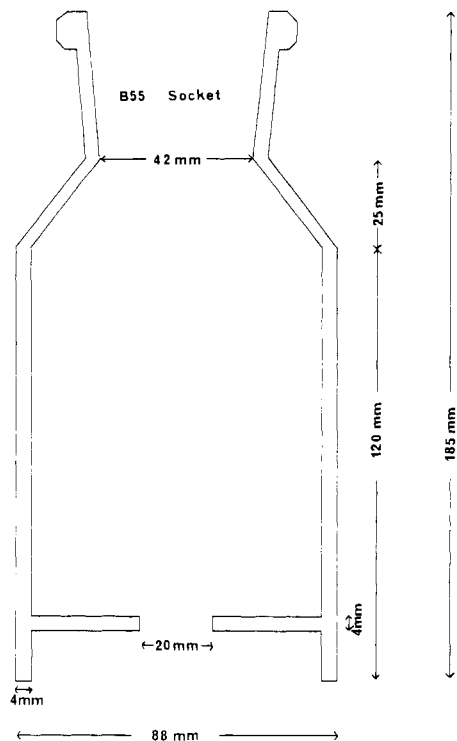


Figure 1. Glass gas-tight blender jar; neck reduced to B14 using B55 to B14 adapter.

(Dieterich et al., 1967; Berck, 1968) methods.

EXPERIMENTAL SECTION

Apparatus. Gas Concentrate Flasks. The gas was generated by the addition of water to a weighed amount of Phostoxin tablet in a glass Büchner filter flask. The latter was fitted with a stopcock adapter in the neck and a rubber septum in the side arm. It was evacuated before the gas was generated and brought back to atmospheric pressure after generation was complete. The amount of tablet taken was dependent on the size of the flask. The volume of air removed by evacuation had to be greater than the volume of the gases generated by the tablet.

Phosphine Standards. A range of working standards was prepared by diluting appropriate volumes of this concentrate in conical flasks of known volume and fitted with septa. [The septa that fit 1-oz "Clinbritic" bottles were found to be a suitable size for a B14 Quickfit flask neck (available from Townson & Mercer (Vic) P/L., Australia)].

Fumigation Flasks. Thirty-seven milliliter hypovials fitted with butyl rubber septa and aluminum seals (Pierce Chemical Company, Ill.), or 50-mL conical flasks fitted with the "Clinbritic" septa were used.

Grinding Equipment. A Waring Blendor with a glass gas-tight blender jar, fitted with a septum, was used to grind the wheat. The blender jar, illustrated in Figure 1, was made to specification by Halu Glass Manufacturing, Victoria, Australia. Silicone grease was used on the ground glass joint.

Syringe. Hamilton gas-tight syringe, 500 μ L.

Gas Chromatograph. A Hewlett Packard 7620A G.C. equipped with a Tracor FPD and a 190 cm \times 4 mm i.d. glass column, packed with 3% Carbowax 20 M on Gas-Chrom Q, 80-100 mesh, was used. Temperatures were 140, 50, and 160 $^{\circ}$ C for the injection port, column and detector, respectively, and flow rates for H₂, O₂, and N₂ were 160, 40, and 30 mL/min, respectively.

Procedure. Fumigation of Samples. Ten samples of wheat were fumigated and aired in the laboratory. Fu-

Table I. Field-Treated Samples: History and Residual Phosphine

Sample		
Cell 15		Cell 41
History		
Phostoxined 24/6/76		Phostoxined 17/2/77
5 pellets/ton		7 pellets/ton
Turned for 40 min		Aerated 24 h on 14-15/3/77
		Sample taken 16/3/77
Residual Phosphine, mg/kg		
	Cell 15	Cell 41
23/3/77	0.002	0.001
24/3/77	0.001	0.001

migation was carried out in hypovials or 50-mL conical flasks. These were filled with a weighed amount of wheat and sealed. A measured volume of phosphine was added by means of syringe, and the samples were left to stand for a number of days (fumigation period). To air the fumigated wheat, the contents of the containers were placed in open dishes and left for several hours (airing period). Gas was not circulated through the wheat and there was no agitation during airing.

Method. Thirty grams of wheat were ground for 3 min in the sealed blender jar. An aliquot of the headspace gas was injected directly into the GLC and the response compared with standards. Injections were repeated every 15 min until the response of the headspace gas had stabilized. This was almost immediately for low levels of phosphine. For higher levels, e.g., 0.1 mg/kg, the system took from 30 to 45 min to equilibrate.

Efficiency of Method. The efficiency of the method was determined in two ways. The first involved the measurement of the phosphine distribution, at room temperature, between the ground wheat and the headspace gas in the blender jar. Thirty grams of wheat were placed in the jar, the system was sealed, and the wheat was ground for 1 min. A measured amount of phosphine was injected into the jar and the wheat was reground for 2 min. A sample of the headspace gas was injected into the GLC and the response compared with standards. Injections were repeated at intervals up to 1 h and the final phosphine content of the headspace gas after 1 h was calculated.

