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METHYL BROMIDE FUMIGATION
Prepared in the Division of Control Investigations

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Introduction

The use of methyl bromide as a fumigant is relatively recent, and many requests have come to the Bureau for information concerning it. The following information has been assembled in order to acquaint those interested with its general characteristics and uses.

Uses of Methyl Bromide

Methyl bromide has been found effective against a wide variety of insects, as well as red spiders and other mites, and against all stages. It has properties of penetration which make possible the destruction of certain sheltered pests such as leaf miners, borers, mites, and other internal feeders. In common with certain other fumigants, its lethal action is delayed for a time following fumigation. This period may be several days with some species, and will vary according to the excess above the minimum lethal dosage.

The uses of methyl bromide have increased rapidly in the last 5 years, as more and more entomologists have utilized it in the solving of their insect-control problems. In its gaseous state its employment is usually limited to fumigation in tight enclosures.

It has been widely applied for the fumigation of plant material to allow movement from within quarantined areas. Its use is authorized under Federal or State regulations for the treatment of most imported plant material for propagation, as well as for imported green pod vegetables, cipollini bulbs, and chestnuts; for domestic nursery and greenhouse plants, and shipments of fresh vegetables and fruits for certification under the Japanese beetle quarantine; for nursery hosts of the oriental fruit moth and the white-fringed beetle; for azaleas infested with the azalea leaf roller; and for hosts of the camellia scale. It also has been authorized for the fumigation of the potato tuber moth in white potatoes, the sweetpotato weevil in sweetpotatoes and sweetpotato draws and vine cuttings, the strawberry crown borer in strawberry plants, Hypera brunneipennis in baled hay, host plants of the European corn borer and the citrus whiteflies, carriers of the pear psylla, the grape phylloxera on grapevines, Christmas trees for certification under the gypsy moth quarantine, narcissus bulbs from certain producing areas, and probably others.

In commercial insect control it is used in many ways: For greenhouse plants, especially those infested with cyclamen and other related mites; for various coccids on potted plants; for the codling moth in pears; for the tomato pinworm; and for the gladiolus thrips on corms. It is also used for storage-infesting insects in milled flour and feeds, and in seeds, and for their control in rice and wheat mills, seed houses, and candy manufacturing plants. Other uses include the fumigation of dried fruits, nut meats, dry beans and peas, green coffee beans, wooden antiques, chicory, spices, chestnuts, macaroni products, dehydrated soups and vegetables, cocoa and chocolate, dairy products including cheese, dried milk, and butter, and margarine.

Methyl bromide is mixed with ethylene dichloride and carbon tetrachloride as a fumigant for stored grains, and with hydrocyanic acid for certain treatments applied by private commercial entomologists.

Methyl bromide is also used as a soil fumigant by injection as a liquid, but it is injurious to plant life when used in this manner. It has been authorized for the treatment of potting soil and soil plots or plunging beds under the white-fringed beetle quarantine. It has also been widely used for control of colonies of the Texas leaf-cutting ant by injection into the colony entrances. It can also be diluted with water and used as a soil fumigant in quarantine treatments against the Japanese beetle and the white-fringed beetle.

Properties of Methyl Bromide

Methyl bromide (CH_3Br) is a colorless, odorless, volatile liquid, with a specific gravity of 1.732 at 0°C ., and a boiling point of 40.1°F . It is a gas at ordinary temperatures, in which state it is approximately 3.3 times as heavy as air. It is soluble in most common organic solvents but is only slightly soluble in water. It has been used as a fire extinguisher.

It is normally procurable in 10-, 50-, and 150-pound cylinders, or in 1-pound cans. It is obtainable from the following manufacturers:^{1/}

The Dow Chemical Company, Midland, Mich.
E. I. duPont de Nemours & Company, Wilmington, Del.
Michigan Chemical Corporation, St. Louis, Mich.
Pittsberg Chemical Company, Vernon, Calif.

Methyl bromide will soon be obtainable in glass ampules of various sizes. The names of possible sources from which these may be purchased will be given upon request.

Detection of the Gas

A halide detector, several types of which are marketed by refrigeration supply companies as refrigerant leak detectors, is the easiest and most useful means of determining the presence or absence of harmful concentrations of methyl bromide gas. The detector consists of an alcohol or acetylene torch which heats a copper cone or tube, and an air tube or hose through which the air to be tested is passed over the copper. This tube facilitates drawing samples from between or within containers. A green flame is produced when fumes of a halide pass over red-hot copper. Best results have been obtained with the alcohol torch type.

