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FOOD FUMIGATION

Bromide Residues from Methyl Bromide Fumigations of Cocoa Beans, and Processed Fractions from Fumigated Beans

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Cocoa beans were fumigated with methyl bromide in a series of studies. Bromide residues were determined on the beans and their fractions after milling. Under the conditions used, bromide residues in cocoa beans did not exceed the tolerance of 50 p.p.m. after fumigation 5 times with 1.5 pounds of methyl bromide per 1000 cubic feet for 24 hours, 7.5 pounds in one fumigation, or with 4.5 pounds for 24 hours followed by 4.5 pounds for 12 hours. The shells from fumigated beans contained 4 to 6 times the amount of residue in the whole bean. Cocoa had a residue level about the same as the fumigated beans, and the other fractions all had lower residues. Reducing the chamber load from 75% to 15% did not affect the residue deposition.

IN THE harvesting, storage, shipping, and other handling of cocoa beans prior to processing, there is ample opportunity for infestation by insects or rodents. One of the most effective ways of controlling these pests is by fumigation with methyl bromide—for example, Phillips *et al.* (*5*) reported on the fumigation of cocoa beans for control of the tobacco moth.

A tolerance for residues of inorganic bromide in cocoa beans resulting from fumigations with methyl bromide has been established by the U. S. Food and Drug Administration at the level of 50 p.p.m. (*2*). This permits legal use of the fumigant under conditions which are effective in solving these problems. Under some conditions, because of length of storage or handling, reinfestation can occur, making it necessary to fumigate more than once. Some pests require higher concentrations of fumigant than others.

This study was undertaken with the cooperation of members of the cocoa industry to determine the levels of bromide residues resulting from single and multiple fumigations with methyl bromide at different dosages and to determine the pattern of residue deposition in the fractions from fumigated cocoa beans after processing.

Experimental Procedure and Results

Series I. The cocoa beans used in the first experimental series were fumigated in a 36-cu. foot vault, using 1.5 pounds of methyl bromide per 1000 cu. feet (*1*). The exposure period was 16 hours at 75° to 80° F. and 50% relative humidity. After fumigation the beans were removed from the vault, placed on a table in the laboratory, and allowed to air 24 hours before sampling. The sample to be analyzed was sealed in a screw-capped glass jar, and total bromide was determined by the Shrader method (*6*) as soon as possible.

The experiment was carried out so that the beans were exposed to the fumigant four times, each time followed by determination of bromide. Results of the analyses are given in Table I. Aeration of 7 days was allowed between fumigations.

Series II. Cocoa beans for the second series were obtained from the 1964 Nigerian main crop, shipped in commercial 4.4-cu. foot burlap bags, each weighing approximately 120 pounds. The shipment was handled to ensure that the beans would not be fumigated before arrival at the laboratory.

The fumigations were carried out in an air-tight 27-cu. foot chamber, 44 inches long and 35 inches in diameter. A vacuum was drawn on the chamber after samples were introduced and a weighed quantity of methyl bromide was swept in with the air as the pressure in the chamber was brought to atmospheric. A circulating fan in the chamber was run to assure mixing of the gas. After the fumigation period, air was drawn rapidly through the chamber and exhausted through a stack to remove the fumigant from the air prior to opening the chamber.

The fumigations were carried out with five bags in the chamber each time. After each fumigation, one bag was removed and another added. Table II shows the loading scheme. This plan gave duplicate bags of cocoa beans fumigated with 1.5 pounds of methyl bromide 1, 2, 3, 4, and 5 times. The load level of 75% full was kept constant for all of the fumigations in this series.

After aeration for 2 to 3 days, the beans from each bag to be sampled were poured into a fiber drum with several

Table I. Residues of Bromide in Cocoa Beans Fumigated with Methyl Bromide after 24 Hours' Aeration

(Series I)

Number of Fumigations				
0	1	2	3	4
Total bromide, p.p.m.				
19	19	29	36	43
15	10	35	32	33

Table II. Chamber Loading Chart for Series II Fumigations

Fumigation No.	Total Times Each Bag Fumigated: 1	2	3	4	5	5	4	3	2	1
	Bag numbers in chamber									
1	1	2	3	4	5					
2		2	3	4	5	6				
3			3	4	5	6	7			
4				4	5	6	7	8		
5					5	6	7	8	9	
6						6	7	8	9	10

grab samples removed during the pouring to give about 10 pounds of beans. The sample was thoroughly mixed and a 1-pound subsample was removed for assay. A 1-gallon friction-lid can was filled with another subsample and the remainder was returned to the drum containing the bulk sample. The 1-gallon subsample was held under refrigeration until the end of the experiment as a retainer, in case more information was needed on the unprocessed fumigated beans.

