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Application of methyl bromide in fumigation of dairy products

HILAL AHMAD PUNOO*

Department of Food Science and Technology, University of Kashmir, Hazratbal, Srinagar, Kashmir, Jammu and Kashmir

ABSTRACT

Owing to the use of methyl bromide fumigation for insect control in various food industries, the question arises from time to time as to the possible presence and effect of residual bromides in the fumigated foods. Laboratory experiments, as well as commercial fumigations involving millions of pounds of dairy products, were carried out to demonstrate the suitability of methyl bromide for fumigating these products. They may be exposed satisfactorily in vaults, coolers, curing rooms, warehouses, or factories which are tight enough to confine the gas. Pests such as the cheese mite *(Tyroglyphus siro),* cheese skipper *(Piophila casei),* weevils and roaches, which may often be found under the usual manufacturing and aging or storing conditions, are controlled most readily with methyl bromide because of its toxicity to all forms of insect life including the eggs, and because of its effectiveness at low or high temperatures. Methyl bromide also has the advantages of relative insolubility in water, ease of application and rapid venting. The exceptional penetrating property of the gas makes it unnecessary to move or lift stock or to open to reach the pests. Careful inspections of fumigated dairy products revealed no off-tastes or odours, so that the only question to be discussed concerns the magnitude of the bromide retention under various fumigating conditions. Methyl bromide does not penetrate moisture-proof wrapping material such as cellophane with a rubber-like lining. Numerous fumigations of storage rooms and warehouses containing half-pound and two-pound packages of cheese so wrapped were carried out, and no more bromide was found in the cheeses than that in non-fumigated controls. The controls on Brick, Swiss and American process cheese contained no bromide, while a prepared cheese spread contained 5 ppm probably introduced with salt or some other ingredient of the mixture. The amount of bromide retained by fumigated cheese is dependent primarily upon the area exposed and upon the kind of coating or wrapping. In direct fumigations of large cheeses or in fumigations of storage rooms, etc., containing large or small packages of cheese in moisture-proof wrappers, the retentions are for all practical purposes negligible. The residual bromide contents of dried skim milk, butter and several kinds of cheese were determined after fumigation under various laboratory and commercial conditions. After a lapse of reasonable period of the fumigant, the residues are entirely inorganic in nature and are present in insignificant amounts.

Key words: Dairy products, Fumigation, Methyl bromide, Residual bromide, Retention

Methyl bromide is identified as an ozone depleting substance and was banned for applications in food and feed under the Montreal Protocol (TEAP, 2014). Methyl bromide is useable for quarantine and pre-shipment (QPS) and for critical uses after the approval that there is no other fumigant available for the treatment of agricultural products under the protocol as a chemical feedstock and for specific, approved laboratory uses. In relation to the use of methyl bromide fumigation for insect control in various food industries, the question arises from time to time as to the possible presence and effect of residual bromides in the fumigated foods. Some researchers (Dudley et al., 1940; Laug, 1941; Stenger et al., 1939) indicated that while the residues were negligible in many foods, they might be higher in others, particularly those in finely divided form or containing much oil or fat, such

*Corresponding author email: *hilal_punoo@rediff.com*

as milled grains, cheese or nutmeats. During the past few years, however, extensive commercial fumigations of some of these products were conducted successfully and publications (Roehm et al., 1942; Shrader et al., 1942) presented additional information about the bromide residues. These residues are generally low following commercial fumigations than in laboratory experiments, because of the smaller ratio of fumigant to product. After suitable periods of airing, the residues consist entirely of inorganic bromides which are harmless in the amounts ordinarily present.

