Peanut Science (1983) 10, 33-36

Fumigation of Imported Shelled Peanuts with Methyl Bromide[1]

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ABSTRACT

Imported shelled peanuts were fumigated with methyl bromide at temperatures and dosages corresponding to quarantine-type fumigations against khapra beetles, *Trogoderma granarium* Everts. Samples of fumigated peanuts were analyzed independently by four laboratories for bromide residues and five laboratories conducted organoleptic tests of roasted peanuts. Sorption of methyl bromide during fumigation ranged from 89.3 to 71.4% of the dosage applied at temperatures ranging from 27.6 to 4.4 C, respectively. Bromide residues ranged from 70.2 to 286.3 ppm depending upon dosage - temperature combination and source of analysis. Organoleptic tests by 4 of the laboratories showed no flavor differences between treated and untreated peanuts while 1 laboratory obtained significant flavor differences between a paste made of treated peanuts and a paste made from untreated peanuts.

Key Words: quarantine, fumigation, peanuts, methyl bromide, quality, residues, volatiles, khapra beetle.

The poor domestic peanut crop during the 1980 season necessitated the importation of shelled peanuts by U. S. manufacturers to supplement domestic supplies. These peanuts came from countries where indemic populations of khapra beetles, *Trogoderma granarium* Everts exist and this insect is quarantined in the U.S. Such peanuts might require fumigation and this, in turn, might affect the quality of the peanuts.

Quarantine regulations as contained in Animal and Plant Health Inspection Service (APHIS) regulations [Anon. (1)] require that khapra-beetle infested peanuts be fumigated with methyl bromide for 12 hr at various dosages depending on the temperature of the commodity. Many manufacturers importing peanuts became concerned that these dosages of methyl bromide might adversely affect the quality of the peanuts and might produce excessive bromide residues.

Research was initiated to determine if peanuts fumigated according to quarantine regulations would be acceptable for use after the treatment. The Agricultural Research Service (ARS), APHIS and the Peanut Butter and Nut Processors Association (PBNPA) entered into cooperative effort to examine imported shelled peanuts for quality and accumulation of bromide residues after quarantine fumigation with methyl bromide. The 5 com-

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

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mercial processing companies from the PBNPA cooperating in this study were: Fisher Nut Company, St. Paul, MN; Luden's Inc., Reading, PA; M&M/Mars, Snackmaster Division, Albany, GA; The Procter & Gamble Co., Cincinnati, OH; and Swift & Co., Oak Brook, IL.

Materials and Methods

Fumigation - Shelled peanuts imported from China were used in the test. They were comparable in appearance to U.S. No. 1 Medium runners with a moisture content of 6.2 ± 0.1%. Peanuts were sent to the Stored-Product Insects Research and Development Laboratory (SPIRDL) by the Proctor and Gamble Co. where they were divided into 4.54-kg lots for the fumigations. Ten-liter glass jars were used as fumitoria and the peanuts filled the jars to about 70% of capacity. The jar lids were gasketed for sealing and equipped with glass tubes for introducing the fumigant and removing gas samples [Leesch *et al.* (7)]. Eighteen replicate lots of peanuts were fumigated for 12 hr according to the temperature/dosage schedule as follows:

Temperature C	Dosage of methyl bromide
27.6 (80 F)	56 mg/L (3.5 lb/1000 ft^3)
21.1 (70 F)	72 mg/L (4.5 lb/1000 ft^3)
15.6 (60 F)	96 mg/L (6.0 lb/1000 ft^3)
4.4 (40 F)	144 mg/L (9.0 lb/1000 ft^3)

Seventy-two hours prior to fumigation, each replicate (18 jars) was placed in a controlled-temperature chamber to equilibrate at one of the 4 temperatures being tested. After applying methyl bromide as gas to each fumitorium, each was inverted 4 times to thoroughly mix the fumigant with the peanuts in the jar. Immediately after dosing and mixing, each fumitorium was placed in the controlled-temperature chamber.

During the fumigation, gas samples were removed at 1.5, 2, 6 and 12 hr to determine the leakage and sorption of methyl bromide. At each temperature, 4 empty fumitoria were treated with methyl bromide and sampled at the same sampling periods. This procedure allowed us to estimate the amount of fumigant that was lost due to leakage. Analysis of gas samples was accomplished by the GLC method described by Dennis *et al.* (3) except that a Tenax® column support was used.

Twelve hours after applications, the fumitoria were removed to a hood and aerated for 10 min with a stream of air. After forced aeration, peanuts from the 18 jars were pooled into 3 equal parts in paperboard boxes (each containing peanuts from 6 jars) and allowed to stand 28 hr at room temperature (25 ± 2C) to provide further aeration. Each box (a pooled replicate) was then mixed and divided into 6 equal sublots for residue and organoleptic analyses by the cooperators. Untreated controls, handled like treated samples were provided for comparison.