The beans were shipped in the fiber drums to the Nestlé Co., Fulton, N. Y., where they were put through a normal milling procedure. One-gallon samples of roasted beans, shells, nibs, and cocoa, and 5 pounds of liquor and cocoa butter from each fumigated bag were returned to The Dow Chemical Co., Midland, Mich., for determination of bromide residues. All samples were analyzed by an x-ray fluorescence procedure (*3*). Before assay, the cocoa beans were ground and thoroughly mixed in a meat grinder or blender. A standard curve was prepared for cocoa beans by adding to ground beans known amounts of sodium bromide and determining instrument response. Because of the similarity of the fractions to the whole beans, the instrument response factor obtained on the beans was used for all the fractions. As a check on these determinations some samples were also analyzed by the chemical method of Shrader *et al.* (*6*).

Good agreement between the two methods was obtained on all types of samples, as shown in Table III. Both procedures determine the bromine content in the sample regardless of its chemical form.

A sample from each container of the roasted beans, shells, nibs, and cocoa from the milling was removed by a 1-inch-diameter probe inserted to a depth of 8 to 9 inches. The chocolate and cocoa butter bars were sampled by removing a strip $^1/_2$ to $^3/_4$ inch wide from the end of each of 4 to 5 bars in each sample, to fill a 6 ounce jar.

The results of Series II fumigations, with subsequent milling of beans and analysis of fractions, are given in Table III. Data on the milled fractions of fumigated beans show that roasting increases the residue somewhat, probably because of moisture loss; shells contain 5 to 10 times more bromide than the raw beans; residues in cocoa butter samples are all 5 p.p.m. or less; nibs and liquor both have residues somewhat lower than the beans; and cocoa contains about the same level of residue as the beans.

Series III. In the third series of fumigations the 27-cu. foot chamber loaded with five bags was used. Fumigation data are given in Table IV along with results of analyses of samples of the beans. The two bags of beans with the highest residue, samples 32,528 and 32,530, were milled in the same way as Series II samples, and the fractions analyzed. These data are included with the former data in Table III. The generalizations applying to fractions from cocoa beans fumigated with multiple 1.5 pounds of methyl bromide per 1000 cu. feet apply also to these fumigations with the higher dosages.

Series IV. A single fumigation at the rate of 1.5 pounds of methyl bromide per 1000 cu. feet was conducted with a single bag of cocoa beans in the chamber, at a 15% load (Table IV).

The data from Series I to IV fumigations indicate that the residue is directly proportional to the time of exposure, is about the same for the same total exposure whether exposed once with a high dose or several times with low dosages, and is directly proportional to the concentration of fumigant; relatively high residues can result from several fumigations with a large cumulative dose; and the residue was about the same when 15% full of beans as when it was 75% full during fumigation.

These conclusions may vary under different fumigation conditions, or with different cocoa beans.

Series V. A commercial warehouse fumigation was carried out in which cocoa beans were sampled before and after exposure (Table V). The beans from all seven sources picked up a residue of approximately the same magnitude. The increase of residues corresponds to those of Table III for a single chamber fumigation. Cocoa beans from some locations either had a natural bromide content as high as 28 p.p.m. (Ghana) or had been fumigated previously. The fumigation history of these beans prior to this test was unknown.

If the fumigation history of shipments of beans, or the natural content of bromide residues, is unknown, it will not

Table III. Residues of Bromide in Cocoa Beans and Milled Fractions from Repeated Fumigations

Rep. No.	Sample	Times Fumigated: 0		1[a]		2[a]		3[a]	4[a]	5[a]		3[b]
		Cumulative, Lb. MeBr/1000 Cu. Ft.: 0		1.5		3		4.5	6	7.5		16.5
		X[c]	C	X	C	X	C	X	X	X	C	X
		Gross P.P.M. Bromide Residue										
1	Cocoa beans	5, 8	...	7	...	12	...	16	20	26	...	64
2	Cocoa beans	...	...	9	...	14	...	21	27	31	...	70
1	Roasted cocoa beans	<5	5, 6	9	8, 8	14	14, 16	24	33	36	...	79
2	Roasted cocoa beans	...	...	10	...	16	...	22	31	33	29, 30	74
1	Shells	<5	4, 4	42	38, 36	96	81, 89	153	150	192	...	366
2	Shells	...	...	36	...	84	...	102	159	162, 156	152, 146	318
1	Nibs	<5	4, 3	6, 7	1, 2	5	2, 2	8	11	10	...	41
2	Nibs	...	...	7	...	10	...	13	14	19, 15	19, 16	51
1	Cocoa	<5	1, 3	<5	3, 4	<5	4, 2	12	21	18	...	80
2	Cocoa	...	...	10	...	12	...	18	30	24, 24	21, 24	95
1	Liquor	<5	1, <1	<5	1, 1	<5	3, 2	8	11	12	...	40
2	Liquor	...	...	<5	...	10	...	8	16	20, 15	13, 13	50
1	Butter	<5	1, 1	<5	5, 3	<5	<1, <1	<5	<5	<5	...	<5
2	Butter	...	...	<5	...	<5	...	<5	<5	<5, <5	1, 2	<5

[a] $1^1/_2$ pounds of methyl bromide per 1000 cu. feet, 75–80° F., 24 hours (Series II).
[b] Milled fraction from samples 32,528 and 32,530, fumigation schedule given in Table IV.
[c] Analysis by: X, x-ray fluorescence; C, chemical method.

