

IRRITATION FROM RESIDUAL BROMIDES

AFTER METHYL BROMIDE FUMIGATION

Ben H. Miller, B.Ch.E.

Remo Navone, B.S.

Minoru Ota, B.A.

AFTER a private home in California was fumigated with methyl bromide gas, the local county health officer called the California State Health Department about a severe irritation experienced by the occupants.

Investigators from the bureau of occupational health of the State department of public health were assigned to visit the home. They learned that after the house had been fumigated to eliminate termites, it was "aired out," and the family who had occupied the house moved back in. Almost immediately the family experienced an irritation which they associated with the fumigation. All four members of the family, particularly the 2-year-old child, suffered from irritation of the eyes, nose, throat, and skin. Even the dog was affected. The irritation was persistent and was particularly severe on damp nights. The family finally felt they could not continue to live in the house and moved out into the garage and a tent, where they were living at the time of the State health department investigation.

Although the effects reported seemed to be associated with the fumigation, the precise origin or the nature of the substance that caused the irritation was not known. Methyl bromide

liquid is highly volatile and would be expected to vaporize completely and be lost to the outside atmosphere during the "airing out" procedure.

The Investigation

The fumigator, a qualified contracting pest control operator, stated that he did not know the source of the irritation, but remarked that after the fumigation he had found the kitchen stove was corroded and had replaced it. However, in his work on about 200 such jobs, he had never known of a similar occurrence. He said that 40 pounds of methyl bromide had been used, about 10 pounds from one container and 30 pounds from another. During the interview he mentioned that possibly a pilot light had been left burning during the fumigation. Later it was learned that the instructions for using methyl bromide gas require that all flames be extinguished prior to fumigation.

It was then discovered that about 2 years previously a similar incident had occurred in another southern California home, where a pilot light had been left on during methyl bromide fumigation. Most of the metal objects in that house had become corroded and had to be replaced. The residents there too had experienced skin and respiratory irritation.

In an attempt to identify the corrosive and irritating substance, the health department laboratory impregnated paper, wood, and metal with various forms of bromides to determine which bromide would cause corrosion. The laboratory tests indicated that hydrobromic

All the authors are with the California State Department of Health. Mr. Miller is industrial hygiene engineering associate in the division of preventive medical services, bureau of occupational health, Berkeley. Mr. Navone is chief of the branch public health laboratory and Mr. Ota is associate public health chemist. Both are with the division of laboratories in Los Angeles.

acid was quite corrosive, and also that it was persistent as a residual material. Moreover, hydrobromic acid is a powerful irritant to the eyes, skin, and respiratory system, and it can be formed from methyl bromide by decomposition in a flame. Since hydrobromic acid can react with fabrics, wood, and metal to form bromides and methyl bromide cannot, it appeared that hydrobromic acid might be the cause of the distress. An investigation to ascertain the presence of residual bromides on surfaces within the house disclosed substantial quantities of bromides on the ceilings, walls, door frames, and other surfaces.

The sampling method consisted of wiping about 200 square inches of each surface with a folded industrial paper wiper which had previously been dampened in 1 percent sodium bicarbonate solution. The samples obtained were then analyzed for bromides by the phenol red colorimetric method of Houghton (1). The results of those wipe tests are shown in table 1.

Wipe samples were also obtained in two other homes where no pilot light had been left burning during fumigation. Bromide residuals found in the "control" homes are listed in table 2.

Definite quantities of residual bromides were present in the home where the pilot light was burning (table 1), while residual bromides were almost completely absent in homes where no pilot light was burning during fumigation (table 2).

Further inquiry elicited information about several other homes adversely affected after methyl bromide fumigation during which one or more flames had been left burning. In one

Table 1. Bromide residuals in home where pilot light was burning during fumigation

Location	Milligram of bromide per sample
Kitchen ceiling.....	0. 37
Kitchen door frame.....	. 75
Kitchen cabinets.....	. 48
Bottom of kitchen table.....	. 23
Ledge in kitchen.....	. 34
Hall door frames.....	. 74
Rear of hall picture.....	. 39
Wall of living room.....	. 37
Under house.....	. 37

of these homes sufficient gas to keep a pilot light burning for hours was reported to have remained in the supply line even though the fuel gas supply service valve was shut off. Tests of wipe samples taken at two of these homes where fumigation had been completed 4 to 6 months previously show that bromides were still present (table 3).