Residue Analysis - Subsamples (100 g) of each sublot retained at SPIRDL plus untreated controls were sent to Dow Chemical Co., Midland, MI for residue analysis. Total bromide residues were determined there by neutron activation analysis. In addition, The Fisher Nut Co. and Swift & Co., had residue analyses performed on subsamples taken from the sublots they received. Residue analyses were conducted by Medallion Laboratories of Minneapolis, MN for the Fisher Nut Co. and by Swift & Co. in their laboratories according to a modified method based on methods described by Shrader *et al.* (8) and Heuser (5). Subsamples from the SPIRDL sublots were sent to Dr. Joseph Ford, APHIS, Plant Protection and Quarantine National Monitoring & Residue Analysis Laboratory in Gulfport, MS where they were analyzed by two methods: a GLC method described by Heuser and Scudamore (6) and an ashing method described by Shrader *et al.* (8).

Headspace Analyses - Also, subsamples of each sublot (100 g) were sent to Dr. Clyde T. Young at North Carolina State University, Department of Food Science, Raleigh, NC for headspace analysis of roasted peanuts. Methods used for the headspace analyses were those of C. T. Young (10). These headspace analyses were designed to locate any volatile which might contribute off-flavors to peanuts fumigated with methyl bromide.

Organoleptic Tests - The following tests were conducted by the 5 cooperating companies:

Fisher Nut Company - Quality was determined on unblanched, oil roasted peanuts by an informal taste panel. Subjective comments were solicited from panel members comparing two samples of treated peanuts and one sample of untreated peanuts.

Ludens, Inc. - Peanuts were dry roasted for 15 min in a rotary roaster and then allowed to cool for 15 min. A rating test was conducted on unblanched peanuts by 48 persons who rated eight samples each (4 treated samples and 4 untreated samples). All samples were rated on a scale of 1 (poor) to 10 (excellent). Treated and untreated samples were rotated so that each sample occurred the same number of times in the sampling sequence. Also, a triangulation test was conducted by 12 persons with tasting experience. The panelists were given two samples of the same treatment along with one control sample and asked to match the two like samples. Untreated peanuts held at 27.6 C were used as control samples.

M&M Mars, Inc., Snackmaster Div. - Treated and untreated peanuts were roasted separately in hydrogenated peanut oil and hand blanched. Samples were ranked for flavor in 4 tests of 4 samples each by a select taste panel. Ranks were converted to scores according to the method of Fisher and Yates (4) and subjected to an analysis of variance and subsequently to Tukey's Test.

Procter & Gamble Co. - Each treated and untreated sublot of peanuts was roasted separately in a spouting bed roaster for 4 min at 204 C (400 F), cooled for 5 min with ambient air and blanched to remove skins. Blanched peanuts were ground to a fine particle size in a food processor and graded by an experienced panel of judges for flavor quality. Ranking was done on a scale of 1 (poor) to 10 (excellent) in 2 sessions on different days where samples were presented blind.

Swift & Company - Each treated and untreated sublot of peanuts was roasted separately in a laboratory roaster to a controlled roast level of 8.90 ± 0.3 on the A-coordinate of the Hunter color scale. The color was determined with a Gardner Model XL-23 colorimeter. Peanuts were hand blanched and ground to a smooth paste in a laboratory peanut mill. The resulting pastes were then sensory evaluated for flavor differences using a one-way directional difference from the reference test. The reference used in each case was the corresponding untreated roasted peanut paste. Each treatment was sampled in 3 sessions by eight experienced judges. In each series, a 4-sample balanced complete block design was used where each judge received the untreated control as a reference and as a blind test sample along with treated samples. Red-panel booth lighting was used to assure that all samples presented appeared the same. Samples presented were rated on a scale of 1 (same as untreated sample) to 6 (extremely different from untreated sample). Data were analyzed using analysis of variance and then further analyzed to determine differences among the methyl bromide-treatment levels by a series of t-tests.

Results and Discussion

The sorption of methyl bromide on peanuts during fumigation is shown in Table 1. Mean loss of methyl bromide from empty fumitoria during the fumigation ranged from 4.7 to 6.5% of the dosage applied. With 70%

Table 1. Mean concentration of methyl bromide (± Std. Dev.) during 12-hour fumigation of imported peanuts.

