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Phosphine and Methyl Bromide Fumigation of Shelled Peanuts[1]

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ABSTRACT

In laboratory studies, neither germination nor quality of peanuts was adversely affected by fumigation with phosphine, regardless of the dosage or the number of times the peanuts were fumigated. Sorption of phosphine ranged from 55.3 to 71.1% and was highest for peanuts with 7% moisture content. Residues of phosphine generally increased with dosage and the number of fumigations; however, the highest residue (11.3 ppb) occurred after 3 fumigations at the highest dosage (1.12 mg/liter).

Methyl bromide fumigation of peanuts in the laboratory reduced germination and quality in direct proportion to the dosage applied and the number of fumigations. Sorption ranged from 88.8% to 92.9%, was inversely proportional to the dosage, and increased with an increase in moisture content of the peanuts. Also, total bromide residues increased proportionately with the dosage and the number of fumigations. Residues of >200 ppm were found on peanuts after 3 fumigations at the highest dosage tested (64 mg/liter), regardless of the moisture content, and after 3 fumigations at 48 mg/liter on peanuts of 7% moisture content.

When 900-kg (1-short ton) corrugated paper bulk containers were fumigated with phosphine, the gas that penetrated the containers killed all insects exposed at the center of the peanut mass; there was no effect of phosphine on the germination or quality of the peanuts, and residues of phosphine were well below the tolerance regardless of the dosage or the number of times fumigated. When the containers were fumigated with methyl bromide, the gas that penetrated the containers killed all insects exposed in the center of the mass only at the highest dosage tested (64 mg/liter); germination was reduced, quality decreased with successive fumigations, and residues increased in proportion to the dosage and the number of times fumigated. Unlike the laboratory test, bromide residues exceeded 200 ppm only after 3 fumigations at the highest dosage tested.

Key Words: phosphine, methyl bromide, germination, quality, shelled peanuts, gas concentration, sorption, residues, *Plodia, Sitophilus, Tribolium.*

The peanut-shelling and -processing industries are beginning to use corrugated paperboard bulk containers to replace or supplement the use of burlap bags for the storage and shipment of shelled peanuts. Several different configurations, constructions, and sizes of containers are available, but the ones apparently of greatest interest are those designed to hold ca. 1 short ton (900 kg) of shelled peanuts.

[1]This paper reports the results of research only. Mention of a pesticide in this paper does not constitute a recommendation for use by the U. S. Department of Agriculture nor does it imply registration under FIFRA as amended. Also, mention of a commercial or proprietary product in this paper does not constitute an endorsement for use by the U. S. Department of Agriculture.

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This change in marketing procedures immediately raises questions relating to insect control, e.g., whether (1) methyl bromide (bromomethane) as now used to fumigate peanuts in burlap bags will be effective for fumigating shelled peanuts in bulk containers: (2) another fumigant would be more suitable for shelled peanuts in bulk containers; (3) quality of shelled peanuts would be affected by fumigation.

Research was implemented in 1975 at the USDA Stored-Product Insects Research and Development Laboratory, Savannah, Georgia, to answer these questions. The results reported here involved two experiments: one used 4.5-kg (10-1b) lots of peanuts under laboratory-controlled conditions and the other used 900-kg lots of peanuts under ambient conditions in a warehouse.

Materials and Methods

The laboratory and warehouse tests were conducted concurrently, and Spanish No. 1 shelled peanuts were used in both tests. The peanuts were in storage about 5 months and their moisture content was 5% when received as shelled peanuts. The moisture content was monitored during the test period with a Steinlite(R) moisture meter model PT2.

The fumigants used in the tests were phosphine and methyl bromide. Phosphine was evolved from pre-prepared 3-g packets of the Detia(R) Gas Ex-B formulation of aluminum phosphide. Methyl bromide was metered from 454-g (1-1b) cans containing 100% methyl bromide.

Four dosages of each fumigant were tested. Phosphine was applied at 0.14, 0.42, 0.70, and 1.12 mg/liter in the laboratory test and at 0.60, 1.20, 1.80, and 2.40 mg/liter in the warehouse test. Methyl bromide was applied at 16, 32, 48, and 64 mg/liter in both the laboratory and warehouse tests. Each fumigant dosage was replicated 3 times, and each lot of peanuts was fumigated at 2-wk intervals until 3 fumigations were accomplished. Fumigations with phosphine and methyl bromide were for 120 and 24 hr, respectively.

Concentrations of each fumigant were monitored during fumigation and aeration. Phosphine concentrations were determined by the detector tube method during fumigation in the warehouse test. The gas-liquid chromatographic (GLC) method of Dennis et al. (1972), modified to use a flame photometric detector was used in the laboratory test and during aeration in the warehouse test. Methyl bromide concentrations were determined by the GLC method described by Dennis et al. (1972).

After aeration, samples of peanuts from each replicate were collected for residue analysis and for germination and organoleptic tests. Samples for residue analysis consisted of 454 and 250 g for each analysis of phosphine and bromide, respectively; 454 g for each germination test; and 1360 g for each organoleptic test. Each sample was sealed in a polyethylene bag and stored at 12°C until analyzed. Samples fumigated with methyl bromide were analyzed by neutron activation at Dow Chemical Company, Midland, MI, for total bromide residue (organic and inorganic). Samples fumigated with phosphine were analyzed for residue by the method described by Rosebrook (1972). The germination tests were conducted by the Georgia Department of Agriculture, State Seed Laboratory,

Atlanta, GA. The organoleptic (quality: aroma and flavor) tests were made by Hershey Foods, Inc., Hershey, PA, and were conducted according to their standard methods for flavor and aroma of roasted nuts and the multiple comparison difference analysis method described by Larmond (1970).

Analysis of variance was conducted on the data from the laboratory test, except the quality evaluations performed by Hershey Foods, Inc. In addition, regression analysis on the data collected was conducted to determine linear relationships. These analyses were performed using the Statistical Analysis System (SAS) procedures developed by Barr et al. (1976).