After the surfaces of Mrs. G's house had been thoroughly washed, only two of five additional wipe samples contained any detectable amount of bromide. One sample contained only 0.01 and the other only 0.03 milligrams of bromide.

One other house in which pilot lights had been left on during a recent fumigation was located during the study. Shortly after the fumigation all surfaces in this house had been thoroughly washed. Five wipe samples were

Table 2. Bromide residuals in homes where pilot light was not burning during fumigation

Location	Milligram of bromide per sample
Home of Mrs. W:	
Attic at impregnation points.....	0. 06
Rear of stove.....	. 01
Under kitchen sink.....	0
Kitchen walls.....	. 03
Bedroom surfaces.....	0
Home of Mrs. S:	
Hot water heater.....	0
Behind kitchen stove.....	0
Under kitchen sink.....	0
Inside kitchen cabinet.....	. 01
Walls of den.....	0

Table 3. Bromide residuals found 4-6 months after fumigation in homes where pilot light was burning during fumigation¹

Location	Milligrams of bromide per sample
Home of Mrs. G:	
Underside of kitchen shelves.....	1. 7
Vent over stove.....	1. 8
Kitchen ceiling.....	1. 8
Home of Mrs. P:	
Kitchen ceiling.....	. 84
Kitchen vent.....	1. 5
Top of hot water heater.....	2. 2
Kitchen window frames.....	. 8

¹ After fumigation some irritation of the hands was reported in both instances.

obtained for analysis, and none disclosed a detectable amount of bromide ion.

Discussion

From these results, it was concluded that bromides remaining after methyl bromide fumigation were removed by washing the surfaces thoroughly.

Under ordinary conditions of fumigation, 40 pounds of methyl provides a concentration of methyl bromide vapor in air of about 1.5 percent (15,000 ppm) in an average house (area, 1,250 square feet; volume, 10,000 cubic feet). According to Nuckolls (2) and von Oettingen (3), 0.7 percent by volume methyl bromide vapor in a room was decomposed by a gas flame to give 0.003 percent volume of hydrogen bromide. A 2.2 percent by volume methyl bromide was similarly decomposed to give 0.011 percent by volume hydrobromide.

Interpolation, assuming decomposition follows a straight-line function, indicates that a 1.5 percent concentration of methyl bromide under such circumstances would decompose to give 72 ppm (0.0072 percent by volume) of hydrogen bromide. (The threshold limit value for hydrogen bromide in air, according to the list for 1959 issued by the American Conference of Governmental Industrial Hygienists, is 5 ppm, or 0.0005 percent by volume.)

In view of von Oettingen's work, indicating the decomposition of methyl bromide by gas flame, and the results of this investigation, it seems probable that the methyl bromide used to fumigate the homes studied was decomposed by burning pilot lights. The decomposition was accompanied by formation of hydrogen bromide, which in turn produced the persistent

and irritating condition which was the basis for the complaints.

Recommendations

Since this explanation fits all the circumstances, it is believed to be correct. Therefore, it is recommended that a very careful effort be made to insure that all flames, including pilot lights, be extinguished before fumigating any residence with methyl bromide. There is little doubt that the presence of any open flame during methyl bromide fumigation will result in the irritating and distressing conditions.

If metallic objects such as stoves, hot water heaters, or floor furnaces appear corroded, or if any irritation is experienced following fumigation, it is inadvisable to occupy the house until it has been thoroughly decontaminated. All exposed surfaces and fabrics should be decontaminated by washing them with a mild alkaline solution, such as sodium carbonate (washing soda) dissolved in water. An alkaline solution will neutralize any residual hydrogen bromide.

REFERENCES

- (1) Houghton, G. U.: The bromide content of underground waters. *J. Chem. Soc. London* 65: 277-280, September 1946.
- (2) Nuckolls, A. H.: Underwriters Laboratories' report on the comparative life, fire and explosion hazards of common refrigerants. *Miscellaneous Hazards No. 2375*. Chicago, Underwriters Laboratories, Nov. 13, 1933, 118 pp.
- (3) von Oettingen, W. F.: The toxicity and potential dangers of methyl bromide, with special reference to its use in the chemical industry, in fire extinguishers, and in fumigation. *Nat. Inst. Health Bull. No. 185*. Washington, D.C., U.S. Government Printing Office, 1946, 41 pp.