The second way measured the phosphine released when the wheat was ground a second time. Samples were treated as in the method, and the phosphine content of the headspace gas was calculated. The septum was then removed from the blender jar and the phosphine was allowed to escape. The wheat was not agitated in any way during this airing. After 30 min a new septum was placed in the blender jar and the wheat was reground for another 3 min. The phosphine content of the headspace gas was measured as before.

Test of Method on Field Treated Samples. Two samples were supplied by the Wheat Board. The history of each is given in Table I. The samples were analyzed, as outlined in the method, on the 23/3/77 and repeated on the 24/3/77.

RESULTS AND DISCUSSION

Phosphine was eluted from the column after approximately 30 s. Figure 2 shows the peaks obtained. Peak heights were used for measuring the response as retention times and peak shapes were consistent throughout the experiments.

Samples Fumigated in the Laboratory. Table II lists the results for residual phosphine in the wheat. The figures show that most of the phosphine was removed from the wheat during the airing step. As was expected, ex-

Table II. Residual Phosphine in Wheat Fumigated and Aired for Various Periods in the Laboratory

Sample no.	Phosphine dosage, μg	Wheat, g	Equiv tab/tonne	Period of fumigation, days	Period of airing, h	Residual phosphine, mg/kg
1	202	30	6.7	4	4	0.15
2	202	30	6.7	4	21	0.06
3	303	30	10.1	6	27	0.10
4	303	30	10.1	6	30	0.08
5	218	50	4.4	5	3.5	0.03
6	218	50	4.4	5	4.5	0.03
7	218	50	4.4	1	4	0.03
8	218	50	4.4	4	4.5	0.02
9	218	30	7.3	5	3	0.12
10	218	30	7.3	5	8	0.11

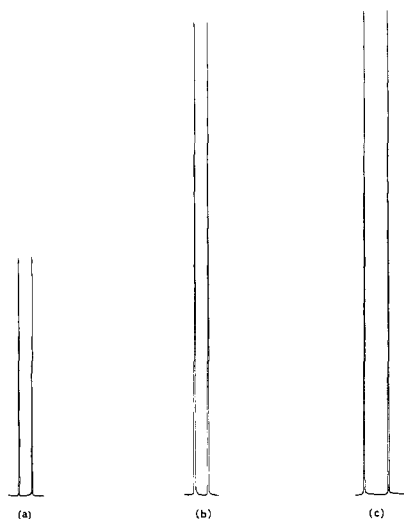


Figure 2. (a) and (b) phosphine standards: 268 and 536 pg, respectively; (c) laboratory-fumigated sample no. 2; phosphine content = 0.06 mg/kg.

tension of the airing period resulted in a decrease in the phosphine content of the wheat (compare samples 1 and 2).

The optimum time for grinding the wheat was 3 min. Grinding for a shorter period than this increased the time required for equilibrium to be reached, and grinding for a longer period did not noticeably reduce it.

The laboratory-fumigated samples were not aerated by passing nitrogen through them, as, when this was done, only trace amounts of phosphine were detected. The larger residues obtained, using the procedure outlined, were preferred for testing the method. Consequently, these levels are not indicative of those likely to be found in field-treated samples.

Care had to be taken with the amount of silicone grease used on ground glass joints. Phosphine escaped when no grease was used and appeared to be absorbed when too much was used.

Detector sensitivity was 10 pg of phosphine for a 10% recorder scale deflection. The phosphine response was linear in the range tested.

Distribution of Phosphine between the Phases. This was tested at three levels: 0.01, 0.06, and 0.14 mg/kg. Table III lists the results. Seventy-nine percent or more of the phosphine remained in the headspace 1 h after grinding.

Table III. Partitioning of Phosphine between Headspace and Ground Wheat in Blender Jar

Wheat, g	Phosphine dosage, μg	Phosphine dosage, mg/kg	% phosphine in headspace after 1 h	Phosphine in headspace after 1 h, mg/kg
30	4.184	0.139	80.4	0.112
30	4.184	0.139	79.0	0.110
30	1.802	0.060	80.1	0.048
30	1.802	0.060	80.3	0.048
30	0.361	0.012	84.3	0.010
30	0.361	0.012	85.0	0.010

Table IV. Phosphine Released by Two Successive Grindings of the Wheat with Airing between Them

Sample no.	First grinding, mg/kg	Second grinding, mg/kg
7	0.03	0.003
8	0.02	0.001
9	0.12	0.01
10	0.11	0.01

Second Grinding of the Wheat. Four of the samples that were fumigated in the laboratory were subjected to a second grinding. The phosphine released was of the order of 10% of the phosphine value obtained with the first grinding. Results are listed in Table IV.

Field-Treated Samples. Residual phosphine was of the order of 0.001 mg/kg (Table IV). This was well below the Codex Alimentarius limit of 0.1 mg/kg for phosphine in raw cereals (Report of 8th Session, 1975).

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