Table IV. Residues of Bromide in Cocoa Beans Fumigated with Methyl Bromide

(Series III and IV)

Sample	Rate[a]	Hours[b]	Rate[a]	Hours[b]	Rate[a]	Hours[b]	Bromide Residues, P.P.M.[c]
			Series III				
32,534	4.5	24	...	...	...	...	23
32,535	4.5	24	4.5	12	...	...	34
32,523	...	...	4.5	12	...	...	13
32,530	4.5	24	4.5	12	7.5	24	70
32,529	4.5	24	4.5	12	7.5	24	60
32,528	4.5	24	4.5	12	7.5	24	64
32,541	...	...	...	...	7.5	24	42
32,525	...	...	...	...	7.5	24	40
			Series IV				
32,518	1.5	24[d]	...	...	...	...	9

[a] Pounds per 1000 cu. feet.
[b] Hours' exposure to fumigant. All samples aerated 24 hours before sampling.
[c] All analyses by x-ray fluorescence.
[d] Chamber 15% full. All other fumigations at 75% chamber load.

Table V. Residues of Bromide in Cocoa Beans Following Commercial Fumigation with Methyl Bromide

(1.5 lb. per 1000 cu. ft. for 24 hours at 75–80° F.)

Sample	Source	Bromide Residues, P.P.M. Untreated	Bromide Residues, P.P.M. Treated
8–1	Mexico	<5	8
8–2	Mexico	<5	6
6–1	Dominican Republic	11	14
5–1	Dominican Republic	5	8
4–1	Dominican Republic	<5	14
3–1	Dominican Republic	9	20
8–3	Ghana	28	33
5–3	Brazil	<5	14
7–1	Ivory Coast	6	7
7–3	Ivory Coast	<5	16
6–2	Ivory Coast	<5	7
6–3	Ivory Coast	<5	11
5–2	New Guinea	<5	6
3–3	New Guinea	<5	11
4–2	New Guinea	8	17
3–2	Nigeria	8	19
4–3	Nigeria	9	11

Table VI. Bromide Content of Unfumigated Cocoa Beans

Source	Total Bromide, P.P.M.
Ghana	
Sample 1	<5
Sample 2	<5
Ivory Coast	<5
Nigeria	
Main crop 1964 (composite)	<5
Bag 32,510	<5
Bag 32,515	<5
Bag 32,520	<5
Bag 32,523	8
Bag 32,531	6
Bag 32,533	6
Bag 32,536	<5
Bag 32,539	5
Bag 32,512	5
Bag 32,518	<5

be possible to predict the total bromide content of beans after a given fumigation.

Unfumigated Controls. Table VI gives results of analyses on unfumigated beans. The Ghana and Ivory Coast samples were obtained as a check on blank values of beans from these areas. The Nigerian sample labeled "composite" was removed from the shipment before arrival at the laboratory and analyzed immediately, to confirm that the natural bromide content was low enough to proceed with the experiments. The following 10 samples were removed from individual bags of the Nigerian shipment of 32 bags by a sampling thief. More than half of the bags contained less than 5 p.p.m. of bromide, while the others ranged from 5 to 8 p.p.m. The data given in Tables I to VI are "gross" figures, not corrected for naturally occurring bromide.

Discussion

In the studies conducted particular attention was paid to sampling. Since cocoa beans are often fumigated in large quantity, it may be difficult, if not impossible, to take truly representative samples. In a loaded railroad car, warehouse, ship, or silo, it may not be practical to sample adequately. Samples sent to the laboratory for analysis often weigh less than one-half pound. Cocoa beans are large compared to cereal grains, a typical sample having about 425 beans per pound. Thus, a half-pound sample of 212 beans may represent 500 bags, only one bean per 280 pounds. If good composite samples are taken and reduced by quartering or proper splitting, this may be adequate. However, if great care is not exercised, the analytical result may be misleading.

On occasion, the finding of a residue content of relatively large magnitude in cocoa beans might be alarming. However, as Tables V and VI show, cocoa beans may contain bromide before a particular fumigation. The only safe way is to determine the bromide content before conducting a fumigation, to assure that postfumigation residues will be within tolerance levels.

Cocoa products are sometimes included in cattle feed (*4*). Cocoa offered for use as cattle feed, called "cocoa meal," has an exceedingly low feed value. Only 27% of the crude protein in cocoa shells is digestible on the average, so they have no higher feeding value per pound than good roughage. In addition, because of the theobromine and caffeine in both these products, any appreciable amount is injurious to animals. A maximum of 2 pounds per head of cocoa shells may be fed daily to mature cattle without harm. Cocoa meal also can be safely fed only at low levels.

Cocoa actually has a lower bromide residue than the beans from which it is derived (Table III), but cocoa shells may have a bromide residue 6 times higher than the corresponding cocoa beans. Because the maximum feeding level is in the range of 5% of the total diet, the contribution of bromide would be very small from either source.

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