After the torch is lighted it should be allowed to burn until the copper cone or tube glows at red heat and a blue inner flame shows above the copper. The valve can then be regulated until the blue flame just disappears beneath the end of the copper cone or tube when viewed horizontally.

^{1/} The accompanying list of concerns and their products is included for the information of the users of this circular without any given or implied guarantee of the reliability of the firms or endorsement of their individual products. No attempt has been made to make the list fully complete, and no discrimination is intended or implied against firms whose names or products are not listed.

When the sampling tube is placed in air containing methyl bromide a green or blue flame will be seen in the torch, depending on the concentration. The following tabulation, prepared by one of the manufacturers of methyl bromide, gives the approximate methyl bromide concentration associated with color intensity in the flame.

<u>Parts CH₃Br</u> <u>per million,</u> <u>by volume</u>	<u>Pounds CH₃Br</u> <u>per 1,000 cubic feet</u>	<u>Flame color</u>
0	0	Almost invisible
40	0.010	Rather faint green
60	.014	Moderate green
100	.024	Moderate green
130	.031	Strong green; slightly blue at edges
180	.043	Strong green; rather blue
240	.058	Strong blue-green
360	.086	Strong blue-green
800	.192	Strong blue

The detector should be cleaned before each use, as lint often lodges in the throat. The cone in the alcohol torch will become red hot only when the flame is strong and direct through the center of the cone. If the flame spreads around the cone, it will not heat properly and often a green color will show in the absence of any halide. In the latter event the lamp should be cooled and cleaned and another attempt made.

Protection to Operator

Since methyl bromide is injurious to all forms of animal life, proper caution should be observed when handling it. Continued exposure to low concentrations is especially to be avoided. An operator should use an approved gas mask when exposed to the gas at fumigation concentrations. The mask should be equipped with a black canister, type B, for organic vapors, as approved by the Bureau of Mines as per schedule 14D or 19A. The manufacturer's instructions on each canister should be followed rigidly. Do not use a mask in known concentrations stronger than the limit stated on the canister, nor for total exposure periods longer than those recommended. Canisters can be procured from the following firms (see footnote 1, page 3):

	<u>Type</u>	<u>Canister recommended</u>
Mine Safety Appliance Co.	AB	CMA
E. D. Bullard Company	CM	CM-1
Davis Emergency Equipment Co.	M-1	C-1

Considerable information is available on the effect of methyl bromide gas on warm-blooded animals.^{2/} It has been shown that they can survive high concentrations for brief periods, but that prolonged exposures to low concentrations may be injurious or perhaps lethal. From these studies it is considered that momentary exposure of operators to fumigation concentrations by accident, as might result from opening a vault door before venting and thus being subjected to a few seconds of exposure, is not likely to cause injury, but working many hours in a low concentration may be harmful. It is indicated in the studies on animals that prolonged and repeated exposures to concentrations as low as 33 PPM can be injurious.

Two effects are produced, (1) a paralysis, resulting from continued exposure to low concentrations, from which animals can completely recover when removed from the environment of the gas, and (2) with higher concentrations, lung irritation which can become severe and acute, often developing into typical confluent broncho-pneumonia.

The effects are additive during a given exposure period or in closely repeated exposures, but where exposures are irregular and at intervals of several days the effects can apparently be thrown off by the body.

Liquid methyl bromide when spilled on the skin will sometimes cause burning on certain persons. It has been observed that a few individuals become sensitive to methyl bromide and are easily burned by contact with it in liquid form. Burns on the feet of men applying quantities of liquid methyl bromide as a soil fumigant have also been reported. It is inadvisable for any except experienced technical personnel to attempt to handle liquid methyl bromide.

^{2/} Irish, D. D., Adams, E. M., Spencer, H. C., and Rowe, V. K. 1940. The response attending exposure of laboratory animals to vapors of methyl bromide. Jour. Indus. Hyg. and Toxicol. 22(6): 218-230.

Sayers, E. R., Yant, W. P., Thomas, B. G. H., and Berger, L. B. 1929. Physiological response attending exposure to vapors of methyl bromide, methyl chloride, ethyl bromide, and ethyl chloride. U. S. Pub. Health Serv. Bul. 185. 56 pp.

Types of Fumigation Chambers

Successful methyl bromide fumigation can be done in almost any tight enclosure, such as fumigation vaults, converted drums, tents or tarpaulins, storage rooms, van or refrigerator trucks, and refrigerator or freight cars. Conditions associated with various materials to be fumigated limit the use of certain of these. In general, fumigation to meet quarantine requirements must either be done in a standard enclosure (usually a metal-lined vault) or the dosage schedules must be increased to compensate for probable leakage. For commercial insect control, dosage schedules can be developed for the specific enclosure used.

For atmospheric vault fumigation, the best type of vault is longer than wide and is provided with a blower to be used for circulation and for venting. In this arrangement, as shown in figure 1, the blower is mounted on the back wall next to the ceiling, directing the air flow along the ceiling toward the front. For venting, a trap door is dropped in front of the blower, thus directing its discharge to the outside, and at the same time fresh air is admitted, either through a small intake or by slightly opening the front door.

For most uniform results the vault should be lined with sheet metal, but good results are also obtained with plywood or pressed wood linings. All joints should be soldered or sealed with a nonhardening bituminous compound (caulking compound). The whole end may serve as a door, as shown in figure 1, or in small installations the side can be used as the door. The door should be clamped against two parallel strips of molded sponge-rubber gasket. All other openings should be similarly gasketed.

If temperature control is desired, the vault can be made self contained by adding thermostatically controlled electric heaters. The walls can be insulated or not, as desired. Plans are available upon request.

Methyl bromide can be used satisfactorily in equipment for vacuum fumigation.

A small type of fumigation chamber can be made from a steel drum by providing a water-sealed lid. Plans of this unit are available upon request. Drums, tight boxlike hoods, wooden barrels, or cylinders can also be used by inverting them over objects to be fumigated.

Tent or tarpaulin fumigation can be performed by using cloth coated with ethyl cellulose, vinyl resin, or other similar coating materials. Ordinary canvas duck tarpaulins apparently do not retain methyl bromide sufficiently well to insure satisfactory fumigation. Refrigerated freight cars and trucks make good

fumigation chambers. Other enclosures that would normally be too leaky, such as freight cars, van trucks, and rooms, can be made usable by sealing all cracks with masking tape, a product sold by automobile supply companies, or with flour-oil paste.

Dosage Schedules

Dosage schedules for methyl bromide fumigation are composed of three elements, each equally important: (1) Amount of methyl bromide, (2) exposure period, and (3) temperature. It has been found that generally one-half pound of methyl bromide and one-half hour of exposure have about the same value, so that any modification of a dosage schedule can be either in dosage or in exposure in those proportions. Methyl bromide is more effective at higher than at lower temperatures, and the change in effectiveness is at a fairly constant rate for any given insect or environment. Available data indicate that a 5° to 10° change in temperature is equivalent to one-half hour of exposure or one-half pound of dosage. This ratio of course changes as the schedules approach dosages of less than 1 pound, exposures of less than 1 hour, or extreme temperatures.

This fairly constant rate of change has made it possible to establish series of dosage schedules ranging from low to high temperatures all of which have approximately the same effectiveness on a given insect and the same degree of tolerance from the plant host. In instances where the schedules are near the minimum lethal amount, the series have small temperature differences. Where the schedules of a series are considerably over the minimum, they are fewer with greater temperature differences.

Fumigation schedules developed to date are too numerous to be discussed here. At 70° F. the minimum schedules for accessible insects appear to be about 2.5 pounds for 1.5 hours (or 2 pounds for 2 hours).

A moderate dosage schedule sufficient for most insects and well tolerated by most plants is 3 pounds for 2 hours at 70° .

For some insects imbedded in vegetables, fruits, and nuts it is sometimes necessary to use dosages of 4 to 5 pounds for 3 to 5 hours, but many succumb to 2 pounds for 2 hours at 70° .

Insect larvae in soil balls on nursery plants require 1.5 pounds for 2.5 hours at 73° for the Japanese beetle and 3.5 pounds for 1.5 hours at 70° in vacuum for the white-fringed beetle.

For the fumigation of grain or inert materials, a schedule of 1 pound for 24 hours at prevailing temperatures is generally recommended.

Successful fumigation has been done with methyl bromide from 0° to 95° F.

Method of Applying Dosages

The dosage of methyl bromide is released within the chamber through a closed system from the outside. It can be released either by spraying through an ordinary spray nozzle into the air stream in front of the blower, by allowing it to evaporate from a shallow pan, or by volatilizing it through a heated coil.

Where the calculated dosage of methyl bromide is 1 pound or more it can be measured by weight. To do this, the cylinder of methyl bromide is placed on platform scales and accurately weighed. The desired amount is then subtracted from the total and the scales are set at that point. The gas is slowly released, and when the weight bar again balances the valve is closed. In this case the cylinder of gas is connected directly with the fumigation vault by light copper or plastic tubing. Near the cylinder the tubing should be arranged in a spiral coil of two or three turns to reduce to a minimum its influence on the weight of the cylinder.