Laboratory experiments, as well as commercial fumigations involving millions of pounds of dairy products, were carried out to demonstrate the suitability of methyl bromide for fumigating these products. They may be exposed satisfactorily in vaults, coolers, curing rooms, warehouses, or factories which are tight enough to confine the gas. Pests such as the cheese mite (*Tyroglyphussiro*), cheese skipper (*Piophilacasei*), weevils and roaches, which may often be found under the usual manufacturing and aging or storing conditions, are controlled most readily with methyl bromide because of its toxicity to all forms of insect life including the eggs, and because of its effectiveness at low or high temperatures. Although a larger dosage is required at lower temperatures, it is noteworthy that this fumigant is effective under such conditions; many common fumigants become ineffective when the temperature drops. Methyl bromide also has the advantages of relative insolubility in water, ease of application and rapid venting. The exceptional penetrating property of the gas makes it unnecessary to move or lift stock or to open boxes to reach the pests. Careful inspections of fumigated dairy products revealed no off-tastes or odours, so that the only matter to be discussed in this paper concerns the magnitude of the bromide retention under various fumigating conditions.

MATERIALS AND METHODS

Analyses for total and inorganic bromides, with organic bromide by difference, were made as per Shrader et al. (1942).

Method developed by Shraderet al. (1942) was used for distinguishing between inorganic and organic bromide. This method also gave the results of a laboratory fumigation of American cheese.

Fumigation of cheese: Dudley et al. (1940) reported bromide residues in American cheese corresponding to about 80 ppm (parts per million) Br after laboratory fumigation and 34 ppm after commercial fumigation. Laug (1941) obtained much higher residues by treating grated Italian cheese with extreme dosages, and he reported that most of the bromide was non-volatile. A method for distinguishing between inorganic and organic bromide was developed by Shrader et al. (1942), who also gave the results of a laboratory fumigation of American cheese. They concluded that methyl bromide does not penetrate more than a quarter of an inch inside the surface of the cheese. Using an unwrapped 200g of cheese, the outside 6.4 mm layer after aeration contained 80 ppm Br, corresponding to 43 ppm on the entire sample. This cheese had been fumigated for 12 h at 24–25°C, with a methyl bromide concentration of 32 g m^{-3}.

Table 1 prevents the retentions of bromide by whole Longhorn cheeses fumigated under conditions, which might be encountered in practice, except that the dosage was higher than is ordinarily required (The normal dosage is from 16–32 g m^{-3}, depending on the temperature.)

The cheeses, weighing about 12 pounds each and having their original cloth and wax coatings, were exposed for 24 h @ 80 g m^{-3} methyl bromide at 10°C. After various periods of standing in air at about 24°C, the cloth was removed from 2.54 cm sections of each cheese and samples were taken from the outer 6.4 mm and from interior sections. Analyses for total and inorganic bromides, with organic bromide by difference, were done as per Shrader et al. (1942). Since within experimental error no more bromide was ever found in the interior portions than in the controls, only the results obtained on outside samples are shown in the Table 1. Cheese B appears to have taken up more bromide than Cheese A, apparently because it had a thinner coating of wax.

The results showed that all of the absorbed methyl bromide was lost either by volatilization or by conversion into inorganic bromide, within two or three days after removal from the fumigation chamber. In another set of experiments, the magnitude of the residual bromide content after a week of airing was studied as a function of dosage. Whole Longhorn cheeses were fumigated with different concentrations of methyl bromide for 24 h at 10°C, and later analyzed for total bromide in the outer 6.4 mm section (after removal of the cloth). About 6.4 mm layer from the top of each cheese was also tested; this was not covered with cloth, but had a wax coating, which was included in the samples. The data (Table 2) showed a general tendency toward higher retention with higher dosage, but the effect appears to be modified somewhat by the condition of the coating, since considerable variations occur between samples from different positions. Interior samples again were found to be free from bromide.

Table 1 Fumigation of whole Longhorn cheeses applying 80 g m^{-3} CH_3Br for 24 h at 10°C

Hours aired at 24ºC	ppm (parts per million) bromide remaining in outer 6.4 mm					
	Cheese A			Cheese B		
	Total	Inorganic	Organic	Total	Inorganic	Organic
0.5	77	15	62	101	23	78
4	61	21	40	84	30	54
24	42	22	20	47	38	9.0
48	25	25	0.0	43	39	4.0
96	24	24	0.0	39	38	1.0
168	26	25	1.0	38	36	2.0