Laboratory Test

The test was conducted in a controlled-temperature room maintained at 25° ± 2°C. Peanuts were preconditioned to moisture contents of 5, 7, and 8% in rooms maintained at proper conditions to achieve the desired moisture content as described by Karon and Hillery (1949). The time for peanuts to achieve the desired moisture content levels varied from 28 to 35 days.

Ten-liter wide-mouth jars with sealable lids were used as fumitoria. Each lid contained a gas-transfer tube fitted with a 5-cm length of rubber tubing that was sealed with a pinch clamp. By attaching a gas-tight syringe to the rubber tubing, the fumigant doses were applied and gas samples were removed while maintaining a closed system.

Each fumitorium was filled to about 70% of capacity with 4.5 kg of peanuts. Three fumitoria were prepared for each of the 4 dosages of each fumigant, the 3 fumigations at each dosage, and the 3 levels of moisture content of the peanuts. Thus, of the 144 fumitoria prepared, 108 were fumigated and 36 were held as untreated controls.

By using calibrated gas-tight syringes, both phosphine and methyl bromide were applied through the gas-transfer tubes into the fumitoria. Just before application, a volume of air slightly greater than the volume of gas to be applied was removed from each fumitorium. After application, the closed system was opened momentarily to equalize the pressure. Phosphine was applied as gas taken from a 20-liter bottle containing a "parent" concentration (in nitrogen) that had evolved from a 3-g packet of Detia formulation. Methyl bromide was applied as saturated gas. It was collected in a syringe attached to the metering valve of the 454-g can of methyl bromide. The accuracy of the dosing technique and the sorption of the fumigants by the fumitoria were assessed by fumigating and monitoring concentrations of gases in empty fumitoria. Sorption of the fumigants by the peanuts was determined by monitoring concentrations of gases in each fumitorium. Concentrations were determined by gas chromatographic analyses of 10-cc samples of gas taken from each fumitorium at regular intervals throughout each fumigation period.

Aeration was accomplished by removing the gas-transfer tubes from the lids and inserting lengths of polyethylene tubing attached to a vacuum manifold. This procedure provided about one air exchange per 5 min. for each fumitorium. Vacuum aeration was conducted for at least 4 hr. or until no fumigant could be detected by analysis of gas samples. The open fumitoria were then held for 44 hr. before samples of peanuts were collected for the residue, germination, and organoleptic analyses. Samples were taken by mixing and then dividing the contents of each jar being sampled into the given sample quantities.

Warehouse Test

The temperature and RH in the warehouse were monitored but not controlled. Peanuts of 6% moisture content were divided into 900-kg lots and held in paperboard, bulk-type containers on wood pallets.

The containers, a product of the St. Regis Paper Company, were constructed of double-wall, corrugated paperboard. The sides of the container were formed by a single piece (octagonal tube) with folded sheets fitted inside to form 2 compartments. Caps made of similar material formed the bottom and top of each container. The caps overlapped the sides 20 cm (8 in) and were held in place by metal bands.

Each container was covered with a 0.15-mm (6-mil) polyethylene film that was subsequently sealed to the floor with damp sand. Each container designated for fumigation with methyl bromide was prepared to provide recirculation of the fumigant under the film by use of a 2.38 m^3/min (100-cfm) blower.

Methyl bromide was applied as liquid and was preweighed into glass ampules to provide dosages of 16, 32, 48 and 64 mg/liter. The liquid was applied through a polyethylene tube into a wad of filter paper attached to the end of the tube. The filter paper was held in the airstream of a 100-cfm blower to assure complete volatilization of the liquid. The blower was operated after each application for 20 min.

Specially prepared packets of the Detia formulation of aluminum phosphide were used for the phosphine fumigations. On the basis of evolution of 1 g of phosphine/3 g of formulation, the phosphine dosages used were 0.6, 1.2, 1.8, and 2.4 mg/liter (50, 100, 150, and 200 g of formulation/1,000 cu. ft.), respectively.

Distribution of methyl bromide and phosphine within each container was determined by monitoring concentrations of each fumigant at regular intervals throughout each fumigation period. Concentrations were determined under the film, at a depth of 30 cm into the mass of peanuts, and near the geometric center (60 cm depth) of each container by equipping the containers with 4 mm ID stainless steel probes sealed to the outer wall of each container and the polyethylene film.

Aeration was accomplished by removing the film covering each container of peanuts. Concentrations of each fumigant within the containers were monitored for 6 days during aeration or until no fumigant gas could be detected among the peanuts.

After aeration, the containers were opened and samples of peanuts were collected for the residue, germination, and organoleptic analyses. The samples of peanuts were collected by use of a 2-m compartmented probe inserted several times, as described by Leesch et al. (1974).

Bioassays with 3 species of insects were conducted during 2 fumigations of the containers at each fumigant dosage tested. The insects were from stock cultures of susceptible strains maintained at the Savannah laboratory. They were as follows: (1) the red flour beetle, *Tribolium castaneum* (Herbst), 2-wk-old adults and 0- to 3-day-old eggs; (2) the rice weevil, *Sitophilus oryzae* (L.), 1-wk-old adults and a mixture of immature stages ranging from 1-day-old eggs to pre-emerged adults, and (3) the Indian meal moth, *Plodia interpunctella* (Hubner), late instar larvae. Except for the moth larvae, the insects were exposed in the cages described by Leesch et al. (1974). These were placed near the geometric center of the mass of peanuts in each container. Moth larvae were exposed in 235-ml jars with filter paper lids, and the jars were placed 15 cm (6 inches) under the surface of the peanuts. The insects were removed after fumigation and aeration were completed. Biological efficacy of the fumigations was assessed on the basis of observed mortality of adult insects, emergence of adult moths from the larval cultures, hatch of flour beetle eggs, and emergence of the rice weevil adults from the mixture of immature stages. Three containers of untreated peanuts were used to assess natural mortality of the insects during the test.

Stacked Containers

After the fumigations of individual containers were completed, tests were made to assess gas penetration and distribution within the peanut mass when the containers were placed in a close stacked configuration. A stack of 12 of the octagonal containers was constructed 2 units high and covered with 6-mil polyethylene film. As with the individual containers, probes were inserted for collecting gas samples from under the film and from within the peanut mass of each container. A second stack was similarly constructed with rectangular containers, a product of the International Paper Company. These containers also held about 900 kg of peanuts per con-

tainer and were made of double-wall, corrugated paperboard, but they had 4 internal compartments. The stacks were alternately fumigated with phosphine and methyl bromide until 3 fumigations of each stack with each fumigant were accomplished. Phosphine was applied at 1.2 mg/liter (3 standard packets of Detia Gas Ex-B formulations per 1,000 cu ft) and methyl bromide was applied at 48 mg/liter (3 lb per 1,000 cu ft). Four of the blowers used during individual container fumigation were used to recirculate the methyl bromide gas. Analyses of gas samples were made by the methods previously described. No residue, germination, or organoleptic analyses were conducted on peanuts from the stacked containers.

Results and Discussion

Laboratory Test

Phosphine. Moisture content (MC) of the peanuts influenced the concentration of phosphine sustained in the 10-liter fumitoria as shown in Fig. 1. Because of the space occupied by the peanuts, the initial concentration of phosphine was about twice as high as the initial level in the empty fumitoria. Regardless of the MC of the peanuts, the concentration decreased rapidly during the 1st 20 h; then there was a more gradual decrease during the remaining 100 h of fumigation. The greatest decrease in concentration occurred in peanuts of 7% MC. As this pattern of decrease in concentration occurred each time the peanuts were fumigated, regardless of the phosphine dosage applied, the 7% MC may be a critical level for maximum sorption of phosphine by peanuts.

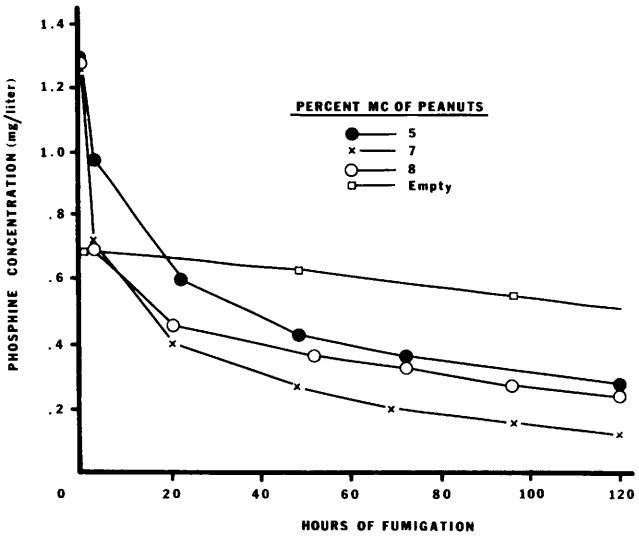

Fig. 1. Concentrations of phosphine in 10-liter fumitoria during fumigation of 2.54-kg lots of shelled peanuts at 25°C for 120 h; 500 ppm (0.7 mg/liter) dosage of phosphine applied as gas.

Phosphine sorbed by the peanuts ranged from 55.3 to 71.1%, depending on the dosage applied and the MC of the peanuts. Sorption by peanuts of 5, 7, and 8% MC ranged form 55.3 to 60.5, 70.1 to 71.1, and 60.8 to 65.8, respectively. Sorption was significantly ($P < 0.05$) greater for peanuts of 7% MC as compared to those of 5% and 8% MC. The percent sorption by the 5% MC peanuts decreased significantly ($P < 0.05$) as the dosage of phosphine increased, but the dosage had no significant effect on the percent sorption by peanuts of 7 and 8% MC.

In general, residues of phosphine on the peanuts of 5 and 7% MC increased with the increase in dosage applied and with the number of times they were fumigated (Fig. 2). However, 8% MC peanuts were an exception; in this case residues after 3 fumigations were equal to or less than residues found after 1 and 2 fumigations. Regression analysis showed that fairly good linear relationships existed for peanuts of 5 and 7% MC; however, peanuts of 8% MC could not be fitted to a linear model because the third fumigation produced consistently lower residues than those of the second fumigation. Within each fumigation at 8% MC, the correlation of residues to dosage was linear. Equations for these relationships were as follows: (1) for fumigation 1, $\hat{R} = 0 + 1.87$ (dosage with $r^2 = 0.72$, (2) for fumigation 2, $\hat{R} = 0.40 + 3.59$ (dosage) with $r^2 = 0.82$, and (3) for fumigation 3, $\hat{R} = 0.15 + 1.15$ (dosage) with $r^2 = 0.79$. The reason for the low residue resulting from the third fumigation of the 8% MC peanuts was not determined. The highest residue found was 11.3 ppb on peanuts of 5% MC after 3 fumigations at 1.12 mg/liter. All other residues found were below the tolerance of 10 ppb of phosphine for certain processed foods. Peanuts of 5% MC accumulated significantly higher residues ($P < 0.05$) than those of 7 and 8% MC.

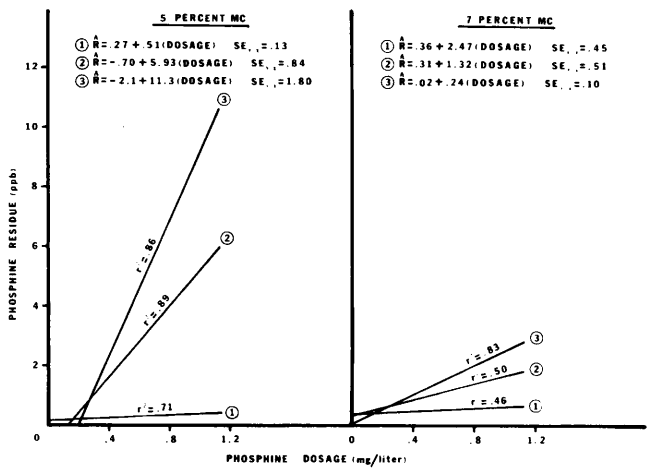

Fig. 2. Linear regression between residues of phosphine on peanuts and dosage after 120-h fumigations in 10-liter fumitoria at 25°C. The number of fumigations is circled for each moisture content (MC).

Phosphine had no adverse effect on germination of the peanuts regardless of dosage or the number of times fumigated. Germination ranged from 72-82% for the treated and from 69-76% for untreated peanuts of 5% MC; from 64-80% for treated and from 62-71% for the untreated of 7% MC; and from 10-61% for the treated and from 15-48% for the untreated peanuts of 8% MC. The phosphine-fumigated peanuts, in general, showed a higher percentage of germination than the untreated peanuts. Mold and general deterioration of the 8% MC peanuts was evident, which may have contributed to the low percentage of germination of these peanuts.

Quality tests of the phosphine-fumigated peanuts

showed that no adverse aroma or flavor resulted from the fumigations. However, only the peanuts of 5% MC were fully evaluated for quality. Because of the development of mold and general deterioration of some peanuts as the test progressed, quality evaluations became impractical. This deterioration was, in general, proportional to the MC. Subsequently, peanuts of 7% MC fumigated 3 times could not be tested, and those of 8% MC fumigated once could be tested only for aroma.

Methyl Bromide. The effect of MC of the peanuts on the concentration of methyl bromide sustained in the 10-liter fumitoria is shown in Figure 3. In this example, the initial concentration of methyl bromide among the peanuts (76.5 mg/liter) was more than 2 times the initial level in the empty fumitoria (32 mg/liter). This high concentration lasted only a short time since the peanuts rapidly sorbed the methyl bromide. The rate of sorption was proportional to MC of the peanuts and was greatest on peanuts of 8% MC. Six hours after dosing, only 4, 7, and 14 mg/liter were detected in peanuts of 8, 7, and 5% MC, respectively. The concentration then continued to decrease, and only 1.5 to 2.6 mg/liter was detected after 24 h of fumigation. Within each dosage, the sorption was highly correlated (r = 0.77 to 0.87) to the MC of the peanuts. Sorption on peanuts ranged from 88.8-90.4% 90.0-92.5% and 91.0-92.9% for peanuts of 5, 7 and 8% MC, respectively. Also, sorption by peanuts of the 3 MC levels decreased with an increase in dosage.

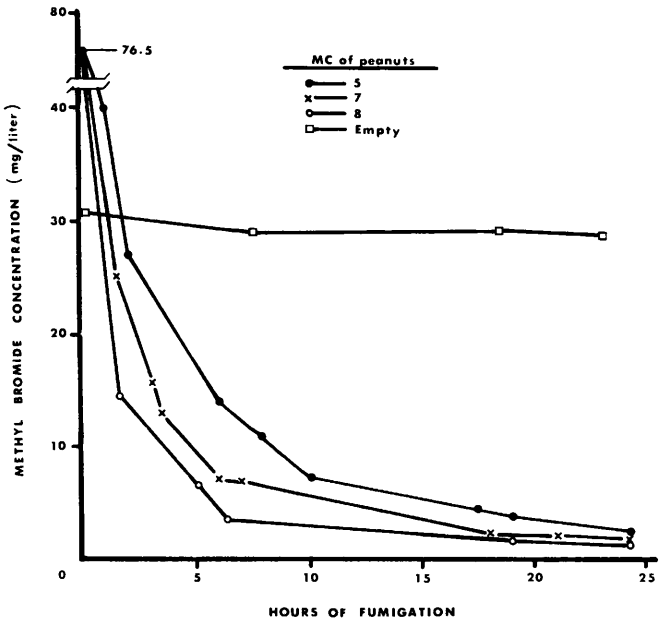

Fig. 3. Concentrations of methyl bromide applied at 32 mg/liter in 10-liter fumitoria during fumigation of 2.54-kg lots of shelled peanuts at 25°C for 24 h.

Methyl bromide concentrations sustained among the peanuts were, in general, proportional to the dosage applied. However, regardless of the dosage applied, about 90% of the methyl bromide was sorbed by the peanuts during the 24-hr fumigations. Fumigations of the empty fumitoria show that another 5% of the gas applied was lost due to leakage or sorption by the container. With this high rate of sorption by the peanuts and a greater than 5% loss of gas (leakage, etc.) expected during most practical fumigations, one can readily visualize the difficulty of maintaining a concentration of methyl bromide in shelled peanuts that would be effective against insects.

Residues of bromide increased in proportion to the dosage and the number of times the peanuts were fumigated and MC had no significant effect on residue accumulation (Fig. 4). For example, residues from 2 fumigations at 16 mg/liter were comparable to residues from 1 fumigation at 32 mg/liter, 3 at 16 were comparable to 1 at 48, 2 at 32 were comparable to 1 at 64, etc. Residues of bromide were in excess of 200 ppm on peanuts after 3 fumigations with methyl bromide at 64 mg/liter. In one instance, a dosage of 48 mg/liter produced residues in excess of 200 ppm on peanuts of 7% CM after 3 fumigations. The interaction of dosage and number of fumigations on residue was highly significant ($P < 0.01$). This linear relationship became slightly curvilinear with the increase in dosage applied and number of times the peanuts were fumigated.