Dosage (mg/L)	Temp. C	Methyl Bromide Concentration (mg/L) Hours After Application 0	1.5	3.0	6.0	12.0	Percent Loss[a] During Fumigation
		70% Loaded					
56	27.6	123.9 (±3.5)	58.8 (±2.7)	34.8 (±1.9)	14.8 (±0.6)	6.3 (±0.3)	89.3
72	21.1	143.0 (±3.7)	74.2 (±2.1)	52.1 (±1.9)	26.3 (±1.1)	10.9 (±0.5)	86.5
96	15.6	211.1 (±6.5)	115.4 (±3.7)	80.9 (±3.3)	44.9 (±2.7)	19.9 (±1.2)	85.9
144	4.4	273.0 (±8.1)	163.9 (±3.3)	129.8 (±2.4)	94.3 (3.4)	60.4 (±3.2)	71.4
		Empty Fumitoria					
56	27.6	66.4 (±1.2)	64.4 (±1.2)	63.7 (±1.2)	63.1 (±1.4)	62.7 (±1.1)	5.6
72	21.1	83.1 (±0.7)	80.6 (±0.8)	79.4 (±0.4)	78.7 (±0.2)	78.2 (±0.6)	5.9
96	15.6	107.5 (±2.0)	105.3 (±0.8)	103.7 (±0.9)	102.6 (±0.4)	102.4 (±1.0)	4.7
144	4.4	157.4 (±1.9)	151.2 (±1.5)	149.3 (±0.7)	147.7 (±1.2)	147.1 (±1.5)	6.5

a/ Percent loss of methyl bromide from 70% loaded jars corrected for loss from empty jars treated at the same dosage and temperature.

of the capacity of each jar filled with peanuts, mean sorption (subtracting loss of empty jars) was 89.3, 86.5, 85.9, and 71.4% for treatments at 27.6, 21.1, 15.6 and 4.4 C, respectively. Thus, there appears to be little or no difference in the amount of sorption occurring at 15.6 C or higher but there was about 15% less sorption occurring at 4.4 C. The reason may be that 4.4 C is approaching the boiling point of methyl bromide and the molecular forces which contribute to adsorption are somewhat weaker at this temperature. The sorption of methyl bromide by peanuts treated at 15.6 C or higher agrees well with that found by Leesch *et al.* (7).

The accumulation of total bromide residues on peanuts after fumigation is shown in Table 2. The variation between the results obtained from different analysts and methods of analysis is small except for the GLC method employed by the APHIS laboratory which gave results that were higher than the others. Residues did not increase with dosage as they did when the temperature was held constant in a study by Leesch *et al.* (7). This difference apparently indicates that the shorter exposure period and lower temperature offset the higher accumulation of residues expected when treating the peanuts with a higher dosage. Thus the two independent variables offset the bromide accumulation when they are changed in opposite directions. Although sorption was similar except at the 4.4 C temperature, it appears that at low temperatures, much of the sorption is adsorption in which the fumigant is less permanently bound to the peanuts. High temperatures should increase the amount of methyl-S-methionine sulfonium bromide or its breakdown product in the peanuts [Bills *et al.* (2)].

Analysis of the headspace vapors produced during roasting of peanuts revealed that for each of the treated samples a peak appeared during GLC analysis of vapors at a retention time of between 3.06 and 3.13 min (Fig. 1). For untreated samples, no peak was present. The identity of the compound eluting between 3.06 and 3.13 min remains unknown but it may be either methyl bromide or a volatile reaction product. The latter seems most plausible as it has been postulated that methyl bromide reacts with sulfur-containing amino acids such as methionine to produce volatile compounds, possibly dimethyl sulfide [Winteringham *et al.* (9)]. Also, methyl bromide should elute from the column in less time than was found here.

Organoleptic testing by the 5 companies gave results shown in Table 3. Only one source of testing, Swift & Co., detected significant differences in the flavor of treated as compared to untreated peanuts. None of the judges described the off-flavor as chemical but rather as stale or sour in nature. The different results may arise from different methods of preparation of the peanuts for tasting. Swift & Co. personnel tasted a paste preparation of the roasted peanuts while all the other testing firms used whole roasted nuts or ground-roasted nuts. The final product (i.e. the amount of grinding of the peanuts), might be a factor in detecting off-flavors or aromas in treated