Special glass measures, or dispensers, have been devised to measure small quantities of methyl bromide. One type is inserted in the line between the supply cylinder and the vault. By use of valves the desired amount is admitted to the measure, which is graduated in cubic centimeters. The methyl bromide remains as a liquid in the measure, since it is still under pressure. To release, valves on the other side are opened, and its own pressure forces the dosage into the vault.

Another type of dispenser holds the contents of a 1-pound can and the dosage is removed by subtraction. A third type delivers the entire contents of a can into the vault and is useful where the amount of fumigant desired is in multiples of 1 pound.

These dispensers can be procured from the Arrow Products Company, Carlstadt, N. J., the Dow Chemical Company, Midland, Mich., or Bobbink and Atkins, East Rutherford, N. J. (See footnote 1 on page 3.)

Calculation of Dosage

When a dosage of methyl bromide is calculated by weight the following formula is used:

Divide the volume of the vault in cubic feet by 1,000, then multiply this quotient by the dosage rate as expressed in pounds per 1,000 cubic feet. (Example, for a dosage of 2.5 pounds per 1,000 cubic feet in a 1,400-cubic-foot vault it would take $\frac{1400}{1000} \times 2.5 = 3.5$ pounds.)

When a dosage of methyl bromide is to be measured the following formula is used:

Multiply the index of the desired rate (see below) by the capacity of the vault in cubic feet. (Example, for a dosage of 2 pounds per 1,000 cubic feet in a 31-cubic-foot vault, $0.52 \times 31 = 16.12$ cc.) (The basic index is 0.26 cc. per cubic foot per pound per 1,000 cubic feet.)

<u>Rate per 1,000 cubic feet</u>	<u>Index</u>
1 pound	0.26 cc. per cubic foot
1.5 pounds	0.39 cc. per cubic foot
2 pounds	0.52 cc. per cubic foot
2.5 pounds	0.65 cc. per cubic foot
3 pounds	0.78 cc. per cubic foot
3.5 pounds	0.91 cc. per cubic foot
4 pounds	1.04 cc. per cubic foot

Effect of Humidity

The efficiency of methyl bromide apparently is not impaired by the presence of moisture; in fact, better results are often obtained under conditions of high humidity. Enough water to form a protective film, however, will sometimes reduce the expected efficiency.

Circulation and Venting

Methyl bromide gas will stratify if no circulation is provided in the fumigation chamber, and an overdosage or lengthened exposure is necessary to offset that condition.

If fumigation is done at prevailing temperatures, a short period of circulation during and following the application of methyl bromide is sufficient to mix the gas and air thoroughly. If temperature control is necessary, circulation should continue for the duration of the exposure, since heat stratification will occur otherwise. If rapid penetration is desired in a short exposure period, continuous circulation will probably be desirable.

The fumigation chamber should not be entered, except by men wearing gas masks, until the gas in the free air spaces has been exhausted through the venting system. This can be determined with the halide test lamp. Gas will continue to be present in the containers or load for a period of 1 hour or more but it is generally safe to handle such material if the exhausting continues, as this will keep a drift of fresh air moving toward the rear of the chamber.

Plant Reaction

In general, living plant material is unaffected by ordinary dosages of methyl bromide, although any plant can be injured by overdosages or careless attention to details. In the fumigation of living plants the directions as to dosage, temperature, and length of exposure should be followed rigidly.

Dormant plant material is more tolerant than growing plants. Nonfoliated dormant material (deciduous woody plants, bulbs, corms, roots, tubers, etc.) is more generally tolerant than foliated dormant plants. There are some plants that are injured consistently by moderate dosages, such as a few azaleas, certain coniferous evergreens in a partially dormant or nondormant state, a scattering of perennials, and a few potted greenhouse varieties, particularly rooted chrysanthemum cuttings. The list of plant varieties successfully fumigated runs into the thousands.

Vegetable produce generally has been uninjured in experimental and commercial treatments to date. Potatoes, sweet-potatoes, tomatoes, onions, cabbage, snap beans, lima beans, pigeon peas, turnips, sweet corn, carrots, and beets all have been fumigated in carload lots. Eggplant and peppers are considered to be easily injured but have been fumigated successfully in mixed carlots. Cauliflower, celery, honeydew melons, cantaloupes, papayas, pod peas, bunch radishes, and dried garlic have been fumigated experimentally without injury. Cucumbers, however, have been consistently injured.

Apples, peaches, and pears have been fumigated in carload lots, and apricots, cherries, grapes, and plums have been treated experimentally.