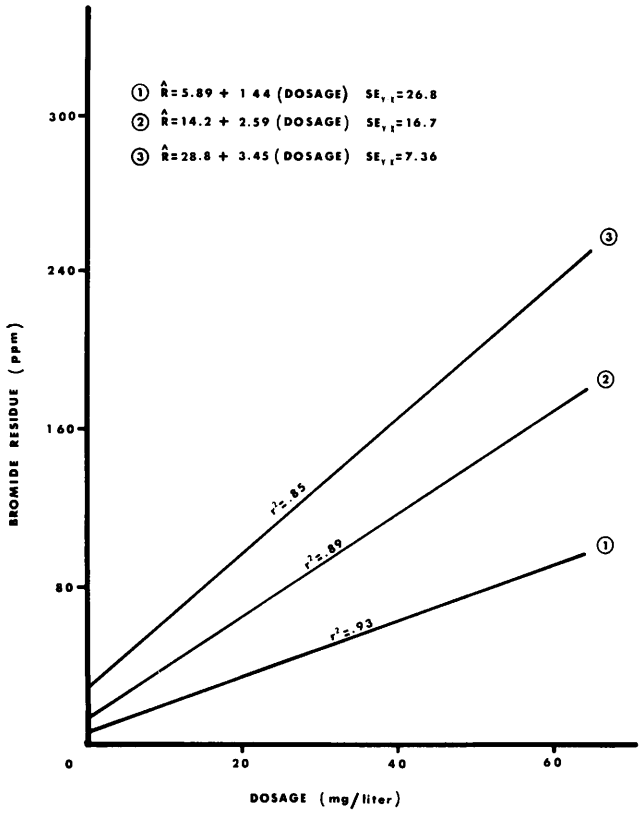

Fig. 4. Linear regression between bromide residues and dosage within each fumigation (circled) of peanuts for 24 h with methyl bromide. (Data are grouped across the 3 moisture content levels because no difference caused by different moisture content levels was found.)

This upward trend with increased dosage is reflected in the increase of slope of the regression lines with successive fumigations. Within each dosage, residues were highly correlated ($P < 0.01$) to the number of times the peanuts were fumigated, with correlation

coefficients ranging from 0.91 to 0.93. Within MC and across dosages, and the number of fumigations, there was a negative linear correlation between residues and percent germination. Linear equations for germination (G) are as follows: (1) 5% MC, $\hat{G}$ = 68.5 - 0.26 (residue) with r^2 = 0.75; (2) 7% MC, $\hat{G}$ = 61.2-0.20 (residue) with r^2 = 0.70; and (3) 8% MC, $\hat{G}$ = 40.6-0.19 (residue) with r^2 = 0.50. Due to the deterioration of peanuts of 8% MC, the equation relating the linear correlation of germination and residues has a low intercept and more variation; however, the slope is not significantly different from the slopes of 5 and 7% MC.

Methyl bromide adversely affected germination of the peanuts (Fig. 5). Germination was inversely proportional to the dosage and the number of times the peanuts were fumigated. At a dosage of 32 mg/liter, peanuts of 5 and 7% MC began to show a reduction in germination after 1 fumigation. Peanuts of 8% MC showed a loss of germination after 1 fumigation at a dosage of 48 mg/liter. All peanuts fumigated twice with methyl bromide showed a significant ($P < 0.05$) reduction in germination. Untreated peanuts of 8% MC deteriorated rapidly during the test period, and no attempt was made to determine any differences between these and the other peanuts. There was a significant negative correlation ($P < 0.01$) of either the dosage or the number of fumigations with percent germination, but there was no significant negative correlation of the combined dosage and number of fumigations on the percent germination. There was no significant difference between 5 and 7% MC peanuts in the germination response.

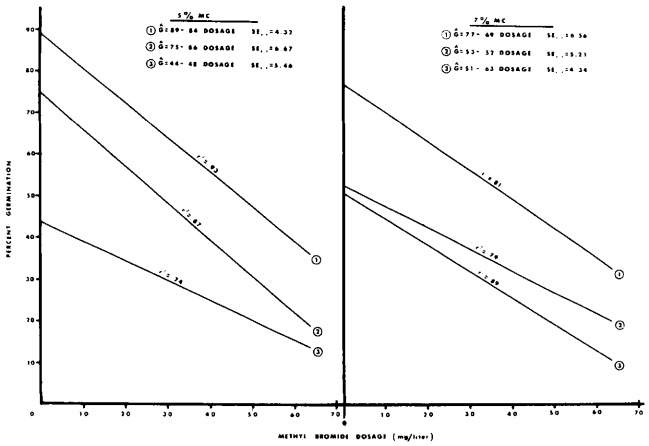

Fig. 5. Linear regression between percent germination of peanuts after fumigation and the dosages of methyl bromide applied to peanuts in 10-liter fumitoria for a 24-h period at 25°C. (The number of fumigations is circled.)

A summary of the results of quality evaluation show that methyl bromide had adverse effects on both the aroma and flavor of peanuts (Table 1). At the 5% MC, peanuts fumigated once at dosages of 32, 48, and 64 mg/liter were significantly poorer in aroma than untreated peanuts. Flavor was not adversely affected until the peanuts were fumigated twice. After 2 fumigations, only the dosage of 16 mg/liter of methyl bromide had no adverse effect on flavor. After 3 fumigations, all dosages of methyl bromide tested adversely affected the flavor of shelled peanuts. Peanuts of 7% MC showed significant aroma and flavor losses after a single fumigation. Because of general deterioration of the peanuts of 8% MC only those that had been fumigated once were evaluated for aroma. Peanuts of 8% MC treated at 32 mg/liter or more were significantly poorer in aroma than untreated peanuts.

Table 1. A summary of the effect of methyl bromide on the aroma and flavor of peanuts roasted after 24-hr fumigations in 10-liter fumitoria at 25°C.[1]

Peanut moisture	Times fumigated	Dosage (mg/liter)	Untreated peanuts significantly better than treated peanuts in: 2/	
			Aroma	Flavor
5	1	16	No	No
		32	Yes	No
		48	Yes	No
		64	Yes	No
	2	16	No	No
		32	Yes	Yes
		48	Yes	Yes
		64	Yes	Yes
	3	16	Yes	Yes
		32	Yes	Yes
		48	Yes	Yes
		64	Yes	Yes
7	1	16	Yes	Yes
		32	No	Yes
		48	Yes	Yes
		64	Yes	Yes
	2	16	No	No
		32	Yes	Yes
		48	Yes	Yes
		64	Yes	Yes
8	1	16	No	---
		32	Yes	---
		48	Yes	---
		64	Yes	---

1/ Samples fumigated 3 times at 7% moisture and 2 and 3 times at 8% moisture were not tested for quality.

2/ Samples were analyzed using an analysis of variance method described by Larmond (1970). Significance is at the $P < 0.05$ level.