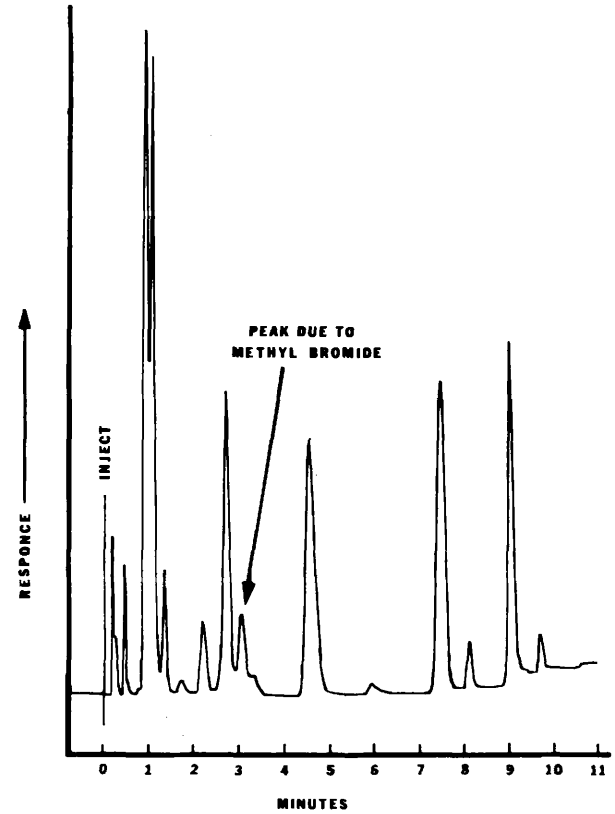

Fig. 1. Chromatogram of the headspace gases after heating peanuts which had been treated with methyl bromide. Arrow shows peak due to methyl bromide treatment which appears in the analysis.

Table 2. Bromide residues found in imported peanuts after a 12-hour fumigation with methyl bromide.

Dosage (mg/L)	Temperature C	Mean Bromide Residues (ppm) on Peanuts[a/]				
		A[b/]	B[c/]	C[c/]	D[b/]	E[c/]
56	27.6	83.7	75.0	109.1	95.0	70.1
72	21.1	91.3	80.0	146.4	98.1	86.5
96	15.6	119.7	86.7	161.8	113.8	91.3
144	4.4	116.0	91.7	186.3	118.4	92.3
0	27.6	4	5	1.0	16.1	3.8
0	21.1	2	5	0.9	25.3	1.9
0	15.6	3	5	2.9	22.9	3.8
0	4.4	2	5	3.0	37.9	8.5

a/ Means of 3 replications; letters used indicate the source of analysis: A = Dow Chemical Co.; B = Fisher Nut Co. (Medallion Laboratories); C and D = APHIS - National Monitoring and Residue Analysis Laboratory, C is GLC method, D is ashing method; E = Swift & Co.

b/ Total bromide residues = inorganic plus organic bromide.

c/ Inorganic bromide residues.

Table 3. Results of several organoleptic evaluations of imported peanuts fumigated 12 hours with methyl bromide.

Dosage (mg/L) Treated Peanuts[b/]	Treated Temperature (C)	Source[a/]				
		A	B	C	D	E
56	27.6	No	No	No	No	Yes[c/]
72	21.1	No	No	No	No	Yes[b/]
96	15.6	No	No	No	No	Yes[c/]
144	4.4	No	No	No	No	Yes[c/]

a/ Sources of testing flavor were as follows: A = Fisher Nut Co. (oil roasted, unblanched); B = Luden's, Inc. (oven roasted, unblanched); C = M&M Mars, Inc. (oil roast, blanched); D = Procter & Gamble Co. (oven roasted, blanched, granulated); E = Swift & Co. (oven roasted, blanched, smooth paste). No means - no difference from untreated peanuts; yes means - taste was significantly different from untreated peanuts.

b/ Flavor of treated significantly different from untreated at $p = 0.05$

c/ Flavor of treated significantly different from untreated at $p = 0.01$

peanuts. The amount of residue found and dosages used place these treated peanuts in an area which, according to Leesch *et al.* (7), may result in adverse flavor effects. According to that study, peanuts with 5% moisture content and residues above 131 ppm always had off-flavors whereas peanuts with lower residues variably exhibited significantly different flavor from untreated peanuts.

It appears that quarantine dosages of methyl bromide which might be used to fumigate peanuts probably would not adversely affect their quality and would permit production of an acceptable finished product; however, the appearance of off-flavor may depend upon the nature of the final product. With the exception of one source of testing, the peanuts did not exhibit significantly different flavors from untreated peanuts from the same lot. Residues found on treated peanuts probably would not be excessively high if only one fumigation was performed. If peanuts had been fumigated previously with methyl bromide, there may be excessive residues (i.e., greater than the tolerance of 200 ppm) if the peanuts received a subsequent quarantine fumigation. In addition, a previous fumigation with methyl bromide might cause significant flavor degradation if a subsequent quarantine fumigation with methyl bromide were applied. Therefore, the history of the imported peanuts should be determined and the final product should be considered before they are subjected to a fumigation for quarantine purposes.

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Accepted April 19, 1983