The same species or varieties of plants often react differently under different conditions. Therefore, wherever possible, trial tests should be made prior to the fumigation of plant materials or produce in any quantity, or where new installations, new conditions, or new plant varieties are involved. This is most important in regard to potted greenhouse plants.

CAUTION

Since methyl bromide is known to be injurious to humans, persons not familiar with handling fumigants are cautioned against using it until they have thoroughly familiarized themselves with the necessary precautions.

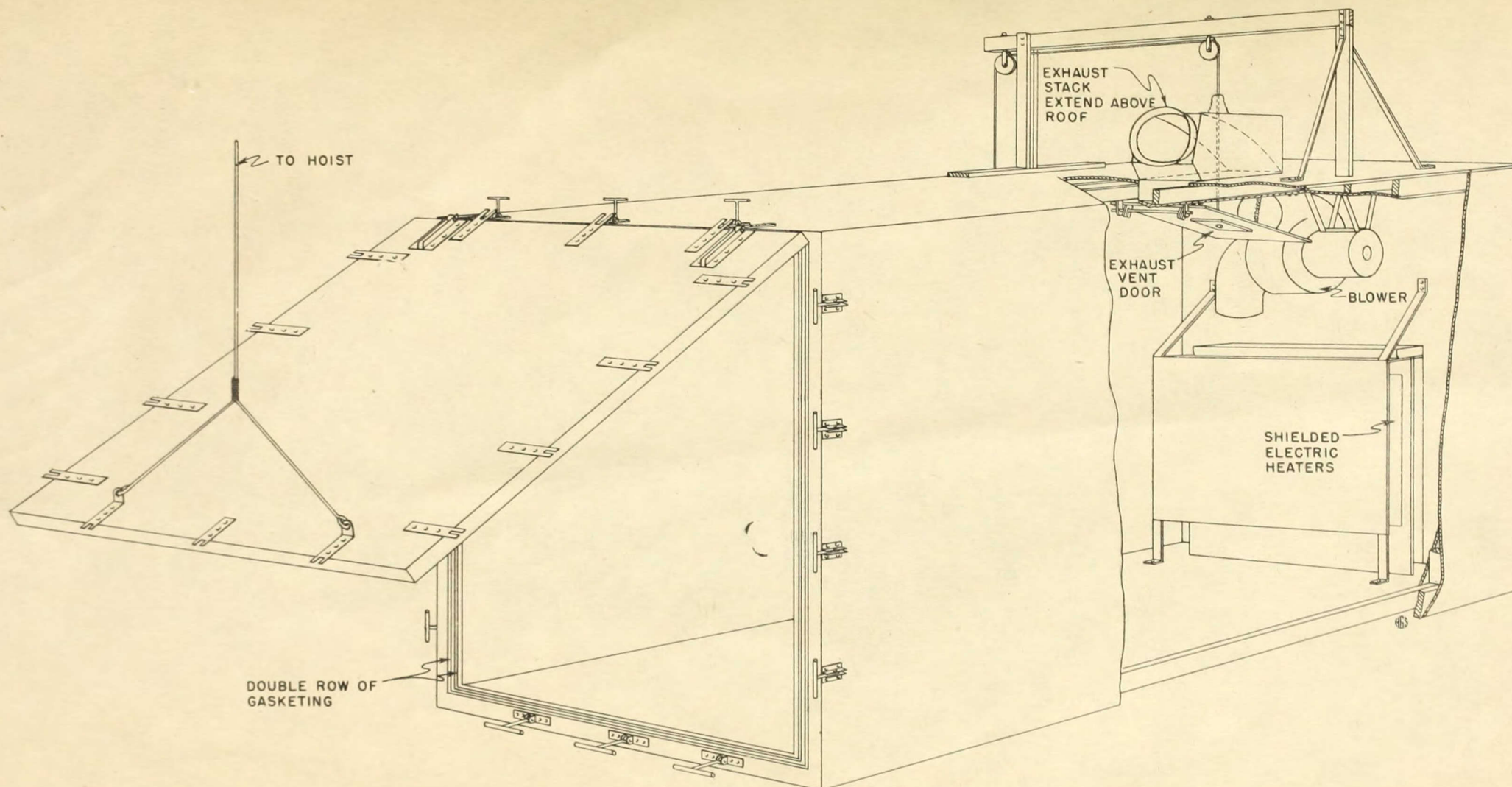


Figure 1.--Approved type of methyl bromide fumigation vault. The exhaust vent door is closed for circulation, and opened for venting as shown. Electric heaters and insulated walls are necessary only where temperature control is desired.

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