The quality evaluations did not show a direct correlation between adverse effects and accumulation of bromide residue on the peanuts. In general, both aroma and flavor were more adversely affected by fumigations which resulted in lower residue levels on peanuts of 7% MC than on peanuts of 5% MC. The aroma of peanuts of both 5 and 7% MC was more readily affected by fumigations resulting in low residue levels than was flavor. For example, when residues were as low as 28 ppm on peanuts of 7% MC, both aroma and flavor were affected adversely, but neither aroma nor flavor was affected when residues were as high as 67 ppm. At a residue level of 73 ppm or more, both aroma and flavor were always affected adversely. With the peanuts of 5% MC, the aroma was affected adversely at a residue level as low as 50 ppm but not at 56 ppm. At a residue level of 71 ppm or more, the aroma was always affected adversely. Though the flavor of the peanuts of 5% MC was affected adversely at a residue level of 72 ppm, this effect was not detected at a residue level of 98 ppm. At the next highest level of residue measured (131 ppm) and at higher levels, the flavor

was always affected adversely. Obviously, the presence of bromide residue could be a factor that affects the quality of peanuts fumigated with methyl bromide. However, the variability of the correlation between adverse effects and accumulation of bromide residue indicates that other factor(s) not determined in these tests may be involved. Until this factor(s) is identified, the measurement of bromide residues on peanuts apparently is not the best criteria for predicting adverse effects on quality (aroma and flavor) of peanuts fumigated with methyl bromide.

Warehouse Test

Conditions in the warehouse ranged from 39°C and 43% RH during the day to 25°C and 94% RH at night. However, the temperature of the peanuts in the container remained at 25°±4°C and there were only minor changes in the MC of the peanuts (6±0.1%).

Phosphine. The concentrations of phosphine under the film (tarpaulin) and at 2 positions within the peanut mass in the container resulting from the dosage of 1.8 mg/liter are shown in Fig. 6 as a typical example of the phosphine fumigations. A similar pattern of concentrations occurred at each position during each fumigation, except that the concentrations were proportionately higher or lower according to the dosage applied. The minor differences in concentration of phosphine at the center of the peanut mass and under the film indicate rapid penetration of the container and peanut mass by the phosphine gas. The decrease in concentration after 24 hr is considered normal for this method of fumigation and indicates that the formulation applied had about completed its evolution of phosphine. Also, this decrease is in agreement with the laboratory tests, which showed that about 50 to 70% of the phosphine was sorbed by the peanuts.

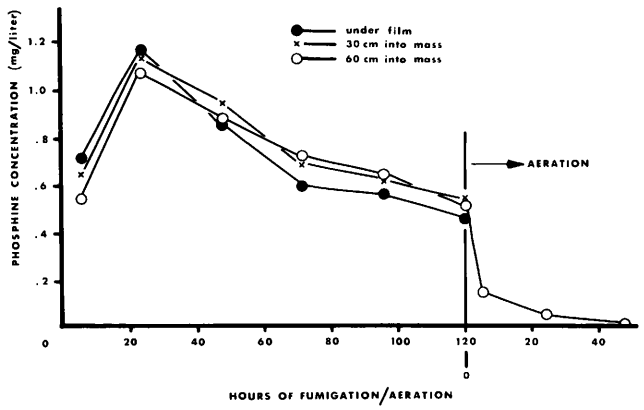

Fig. 6. Concentrations of phosphine in 900-kg bulk containers of shelled peanuts during fumigation and aeration at 25±4°C; 1.8 mg/liter dosage of phosphine applied.

Removal of the films from the containers resulted in rapid dissipation of phosphine. Only trace amounts could be detected at the center of the peanut mass after 48 h of aeration. Measurements of concentrations during aeration of the other fumigations showed that phosphine dissipated at about the same rate regardless of the concentrations present at the onset of aeration.

The residue of phosphine remaining on shelled peanuts after fumigation in bulk containers were well below the tolerance level of 10 ppb for certain processed foods. The residues increased with dosage and, with one exception, the number of times fumigated (Fig. 7). Residues from the first and second fumigations were not significantly different; however, the third fumigation resulted in a significantly higher ($P < 0.05$) accumulation of residue.

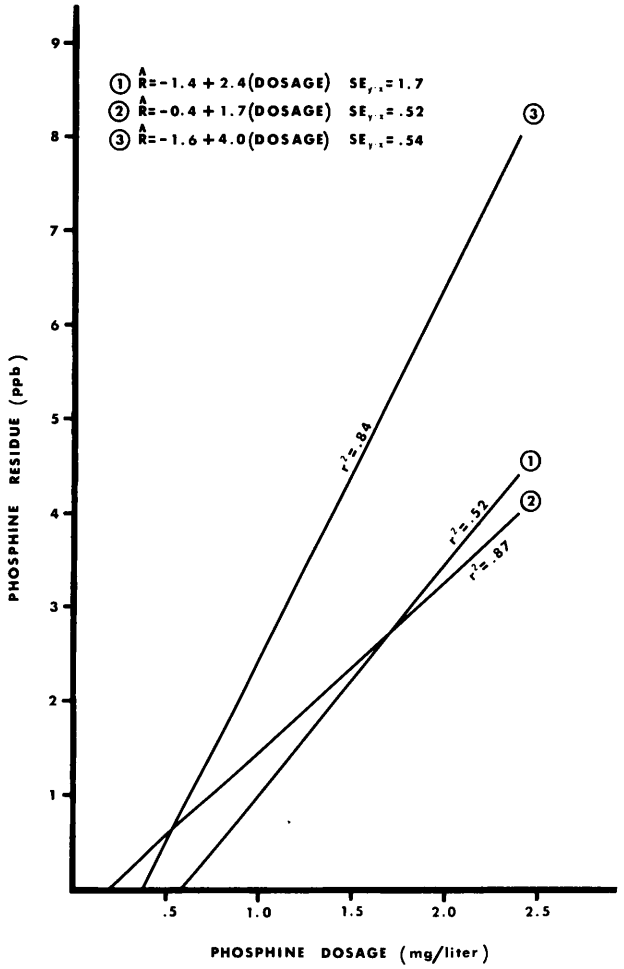

Fig. 7. Linear regression between residues of phosphine accumulated and the dosage applied to peanuts in 900-kg bulk containers under a 6-mil polyethylene film; fumigations (circled) were for 120 h at 25±4°C.

Phosphine fumigation of shelled peanuts in bulk containers had no significant adverse effect on the germination of the nuts. Even peanuts fumigated 3 times with phosphine at the highest dosage tested (2.4 mg/liter) showed no decrease in germination. Germination of treated peanuts ranged from 64 to 85% while that of untreated peanuts ranged from 67 to 85%.

Quality evaluations of the phosphine-fumigated peanuts in bulk containers resulted in no adverse flavor variation from untreated nuts regardless of the dosage or the number of times fumigated. However, the tests showed that peanuts fumigated twice at 0.60 and 1.20 mg/liter were significantly better in aroma than those fumigated twice at 1.80 and 2.40 mg/liter

but were not significantly different in aroma from the untreated nuts. This difference in aroma did not develop a trend because, in peanuts tested after the third fumigation, neither the aroma nor flavor differed significantly among treatments nor from those of untreated peanuts.

All insects exposed in containers fumigated with phosphine were killed, even at the lowest dosage tested (0.06 mg/liter). Average phosphine concentrations for the 120-h fumigations were 0.18±0.02 mg/liter for the lowest dosage and increased proportionately with dosage to 1.02±0.07 mg/liter at the highest dosage.

Methyl Bromide. The concentrations of methyl bromide under the film and at 2 positions within the peanut mass during fumigation at 48 mg/liter are given in Fig. 8 as a typical example of the methyl bromide fumigations. The concentrations of gas at any time at each site in the lower dosages tests were progressively higher as the dosage was increased from 16 to 48 mg/liter. The product of concentration multiplied by time (CT) increased with dosage as shown in Table 3, but although the 64-mg/liter dosage provided the highest concentrations of gas, these concentrations were low in proportion to the dosage applied.

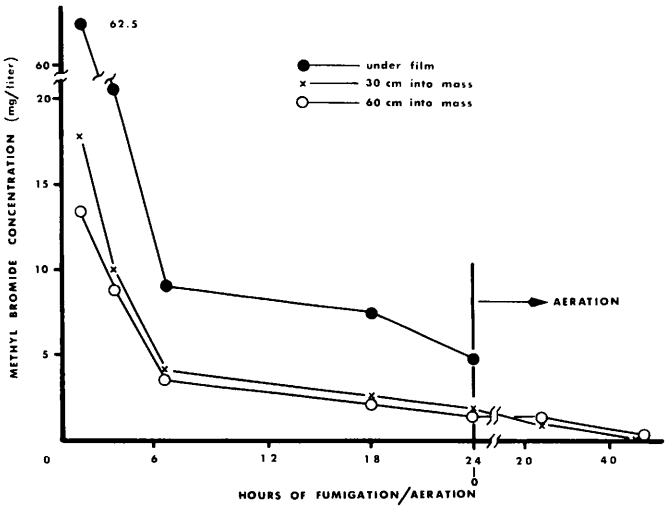

Fig. 8. Concentrations of methyl bromide in 900-kg bulk containers of shelled peanuts during fumigation and aeration at 25±4°C; 48 mg/liter dosage of methyl bromide applied.

As shown in Fig. 8, methyl bromide penetration of the container and peanut mass was rapid: the highest concentration at the center of the mass was achieved within 2 h. However, the concentration was much lower (ca. 30%) than the dosage applied, and most of the gas was sorbed or lost by leakage within 6 h after application. After 24 h of fumigation, the concentrations of methyl bromide had decreased in proportion to the dosages applied and ranged from about 2 mg/liter for the 64-mg/liter dosage to only trace amounts (<0.4 mg/liter) for the 16-mg/liter dosage. Aeration of methyl bromide from the center of the peanut mass also was rapid, and the rate of dissipation was the same regardless of the methyl bromide concentration at the time the films were removed. After 48 h of aeration, only trace amounts of methyl bromide could be detected in a few of the containers.

Residues of bromide resulting from fumigation of the peanuts in containers are shown in Fig. 9. In only one replicate fumigated 3 times at 64 mg/liter did the residue exceed 200 ppm. The residues found were linearly correlated to the dosage applied and to the number of times the peanuts were fumigated at each dosage. The data show that each fumigation had an equal effect upon the accumulation of bromide residues. By plotting the residues against the sum of the dosage(s) across fumigations, a linear relation was shown to hold. Thus, the residues accumulated after 2 fumigations at 16 mg/liter were the same as those accumulated after 1 fumigation at 32 mg/liter, etc. The accumulation of residues was lower per equivalent dosage of methyl bromide on peanuts in the containers than in the 10-liter fumitoria. This difference was probably the result of sorption by the containers and the greater efficacy in retaining the gas in the 10-liter fumitoria than in the containers.

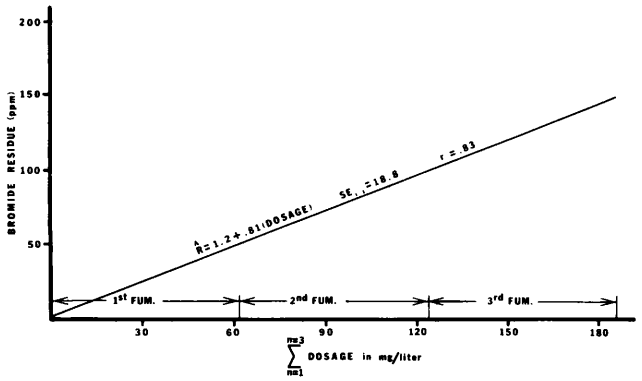

Fig. 9. Linear regression between bromide residues accumulated and the sum of the dosage(s) of methyl bromide across fumigations(n) applied to peanuts in 900-kg bulk containers under a 6-mil polyethylene film; fumigations were for 24 h at 25±4°C.

As in the laboratory test, the peanuts in the containers decreased in percent germination after 1 fumigation at a dosage of 32 mg/liter or more (Fig. 10). After 3 fumigations, germination was adversely affected by all dosages tested. Like the bromide residue accumulation, the percentage of germination decreased according to the sum of the dosages applied. These results compare well to the results of the laboratory study in 10-liter fumitoria; but, again, like the residue accumulation, the effect on germination per equivalent dosage of methyl bromide was not as great on peanuts in the containers as on those in the 10-liter fumitoria.

A summary of the quality evaluations of the peanuts fumigated in containers with methyl bromide shows that both aroma and flavor were adversely affected after 1 fumigation at dosages of 48 and 64 mg/liter (Table 2). The quality of the peanuts decreased with each successive fumigation so that after 3 fumigations the untreated peanuts were better in aroma and flavor than the fumigated peanuts regardless of dosage. As in the laboratory test, the correlation between bromide residue accumulation and adverse effects on flavor

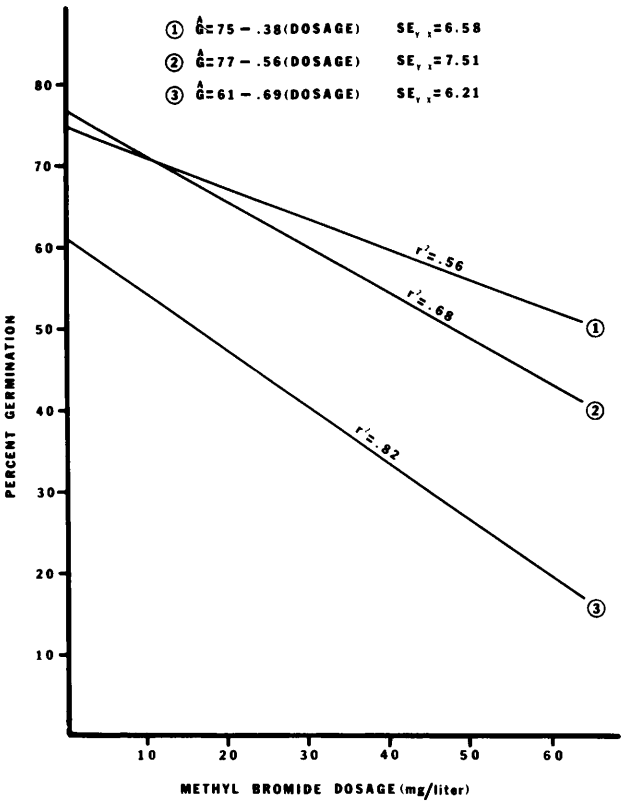

Fig. 10. Linear regression between percent germination and the dosages of methyl bromide applied to peanuts in 900-kg bulk containers for 24 h at 25±4°C. (The number of fumigations is circled.)

Table 2. A summary of the effect of methyl bromide on the aroma and flavor of peanuts roasted after 24-hr fumigations in bulk containers at 25±4°C.

Times fumigated	Dosage (mg/liter)	Untreated peanuts significantly better than treated peanuts in: 1/	
		Aroma	Flavor
1	16	No	No
	32	No	No
	48	Yes	Yes
	64	Yes	Yes
2	16	No	No
	32	No	No
	48	Yes	No
	64	Yes	No
3	16	Yes	Yes
	32	Yes	Yes
	48	Yes	Yes
	64	Yes	Yes

1/ Samples were analyzed using an analysis of variance method described by Larmond (1970). Significance is at the P <0.05 level.

and aroma was not linear. Both flavor and aroma were adversely affected at a residue level as low as 43 ppm but flavor was not affected at 86 ppm, nor aroma at 61 ppm. However, at residue levels greater than these, both flavor and aroma were always affected, which agrees well with the results of the laboratory studies.

As shown in Table 3, both the 48- and 64-mg/liter dosages of methyl bromide were highly effective against the insects exposed in the containers, but only the 64-mg/liter dosage killed all of them. There was a

Table 3. Mortality of insects exposed and CT values obtained during methyl bromide fumigation of peanuts in bulk containers for 24 hr at 25±4°C; data are the averages of 3 replications of each dosage fumigated twice.

Insecticide and dosage (mg/liter)	Insect mortality (%)					Concentration x time (CT) ±S.E. at center of peanut mass (mg hr/liter)
	Tribolium		Sitophilus		Plodia larvae 1/	
	Eggs	Adults	Immature stages	Adults		
16	0	7	0	99	66	17.2± 2.4
32	17	4	39	100	86	44.0± 1.8
48	100	100	98	100	99.5	105.5±30.8
64	100	100	100	100	100	135.9±20.3
0 (control)	0	9	0.5	0	8	0

1/ Data are based on 3 replicates of one fumigation.

high percentage of survival of red flour beetle eggs and adult and immature stages of rice weevils exposed to the dosages lower than 48 mg/liter. The low concentration x time (CT) values obtained for some of these fumigations agree with the frequency of insect survival. Brown (1959) reported minimum CT values needed for at least 99.9% kill of a variety of stored-product insects ranged from 70 mg h/liter at 25°C to 100 mg h/liter at 30° C. the CT values obtained at the center of the peanut mass show that efficacious concentrations of methyl bromide were not obtained until a dosage of 48-64 mg/liter was applied. Leesch et al. (1974) found that a dosage of 32 mg/liter was adequate to kill insects at the center of a peanut mass in 900-kg containers. However, the CT values obtained with the 32-mg/liter dosage correlate well with the CT values in Table 3, which correspond to an efficacious treatment.

Fumigation of shelled peanuts with methyl bromide at the dosages found effective against the exposed insects could result in adverse effects on aroma and may attribute an adverse flavor to the roasted nuts.

Stacked Containers. Penetration and distribution of gases of both phosphine and methyl bromide under the film and within the peanut mass of both types of containers fumigated in a close stacked configuration were determined to be the same as for the respective gases during fumigation of individual octagonal containers; that is, there was little or no difference in concentration and distribution of either fumigant due to the type of container used nor to the size of the stack when compared with individual containers fumigated at the same dosages.

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