It should be mentioned that while methyl bromide does not penetrate solid cheese, it enters any hole or crevice which is open to the air. Therefore infestations on either external or open internal surfaces can be controlled. With porous cheese, the retention of bromide in interior portions is practically the same as that on the outside. For example, during a commercial fumigation a sample quarter of a rather porous cheddar cheese was exposed, unwaxed, to 29 g m^{-3} for 8 h at 15–21°C, then it was immediately waxed and shipped to the laboratory for analysis. The total bromide, which was entirely inorganic at the time of analysis, amounted to 12 ppm on the outer 6.4 mm (average from top, curved side and cut side after removal of the wax) and to 11 ppm at a region about 76.2 mm inside the cheese. Another more solid cheese (American cheddar), treated in a comparable way, showed bromide on the outer portions, but no more in the center than was found in a duplicate un-fumigated portion.

In another commercial fumigation, unwrapped 500 g bricks of limburger cheese were fumigated in a curing room at 21°C. A dosage of 24 g m^{-3}of methyl bromide was employed and about 2,300 kg of cheese was present in the room. After fumigation the room was aired for 3 h, then two bricks of the cheese were wrapped in waxed paper and shipped to the laboratory where they were analyzed six days later. Cheese 1, the less ripe of the two, contained 21 ppm bromide in the outer 6.4 mm and 6 ppm in the interior. The corresponding figures for Cheese 2 were 38 ppm and 12 ppm. Controls on similar un-fumigated bricks showed contents of the same magnitude as those of the centers of the fumigated samples, but there were individual variations which may be associated with the salt content. Common salt ordinarily contains up to 2,000% bromide.

Methyl bromide does not penetrate moisture-proof wrapping material such as cellophane with a rubber-like lining. Numerous fumigations of storage rooms and warehouses containing 200-900g packages of cheese so wrapped were carried out, and no more bromide was found in the cheeses than that in controls. The controls on Brick, Swiss and American process cheese contained no bromide, while a prepared cheese spread contained 5 ppm probably introduced with salt or some other ingredient of the mixture. When a 200 g tin foil wrapped package of this cheese spread

Table 2 Fumigation of whole Longhorn cheeses applying various dosages for 24 h at 10°C airing for 168 h

Cheese	Methyl bromide (g m^{-3})	Temperature during airing (°C)	ppm (parts per million) total bromide found	
			Outer 6.4 mm	Top 6.4 mm
A	80	24	26	29
B	80	24	38	32
C	48	–1 to 10	35	30
D	48	–1 to 10	29	28
E	32	–1 to 10	25	17
F	32	–1 to 10	21	25
G	16	–1 to 10	18	19
H	16	–1 to 10	20	15
I	Non-fumigated control		0.0	2.0

was fumigated for 9 h at 21°C @ 48 g $m^{-3}$of methyl bromide, the bromide content rose only to 9 ppm.

From the above it is evident that the amount of bromide retained by fumigated cheese is dependent primarily upon the area exposed and upon the kind of coating or wrapping. In direct fumigations of large cheeses or in fumigations of storage rooms, etc., containing large or small packages of cheese in moisture-proof wrappers, the retentions are for all practical purposes negligible.

Fumigation of dried skim milk: Samples of skim milk powders, which had been dried by different processes were fumigated for a 12 h period at 21°C and 30% relative humidity with 32 g of methyl bromide per m^3. The milk powders were fumigated in 2.3 kg paper bags, in a 14 m^3 chamber at atmospheric pressure. After fumigation the bags were removed to a large room and were allowed to stand in normal air for definite time intervals. Before each sampling the contents of each bag were well mixed. The amounts of bromide retained after various periods of standing are shown in Table 3. The non-fumigated controls contain much more bromide than is added by the fumigation. All of the retained bromide is inorganic after four days of airing. These observations are consistent with those of Laug (1941) who fumigated skim milk powder with much higher dosages of methyl bromide and found relatively little bromide retained after sufficient airing.

Portions of the same fumigated samples were later refumigated in the same manner with the same concentration of methyl bromide, but for 16 h at 20°C and 70-80% relative humidity. After four days of airing the parts per million of bromide were 26 pp min the spray-dried milk and 58 ppm in the roll-dried material. The data indicated that no difficulty with high bromide residues is to be expected in fumigations of skim milk powders.

Table 3 Fumigation of skim milk powders applying 32 g m^{-3} CH_3Br for 12 h at 21°C and 30% r.h.

Hours aired	ppm (parts per million) total bromide	
	Spray-dried product	Roll-dried product
0.5	29	59
4	29	50
24	28	54
51	27	54
96	24	48
Non fumigated control	24	44

Fumigation of butter: There is no point in fumigating butter itself, but since it might be stored in creameries or warehouses undergoing general fumigation, an experimental fumigation was carried out. A cube of butter 6.4 mm on a side was exposed for 12 h @ 16 g m^{-3} of methyl bromide, at 22–25°C. Immediately after fumigation the outer 6.4 mm was cut off and the outer and inner portions were aired separately, being analyzed from time to time for total and inorganic bromide. The findings reported in Table 4 showed that methyl bromide did not penetrate more than 6.4 mm into the butter, and that most of it escapes by volatilization, but a small part is converted to inorganic bromide. No analyses have yet been made of packaged butter fumigated under commercial conditions.

Some packaged oleomargarine, which had been present during fumigation of a cold storage room, contained very little bromide, the highest results amounting to 7 ppm Br in the outer 6.4 mm and 3 ppm Br in interior portions. It may be concluded that fumigation of rooms containing butter or oleo will produce no objectionable bromide residues in these products.

In no case does methyl bromide remain as such in any of these dairy products for more than two or three days after removal from the fumigation chamber. The bromide residues are entirely inorganic. Flinn (1941) showed that no injurious effects were produced in adults who consumed 30 to 45 grains (2 to 3 g) of sodium bromide daily over a period of four months. Assuming that an adult might eat a kilogram of fumigated foods each day (a liberal allowance) and that the bromide residues in these foods might average 100 ppm (which is more than that was found in any of the above experiments), the possible daily bromide

Table 4 Fumigation of butter applying 16 g m^{-3} CH_3Br for 12 h at 22–25°C

Hours aired	ppm (parts per million) bromide remaining			
	In outer 6.4 mm		In inner portions	
	Total	Inorganic	Total	Inorganic
0.5	58	3.0	1.0	…….
4	56	4.0	1.0	2.0
24	27	4.0	2.0	……
48	16	5.0	…….	…….
96	10	11	…….	…….
168	9.0	10	…….	
Non-fumigated controls	1.0	1.0	…….	…….

intake would amount to only 0.10 g, or 0.13 g as sodium bromide. It is evident that an ample margin of safety exists.

CONCLUSION

The use of methyl bromide for fumigating dairy products was discussed and its advantages mentioned. The residual bromide contents of dried skim milk, butter and several kinds of cheese were determined after fumigation under various laboratory and commercial conditions. After a reasonable period has been allowed for escape of the fumigant, the residues are entirely inorganic in nature and are present in insignificant amounts.

REFERENCES

Dudley HC, Miller JW, Neal PA, Sayers RR (1940) Studies on foodstuffs fumigated with methyl bromide. Pub. Health Reports **55**: 22.

Flnn FB (1941) The Appearance of blood bromide after oral ingestion. Journal of Laboratory and Clinical Medicine **26**: 1325.

Laug EP (1941) Bromide residues in foodstuffs. Industrial and Engineering Chemistry **33**: 803.

Roehm LS, Shrader SA, Stenger VA (1942) Bromide residues in cereals fumigated with methyl bromide. Cereal Chemistry **19**: 235.

Shrader SA, Beshgetoor AW, Stenger VA (1942) Determination of Total and Inorganic Bromide in Foods Fumigated with Methyl Bromide. Industrial and Engineering Chemistry, Analytics Ed. **14**: 1.

Stenger VA, Shrade SA, Beshgetoor AW (1939) Analytical Methods for Methyl Bromide. Industrial and Engineering Chemistry, Analytics Ed. **11**: 121.

Teap (2014) Report of the Technology and Economic Assessment Panel, Progress Report, Montreal Protocol on Substances that Deplete the Ozone Layer, United Nations Environment Programme, Ozone Secretariat, October 2014, Nairobi, Kenya: